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R. GÁSPÁR, L. JÁNOSSY, K. NAGY, L. PÁL, A. SZALAY, I. TARJÁN

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HOROSPHERIC BASIS OF THE SL(2, C) GROUP

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Representations of the $SL(2,C)$ groups are reduced with respect to the horospheric subgroup $\begin{pmatrix}1 & \beta\\ 0 & 1\end{pmatrix}$ isomorphic to the translation group in two dimensions. The matrix elements of unitary representations of the principal and supplementary series are derived in a basis defined by a two-dimensional momentum corresponding to the above subgroup. Matrix elements of unitary representations expressed in this basis assume a simpler form than in any other basis considered so far. The two-dimensional momentum introduced proves to be essentially identical with the impact parameter.

Introduction

Irreducible representations of the $SL(2, C)$ group can be realized on the functions space D^{χ} [1] elements of which are infinitely differentiable functions $\varphi(z, z^*)$ with infinitely differentiable inversion

$$\hat{\varphi}(z, z^*) = z^{2j} z^{*2k} \varphi\left(-\frac{1}{z}, -\frac{1}{z^*}\right);$$

where $\chi = (j, k)$ labels an irreducible representation. From the point of view of classification of the representations it is convenient to introduce j_0 and σ by the relations $2j = j_0 - 1 + i\sigma$, $2k = -j_0 - 1 + i\sigma$. In particular, representations are unitary if on D^{χ} there is a positive definite Hermitean functional. This exists in two cases: either $2j_0$ is integer and σ real (principal series) or, $j_0 = 0$ and σ is pure imaginary, $i\sigma = \varrho$, $-1 < \varrho < 1$ (supplementary series). Explicit forms of the Hermitean functionals differ from each other in the two cases.

If one chooses a particular basis within an irreducible representation, an integral representation for the matrix elements of unitary representations (UR) can be written down with the aid of the above functional. This can be evaluated in principle and the result depends first of all on the basis used. Relativistic expansions of the scattering amplitude required the knowledge of the explicit form of matrix elements of UR [2—5]. Representations were investigated then mainly in $SU(2)$, $SU(1, 1)$, $E(2)$* bases [6—10]. There are several possibilities for evaluation of the matrix elements in the above bases, namely, solution of recurrence relations, calculation of the integral representation for the matrix elements, solution of the eigenvalue equations of the Casimir operators etc. However, any one of these methods is used the matrix elements of UR in the above bases can be expressed only in terms of rather complicated formulas containing multiple sums. For instance, in angular momentum basis representations can be given only in terms of a triple sum over Wigner D-functions and hypergeometric function. As these special functions are sums themselves, the final result is actually a sixfold sum. Perhaps it is needless to emphasize that we face here representations of a fundamental symmetry of nature rather than a solution of an artificial model or something like that. Therefore the obvious question arises as to which is the basis preferred by the internal structure of the Lorentz group in the sense that the matrix elements of UR take a simple form in it. A considerable simplification can be achieved in an $O(2)\times O(1, 1)$ basis [11] but it seems that the so-called horospheric subgroup [1, 12, 13] which is formed by the matrices $\begin{pmatrix} 1 & \beta \\ 0 & 1 \end{pmatrix}$ plays a distinguished role in the $SL(2, C)$ group. Namely, in the basis labelled by a two-dimensional momentum $\mathbf{P} = (P_1, P_2)$ corresponding to the horospheric subgroup, isomorphic to the translation group in two dimensions, the matrix elements of UR assume a form simpler than in any other basis considered so far. Actually, this in not surprising since the horospheric subgroup is of fundamental significance in the geometrical approach presented to the representation theory in [1].

It is worth noting that the two-dimensional momentum, used in the present paper has bearing on a relativistic generalization of the impact parameter, however, for proving this the Poincaré group ought to be considered. It can be shown [14] that the components of the impact parameter can be defined as the eigenvalues of the operators $(M_1 - N_2)/(p^0 - p^3)$ and $(M_2 + N_1)/(p^0 - p^3)$ where p^0 and p^3 denote the zeroth and third components of the momentum. Since the infinitesimal generators of the horospheric subgroup $\begin{pmatrix} 1 & \beta \\ 0 & 1 \end{pmatrix}$ are just $(M_1 - N_2)$, $(M_2 + N_1)$ and the two-dimensional momenta P_1, P_2 are the eigenvalues of the above generators, therefore, the components of the impact parameter can be given in the form $P_1/(p^0 - p^3)$, $P_2/(p^0 - p^3)$. It should be emphasized that the subgroup $\begin{pmatrix} 1 & \beta \\ 0 & 1 \end{pmatrix}$, isomorphic to the two-dimensional translation group, has nothing to do with spatial translations, therefore, the "momenta" P_1, P_2 are connected with horospheric translations

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* Strictly speaking we mean here the reduction $SL(2,C) \supset E(2) \supset O(2)$

$\begin{pmatrix}1 & \beta \\ 0 & 1\end{pmatrix} \subset SL(2, C)$ rather than with translations of space-time coordinates. The relation of the momenta P_1, P_2 to the impact parameter is treated in [14], here representations of the Lorentz group are considered only.

The paper is organized as follows. First the rigorous meaning of the matrix elements of representations is given. This is required since the horospheric basis in z-representation takes the form of a two-dimensional plane wave $\exp(-Pz + P^* z^*)$ with P continuous. It is well known that the treatment of group representation in continuous bases requires more rigour than usual, namely, the above two-dimensional plane wave has to be considered as a functional on D^χ space rather than an ordinary function. In this manner the strict meaning of the matrix elements of UR can be given and an integral representation can be obtained for them. This, however, is not the best way to evaluate the matrix elements. They can be derived in a more simple way by solving the eigenvalue equations of the Casimir operators. The simplicity of the matrix elements obtained is striking in the case of the "zeroth column" of representations which is nothing but a spherical function. It will be shown that apart from a normalization factor these are simple elementary (trigonometric, exponential) functions. This occurs in no other basis of the $SL(2, C)$ group. In Section 2 the supplementary series of UR is treated. It is shown that its matrix elements can be reduced to those of the principal series.

1. Unitary representations of the principal series

The infinitesimal generators of the $SL(2, C)$ group satisfy the Lie algebra

$$[M_k, M_l] = i\varepsilon_{klm} M_m, \quad [M_k, N_l] = i\varepsilon_{klm} N_m, \qquad (1.1)$$
$$[N_k, N_l] = -i\varepsilon_{klm} M_m,$$

where M_k are generators of rotations about, and N_k are generators of boosts along the x_k-axis ($k = 1, 2, 3$). It is convenient to introduce the familiar combinations $J_k = (M_k + iN_k)/2$, $K_k = (M_k - iN_k)/2$ as they satisfy formally the commutation relations of two independent angular momenta:

$$[J_k, J_l] = i\varepsilon_{klm} J_m, \quad [K_k, K_l] = i\varepsilon_{klm} K_m, \qquad (1.2)$$
$$[J_k, K_l] = 0.$$

In the following, instead of the six Hermitean generators M_k, N_k the combinations

$$J_+ \equiv J_1 + iJ_2 = \frac{1}{2}[M_1 - N_2 + i(M_2 + N_1)], \; J_2, J_3, \qquad (1.3)$$
$$K_- \equiv K_1 - iK_2 = \frac{1}{2}[M_1 - N_2 - i(M_2 + N_1)], \; K_2, K_3$$

will be used since J_+ and K_- generate the subgroup according to which the irreducible representations of the $SL(2, C)$ group will be reduced. The parameters belonging to these can be determined from the invariance of the bilinear form $\Sigma\,(\chi_k M_k + u_k N_k)$, where χ_k is a real rotation angle about the χ_k-axis and u_k is a rapidity of the boost along the x_k-axis ($k = 1, 2, 3$):

$$\begin{aligned}\sum_{k=1}^{3} (\chi_k M_k + u_k N_k) &= J_+(\chi_1 - iu_1) + K_-(\chi_1 + iu_1) + \\ &+ J_2(\chi_2 - i\chi_1 - u_1 - iu_2) + K_2(\chi_2 + i\chi_1 - u_1 + iu_2) + \\ &+ J_3(\chi_3 - iu_3) + K_3(\chi_3 + iu_3)\,.\end{aligned} \tag{1.4}$$

It follows from this that the parameters corresponding to the generators (J_+, K_-), $(J_2 K_2)$ and $(J_3 K_3)$ are pairwise complex conjugate to each other.

Irreducible representations of $SL(2, C)$ can be given in the D^χ space in the following way [1]:

$$T^\chi(g)\,\varphi(z) = (-\gamma z + \alpha)^{2j}\,(-\gamma^* z^* + \alpha^*)^{2k}\,\varphi\left(\frac{\delta z - \beta}{-\gamma z + \alpha}\right), \qquad (\varphi \in D^\chi) \tag{1.5}$$

where D^χ is the space of all infinitely differentiable functions $\varphi(z, z^*)$ with infinitely differentiable inversions $\hat{\varphi}(z, z^*) \equiv z^{2j} z^{*2k} \varphi\left(-\frac{1}{z}, -\frac{1}{z^*}\right)$. Here j and k are labels characterizing irreducible representations which can be written in the form

$$2j = j_0 - 1 + i\sigma\,,\; 2k = -j_0 - 1 + i\sigma\,,$$

where j_0 takes integer and half-integer values and σ is an arbitrary complex number. For the principal series of representations σ is real and the scalar product is defined by

$$\begin{gathered}(\varphi_1, \varphi_2) = \int d^2z\, \varphi_1^*(z)\, \varphi_2(z) \\ (\varphi_1, \varphi_2 \in D^\chi,\; d^2z = d\mathrm{Re}z\, d\mathrm{Im}z)\,.\end{gathered} \tag{1.6}$$

In the present section we concern ourselves with the principal series, i.e. σ is real and hence $k = -j^* - 1$.

Irreducible representations of $SL(2, C)$ will be reduced according to the horospheric subgroup $\begin{pmatrix}1 & \beta\\ 0 & 1\end{pmatrix}$, isomorphic to the two-dimensional translation group. Therefore, the basis within an irreducible representation will be labelled by a two dimensional continuous momentum. Since the infinitesimal generators of the above horospheric subgroup are J_+ and K_-, the basis is defined by the equations

$$J_+\Phi^{jk}_{PP*}= P\Phi^{jk}_{PP*},\ K_-\Phi^{jk}_{PP*}= P^*\Phi^{jk}_{PP*}. \tag{1.7}$$

where

$$P=\frac{1}{2}(P_1+iP_2)\,,\ P^*=\frac{1}{2}(P_1-iP_2)\,. \tag{1.8}$$

These eigenvalue equations can be written in terms of the Hermitean generators (1.1) alternatively as

$$(M_1-N_2)\Phi^{jk}_{PP*}= P_1\Phi^{jk}_{PP*},\ (M_2+N_1)\Phi^{jk}_{PP*}= P_2\Phi^{jk}_{PP*}. \tag{1.9}$$

It is easily inferred from (1.5) that the generators J_+ and K_- can be represented on D^χ in the form $J_+ = -\partial/\partial z$, $K_- = \partial/\partial z^*$. The solution of the equations (1.7) is a two-dimensional plane wave of the form

$$\Phi_{PP*}(z) = \Phi^{jk}_{PP*}(z) = (2\pi)^{-1}e^{-Pz+P^*z^*}\,. \tag{1.10}$$

It has been mentioned that the irreducible representations of the $SL(2, C$ group can be built up on the function space D^χ. If the basis functions (1.10) were elements of D^χ, the matrix elements of representations could be put down easily since the scalar product is known for both the principal and supplementary series, (cf. Eqs. (1.6) and (2.2)) as well as the action of representations onto the basis functions $\Phi_{PP*}(z)$. However, it is seen immediately that the inversion of the basis functions (1.10) $\hat{\Phi}_{PP*}(z) = (2\pi)^{-1}z^{2j}z^{*2k}.\ \exp\left(P\frac{1}{z}-P^*\frac{1}{z^*}\right)$ is not infinitely differentiable at $z = 0$ and therefore, not an element of D^χ. The question arises what is the rigorous meaning of the matrix elements of representations which one would obtain naïvely with the aid of the basis functions (1.10) and scalar product (1.6). It is a standard procedure [1] how to treat the bad behaved functions like (1.10). They should be considered as functionals on D^χ namely

$$\psi(P, P^*) = (\Phi, \varphi(z)) = \int d^2z\Phi_{PP*}(z)\,\varphi(z)\,, \qquad (\varphi(z) \in D^\chi)\,. \tag{1.11}$$

Loosely speaking we have changed over to the well behaved functions $\psi(P, P^*)$ by smearing the bad behaved plane waves with an element $\varphi(z)$ of D^χ. The action of the representations on the functions $\psi(P, P^*)$ are defined as

$$T^\chi_g\psi(P, P^*) = \int d^2z(-\gamma z+\alpha)^{2j}(-\gamma^*z^*+\alpha^*)^{2k}\,\Phi_{PP^*}\left(\frac{\delta z-\beta}{-\gamma z+\alpha}\right)\varphi(z)\,.$$

Expressing $\varphi(z)$ from (1.11) and substituting here we get

$$T_g^\chi \psi(P, P^*) = (2\pi)^{-2} \int d^2z\, e^{-P^*z'+P^*z'^*} (-\gamma z + \alpha)^{2j} (-\gamma^* z^* + \alpha^*)^{2k} ;$$
$$\int d^2Q\, e^{Qz-Q^*z^*} \psi(Q, Q^*)\,, \tag{1.12}$$

where

$$z' = \frac{\delta z - \beta}{-\gamma z + \alpha}\,,\; d^2Q = dQ_1\, dQ_2\,,\; Q = \frac{1}{2}(Q_1 + iQ_2)\,.$$

In this way the matrix elements of the operators T_g^χ appear as the kernel of the integral transformation (1.12),

$$T_g^\chi \psi(P, P^*) = \int d^2Q T^j_{\mathbf{QP}}(g)\, \psi(Q, Q^*) \tag{1.13}$$

with

$$T^j_{\mathbf{QP}}(g) = (2\pi)^{-2} \int d^2z\, e^{Qz-Q^*z^*} (-\gamma z + \alpha)^{2j} (-\gamma^* z^* + \alpha^*)^{2k}\, e^{-Pz'+P^*z'^*}\,. \tag{1.14}$$

Here we have tacitly interchanged the order of integrations with respect to z and Q, however, a detailed investigation shows that this is not legitimate if either $P = 0$ or $\gamma = 0$. This indicates that in (1.12) the operators of representations are well defined, but their matrix elements have slightly restricted meaning. We shall return to this point later on.

It would be hard to evaluate the integral representation (1.14) directly, therefore the matrix elements of representations will be obtained by solving the eigenvalue equations of the Casimir operators $\mathbf{J}^2 = J_1^2 + J_2^2 + J_3^2$ and $\mathbf{K}^2 = K_1^2 + K_2^2 + K_3^2$. To this end, a parametrization which fits the horospheric basis well should be introduced. Namely, it can be shown that each $g = \begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix} \in SL(2, C)$ can be decomposed as

$$g = \begin{pmatrix} 1 & -i\varphi \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\frac{\vartheta}{2} & -\sin\frac{\vartheta}{2} \\ \sin\frac{\vartheta}{2} & \cos\frac{\vartheta}{2} \end{pmatrix} \begin{pmatrix} 1 & -i\psi \\ 0 & 1 \end{pmatrix} \tag{1.15}$$

unless $\gamma = 0$. For the proof as well as the discussion of the singular case $\gamma = 0$ we refer to [15]. Here φ, ϑ, ψ are complex parameters $\varphi = \varphi_1 + i\varphi_2$, $\vartheta = \vartheta_1 + i\vartheta_2$, $\psi = \psi_1 + i\psi_2$ which vary between the limits

$$-\infty < \varphi_1, \varphi_2, \psi_1, \psi_2, \vartheta_2 < \infty\,, \qquad -\pi < \vartheta_1 \leqq \pi\,. \tag{1.16}$$

It is easy to recognize an analogy between the above parametrization and the Euler decomposition of the $SU(2)$ group. This is retained by the structure of the matrix elements as well. It is not only of formal nature but rests upon the homomorphy between $SL(2, C)$ and the three-dimensional complex rotation group. Elements of the $SL(2, C)$ group can be parametrized with complex Euler angles by sandwiching a complex rotation about the x-axis with two elements of the $O(2)\times O(1, 1)$ group, i.e. with $\begin{pmatrix} e^{-i\varphi/2} & 0 \\ 0 & e^{i\varphi/2} \end{pmatrix}$ and $\begin{pmatrix} e^{-i\psi/2} & 0 \\ 0 & e^{i\psi/2} \end{pmatrix}$. By means of a deformation within the $SL(2, C)$ group, this subgroup can be contracted into the horospheric subgroup, i.e. $\begin{pmatrix} e^{-i\varphi/2} & 0 \\ 0 & e^{i\varphi/2} \end{pmatrix} \to$ $\to \begin{pmatrix} 1 & -i\varphi \\ 0 & 1 \end{pmatrix}$, $\begin{pmatrix} e^{-i\psi/2} & 0 \\ 0 & e^{i\psi/2} \end{pmatrix} \to \begin{pmatrix} 1 & -i\psi \\ 0 & 1 \end{pmatrix}$ where the arrow stands for "deforms into". In this way the Euler decomposition deforms into the parametrization (1.15) used here. For details refer to [16].

With the aid of the above parametrization the infinitesimal generators and the Casimir operators can be expressed as differential operators with respect to the group parameters. The matrix elements of representations $T^j_{\mathrm{QP}}(g)$ can be evaluated by solving the eigenvalue equations

$$[\mathbf{J}^2 - j(j+1)]\, T^j_{\mathrm{QP}}(g) = 0\,, \quad [\mathbf{K}^2 - k(k+1)]\, T^j_{\mathrm{QP}}(g) = 0$$

which can be written in terms of the parameters φ, ϑ, ψ as

$$\Bigg[\tan^2\frac{\vartheta}{2}\;\frac{\partial^2}{\partial\vartheta^2} + \frac{1}{2}\;\tan\frac{\vartheta}{2}\left(3 + \tan^2\frac{\vartheta}{2}\right)\frac{\partial}{\partial\vartheta} + \frac{i}{\cos^2\dfrac{\vartheta}{2}}\left(\frac{\partial}{\partial\varphi} + \frac{\partial}{\partial\vartheta}\right)\frac{\partial}{\partial\vartheta} +$$

$$-\frac{1}{\sin^2\vartheta}\left(\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial\psi^2} - 2\cos\vartheta\frac{\partial^2}{\partial\varphi\,\partial\psi}\right) + \frac{i}{4\sin\dfrac{\vartheta}{2}\cos^3\dfrac{\vartheta}{2}}\left(\frac{\partial}{\partial\varphi} + \frac{\partial}{\partial\psi}\right) -$$

$$- j(j+1)\Bigg]\, T^j_{\mathrm{QP}}(g) = 0,$$

$$\Bigg[\tan^2\frac{\vartheta^*}{2}\;\frac{\partial^2}{\partial\vartheta^{*2}} + \frac{1}{2}\tan\frac{\vartheta^*}{2}\left(3 + \tan^2\frac{\vartheta^*}{2}\right)\frac{\partial}{\partial\vartheta^*} -$$

$$-\frac{i}{\cos^2\dfrac{\vartheta^*}{2}}\left(\frac{\partial}{\partial\varphi^*} + \frac{\partial}{\partial\psi^*}\right)\frac{\partial}{\partial\vartheta^*} - \frac{1}{\sin^2\vartheta^*}\left(\frac{\partial^2}{\partial\varphi^{*2}} + \frac{\partial^2}{\partial\psi^{*2}} -\right.$$

$$\left.- 2\cos\vartheta^*\frac{\partial^2}{\partial\varphi^*\,\partial\psi^*}\right) - \frac{i}{4\sin\dfrac{\vartheta^*}{2}\cos^3\dfrac{\psi^*}{2}}\left(\frac{\partial}{\partial\varphi^*} + \frac{\partial}{\partial\psi^*}\right) -$$

$$- k(k+1)\Bigg]\, T^j_{\mathrm{PQ}}(g) = 0\,.$$

Here

$$j \equiv \frac{1}{2}(j_0 - 1 + i\sigma)\,, \quad k \equiv \frac{1}{2}(-j_0 - 1 + i\sigma)\,.$$

For the principal series treated in the present section σ takes real values. These equations are rather complicated, nevertheless their solutions take a simple form. First, the dependence on parameters φ, φ^* and ψ, ψ^* can be separated,

$$T^j_{QP}(g) = e^{-i(Q\varphi + Q^*\varphi^* + P\psi + P^*\psi^*)}\, d^j_{QP}(\vartheta, \vartheta^*)\,. \tag{1.17}$$

The remaining eigenvalue equations for d^j_{QP} have a regular solution only if 2_{j_0} takes integer values. The solution reads

$$d^j_{PQ}(\vartheta, \vartheta^*) = n^j_{PQ}\, \frac{\exp\left[(Q+P)\cot(\vartheta/2) - (Q^* + P^*)\cot(\vartheta^*/2)\right]}{\sin(\vartheta/2)\sin(\vartheta^*/2)}\,\cdot$$

$$\left[I_{2j+1}(t)\, I_{2k+1}(t^*) - I_{-2j-1}(t)\, I_{-2k-1}(t^*)\right], \tag{1.18}$$

where

$$t = \frac{2\sqrt{QP}}{\sin\dfrac{\vartheta}{2}} \quad \text{and} \quad n^j_{QP} = -\frac{1}{4\sin(2\pi j)}\left(\frac{P}{Q}\right)^{j+\frac{1}{2}}\left(\frac{P^*}{Q^*}\right)^{k+\frac{1}{2}}.$$

Here $I_\nu(t)$ denotes the Bessel function of imaginary argument [17]. It is defined by the series

$$I_\nu(t) = \sum_{m=0}^{\infty} \frac{(t/2)^{\nu+2m}}{m!\,\Gamma(m+\nu+1)}\,.$$

In order to determine $I_\nu\left(\dfrac{2\sqrt{Q}\sqrt{P}}{\sin\vartheta/2}\right)$ unambiguously the $\sin\dfrac{\vartheta}{2}$ as well as Q and P planes have to be cut. However, the discontinuities of d^j_{QP} across the cuts can be shown to vanish simply as a consequence of the quantization of j_0. Indeed, encircling the infinity in the $\sin(\vartheta/2)$ plane in the positive direction $I_{2j+1}(t)\, I_{2k+1}(t^*)$ and $I_{-2j-1}(t)\, I_{2k-1})\, (t^*)$ are multiplied by $\exp(-4\pi i j_0) = 1$ and $\exp(+4\pi i j_0) = 1$, respectively. Vanishing of the discontinuities in Q and P planes can be seen in a similar simple way.

It has been mentioned that at $P = 0$ the order of integrations cannot be interchanged in (1.12); i.e. in this case $T^j_{QP}(g)$ cannot be interpreted as the kernel of the integral transformation (1.12). Indeed, in (1.17) and (1.18) in the explicit form of T^j_{QP} we meet an oscillating expression undetermined when P tends to zero. Due to the symmetry of the matrix elements a similar statement can be made on $Q \to 0$ too. At the same time, however, if the limit

$P \rightarrow 0$ is performed in (1.14) in the integrand, the integral yields a definite result:

$$T^j_{QP=0}(g) \equiv (2\pi)^{-2} \int d^2 z e^{Qz - Q^* z^*} (-\gamma z + \alpha)^{2j} (-\gamma^* z^* + \alpha^*)^{2k} =$$

$$= N^j_Q \left(\sin \frac{\vartheta}{2} \right)^{2j} \left(\sin \frac{\vartheta^*}{2} \right)^{2k} e^{Q \cot \frac{\vartheta}{2} - Q^* \cot \frac{\vartheta^*}{2}} \cdot e^{-i(Q\varphi + Q^*\varphi^*)}, \tag{1.19}$$

where

$$N^j_Q = (4\pi)^{-1} \frac{\Gamma(2j+1)}{\Gamma(-2k)} Q^{-2j-1} Q^{*-2k-1}.$$

Let us now introduce the functions

$$Y^j_Q(\vartheta, \varphi) \equiv \left[\frac{(2j+1)(-2k-1)}{8\pi^2} \right]^{1/2} T^j_{QP=0}(g)^* \tag{1.20}$$

which form a complete orthonormal set of functions in the space of square integrable functions defined on the spinors u, v. It has been shown in [22] that u and v are expressed in terms of parameters ϑ, φ as

$$u = \cos(\vartheta/2) - i\varphi \sin(\vartheta/2), \quad v = \sin(\vartheta/2).$$

Functions (1.20) satisfy the orthogonality relations

$$\int Y^{j'}_{Q'}(\vartheta, \varphi)^* \, Y^j_Q(\vartheta, \varphi) \, d^2 u d^2 v = \delta_{j_0', j_0} \delta(\sigma' - \sigma) \, \delta(Q_1' - Q_1) \, \delta(Q_2' - Q_2),$$

where

$$d^2 u d^2 v = d \operatorname{Re} u d \operatorname{Im} u d \operatorname{Re} v d \operatorname{Im} v = \sin \vartheta \sin \vartheta^* \, d \operatorname{Re} \vartheta \, d \operatorname{Im} \vartheta d \operatorname{Re} \varphi d \operatorname{Im} \varphi.$$

It is a remarkable fact that the spherical functions (1.20) are, apart from the normalization factor, elementary functions. In the next section we proceed to the evaluation of the matrix elements of the supplementary series.

2. Supplementary series of the unitary representations

The supplementary series is characterized by the values $j_0 = 0$ and $i\sigma = \varrho$ $(-1 < \varrho < 1)$, i.e. between j and k defined previously the relation

$$2j + 1 = 2k + 1 \equiv \varrho \tag{2.1}$$

holds. The Hermitean functional on D^χ now reads [1, 12]

$$\{\varphi_1, \varphi_2\} = \Gamma(-\varrho)^{-1} \int d^2_{z_1} d^2_{z_2} \, |z_1 - z_2|^{-2-2\varrho} \cdot \varphi_1(z_1)^* \, \varphi_2(z_2) \quad (\varphi_1, \varphi_2 \in D^\chi). \tag{2.2}$$

This functional is convergent and positive definite for $-1 < \varrho < 1$, but it can be extended to the values $|\varrho| > 1$ by means of regularizaton. Then, however, it fails to remain positive definite and therefore cannot be used as a scalar product [1].

Equations defining the horospheric basis take the form of (1.7) or (1.9), again:

$$J_+ \Phi^{\varrho}_{PP*} = P\Phi^{\varrho}_{PP*}\,, \quad K_- \Phi^{\varrho}_{PP*} = P^* \Phi^{\varrho}_{PP*}$$

with

$$P = \frac{1}{2}(P_1 + iP_2)\,. \quad P^* = \frac{1}{2}(P_1 - P_2)\,.$$

In the z-space the generators are given in the form $J_+ = -\partial/\partial z$, $K_- = \partial/\partial z^*$ and thus the basis functions are of the form $\Phi^{\varrho}_{PP*}(z) = N \exp(-Pz + P^*z^*)$. These functions are orthogonal with respect to the scalar product of the supplementary series (2.2), however, the normalizing factor differs from that of the principal series. It is determined from the requirement

$$\{\Phi^{\varrho}_{QQ*}, \Phi^{\varrho}_{PP*}\} = N^2 \Gamma(-\varrho)^{-1} \int d^2 z_1\, d^2 z_2\, |z_1 - z_2|^{-2-2\varrho} \Phi^{\varrho}_{QQ*}(z)^* \Phi^{\varrho}_{PP*}(z) =$$
$$= \delta(Q_1 - P_1)\, \delta(Q_2 - P_2)\,.$$

Integration with respect to z_1 can be easily performed by introducing the variable $z = z_1 - z_2$ and subsequently polar coordinates in the z-plane,

$$\int d^2 z_1 \frac{|z_1 - z_2|^{-2-2\varrho}}{\Gamma(-\varrho)} e^{Qz_1 - Q^* z_1^*} = 2\pi e^{Qz_2 - Q^* z_2^*}\, \Gamma(-\varrho)^{-1}\,,$$
$$\int_0^\infty d|z|\; |z|^{-1-2\varrho} J_0(2|z|\,|Q|) = \pi \frac{|Q|^{2\varrho}}{\Gamma(1+\varrho)} e^{Qz_2 - Q^* z_2^*}\,. \tag{2.3}$$

Here J_0 denotes the Bessel function of zero order. From this it follows immediately that $N = (2\pi)^{-1} |P|^{-\varrho} \sqrt{\Gamma(1+\varrho)/\pi}$ and the basis functions are

$$\Phi^{\varrho}_{PP*}(z) = (2\pi)^{-1} |P|^{-\varrho} \sqrt{\frac{\Gamma(1+\varrho)}{\pi}}\; e^{-Pz + P^* z^*}\,. \tag{2.4}$$

Similarly to the basis for the principal series these functions are not elements of space D^{χ} either, therefore they are to be considered as functionals on D^{χ}, which, in the present case can be written as

$$\psi(P, P^*) = \int d^2 z_1 d^2 z_2 \Phi^{\varrho}_{PP*}(z_1)\, K(z_1; z_2)\, \varphi(z_2)\,, \tag{2.5}$$

where

$$K(z_1, z_2) = |z_1 - z_2|^{-2-2\varrho}\, \Gamma(-\varrho)^{-1}.$$

The action of the representations T_g^χ is defined now by

$$T_g^\chi \psi(P, P^*) = \int d^2z_1 d^2z_2 (-\gamma z_1 + \alpha)^{\varrho-1} (-\gamma^* z_1^* + \alpha^*)^{\varrho-1} \cdot \Phi^\varrho_{PP^*}\left(\frac{\delta z_1 - \beta}{-\gamma z_1 + \alpha}\right) K(z_1, z_2)\, \varphi(z_2)\,. \tag{2.6}$$

With the aid of (2.3) $\varphi(z)$ can be expressed from (2.5)

$$\varphi(z) = \int \Phi_{QQ^*}(z)^* \, \psi(Q, Q^*)\, d^2Q\,.$$

Substituting this in (2.6) one gets

$$T_g^\chi \psi(P, P^*) = \int d^2z_1 d^2z_2 (-\gamma z_1 + \alpha)^{\varrho-1} (-\gamma^* z_1^* + \alpha^*)^{\varrho-1}$$

$$\Phi^\varrho_{PP^*}\left(\frac{\delta z_1 - \beta}{-\gamma z_1 + \alpha}\right) K(z_1; z_2) \int d^2Q \Phi^\varrho_{QQ^*}(z_2)^* \, \psi(Q, Q^*)\,.$$

Consequently, the matrix elements of the supplementary series can be defined as the kernel of the integral transformation

$$T_g^\chi \psi(P, P^*) = \int d^2Q T^\varrho_{\{QP\}} \psi(Q, Q^*)$$

provided the interchange of the order of integrations is legitimate. The kernel takes the form

$$T^\varrho_{\{QP\}}(g) = \int d^2z_1 d^2z_2 \Phi^\varrho_{QQ^*}(z_2)^* \, K(z_1; z_2)\,, \\ (-\gamma z_1 + \alpha)^{\varrho-1} (-\gamma^* z_1^* + \alpha^*)^{\varrho-1} \, \Phi^\varrho_{PP^*}\left(\frac{\delta z_1 - \beta}{-\gamma z_1 + \alpha}\right). \tag{2.7}$$

The labels Q, P have been put in curly brackets to indicate that the scalar product differs from that given for the principal series.

Even though (2.7) seems to be more complicated than (1.14), it can nevertheless be easily reduced to (1.14). We use (2.3) again, then (2.7) becomes [18]

$$T^\varrho_{\{QP\}}(g) = \Gamma(-\varrho)^{-1} \int d^2z_1 d^2z_2 \, |z_1 - z_2|^{-2-2\varrho} \Phi^\varrho_{QQ^*}(z_1)^* \cdot$$

$$(-\gamma z_2 + \alpha)^{\varrho-1} (-\gamma^* z_2^* + \alpha^*)^{\varrho-1} \, \Phi^\varrho_{PP^*}\left(\frac{\delta z_2 - \beta}{-\gamma z_2 + \alpha}\right) =$$

$$= (2\pi)^{-2} \int d^2z \, e^{Qz - Q^*z^*} (-\gamma z + \alpha)^{\varrho-1} (-\gamma^* z^* + \alpha^*)^{\varrho-1} \, e^{-Pz' + P^*z'^*}\,. \tag{2.8}$$

It is concluded that

$$T^\varrho_{\{QP\}}(g) = T^j_{QP}(g) \,|_{2j+1=\varrho}\,.$$

i.e., the matrix elements of the supplementary series in horospheric basis coincide with those of the principal series, merely $2j + 1 = 2k + 1 = \varrho$ have to be substituted. Therefore, one gets from (1.17) and (1.18),

$$T^{\varrho}_{\{QP\}}(g) = e^{-i(Q\varphi+Q^*\varphi^*+P\psi+P^*\psi^*)}\, d^{\varrho}_{\{QP\}}(\vartheta, \vartheta^*)$$

with

$$d^{\varrho}_{\{QP\}}(\vartheta, \vartheta^*) =$$

$$= n^{\varrho}_{QP} \cdot \frac{\exp[(Q+P)\cot(\vartheta/2) - (Q^*+P^*)\cot(\vartheta^*/2)]}{\sin(\vartheta/2)\sin(\vartheta^*/2)} [I_{\varrho}(t)\, I_{\varrho}(t^*) - I_{-\varrho}(t)\, I_{-\varrho}(t^*)]$$

where again

$$t = \frac{2\sqrt{QP}}{\sin(\vartheta/2)} \text{ and } n^{\varrho}_{QP} = -\frac{1}{4\sin(\varrho\pi)} \left|\frac{P}{Q}\right|^{\varrho}.$$

It has been mentioned in the case of principal series that the discontinuity across the cuts in t and t^* planes vanishes due to the quantization of j_0. It is easy to see that this is true for the supplementary series as well. At $t = 0$ the Bessel function $I_{\varrho}(t)$ has a branch point of order ϱ, that is, when encircling the origin once in the positive direction $I_{\varrho}(t)$ $I_{\varrho}(t^*)$ and $I_{\varrho}(t)$ $I_{\varrho}(t^*)$ are multiplied by $\exp(2\pi i\varrho)\exp(-2\pi i\varrho) = 1$. Completing this by the observation that in the given range of ϑ the value of $\cot\dfrac{\vartheta}{2}$ is unambiguously determined by the value of $\sin\dfrac{\vartheta}{2}$, we can see that the discontinuity vanishes. A similar statement can be made on the discontinuities in the Q, Q^* and P, P^* planes.

Finally, I would add that the impact parameter may prove to be not only useful but a fundamental variable in the description of high energy phenomena. In this case the expansion of scattering amplitude would enable the above representations to incorporate a great deal of dynamics.

REFERENCES

1. I. M. GEL'FAND, M. I. GRAEV and N. YA. VILENKIN, "Integral Geometry and Representation Theory", Generalized Functions, Vol. 5. Academic Press, New York, London, 1966.
2. M. TOLLER, Nuovo Cim., **53A**, 671, 1968.
3. G. FELDMAN and P. T. MATTHEWS, ICTP, 33, 68.
4. M. SHEFTEL, J. SMORODINSKY and P. W. WINTERNITZ, Phys. Lett., **26B**, 241, 1968.
5. R. DELBOURGR, A. SALAM and J. STRATHDEE, Phys. Rev., **164**, 1981, 1967.
6. S. STRÖM, Ark. Fys. **23**, 467, 1965, ibid. **33**, 465, 1957, **38**, 373, 1968.
7. J. A. VERDIEV and L. A. DADASHEV, Sov. J. Nucl. Phys., **6**, 795, 1968.
8. N. MUKUNDA, J. Math. Phys., **9**, 50, 1968.
9. G. J. IVERSON and G. MACK, J. Math. Phys., **11**, 1581, 1970.
10. N. W. MACFADYEN, J. Math. Phys. **12**, 492, 1971.
11. M. HUSZÁR and J. SMORODINSKY, JINR E2-4225 (1968); Theor. Math. Phys., **4**, 328, 1970.
12. M. A. NAIMARK, Linear Representations of the Lorentz Group, Pergamon, Oxford, 1964.
13. CHANG-SHAN-JIN and O'RAIFEARTAIGH, J. Math. Phys., **10**, 21, 1969.
14. M. HUSZÁR, Impact parameter states and infinite momentum frame kinematics, KFKI Report 75—4. Nuovo Cim. in print.
15. M. HUSZÁR, J. Math. Phys., **14**, 1620, 1973.
16. M. HUSZÁR, ibid. **15**, 659, 1974.
17. H. BATEMAN and A. ERDÉLYI, "Higher Transcendental Functions", Vol. 2. McGraw Hill, New York, Toronto, London, 1953.
18. It should be noted that (2.8) could be obtained in a simpler way if in (2.5) the relation (2.3) is applied immediately, however, we have attached importance to Eq. (2.7) since this is the formula which would be obtained directly from (2.2) if $\exp(-Pz+P^*z^*)$ were an element of D^{χ}.

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EXPLANATION OF THE MAGNETIC BEHAVIOUR OF OXYGEN IN THE LIQUID STATE

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The experimentally well known decrease of the magnetic susceptibility of oxygen in the liquid state compared with Curie's law is explained. A physical reason is given for this phenomenon (spin exchange forces), and the reduction of magnetic susceptibility is calculated on the basis of the interaction of pairs of oxygen molecules. The critical point is also considered, but no special critical phenomenon is taken into account. The values are therefore reference values for vanishing critical effects.

I. Introduction

The oxygen molecule is known to be paramagnetic. The reason for this phenomenon is that in the ground state — which will be the only state considered here — a non-compensated spin exists. Of the 16 electrons present, 14 are spin-saturated, the remaining two, which are in π_g-orbitals, have parallel spins [1].

Since there is no total orbital angular momentum, the molar magnetic susceptibility according to Curie's law is given by [2]:

$$\chi_{\mathrm{mol}} = 1.00/T \ \mathrm{cm^3 mol^{-1}} \ (\mathrm{cgs}),^* \tag{1}$$

where T is the absolute temperature.

In the gaseous phase, the experimental values due to measurements of KAMERLINGH ONNES [3] agree very well with this formula, but in the liquid state the susceptibility is reduced by 30—50%; in the solid phase the reduction is even greater [4], [5]. In this paper, we restrict our attention to the liquid state.

Fig. 1 shows the molar susceptibility in the gaseous and the liquid phases (boiling point: 90.2 K; melting point: 54.3 K). The full line is the experimental χ_{mol}, the dotted curve shows the corresponding values given by Curie's law. Fig. 2 shows the relative deviation of the experimental values from Curie's law.

After the measurements carried out by KAMERLINGH ONNES several attempts were made to explain the decrease of susceptibility, but without

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[*] $\chi_{\mathrm{mol}}(S\,I)/\mathrm{m^3\,mol^{-1}} = 4\pi/10^6\, \chi_{\mathrm{mol}}(\mathrm{cgs})/\mathrm{cm^3\,mol^{-1}}$.

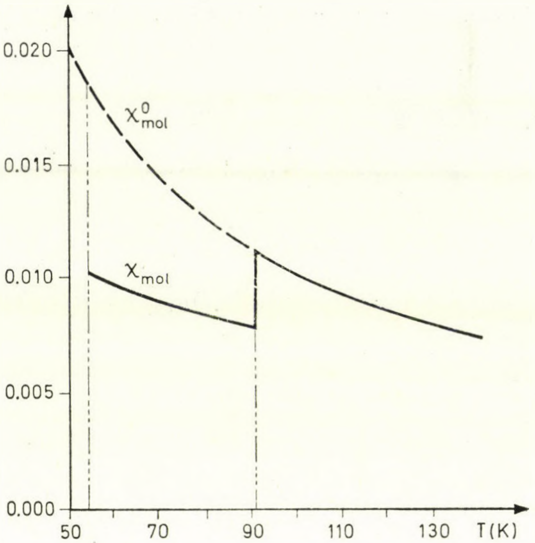

Fig. 1. Molar magnetic susceptibility of gaseous and liquid oxygen
χ_{mol}: experimental values
χ°_{mo} : susceptibility according to Curie's law

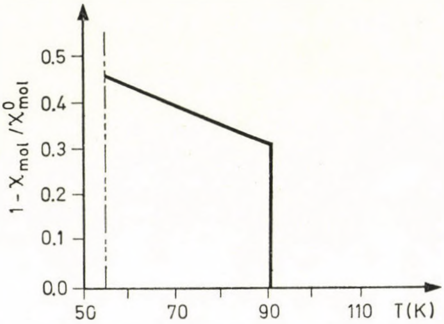

Fig. 2. Relative deviation from Curie's law in the liquid phase

success. One of the most important steps was the assumption of the existence of an O_4-molecule in the condensed states in addition to the O_2-molecules, as proposed by Lewis [6]. The spin would be saturated in the O_4-molecule, therefore the decrease of susceptibility seemed to be explained. But this was no real explanation since the existence of O_4 was only a postulate.

Knobler [7] tried to explain the reduction effect by antiferromagnetic spin exchange but was not successful.

A mathematical description of a possible decrease of susceptibility independent of the physical reason was found by Buckingham and Pople [8]. It consists in a virial expansion of χ_{mol}:

$$\chi_{\mathrm{mol}} = \frac{1.00}{T}\left[1 + \varrho_{\mathrm{mol}}\cdot\frac{L}{2}\cdot\frac{\int d^3r\cdot d\Omega\left(-\frac{2}{9}\exp(-E_s/kT)-\frac{3}{9}\exp(-E_T/kT)+\frac{5}{9}\exp(-E_Q/kT)\right)}{\int d^3r\cdot d\Omega} + \varrho_{\mathrm{mol}}^2\cdots\right], \qquad (2)$$

where L is the Avogadro constant, k is the Boltzmann constant, ϱ_{mol} the molar density, Ω symbolizes the angles for all possible relative orientations of two O_2-molecules (three angles needed), and E_S, E_T, E_Q designate the interaction potential energy of two molecules in the possible three states singlet, triplet and quintuplet, respectively (the single molecule is in the triplet state as mentioned). The first term of formula (2) is the term of Curie's law. The second term takes complexes of two O_2-molecules into account (independent of whether there exist "real" O_4-molecules or not since it is only a mathematical formalism).

The present paper is based on this formalism. The 3-, 4-... body interactions are neglected as the paper only deals with the liquid state, where specific 3-body forces are found to be comparatively small. Consideration of 2-body forces will be sufficient to clarify whether the decrease of the susceptibility can be explained qualitatively and, maybe, even quantitatively, which was not possible so far.

II. The physical reason for the decrease of susceptibility

II.1 Murrel's formalism

Now, the physical reason for the difference of E_S, E_T, E_Q has to be found. We have to study the interaction potential of two O_2-molecules at any distance and orientation. This constitutes a rather complex 32-electron problem. To simplify this problem, the 14 spin-saturated electrons of one molecule were assumed to compensate 14 charges of the nuclei (7 of each), the remaining quasi-molecule being: 2 positive charges in the distance of 1.21×10^{-10} m, as in the oxygen molecule. Two electrons with parallel spins remain in the π_g-orbitals. Thus, the interaction of two oxygen molecules is reduced to a four-electron problem, which is much easier to handle as far as the antisymmetrization rule is concerned.

With this simplified model, we can ask which part of the interaction potential is spin-dependent and, therefore, gives rise to different E_S, E_T, E_Q.

To answer this question, we follow the ideas of MURRELL [9] who used perturbation theory to expand the energy of a system of two molecules:

$$E = E_0 + E^{10} + E^{20} + E^{12} + E^{22} + \dots , \tag{3}$$

where E_0 is the energy of the ground state (two independent molecules) which is of no interest. E^{10} and E^{20} are the usual first- and second-order terms in perturbation theory which are spin-independent. The average potential is given by these terms, which was taken from the literature in this paper (LENNARD-JONES and hard-sphere potentials). E^{12} and E^{22} are exchange terms and can be derived by using the antisymmetrization rule for the electron wave functions. Both terms are spin-dependent. According to MURRELL, E^{22} is much smaller than E^{12}, and we estimated E^{22} to be negligible in the case of oxygen.

Therefore, as the interesting term remains E^{12}:

$$E^{12} = \langle \sum_{ij} P_{ij}^{+}(\psi_{\mathrm{I}}\psi_{\mathrm{II}}) \mid \psi_{\mathrm{I}}\psi_{\mathrm{II}} \rangle \cdot \langle \psi_{\mathrm{I}}\psi_{\mathrm{II}} \mid U \mid \psi_{\mathrm{I}}\psi_{\mathrm{II}} \rangle - \langle \sum_{ij} P_{ij}^{+}(\psi_{\mathrm{I}}\psi_{\mathrm{II}}) \mid U \mid \psi_{\mathrm{I}}\psi_{\mathrm{II}} \rangle . \tag{4}$$

ψ_{I} (ψ_{II}) is the wave function (including the spin component) of the first (second) molecule. 1,2: electrons of molecule I, 3,4: electrons of molecule II. U is the interaction operator which includes the attraction of the electrons of one oxygen molecule to the nuclei of the other one, as well as the electron-electron and nuclei-nuclei repulsion. P_{ij}^{+} designates the exchange of one electron of one molecule with one electron of the other molecule, e.g.:

$$P_{23}^{+}\, a(1) \cdot b(2) \cdot c(3) \cdot d(4) = a(1) \cdot b(3) \cdot c(2) \cdot d(4) , \tag{5}$$

where a, b, c, d are wave functions (including spin).

In our particular case, it is possible to separate the space and spin parts, which takes expression (4) into

$$\begin{aligned} E^{12} = {} & \langle P_{13}^{+}(\xi_{\mathrm{I}}\xi_{\mathrm{II}}) \mid \xi_{\mathrm{I}}\xi_{\mathrm{II}} \rangle \times \{ S_{00}^{+} \cdot \langle \varphi_{\mathrm{I}}\varphi_{\mathrm{II}} \mid U \mid \varphi_{\mathrm{I}}\varphi_{\mathrm{II}} \rangle - \\ & - \langle \sum_{ij} P_{ij}^{+}(\varphi_{\mathrm{I}}\varphi_{\mathrm{II}}) \mid U \mid \varphi_{\mathrm{I}}\varphi_{\mathrm{II}} \rangle \} \doteq \langle P_{13}^{+}(\xi_{\mathrm{I}}\xi_{\mathrm{II}}) \mid \xi_{\mathrm{I}}\xi_{\mathrm{II}} \rangle \cdot A . \end{aligned} \tag{6}$$

where

$$S_{00}^{+} = \langle \sum_{ij} P_{ij}^{+}(\varphi_{\mathrm{I}}\varphi_{\mathrm{II}}) \mid \varphi_{\mathrm{I}}\varphi_{\mathrm{II}} \rangle . \tag{6a}$$

Here, φ is the spatial part of the wave function, and ξ is the spin part. The first term of (6) is exclusively spin-dependent, whereas the exchange energy A is not spin-dependent.

Orthogonalizing the spin-dependent term leads to

$$E^{12}(S) = -A/2, \quad E^{12}(T) = 0, \quad E^{12}(Q) = +A\,. \tag{7}$$

Therefore, the energies needed to use the Buckingham-formalism (2) are:

$$\begin{aligned} E &= E^{10} + E^{20} - A/2\,,\\ E &= E^{10} + E^{20}\,,\\ E &= E^{10} + E^{20} + A\,. \end{aligned} \tag{8}$$

The remaining problem is the determination of the exchange energy A. Therefore, the explanation of the reduction of susceptibility leads to the calculation of the exchange energy A — a completely non-magnetic problem.

II.2. The calculation of the exchange energy

For the calculation of A we need the spatial wave function of the electrons in the π_g-orbitals. These orbitals are taken as a linear combination of the atomic $p_{x,y}$-orbitals. The formulae for the $p_{x,y}$-functions have been taken from TUTIHASI [10] and are given by

$$\begin{Bmatrix} p_x \\ p_y \end{Bmatrix} = r \cdot [9.62 \exp(-3.16\, r) + 1.47 \exp(-1.32\, r)] \cdot$$

$$\cdot \sqrt{3/4\pi} \cdot \sin\theta \cdot \begin{Bmatrix} \cos\varphi \\ \sin\varphi \end{Bmatrix}, \tag{9}$$

where r, θ, φ are spherical coordinates (with the z-axis as the symmetry axis of the O_2-molecule). r is measured in a.u. $= 5.292 \times 10^{-11}$ m. (9) represents an analytical fit to SCF-results (self consistent field-method).

Now, we should be able to calculate A, but this problem still seems to be too complicated. MURRELL [9] has shown that, in the case of H—H and C—C interaction, A can be reduced to

$$A = k \cdot \frac{S^2(R)}{R}\,, \tag{10}$$

where $S(R)$ is the overlap integral $\int d^3r_1 \varphi(1)\, \overline{\varphi}(1)$; $\varphi, \overline{\varphi}$ are spatial wave functions around centres at a distance R in a.u.). If the energy is expressed in Hartree units (4.36×10^{-18} J), k turns out to be of the order of 1 in the cases studied by MURRELL.

The case of oxygen is much more complicated, since there are now two electrons of each molecule overlapping, and the molecules are not spherically symmetric. Replacing S^2 by S_{00}^+ (defined in Eq. (6a)) takes this fact into account. S_{00}^+ depends on the distance of the 2 molecules and on the relative orientation.

The author [11] found out that, in good approximation, the following formula holds:

$$A = k \cdot \frac{S_{00}^+}{R}. \tag{11}$$

S_{00}^+ can be expressed analytically by the distance and the relative orientation of the oxygen molecules. Therefore, the remaining problem is to determine k. This was done by computer and found out to be $+1.8 \pm 0.5$. The inaccuracy derives from the reduction of 3- and 4-centre integrals to 2-centre integrals and from the fact that the remaining terms, which had to be subtracted from each other, had almost equal values.

II.3. Spin-independent interaction potential

The spin-independent interaction potential was taken from the literature, i.e. a LENNARD-JONES potential (spherically symmetric) with $\varepsilon = 115$ K (1.59×10^{-21} J) and $\sigma = 3.46 \times 10^{-10}$ m was chosen [12], [13].

To assess whether the angular dependence of the interaction has to be taken into account, a realistic angular dependence according to CORNER [14]

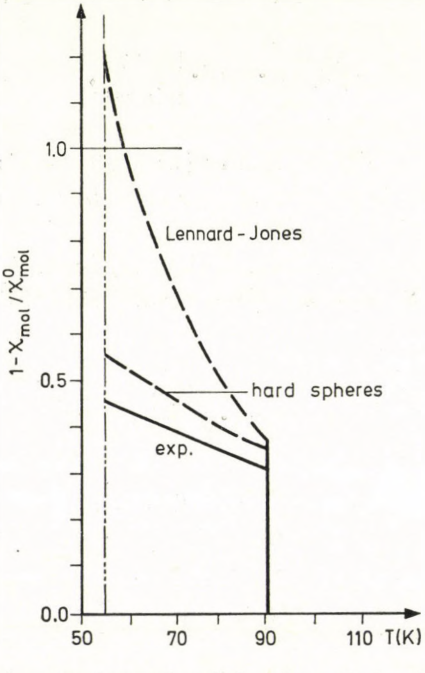

Fig. 3. Comparison of the experimental and the theoretical values of $(1 - \chi_{\mathrm{mol}}/\chi^{\circ}_{\mathrm{mol}})$

was used. However, the difference between these results and those obtained with the symmetric potential turned out to be minimal so that this more complicated potential was no longer used. We also made use of a model potential, i.e. the hard-sphere potential with $\sigma = 3.46 \times 10^{-10}$ m (point of zero value of the LENNARD-JONES potential used).

III. Results

Taking into account the potentials mentioned, the decrease of the susceptibility according to the BUCKINGHAM formalism (2) was determined (Fig. 3). There is really a decrease of susceptibility, and even greater than that measured. In the vicinity of the boiling point, the results are rather good. Interestingly enough, the hard-sphere potential gives better results than the LENNARD-JONES potential. The neglect of the 3-body forces seems to make the values too high, which is in accordance with results of MCMAHAN, GUYER [15]. Summarizing, we can say that the decrease of the susceptibility of oxygen in the liquid state could be explained, but an improvement of the accuracy would be highly desirable.

The critical point was considered, too, the result for the relative decrease being 0.0595 (LENNARD-JONES) and 0.0850 (hard spheres), respectively. These are reference values without consideration of any special critical phenomenon. The corresponding experiment is being done at the I. Physikalisches Institut der Universität Wien.

*

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LITERATURE

1. J. SLATER, Quantum Theory of Molecules, Vol. 1, p. 117, 1963.
2. J. VAN VLECK, The Theory of Electric and Magnetic Susceptibilities, p. 266, 1932.
3. A. PERRIER and H. KAMERLINGH ONNES, Comm. Leiden Nr. 139 c, d, 1914.
4. E. KANDA et al., Sci. Repts. Res. Inst. Tohoku Univ., A7, Nr. 1, 1955.
5. H. JAMIESON and A. HOLLIS HALLET, Proc. 10th Conf. on Low Temperature Physics, Moscow, 1966.
6. G. LEWIS, J. Am. Chem. Soc., **46**, 2027, 1924.
7. C. KNOBLER, Thesis, Leiden, 1961.
8. A. BUCKINGHAM and J. POPLE, Disc. Faraday Soc., **22**, 17, 1956.
9. J. MURRELL et al., Proc. Roy. Soc. (London), A **284**, 566, 1965.
10. S. TUTIHASI, J. Phys. Soc. Jap., **3**, 135, 1948.
11. K. KRATKY, Doctoral Thesis, Vienna, 1974.
12. H. JOHNSTON, J. Chem. Phys. **44**, 1038, 1940.
13. D. NEWITT, Design of High Pressure Plant and Properties of Fluids at High Pressures, 1940.
14. J. CORNER, Proc. Roy. Soc. (London), **192**, 275, 1948.
15. A. MCMAHAN and R. GUYER, Phys. Rev. A7, 1105, 1973.

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UNSTEADY FLOW OF A DUSTY VISCOUS LIQUID IN A ROTATING CHANNEL

By

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The unsteady flow of a dusty viscous liquid in a parallel plate channel rotating with an angular velocity Ω is analysed. Analytical expressions for the velocities of the liquid and the dust particles are obtained. These expressions contain two parameters: the dimensionless decay factor λ and K^2 which is the reciprocal of the Ekman number. The effects of these parameters on the velocity distributions are studied.

Introduction

Saffman [1] has discussed the stability of the laminar flow of a dusty gas in which the dust particles are uniformly distributed. He has assumed that the dust particles are uniform in size and shape and the bulk concentration of the dust is very small to be neglected. On the other hand the density of the dust material is large compared with the gas density so that the mass concentration of dust is an appreciable fraction of unity. Michael [2] has investigated the Kelvin–Helmholtz instability of the dusty gas. Rao [3] has discussed the unsteady laminar flow of a dusty viscous liquid under the influence of exponential pressure gradient through a circular cylinder.

In the present paper we consider the unsteady flow of a dusty viscous liquid confined between two parallel infinite walls rotating with an angular velocity Ω about an axis perpendicular to their planes. Exact solutions of the governing equations are obtained in closed form. There are two parameters involved, viz. λ which is a dimensionless decay factor and $K^2 = \dfrac{\Omega z_0^2}{\nu}$ which is the ratio of Coriolis and viscous forces. Velocity profiles for small and large values of these parameters have been drawn.

The importance of the study of fluid flow problems taking into account the simultaneous effects of dust and Coriolis force lies in their application in many fields of interest. Therefore it is desirable to study their effects in specific flow problems.

1. Equations of motion

The equations of motion and continuity in a rotating frame of reference for a viscous incompressible fluid with uniform distribution of dust particles are given by

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u}\cdot\nabla)\,\mathbf{u} + 2\mathbf{\Omega}\times\mathbf{u} = -\frac{1}{\varrho}\operatorname{grad} p + \nu\nabla^2\mathbf{u} + \frac{K'N_0}{\varrho}(\mathbf{v}-\mathbf{u}), \tag{1.1}$$

$$m\left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\,\mathbf{v} + 2\mathbf{\Omega}\times\mathbf{v}\right] = K'(\mathbf{u}-\mathbf{v}), \tag{1.2}$$

$$\operatorname{div}\mathbf{u} = 0, \tag{1.3}$$

$$\operatorname{div}\mathbf{v} = 0. \tag{1.4}$$

In these equations $\mathbf{u}$, $\mathbf{v}$ are velocities of liquid and dust particles, respectively, $\mathbf{\Omega}$ is the angular velocity of the system (consisting of the plates and the dusty liquid) referred to a fixed inertial frame and $p = p' - \frac{\varrho}{2}|\mathbf{\Omega}\times\mathbf{r}|^2$, p' denoting the fluid pressure and $\mathbf{r}$ denoting the position vector from the axis of rotation, m the mass of a dust particle, K' the Stokes resistance coefficient which for spherical particles of radius ε is $6\pi\mu\varepsilon$, μ being the viscosity of the liquid, N_0 the number density of dust particles which is a constant throughout the motion, ν, ϱ are respectively the kinematic coefficient of viscosity and density of the liquid.

We choose a cartesian system such that z-axis is perpendicular to the plates, $z = \pm z_0$. The x-axis is in the direction of the pressure gradient. For simplicity the angular velocity is taken to be parallel to the z-axis. Since the plates are infinite in the x and y-directions, the fields set up for the unsteady state will depend only on z and t.

The velocities $\mathbf{u}$, $\mathbf{v}$ may reasonably be assumed as

$$\mathbf{u} = (u_1, u_2, 0), \tag{1.5}$$

$$\mathbf{v} = (v_1, v_2, 0). \tag{1.6}$$

The equations of motion then reduce to

$$\frac{\partial u_1}{\partial t} - 2\Omega\, u_2 = -\frac{1}{\varrho}\frac{\partial p}{\partial x} + \nu\frac{\partial^2 u_1}{\partial z^2} + \frac{K'N_0}{\varrho}(v_1 - u_1), \tag{1.7}$$

$$\frac{\partial u_2}{\partial t} + 2\Omega\, u_1 = -\frac{1}{\varrho}\frac{\partial p}{\partial y} + \nu\frac{\partial^2 u_2}{\partial z^2} + \frac{K'N_0}{\varrho}(v_2 - u_2), \tag{1.8}$$

$$0 = -\frac{1}{\varrho}\frac{\partial p}{\partial z}, \tag{1.9}$$

$$m\left[\frac{\partial v_1}{\partial t} - 2\Omega\, v_2\right] = K'(u_1 - v_1), \tag{1.10}$$

$$m\left[\frac{\partial v_2}{\partial t} + 2\Omega\, v_1\right] = K'(u_2 - v_2). \tag{1.11}$$

Eqs. (1.3) and (1.4) are identically satisfied and Eq. (1.9) shows the constancy of the fluid dynamic pressure along the axis of rotation. We shall assume now that the fluid flows under the influence of exponential pressure gradient in the direction of the x-axis between the parallel plates, $z = \pm z_0$. The boundary conditions to be satisfied are

$$z = \pm z_0\colon\ u_1 = 0,\ u_2 = 0;\ v_1 = 0,\ v_2 = 0. \tag{1.12}$$

We now make Eqs. (1.7), (1.8), (1.10) and (1.11) dimensionless by introducing the following non-dimensional quantities:

$$\bar{x} = \frac{x}{z_0},\ \bar{z} = \frac{z}{z_0},\ \bar{u}_1 = \frac{u_1 z_0}{\nu},\ \bar{u}_2 = \frac{u_2 z_0}{\nu},\ \bar{v}_1 = \frac{v_1 z_0}{\nu},$$

$$\bar{v}_2 = \frac{v_2 z_0}{\nu},\ \bar{p} = \frac{p z_0^2}{p \nu^2},\ K^2 = \frac{\Omega z_0^2}{\nu},\ c = \frac{m N_0}{\varrho},\ \sigma = \frac{m\nu}{K' z_0^2},$$

$$\bar{t} = \frac{\nu t}{z_0^2},\ \bar{\lambda} = \frac{\lambda z_0^2}{\nu}.$$

After dropping the bars, Eqs. (1.7), (1.8), (1.10) and (1.11) become

$$\frac{\partial q_1}{\partial t} + 2\,iK^2 q_1 = -\frac{\partial p}{\partial x} + \frac{\partial^2 q_1}{\partial z^2} + \frac{c}{\sigma}(q_2 - q_1), \tag{1.13}$$

$$\frac{\partial q_2}{\partial t} + 2\,iK^2 q_2 = \frac{1}{\sigma}(q_1 - q_2), \tag{1.14}$$

where $q_1 = u_1 + iu_2$ and $q_2 = v_1 + iv_2$.

The boundary conditions then reduce to

$$z = \pm 1,\ q_1 = 0,\ q_2 = 0. \tag{1.15}$$

We now assume that

$$-\frac{\partial p}{\partial x} = e^{-\lambda t}. \tag{1.16}$$

In view of (1.16), we can express

$$q_1 = f(z)\, e^{-\lambda t}. \tag{1.17}$$

Substituting (1.16), (1.17) in (1.13) and solving that using the boundary conditions $f(\pm 1) = 0$, we get

$$q_1 = \frac{1}{\alpha^2}\left(\frac{\cos \alpha z}{\cos \alpha} - 1\right) e^{-\lambda t}, \tag{1.18}$$

where

$$\alpha^2 = \frac{(\lambda - 2\, iK^2)\left[(1 + c) - \sigma\lambda + 2\, iK^2\sigma\right]}{(1 - \sigma\lambda) + 2\, iK^2\sigma}.$$

Eq. (1.14) then gives

$$q_2 = \frac{[1 - \sigma\lambda - 2\, iK^2\sigma]}{(1 - \sigma\lambda)^2 + 4\, K^4\sigma^2} \cdot \frac{1}{\alpha^2}\left(\frac{\cos \alpha z}{\cos \alpha} - 1\right) e^{-\lambda t}. \tag{1.19}$$

Separating real and imaginary parts in (1.18), we get

$$u_1 = \left[\frac{(A^2 - B^2)\, P - 2\, ABQ}{(A^2 + B^2)^2\, R} - \frac{(A^2 - B^2)}{(A^2 + B^2)^2}\right] e^{-\lambda t}, \tag{1.20}$$

$$u_2 = \left[\frac{(A^2 - B^2)\, Q + 2\, ABP}{(A^2 + B^2)^2\, R} - \frac{2\, AB}{(A^2 + B^2)^2}\right] e^{-\lambda t}, \tag{1.21}$$

where

$$\begin{aligned}
P &= \cos A \cos hB \cos Az \cos hBz + \sin A \sin hB \sin Az \sin hBz,\\
Q &= \cos A \cos hB \sin Az \sin hBz - \sin A \sin hB \cos Az \cos hBz.\\
R &= \cos^2 A \cos h^2 B + \sin^2 A \sin h^2 B,\\
TA &= \alpha_1(\beta_1\gamma_1 + \beta_2\gamma_2) - \alpha_2(\beta_1\gamma_2 - \beta_2\gamma_1),\\
TB &= \alpha_1(\beta_1\gamma_2 - \beta_2\gamma_1) + \alpha_2(\beta_1\gamma_1 + \beta_2\gamma_2),\\
T^2 &= (1 - \sigma\lambda)^2 + 4K^4\sigma^2,\\
\sqrt{2}\,\alpha_1 &= \left[\lambda + \sqrt{\lambda^2 + 4\, K^4}\,\right]^{1/2},\\
\sqrt{2}\,\alpha_2 &= \left[-\lambda + \sqrt{\lambda^2 + 4\, K^4}\,\right]^{1/2},\\
\sqrt{2}\,\beta_1 &= \left[(1 + c) - \sigma\lambda + \sqrt{\{(1 + c) - \sigma\lambda\}^2 + 4\, K^4\sigma^2}\,\right]^{1/2},\\
\sqrt{2}\,\beta_2 &= \left[\sigma\lambda - (1 + c) + \sqrt{\{(1 + c) - \sigma\lambda\}^2 + 4\, K^4\sigma^2}\,\right]^{1/2},\\
\sqrt{2}\,\gamma_1 &= \left[1 - \sigma\lambda + \sqrt{(1 - \sigma\lambda)^2 + 4\, K^4\sigma^2}\,\right]^{1/2},\\
\sqrt{2}\,\gamma_2 &= \left[\sigma\lambda - 1 + \sqrt{(1 - \sigma\lambda)^2 + 4\, K^4\sigma^2}\,\right]^{1/2}.
\end{aligned} \tag{1.22}$$

From (1.19), we get

$$v_1 = \frac{(1 - \sigma\lambda)\, u_1 + 2\, K^2 \sigma u_2}{T^2}\,, \tag{1.23}$$

$$v_2 = \frac{(1 - \sigma\lambda)\, u_2 - 2K^2 \sigma u_1}{T^2}\,. \tag{1.24}$$

2. Discussion

Typical non-dimensional velocity profiles are shown in Figs. 1 to 12 when $c = 0.2$, $\sigma = 0.8$ and $t = 1$.

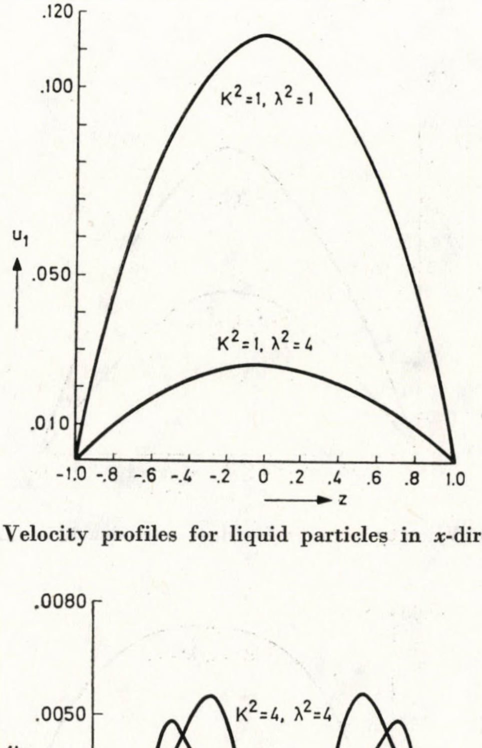

Fig. 1. Velocity profiles for liquid particles in x-direction

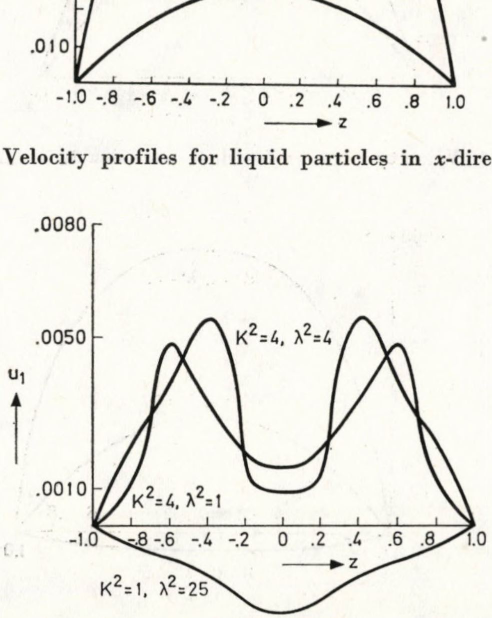

Fig. 2. Velocity profiles for liquid particles in x-direction

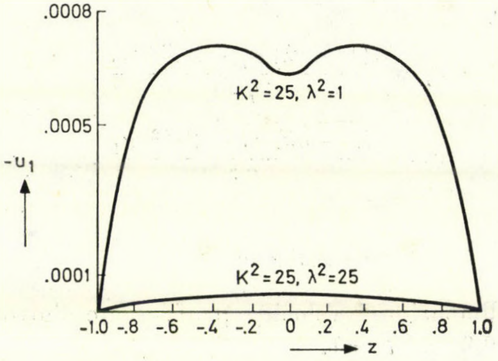

Fig. 3. Velocity profiles for liquid particles in x-direction

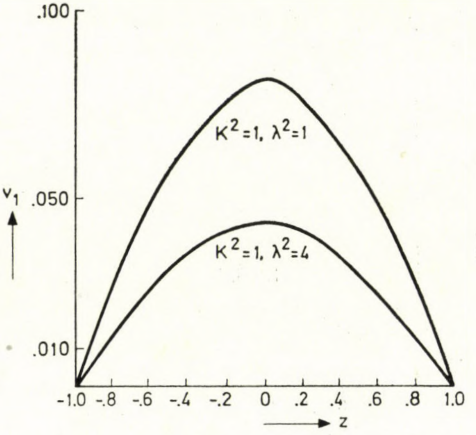

Fig. 4. Velocity profiles for dust particles in x-direction

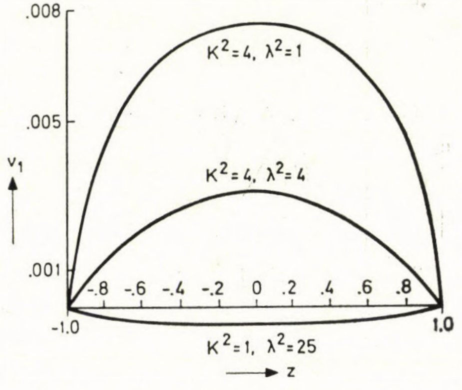

Fig. 5. Velocity profiles for dust particles in x-direction

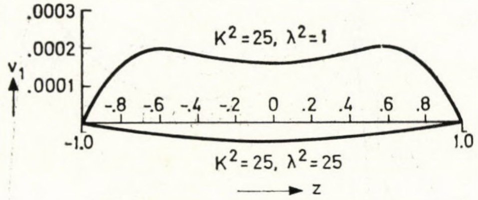

Fig. 6. Velocity profiles for dust particles in x-direction

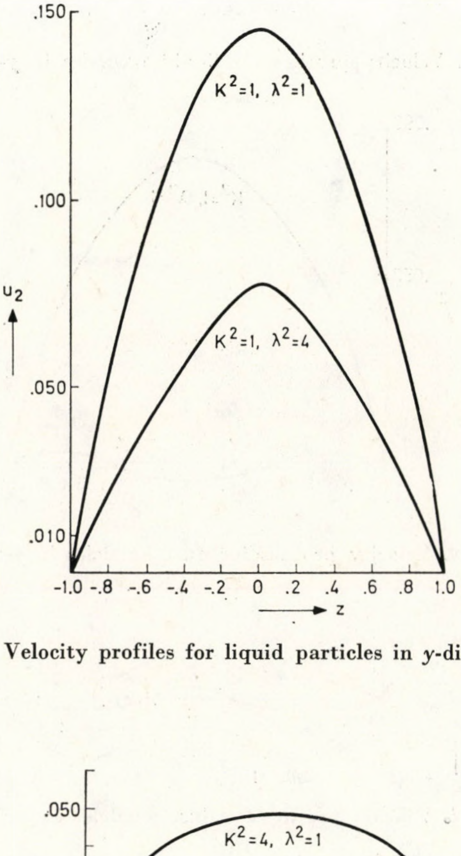

Fig. 7. Velocity profiles for liquid particles in y-direction

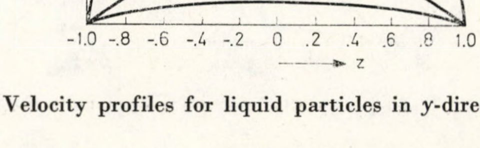

Fig. 8. Velocity profiles for liquid particles in y-direction

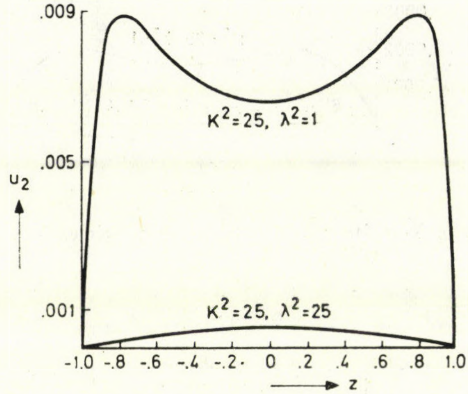

Fig. 9. **Velocity profiles for liquid particles in *y*-direction**

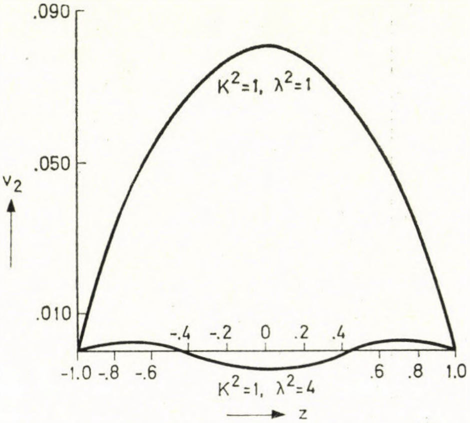

Fig. 10. **Velocity profiles for dust particles in *y*-direction**

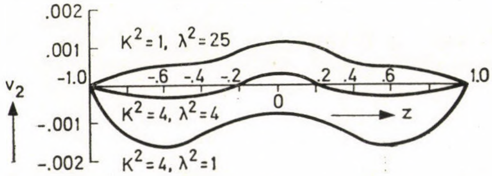

Fig. 11. **Velocity profiles for dust particles in *y*-direction**

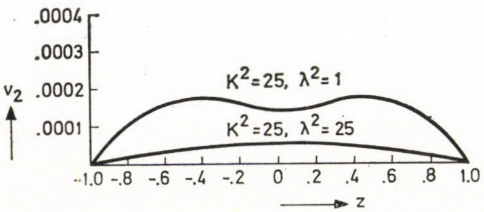

Fig. 12. **Velocity profiles for dust particles in *y*-direction**

Consider first the velocity profiles of the liquid and the dust particles in the direction of the pressure gradient. We observe the following points:

(i) Figs. 1 and 2 show that for small values of K^2 and λ^2, the velocity profiles for liquid particles are nearly parabolic, the maximum of u_1 occurring at the centre. From these two Figures we also note that for small K^2, u_1 decreases as λ^2 increases and after λ^2 exceeds a certain critical value λ_c^2, say, flow is reversed.

(ii) Figs. 2 and 3 show that for small values of λ^2, the maximum of u_1 no longer occurs at the centre as we increase K^2, but is shifted towards the walls. These two Figures also show the oscillatory character of u_1 for large K^2 and small λ^2. From Figs. 2 and 3 we also note that for large K^2, u_1 decreases with the increase of λ^2 and after λ^2 exceeds a certain critical value, flow is reversed.

(iii) Figs. 4 and 5 show that for small K^2, v_1 decreases with the decrease of λ^2 and after λ^2 crosses a certain critical value, flow is reversed. We also note from these two Figures that for small values of K^2 and λ^2, the velocity profiles for dust particles are nearly parabolic. From Fig. 6 we observe that for large values of K^2, v_1 decreases as λ^2 decreases and flow is reversed after λ^2 crosses a certain critical value.

From the above discussion it is clear that the motion of the liquid particles in the positive direction of the x-axis does not imply that the dust particles also move in that direction. This difference is due to the fact that the pressure gradient is directly exerted on the fluid, then the dust particle is moved by Stokes drag due to the difference between the velocities of fluid and dust.

Let us consider now the velocity profiles of the secondary flow of the liquid and dust particles.

(iv) Figs. 7, 8 and 9 show that the profiles for u_2 always increase when both K^2 and λ^2 increase. The shapes of the profiles are similar to those of u_1 for small values of K^2 and λ^2. The profiles for u_2 never cut the axis of rotation (at least for values of K^2 and λ^2 considered), thereby discounting the possibility of flow reversal in the y-direction. From Fig. 9 we also see the oscillatory character of the profiles for u_2 when K^2 is large and λ^2 is small.

(v) Fig. 10 shows that the profiles for dust particles v_2 are nearly parabolic for small values of K^2 and λ^2. For small K^2, the oscillatory character of v_2 is clearly evident from this Figure when we increase λ^2. These oscillations cause reversal of the velocity.

(vi) For large K^2 and λ^2, the oscillatory character of the flow is again evident from the Figs. 11 and 12 and due to these oscillations there is a reversal of flow.

From the above discussion we note that the liquid particles will move in the negative direction of the y-axis (at least for values of K^2 and λ^2 considered) whereas the dust particles will move in both the directions of the y-axis.

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REFERENCES

1. P. G. Saffman, J. Fluid Mech., **13,** 120, 1962.
2. D. H. Michael, Proc. Camb. Phil. Soc., **61,** 569, 1965.
3. P. S. S. Rao, Defence Sci. J., **19,** 135, 1969.

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A GENERALIZATION OF THE KLEIN—GORDON EQUATION

By

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The Einstein—Maxwell Lagrangian is completed by a highly non-linear term describing a scalar particle. By means of the usual variation technique the coupled equations of motion are obtained for the particle as well as for electromagnetic and gravitation fields.

Introduction

Einstein's general theory of relativity was the first essentially non-linear theory which registered enormous success in describing numerous macroscopic phenomena. Nevertheless, its application to microphysics is full of difficulties [1]. We do not intend to solve these problems here, merely we wish to indicate that the field equations describing elementary particles are probably non-linear, too. In the present paper an example is given of how a spin-zero particle can be described by a simple non-linear term in the presence of gravitation and electromagnetic fields. From the Lagrangian the coupled Maxwell—Einstein equations and the field equation for the particle are obtained. Maxwell equations contain a slightly more complicated current density which can be derived from the familiar Klein—Gordon equation. The presence of the matter is exhibited by a contribution to the energy-momentum tensor on the right hand side of the Einstein equations. The particle field satisfies a highly non-linear equation coupled to the electromagnetic and gravitation fields through the vector potential and the metric tensor, respectively.

The Lagrangian

The electromagnetic and gravitation fields are described by the familiar Lagrangians. The total Lagrangian investigated in the present paper has the form:

$$L = \frac{c^4}{16\,\pi\gamma} R + \frac{1}{4\,\mu_0} F_{ts} F^{ts} - c\sqrt{-\,\psi\psi^*\, a^t a_t^*}. \tag{1}$$

(Here R is the scalar curvature

F_{ik} is the electromagnetic field tensor: $\mu_0(A_{k;\,i} - A_{i;\,k})$

ψ is a generalized wave function

$$a_i = \frac{\hbar}{i}\,\psi_{;\,i} - \mu_0 e \psi A_i$$

$*$ stands for complex conjugation.)

It can be established that L is a real scalar.

The action is: $s = \iiiint L \sqrt{-g}\; dX$.

The first variation of s must be set equal to zero. This action can be varied with respect to A_i, g_{ik}, ψ (or ψ^*).

Field equations

The equation obtained by the variation of ψ^* has the following form:

$$\sqrt{\frac{\psi\psi^*}{-a^t a_t^*}}\left(\frac{\hbar}{i}\nabla_i - \mu_0 e A_i\right)\left[\sqrt{\frac{\psi\psi^*}{-a^r a_r^*}}\left(\frac{\hbar}{i}\nabla^i - \mu_0 e A^i\right)\psi\right] = \psi\,. \tag{2}$$

The result of the variation of the vector potential is the Maxwell equation:

$$\frac{1}{\mu_0} F^t_{i;\,t} = ce\sqrt{\frac{\psi\psi^*}{-a^t a_t^*}}\left[\frac{\hbar}{2i}\left(\psi^*\psi_{;i} - \psi\psi^*_{;i}\right) - \mu_0 e \psi\psi^* A_i\right]. \tag{3}$$

The variation of g_{ik} results in the Einstein equations:

$$-\frac{c^4}{8\pi\gamma}\left(R_{ik} - \frac{1}{2} g_{ik} R\right) = \frac{1}{\mu_0} F_{it} F_k^t - \frac{1}{4\mu_0} F_{ts} F^{ts} g_{ik} +$$

$$+ c\sqrt{-\psi\psi^* a^t a_t^*}\, g_{ik} + \frac{c}{2}\sqrt{\frac{\psi\psi^*}{-a^t a_t^*}}\left(a_i a_k^* + a_k a_i^*\right). \tag{4}$$

Eq. (2) looks like the familiar covariant wave equation of a spin-zero particle, however, the operator $\frac{1}{mc}\left(\frac{\hbar}{i}\nabla_i - \mu_0 e A_i\right)$ is replaced by $\sqrt{\frac{\psi\psi^*}{-a^t a_t^*}}$ $\left(\frac{\hbar}{i}\nabla_i - \mu_0 e A_i\right)$.

For the interpretation of Eqs. (2) and (3) let us consider them under the following conditions:

$$\psi = \varphi(x^1, x^2, x^3)\;\exp\left[\frac{i}{\hbar}\left(mc + \mu_0 e A_4\right) x^4\right],$$

$$\frac{\partial m}{\partial x^i} = 0\,,\quad \frac{\partial A_4}{\partial x^4} = 0\,,\quad (g^{ik}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}.$$

Apart from the factor $mc\sqrt{\frac{\psi\psi^*}{-a^t a_t^*}}$ Eq. (2) reduces to the covariant Klein–Gordon equation, and the formula (3) has now the form

$$\frac{1}{\mu_0} F^t_{4\,;t} \cong ce\,\psi\psi^*\,,$$

$$\frac{1}{\mu_0} F^t_{\alpha\,;t} \cong \frac{e}{m}\left[\frac{\hbar}{i}\left(\psi^*\psi_{;\alpha} - \psi\psi^*_{;\alpha}\right) - \mu_0 e\,\psi\psi^* A_\alpha\right],$$

(here $\alpha = 1, 2, 3$). This current density is identical to that well known from quantum mechanics.

It is worth mentioning that the current conservation can be derived from Eqs. (2) and (3).

Finally, we mention that the Lagrangian could be modified instead of $\sqrt{-\psi\psi^* a^t a_t^*}$, by the expression

$$\sqrt{-\psi\psi^*\,a^t a_t^*}\;F\left[\frac{\psi\psi^*\,a^s a_s^*}{\varrho^r \varrho_r}\right]$$

too, where

$$\varrho_i = \frac{\hbar}{2i}\left(\psi^*\psi_{;i} - \psi\psi^*_{;i}\right) - \mu_0 e\,\psi\psi^* A_i\,,$$

and F is an arbitrary function.

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REFERENCE

1. ABDUS SALAM, Impact of Quantum Gravity Theory on Particle Physics, Preprint ICTP, 1974.

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ANGULAR FORCES AND NORMAL VIBRATIONS IN NIOBIUM AND TANTALUM: I

By

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The angular force model proposed by Clark, Gazis and Wallis [2] is taken into account to incorporate the effect of electron—ion interaction term from Krebs [11] model. The model thus obtained is applied to compute the phonon dispersion curves for normal modes of vibration in Niobium and Tantalum along three principal symmetry directions and it is found that it gives an excellent agreement with the experimental neutron scattering data.

I. Introduction

Angular forces were introduced for the study of lattice dynamical properties long ago by **Born** [1] in his study of the diamond structure. Later on, **Clark** et al. [2] and **de Launay** [3] proposed their angular force models (known as CGW and DAF models, respectively) to explain the Cauchy discrepancy in cubic metals. **Clark** et al. have studied the lattice dynamics of iron and vanadium (bcc) and later the same process was extended for the study of copper (fcc) by **Yuen** and **Varshni** [4]. A similar calculation for copper with **de Launay** type angular forces was also made by **Yuen** and **Varshni** [5].

Quite recently, **Bihari** and **Tripathi** [6, 7] suggested a modification of the CGW and DAF angular force models by incorporating the effect of conduction electrons on lattice dynamics of metals in a manner outlined by results as compared to those given by DAF model for fcc structure. However. both models give almost the same results for bcc metals (**Bose** et al. [10]), But the major shortcoming of these approaches is that they violate the symmetry requirements in the sense that frequencies obtained are not periodic in the reciprocal space. To overcome such a difficulty, it is worththile to incorporate the effect of electron—ion interaction on lattice dynamics of metals as proposed by **Krebs** [11] which is superior to other models (**de Launay** [12], **Bhatia** [13], **Bhatia** and **Horton** [14], **Sharma** and **Joshi** [8, 9]) in the sense that frequencies given by it satisfy the symmetry requirements of cubic lattices and has been employed successfully for the study of lattice dynamical properties of a number of cubic metals (**Shukla** and **Dayal** [15], **Mahesh** and **Dayal** [16], **Singh** and **Sharma** [17], **Pal** and **Singh** [18]).

In the present paper, we have made a detailed study of the phonon dispersion of two representative elements of transition group, namely Niobium and Tantalum, by taking into account the effect of conduction electrons on lattice vibration in the same way as outlined in KREBS [11] model. Total interaction governing the lattice vibrations has been considered to consist of three parts: (i) the ion—ion central interaction depending on the distance between the ions, (ii) the angular interaction (CLARK et al. [2]), which arises due to the resistance to deformation of certain angles formed by the ions in question and (iii) an electron—ion interaction term (KREBS [11]) that is introduced because of the presence of conduction electrons in metals. The central and angular interactions are assumed to be effective only up to second neighbours. An independent stimulus to the present study was imparted by the availability of a detailed picture of phonon frequencies along principal symmetry directions obtained from the latest neutron scattering experiments.

II. Theoretical formulation

Proceeding in the usual way the secular determinant for frequencies may be written as

$$| D(q) - \prod^{2} \nu^2 m I | = 0 , \tag{1}$$

where q is the phonon wave vector, ν is the frequency, m is the mass of the ion, and I is a unit matrix of order three. There will be nine elements D_{ij} $(i, j = 1, 2, 3)$ of the (3×3) dynamical matrix D, and each of these elements can be represented as the sum of the three interaction terms, as explained above. The expressions for two typical elements are given below; the expressions for the remaining elements can be derived in cyclic order from them:

$$\begin{aligned} D_{ii}(q) = {} & 8(\alpha + 2\gamma_1 + \gamma_2)(1 - C_i C_j C_k) + 4\beta S_i^2 - 2\gamma_1 \\ & (4 \cos a_{qi} - \cos a_{qj} - \cos a_{qk} - 2) + 3\gamma_2 \ \ (2 - \cos a_{qj} - \cos a_{qk}) \\ & + A \sum_G \left[\frac{(q+G)_i (q+G)_i}{|q+G|^2 + k_c^2} \cdot g^2(|q+G| r_s) \right. \\ & \left. - \frac{G_i G_i}{|G|^2 + k_c^2} \cdot g^2(|G| r_s) \right], \end{aligned}$$

$$\begin{aligned} D_{ij}(q) = {} & 8\left(\alpha - \gamma_1 + \frac{3}{2}\gamma_2\right) S_i S_j S_k \\ & + A \sum_G \left[\frac{(q+G)_i (q+G)_j}{|q+G|^2 + k_c^2} \cdot g^2(|q+G| r_s) \right. \\ & \left. - \frac{G_i G_j}{|G|^2 + k_c^2} \cdot g^2(|G| r_s) \right], \end{aligned} \tag{2}$$

where

$$C_i = \cos\left(\frac{1}{2}\, a_{qi}\right), \quad S_i = \sin\left(\frac{1}{2}\, a_{qi}\right), \quad g(x) = \frac{3(\sin x - x\cos x)}{x^3}$$

and q_i is the ith cartesian component of the phonon wave vector q, G is the reciprocal lattice vector, a is the lattice constant, r_s is the radius of a sphere of atomic volume, k_c is the screening parameter, A is a constant which depends on the effective charge of the ions, α and β are the force constants associated with the central forces between nearest and next nearest neighbours, and γ_1 and γ_2 are the corresponding ones for the angular interaction.

The screening parameter k_c as obtained by PINES [19] is

$$K_c = 0.253\left(\frac{3}{4\pi\, n_e\, a_0^3}\right)^{1/6} \cdot k_F\,,$$

where n_e is the electron density, a_0 the Bohr radius, and k_F the Fermi radius.

The five unknown (α, β, γ_1, γ_2, and A) involved in the solution of Eq. (1) are determined by expanding the element of the determinant in the long-wave length limit and relating it to the three elastic constants and two zone boundary frequencies (ν_{T_1} and ν_{T_2} both transverse) in [ξ00] and [$\xi\xi\xi$] directions, respectively. The resulting expressions are

$$aC_{11} = 2\alpha + 2\beta + 12\gamma_1 + 6\gamma_2 + \frac{2A}{a^2k_c^2}\,, \tag{3a}$$

$$a(C_{11} - C_{12}) = 2\beta + 18\gamma_1 + 9\gamma_2\,, \tag{3b}$$

$$aC_{44} = 2\alpha + 2\gamma_1 + 9\gamma_2\,, \tag{3c}$$

$$\overset{2}{\Pi}\, m\nu_{T_1}^2 = 4(\alpha + 2\gamma_1 + 3\gamma_2)\,, \tag{3d}$$

$$\overset{2}{\Pi}\, m\nu^2{}_{T_2} = 2\alpha + \beta + 6\gamma_1 + 9\gamma_2\,. \tag{3e}$$

It is evident from above equations that our expression for the Cauchy discrepancy ($C_{12} - C_{44}$), which arises because of non-central interactions (FUCHS 20]), contains terms due to angular (ion—ion) and volume (electron—ion) forces only. Various parameters and the calculated values of force constants are shown in Table I.

III. Results and discussion

The computed phonon frequencies, obtained from the solution of secular equation (1) along principal symmetry directions [ξ00], [$\xi\xi$0] and [$\xi\xi\xi$] of two representative elements of transition group, namely the Niobium and

Table I

Constants and calculated parameters for Niobium and Tantalum

Conntstas/parameters (calculated)	Niobium	Tantalum
(10^{11} dyn/cm^2) C_{11}	24.6	26.10
(10^{11} dyn/cm^2) C_{12}	13.4	15.74
(10^{11} dyn/cm^2) C_{44}	2.87	8.18
(10^{-8} cm) a	3.3008	3.303
(10^{12} c/s) ν_{T_1}	6.49	6.03
(10^{12} c/s) ν_{T_2}	5.04	3.78
(10^3 dyn/cm) α	27.0811	20.5530
(10^3 dyn/cm) β	17.6497	6.6389
(10^3 dyn/cm) γ_1	2.8974	2.1893
(10^3 dyn/cm) γ_2	-5.6093	-2.0518
(10^3 dyn/cm) A	-27.2512	51.9378

Tantalum, are shown in Figs. 1 and 2. To evaluate the values of five force constants involved in the scheme under study, we have taken the experimental values of elastic constants obtained from the measurements of BOLEF [21] for Niobium and of FEATHERSTON et al. [22] for Tantalum. Experimental values of phonon frequencies taken from the measurements of recent neutron scattering experiments (NAKAGAWA and WOODS [23] for Niobium and WOODS [24] for Tantalum) also have been shown in the Figure together with computed frequencies.

Figs. 1 and 2 show that computed phonon frequencies for all symmetry directions give an adequate interpretation of phonon dispersion curves obtained from the experiments. Phonon frequencies for both the metals along [ξ00] and [$\xi\xi\xi$] directions fully satisfy the symmetry requirements of bcc structure at zone boundary. We find a fairly good agreement between experimental and theoretical values for both the metals: Niobium and Tantalum along [ξ00] and [$\xi\xi\xi$] directions except some small deviations in the region of large wave vectors. However, the discrepancy along [$\xi\xi$0] is comparatively significant for shorter waves. The small deviations from the measured values may be attributed to the approximate calculation of electron lattice interaction and assumption of short range forces. The analysis of the data on Born—Von Karman theory indicates that interatomic forces in these metals are of long range nature. Comparatively a large cohesive energy in case of transition metals due to the presence of d-electronic shells (MOTT [25]) is also expected to play a significant role to govern the lattice vibration.

However, as the results reveal, we may conclude that the results obtained here are quite satisfactory and able to give an adequate interpretation of pho-

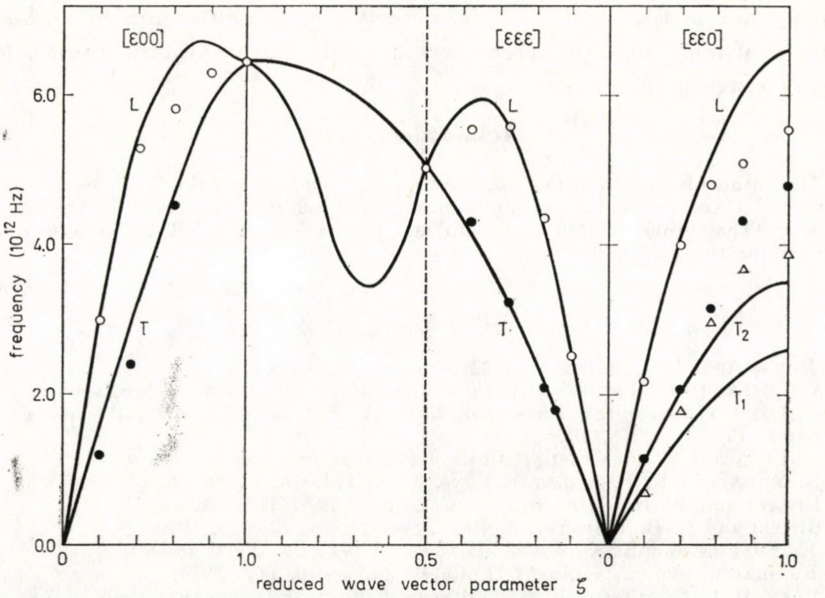

Fig. 1. **Dispersion curves along the symmetry directions for Niobium. Solid curves correspond to computed frequencies. Experimental points are shown by ○, •, △ (Nakagawa and Woods [23])**

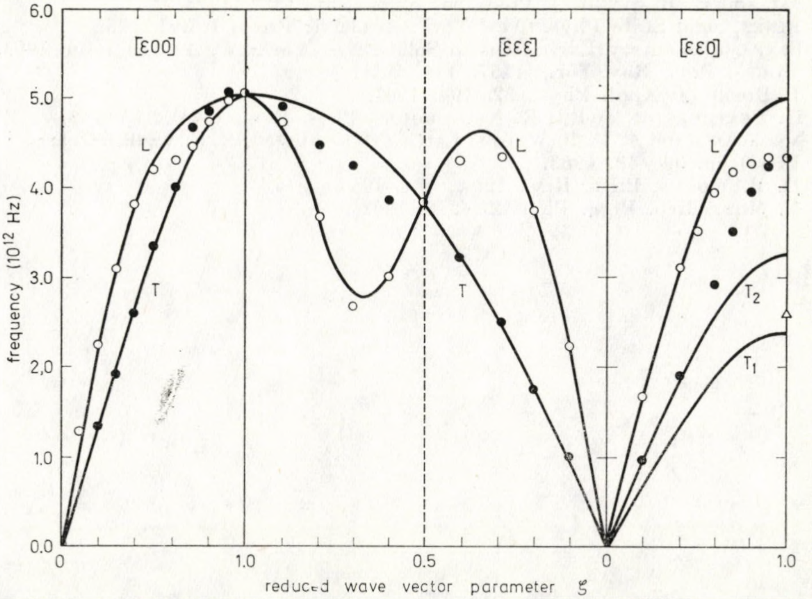

Fig. 2. **Dispersion curves along the symmetry directions for Tantalum. Solid curves correspond to present calculations. Experimental points are shown by ○, •, △ (Woods [24])**

non dispersion in transition metals, namely the Niobium and Tantalum. Consideration of more distant neighbours may also improve our results to great degree of extent.

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REFERENCES

1. M. BORN, Ann. Phys. (Germany) **44,** 605, 914.
2. B. C. CLARK, D. C. GAZIS and R. F. WALLIS, Phys. Rev., **134,** A1486, 1964.
3. J. DE LAUNAY, Solid State Phys. Vol. **2,** eds. F. Seitz and D. Turnbull (New York: Academic Press) p. 276, 1956.
4. P. S. YUEN and Y. P. VARSHNI, Phys. Rev., **164,** 895, 1967.
5. P. S. YUEN and Y. P. VARSHNI, Phys. Rev., **174,** 766, 1968.
6. J. BIHARI and B. B. TRIPATHI, Phys. Letters, **29A,** 313, 1969.
7. J. BIHARI and B. B. TRIPATHI, J. Phys. Soc. Japan, **28,** 346, 1970.
8. P. K. SHARMA and S. K. JOSHI, J. Chem. Phys., **39,** 2633, 1963.
9. P. K. SHARMA and S. K. JOSHI, J. Chem. Phys., **40,** 662, 1964.
10. G. BOSE, H. C. GUPTA and B. B. TRIPATHI, J. Phys., F**2**, 426, 1972.
11. K. KREBS, Phys. Rev., **138,** 143, 1965.
12. J. DE LAUNAY, J. Chem. Phys., **21,** 1975, 1953.
13. A. B. BHATIA, Phys. Rev., **97,** 363, 1955.
14. A. B. BHATIA and G. K. HORTON, Phys. Rev., **98,** 1715, 1955.
15. M. M. SHUKLA and B. DAYAL, J. Phys. Chem. Solids, **26,** 1343, 1965.
16. P. S. MAHESH and B. DAYAL, Phys. Rev. **143,** 443, 1966.
17. A. K. SINGH and P. K. SHARMA, J. Phys. Soc. Japan, **26,** 425, 1969.
18. S. PAL and R. B. SINGH, J. Phys. Soc. Japan, **36,** 1487, 1973.
19. D. PINES, Solid State Phys. (New York: Academic Press) **1**, 394, 1955.
    D. PINES, Elementary Excitations in Solids, New York: W. A. Benjamin, 1963.
20. K. FUCHS, Proc. Roy. Soc., **A157,** 444, 1936.
21. D. I. BOLEF, J. Appl. Phys., **32,** 100, 1961.
22. F. H. FEATHERSTON and J. R. NEIGHBOURS, Phys. Rev., **130** 1324, 1963.
23. Y. NAKAGAWA and A. D. B. WOODS, Lattice Dynamics ed. R. F. Wallis (Oxford: Pergamon Press) pp. 39—48, 1963.
24. A. D. B. WOODS, Phys. Rev., **126A,** 781, 1964.
25. N. F. MOTT, Rep. Prog. Phys. **25,** 218, 1962.

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LATTICE DYNAMICS OF CALCIUM AND STRONTIUM

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Phonon dispersion curves and heat capacities of calcium and strontium are calculated on the basis of a model proposed by us recently. In the absence of experimental observations, computed results are compared with the other theoretical predictions.

1. Introduction

One of the outstanding problems for theoreticians in the study of lattice dynamics of cubic metals is to compare and reproduce as far as possible some of the experimental results i.e. phonon dispersion curves along the principal symmetry directions, $g(\nu) - \nu$ curves and $(\theta - T)$ curve. A critical study of literature may reveal that while for various metals of cubic structure extensive experimental data for phonon frequencies and heat capacities exist such kinds of measurements have not been carried out for calcium and strontium. On the other hand, theoretical studies of lattice dynamics of these two rare earth metals have become very popular quite recently as can be seen from the works of Animalu [1], Grasko and Gruski [2], Moriarty [3], Swaroop et al. [4] and that of Prasad and Srivastava [5]. It has been found that theoretical results of all the authors were differing in the entire frequency range. The purpose of this paper is to present a new study of lattice dynamics of these two metals on the basis of a new model to throw some light on the existing diversity. The model chosen by us consists of taking the ionic shell interaction on the basis of axially symmetric forces (see Lehman et al. [6]) and the electron ion interaction on the basis of Krebs' [7] approach. The choice of this model was also encouraged by the fact that such scheme has been found very successful in predicting lattice dynamics of several cubic metals (see for example Shukla and Closs [8], Closs and Shukla [9], Shukla et al. [10] and Lima et al. [11]).

2. Theory

The phonon frequencies are given by the solution of the secular determinant

$$| D - m\omega^2 I | = 0 , \tag{1}$$

where D is the dynamical matrix, ω is angular frequency, m is ionic mass and I is 3×3 unitary matrix. The typical diagonal and non-diagonal part of the dynamical matrix D is given by

$$D_{ii} = 4A_1(3 - C_iC_j - C_jC_k - C_kC_j) + 2B_1(2 - C_iC_j - C_iC_k)$$
$$+ \frac{a^3\lambda^2}{4} k_e \sum_h \left[\frac{(q_i + h_i)}{|\vec{q} + \vec{h}|^2 + \frac{a^2\lambda^2}{4\pi^2} f(t_1)} g^2(u_1) - \frac{h_i^2}{h^2 + \frac{a^2\lambda^2}{4\pi^2} f(t_2)} g^2(u_2) \right], \quad (2)$$

$$D_{ij} = 2B_1S_iS_j + \frac{a^3\lambda^2}{4} k_e \sum_n \left[\frac{(q_1 + h_i)(q_j + h_j)}{|\vec{q} + \vec{h}|^2 + \frac{a^2\lambda^2}{4\pi^2} f(t_1)} g^2(u_1) - \right.$$
$$\left. - \frac{h_ih_j}{h^2 + \frac{a^2\pi^2}{4\pi^2} f(t_2)} g^2(u_2) \right], \quad (3)$$

where A_1 and B_1 are the axially symmetric force constants for the first nearest neighbour.

$$S_i = \sin(\pi a k_i), \quad C_i = \cos(\pi a k_i), \quad q_i = \frac{ak_i}{2\pi},$$

$$\lambda = C(r_s/a_0)^{1/2} K_F \text{ with } \cdot 353 < C < \cdot 814,$$

$$g(u) = \frac{\sin u - u \cos u}{u^3}, \quad f(t) = \frac{1}{2} + \frac{1 - t^2}{4t} \ln \frac{1 + t}{1 - t},$$

$$t_1 = \frac{\pi |\vec{q} + \vec{h}|}{aK_F}, \quad t_2 = \frac{\pi h}{aK_F}, \quad u_1 = \frac{2\pi r_s}{a} |\vec{q} + \vec{h}|, \quad u_2 = \frac{2\pi r_s}{a} h,$$

$k_i (i = 1, 2, 3)$ are cartesian components of the wave vector.

$h_i (i = 1, 2, 3)$ are cartesian components of the reciprocal wave vector.

a = lattice parameter

K_F = Fermi wave vector

r_s = radius of atomic sphere

a_0 = Bohr radius

K_e = bulk modulus of electron gas.

By expanding the secular determinant in the longwave length limit ($q \rightarrow 0$), the following relations are obtained between the elastic constants and force constants:

$$ac_{11} = 4A_1 + 2B_1 + ak_e, \quad (4)$$

$$ac_{12} = -4A_1 + B_1 + ak_e, \quad (5)$$

$$ac_{44} = 4A_1 + B_1. \quad (6)$$

3. Numerical computations

The three disposable parameters of the model are evaluated in terms of the elastic constants alone by means of the following relations:

$$B_1 = a(2C_{44} + C_{12} - C_{11}) , \tag{7}$$

$$A_1 = \frac{a}{4}(C_{11} - C_{12} - C_{44}) , \tag{8}$$

$$ak_e = a(2C_{11} - C_{12} - 3C_{44}) . \tag{9}$$

The elastic constants of calcium and strontium were taken from the work of Koster and Franz [12]. The lattice parameters were taken from Pearson [13]. While input data to claculate force constants are given in Table I, output values of force constants are listed in Table II.

Table I

Input data to calculate force constants

Metal	Elastic constants			Lattice parameter A 10^{-8} cm	Atomic mass M 10^{-22} gm
	C_{11}	C_{12}	C_{44}		
	10^{12} dyn cm^{-2}				
Calcium	.2456	.1106	.0735	5.56	.665
Strontium	.2034	.0791	.0608	6.05	1.455

Table II

Output value of force constants in units of 10^3 dyn cm^{-1}

Metal	A_1	B_1	ak_e
Calcium	.855	.667	8.901
Strontium	.960	$-.163$	8.791

Calculated phonon dispersion curves of calcium and strontium are plotted in Figs. 1 and 2 together with the theoretical curves of Moriarty [3] also shown for comparison purposes. The present results are shown by continuous lines.

To calculate $(\theta - T)$ curves of these metals we have solved the secular determinant (1) for 8000 miniature cells equally spaced in the first Brillouin zone. The crystal symmetry made it possible to calculate phonon frequencies for only 262 non-equivalent wave vectors including the origin. The resulting frequency distribution functions were utilised to calculate c_v on the basis of

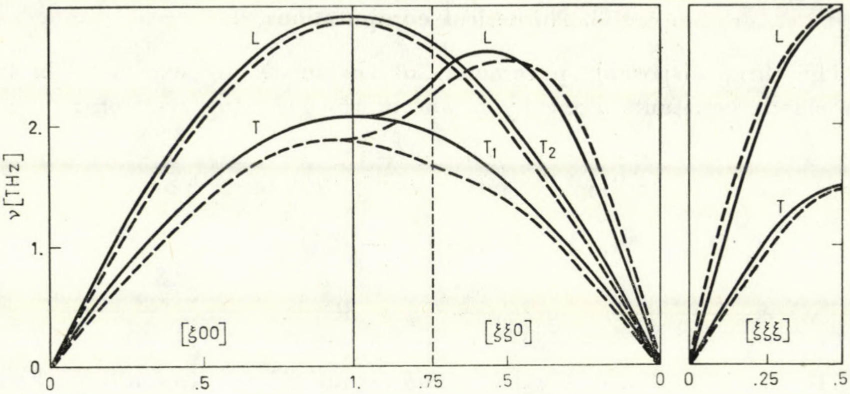

Fig. 1. Dispersion curves of calcium along the principal symmetry directions. Solid curves show the present results. Broken curves are from the theoretical computation of MORIARTY

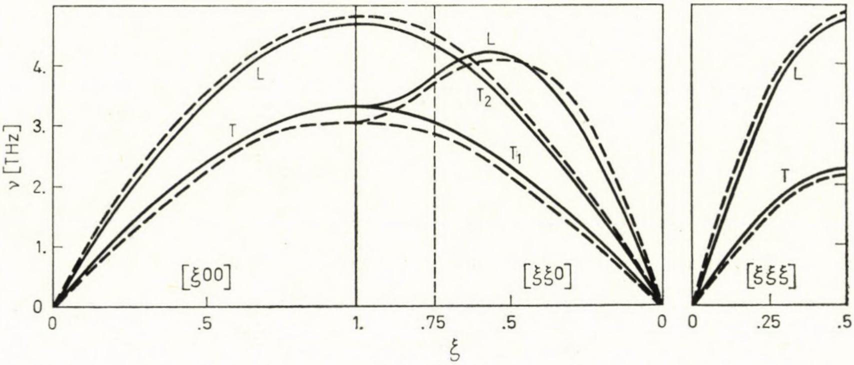

Fig. 2. Dispersion curves of strontium. Solid curves show the present results. Broken curves are from the theoretical computation of MORIARTY

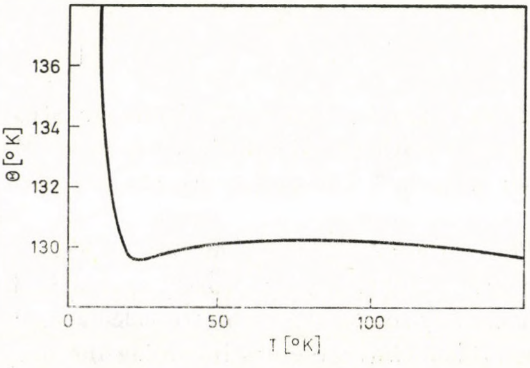

Fig. 3. ($\theta - T$) curve of calcium

Blackman's sampling technique. The resultant c_v was utilised to plot $(\theta - T)$ curves of calcium and strontium in Figs. 3 and 4.

A comparative study of Figs. 1 and 2 shows the fact that the present result of phonon dispersion curves of calcium and strontium are in quite good agreement with **Moriarty**'s [3] results. The theoretical results of **Prasad** and **Srivastava** and those of **Grasko** and **Gruski** [2] were also found very close to the present results. The theoretical results of **Swaroop** et al. [4] diverted in low frequency ends with the present results. Also, the results of **Animalu** [1] differed a lot near the zone boundaries.

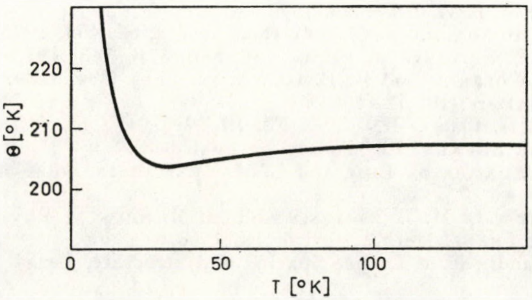

Fig. 4. $(\theta - T)$ curve of strontium

4. Discussion and conclusion

The lattice dynamics and heat capacities of calcium and strontium have been calculated on the basis of a phenomenological model which has been found quite successful in interpreting experimental data on other cubic metals. In the absence of experimental data, theoretical phonon dispersion curves have been compared with the theoretical results of **Moriarty** [3]. The reason for comparing the present calculations with **Moriarty** was twofold, i.e. firstly, that his calculations were based on a model on first principles, secondly, that his results were the latest. The model employed by us here is not very much realistic in the sense that we have assumed that the conduction electrons of these rare-earth metals behave like a free electron gas, which is not true. We have also assumed them to be a divalent metal which means that the conduction electrons of these metals lie in well defined orbits, a hypothesis which is also open to objection. We have further assumed that electron screening in these metals is governed by the theory of Bohm and Pines. For the justification of all these criteria as well as the validity of the present calculation, one would expect experimental phonon dispersion relations of these metals to be determined.

Nevertheless, the present study shows that the modified axially symmetric model could explain satisfactorily well lattice dynamics of calcium and strontium.

*

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REFERENCES

1. A. O. E. Animalu, Phys. Rev., **161**, 445, 1957.
2. Z. A. Gruski and G. L. Grasko, Soviet Physics Doklady, **16**, 298 1971.
3. J. A. Moriarty, Phys. Rev., B**6**, 4445, 1972.
4. A. Swaroop, B. M. Bohra and L. M. Tewari, Physica, **66**, 403, 1973.
5. B. Prasad and R. S. Srivastava, Phys. Stat. Sol., **57B**, 743, 1973.
6. G. W. Lehman, T. Wolfram and R. E. DeWames, Phys. Rev., **128**, 1593 1962.
7. K. Krebs, Phys. Letters, **10**, ;12, 1964.
8. M. M. Shukla and H. Closs, Jr. Phys., F**3**, LI 1973.
9. H. Closs and M. M. Shukla, Physica (to be published).
10. M. M. Shukla, I. C. da Cunha Lima and L. M. Brescansin, Solid St. Comm., **11**, 1431 1972.
11. I. C. da Cunha Lima, L. M. Brescansin and M. M. Shukla, Physica, **72**, 179, 1974.
12. W. Koster and H. Franz, Metall. Rev. **6**, 18, 1968.
13. W. B. Pearson, Handbook of Lattice Spacing and Structure, Pergamon Press, London, 1968.

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LATTICE DYNAMICS OF NOBLE METALS ON MODIFIED BHATIA'S MODEL

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Phonon spectra and lattice heat capacities of copper, silver and gold have been calculated on the basis of modified Bhatia's model. Calculated phonon dispersion curves as well as ($\theta - T$) curves of copper, silver and gold are found to give reasonable agreements with the experimental data.

1. Introduction

Several phenomenological models for cubic metals have been developed so far (see for example Joshi and Rajgopal [1] and Shukla et al. [2]). The basic aim of all these models has been the same i.e. to propound a theory which can successfully reproduce the lattice dynamical properties (phonon dispersion curves along the principal symmetry directions and the variation of θ with temperature) with only a few free parameters.

The interpretation of the experimental phonon dispersion curves of several cubic metals has revealed the fact that the conduction electrons play an important role in the evaluation of the theoretical phonon frequencies of metals. This indicated that the electron—ion interaction term of the dynamical matrix should be handled with a proper attention.

Bhatia [3] has propounded a phenomenological model for lattice dynamics of cubic metals as early as 1955. His model consists of evaluating the ion—ion interaction on axially symmetric forces extending between the first nearest neighbours. The electron—ion interaction in his model has been considered on the Thomas—Fermi theory of metallic screening. Three force parameters of the model were evaluated in terms of the three independent elastic constants available and lattice dynamics and heat capacities of several cubic metals have been studied on its basis (for a detail see Sangal and Sharma [4] and references therein). Quite recently Shukla and Camargo [5] have discovered that Bhatia's [3] scheme to estimate the Thomas—Fermi screening parameter of a metal in terms of the elastic constants is wrong which means that the calculated phonon frequencies of all the metals by several authors are wrong. Shukla and Salzberg [6, 7] have thus modified the electron—ion interaction part of the dynamical matrix. Such modifications also permitted to vary the electron screening in metals in between the limits predicted by the theory of Bohm—Pines and Thomas—Fermi. They have also extended the interionic interactions present in metals out to third neighbours. The inclusion of interionic interactions beyond the first neighbour was deemed necessary owing to the fact that experimentalists on interpreting their experimental phonon frequencies have found that interatomic interactions in metals are of a long range in nature. We (SHUKLA and SALZBERG [6, 7]) were of the opinion that restricting the interionic interaction in BHATIA's model up to first nearest neighbour only had put a limitation over the success of the model. The scheme of SHUKLA and SALZBERG [6, 7] was extremely successful in reproducing the experimental phonon dispersion relations along the principal symmetry directions of sodium and copper within the limits of the experimental error. In the present paper we have combined together the lattice dynamics of all noble metals.

The choice of noble metals for the present study was done due to the following reasons:

(1) All these metals belong to the same crystallographic structure i.e. f.c.c. structure.

(2) They all are monovalent metals.

(3) Experimental measurements of the phonon dispersion relations exist for all of them along the principal symmetry directions.

(4) Numerous elastic and thermal data exist for all of them.

2. Theory

The secular determinant to determine phonon frequency is given by

$$|D - m\omega^2 I| = 0\,, \tag{1}$$

where D is dynamical matrix, m is ionic mass, ω is angular frequency and I is unit matrix.

Each element of the dynamical matrix is split up into two parts, the ion—ion interaction part D_{ij}^{ii} and the electron—ion interaction part, D_{ij}^{ie}. Written mathematically,

$$D_{ij} = D_{ij}^{ii} + D_{ij}^{ie}\,. \tag{2}$$

Taking the ion—ion interactions up to third neighbours, the typical diagonal and non—diagonal part of the dynamical matrix is given by

$$\begin{aligned} D_{ii}^{ii} = {} & 2(2\alpha_1 + \beta_1)\,[2 - c_i(c_j - c_k)] + 4\alpha_1(1 - c_j c_k) + 4(\alpha_2 + \beta_2) \\ & [(1 - c_j^2) + 4\alpha_2 2 - (c_j^2 + c_k^2)] + 8/3(2\beta_3 + 3\alpha_3) \\ & [1 + c_j c_k(1 - 2c_i^2)] + 8/3(\beta_3 + 6\alpha_3)\left[1 + \frac{c_i}{2}(c_j + c_k)\,(1 - 2c_j c_k)\right], \end{aligned} \tag{3}$$

$$D^{ii}_{ij} = 2\beta_1 S_i S_j + \frac{4}{3} S_i S_j \beta_3 [4c_k(c_i + c_j)(1 - 2c_k)^2] . \tag{4}$$

The electron=ion interaction has been taken on the basis of the work of SHUKLA and CAMARGO [5] given by

$$D^{ie}_{ii} = \frac{k_e q_i^2 n^{-1}}{1 + q^2/k_c^2} , \tag{5}$$

$$D^{ie}_{ij} = \frac{k_e q_i q_j n^{-1}}{1 + q^2/k_c^2} , \tag{6}$$

where $S_i = \sin (q_i a)$
$C_j = \cos (q_i a)$
a = lattice parameter
q_i = ith component of phonon wave vector
$k_c = (r_s/a_0) k_F \beta$; r_s = radius of atomic sphere, a_0 = Bohr radius
k_F = Fermi wave vector

(α_i, β_i) are force constants for ith neighbour

$$\cdot 353 \leq \beta \leq \cdot 814 ,$$

$$n = \frac{4}{a^3} .$$

By expanding the secular determinant in the long wavelength limit ($q \to 0$), the following relations were found between elastic constants and force constants:

$$ac_{11} = 4\alpha_1 + 2\beta_1 + 4\alpha_2 + 4\beta_2 + 24\alpha_2 + 12\beta_3 + ak_e , \tag{7}$$

$$ac_{12} = -4\alpha_1 + \beta_1 - 4\alpha_2 - 24\beta_3 + 6\alpha_3 + ak_e , \tag{8}$$

$$ac_{44} = 4\alpha_1 + \beta_1 + 4\alpha_2 + 24\alpha_3 + 6\beta_3 , \tag{9}$$

where k_e is bulk modulus of electron gas and is given by

$$k_e = (c_{12} - c_{44}) + \frac{8}{a} (\alpha_1 + \alpha_2 + 6\alpha_3) . \tag{10}$$

3. Numerical computations

In order to determine the phonon frequencies, the evaluation of force constants was necessary. The seven disposable parameters of the model were evaluated by using the equations relating them with the three elastic constants and four experimental phonon frequencies corresponding to four wave vectors at the zone boundaries. After making several choices finally longitudinal and transversal zone boundary frequencies from the directions $[\zeta 00]$ and $[\zeta\zeta\zeta]$ were taken. Elastic constants were taken at the same temperature at which phonon frequencies were measured. Phonon dispersion relations for copper, silver and gold have been measured respectively by SVENSSON and BROCKHOUSE [8], KAMITAKAHARA and BROCKHOUSE [9] and by LYNN et al. [10]. All these measurements have been carried out at room temperature only. The room temperature values of the elastic constants of copper were taken from the work of OVERTON and GAFFNEY [11] and those of silver and gold from the work of NEIGHBOURS and ALERS [12]. The input data to calculate atomic force constants are given in Table I. Calculated values of the force constants are shown in Table II.

A knowledge of the numerical values of the force constants made it possible to calculate the phonon dispersion relations in copper, silver and gold. Computed phonon dispersion curves of silver and gold are presented in Figs. 1 to 2 together with the experimental points shown for comparison purpose. While theoretical curves are shown by continuous lines, experimental points are shown by the different symbols given in the captions. Phonon dispersion curves of copper are not given here as it has been already reported by one of us (SHUKLA and SALZBERG [6]) earlier.

The calculation of specific heat of these metals has been made on a numerical sampling of the vibration spectrum. To evaluate the frequency spectrum,

Table I

Input data to calculate force constants

Metal	Lattice parameter a (Å)	Elastic constants			Atomic mass M (10^{-22}g)	Phonon frequencies			
		c_{11}	c_{12}	c_{44}		$\nu_L\ \zeta 00$	$\nu_T\ \zeta 00$	$\nu_L\ \zeta\zeta\zeta$	$\nu_T\ \zeta\zeta\zeta$
		(10^{11} dyn cm^{-1})				(10^{12} Hz)			
Copper	3.618	16.84	12.15	7.55	1.056	7.19	5.08	7.40	3.38
Silver	4.078	12.40	9.37	4.61	1.791	4.71*	3.25*	5.07	2.24
Gold	4.07	19.23	16.30	4.20	3.270	4.61	2.75	4.70	1.86

* For the wave vector (·8,0,0)

Table II

Output values of the force constants (10^3 dyn cm^{-1})

Metal	α_1	β_1	α_2	β_2	α_3	β_3	ak_e
Copper	−1.7809	29.513	−.2615	.7689	−.2189	1.8726	−10.204
Silver	−1.7177	26.104	− 4499	−.1651	−.1651	.9048	− 5.875
Gold	− .9410	33.574	−.1751	−.2385	−.2385	−1.0485	− 1.8869

the entire Brillouin zone was divided into 8000 miniature cells and the frequencies were calculated for the central point of each cell. This gave rise to 24 000 frequencies. The entire frequency spectrum was divided into small intervals of width $\Delta\nu = .05 \times 10^{12}$ Hz and the specific heat was evaluated through BLACKMAN's sampling technique [13]. The calculated values of c_v were utilised to compute $(\theta - T)$ curves of copper, silver and gold and these are plotted in Figs. 3 to 5 together with some experimental points for comparison purpose. The experimental c_v of copper, silver and gold were taken respectively from the works of MARTIN [14], MEADS et al. [15] and that of GEBALLE and GIAUQUE [16]. In order to estimate the lattice heat capacities the coefficient of the electronic specific heat has been subtracted from the experimental c_v. Such coefficient, γ, has the value of 164.4, 155.5 and 177.6, all in the units of 10^{-6} cal deg^{-2} g atom^{-1} respectively for copper, silver and gold. These correspond to the experimental measurement of CORAK et al. [17] for copper and gold and to those of YATES and HOARE [18] for silver.

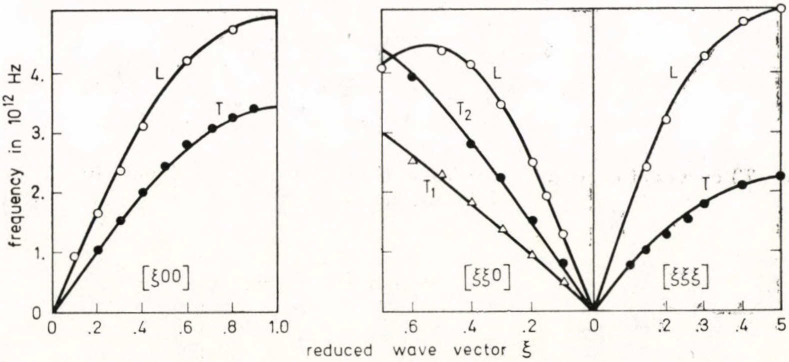

Fig. 1. Phonon dispersion relations in silver. Calculated curves are shown by solid line. Experimental points are shown by ○, ● and △

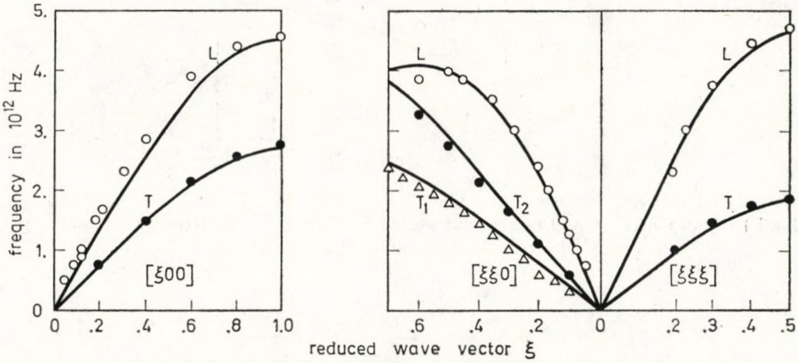

Fig. 2. Phonon dispersion relations in gold. Calculated curves are shown by solid line. Experimental points are marked by ○, ● and △

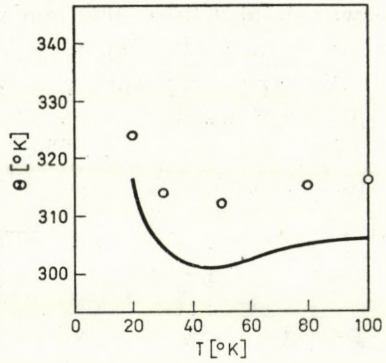

Fig. 3. **($\theta - T$) curves of copper. Theoretical curve is shown by continuous line. Experimental points are marked by ○**

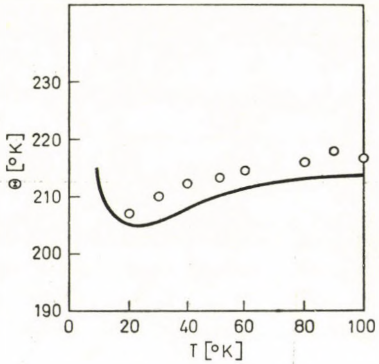

Fig. 4. **($\theta - T$) curves of silver. Theoretical curve is shown by continuous line. Experimental points are marked by ○**

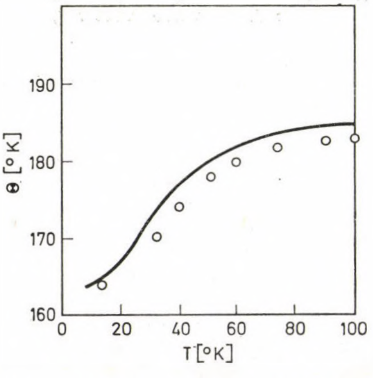

Fig. 5. **($\theta - T$) curves of gold. Theoretical curve is shown by continuous line. Experimental points are marked by ○**

4. Comparison with experimental results

We shall compare each metal separately.

Copper

Phonon dispersion relations of copper along all the principal symmetry directions have given an excellent fit with the experimental results (see Shukla and Salzberg [6]).

The study of Fig. 3 shows that the calculated $(\theta - T)$ curve of copper has reproduced exceedingly well the entire course of the experimental curve. Our curve lies about 3% below the experimental curve. Had we used zero degree Kelvin values of elastic constants and extrapolated values of zero degree phonon frequencies to calculate this curve, probably this difference could have been dropped a little bit.

Silver

A critical study of Fig. 1 shows that the calculated phonon dispersion curves of silver have given an excellent description of the experimental curves of Kamitakahara and Brockhouse [9]. At low wave vectors our curves have almost reproduced the experimental results. A little discrepancy exists between the calculated and experimental curve near the zone boundaries. The maximum deviation existing between the two sets of results does not exceed more than 8%.

The study of Fig. 4 reveals the information that theoretical $(\theta - T)$ curve of silver has reproduced the entire course of the experimental result. The calculated curve has been found to lie about 2% below the experimental curve.

Gold

The study of Fig. 2 shows that the calculated phonon dispersion curves of gold along all the principal symmetry directions have given an excellent description of the experimental results of Lynn et al. [10]. Except at few wave vectors at the high frequency region, the calculated curves have almost reproduced the experimental ones within the limits of the experimental errors.

A critical study of Fig. 5 reveals the fact that the calculated $(\theta - T)$ curve of gold has reproduced the entire course of the experimental findings. The calculated curve lies about 2% above the experimental one.

5. Conclusion

The lattice dynamics and heat capacities of copper, silver and gold have been studied on the basis of modified **Bhatia**'s model. A critical study of the results presented here indicates that the present scheme has been extremely helpful in explaining the experimental phonon dispersion curves as well as the heat capacities of all the noble metals combined together. The maximum deviation between the calculated and experimental phonon frequencies of all these metals has been found of the order of 10%. The calculated and experimental θ does not differ more than 5%. The agreements between the calculated and experimental θ could have been improved had we used zero degree values of experimental constants for such calculations. Owing to the fact that our model is not very rigorous as far as the calculation of electron—ion interaction is concerned, since it does not modify the transversal branches, this kind of result is very much encouraging. To achieve similar success experimentalists **Svensson** and **Brockhouse** [6], **Kamitakahara** and **Brockhouse** [9] and **Lynn** et al. [10] have used as many as 12 to 16 free parameters. The original model of **Bhatia** also had only a limited success in the interpretation of experimental $(\theta - T)$ curves of these metals. It is thus clear from the present study that the idea underlying the modification of the **Bhatia**'s model is quite justified. One can say definitively that interatomic interactions in cubic metals (noble metals for the present studies) extend out to third neighbours at least.

While the original model of **Bhatia** [3] was linked with the Thomas—Fermi theory of electron screening, we varied such screening in noble metal ions in between the theories of Bohm and Pines and that of Thomas and Fermi. We came to the conclusion that the best results are obtained when the electron screening in all these three metals is considered on the theory of Bohm and Pines. Present result does not confirm with the hypothesis of **Shukla** and **Dayal** [19] that electron screening in noble metals is connected with their ionic radii. Our calculations appear to be more justified in the sense that it was based on reproducing the experimental phonon dispersion curves of all the noble metals. **Shukla** and **Dayal** [19] had come to that conclusion while fitting the experimental $(\theta - T)$ curves of silver and gold due to the lack of experimental phonon dispersion curves of silver and gold at that time.

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REFERENCES

1. S. K. Joshi and A. K. Rajgopal, Solid State Physics, A. P., New York, 1968.
2. M. M. Shukla, I. C. da Cunha Lima and L. M. Brescansin, Solid St. Comm., **11,** 1431, 1972.
3. A. B. Bhatia, Phys. Rev., **97,** 363, 1955.
4. S. K. Sangal and P. K. Sharma, Acta Phys. Hung., **29,** 107, 1970.
5. M. M. Shukla and F. P. Camargo, Ciencia e Cultura, **26,** 579, 1974.
6. M. M. Shukla and J. B. Salzberg, Physics Letters, **43A,** 429, 1973.
7. M. M. Shukla and J. B. Salzberg, Jr. Phys. F**3,** L99, 1973.
8. E. C. Svensson, B. N. Brockhouse and J. M. Rowe, Phys. Rev., **155,** 619, 1967.
9. W. A. Kamitakahara and B. N. Brockhouse, Physics Letters, **29A,** 639, 1969.
10. J. W. Lynn, H. G. Smith and R. M. Nicklow, Phys. Rev., B**8,** 3493, 1973.
11. W. C. Overton and J. Gaffney, Phys. Rev., **98,** 969, 1955.
12. J. R. Neighbours and G. A. Alers, Phys. Rev., **111,** 707, 1958.
13. M. Blackmann, Handbuch der Physik, pt. 1, Vol. 7, Springer Verlag, Berlin, 1955.
14. D. L. Martin, Canad. Jr. Phys., **38,** 17, 1960.
15. P. F. Meads, W. R. Forsythe and W. F. Giauque, J. Am. Chem. Soc., **63,** 1962, 1941.
16. T. H. Geballe and W. F. Giauque, J. Amer. Chem. Soc., **74,** 2368, 1952.
17. W. S. Corak, M. P. Garfunkel, C. B. Satterthwarte and A. Wexler, Phys. Rev., **98,** 1599, 1956.
18. B. Yates and F. E. Hoare, Proc. Royal Soc., A **240,** 42, 1957.
19. M. M. Shukla and B. Dayal, Jr. Phys. Chem. Solids, **26,** 1343, 1965.

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RO-VIBRATIONAL ENERGY JACOBIANS WITH RESPECT TO CORIOLIS ZETA COEFFICIENTS*

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Algebraic Jacobian expressions are given describing the sensitivity of upper-state ro-vibrational energy levels to changes in Coriolis zeta coefficients. For two and three interacting states closed formulae are derived. For non-degenerate, multiple interactions two alternative approaches are used. One method is novel and consists of the application of the "*mixing matrices*", the other is the use of first-order perturbation theory.[1]

1. Introduction

In order to determine vibrational-rotational interaction parameters in molecular spectra a frequently used procedure is that of computer simulation. When several parameters are to be determined from a great number of observables, such as rotational transitions in a vibrational spectrum, the obvious procedure to apply — in addition to combination differences — is the method of least-squares. The analysis of different resonances rarely proceeds along this line, because it is difficult to obtain physically meaningful effective rotational constants for the upper states by the least-squares technique. In most cases the resonance parameters are obtained in the simulation method by trial-and -error, starting from some acceptable set.

This paper deals with Coriolis perturbations, and its purpose is to derive expressions for the Jacobian elements of the upper-state levels with respect to Coriolis zeta coefficients. The expected use of these formulae is in the analysis of multiple, non-degenerate interactions, where several Coriolis zeta coefficients participate in the rotational perturbations. Multiple interactions are allowed by symmetry in asymmetric tops, providing for a complex structure in the spectrum, even when the molecule is built only from a few atoms.

First we shall deal with two and three interacting vibrational states, then discuss the problem generally.

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[1] In a recent paper **Rowe** and **Wilson** [9] have also derived formulae for the derivatives of rotational energy levels in perturbed spectra, utilizing the Hellmann—Feynmann theorem as described in [8]. Their Equation 9. in [9] can be shown to be equivalent to the a-type perturbation expression in *Section* 5.2 if $F = 2A\,\zeta^a_{rs}\,\Omega_{rs}$, the approximation specified in *Footnote* 7 here is used, and it is realized that in this work the vibrational wavefunctions are phased.

2. Interactions between two vibrational states

The simplest case to start with is the *a*-type Coriolis interaction between two vibrational-rotational level systems. Mills [1] gave analytical descriptions both for the perturbed energy levels and for the corresponding wavefunctions.

The analytical derivatives are obtained in a straightforward manner from the formula of perturbed energies:

$$E^{\pm}(J,K) = \frac{1}{2}(\nu_r + \nu_s) + F(J,K) \pm \frac{1}{2}\Delta_K ,$$

where

$$\Delta_K^2 = 16A^2K^2(\zeta_{rs}^a)^2\,\Omega_{rs}^2 + \delta^2 ,$$

where ν_r and ν_s are the frequencies of band-origins, $F(J, K)$ is the rotational energy, A is the equilibrium rotational constant, ζ^a_{rs} is the *a*-type Coriolis zeta coefficient connecting the two states,

$$\Omega_{rs} = \frac{1}{2}\left[\left(\frac{\nu_r}{\nu_s}\right)^{1/2} + \left(\frac{\nu_s}{\nu_r}\right)^{1/2}\right]$$

and

$$\delta^2 = (\nu_r - \nu_s)^2 .$$

It follows that

$$\frac{\partial E^{\pm}(J,K)}{\partial \zeta_{rs}^a} = \frac{\partial E^{\pm}(K)}{\partial \zeta_{rs}^a} = \pm\frac{\Delta_K^2 - \delta^2}{2\Delta_K\,\zeta_{rs}^a} , \tag{1}$$

where the + and — signs refer to the perturbed upper and lower levels, respectively.

The corresponding derivatives of the $\Delta J = 0$, $\Delta K = \pm 1$ transitions are obtained as the energy derivatives belonging to $(K + 1)$ and $(K - 1)$, since the vibrational ground state is unperturbed, thus its derivative with respect to ζ^a_{rs} is identically zero:

$$\frac{\partial R^{\pm}_{Q_K}}{\partial \zeta_{rs}^a} = \frac{\partial E^{\pm}(K+1)}{\partial \zeta_{rs}^a} - \frac{\partial E^{\circ}(K)}{\partial \zeta_{rs}^a} = \frac{\partial E^{\pm}(K+1)}{\partial \zeta_{rs}^a} ,$$

and

$$\frac{\partial P^{\pm}_{Q_K}}{\partial \zeta_{rs}^a} = \frac{\partial E^{\pm}(K-1)}{\partial \zeta_{rs}^a} - \frac{\partial E^{\circ}(K)}{\partial \zeta_{rs}^a} = \frac{\partial E^{\pm}(K-1)}{\partial \zeta_{rs}^a} .$$

3. Interactions between three vibrational states

Although, strictly speaking, there are no closed analytical expressions for the eigenvalues of a (3×3) Hamiltonian matrix, it is still possible to give practically useful formulae. Kovács and Singer [2] gave formulae to calculate the roots of a third-order secular equation utilizing a Mac-Laurin-type series expansion. The advantage of these expressions is that the precision of the eigenvalues can be improved beyond any given degree by extending the summations involved over more terms.

The diagonal terms of a hermitian, symmetric matrix are reduced by the quantity W:

$$W = w + \frac{W_1 + W_2 + W_3}{3} \tag{2}$$

where the W_i's are the diagonal terms.

The three reduced roots are given by (see Eq. 12 in [2]):

$$\begin{aligned} w_1 &= -a^{1/2} - b/2a + \sum_{n=2}^{\infty} (-1)^n \frac{3}{2n} \begin{pmatrix} \frac{3n-5}{2} \\ n-1 \end{pmatrix} \frac{b^n}{a^{(3n-1)/2}}, \\ w_2 &= b/a + \sum_{n=2}^{\infty} [1-(-1)^n] \frac{3}{2n} \begin{pmatrix} \frac{3n-5}{2} \\ n-1 \end{pmatrix} \frac{b^n}{a^{(3n-1)/2}}, \\ w_3 &= a^{1/2} - b/2a - \sum_{n=2}^{\infty} \frac{3}{2n} \begin{pmatrix} \frac{3n-5}{2} \\ n-1 \end{pmatrix} \frac{b^n}{a^{(3n-1)/2}}, \end{aligned} \tag{3}$$

where the definitions of a and b are given in Eq. (6) in [2].

Since the above expressions converge very rapidly, provided $|3^{3/2} b/2a^{3/2}| \leqq 1$ — which is always true for secular equations — useful approximate expressions are obtained for the roots W_i when only the first two terms in the summations of Eqs. (3) are retained. The resulting simplified expressions are given in Eqs. (15) in [2], and are reproduced here:

$$\begin{aligned} W''_1 &= \frac{1}{3} \sum_i W_i - \left[\sum_{i,k} \left[\frac{W_{ik}^2}{6} + |H_{ik}|^2 \right] \right]^{1/2} - \\ &- \frac{\frac{1}{6} \sum_{i,k,l,} \left\{ \left[\left(\frac{W_{ik}}{3} \right)^2 + |H_{ik}|^2 \right] (W_{li} + W_{lk}) - 2R(H_{ik} H_{kl} H_{li}) \right\}}{\sum_{i,k} \left[\frac{W_{ik}^2}{6} + |H_{ik}|^2 \right]} \\ W''_2 &= \frac{1}{3} \sum_i W_i + \\ &+ \frac{\frac{1}{3} \sum_{i,k,l,} \left\{ \left[\left(\frac{W_{ik}}{3} \right)^2 + |H_{ik}|^2 \right] (W_{li} + W_{lk}) - 2R(H_{ik} H_{kl} H_{li}) \right\}}{\sum_{i,k} \left[\frac{W_{ik}^2}{6} + |H_{ik}|^2 \right]} \end{aligned} \tag{4}$$

$$W_3'' = \frac{1}{2}\sum_i W_i + \left[\sum_{i,k}\left(\frac{W_{ik}^2}{6} + |H_{ik}|^2\right)\right]^{1/2} - \tag{4}$$

$$- \frac{\frac{1}{6}\sum_{i,k,l,}\left\{\left[\left(\frac{W_{ik}}{3}\right)^2 + |H_{ik}|^2\right](W_{li} + W_{lk}) - 2R(H_{ik}H_{kl}H_{li})\right\}}{\sum_{i,k}\left[\frac{W_{ik}^2}{6} + |H_{ik}|^2\right]},$$

where $W_{ik} = W_i - W_k$, and R denotes the real part of the off-diagonal Hamiltonian matrix elements. Provided we have constructed the Hamiltonian matrix on the basis of phased wavefunctions of the interacting vibrational states, the Hamiltonian matrix contains only real elements.

By differentiating the expressions in Eqs. (4) with respect to H_{ik} we can obtain closed form expressions for the Jacobian elements of W_1'', W_2'' and W_3'' with respect of the off-diagonal Hamiltonian matrix elements.

Denoting by A and B the following summations in Eqs. (4):

$$A = \sum_{i,k}\left[\frac{W_{ik}^2}{6} + |H_{ik}|^2\right],$$

$$B = \frac{1}{6}\sum_{i,k,l,}\left[\left(\frac{W_{ik}}{3}\right) + |H_{ik}|^2\right](W_{lk} + W_{li}).$$

the Jacobian element expressions are the following:

$$\frac{\partial W_1''}{\partial H_{ik}} = \frac{\text{sign of } H_{ik}}{A^2}\left\{- H_{ik}A^{3/2} - \right.$$

$$\left. 2\left[\frac{W_{li} + W_{lk}}{6}A - B\right]H_{ik} + H_{kl}H_{li}(A - H_{ik}^2)\right\}, \tag{5}$$

$$\frac{\partial W_2''}{\partial H_{ik}} = \frac{\text{sign of } H_{ik}}{A^2}\left\{4\left[\frac{W_{li} + W_{lk}}{6}A - B\right]H_{ik} - 2H_{kl}H_{li}(A - H_{ik}^2)\right\}$$

while

$$\frac{\partial W_3''}{\partial H_{ik}} = -\left[\frac{\partial W_1''}{\partial H_{ik}} + \frac{\partial W_2''}{\partial H_{ik}}\right],$$

where the last equation follows from the trace rule:

$$\sum_i \frac{\partial W_i}{\partial H_{ik}} = 0. \tag{6}$$

Eqs. (5) are, in fact, generally true for any type of off-diagonal elements, therefore for any type of perturbations. In the case of Coriolis interactions the Jacobian elements are obtained from

$$\frac{\partial W_i}{\partial \zeta^a_{ik}} = \frac{\partial W_i}{\partial H_{ik}} \frac{\partial H_{ik}}{\partial \zeta^a_{ik}} .$$

For the simple case of a-type Coriolis interactions, where $H_{ik} = 2iAK\zeta^a_k\,\Omega_{ik}$:

$$\frac{\partial W_i}{\partial \zeta^a_{ik}} = 2iAK\,\Omega_{ik} \frac{\partial W_i}{\partial H_{ik}} .$$

4. The case of multiple Coriolis interactions

The eigenvalues of the vibrational-rotational Hamiltonian matrix are obtained by a similarity transformation:

$$\mathbf{E} = \mathbf{U}^T\,\mathbf{HU} ,$$

where $\mathbf{U}^T$ is the transpose of the eigenvector matrix. The rigorous way to calculate the derivatives of $\mathbf{E}$ with respect to some parameter P is given by:

$$\frac{\partial \mathbf{E}}{\partial P} = \frac{\partial \mathbf{U}^T}{\partial P}(\mathbf{HU}) + \mathbf{U}^T \frac{\partial H}{\partial P}\mathbf{U} + (\mathbf{U}^T\mathbf{H})\frac{\partial \mathbf{U}}{\partial P} . \tag{7a}$$

Under the approximation that $\mathbf{U}$ is much less sensitive to changes in P than $\mathbf{H}$, Eq. (7a) is simplified:[2]

$$\frac{\partial E}{\partial P} \simeq \mathbf{U}^T \frac{\partial H}{\partial P}\mathbf{U} . \tag{7b}$$

As discussed in *Section* 6 the above approximation holds only for the case when all interactions are weak. Eq. (7b) can be tested against the case of two interacting vibrational states (*Section* 2), using the eigenvector matrix elements given by MILLS [1]

$$\begin{vmatrix} \dfrac{\partial E^+}{\partial \zeta^a_{rs}} & 0 \\ 0 & \dfrac{\partial E^-}{\partial \zeta^a_{rs}} \end{vmatrix} \simeq \mathbf{U}^T \begin{vmatrix} \dfrac{\partial H_{11}}{\partial \zeta^a_{rs}} & \dfrac{\partial H_{12}}{\partial \zeta^a_{rs}} \\ \dfrac{\partial H_{21}}{\partial \zeta^a_{rs}} & \dfrac{\partial H_{22}}{\partial \zeta^a_{rs}} \end{vmatrix} \mathbf{U} =$$

$$= \begin{vmatrix} u_{11} & u_{21} \\ u_{12} & u_{22} \end{vmatrix} \begin{vmatrix} 0 & 2AK\,\Omega_{rs} \\ 2AK\,\Omega_{rs} & 0 \end{vmatrix} \begin{vmatrix} u_{11} & u_{12} \\ u_{21} & u_{22} \end{vmatrix} \text{[3]} .$$

---

[2] CASTELLANO and BOTHNER-BY [8] have shown that with respect to the diagonal elements of $\partial\mathbf{E}/\partial P$ the approximate equality in Eq. (7b) is a rigorous one. From this fact it follows that the trace-rule in Eq. (6) here is, in fact, an exact one.

[3] The construction of the Hamiltonian matrix is done on the basis of phased wavefunctions: Ψ_r and $-i\Psi_s$.

Carrying out the matrix multiplications we obtain:

$$\begin{vmatrix} \dfrac{\partial E^+}{\partial \zeta^a_{rs}} & 0 \\ 0 & \dfrac{\partial E^-}{\partial \zeta^a_{rs}} \end{vmatrix} = 2AK\,\Omega_{rs} \begin{vmatrix} 2u_{11}u_{21} & u_{12}u_{21} + u_{11}u_{22} \\ u_{12}u_{21} + u_{11}u_{22} & 2u_{12}u_{22} \end{vmatrix} . \tag{8}$$

The eigenvector elements are:

$$u_{11} = a_K\,, \quad u_{12} = -\,b_K\,, \quad u_{21} = b_K \text{ and } u_{22} = a_K\,,$$

where a_K and b_K are coefficients in the linear combinations of unperturbed vibrational wavefunctions.

$$| \psi^+ > = a_K \,|\, \psi_r > -\, ib_K \,|\, \psi_s >,$$
$$| \psi^- > = -\, ib_K \,|\, \psi_r > +\, a_K \,|\, \psi_s > .$$

The expressions for the coefficients a_K and b_K are:

$$a_K = \left[(\Delta_K + \delta)/2\Delta_K\right]^{1/2}, \quad b_K = \left[(\Delta_K - \delta)/2\Delta_K\right]^{1/2}.$$

Since from Eq. (8):

$$\frac{\partial E^+}{\partial \zeta^a_{rs}} = 4u_{11}u_{21}\,AK\,\Omega_{rs}\,; \qquad \frac{\partial E^-}{\partial \zeta^a_{rs}} = 4u_{12}u_{22}\,AK\,\Omega_{rs}$$

and since

$$-\,u_{12}u_{22} = u_{11}u_{21} = a_K b_K = \frac{(\Delta_K^2 - \delta^2)^{1/2}}{2\Delta_k}\,,$$

furthermore:

$$4AK\,\Omega_{rs} = \frac{(\Delta_K^2 - \delta^2)^{1/2}}{\zeta^a_{rs}}\,,$$

we obtain that

$$4u_{11}u_{21}\,AK\,\Omega_{rs} = +\,\frac{\Delta_K^2 - \delta^2}{2\zeta^a_{rs}\,\Delta_k} = \frac{\partial E^+}{\partial \zeta^a_{rs}}$$

and similarly

$$4u_{12}u_{22}\,AK\,\Omega_{rs} = -\,\frac{\Delta_K^2 - \delta^2}{2\zeta^a_{rs}\,\Delta_K} = \frac{\partial E^-}{\partial \zeta^a_{rs}}\,.$$

It should be noted that since for weak interactions, as will be shown, $u_{11}u_{22} + u_{12}u_{21} \neq 0$, the right hand side matrix of Eq. (8) will not be diagonal. Numerical calculations show the off-diagonal elements to be often larger than the diagonal ones.

One can prove easily that the energy Jacobian matrix is diagonal only for strong interactions — for which the results reported in *Sections* 4, 5 and 6 are not applicable. The off-diagonal element is, from Eq. (8), proportional to $u_{11}u_{22} + u_{12}u_{21}$. The requirement that the former be zero can be reformulated:

$$u_{11}u_{22} - u_{12}u_{21} = -\,2u_{12}u_{21}\,.$$

Since the left-hand side is equal to unity — **U** being ortho-normal — we obtain:

$$-2u_{12}u_{21} = 2b_K^2 \simeq 1 .$$

The existence of a diagonal Jacobian matrix then requires

$$2b_K^2 = \frac{\Delta_K - \delta}{\Delta_K} \simeq 1 ,$$

which condition is met only for $\delta \ll \Delta_K$, i.e., for strong resonance.

5. The construction of Jacobian element expressions for multiple interactions

The binary interaction serves as recipe for constructing the matrix equations for other interaction situations. In the following we seek a simplification of the algebra — inherent already in the (2×2) case — that allows us to circumvent matrix notation and give simple algebraic expressions for the Jacobian elements concerned.

We shall deal with two particular cases, first with multiple *a*-type interactions in asymmetric tops, then with multiple simultaneous *a*, *b* and *c*-type interactions in planar C_s asymmetric tops. The treatment given allows one to develop special expressions for other cases.

The essential part of the method is that in all interaction cases the problem of differentiating the matrix product $\mathbf{U}^T\mathbf{H}\mathbf{U}$ can be reformulated as

$$\frac{\partial E}{\partial \zeta_{rs}^a} \simeq \text{constant}\,\mathbf{U}^T\mathbf{M}\mathbf{U} , \tag{9}$$

where **M** is a matrix called here the "*mixing matrix*", composed of elements 0 and ± 1.[4] The position of the ± 1's in the *mixing matrix* depends on the way the Hamiltonian matrix is set up, but once some construction principle is adopted, **M** becomes the same constant matrix for all rotational quantum numbers. As we shall see later the function of the *mixing matrix* is to permute pairs of columns of the $\mathbf{U}^T$ matrix, or to combine some columns of $\mathbf{U}^T$ and permute these combinations in building the $\mathbf{U}^T\mathbf{M}$ matrix. All other columns of $\mathbf{U}^T$ — not affected by other permutations — will be missing from the final matrix $\mathbf{U}^T\mathbf{M}\,\mathbf{U}$, therefore relatively simple expressions will be obtained for the combination of the eigenvector matrix elements.

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[4] The condition for this is that the perturbation Hamiltonian matrix is constructed on the basis of phased wavefunctions; then all matrix elements are real quantities.

The way in which a particular **M** matrix produces this permutation/combination effect is closely related to the function of the so-called elementary similarity transformations; in particular, to the properties of permutation matrices [3]. The *mixing matrix* is, however, not identical to either of these elementary matrices. The simplest type of *mixing matrices* is encountered in the example of multiple a-type interactions in asymmetric tops.

5.1 *Multiple a-type Coriolis interactions*

The construction of the perturbation Hamiltonian matrix in this case is such that the corresponding mixing matrix is symmetric and has $+1$ elements along its co-diagonals. The matrix transformations can be illustrated by using a matrix $\mathbf{M}_{rs}$ relating to just one interaction element.[5] The corresponding parts of the Hamiltonian matrix and $\mathbf{M}_{rs}$ are:

$$\begin{array}{cc} & \begin{array}{cc} r & s \end{array} \\ \mathbf{H}: & \begin{vmatrix} E_r & \mathit{\Delta}_{rs} \\ \mathit{\Delta}_{sr} & E_s \end{vmatrix} \end{array} ; \quad \begin{array}{cc} & \begin{array}{cc} r & s \end{array} \\ \mathbf{M}_{rs}: & \begin{vmatrix} 0 & +1 \\ +1 & 0 \end{vmatrix} \end{array}$$

where

$$\mathit{\Delta}_{rs} = \mathit{\Delta}_{sr} = 2AK\,\Omega_{rs}\zeta'_{rs},$$

$$E_r = \nu_r + F_r(J, K)\,.$$

In the above case the product matrix $\mathbf{U}^T\mathbf{M}$ will contain two columns which are the interchanged r-th and s-th columns of $\mathbf{U}^T$.

$$\begin{array}{ccc} \begin{array}{cc} r & s \end{array} & \begin{array}{cc} r & s \end{array} & \\ \begin{vmatrix} \ldots u_{r1}\ldots & u_{s1}\ldots \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ u_{rr} & u_{sr}\ldots \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ \ldots u_{rs}\ldots & u_{ss}\ldots \\ & \\ & \\ & \end{vmatrix} & \begin{vmatrix} & \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ \ldots 0 & +1 \\ \cdot & \\ & \cdot \\ & \cdot \\ \ldots +1 & 0 \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \end{vmatrix} = & \begin{vmatrix} u_{s1} & u_{r1} \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ u_{sr} & u_{rr} \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ u_{ss} & u_{rs} \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \end{vmatrix}. \\ \mathbf{U}^T & \mathbf{M}_{rs} & \mathbf{U}^T\mathbf{M}_{rs} \end{array}$$

---

[5] Again, the problem is set up on the basis of phased vibrational wavefunctions. Such $\mathbf{M}_{rs}$ matrices are closely related to matrices $\mathbf{I}_{ij}$ [3], $\mathbf{M}_{rs}$ corresponds to the non-diagonal block of $\mathbf{I}_{ij}$.

If now $\mathbf{U}^T\mathbf{M}_{rs}$ is right-multiplied by $\mathbf{U}$, the i-th diagonal element of the resulting product matrix is given as:

$$[\mathbf{U}^T\mathbf{M}\mathbf{U}]_{ii} = 2u_{ri}u_{si}\,.$$

Multiplying this expression by the constant factor in Eq. (9), which is presently $2AK\Omega_{rs}$, the Jacobian element, giving the sensitivity of the rovibrational levels in the excited state: $(v_i = 1, \sum_{j\neq i} v_j = 0)$ towards the Coriolis coefficient ζ^a_{rs} is given by the formula:

$$\left[\frac{\partial E(K)}{\partial \zeta^a_{rs}}\right]_{ii} = 4AK^{\text{upper}}\,\Omega_{rs}u_{ri}u_{si}\,, \tag{10}$$

where u_{ri} and u_{si} are elements of the eigenvector matrix belonging to some upper state K rotational quantum number.

5.2 *Multiple a, b and c-type Coriolis interactions in planar C_s asymmetric top molecules*

The somewhat more complicated problem of simultaneous *a*, *b* and *c*-type interactions in planar C_s asymmetric tops, such as isocyanic acid HNCO [4] can be similarly handled. Here one has three different types of off-diagonal elements in the Hamiltonian matrix:

$$\begin{aligned}
\langle J, K \mid \mathbf{H}^a_{rs} \mid J, K\rangle &= 2iA\,\zeta^a_{rs}\Omega_{rs}K\,,\\
\langle J, K \mid \mathbf{H}^c_{rs} \mid J, K \pm 1\rangle &= iC\,\zeta^c_{rs}\Omega_{rs}[J(J+1) - K(K\pm 1)]^{1/2}\,,\\
\langle J, K \mid \mathbf{H}^b_{rs} \mid J, K \pm 1\rangle &= \pm B\,\zeta^b_{rs}\Omega_{rs}[J(J+1) - K(K\pm 1)]^{1/2}\,.
\end{aligned}$$

To illustrate the problem we consider the interactions connecting $\nu_4(a')$, $\nu_5(a')$ and $\nu_6(a'')$ of isocyanic acid. Having removed the imaginary off-diagonal elements by proper phasing of the vibrational wavefunctions, we obtain, for a given value of J, a symmetric (9×9) matrix, which subdivides into three (3×3) blocks for $(K+1)$, K and $(K-1)$, respectively. The structure of the Hamiltonian matrix is shown in Table I.

If furthermore we approximate $[J(J+1) - K(K\pm 1)]^{1/2} \cong [J(J+1) - K^2]^{1/2}$, the problem can again be formulated in terms of the *mixing matrices*, whose construction for the different Coriolis zeta coefficients is shown in Figs. 1 and 2.

The rest of the above matrices **M** is filled with zeros.[6]

---

[6] Off-diagonal perturbation matrix elements diagonal in K produce co-diagonal, orthonormal matrices, those off-diagonal in K by one unit give rise to anti-diagonal, orthogonal matrices **M**.

Table I

Perturbation Hamiltonian matrix for

$J, K+1$	$J, K+1$	$J, K+1$	J, K	J, K
$\nu_4(a') + F_4(J, K+1)$	0	$2A(K+1)\,\zeta^a_{4,6}$	0	$C[J, K]^{1/2}\,\zeta^c_{4,5}$
	$\nu_5(a') + F_5(J, K+1)$	$2A(K+1)\,\zeta^a_{5,6}$	$C(J, K)^{1/2}\,\zeta^c_{4,5}$	0
		$\nu_6(a'') + F_6(J, K+1)$	$B[J, K]^{1/2}\,\zeta^b_{4,6}$	$B[J\ K]^{1/2}\,\zeta^b_{5\cdot 6}$
			$\nu_4(a') + F_4(J, K)$	0
	Symmetric			$\nu_5(a') + F_5(J, K)$

The constant factors corresponding to the above matrices in Eq. (9) are:[7]

$$\text{(a, b): } 2AK\,\Omega_{rs}, \quad \text{(c): } C[J, K]^{1/2}\,\Omega_{rs}, \quad \text{(d, e): } B[J, K]^{1/2}\,\Omega_{rs}.$$

The practical way to construct Jacobian element expressions is based on the observation that in the final u_{ij} combinations those elements are found in products whose row-indices are permuted by the particular **M** matrix, therefore for each interaction matrix element Δ_{rs} there will be products of the form $u_{r,i}u_{s,i}$. In multiple a-type interactions —where the perturbation problem is diagonal in K— this is the end result itself (see Eq. (10)), but the situation is somewhat more involved in *Section* 5.2.

To obtain the Jacobian element expressions in this example, we split the full matrices of dimension (9×9) into two (6×6) submatrices, one containing the $K+1$ and K sub-blocks, the other containing the K and $K-1$ sub-blocks. The reason for this division is that one two-block system corresponds to the $(K+1)/K$ interactions, while the other to the $K/(K-1)$ interactions. Then simply the products of the u_{ij} elements are written down using the indices of the zetas as row-indices in the u_{ij} products.

---

[7] $[J, K]^{1/2} \equiv [J(J+1) - K^2]^{1/2}$

$\nu_4(a')$, $\nu_5(a')$ and $\nu_6(a'')$ of isocyanic acid

J, K	$J, K-1$	$J, K-1$	$J, K-1$
$B[J, K]^{1/2} \zeta^b_{4,6}$	0	0	0
$B[J, K]^{1/2} \zeta^b_{5,6}$	0	0	0
0	0	0	0
$2AK \zeta^a_{46}$	0	$C[J, K-1]^{1/2} \zeta^c_{45}$	$-B[J, K-1]^{1/2} \zeta^b_{46}$
$2AK \zeta^a_{56}$	$C[J, K-1]^{1/2} \zeta^c_{45}$	0	$-B[J, K-1]^{1/2} \zeta^b_{56}$
$\nu_6(a'') + F_6(J, K)$	$-B[J, K-1]^{1/2} \zeta^b_{46}$	$-B[J, K-1]^{1/2} \zeta^b_{56}$	0
	$\nu_4(a') + F_4(J, K-1)$	0	$2A(K-1) \zeta^a_{46}$
		$\nu_5(a') + F_5(J, K-1)$	$2A(K-1) \zeta^a_{56}$
			$\nu_6(a'') + F_6(J, K-1)$

The resulting Jacobian element expressions are given below and are derived for the general planar C_s asymmetric top molecule with total vibrational dimension of N. $N = n_1 + n_2$, n_1 and n_2 being the dimensions for species a' and a'', respectively. For the i-th vibration

$$\frac{\partial E_i}{\partial \zeta^a_{rs}} = 4AK\, \Omega_{rs}[u_{r,i} u_{s,i} + u_{r+N,i} u_{s+N,i} + u_{r+2N,i}\, u_{s+2N,i}]\,,$$

where r and s span the species a' and a'', respectively.

$$\frac{\partial E_i}{\partial \zeta^c_{rs}} = 2C[J, K]^{1/2}\, \Omega_{rs}\{u_{r+N,i}(u_{s,i} + u_{s+2N,i}) + u_{s+N,i}(u_{r,i} + u_{r+2N,i})\}\,,$$

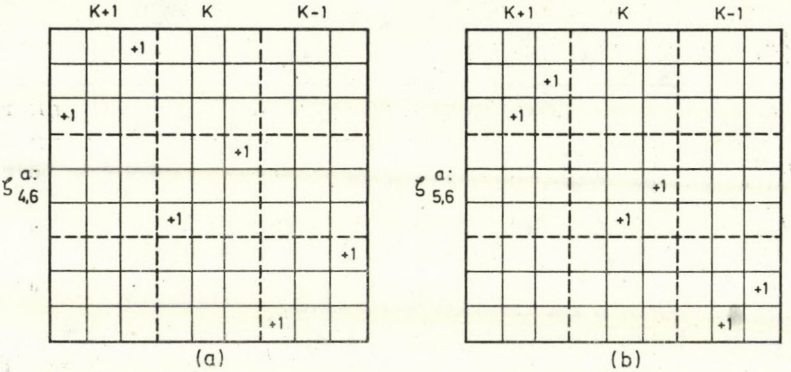
where r and s both span species a', but $r \neq s$.

$$\frac{\partial E_i}{\partial \zeta^b_{rs}} = 2B[J, K]^{1/2}\, \Omega_{rs}\{u_{r+N,i}(u_{s,i} - u_{s+2N,i}) + u_{s+N,i}\,(u_{r,i} - u_{r+2N,i})\}\,,$$

where r and s span again a' and a'', respectively.

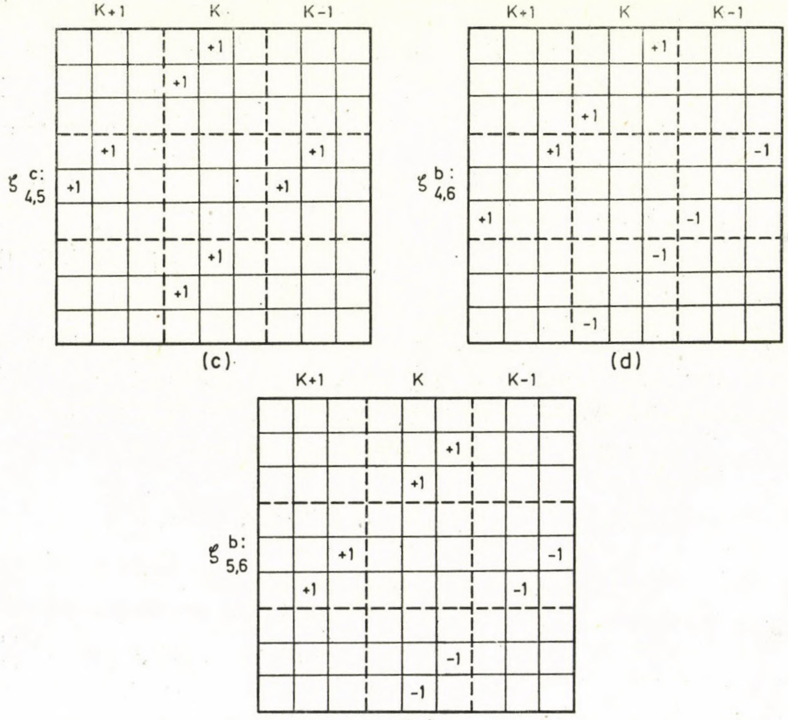
The vibrational index i runs three times from 1 to N in the $(3N \times 3N)$ matrix:

i: $1 \to N$ in all three K sub-blocks.



(a) (b)

Fig. 1. Mixing matrices for *a*-type Coriolis interactions



(c) (d)

(e)

Fig. 2. Mixing matrices for *b*-, and *c*-type Coriolis interactions

It can be noted that in all three expressions the same u_{ij} elements are used in different products and combinations. Fig. 3 shows how to select and combine the u_{ij} elements for a given vibrationally excited state for different interaction coefficients. Similar diagrams can be constructed for any molecule and scheme of perturbation to ease the writing of a computer programme.

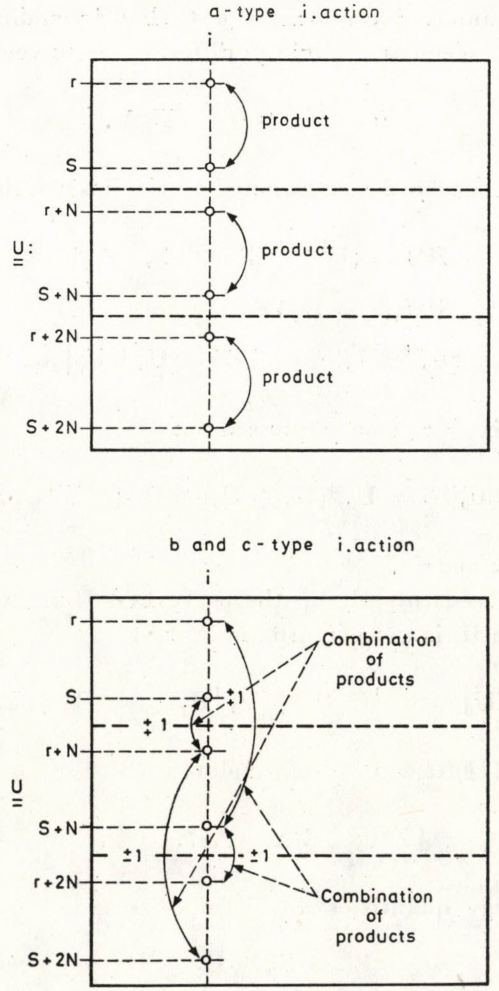


Fig. 3. **Diagram for the selection and combination of u_{ij} elements**

6. Application of first-order perturbation theory

In this *Section* it will be shown that the results previously obtained by the *mixing matrix* technique can also be derived from perturbation theory, provided the perturbation Hamiltonian matrix has small off-diagonal elements, i.e. when the perturbations are weak. The basis for this treatment is found in WILSON's book [5].

The diagonalization of the perturbation Hamiltonian matrix yields the eigenvalues. Starting from an unperturbed set of Hamiltonian matrix elements:

$$\mathbf{E}_0 = \mathbf{U}_0^T \mathbf{H}_0 \mathbf{U}_0 = \mathbf{U}_0^{-1} \mathbf{H}_0 \mathbf{U}_0 .$$

Now if the Hamiltonian matrix is perturbed by adding small increments to its off-diagonal elements, slightly different eigenvectors are obtained:

$$\mathbf{U} = \mathbf{U}_0 + \mathbf{U}_1 = \mathbf{U}_0\mathbf{A}\,.$$

The perturbed problem can be constructed on the basis of the unperturbed one:

$$\begin{aligned} \mathbf{HU} &= (\mathbf{U}^T)^{-1}\mathbf{E} = \mathbf{UE}\,, \\ \mathbf{HU}_0\mathbf{A} &= \mathbf{U}_0\mathbf{AE}\,, \\ [\mathbf{U}_0^{-1}\mathbf{HU}_0]\,\mathbf{A} &= \mathbf{AE} = [\mathbf{U}_0^T\mathbf{HU}_0]\,\mathbf{A}\,. \end{aligned} \tag{11}$$

Furthermore matrix **A** can be expressed as:

$$\mathbf{A} = \mathbf{U}_0^{-1}\mathbf{U} = \mathbf{U}_0^{-1}(\mathbf{U}_0 + \mathbf{U}_1) = \mathbf{I} + \mathbf{U}_0^{-1}\mathbf{U}_1 \cong \mathbf{I}\,,$$

where **I** is the unit matrix.

We then proceed to split up the perturbed Hamiltonian matrix: $\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_1$, where $\mathbf{H}_1$ is the perturbation term:

$$\mathbf{E}^x = \mathbf{U}_0^{-1}\mathbf{HU}_0 = \mathbf{U}_0^{-1}\mathbf{H}_0\mathbf{U}_0 + \mathbf{U}_0^{-1}\mathbf{H}_1\mathbf{U}_0 = \mathbf{E}_0 + \mathbf{U}_0^{-1}\mathbf{H}_1\mathbf{U}_0\,.$$

Returning to Eq. (11) it can be reformulated as

$$\mathbf{E}^x\mathbf{A} = \mathbf{AE}\,. \tag{12}$$

The different energy quantities are defined as:

$$\begin{gathered} \mathbf{E}^x = \mathbf{E}_0 + \mathbf{E}_1 \cong \mathbf{E}\,, \\ \mathbf{E}_0 = \mathbf{U}_0^T\mathbf{H}_0\mathbf{U}_0\,, \quad \mathbf{E}^x = \mathbf{U}_0^T\mathbf{HU}_0\,, \quad \mathbf{E}_1 = \mathbf{U}_0^T\mathbf{H}_1\mathbf{U}_0\,, \\ \mathbf{E} = \mathbf{U}^T\mathbf{HU}\,. \end{gathered} \tag{13}$$

Eq. (12) can be written as follows

$$\sum_j E_{ij}^x A_{jk} = A_{ik}E_k\,.$$

The solution of this system of equations is obtained from the secular equation:

$$|\,\mathbf{E}^x - \mathbf{EI}\,| = 0\,.$$

If the roots of this matrix are resubstituted in Eq. (12) the eigenvectors building the matrix **U** are obtained.

From Eq. (13) we can derive *via* first-order perturbation theory [5]:

$$\mathbf{E} - \mathbf{E}_0 = \mathbf{E}_1 \cong \mathbf{U}_0^T \mathbf{H}_1 \mathbf{U}_0 , \tag{14}$$

whose k-th diagonal element is:

$$(E_1)_k = [U_0^T H_1 U_0]_{kk} = \sum_u \sum_v (U_0)_{uk} (U_0)_{vk} (H_1)_{uv} , \tag{15}$$

where k is the vibrational index, while u and v refer to normal-coordinates among which the interactions occur.[8]

If we let $H_1 \to 0$ and $E_1 \to 0$ in Eq. (15) the interaction Jacobian element fort the i-th vibrational state is obtained as:

$$\partial E_i / \partial H_{uv} = 2 u_{ui} u_{vi} . \tag{16}$$

(It is to be remarked that for asymmetric tops the diagonal terms

$$\partial E_i / \partial H_{uu} = u_{ui}^2$$

are undefined, since H_{uu} is not altered when the Hamiltonian is perturbed.)

Since in the a-type interaction problem $H_{uv} = 2AK^{\text{upper}}\,\Omega_{uv}\zeta_{uv}^a$, we obtain:

$$\partial E_i / \partial \zeta_{uv}^a = 4AK^{\text{upper}}\,\Omega_{uv} u_{vi} u_{ui} ,$$

which is identical to our previous result: (see Eq. (10)).

For the elements of the matrix **A** the following formula can be given by substituting Eq. (14) back to Eq. (12), and retaining linear terms only:

$$A_{ik} = \frac{E_{ik}^x}{E_k - E_i} A_{kk} \cong \frac{E_{ik}^x}{E_k - E_i}$$

for $i \neq j$.

Using the relationship $\mathbf{E}^x = \mathbf{E}_0 + \mathbf{U}_0^T \mathbf{H}_1 \mathbf{U}_0$ the result is:

$$A_{ij} = \sum_u \sum_v \frac{(U_0)_{ui} (U_0)_{vj} (H_1)_{uv}}{E_j - E_i} , \text{ for } i \neq j , \tag{17}$$

which may be rewritten as:

$$A_{ij} = 2AK^{\text{upper}}\,\Omega_{uv} \sum_u \sum_v \frac{(U_0)_{ui} (U_0)_{vj} \zeta_{uv}^a}{\nu_j^x(K) - \nu_i^x(K)}$$

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[8] Expressions (14) and (15) are basically identical to Kovács' formulae (14) and (15) in [7].

for $i \neq j$, and where $\nu_j^x(K)$ and $\nu_i^x(K)$ are perturbed vibrational origins for the different K sub-branches obtained from the diagonalization of the perturbation Hamiltonian matrix.

The criterion of applicability of first-order perturbation theory is that **A** should have relatively small off-diagonal elements, which is seen to be the case if $2AK^{\text{upper}}\ \Omega_{uv}\zeta_{uv}^a \ll \nu_j^x(K) - \nu_i^x(K)$, that is, when the Coriolis perturbation is weak indeed.

7. Conclusions

The present paper offers algebraic Jacobian element expressions for Coriolis interactions. Apart from the cases dealt with in *Sections* 2 and 3 the formulae apply for weak interactions. Although in actual perturbations the strength of interactions will be different among different vibrational states, the presently given expressions for $n > 3$ are satisfactory to get a rough fit to the interaction parameters. In the case of strong interactions numerical Jacobian element calculations are advisable.

It may be added that, due to the existence of quadratic Coriolis zeta sum rules, not all zeta coefficients can be independently refined. Least-squares refinement procedures applied for this purpose should contain constraints to take these sum rules into account. Such a programme is in development in our laboratory [6].

REFERENCES

1. I. M. Mills: Pure and Applied Chem., **11**, 325, 1965.
2. I. Kovács and S. Singer: Phys. Zeitschrift, **43**, 362, 1942.
3. J. H. Wilkinson: The Algebraic Eigenvalue Problem, Clarendon Press, Oxford, 1965.
4. R. A. Ashby and R. L. Werner: J. Molecular Spectr., **18**, 184, 1965.
5. E. B. Wilson, J. C. Decius and P. C. Cross: Molecular Vibrations, p. 231, McGraw Hill, New York, 1955.
6. L. Nemes: to be published.
7. I. Kovács: Rotational Structure in the Spectra of Diatomic Molecules, Akadémiai Kiadó/Adam Hilger Ltd., Budapest—London, 1969.
8. S. Castellano and A. A. Bothner-By, J. Chem. Phys., **41**, 3863, 1964.
9. W. F. Rowe and E. B. Wilson, J. Mol. Spectr., **56**, 163, 1975.

RECENSIONES

R. Behrisch, W. Heiland, W. Poschenrieder, P. Staib and H. Verbeek:

Ion Surface Interaction, Sputtering and Related Phenomena

Gordon and Breach Science Publishers, London, New York, Paris, 1974. 319 pages

Sputtering and cleaning of solid surfaces by ion bombardment is a classical tool of materials science and technology. In the last 15 years the interaction of ions with solid surfaces became a powerful method of surface studies and surface science. A great number of outstanding laboratories was devoted to reveal physical processes taking place in ion bombardment. Various methods based on ion bombardment have been developed providing information on the composition of the surface and depth profile, electronic structure and even on surface topography of solids.

In September 1972, an international conference was held on ion-surface interactions and sputtering processes in the Max-Planck-Institut für Plasmaphysik, Garching bei München. The book compiles the full text of 50 papers presented at the conference. Unfortunately 18 papers have not been submitted for publication.

The main aspect of the conference was to discuss the physical processes of sputtering, scattering and emission (ion electron, photon) produced by ions. Many papers deal with applications.

The main chapters of the book are:

— *Sputtering* of single crystals (**Jackson**, **Hofer** etc.), compounds, adsorbed layers, oxides (**Kelly**), polycrystalline sputtering (**Andersen**, **Colligon**, **Eckstein** etc.), theory, computer simulation and experiments.

— *Surface and depth analysis* by sputtering and Auger spectroscopy (**Staib**), secondary ion mass spectroscopy (**Schulz**, **Werner**, **Biersack** etc.).

— *Scattering of ions*, models for scattering processes (**Parilis**, **Mashkova**, **Skripka** etc.), energy distribution of backscattered protons (**Verbeek**), ion bombardment induced radiation damage (**Heiland** etc.), surface study by application of ion scattering (**Akashi**, **Heiland**, **Taglauer**).

— *Secondary ion emission*, physical processes (**Joyes**, **Blaise**, **Jurela** etc.), yields (**Abdullayeva** etc.), clusters, polyatomic ions (**Herzog**, **Staudenmaier**, **Richards**, **Kelly** etc.).

— *Surface damage and topography* (**Nelson**, **Hermanne**, **Wilson**, **Blewer**, **Kaminsky**, **McCracken**, **Cavaleru**, **Bayly** etc.).

— *Photon emission by ion bombardment*, of metals (**Kerkdijk**, **Martel** etc.) and insulator compounds (**Tolk** etc.).

— *Secondary electron emission* distribution (**Colombié**, **Parilis**, **Arifov** etc.), yield (**Kishinevsky**).

— *SIMS applications* (**Werner**).

The great deal of data recollected in the papers, especially the yields of ion bombardment are very important for SIMS studies. The sputtering yield and damage are of great interest for LEED and AES work. Scattering processes and photon emission are nowadays in the focus of interest of current research.

The material published, although not complete, provides an excellent review of research done in this field. The list of participants and their institutes provides information about the research centres.

The book is indispensable for research laboratories, universities and industry, working with surface studies, analysis and technology.

G. Gergely

M. G. Bowler: Nuclear Physics

Pergamon Press Ltd. Oxford, 1973, 420 pages

This book sets out clearly and logically the fundamental concepts of low energy nuclear physics. From the outset the concepts developed are treated from the point of view of quantum mechanics, although the author assumes an initial knowledge of the Schrödinger equation, some perturbation theory and basic electromagnetic theory. The book contains little on experimental techniques and nothing on the subject of the interaction of radiation with matter. Chapter 1 is primarily concerned with nuclear structure at a fairly basic level. Chapter 2 deals with spin and static electric and magnetic moments. Chapter 3 is on nuclear decay treating both electromagnetic and β-decay using quantum mechanics. Chapter 4 is devoted to the theory of nuclear reactions and discusses the concepts of cross-section and of resonance in considerable detail. In Chapter 5 the nuclear physics of the fission reaction, the nuclear aspects of stellar physics and further application of the theory of thermonuclear reactions: the problems of devising a thermonuclear power-plant are treated. Finally, the last chapter introduces the important concept of isospin and establishes links with high energy physics.

Students attending courses on nuclear physics, astrophysics and nuclear engineering will find this book an extremely lucid introduction to more complex and specialised texts.

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K. H. Hellwege: Einführung in die Physik der Molekeln

Springer Verlag, Berlin, 1974., 162 S.

Dieser Band enthält eine kurze und elementare Einführung in die Molekülphysik und soll nicht mehr sein als ein hoffentlich nützliches Hilfsmittel für Anfänger. Deshalb wurde auf stoffliche Vollständigkeit ebenso verzichtet wie auf anspruchsvollere theoretische Methoden. Vorausgesetzt sind nur die Grundlagen der Quantentheorie und der Atomphysik. Der Band befasst sich mit dem Modell für zweiatomige Molekeln und mit der Rotations-, Schwingungs-, Elektronenenergie und der Gesamtenergie zweiatomiger Molekeln, mit den Bandenspektren und der chemischen Bindung bei zweiatomigen Molekeln. Im weiteren Teil des Bandes liegen Besprechungen über mehratomige Molekeln, den Raman-Effekt und die Kernspin-Effekte vor. Die Werte der atomaren Konstanten und eine Energie-Umrechnungstabelle befinden sich am Ende des Bandes.

Es ist zu bedauern, dass der Autor als Quellenwerke grösstenteils verhältnismässig ältere Bücher verwendet hat. Daraus ergibt sich, dass einige Bezeichnungen altmodisch sind (zum Beispiel: in Hundschem Fall b wird statt dem vom Autor verwendeten Vektor und der Quantenzahl K heutzutage N gebraucht und statt dem von ihm bezeichneten N ist R gebräuchlich).

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D. G. Holloway: The Physical Properties of Glass

Wykeham Publications (London) Ltd., London and Winchester, 1973 pp. xii + 220

Belonging to the Wykeham Science Series, this book provides an elementary and highly pedagogical introduction to the present state of glass science for students approaching or starting their careers in university. As with other volumes in the series, the main author, a distinguished research worker in the field, is assisted by an experienced schoolmaster, D. A. Tawney in the present case. Judged by the result, this arrangement seems to serve its purpose to reinforce the link between school and higher education excellently.

Following a general introduction, the composition and structure of glasses are described in Chapter 1. The limits to our present understanding of the structure of glass are also discussed.

The thermal properties of glass (heat capacity, thermal expansion, thermal conductivity) are dealt with in Chapter 2.

Chapter 3 is devoted to the electrical properties of glass, such as d.c. conductivity, the mechanism of ionic conduction in solids, dielectric properties and relaxation, high frequency phenomena, etc.

The optical properties of glass (refractive index, dispersion, absorption, optical glasses, colouring) are described in Chapter 4.

Chapter 5 deals with the elastic properties (anelasticity, relaxation, hardness) of glass.

Chapter 6 is on the fracture of glass, the field of research interest of the author.

The text is clear and lucid throughout, the reader is helped by many illustrations (diagrams, drawings and photographs), by careful interpretations attached to the formulae and by a list of symbols and an index at the end, where he can also find some suggestions for further reading.

It is important to point out that while the primary aim of the book is to give a simple qualitative account of the physical properties of glass as determined by its microscopic structure, this also involves introducing most of the fundamental concepts of solid state physics, which gives the author the opportunity to make a comparison between glasses and crystalline solids. This way the book may, in fact, serve as an introduction to the physics of solids in general and as such it is highly recommended to students and teachers of condensed matter physics and materials science.

The only word of criticism should go to the publisher: if all copies are as poorly bound as mine, this will considerably limit their use; even a paperback should be able to withstand wear without falling apart to pages.

I. Kondor

Printed in Hungary

A kiadásért felel az Akadémiai Kiadó igazgatója Műszaki szerkesztő: Botyánszky Pál
A kézirat nyomdába érkezett: 1975. VIII. 25. — Terjedelem: 7 (A/5) ív, 29 ábra

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Papers may be either articles with abstracts or short communications. Both should be as concise as possible, articles in general not exceeding 25 typed pages, short communications 8 typed pages.

II. MANUSCRIPTS

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ANALYTIC 3*d* RADIAL WAVE FUNCTIONS FOR THE POSITIVE IONS AND ATOMS OF THE IRON GROUP ELEMENTS

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Hartree—Fock variational procedure was carried out for the iron group atoms in singly ionized and neutral states to optimize the 3*d* orbital in a two exponential form. For the inner orbitals a simplified description was given and they were assumed to be fixed during the variational procedure. The analytic wave functions presented here are proposed first of all for use in molecular and solid state physics applications.

The construction of analytic wave functions has not lost its importance even now when a large number of self-consistent field (SCF) functions have been tabulated (e.g. [1]) for the different ionized states of the elements. Whereas the analytic form is convenient also in atomic physics application, its advantage is striking in molecular and solid state physics applications, since here, in the description of the electrons taking part in the bonding, the atomic functions appear just as the input data of the calculation. In this case, first, the calculations can be carried out much more easily by using a simple analytic form while the loss of accuracy is irrelevant. Secondly, the flexibility of the analytic functions due to their variable parameters makes it eventually possible to take into account the rearrangement of the electrons in the bonding.

For the iron group elements the analytic approximations are partly highly accurate functions consisting of numerous basis functions [2], [3], [4], [5], [6], partly simpler, but less accurate wave functions appropriate for molecular and solid state physics applications [7], [8], [9], [10], [11], using, for example, a minimum basis set of STO-s (Slater-type orbitals). As has long been known, the minimum basis set approximation, which describes an electron of $(n, 1)$ quantum numbers by $n - 1$ STO-s, reproduces fairly well the inner *s* and *p* functions. In the case of the 3*d* orbital, however, this approximation breaks down [12], [13], [9], [14]; at least two STO-s are needed to reproduce the characteristic shape of the 3*d* radial function [9], [10], [11] (An *ad hoc* two-STO 3*d* radial function was used earlier by Fletcher [15] for the energy band calculation of nickel). In these papers the parameters of the 3*d* radial wave function were determined by fitting to the SCF numerical function [9], [10] or by minimizing the Hartree—Fock (HF) energy with respect to them [11]. This paper follows the latter procedure as an extension of an earlier work [11]. While this previous paper contains results only for the singly ionized states of Ti, Cr, Fe and Cu, in this work the variation was carried out with higher accuracy for the neutral atoms of $3d^{n-1}4s$ configuration and the positive ions of $3d^n$ configuration of the iron group elements. For the determination of the variational energy the 'average of configuration' method [12] was used, and the inner orbitals were assumed to be fixed.

It should be emphasized again that the two-STO approximation presented here is by no means intended to compete in *accuracy* with some of the earlier, much more elaborate approximations mentioned above. In many applications, however, the two-STO form, which brings the conditions of *simplicity*, *flexibility* and *relative accuracy* together, is more appropriate than the more complicated many-STO approximations.

Model wave functions for the *s*, *p* and *d* orbitals

Since our purpose was to determine the parameters of the $3d$ radial wave function, we assumed for the inner s and p orbitals the simplest possible form still reflecting the main features of the HF functions. Instead of the Schmidt orthogonalization procedure we used the so called Fock—Petrashen orbitals (FPO) for the description of the inner s and p radial functions, which have the form

$$R_{nl} = Q_{nl}(r) \exp(-\alpha_{nl} r), \tag{1a}$$

where Q_{nl} is a polynomial

$$Q_{nl} = \sum_{k=l}^{n-1} A_{nl}^{k} \frac{(2\alpha_{nl})^{k+3/2}}{[(2k+2)!]^{1/2}} r^k \tag{1b}$$

and the coefficients A_{nl}^k are determined so as to make R_{nl} orthogonal to all inner orbitals of the same symmetry. Although in total energy calculations the FPO-s do not provide such an accuracy than those made by Schmidt orthogonalization [16], they are sufficiently accurate for the present purpose where only the d-part of the total energy is needed. This is because the FPO-s deviate considerably from the HF functions in the neighbourhood of the nucleus only, and — with an adequate choice of the α_{nl} screening constants — they can fit the HF radial wave functions fairly well in the region where they overlap with the $3d$ orbital. The screening constants of the $1s$, $2s$ and $2p$ orbitals were determined by the traditional Slater's rule

$$\begin{aligned} \alpha_{1s} &= 18.70 + m, \\ \alpha_{2s} = \alpha_{2p} &= \frac{1}{2}(14.85 + m), \end{aligned} \tag{2a}$$

Table I

The A_{nl}^{k} coefficients defined in (1b) for the iron group elements

Shell (n, l)	k	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
1s	0	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
2s	0	0.81830	0.82644	0.83389	0.84073	0.84703	0.85285	0.85825	0.86327
	1	−1.62113	−1.62635	−1.63110	−1.63545	−1.63944	−1.64312	−1.64651	−1.64966
2p	1	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
3s	0	0.40715	0.41410	0.42047	0.42631	0.43170	0.43668	0.44129	0.44558
	1	−2.01656	−2.03393	−2.04970	−2.06410	−2.07729	−2.08942	−2.10061	−2.11096
	2	2.41811	2.42782	2.43663	2.44464	2.45197	2.45869	2.46488	2.47060
3p	1	0.97208	0.98481	0.99628	1.00665	1.01609	1.02470	1.03260	1.03986
	2	−1.80526	−1.81463	−1.82302	−1.83060	−1.83746	−1.84371	−1.84943	−1.85468

where m is the number of d electrons both for the atoms and ions with the assumed $3d^m\,4s$ and $3d^m$ configurations, respectively. In the case of the $3s$ and $3p$ shells, however, we modified Slater's rule by introducing some screening for the s and p electrons by d electrons. Such a modification is straightforward in view of the fact that the maximum radial densities for all $3s$, $3p$ and $3d$ electrons occur at about the same radii. In addition to this, a constant term was added as a correction to α_{3s} and α_{3p} so as to optimize the orbital of the form (1) for the $3s$ and $3p$ shells. The values of these corrections were determined by the condition that the first moments of the radial charge densities should be in optimal agreement with the HF values for the iron group elements. Thus the screening constants of the $3s$ and $3p$ shells as a function of m are

$$\begin{aligned} \alpha_{3p} &= \frac{1}{3}(7.75 + 0.76\, m) + 0.39\,, \\ \alpha_{3s} &= \alpha_{3p} + 0.50\,. \end{aligned} \tag{2b}$$

The A_{nl}^{k} coefficients in (1) determined by the screening constants given by (2) are shown in Table I. from Ti to Cu. As an example, in Fig. 1 the $2p$ and $3s$ radial functions $P_{nl} = rR_{nl}$ are compared to the HF functions of SYNEK [4]. One can see from the Figure, first, that the one-STO function is a rather good approximation for the $2p$ shell, just as expected. Secondly, our approximate FPO function follows generally with sufficient accuracy the function given by SYNEK [4] for the $3s$ shell except the region neighbouring to the nucleus,

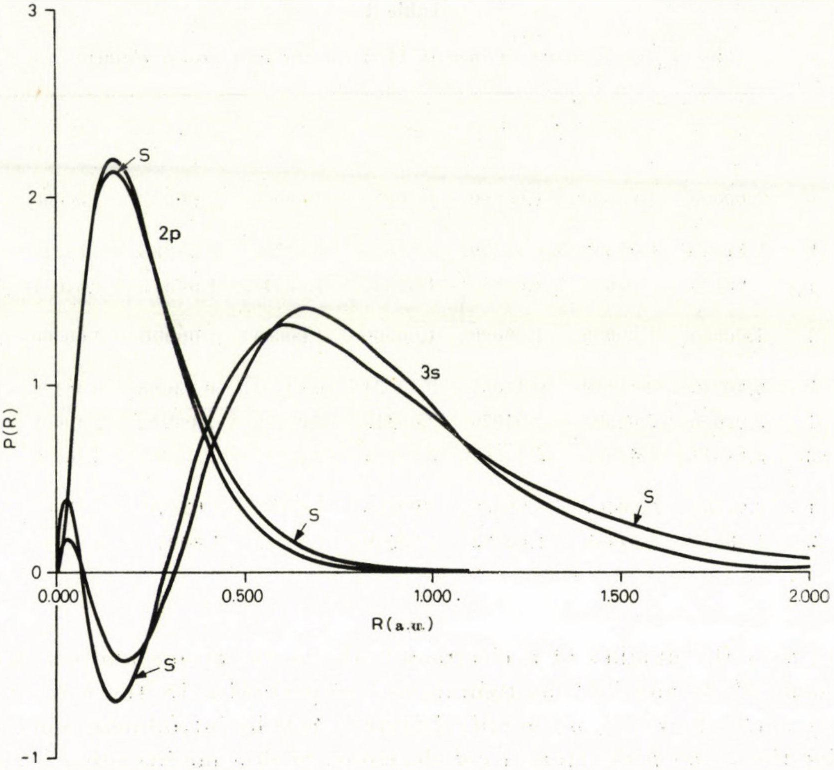

Fig. 1. Comparison of the $P(r) = rR(r)$ radial wave functions given by Eq. (1) for the $2p$ and $3s$ orbitals of Cu^+ ion with the corresponding HF results of SYNEK (S) [4]

where it deviates considerably from the HF function. This inner region, however, is irrelevant from the point of view of calculating the d-part of the total energy.

Since atomic $4s$ functions of $3d^m4s$ configuration have not been available for all the iron group elements, we used CLEMENTI's $4s$ wave functions [5] of the $3d^{m-1}4s^2$ configuration, and it is expected that no significant error in the resulting d-orbitals was thereby introduced.

As it was mentioned before, the $3d$ orbital cannot be described even qualitatively by using a simple one-STO function. In this paper a two-STO form was assumed for the $3d$ shell, which — as was pointed out earlier [13], [14], [10], [11] — already reproduces the main effect in the characteristic deviation of the $3d$ orbital from the hydrogenic shape. Thus the $3d$ radial function has the form

$$R_{3d} = r^2 \left\{ A_1 \left(\frac{(2\alpha_1)^7}{6!} \right)^{1/2} e^{-\alpha_1 r} + A_2 \left(\frac{(2\alpha_2)^7}{6!} \right)^{1/2} e^{-\alpha_2 r} \right\}, \tag{3}$$

Table II

Parameters of the model 3*d* radial wave functions of the form (3) for the atoms (A) and ions (I) of the 3*d* transition series in $3d^m4s$ and $3d^m$ configuration, resp.

		Orbital exponents		Expansion coefficients	
		α_1	α_2	A_1	A_2
Ti	A	4.3067	1.6331	0.42885	0.72984
	I	4.4487	1.7413	0.40722	0.73996
V	A	4.7140	1.8323	0.43661	0.71737
	I	4.8193	1.9161	0.42006	0.72568
Cr	A	5.0887	2.0058	0.44325	0.70830
	I	5.1821	2.0789	0.42862	0.71634
Mn	A	5.4444	2.1648	0.44920	0.70103
	I	5.5276	2.2303	0.43587	0.70878
Fe	A	5.7891	2.3144	0.45437	0.69519
	I	5.8815	2.3821	0.43976	0.70452
Co	A	6.1353	2.4624	0.45770	0.69131
	I	6.2170	2.5226	0.44529	0.69931
Ni	A	6.4600	2.6000	0.46295	0.68600
	I	6.5528	2.6631	0.44913	0.69558
Cu	A	6.7810	2.7329	0.46761	0.68155
	I	6.8769	2.7966	0.45400	0.69119

where α_1, α_2, A_1 and A_2 are variational parameters; one of them is fixed by the normalizing condition (in the calculation A_1).

The results of the HF variational procedure discussed in the next section are shown in Table II and Fig. 2. In the Table the values of the parameters of the 3*d* radial wave function are shown for the singly ionized and neutral states (with $3d^m$ and $3d^m4s$ configuration, respectively) of the iron group elements from Ti to Cu. One can see from the Table that the screening constants show an approximate linear dependence on the *d* electron number *m*, which has the form

$$\left.\begin{aligned}\alpha_1 &= 0.34671\, m + 3.4346\\ \alpha_2 &= 0.15006\, m + 1.3160\end{aligned}\right\}\ \text{for ions}$$

$$\left.\begin{aligned}\alpha_1 &= 0.35160\, m + 3.3045\\ \alpha_2 &= 0.15543\, m + 1.2079\end{aligned}\right\}\ \text{for atoms}$$

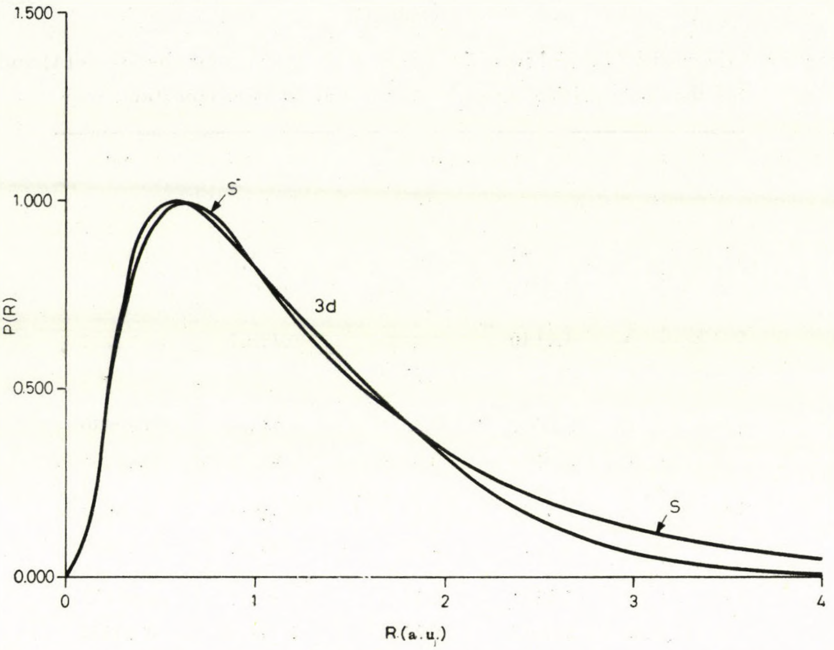

Fig. 2. Comparison of the $P_{3d} = rR_{3d}$ radial wave function given by Eq. (3) for copper ion with the HF result of SYNEK (S) [4]

These expressions are satisfied within 0.5 and 1 per cent for α_1 and α_2, respectively. As for the amplitudes of the $3d$ wave function, though they show a pronounced monotonic dependence on the d electron number — A_2 decreases and A_1 increases with m — they vary very slowly through the series. From Ti to Cu the variation of A_2 and A_1 is 7 and 9 per cent, respectively. In Fig. 2 the radial function $P_{3d} = rR_{3d}$ is plotted for Cu^+ together with the highly accurate 6-STO result by SYNEK [4]. The comparison shows that the two-STO form simulates well the HF function in the region $0 < r < 2$ a.u., while beyond this region it cuts off too sharply. This shows the limits of the two-STO approximation, since more STO basis functions with smaller screening constants ('effective charge') are needed to get better agreement in this outer region as well.

Calculation of the total energy and the variational procedure

To determine the optimized values of the parameters of the $3d$ radial wave function the conventional HF variational procedure was used with two restrictions. First, we varied only the parameters of the $3d$ orbital, the inner wave functions (in the case of neutral atoms the $4s$ function as well) being kept fixed. Secondly, the average energy of the configuration [12] was minimized instead of the energy of the ground state multiplet of the given configuration. This latter assumption results in orbitals somewhat more extended [3] than those which could have been obtained by varying the ground state multiplet energy. Taking into account the accuracy of the two-STO approximation, however, this effect is of no importance here.

With these assumption one has to minimize the *d*-part of the 'average of configuration' HF energy which has the form

$$E^d_{av} = \sum_{i}^{(3d)} I(i) + \sum_{\text{pairs } i,j}^{(3d)} \{(ij|g|ij) - (ij|g|ji)\}_{av}\,, \tag{4a}$$

where the one- and two-electron terms are defined by

$$I(i) = \int \psi_i^*(r) \left(-\nabla^2 - \frac{2Z}{r}\right) \psi_i(r)\, dr\,, \tag{4b}$$

$$(ij|g|rt) = \iint \psi_i^*(r_1)\, \psi_j^*(r_2) \frac{2}{r_{12}} \psi_r(r_1)\, \psi_t(r_2)\, dr_1\, dr_2\,. \tag{4c}$$

The superscript (3*d*) denotes that at least one of the indices should mean a 3*d* orbital, the index *av* means the average over all multiplets of the given configuration. *Z* stands for the total nuclear charge. The energy is given in rydbergs. From (4) one can get in a straightforward way [12] the following expressions containing only radial functions

$$E^d_{av} = mI(3d) + \frac{m(m-1)}{2}(3d, 3d) + \sum_{i \neq 3d} mq_i(3d, i)\,, \tag{5a}$$

where

$$I(i) = \int_0^\infty rR_{n_i l_i}(r) \left[-\frac{d^2}{dr^2} + \frac{l_i(l_i+1)}{r^2} - \frac{2Z}{r}\right] rR_{n_i l_i}(r)\, dr\,, \tag{5b}$$

$$(i,i) = F^\circ(n_i\, l_i, n_i\, l_i) - \sum_{k \neq 0} \frac{c^k(l_i\, 0, l_i\, 0)}{4\, l_i + 1} F^k(n_i\, l_i, n_i\, l_i)\,, \tag{5c}$$

$$(i,j) = F^\circ(n_i\, l_i, n_j\, l_j) - \sum_{k} \frac{c^k(l_i\, 0, l_j\, 0)}{(4l_i+2)^{1/2}\,(4l_j+2)^{1/2}} G^k(n_i\, l_i, n_j\, l_j)\,. \tag{5d}$$

Here q_i is the number of electrons contained actually in the *i*-th shell, *F* and *G* are the CONDON—SLATER coulomb and exchange integrals defined in SLATER's book [12] and the coefficients c^k are also tabulated there. By using (5) and the analytic forms for the wave functions detailed in the previous section, one can easily obtain simple analytic expressions for the *d*-part of the total energy as a function of the $\alpha_i\, A_i$ variational parameters. For example, the one- and two-electron integrals containing only $3d$ wave functions have the form

$$I(3d) = \sum_{i,j=1}^{2} A_i A_j (\eta_{ij}/\xi_{ij})^{2n+1} \left[\eta_{ij}^2 - \frac{2Z}{n}\xi_{ij}\right],$$

$$(3d, 3d) = F^\circ - \frac{2}{63}(F^2 + F^4),$$

where

$$F^k = 8\,\frac{(2n+k)!\,(2n-k-1)!}{(2n)!\,(2n)!} \sum_{ijuv=1}^{2} A_i A_j A_u A_v \left(\frac{\eta_{ij}\,\eta_{uv}}{\xi_{ij}\,\xi_{uv}}\right)^{2n+1} \xi_{uv}$$

$$\left[\left(\frac{\xi_{uv}}{\xi_{ij}}\right)^k - \left(\frac{\xi_{uv}}{\xi_{ij}+\xi_{uv}}\right)^{2n} \sum_{l=0}^{2n+k} \frac{(2n+l-k-1)!}{(2n-k-1)!\,l!} \left(\frac{\xi_{ij}}{\xi_{ij}+\xi_{uv}}\right)^{l-k}\right].$$

Here we used the notations

$$\xi_{ij} = \frac{\alpha_i + \alpha_j}{2} \quad \text{and} \quad \eta_{ij} = \sqrt{\alpha_i\,\alpha_j}.$$

In the above expressions n is the principal quantum number that equals 3 for the $3d$ orbital.

In the optimization procedure α_1, α_2 and A_2 were varied. The minimum value of the energy was stabilized, on average, within $5 \cdot 10^{-8}$ ry.

In order to check the results — besides the direct comparison of the $3d$ radial functions in Fig. 2 — the energy parameters were compared with the HF values. Such a comparison is presented for the F^4/F^2 ratios and the one-electron energy values of the iron group elements. The ratio F^4/F^2 plotted in Fig. 3 is characteristic for the non-hydrogenic shape of the $3d$ shell (as discussed by Slater [12] and Watson [3]), since the hydrogenic value is equal to 0.6522 independently of the d electron number. The good agreement between our results and the HF values [3] shows that the two-STO form is already suitable to reproduce the characteristic deviation of the $3d$ orbital from the hydrogenic shape. The ratio F^4/F^2 calculated by using the two-STO $3d$ wave function by Richardson et al. [9] are also plotted in the Figure.

In Fig. 4 the one-electron energies of the $3d$ orbitals are plotted both for the ions and atoms of the $3d$ transition series. The one-electron energy is defined by

$$\epsilon_{3d} = I(3d) + (m-1)(3d, 3d) + \sum_{i \neq 3d} q_i(3d, i)\,. \tag{6}$$

Here the same notations were used as in (5). In the Figure the $3d$ one-electron energies of the positive ions are compared with Watson's available HF 'average of configuration' values [3] and the experimental ionization energies

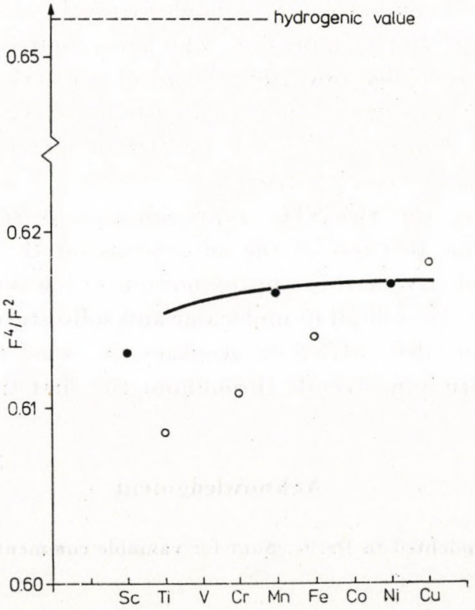

***Fig. 3.* F^4/F^2 for the iron group elements in singly ionized state. The present results (solid line) are compared with the HF values of [3] (heavy dots) and the results of [9] (empty circles). The hydrogenic value is also plotted.**

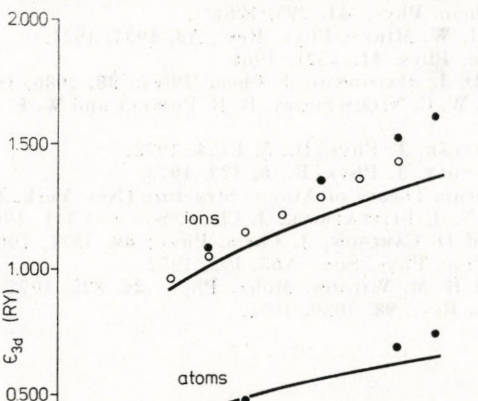

***Fig. 4.* ϵ_{3d} one-electron energies for the atoms and ions of the iron group elements. Besides the present results (solid lines) the HF [4] and the HFS [1] values are also plotted (heavy dots). For ions the experimental ionization energies are also shown (empty circles).**

[17]. For atoms the comparison was made with the results of HERMAN and SKILLMAN [1] for $3d^m4s$ configuration. The agreement is plainly less satisfactory in this case, especially towards the end of the series. This is because the one-electron energy is rather sensitive to the small variation of the energy integrals (e.g. $d - d$ interaction) and this effect increases with increasing d electron number, as one can see from (6).

In conclusion, the two-STO approximation is seen to reproduce the main non-hydrogenic features of the $3d$ orbitals for the iron group elements. Owing to the simplicity of this approximation the wave functions presented here are appropriate first of all in molecular and solid state physics calculations, though they assure also sufficient accuracy in some less elaborate atomic applications, like studying trends throughout the first transition series.

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REFERENCES

1. F. HERMAN and S. SKILLMAN, Atomic Structure Calculations, New Jersey: Prentice Hall, 1963.
2. P. O. LÖWDIN and K. APPEL, Phys. Rev., **103**, 1746, 1956.
3. R. E. WATSON, Phys. Rev., **118**, 1036, 1960.
4. M. SYNEK, Phys. Rev., **131**, 1572, 1963.
5. E. CLEMENTI, J. Chem. Phys., **41**, 295, 1964.
6. J. M. MINOR and R. W. MIRES, Phys. Rev., **A3**, 1937, 1971.
7. G. BURNS, J. Chem. Phys. **41**, 1521, 1964.
8. E. CLEMENTI and D. L. RAIMONDI, J. Chem. Phys., **38**, 2686, 1963.
9. J. W. RICHARDSON, W. C. NIEUWPOORT, R. R. POWELL and W. F. EDGELL, J. Chem. Phys., **36**, 1057, 1962.
10. G. SOLT and J. KOLLÁR, J. Phys. B., **5**, L124, 1972.
11. J. KOLLÁR and G. SOLT, J. Phys. B., **6**, 329, 1973.
12. J. C. SLATER, Quantum Theory of Atomic Structure (New York: McGraw Hill, 1960).
13. D. A. BROWN and N. J. FITZPATRICK, J. Chem. Soc. (A) 941, 1966.
14. C. R. CLAYDON and D. CARLSON, J. Chem. Phys., **49**, 1331, 1968.
15. G. L. FLETCHER, Proc. Phys. Soc., **A65**, 192, 1952.
16. F. R. BURDEN and R. M. WILSON, Molec. Phys., **24**, 825, 1972.
17. J. C. SLATER, Phys. Rev., **98**, 1039, 1955.

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HYDROMAGNETIC FREE CONVECTION FLOW BETWEEN TWO HORIZONTAL PLATES

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The paper deals with the free convection flow between two infinite horizontal plates when the applied magnetic field is transverse to the flow. An exact solution of the momentum and energy equations is obtained for fully developed flow. The velocity, the skin-friction and the rate of heat transfer are found to decrease as the magnetic effect increases.

Introduction

The free convection flow past horizontal plates has received considerable attention in the recent years [1, 2, 3, 4] while effect of magnetic forces on electrically conducting free convection horizontal flows is almost neglected. NANDA [5] has initiated this field by deducing the equations of hydromagnetic free convection boundary layer flow on the horizontal plate. SINGH [6, 7] has considered the solution of the boundary layer equations of the conducting fluid on the horizontal plate. In the following, we consider the free convection flow between two infinite horizontal plates under the effect of the constant transversely applied magnetic field.

We take the x-axis along the lower plate and y-axes normal to it. The hydromagnetic system of equations pertinent to the problem are

$$\nabla\cdot\mathbf{v}=0\,, \tag{1}$$

$$(\mathbf{v}\cdot\nabla)\mathbf{v}=-\frac{1}{\varrho}\nabla p+\nu\nabla^2\mathbf{v}+\frac{1}{\varrho}\mathbf{J}\times\mathbf{B}\,, \tag{2}$$

$$(\mathbf{v}\cdot\nabla)T=\alpha\Delta^2 T+\frac{\mu}{\varrho c_p}\Phi+\mathbf{J}^2/\varrho c_p\sigma\,, \tag{3}$$

$$\nabla\times\mathbf{H}=\mathbf{J}\,, \tag{4a}$$

$$\nabla\cdot\mathbf{B}=0\,, \tag{4b}$$

$$\nabla\times\mathbf{E}=0\,, \tag{4c}$$

$$\nabla\cdot\mathbf{E}=0\,, \tag{4d}$$

$$\mathbf{J}=\sigma[\mathbf{E}+\mathbf{v}\times\mathbf{B}]\,, \tag{4e}$$

$$\mathbf{H}=\mu_e'\mathbf{B}\,, \tag{4f}$$

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where μ_e is the magnetic permeability and σ is the electrical conductivity of the fluid.

We shall assume that the applied magnetic field H_0 is constant and is transverse to the plates which are maintained at temperatures $T_0 + Ax$ and $T_1 + Ax$. Consideration will be given to the region far away from the entrance, where the flow is fully developed. In this region the velocity, the magnetic flux density and temperature fields may be assumed as

$$\mathbf{v} = \mathbf{v}(u, 0, 0), \quad \mathbf{H} = \mathbf{H}(H_1, H_2, 0), \quad T = Ax + \Theta .$$

Since the flow is fully developed; u, H_1, H_2 and Θ will be functions of y only.

It can be easily shown from (4c) and (4e) that $E_x = E_y = 0$, and $E_z = E_0$ (constant) everywhere. From (4a) we have $H_2 = H_0$. Eqs. (2), (3) and (4) then reduce to

$$\nu \frac{d^2u}{dy^2} + \frac{\mu_e H_0}{\varrho} \frac{dH_1}{dy} = \frac{1}{\varrho} \frac{\partial p}{\partial x} , \tag{5a}$$

$$\frac{1}{\varrho} \frac{\partial p}{\partial y} = - g[1 - \beta(T - T_0)] - \mu_e H_0 \frac{dH_1}{dy} , \tag{5b}$$

$$\alpha \frac{d^2\Theta}{dy^2} - Au = 0 , \tag{6}$$

$$H_0 \frac{du}{dy} + \eta_1 \frac{d^2H_1}{dy^2} = 0 , \tag{7}$$

where $\eta_1 = (\sigma\mu_e)^{-1}$, T_0 is the reference temperature and it is the temperature of the lower plate at $x = 0$. β is the coefficient of thermal expansion, g is the acceleration due to gravity. In the energy equation Joule and viscous dissipation terms are neglected. Also in (5b), the variation in density is taken into account only in the derivation of the buoyancy force, while other density variations are neglected within the framework of the constant property fluids. Integration of (5b) with respect to y gives [4, 6]

$$\frac{p^* - p_0}{\varrho} = \int_0^y g\beta\,(T - T_0)\,dy = g\beta\,(Ax - T_0)\,y + g\beta \int_0^y \Theta\,dy ,$$

where $p^* = p + \mu_e H_1^2/2$ and p_0 is the pressure at $y = 0$. Differentiation of the above equation with respect to x gives

$$\frac{1}{\varrho} \frac{\partial p}{\partial x} = \pm \beta g \,|\, A \,|\, y + \frac{1}{\varrho} \frac{dp_0}{dx} . \tag{8}$$

Here positive and negative signs correspond to $A > 0$ and $A < 0$, respectively. Eliminating p from (5a) with the help of (8), we have

$$\alpha \frac{d^2u}{dy^2} + \frac{H_0}{\varrho} \mu_e \frac{dH_1}{dy} = \pm \beta g \,|\, A \,|\, y + \frac{1}{\varrho} \frac{dp_0}{dx} . \tag{9}$$

Solution of the equations

We introduce the non-dimensional variables

$$u_1 = \frac{g\beta d^2}{k}\varrho u\,, \quad h_1 = \frac{H_0\varrho g\beta d^3}{\mu k}\mu_e H_1\,,$$

$$\Theta - T_0 = \frac{k\mu}{(\varrho g\beta d)^2}\Phi = \frac{Ad}{k_a}\Phi\,, \quad \eta = y/d\,, \tag{10}$$

where d is the distance between the two plates, k is the thermal conductivity, $k_a = P_r G_r g\beta d/c_p$, is a dimensionless parameter, $P_r = \nu/\alpha$ is the Prandtl number, $G_r = g\beta A d^4/\nu_2$ is the modified Grashof number and c_p is the specific heat. Eqs. (6), (7) and (9) then reduce to

$$\frac{d^2u_1}{d\eta^2} + \frac{dh_1}{d\eta} = \pm\, k_a\eta + \bar{c}\,, \tag{11}$$

$$\frac{d^2\Phi}{d\eta^2} = \pm\, R_a u_1\,, \tag{12}$$

$$\frac{d^2h_1}{d\eta^2} + M^2\frac{du_1}{d\eta} = 0\,, \tag{13}$$

where $M = H_0 d\mu_e\sqrt{\sigma/\mu}$ is the Hartmann number, $\bar{c} = \beta g d^4/2k\; dp_0/dx$ and $R_a = P_r, G_r$ is the modified Rayleigh number.

The boundary conditions for the velocity result from no-slip conditions at the two plates. The magnetic boundary conditions are obtained from the continuity of the tangential component of the magnetic field. Mathematically these are expressed as

$$\eta = 0;\ u_1 = 0,\ h_1 = 0,\ \Phi = 0,$$

$$\eta = 1;\ u_1 = 0,\ h_1 = 0,\ \Phi = N_1, \tag{14}$$

where $N_1 = k_a(T_1 - T_0)/Ad$. The solutions of (11), (12) and (13); satisfying the conditions (14); are

$$u_1 = \frac{c_1}{M}\sinh M\eta + \frac{c_2}{M}(\cosh M\eta - 1) \mp \frac{k_a}{M^2}\eta\,, \tag{15}$$

$$h_1 = \pm\frac{k_a}{2}\eta^2 - \bar{c}\eta - c_1(\cosh M\eta - 1) - c_2\sinh M\eta\,, \tag{16}$$

$$\Phi = \pm\, R_a\left[\frac{c_1}{M^3}(\sinh M\eta - \eta\sinh M) - \frac{c_2}{2M}(\eta^2 - \eta)\right. \tag{17}$$

$$\left.\pm\,\frac{k_a}{6M^2}(\eta^2 - \eta) + \frac{c_2}{M^3}\{(\cosh M\eta - 1) - \eta(\cosh M - 1)\}\right] + N_1\eta\,,$$

where

$$c_1 = \pm \frac{k_a}{2M} \coth \frac{M}{2} - \left(\frac{\bar{c}}{2} \pm \frac{k_a}{4} \right),$$

$$c_2 = \left(\frac{\bar{c}}{2} \pm \frac{k_a}{4} \right) \coth \frac{M}{2} \mp \frac{k_a}{2M} .$$

Flow characteristics

The viscous drag coefficient C_{VL} at the lower wall is given by

$$\begin{aligned} C_{VL} &= \left(\frac{\partial u_1}{\partial \eta} \right)_{\eta=0} \\ &= \pm \frac{k_a}{M} \coth \frac{M}{2} = \left(\frac{\bar{c}}{2} \pm \frac{k_a}{4} \right) \mp \frac{k_a}{M^2}, \end{aligned} \tag{18}$$

while for the upper plate, we have

$$C_{VU} = c_1 \cosh M + c_2 \sinh M \mp \frac{k_a}{M^2} . \tag{19}$$

The rate of heat transfer at the plate $\eta = 0$ is given by

$$\begin{aligned} q_L &= - \frac{kA}{k_a} \left(\frac{\partial \Phi}{\partial \eta} \right)_{\eta=0} \\ &= \mp \frac{kA}{k_a} R_a \left[\frac{c_1}{M^3} (M - \sinh M) - \frac{c_2}{M^3} (\cosh M - 1) + \frac{c_2}{2M} \pm \right. \\ &\qquad \left. \pm \frac{k_a}{6M^2} \right] - \frac{Ak}{k_a} N_1 , \end{aligned} \tag{20}$$

and for the plate at $\eta = 1$, it is

$$\begin{aligned} q_U = \mp \frac{kA}{k_a} R_a \left[\frac{c_1}{M^3} (M \cosh M - \sinh M) + \frac{c_2}{M^3} (M \sinh M - \right. \\ \left. - \cosh M + 1) - \frac{c_2}{2M} \mp \frac{k_a}{3M^2} \right] - \frac{Ak}{k_a} N_1 . \end{aligned} \tag{21}$$

The flow rate $Q = \int_0^1 u_1 \, d\eta$ is

$$Q = \frac{c_1}{M^3} (\cosh M - 1) - \frac{c_2}{M^2} \sinh M - \frac{c_2}{M} \mp \frac{k_a}{2M^2} . \tag{22}$$

Results

The expressions for u_1, h_1 and Φ involve five parameters viz. k_a, M, $\bar{c}$, N_1 and R_a. In order to have some insight into the flow and heat transfer, numerical results are presented in Tables I and II for the case when the two plates are at the same temperature. This corresponds to $N_1 = 0$. The temperature in this case will be proportional to R_a.

Table I

The values of viscous drag, rate of heat transfer and rate of mass flow for $A > 0,\ k_a = 10$

	M	C_{VL}	$-C_{VU}$	$-\frac{k_a}{AkR_a} q_L$	$\frac{k_a}{AkR_a} q_U$	$-Q$
$\bar{c} = 0$	0	1.6666	2.3333	0.1944	0.2222	0.4167
	2	1.7174	3.2826	0.1829	0.2083	0.3913
	4	1.8283	3.1716	0.1578	0.1780	0.3358
	6	1.9408	3.0594	0.1323	0.1472	0.2798
	8	2.0306	2.9604	0.1117	0.1239	0.2341
	10	2.0999	2.8954	0.0856	0.0323	0.2170
$\bar{c} = -1$	0	0.8333	2.8333	0.1528	0.1806	0.3334
	2	1.2174	2.7826	0.1436	0.1689	0.3130
	4	1.3283	2.6716	0.1242	0.1445	0.2678
	6	1.4408	2.5593	0.1044	0.1197	0.2241
	8	1.5306	2.4697	0.0873	0.0873	0.1883
	10	1.5999	2.3998	0.0657	0.0077	0.1542

Table II

The values of viscous drag, rate of heat transfer and rate of mass flow for $A < 0,\ k_a = 10,\ \bar{c}] = -1$

M	$-C_{VL}$	C_{VU}	$\frac{k_a}{AkR_a} q_L$	$-\frac{k_a}{AkR_a} q_U$	Q
0	1.8333	3.8333	0.2360	0.2638	0.5000
2	2.2174	3.7826	0.2221	0.2474	0.4695
4	2.3282	3.6260	0.1869	0.2116	0.4030
6	2.4409	3.5615	0.1603	0.1757	0.3360
8	2.5306	3.4075	0.1362	0.1438	0.2813
10	2.5999	3.4019	0.1057	0.0567	0.2310

We have considered the values of $\bar{c} = 0, -1$ and $k_a = 10$. For $\bar{c} = 0$, i.e. when the flow is purely buoyancy induced the viscous drag coefficient, the rate of heat transfer and the rate of mass flow are found to be the same in magnitude but opposite in sign for $A > 0$ and $A < 0$.

Tables I and II indicate the non-dimensional values of the rate of mass flow, viscous drag and the rate of heat transfer for $k_a = 10$, $\bar{c} = 0, -1$ and for different values of M. The viscous drag at the upper plate decreases with the increase of the Hartmann number while at the lower plate it increases. The rate of mass flow and heat transfer are found to decrease as M increases.

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REFERENCES

1. Y. Mori, Trans. Japan Soc. Aero/Space Sci., **2**, 22, 1959.
2. E. M. Sparrow and R. D. Cess, J. Heat Mass Transfer, **3**, 1, 1961.
3. W. N. Gill and E. D. Casal, A. I. Ch. E. Journal, **8**, 513, 1962.
4. P. Singh and P. C. Sinha, ZAMM, **51**, 167, 1971.
5. R. S. Nanda, Proc. Symposium on Magnetohydrodynamics, I. I. Sc., Bangalore, India, 1965.
6. P. Singh, The laminar viscous flows with body forces, Ph. D. Dissertation, I. I. T. Kharagpur, India, 1967.
7. P. Singh, Acta Phys. Hung., **34**, 1, 1973.

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NON-LINEAR SECULAR-FREE SOLUTION OF A MODEL EQUATION

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The perturbation technique of Krylov—Bogoliubov—Mitropolsky is used to derive a secular-free solution up to third order of a model equation

$$C^2\frac{\partial^2\Phi}{\partial x^2}+\frac{\partial^2\Phi}{\partial t^2}+\omega_0^2\Phi+C^2\Phi^3=0\,,$$

where C and ω_0 are constants in space and time. Expressions are obtained for amplitude dependent frequency shifts and wave number shifts.

1. Introduction

The study of frequency shift and wave number shift is an important problem in the plasma theory. Many authors, for instance, MONTGOMERY and TIDMAN [1], BOYD [2] and DAS [3] have studied frequency shifts and wave number shifts using the same technique. In this paper our aim is to study a model equation following the above authors for two monochromatic waves.

2. Formulation of the problem

Our starting equation is

$$C^2\frac{\partial^2\Phi}{\partial x^2}+\frac{\partial^2\Phi}{\partial t^2}+\omega_0^2\Phi+C^2\Phi^3=0, \tag{1}$$

where C and ω_0 are instants in space and time. Let the solution of the first order approximation for $\Phi^{(0)}$ may be taken as

$$\Phi^{(0)}=(a_1\cos\psi+a_2\sin\psi)\hat{l}y\,, \tag{2}$$

where $\hat{l}y$ is the unit vector along the direction of y and $\psi=k_0x-\omega t$, a_1 and a_2 are real constants.

We seek the Krylov—Bogoliubov—Mitropolsky perturbation expression in the form

$$\Phi=\varepsilon\Phi^{(0)}(a_1,a_2,\psi)+\varepsilon^2\Phi^{(1)}(a_1,a_2,\psi)+\varepsilon^3\Phi^{(2)}(a_1,a_2,\psi)+\ldots, \tag{3}$$

where ε is a small positive parameter.

For a transverse monochromatic wave propagating along the positive direction of x axis, the approximate expression for phase and amplitude variations are

$$\begin{aligned}
\frac{\partial a_1}{\partial t} &= \varepsilon^2 C_1(a_1) + \ldots, \\
\frac{\partial a_2}{\partial t} &= \varepsilon^2 C_2(a_2) + \ldots, \\
\frac{\partial \psi}{\partial t} &= -\omega + \varepsilon^2 B_1(a_1, a_2) + \ldots, \\
\frac{\partial a_1}{\partial x} &= \varepsilon^2 D_1(a_1) + \ldots, \\
\frac{\partial a_2}{\partial x} &= \varepsilon^2 D_2(a_2) + \ldots, \\
\frac{\partial \psi}{\partial x} &= K_0 + \varepsilon^2 A_1(a_1, a_2) + \ldots,
\end{aligned} \tag{4}$$

where A_1, B_1, C_1, C_2, D_1 and D_2 are the functions of amplitude.

Using Eqs. (2)—(4) in Eq. (1), one can obtain

$$\omega_0^2 - (C^2 K_0^2 + \omega^2) = 0, \tag{5}$$

$$(C^2 K_0^2 + \omega^2)\frac{\partial^2 \Phi^{(1)}}{\partial \psi^2} + \omega_0^2 \Phi^{(1)} = 0, \tag{6}$$

$$\begin{aligned}
\left[(C^2 K_0^2 + \omega^2)\frac{\partial^2 \Phi^{(2)}}{\partial \psi^2} + \omega_0^2 \Phi^{(2)}\right] &= (2K_0 C A_1 - 2\omega B_1)(a_1 \cos\psi + a_2 \sin\psi) + \\
&+ (2K_0 D_1 - 2\omega C_1)\sin\psi + (2\omega C_2 - 2K_0 D_2)\cos\psi - \\
&- C^2\left\{\frac{3}{4}(a_1^2 a_2 + a_2^3)\sin\psi + \frac{3}{4}(a_1 a_2^2 + a_1^3)\cos\psi + \right. \\
&\left. + \frac{1}{4}(3a_1^2 a_2 - a_2^3)\sin 3\psi + \frac{1}{4}(a_1^3 - 3a_1 a_2^2)\cos 3\psi\right\}
\end{aligned} \tag{7}$$

for first, second and third order approximation, respectively.

3. Results and discussion

The dispersion relation of the first order equation is given by Eq. (5). Next the solution of the Eq. (6) reduces in the perturbed state to

$$\Phi^{(1)} = 0\,. \tag{8}$$

It is difficult to solve Eq. (7) for $\Phi^{(2)}$ without avoiding ψ proportional terms on the right hand side of Eq. (7). That is why for avoiding secular behaviour in the third order approximation, we equate the coefficient of $\cos\psi$ and $\sin\psi$ to zero and it gives rise to frequency shifts and wave number shifts.

For the coefficient of $\cos\psi$, an expression for frequency shift may be

$$\Delta\omega = -B_1 = \frac{3C^2(a_1^2 + a_2^2)}{8\omega} \text{ for } A_1 = C_2 = D_1 = D_2 = 0 \tag{9}$$

and for the coefficient of $\sin\psi$, the frequency shift is

$$\Delta\omega = -B_1 = \frac{3C^2(a_1^2 + a_2^2)}{8\omega}, \tag{10}$$

for

$$A_1 = C_1 = D_1 = D_2 = 0 .$$

It is observed that single frequency shift is obtained herein and since the terms in the first bracket on the right hand side of (9) and (10) maintain the same sign, the frequency shift increases by the interaction of the second wave.

Proceeding in the same way, one obtains a single wave number shift given by

$$\Delta k = A_1 = \frac{3}{8K_0}(a_1^2 + a_2^2), \tag{11}$$

Here also, the wave number shift increases for the interaction of the second wave.

Again, the solution up to third order approximation for Φ can be written as

$$\Phi = (a_1\cos\psi + a_2\sin\psi) - \frac{C^2}{4}\left\{\frac{a_2(3a_1^2 - a_2^2)\sin 3\psi + a_1(a_1^2 - 3a_2^2)\cos 3\psi}{\omega_0^2 - 9(\omega^2 + C^2K_0^2)}\right\}. \tag{12}$$

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REFERENCES

1. D. Montgomery and D. A. Tidman, Phys. fluids, **7**, 242, 1964.
2. T. J. Boyd, Phys. fluids, **10**, 896, 1967.
3. K. P. Das, Phys. fluids, **11**, 2055, 1968.

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PHOTONEUTRINO ENERGY LOSS RATES UNDER MAGNETIC FIELD

By

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The neutrino energy loss rate is calculated due to the photoneutrino process in a hot plasma, under magnetic field.

The calculations done for low densities and relatively low temperatures may be used for astrophysical estimations in neutron stars.

Introduction

Recent progress in the production of a strong magnetic field in the laboratory [1] has focussed interest on the study of the effect of magnetic fields on various phenomena [2]. The largest field that can now be produced in the laboratory is of the order of 10^6 G, which is much smaller than that existing in neutron stars, which may be of the order of 10^{15} G [3].

Canonical models for the description of the weak interaction among fermions predicts a direct interaction between electron-neutrino pairs [4]. The effective Hamiltonian which describes the electron neutrino interactions is

$$H_w = \frac{-ig}{8m_w^2}\,(\bar{\psi}_e\,\gamma_\mu(1+\gamma_5)\,\psi_\nu)(\bar{\psi}_\nu\,\gamma_\mu\,(1+\gamma_5)\,\psi_e)\,. \tag{1}$$

Such an interaction follows immediately in conventional theories in which the weak interaction is mediated by a few intermediate vector bosons [5], or when the weak coupling has the form phenomenologically at least of current–current interaction.

A Fierz transformation of the Hamiltonian of Eq. (1) yields the equivalent form

$$H_w = \frac{-\,ig^2}{8\,m_w^2}\,[(\bar{\psi}_e\,\gamma_\mu\,\psi_e)(\bar{\psi}_\nu\,\gamma_\mu\,(1+\gamma_5)\,\psi_\nu) + (\bar{\psi}_e\,\gamma_5\,\gamma_\mu\,\psi_e)(\bar{\psi}_\nu\,\gamma_\mu\,(1+\gamma_5)\,\psi_\nu)]\,, \tag{2}$$

which exhibits more explicitly the matrix element for a neutrino–antineutrino pair to be radiated by an electron, by means of a vector or axial vector current. The vector current is analogous to the coupling of an electron to a photon and implies neutrino-pair radiation by any accelerated electron. PONTECORVO [6] first emphasized that such a possibility could have profound significance in some stages of stellar evolution. Just because neutrinos are so weakly coupled to matter they can easily escape from hot dense stellar cores where they are produced, while photon emission is effectively restricted to the relatively cool stellar surface. If the interaction of Eq. (1) does indeed exist, some stars may have a neutrino luminosity over 10^{10} times their visual one. They may for a short period radiate more energy in neutrino pairs than our entire galaxy does in light. Among those neutrino-pair emission mechanisms which have been investigated and have been found to play an important role in certain stages of stellar evolution:

1) $$e^- + e^+ \text{ —— } \nu + \bar{\nu}$$

"pair-annihilation neutrinos" from the annihilation of electron–positron pairs at very high temperatures $T \geqslant 10^9$ °K [7].

2) $$\gamma + e^{\pm} \text{ —— } \nu + \bar{\nu} + e^{\pm}$$

"photoneutrinos" which are thought to be important for low densities, $\varrho/\mu_e \leqslant 10^5$ gm/cm^3 and relatively low temperatures, $T \leqslant 4 \times 10^8$ °K [8].

3) $$\text{Plasmon} \text{ —— } \nu + \bar{\nu}$$

"plasma neutrinos" from the coherent acceleration of electrons in a plasma interacting with an electromagnetic wave [9].

In a previous article [10] we have studied the effect of magnetic field on reaction 1. In this paper the effect of a strong magnetic field on the photoproduction of neutrino pairs will be discussed.

Transition probability

In a previous article [10] we have studied the effect of magnetic field on reaction 1. In this paper the effect of a strong magnetic field on the photoproduction of neutrino pairs will be discussed.

The Feynman diagrams for the photoneutrino process to the lowest order are shown in Fig. 1. Here $k = (\vec{k}, iK)$, $k' = (\vec{k}, iK')$ are the four-momenta of the initial and the final electrons, $q=(\vec{q}, iq_0)$, $q'=(\vec{q}\,', iq_0')$, and $w=(\vec{w}, iw_0)$ are the four momenta of the neutrino, the antineutrino, and the photon, respectively. $\varepsilon^{(\lambda)}$ is the photon polarization vector. The matrix elements

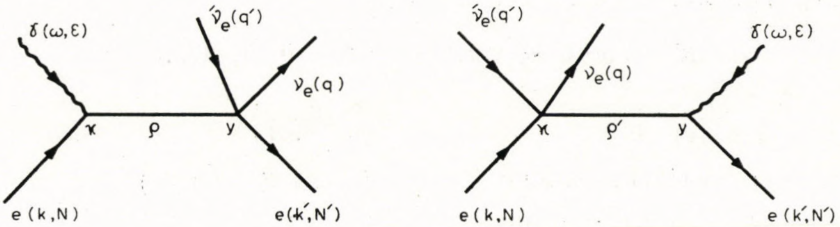

Fig. 1

for this process are

$$S_a = \frac{-ieg^2}{8\, m_w^2 \sqrt{w_0 \Omega}} \iint d^4x\, d^4y\, \overline{\psi}_f(y) \gamma_\mu (1+\gamma_5),$$

$$G(x,y)\hat{\varepsilon}^{(\lambda)}\, \psi_i(x)\, \overline{\psi}_{\nu e}(y)\, \gamma_\mu (1+\gamma_5)\, \psi_{\bar{\nu} e}(y) \exp[+iwx]\,, \tag{3}$$

$$S_b = \frac{-ieg^2}{8\, m_w^2 \sqrt{w_0\, \Omega}} \iint d^4x\, d^4y\, \overline{\psi}_f(y)\, \hat{\varepsilon}^{(\lambda)}\, G(x,y)$$

$$\gamma_\mu (1+\gamma_5)\, \psi_i(x)\, \overline{\psi}_{\nu e}(x)\, \gamma_\mu (1+\gamma_5)\, \overline{\psi}_{-e}(x) \exp[+iwy]\,, \tag{4}$$

where ψ_i, ψ_f, ψ_ν, and $\psi_{\bar{\nu}}$, are the wave functions of the initial electron, the final electron, the neutrino, and the antineutrino. $G(x,y)$, g, and m_w are the propagator, the coupling constant and the mass of the vector boson, respectively.

In the presence of a magnetic field the electron wave function satisfies the Dirac equation:

$$[i(\hat{p} + e\hat{A}) + m]\, \psi(x) = 0, \tag{5}$$

where

$$\hat{p} = -i\gamma_\mu \delta_\mu, \quad \hat{A} = A_\mu \gamma_\mu,$$

m is the mass of the electron, and A_μ is the magnetic vector potential. In the case of a constant homogeneous magnetic field aligned in the z-direction, the following gauge for the vector potential A_μ can be used

$$A_1 = -yB\,, \qquad A_2 = A_3 = A_4 = 0\,.$$

If the representation of the γ-matrices is chosen to be ($k = 1, 2, 3$)

$$\gamma_k \equiv \begin{pmatrix} 0 & i\sigma k \\ i\sigma k & 0 \end{pmatrix}, \quad \gamma_4 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

then the solutions of the Dirac equation are [11]:

$$\psi(x) = \frac{1}{\sqrt{L_1 L_3}} \exp[ik_1 x_1 + ik_3 x_3 - iKt - 1/2\, \xi^2]$$

$$\begin{bmatrix} \alpha A_s \overline{H}_{N-1}(\xi) \\ -S\alpha B_s \overline{H}_N(\xi) \\ s\beta A_s \overline{H}_{N-1}(\xi) \\ -\beta B_s \overline{H}_N(\xi) \end{bmatrix}, \tag{6}$$

where the energy eigenvalue K is given by

$$K = \sqrt{m^2 + k_3^2 + 2\,NeB} \qquad N = 0,\ 1,\ 2, \dots \tag{7}$$

and

$$\begin{aligned} &\xi = \eta y - k_1/\eta\,, && \eta = \sqrt{eB}\,, \\ &\alpha = \sqrt{1/2\,(1 + m/K)}\,, && \beta = \sqrt{1/2(1 - m/K)}\,, \\ &A_s = \sqrt{1/2(1 + sk_3/k)}\,, && S = \pm 1\,, \\ &k = \sqrt{K^2 - m^2}\,, && \end{aligned}$$

$$\bar{H}_N(\xi) = [\xi/\Pi^{1/2}\, 2^N N!]^{1/2} H_N(\xi)\,. \tag{8}$$

Here $H_N(\xi)$ is the Hermite polynomial of order N.

Each energy eigenvalue is infinitely degenerate since the energy does not depend on the canonical momentum k_1, which only determines the position of the electron orbit in the y-direction. For $N \neq 0$ there is additional spin degeneracy because of the quantum number $S = \pm 1$. For $N = 0$ one must have $S = -k_3/|k_3|$; so the electron is polarized against the direction of the magnetic field.

The propagator $G(x, y)$ of the intermediate electron in operator form is:

$$G = -\frac{1}{i(\hat{p} + e\hat{A}) + m}\,, \tag{9}$$

but since its exact expression in the case of a magnetic field is very complicated [12], we have chosen to approximate it by the simpler function

$$G_0 = -\frac{1}{i(\hat{p} + e\,\hat{A}^0) + m} = \frac{i(p + e\hat{A}^0) - m}{(p + e\hat{A}^0)^2 + m^2}\,, \tag{10}$$

where $eA_1^0 = -eBy^0 = \text{constant}$, $A_2^0 = A_3^0 = A_4^0 = 0$. Here y^0 is taken to be equal (k_1/eB), where k_1 is the x-component of the four-momentum of the initial-state electron. Thus G_0 is a free-particle propagator.

The justification for this decision is as follows. According to Eq. (6) the initial wave function is centered at $y^0 = k_1/eB$ in the y-direction, and extends over a range of the order of $\sqrt{2N}\eta^{-1}$ in this direction. The nodes of the wave function (for $N > 0$) are separated by a distance $\Delta y \approx \Pi(\beta N)^{-1/2}\eta^{-1}$. For shorter intervals than this, the initial wave function resembles a free plane wave. Assuming that the lifetime of the virtual electron in the magnetic field is sufficiently short, such that the distance travelled by it does not exceed Δy, the propagation of the virtual electron is essentially free-particle propagation. Thus $\hat{A}$ can be substituted by its average value $\hat{A}^0$ weighted by the initial-state wave function. After substituting the free propagator (10), which is:

$$G_0(n, y) = \frac{i}{(2\pi)^4} \exp[-ik_1(x_1 - y_1)] \int d^4\varrho \exp\,[-i\varrho\,(x - y)]\, \frac{i\hat{\varrho} - m}{\varrho^2 + m^2} \tag{11}$$

in the S-matrix elements (3) and (4), and integrating over x, y, ϱ, and ϱ' one gets:

$$S = S_a + S_b =$$

$$= \sqrt{\frac{2\Pi}{\Omega w_0}} \, \frac{i \eta e g^2}{8 V L_1 L_3 m_w^2} \, \frac{(-1)^{N'-N}}{(2^{N+N'} N! \, N'!)^{1/2}} \, u_{\nu e}(q) \, \gamma_\mu (1+\gamma_5) \, u_{\bar{\nu} e}(q')$$

$$[\sqrt{2N'} \, \alpha' A' H_{N'-1}(0), s' \alpha' B' H_{N'}(0), \sqrt{2N'} \, s' \beta' A' H_{N'-1}(0), \beta' B' H_{N'}(0)]$$

$$M . \begin{bmatrix} \sqrt{2N} \, \alpha A H_{N-1}(0) \\ S \alpha B H_N(0) \\ \sqrt{2N} \, s \beta A H_{N-1}(0) \\ \beta B H_N(0) \end{bmatrix} \delta^4 (w + k - k' - q - q'), \tag{12}$$

in which

$$M = \gamma_4 \hat{\varepsilon} \, \frac{i\hat{\varrho} - m}{\varrho^2 + m^2} \, \gamma_\mu (1+\gamma_5) + \gamma_4 \gamma_\mu (1+\gamma_5) \, \frac{i\hat{\varrho}' - m}{\varrho'^2 + m^2} \, \hat{\varepsilon} \tag{13}$$

and

$$\begin{aligned} \varrho_1' &= (q_1 + q_1') = w_1 , \\ \varrho_2' &= (q_2 + q_2') = w_2 , \\ \varrho_3' &= k_3' + (q_3 + q_3') = k_3 + w_3 , \\ \varrho_0' &= (q_0 + q_0') + K' = K + w_0 , \end{aligned} \tag{14}$$

$$\begin{aligned} \varrho_1 &= -(q_1 + q_1') = -w_1 , \\ \varrho_2 &= -w_2 = -(q_2 + q_2') , \\ \varrho_3 &= k_3' - w_3 = k_3 - (q_3 + q_3') , \\ \varrho_0 &= K' - w_0 = K - (q_0 + q_0') . \end{aligned} \tag{15}$$

Squaring (12), averaging over the possible initial spins of the electrons and photon and summing over the possible final spin states of the electron, the neutrino and the antineutrino, finally integrating over the momenta of the neutrino and the antineutrino by using LENARDS [13] formula, the final result for the matrix element takes the form

$$I = (2\Pi)^4 \, \Sigma\Sigma \, |S|^2 \, d^3q \, d^3q' , \tag{16}$$

$$I = \frac{e^3 B G^2}{3 w_0} F(k, k', w) , \tag{17}$$

where

$$G^2 = \frac{3}{2} \, \frac{g^4}{m_w^4} ,$$

and $F(k, k', w)$ is a function of the variables k, k', and w.

Energy loss rate

Assuming that the stars consist of a completely ionized gas in thermal equilibrium at a temperature T and density ϱ, the number densities of the electron and positrons are given by Fermi—Dirac distributions

$$n_{\mp} = \int dn_{\mp} = \frac{2}{(2\Pi)^3} \int \frac{d_3 p}{\exp\left(\frac{E}{K_B T} \mp \frac{\mu}{K_B T}\right) + 1}, \tag{18}$$

where μ is the chemical potential of an electron (including the electron mass). Photons in thermal equilibrium have a density of states

$$dn_w = \frac{1}{(2\Pi)^3} \left[\exp \frac{w_0}{K_B T} - 1\right]^{-1} d^3 w\,. \tag{19}$$

For the neutrino we have

$$dn_q = \frac{d^3 q}{(2\Pi)^3}, \tag{20}$$

while for an outgoing electron we have

$$dn = \frac{d^3 p}{(2\Pi)^3} \left\{1 - \left[\exp\left(\frac{E}{K_B T} - \frac{\mu}{K_B T}\right) - 1\right\}\right.. \tag{21}$$

Our calculations will be done for the non-relativistic, and non-degenerate case, where photoproduction is thought to be important. For non-relativistic electron $K_B T \ll m$ and for densities below 10^6 gm/cm^3, we may drop the Fermi distribution factor of the final electron relative to the 1 in the integrand of (21). In the non-relativistic limit the electron energy in the presence of a homogeneous magnetic field becomes

$$E(k, N) = m + \frac{2m}{k^2} + N w_c, \tag{22}$$

where

$$w_c = \frac{eB}{m}.$$

The occupation numbers of electron states in a hot plasma in the non-degenerate case follow the Boltzmann statistics

$$f(k, N) = f(0,0) \exp\left[-\left(\frac{k^2}{2m} + N w_c\right) \Big/ K_B T\right], \tag{23}$$

where the coefficient $f(0, 0)$ depends on the electron number density N_e according to

$$f(0,0) = \frac{4\Pi^2 N_e}{w_c m \sqrt{2\Pi m K_B T}} \operatorname{tgh} \frac{w_c}{2 K_B T}. \tag{24}$$

The energy loss rate for electron is now given by

$$Q = \frac{e^3\, BG^2}{6(2\Pi)^3} \int dk_3 f(k_3, N) \int dk'_3 \left(1 - f(k'_3, N')\right),$$

$$\int d^3\, w \left[e^{\frac{w_0}{K_B T}} - 1\right]^{-1} (K + w_0 - K')\, I\,. \tag{25}$$

Integrating over dk_3, dk'_3, and d^3w we obtain

$$\begin{aligned} Q = {} & \frac{e^2\, G^2 \left(\frac{K_B\, T}{m}\right)^{1/2} N_e}{72\,(2\pi)^{3/2}\, m^4}\, \mathrm{tgh}\, \frac{w_c}{2K_B\, T} \exp\left(-\frac{Nw_c}{K_B\, T}\right) \cdot \\ & \cdot \Big\{ m^7 \Big[4K_B\, T - 20\, \frac{NeB\, K_B T}{m^2} + 12\, \frac{NeB\, K_B T}{m^2} + 8.66\, \frac{(K_B\, T)^3}{m^2} + \\ & + 340.76\, \frac{(K_B\, T)^4}{m^3} + 9.33\, \frac{(K_B\, T)^2}{m} \Big] + \\ & + \sqrt{2\Pi}\, m^{5/2} \big[232.74 m\, (K_B\, T)^{9/2} + 77.16 m^2\, (K_B\, T)^{7/2} + \\ & + 17.5\, N'\, eB\, m(K_B\, T)^{5/2} + 32.5\, NeB\, m(K_B\, T)^{5/2} + \\ & + 26.25\, m^3\, (K_B\, T)^{5/2} + m^4\, (K_B\, T)^{3/2} + \\ & + 6\, N'\, eB\, m^2\, (K_B\, T)^{3/2} - 3\, NeB\, m^2\, (K_B\, T)^{3/2} \big] \Big\}\,. \end{aligned} \tag{26}$$

For $N = N' = 0$

$$\begin{aligned} Q = {} & \frac{e^2\, G^2 \left(\frac{K_B\, T}{m}\right)^{1/2} N_e}{72(2\Pi)^{3/2}\, m^4}\, \mathrm{tgh} \left(\frac{w_c}{2K_B\, T}\right) \cdot \\ & \cdot \big\{ \big[4m^7\, (K_B\, T) + 8.66 m^5\, (K_B\, T)^3 + 340.76\, m^4\, (K_B\, T)^4 + \\ & + 9.33\, m^6\, (K_B\, T)^2 \big] + \sqrt{2\Pi}\, \big[232.74\, m^{7/2}\, (K_B\, T)^{9/2} + \\ & + 77.16\, m^{9/2}\, (K_B\, T)^{7/2} + 26.25\, m^{11/2}\, (K_B\, T)^{5/2} + m^{13/2}\, (K_B\, T)^{3/2} \big] \big\}\,. \end{aligned}$$

Eqs. (26) and (27) are the total radiation loss for photoneutrinos for non-degenerate electron in the non-relativistic case at temperatures $T \leqslant 4 \times 10^8\, {}^\circ\mathrm{K}$.

REFERENCES

1. Proceedings of the International Conference on High Magnetic Fields, Cambridge, Mass. (M. I. T. Press, Cambridge, Mass. 1961).
2. T. Erber and H. G. Latal, Bull. Am. Phys. Soc., **10,** 1103, 1965.
2. T. Erber, Rev. Mod. Phys., **38,** 626, 1966; J. J. Klein, Rev. Mod. Phys., **40,** 523, 1968.
3. L. Woltjer, Astrophys. J., **140,** 1309, 1964.
4. R. P. Feynman and M. Gell-Mann, Phys. Rev., **109,** 193, 1958.
5. H. Yukawa, Proc. Phys. Math. Soc. Japan, **17,** 48, 1935; Y. Tanckawa and Watanabe, Phys. Rev., **113,** 1344, 1959; J. Schwinger, Ann. of Phys., **2,** 407, 1957.

6. B. PONTECORVO, Zh. Eksperim. Teor. Fiz., **34**, 275, 1957.
7. H. Y. CHIU and P. MORRISON, Phys. Rev. Letters, **5**, 573, 1960. H. Y. CHIU, Phys. Rev., **123**, 1040, 1961; H. Y. CHIU and R. C. STABLER, Phys. Rev., **122**, 1317, 1961.
8. B. PONTECORVO, Zh. Eksperim. Teor. Fiz., **36**, 1615, 1961; V. PETROSIAN, G. BEOUDET and E. E. SALPETER, Phys. Rev., **154**, 1445, 1967.
9. C. L. INMAN and M. A. RUDERMAN, Astrophys. J., **140**, 1025, 1964; M. H. ZAIDI, Nuovo Cimento, **40**, 502, 1965.
10. M. EL-KHISHEN, A. EL-GOWHARI (to be published).
11. N. P. KLEPIKOV, Zh. Eksperim. Teor. Fiz., **26**, 19, 1954.
12. J. SCHWINGER, Phys. Rev., **82**, 664, 1951; R. KAITNA and P. URBAN, Nucl. Phys., **56**, 518, 1964.
13. A. LENARD, Phys. Rev., **90**, 968, 1953.

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WAVE MECHANICS AND THE PHOTON

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It is shown that the consequent wave mechanical treatment of the interaction of an atom with its own radiation field leads to a process very like that of the emission of photons. It is shown that the radiation reaction causes the transition of an atom in an excited state to a lower state of energy. The radiation emitted has an energy $h\nu$ confined into a narrow cone unless the emitting atom is kept into a volume with dimensions less than the wave length of the emitted light.

Introduction

EINSTEIN's well-known interpretation of the photoelectric effect in terms of photons led to the theory of the dual nature of light. EINSTEIN tried to reconcile to some extent the photon and wave properties of light supposing tentatively the phenomenon of "needle radiation". A suitable electromagnetic source emits radiation into a narrow cone only and such an electromagnetic radiation resembles to what a photon is supposed to be.

The concept of needle radiation seemed, however, to be contradicted by the experimental results of SELÉNYI [1] and of SCHRÖDINGER [2] showing clearly that a sufficiently small source emits coherent radiation into wide solid angles. The latter results seemed thus to support directly the concept according to which atoms radiate like small dipoles with the radiation distributed over a wide range of directions in the well-known manner.

The wave mechanical theory of the emission of atoms seemed to support further the concept of dipole radiation. Indeed, we find from SCHRÖDINGER's formalism that the current distribution inside an atom in a mixed state is that of a small oscillating dipole. Using the one body approximation the dipole is concentrated into a region with linear dimensions of the order of the Bohr radius r_H.

So as to obtain a description of the emission of photons it seemed thus necessary to add to the wave mechanical formalism the second quantization. Thus extending wave mechanics by quantum electrodynamics we are getting back to the concept of the photon.

In this article we intend to show that the concept of the photon can also be obtained from wave mechanics without any additional assumption if we treat the problem in a consequent manner.

It appears that both the emission of radiation somewhat like the needle radiation, and also the experimental results connected with the wide angle interference phenomena can be well understood in terms of wave mechanics— without making use of the second quantization.

Statement of the problem

We thus treat the following problem. Given an atom in an excited state. For sake of simplicity we shall consider the case of the H-atom. The pure excited state is a stationary one and therefore in this state the atom does not emit radiation and the state persists.

The pure excited state is, however, an unstable configuration. If we consider a state which is almost a pure excited state but contains an arbitrarily small admixture of a state of lower energy, then this state emits already a small amount of radiation. The reaction of the radiation field upon the atom causes a perturbation, as a result of this perturbation an avalanche starts and it causes the amplitude of the excited state to diminish and that of the lower state to increase until the configuration of the atom changes into that of the pure lower state.

As the wave equation is in accord with the law of conservation of energy, the process leads to the emission of energy equal to $h\nu$ where ν is the frequency of the emission, thus the process leads to the emission of one photon. Furthermore, as we show in this paper the detailed calculation shows that in general the emission takes place into a narrow cone — thus the emission resembles somewhat to the "needle radiation" proposed by EINSTEIN and others. Besides we shall see that the wave mechanical theory does not contradict the experimentally observed facts concerning the wide angle interference. Indeed, if the emitting atom is concentrated into a sufficiently small region then the opening angle of the cone of the emission becomes large and thus for atoms radiating from sufficiently small regions we obtain a radiation of the form as is emitted by a small dipole.

The method of the calculation

We start from the unperturbed wave equation of the atom

$$H_0\psi = i\hbar\dot{\psi}\,. \tag{1}$$

Considering a solution of (1) corresponding to a mixed state we find that the system described by ψ contains effective current and charge densities, we can denote

$$\mathbf{i} = \bar{\mathbf{i}}(\psi)\,, \qquad \varrho = \bar{\varrho}(\psi)\,. \tag{2}$$

(2) stands for the well-known expression giving current and charge densities of a system described by ψ. The densities (2) produce an electromagnetic field with potentials $\mathbf{A}$, Φ obeying Maxwell's equation, thus

$$\begin{aligned} \nabla^2\mathbf{A} - \frac{1}{c^2}\ddot{\mathbf{A}} &= -4\pi\mathbf{i}\,, \\ \nabla^2\Phi - \frac{1}{c^2}\ddot{\Phi} &= -4\pi\varrho\,, \\ \operatorname{div}\mathbf{A} + \frac{1}{c^2}\dot{\Phi} &= 0\,. \end{aligned} \tag{3}$$

The field obtained from (3) causes a perturbation of the original state, the perturbation operator can be written schematically as

$$P = P(\mathbf{A}, \Phi)\,. \tag{4}$$

Thus considering the reaction of the field of the atom upon itself, (1) has to be replaced by

$$(H_0 + P)\psi = i\hbar\dot{\psi}\,. \tag{5}$$

The emission of the atom can be obtained by solving simultaneously the system of equations (2), (3), (4) and (5).

The problem of the reaction of a wave mechanical system upon itself

The program given above for the wave mechanical treatment of the reaction of a system upon itself has its classical analogy which is obtained replacing (5) by the classical equations of motion of a cloud of charge. In particular taken the electron to be a cloud bound harmonically to the centre of the atom, H. Hertz developed the classical theory of radiation damping and thus obtained a qualitatively correct estimate of the natural line width.

Using in place of the classical equation of motion the wave equation (5) the wave mechanical theory of radiation damping was developed by W. Heitler [3] and others — the latter theory leads to results in quantitative agreement with experiments.

In spite of the success of the wave mechanical treatment of the radiation damping there exists an apparent difficulty which we discuss presently.

An apparent paradox connected with the self-interaction of a system

The wave equation of an H-atom in the presence of a field with potentials $\mathbf{A}$, Φ can be written

$$\frac{1}{2m}\left(i\hbar\nabla+\frac{e}{c}\mathbf{A}\right)^2\psi+(V(r)+e\Phi)\psi=i\hbar\dot{\psi}\,, \tag{6}$$

where $V(r)=-e^2/r$ is the potential of the field of the nucleus; the nucleus is thus taken to be a point particle. Solving (6) we obtain stationary states ψ_ν such that

$$\frac{\partial\varrho_\nu}{\partial t}=0\,,\ \frac{\partial\mathbf{i}_\nu}{\partial t}=0\,, \tag{7}$$

where ϱ_ν and $\mathbf{i}_\nu$ are to be calculated from (2) inserting $\psi=\psi_\nu$. However, the source densities $\bar{\varrho}_\nu$ and $\mathbf{i}_\nu$ thus obtained lead with the help of (3) to potentials corresponding to the field of the electron cloud which (in a stationary manner) surrounds the nucleus. The static part of this field is by no means negligible as it can be seen from qualitative considerations; thus the latter field must be expected to influence to a noticeable extent the distribution of the electron cloud. The stationary solutions of the system (2), (3), (4) and (5) — differ therefore considerably from the stationary solutions obtained from the unperturbed wave equation (1). Since, the solutions of (1) lead to a description of the atom in agreement with experiments, it must be supposed that the solutions of (2), (3), (4) and (5) which differ from the solutions of (1) lead to an incorrect model of the atom.

Because of this difficulty it is usually supposed that (6) leads to a correct description of the atom if we take $\mathbf{A}$ and Φ to be the potentials of the "outer field" only. The field is thus split into

$$\mathbf{A}=\mathbf{A}^{(i)}+\mathbf{A}^{(o)}\,,\qquad \Phi=\Phi^{(i)}+\Phi^{(o)} \tag{8}$$

the upper indexes signifying "inner" and "outer" field. It is supposed that in (6) $\mathbf{A}$ and Φ have to be replaced by $\mathbf{A}^{(o)}$ and $\Phi^{(o)}$, the potentials of the outer field.

The above consideration cannot be altogether valid. Indeed, the theory of radiation damping is just based on considering the effects of the inner field upon the atom. It is true, however, that in the usual procedures this is not done in a consequent manner. The correct description of radiation damping is obtained if we split the field not in accord with (8) but arbitrarily as

$$\mathbf{A}=\mathbf{A}^{(r)}+\mathbf{A}^{(st)}\,,\quad \Phi=\Phi^{(r)}+\Phi^{(st)}\,, \tag{9}$$

where the upper index "r" stands for "radiative" field and "st" for "stationary" field. The usual procedure is to replace in (6) **A** and Φ by $\mathbf{A}^{(r)}$ and $\Phi^{(r)}$. This procedure leads to a correct description of radiation damping and avoids the large distortion which would be caused by the potential of the static field of the electron cloud.

The splitting of the field in accord with (9) is, however, quite unsatisfactory — a splitting of a field into a static and a radiative part cannot be carried out in a consequent manner; among others such a splitting cannot be carried out in a relativistically invariant manner.

Thus a situation arises which compels us to neglect in an arbitrary manner part of the inner field. We can neither neglect the whole of the inner field, nor can we consider the whole of it — in both cases we are led to incorrect results.

The 50% Bohr model

The above apparent discrepancy can, however, be solved in a satisfactory manner. The discrepancy arises from the fact that the wave equation (6) describes the motion of an electron in the field of the nucleus taken as a *point particle*.

In the old theory of Bohr both electron and proton were considered as point particles; the latter theory leads to the difficulty to explain why there is no radiation emitted by the electron moving on a stationary orbit?

The above difficulty is removed by wave mechanics showing that the stationary electron distribution contains stationary charge and current distribution and thus this distribution does not emit radiation.

However, as long as we describe the nucleus as a point particle we have removed only 50% of the difficulty of the Bohr theory. In accord with wave mechanics the nucleus itself cannot be supposed to keep together permanently into a small region. We have to replace the 50% Bohr theory in which the electron is described as a wave but the nucleus is still supposed to be a point particle by the well-known 100% wave description, i.e. by the description in which both electron and proton are taken to be wave packets. Thus the consistent description of the H-atom is obtained only if we use the well-known two-body wave equation.

In the latter description as we have shown in former papers [4], [5] the difficulties which arise in the one body treatment disappear and we obtain cua rrent charge distribution which owing to the diffusion of the nucleus differs appreciably from that obtained for the system of the point nucleus surrounded by the electron.

The charge current distribution obtained in the two-body description of the H-atom is such, that the effects of the "static" part of the field which cause discrepancies in the 50% Bohr theory drop out automatically and the solutions of (2), (3), (4) and (5), if (5) is the wave equation valid for the two-body wave function $\psi(\mathbf{r}^{(1)}, \mathbf{r}^{(2)}, t)$, lead to a correct description of both stationary and mixed states.

The above considerations show that while the one-body description of the H-atom leads to many correct results — this description has its severe limitations and thus it must be replaced by the two-body treatment if we consider e.g. the reaction of an atom upon itself.

The perturbation calculation

Presently, we show in some detail that the perturbation of the radiation emitted by an excited atom causes indeed a reaction on the atom which leads to a fast transition into a lower state of energy. The radiation energy emitted $h\nu$ is equal to the difference of the initial and final states of energy. Furthermore, we shall show that unless the atom is kept together into a volume with dimensions comparable with the wavelength of the emitted radiation — the radiation is emitted into a cone with small opening angle.

We have thus to solve the wave equation

$$(H_0 + P)\psi = i\hbar\dot{\psi} \tag{10}$$

with an initial condition so that ψ represents the distribution of an almost pure excited state at $t = 0$. P is the perturbation operator representing the effect of the radiation emitted by the atom.

We note that in case of a pure excited state obeying

$$H_0\psi_n = i\hbar\dot{\psi}_n \tag{11}$$

no radiation is emitted and thus $P = 0$ and the state ψ_n persists without change. However, as we have already pointed out further above, the pure excited state represents an unstable configuration. If we consider a mixed state e.g. of the form

$$\psi = c_0\psi_0 + c_1\psi_1 \qquad \text{at} \qquad t = t_0 \tag{12}$$

(the suffices 0, 1 represent the lower and excited states, respectively); then radiation with the combination frequency $\omega_1 - \omega_0$ is emitted — and, however small the admixture of the lower state, i.e., however small c_0 at t_0 the radiation emitted starts a perturbation which leads to a transition into the pure lower state. The transition starts slowly, its rate increases at first, it slows down again as soon as the excited state becomes exhausted.

We consider thus a state described by (11) at $t = t_0$ with $c_0 \sim 0$ and solve (10) with this initial condition.

The convenient method to obtain such a solution is to make use of a complete set of normalized orthogonal wave functions ψ_n which are the solutions of the unperturbed wave equation. We can develop the perturbed wave function in terms of these functions, i.e.

$$\psi = \Sigma c_n \psi_n \,, \tag{13}$$

where the c_n are functions of the time. According to Dirac's perturbation theory we have thus

$$\dot{c}_n = -\frac{i}{\hbar} \Sigma P_{nm} c_m \,,$$

$$P_{nm} = \int \psi_n^* P \psi_m d^3\mathbf{r}^{(1)} d^3\mathbf{r}^{(2)} \tag{14}$$

and

$$c_1 = c_1^{(0)} \sim 1, \quad c_0 = c_0^{(0)} \sim 0, \quad \text{at} \quad t = t_0 \,.$$

The unperturbed wave functions are the stationary solutions of the wave equation

$$H_0 \psi_n = i\hbar \dot{\psi}_n \,, \tag{15}$$

$$\psi_n = \Phi_n e^{-i\omega_n t} \,.$$

However, considering a free H-atom the wave equation (11) does not possess stationary solutions which can be normalized. This is indeed the case, since the free atom is subject to wave mechanical diffusion and this diffusion is not a stationary process.

The perturbation method can be applied, however, if we suppose the H-atom to be enclosed into a box the walls of which cannot be penetrated by the atom. The unperturbed wave equation using the two-body treatment can thus be written

$$\left(-\frac{\hbar^2}{2} \sum \frac{\nabla_\nu^2}{m_\nu} - \frac{e^2}{|\mathbf{r}^{(1)} - \mathbf{r}^{(2)}|} + W \right) \psi = i\hbar \dot{\psi} \,, \tag{16}$$

where the suffix $\nu = 1, 2$ refers to measures of proton and electron, respectively, W represents the potential of the walls which prevent the atom to leave its container. If we take the container to be a cubic box with side length L then the stationary solutions can be written in a good approximation as follows

$$\psi_{kl} = \Phi_{kl} e^{-i\omega_{kl} t} \,, \tag{17}$$

where

$$\Phi_{kl} = \frac{1}{L^{3/2}} \varphi_k(\mathbf{s}) e^{i\mathbf{K}_l \mathbf{R}}$$

with the centre of gravity and relative coordinates:

$$\mathbf{R} = \frac{m_1\mathbf{r}^{(1)} + m_2\mathbf{r}^{(2)}}{m_1 + m_2}\,,$$
$$\mathbf{s} = \mathbf{r}^{(1)} - \mathbf{r}^{(2)}. \tag{17a}$$

$\varphi_k(\mathbf{s})$ is the amplitude of the stationary solutions of the one-body wave equation with reduced mass; ω_k is the frequency of that state. Further,

$$\omega_{kl} = \omega_k + \frac{\hbar K_l^2}{2(m_1 + m_2)}\,. \tag{17b}$$

The vector $\mathbf{K}_l$ is the wave number of the translational motion of the state k, l. The solutions (17) define a complete orthogonal set inside the region of the box if we put

$$K_l = \frac{2\pi\mathbf{l}}{L}\,, \tag{17c}$$

where the $\mathbf{l}$ are vectors with integer components. The solutions (17) are slightly inaccurate in the immediate vicinity of the walls; we shall neglect these inaccuracies. Further we suppose

$$\psi_{kl} = 0 \text{ if } \mathbf{r}^{(1)} \text{ or } \mathbf{r}^{(2)} \text{ point outside the box.}$$

So as to obtain the perturbation operator P we have to work out the current densities flowing in the state described by ψ. The six-dimensional current density contains contributions caused by the motions of the electron and those of the proton. We have

$$\mathbf{i}_\nu(\mathbf{r}^{(1)}, \mathbf{r}^{(2)}) = -\frac{ie_\nu\hbar}{2m_\nu c}(\psi^* \operatorname{grad}_\nu\psi - \text{compl. conj.}) - \\ - \frac{e_\nu^2}{m_\nu c^2}\psi\psi^*\mathbf{A}_\nu, \tag{18}$$

where

$$\mathbf{A}_\nu(\mathbf{r}^{(1)},\ \mathbf{r}^{(2)}) = \mathbf{A}(\mathbf{r}^{(\nu)})\,.$$

The current density caused by the protons is proportional to the reciprocal proton mass $1/m_1$; this density will be neglected. The effective current density (in three dimensions) which we consider is thus

$$\bar{\mathbf{i}}(\mathbf{r}) = \int \mathbf{i}_2(\mathbf{r}^{(1)}, \mathbf{r}^{(2)})d^3\mathbf{r}^{(1)}\,. \tag{19}$$

Introducing (13) and (17) into (18) and (19) we obtain a number of terms. We can neglect in a good approximation the terms which arise from the last terms on the right of (18) as these terms are proportional to $1/c^2$.

Introducing (13) into (18) we obtain, cross terms describing oscillating current densities and other terms which describe stationary currents.

From the considerations given further above it is sufficient to consider the oscillating terms as the stationary terms lead only to negligible perturbations.

Supposing for the moment that the wave function ψ can be represented by the linear combination of the states 0 and 1 only, we obtain, neglecting small terms, as the result of a short calculation:

$$\bar{\mathbf{i}}(\mathbf{r}) = -\frac{ic_0^* c_1}{L^3}\frac{e\hbar}{2mc}\mathbf{p}_{01}\exp\{i[(\mathbf{K}_1-\mathbf{K}_0)\mathbf{r}-(\omega_1-\omega_0)t]\}+\text{compl. conj.} \quad (20)$$

where

$$\mathbf{p}_{01} = \int(\varphi_0^* \text{ grad } \varphi_1 - \text{compl. conj.})d^3s$$

and r point inside the box. Here $m_2 = m$.

We note that the current density has the distribution of a plane wave inside the box; we have of course

$$\mathbf{i}(\mathbf{r}) = 0 \text{ if } \mathbf{r} \text{ point outside the box.} \quad (21)$$

From the current distribution (20) the vector potential of the field can be worked out. Introducing (20) into (3) we obtain plane wave solutions for A. Supposing $c_0^* c_1$ varies only slowly in time, we find[1]

$$\mathbf{A}(\mathbf{r}) = \frac{4\pi}{g^2}\mathbf{i}(\mathbf{r}) \quad (22)$$

with $$g^2 = (\mathbf{K}_1 - \mathbf{K}_0)^2 - (\omega_1 - \omega_0)^2/c^2 .$$

The perturbing field is strong if the resonance denominator g^2 is small; this means that a strong perturbation arises if the lower state which is mixed to the original state corresponds to a translational motion equal to that caused by the recoil of the photon with energy $h\nu$.

The matrix elements of the perturbation contain several terms. The most important of them are P_{01} and P_{10} with

$$P_{nm} = \frac{ie\hbar}{mc}\int \psi_n^* (\mathbf{A} \text{ grad}_2)\, \psi_m d^3\mathbf{r}^{(1)} d^3\mathbf{r}^{(2)} . \quad (23)$$

Introducing (20), (22) into (23) we find that only the $n \neq m = 0, 1$ suffices lead to noticeable matrix elements. We find that

$$P_{01} = P_{10}^* \cong i\hbar b c_0 c_1^* , \quad (24)$$

---

[1] We note that the simple field distribution (22) is obtained because we have treated the H-atom as a two-body system. In the "50% Bohr theory" the field obtained has a very complicated distribution. The latter is difficult to deal with — but it seems also void of physical meaning.

where the expression for b does not contain the coefficients c_0, c_1. The equations (14) giving the changes of c_0 and c_1 in time can thus be written

$$\begin{aligned} \dot{c}_0 &= b c_0 c_1 c_1^* , \\ \dot{c}_1 &= - b^* c_1 c_0 c_0^* , \end{aligned} \tag{25}$$

The solutions of the above system are obtained as

$$\begin{aligned} | c_0 |^2 &= 1 - | c_1 |^2 , \\ | c_0 |^2 &= \frac{1}{1 + e^{-\beta(t)}} , \\ \beta(t) &= \int (b + b^*) dt . \end{aligned} \tag{26}$$

Thus if

$$b + b^* > 0 \tag{27}$$

then $\beta(t)$ changes from $-\infty$ to $+\infty$ and thus $| c_0 |$ increases from $0 \to 1$ in the course of time. We see thus that provided (27) is fulfilled the radiation reaction produces a transition from the excited state into the state of lower energy. The transition takes place the faster the smaller g^2.

Mathematically the solutions of (26) of the perturbation equations contain the following kind of processes. During periods when $b + b^* > 0$ the system radiates energy and loses inner energy. During the periods where $b + b^* < 0$ the system absorbs the energy it has emitted previously and during these periods the inner energy of the system increases. In periods when $b + b^* = 0$ the system is in equilibrium with its own radiation field. In this configuration $| c_0 |$, $| c_1 |$ are constants, the phases of the coefficients, however, vary in time.

A qualitative analysis of the emission

In the following we give qualitative arguments as to the mode of emission of the excited atom. These arguments are based upon the result so far obtained. We hope to give a quantitative treatment of the process in a further publication.

The value of b as can be obtained from (20), (22) (23) and (24) is purely imaginary. Thus the perturbation caused by the current as given in (22) corresponds to the configuration in which the radiation field is in equilibrium with the emitting atom and thus it causes no further transition.

The above result is not surprising and it is due to the fact that the expression (22) satisfies the electromagnetic wave equations (3) only inside the box. Thus the field expressed by (22) corresponds to the case where the walls of the box are perfect mirror surfaces and thus the box prevents not only the atom but also the radiation from leaving the box. If in this manner no radiation leaves the box then a state emerges in which there is equilibrium between radiation and atomic state.

If we consider, however, a box which keeps the atom confined but which is transparent to the radiation then the field must be taken to be the solution of (3) where the current distribution is given by (20) and (21).

Without going into mathematical details, from the law of conservation of energy we can estimate the effect of the escaping radiation. The energy leaving the box is compensated by an increase of $| c_0 |$ and decrease of $| c_1 |$ since the energy leaving the system is compensated by inner energy.

Because of this change the amplitude $c_0^* c_1$ changes also in time and we may write

$$c_0^* c_1 = e^{\gamma(t)} , \tag{28}$$

where real $\gamma(t) > 0$ at the beginning of the process, later real $\gamma(t) < 0$.

Considering (28) we find (supposing $\gamma(t)$ to be a slowly varying function) that the frequency of the vector potential will be

$$\Omega = \omega_1 - \omega_0 + i\gamma$$

and thus the resonance denominator

$$g^2 = (\mathbf{K}_1 - \mathbf{K}_0)^2 - \Omega^2/c^2 = \text{complex} . \tag{29}$$

One sees thus easily that the escaping radiation modifies the perturbation operator so that we have

$$b + b^* \neq 0 .$$

The actual value of $b + b^*$ can only be obtained solving exactly the simultaneous systems of equations (3), (4), (5).

However, as both the wave equations and also the electromagnetic equations satisfy strictly the conservation laws it follows that the process continues until the whole of the excess energy of the excited state is transformed into radiation energy, i.e. the process proceeds until the energy is emitted by radiation.

The distribution of the radiation field

The radiation field outside the box in a point with coordinate vector **r** is the field derived from the vector potential

$$\mathbf{A}(\mathbf{r}, t) = \int_{(L^3)} \frac{\mathbf{i}(\mathbf{r}', t')d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} ,$$

$$t' = t - \frac{|\mathbf{r} - \mathbf{r}'|}{c} , \tag{30}$$

Inserting into (30) the $\bar{\mathbf{i}}(\mathbf{r}', t')$ from (20) we find that for a fixed value of $\mathbf{r}$, which represents a point at a large distance from the source, the integrand in (30) oscillates rapidly. The value of $\mathbf{A}(\mathbf{r}, t)$ is therefore in most distant points $\mathbf{r}$ very small.

Larger values of $\mathbf{A}(\mathbf{r}, t)$ are found in such regions whereto the elements of the source emit radiation with identical phases. The mathematical analysis of the integral shows the following:

Regions with appreciable field exist only if

$$|\mathbf{K}_1 - \mathbf{K}_0| \approx \frac{|\omega_1 - \omega_0|}{c}. \tag{31}$$

Unless (31) is satified the emission of the various elements of the source extinguish each other to a large extent everywhere outside the source.

Further, if (31) is satisfied, then noticeable emission occurs in the direction of the vector $\mathbf{K}_1 - \mathbf{K}_0$ moreover noticeable intensity is emitted into a cone with opening angle of the order of

$$\vartheta \sim \sqrt{\frac{\lambda}{L}}$$

thus if $\lambda \ll L$ then the emission takes place inside a narrow cone.

We see thus that if $\lambda \ll L$ the transition of the excited atom into a lower state produces radiation of total energy $h\nu$ and the radiation is emitted into a cone with small opening angle. This emission is just as we picture the emission of a photon. If the region of emission is confined to a region with linear dimensions of the order of λ or into a smaller region then the cone of emission opens up and if $L \ll \lambda$ the radiation becomes of the type of the ordinary dipole radiation. The latter effect is that which was observed by SELÉNYI and SCHRÖDINGER.

Concluding remarks

The process of emission of light by H-atoms enclosed in a volume can be described in the following way. As long as the H-atom is in a pure excited state no emission of radiation takes place. However, because of thermal motion (in case of one atom this may be caused as the result of interaction with the walls of the container) small perturbation in the state of the atom appears. The perturbation gives rise to oscillating current and inner radiation fields. The latter fields are, however, in general rather ineffective. Exceptional case is, if a perturbation happens to arise which is in resonance with a transition from the excited state into a lower state. I.e. a perturbation becomes effective if the value of g^2 as given by (29) attains a sufficiently small value. In the latter case the perturbation initiates an avalanche and a photon is emitted into the direction $\mathbf{K}_1 - \mathbf{K}_0$.

We note, that the value of g^2 does not depend on the direction of $\mathbf{K}_1 - \mathbf{K}_0$ but only on the absolute value of this vector. From this we see that considering a number of excited atoms — they will emit radiation independently of each other whenever the thermal agitation provides a suitable perturbation to initiate an emission process. The directions of such emissions will be distributed at random as the thermal perturbations must be assumed to occur with random directions.

When considering an ensemble of N atoms instead of one H-atom then it is necessary to describe the ensemble of atoms by a wave function with $2N$ coordinate vectors. The latter treatment leads, however, to the same results as the present consideration dealing with one H-atom only. This will be shown in a subsequent publication.

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REFERENCES

1. P. SELÉNYI, Phys. Rev., **56,** 977, 1939.
2. E. SCHRÖDINGER, Ann. d. Phys., **61,** 69, 1920.
3. W. HEITLER, The Quantum Theory of Radiation, Oxford, Clarendon, 1954.
4. L. JÁNOSSY, KFKI preprint, 75—11; Acta Phys. Hung. **37,** 355, 1975.
5. L. JÁNOSSY, Acta Phys. Hung. **27,** 35, 1969.

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NONLINEAR INTERACTION IN COLLISIONAL PLASMA

By

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The interactions between waves for various magnetoionic modes of transverse and longitudinal propagation within a cold plasma have been investigated. The nonlinearity of the medium is introduced through the dielectric tensor. The expressions representing the field components and various interactions exhibit the collision effect through the exponentially damping factor.

1. Introduction

Nonlinear interaction of electromagnetic waves propagating through a cold magnetoplasma has been studied by Kroll, Ron and Rostoker [1], Montgomery [2], Blachier and Bouchet [3], Etievant, Ossakow, Ozizmir and Su [4], Bajwa and Srivastava [5] through different techniques. In most of the cases, the effect of collision has been neglected because of the assumption that the collision time is less than that of the time of interaction. There are some media (ionosphere) where the effect of collision during interaction is not negligibly small and as a result of which different types of coupling are always expected within the ionosphere.

In this paper, we have endeavoured to calculate the electromagnetic intensities of various orders by the help of the tensorial nature of the dielectric constant of the medium with the consideration of the collision effect. In our approach, the field quantities are directly obtained without going through the other variables. Interaction corresponding to the longitudinal propagation as well as ordinary and extra-ordinary waves for transverse propagation have been calculated.

2. Formulation of the problem

We consider an electron-plasma where (i) the ions are stationary and they neutralise the electrons on average, (ii) an external magnetic field acts in the direction of z-axis and (iii) collisional frequency is not a small order quantity.

The Lorentz force equation is

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{v} + \eta\mathbf{v} = \frac{e}{m}\left[\mathbf{E} + \frac{\mathbf{v}\times\mathbf{H}}{c}\right]\ldots, \tag{1}$$

where

e = charge of an electron,
m = mass of an electron,
$\mathbf{v}$ = average velocity of an electron,
η = collision factor,
$\mathbf{E}$ = electric vector,
$\mathbf{H}$ = magnetic vector.

Under Fourier transformation the force equation yields

$$-2\omega^2\mathbf{r} - i\omega\eta\mathbf{r} = \frac{e}{m}\left[\mathbf{E} - i\omega\,\frac{(\mathbf{r}\times\mathbf{H})}{c}\right]. \tag{2}$$

Introducing the polarization vector ($\mathbf{P} = Ne\mathbf{r}$) and $\mathbf{P} = (\sigma)\mathbf{E}$ in (2), we have

$$\sigma^{-1} = -\frac{i\omega m}{Ne^2}\begin{pmatrix} \eta - i2\omega & -\Omega_z & \Omega_y \\ \Omega_z & \eta - i2\omega & -\Omega_{\varkappa} \\ -\Omega_y & \Omega_x & \eta - i2\omega \end{pmatrix}, \tag{3}$$

where

$$\mathbf{\Omega} = \frac{e\mathbf{H}}{mc}.$$

Now, the dielectric tensor $(\bar{\varepsilon})$ can be evaluated as

$$(\bar{\varepsilon}) = I + \frac{i\omega_p^2}{\omega\chi(\eta - i2\omega)} \times$$

$$\begin{pmatrix} \chi_x & \Omega_x\Omega_y + \Omega_z(\eta - i2\omega), & \Omega_z\Omega_x - \Omega_y(\eta - i2\omega) \\ \Omega_z\Omega_y - \Omega_z(\eta - i2\omega), & \chi_y, & \Omega_y\Omega_z + \Omega_x(\eta - i2\omega) \\ \Omega_z\Omega_x + \Omega_y(\eta - i2\omega), & \Omega_y\Omega_z - \Omega_x(\eta - i2\omega), & \chi_z \end{pmatrix}\ldots \tag{4}$$

where

$$\omega_p^2 = \frac{4\pi Ne^2}{m},$$

$$\chi = (\eta - i2\omega)^2 + \Omega^2.$$

Maxwell's equations for field variables are

$$\nabla \times \mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t},$$

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t},$$

$$\nabla \cdot \mathbf{D} = 4\pi e(n - n'), \tag{5}$$

$$\nabla \cdot \mathbf{H} = 0.$$

n = average electron number density,
n' = average ion number density.

To find the solution for different orders, the variables are stretched in the following way

$$(\varepsilon) = \sum_{s=0}^{\infty} (\varepsilon_s), \quad E = \sum_{s=1}^{\infty} E_s,$$

$$H = \sum_{s=0}^{\infty} H_s, \quad n = \sum_{s=0}^{\infty} n_s, \quad v = \sum_{s=1}^{\infty} v_s \tag{6}$$

3. Dispersion relation for the first order variables

For the first order field variables under Fourier transformation we write

$$\nabla \times \mathbf{H}_1 = -\frac{i\omega}{c}(\varepsilon_0)\mathbf{E}_1, \tag{7}$$

$$\nabla \times \mathbf{E}_1 = \frac{i\omega}{c}\mathbf{H}_1, \tag{8}$$

where

$$(\varepsilon_0) = \begin{pmatrix} 1 + \dfrac{i\omega_{p0}^2(\eta - i2\omega)}{\omega\chi_0}, & \dfrac{i\omega_{p0}^2\Omega_{0z}}{\omega\chi_0}, & 0 \\ -\dfrac{i\omega_{p0}^2\Omega_{0z}}{\omega\chi_0} & 1 + \dfrac{i\omega_{p0}^2(\eta - i2\omega)}{\omega\chi_0}, & 0 \\ 0, & 0, & 1 + \dfrac{i\omega_{p0}^2}{\omega(\eta - i2\omega)} \end{pmatrix}. \tag{9}$$

From (7) and (8)

$$\nabla(\nabla \cdot \mathbf{E}_1) - \nabla^2\mathbf{E}_1 = \frac{\omega^2}{c^2}(\varepsilon_0)\mathbf{E}_1,$$

To find the dispersion relation, we assume that

$$\mathbf{E}_1 = \mathscr{E} e^{i(k\cdot r - \omega t)} .$$

In our case, $\mathbf{k} = \hat{y}k_y + \hat{z}k_z$.

Thus the dispersion relation is

$$\begin{vmatrix} k^2 - \frac{\omega_2}{c_2}\left(1 + \frac{i\omega_{p0}^2}{\omega}\frac{\eta - i2\omega}{\chi_0}\right), & \frac{i\omega\omega_{p0}^2\Omega_{0z}}{c^2\chi_0}, & 0 \\ -\frac{i\omega\omega_{p0}^2\Omega_{0z}}{c^2\chi_0}, & k_z^2 - \frac{\omega^2}{c^2}\left(1 + \frac{i\omega_{p0}^2}{\omega}\frac{\eta - i2\omega}{\chi_0}\right), & -k_yk_z \\ 0, & -k_yk_z, & k_y^2 - \frac{\omega^2}{c^2}\left(1 + \frac{i}{\omega}\frac{\omega_{p0}^2}{\omega(\eta - i2\omega)}\right) \end{vmatrix} = 0 . \qquad (10)$$

For longitudinal wave propagation, the dispersion relation is obtained as

$$\left\{k_z^2 - \frac{\omega^2}{c^2}\left(1 + \frac{i\omega_{p0}^2}{\omega}\frac{\eta - i2\omega}{\chi_0}\right)\right\} - \frac{\omega^2}{c^4}\frac{\omega_{p0}^4\Omega_{0z}^2}{\chi_0^2} = 0 . \qquad (11)$$

In case of transverse propagation, the dispersion relation gives

$$k_y^2 = \frac{\omega^2}{c^2}\left(1 + \frac{i}{\omega}\frac{\omega_{p0}^2}{\eta - i2\omega}\right) \qquad (12)$$

and

$$\left\{k_y^2 - \frac{\omega^2}{c^2}\left(1 + \frac{i\omega_{p0}^2}{\omega}\frac{\eta - i2\omega}{\chi_0}\right)\right\}\left(1 + \frac{i\omega_{p0}^2}{\omega}\frac{\eta - i2\omega}{\chi_0}\right) + \frac{\omega_{p0}^4\Omega_{0z}^2}{\chi_0^2 c^2} = 0 . \qquad (13)$$

(12) and (13) correspond to ordinary and extraordinary waves, respectively.

4. Evaluation of first order fields

The intensities corresponding to the extraordinary part may be written as

$$\mathbf{E}_1^{(e)} = A(a\hat{x} + \hat{y})e^{(\mathbf{k}\cdot\mathbf{r} - \omega t)} = \mathscr{E}_e e^{i(kz - \omega t)} \qquad (14)$$

and

$$\mathbf{H}_1^{(e)} = -\hat{z}k_y\frac{cAa}{\omega}e^{i\psi} ,$$

where A is the normalisation factor and

$$A^2 = \frac{|\mathscr{E}_e|^2}{|a|^2 + 1}, \quad a = \frac{i\omega_{p0}^2\Omega_{0z}}{\omega\chi_0 + i\omega_{p0}^2(\eta - i2\omega)}$$

and

$$\psi = k_y - \omega t .$$

Similarly, the intensities for ordinary waves are

$$\left.\begin{aligned} \mathbf{E}_1^{(0)} &= \hat{z}\mathscr{E}_{11}e^{i\varphi} \\ \mathbf{H}_1^{(0)} &= \hat{x}k_y\frac{c}{\omega}\,\mathscr{E}_{11}{}^{i\varphi} \end{aligned}\right\}. \tag{15}$$

For the intensities of longitudinal propagation, we assume that

$$\mathbf{E}_1 = \mathscr{E}_l\, e^{i\Phi} = G\,(\hat{x} + i\hat{y})\, e^{i\Phi}\,. \tag{16}$$

Here,

$$\Phi = k_z z - \omega t$$

and

$$G^2 = \frac{|\mathscr{E}_l|^2}{2}\,.$$

The corresponding magnetic vector is given by

$$\mathbf{H}_1 = \frac{ck_z}{\omega}\, G(i\hat{x} + \hat{y})\, e^{i\Phi}\,. \tag{17}$$

5. Derivation of second order fields

For the second order variables, Maxwell's equation yields

$$\left.\begin{aligned} \nabla\times\mathbf{E}_2 &= \frac{i\omega}{c}\,\mathbf{H}_2\,, \\ \nabla\times\mathbf{H}_2 &= -\frac{i\omega}{c}\,\left[(\varepsilon_0)\,\mathbf{E}_2 + 2(\varepsilon_1)\,\mathbf{E}_1\right], \end{aligned}\right\} \tag{18}$$

where

$$(\varepsilon_1) = \begin{bmatrix} 0, & \dfrac{i\omega_{p0}^2\Omega_{1z}}{\omega\chi_0}, & i\omega_{p0}^2\{\Omega_{0z}\Omega_{1x} - \Omega_{1y}(\eta - i2\omega)\} \\ -\dfrac{i\omega_{p0}^2\Omega_{1z}}{\omega\chi_0}, & 0, & \dfrac{i\omega_{p0}^2}{\omega(\eta - i2\omega)\chi_0}\{\Omega_{0z}\Omega_{1y} + \Omega_{1x}(\eta - i2\omega)\} \\ \dfrac{i\omega_{p0}^2}{\omega(\eta - i2\omega)x_0}\{\Omega_{0z}\Omega_{1x} + \Omega_{1y}(\eta - i2\omega)\}, & \dfrac{i\omega_{p0}^2}{\omega(\eta - i2\omega)\chi_0}\{\Omega_{0z}\Omega_{1y} - \Omega_{1z}(\eta - i2\omega)\}, & 0, \end{bmatrix}. \tag{19}$$

From (18) we get

$$\left[\nabla\nabla\cdot-\nabla^2-\frac{\omega^2}{c^2}(\varepsilon_0)\right]\mathbf{E}_2=\frac{2\omega^2}{c^2}(\varepsilon_1)\,\mathbf{E}_1\,. \tag{20}$$

For transverse propagation, the general solution of (20) can be written as

$$\mathbf{E}_2=\frac{i2e\omega\omega_{p0}^2k_ye^{i2\varphi}}{mc^2\chi_0}(D^{-1})\begin{bmatrix}-\dfrac{A^2a}{\omega}+\dfrac{\Omega_{0z}\mathcal{E}_\parallel^2}{c(\eta-i2\omega)}\\[2ex] \dfrac{A^2a^2}{\omega}+\dfrac{\mathcal{E}_\parallel^2}{c}\\[2ex] \dfrac{\mathcal{E}_\parallel Aa}{c(\eta-i2\omega)}-\dfrac{\mathcal{E}_\parallel A}{c}\end{bmatrix}, \tag{21}$$

where

$$(D)=\begin{bmatrix}4k_y^2-\dfrac{\omega^2}{c^2}\left(1+\dfrac{i\omega_{p0}^2}{\omega}\dfrac{\eta-i2\omega}{\chi_0}\right), & -\dfrac{i\omega_{p0}^2\Omega_{0z}}{\omega c^2\chi_0}, & 0\\[2ex] \dfrac{i\omega_{p0}^2\Omega_{0z}}{\omega c^2\chi_0}, & -\dfrac{\omega^2}{c^2}\left(1+\dfrac{i\omega_{p0}^2}{\omega}\dfrac{\eta-i2\omega}{\chi_0}\right), & 0\\[2ex] 0, & 0, & 4k_y^2-\dfrac{\omega^2}{c^2}\left(1+\dfrac{i\omega_{p0}^2}{\omega}\dfrac{1}{\eta-i2\omega}\right)\end{bmatrix}.$$

For the longitudinal part, we have

$$\mathbf{E}_2=-\hat{z}\,\frac{i4ek_zG^2\omega_{p0}^2\{(\eta-i2\omega)+i\Omega_{0z}\}}{m\omega\chi_0\{\omega(\eta-i2\omega)+i\omega_{p0}^2\}}\,e^{i2\Phi}. \tag{22}$$

6. Different types of interaction

In Eq. (20), the part

$$\mathrm{Re}\ \frac{2\omega^2}{c^2}(\varepsilon_1)\mathbf{E}_1=\mathbf{J}_s\quad\text{(say)}$$

contributes to the process of interaction among various modes of propagation.

We consider the following cases:

(a) Interaction between two ordinary waves

In this case, the interaction produces a current source which is given by

$$\begin{aligned}\mathbf{J}_s=\frac{\omega_\pm^2}{c^2}\mathcal{E}_{\parallel 1}e^{-(k_1''+k_2'')y}\big[\xi_1\{(\zeta_1k_2''+\zeta_2k_2')\cos(k_\pm y-\omega_\pm t)\pm\\ \pm(\zeta_1k_2'-\zeta_2k_2'')\sin(k_\pm y-\omega_\pm t)\}\hat{x}+\xi_2\{(\zeta_3k_2''+\zeta_4k_2')\cdot\\ \cdot\cos(k_\pm y-\omega_\pm t)\pm(\zeta_3k_2'-\zeta_4k_2'')\sin(k_\pm y-\omega_\pm t)\}\hat{y}\big],\end{aligned} \tag{23}$$

where

$$\xi_1 = \frac{e\Omega_{0z}\,\omega_{p0}^2\,\mathcal{E}_{\parallel 2}}{mc\,\omega_2\,\omega_\pm\,(\eta^2+4\omega_\pm^2)\{(\Omega_{0z}+\eta^2-4\omega_\pm^2)^2+16\eta^2\,\omega_\pm^2\}},$$

$$\xi_2 = \frac{e\omega_{p0}^2\,\mathcal{E}_{\parallel 2}}{mc\,\omega_2\,\omega_\pm\,\{(\Omega_{0z}+\eta^2-4\omega_\pm^2)^2+16\eta^2\,\omega_\pm^2\}},$$

$$\zeta_1 = \eta(\Omega_{0z}^2+\eta^2-4\omega_\pm^2-8\eta\omega_\pm^2)\,,$$

$$\eta_2 = \{2\omega_\pm\,(\Omega_{0z}^2+\eta^2-4\omega_\pm^2)+4\eta^2\,\omega_\pm\},$$

$$\zeta_3 = \Omega_{0z}^2+\eta^2-4\omega_\pm^2\,,\quad \zeta_4 = 4\eta\omega_\pm\,,$$

and

$$k_{y1} = k_1' + ik_1''\,,$$

$$k_{y2} = k_2' + ik_2''\,,$$

$$k_\pm = k_1' \pm k_2'\,,$$

$$\omega_\pm = \omega_1 \pm \omega_2\,,$$

Suffixes 1 and 2 are used to denote the propagation vectors and frequencies in electric and magnetic vectors, respectively.

Eq. (23) reveals that the second order wave is an extra-ordinary wave because here the current source is perpendicular to magnetic field. Thus

$$\begin{aligned}\mathbf{E}_2 = {} & \frac{\omega_\pm^2}{c_2}\;\frac{e^{-(\kappa_1''+k_2'')y}}{l_\parallel\,l_{22}-l_{12}\,l_{21}}\,[\hat{x}\,\{l_{22}\,\xi_1\,(\zeta_1\,k_2''+\zeta_2\,k_2')-l_{12}\,\xi_2(\zeta_3\,k_2''+\zeta_1\,k_2')\}\cdot\\ & \cdot\cos\,(k_\pm\,y-\omega_\pm t)\pm\hat{x}\{l_{22}\,\xi_1\,(\zeta_1\,k_2'-\zeta_2\,k_2'')-l_{12}\,\xi_2\,(\zeta_3'\,k_2'-\zeta_4\,k_2'')\,\cdot\\ & \cdot\sin\,(k_\pm\,y-\omega_\pm\,t)+\hat{y}\,\{l_\parallel\,\xi_2\,(\zeta_3\,k_2''+\zeta_1\,k_2')-l_{21}\,\xi_1\,(\zeta_1\,k_2''+\zeta_2\,k_2')\}\cdot\\ & \cdot\cos\,(k_\pm\,y-\omega_\pm t)\pm\hat{y}\,\{l_\parallel\,\xi_2\,(k_2'\,\zeta_3-k_2''\,\zeta_4)-l_{21}\,\xi_1\,(\zeta_1\,k_2'-\zeta_2\,k_2'')\}\,\cdot\\ & \cdot\sin\,(k_\pm\,y-\omega_\pm\,t)\,. \end{aligned} \tag{24}$$

Here

$$l_{11} = k_\pm^2 - \frac{\omega_\pm^2}{c^2}\left(1+2\omega_{p0}^2\,\frac{L-2\eta^2}{L^2+16\,\eta^2\,\omega_\pm^2}\right),$$

$$l_{12} = \frac{\omega_\pm^2}{c^2}\cdot\;\frac{4\omega_{p0}^2\,\Omega_{0z}\,\eta}{L^2+16\,\eta^2\,\omega_\pm^2} = -\,l_{21}\,,$$

$$l_{22} = -\,\frac{\omega_\pm^2}{c^2}\left(1+2\omega_{p0}^2\,\frac{L-2\eta^2}{L^2+16\,\eta^2\,\omega_\pm^2}\right),$$

$$L = \Omega_{0z}^2+\eta^2-4\omega_\pm^2\,.$$

For the collision from field we put $\eta = 0$. In this case

$$\mathbf{J}_s = \frac{e\omega_{p0}^2\,\mathcal{E}_{\parallel 1}\,\mathcal{E}_{\parallel 2}\,k_2'}{m\omega_2\,c^2}\left[\;\hat{x}\;\frac{\Omega_{0z}}{2}\cos\,(k_\pm y-\omega_\pm\,t)\pm\hat{y}\,\omega_\pm\,\sin\,(k_\pm\,y-\omega_\pm\,t)\right]. \tag{25}$$

(b) Interaction between ordinary and extraordinary waves

The current source produced by the interaction between an ordinary and an extraordinary wave can be written as

$$\mathbf{J}_s = \hat{z}\,\frac{\omega_\pm^2}{c^2} A e^{-(k_1''+k_2'')y}\,[\{-\xi_1 a'(\zeta_1 k_2'' + \zeta_2 k_2')$$

$$\pm\, \xi_1 a''(\zeta_1 k_2' - \zeta_2 k_2'') + \xi_2(\zeta_3 k_2'' + \zeta_4 k_1')\}\cos(k_\pm y - \omega_\pm t)$$

$$+ \{\pm\, \xi_1 a'(\zeta_1 k_2' - \zeta_2 k_2'') + \xi_1 a_2'(\zeta_1 k_2'' + \zeta_2 k_2')$$

$$\pm\, \xi_2(\zeta_3 k_2' - \zeta_4 k_2'')\}\sin(k_\pm y - \omega_\pm t)]\,, \text{ where } a = a' + ia''\,. \tag{26}$$

Eq. (26) shows that the interaction of the incident waves generates a second order current source in the direction of *z*-axis. Hence the second order wave will be an ordinary wave.

The corresponding electric field can be written as

$$\mathbf{E}_2 = \mathbf{J}_s\left[k_\pm^2 - \frac{\omega_\pm^2}{c^2}\left(1 - \frac{2\omega_{p0}^2}{\eta^2 + 4\omega^2}\right)\right]^{-1}. \tag{27}$$

(c) Interaction between two extraordinary waves

In this case the expressions for the second order current source and electric field are evaluated as

$$\mathbf{J}_s = \frac{\omega_\pm^2}{c_2} A\xi_3 e^{-(k_1''+k_2'')y}\,[-\hat{x}\{\zeta_6 \cos(k_\pm y - \omega_\pm t)$$

$$\pm\, \zeta_5 \sin(k_\pm y - \omega_\pm t)\} + \hat{y}\{(a'\zeta_6 \pm a''\zeta_5)\cos(k_\pm y - \omega_\pm t)$$

$$+ (\pm\, a'\zeta_5 - a''\zeta_6)\sin(k_\pm y - \omega_\pm t)\}]\,, \tag{28}$$

where

$$\zeta_5 = L(a'k_2' - a''k_2'') - 4\eta\omega(a'k_2'' + a''k_2')\,,$$

$$\zeta_6 = 4\eta\omega(a'k_2' - a''k_2'') + L(a'k_2'' + a''k_2')\}\,,$$

$$\xi_3 = \frac{Ae\omega_{p0}^2}{m\omega_2^2(L^2 + 16\eta^2\omega_\pm^2)}$$

and

$$\mathbf{E}_2 = \mathbf{J}_s(l_{11}l_{22} - l_{12}l_{21})^{-1}\,.$$

(d) Interaction between longitudinal waves

In this case, the current source is produced due to the interaction between the waves generated from the first order electric and magnetic intensities.

The expression for $\mathbf{J}_s$ turns out in the following form:

$$\mathbf{J}_s = -\hat{z}\frac{\omega_\pm^2}{c^2} G^2[\pm G_1 \sin(\Phi_1 \pm \Phi_2) + G_2 \cos(\Phi_1 \pm \Phi_2)$$

$$\pm G_3 \cos(\Phi_1 \pm \Phi_2) + G_4 \sin(\Phi_1 \pm \Phi_2)]e^{-(k_2' + k_2'')z}\,, \tag{29}$$

where

$$G_1 = \frac{e\omega_{p0}^2}{m\omega_\pm\omega_2}\frac{L\chi_1 - 4\eta\omega_\pm\chi_2}{L^2 + 16\eta^2\omega_\pm^2}\,,\quad G_4 = \frac{e\omega_{p0}^2}{m\omega_\pm\omega_2}\frac{4\eta\omega_\pm\chi_2 - L\chi_1}{L^2 + 16\eta^2\omega_\pm^2}\,,$$

$$G_2 = \frac{e\omega_{p0}^2}{m\omega_\pm\omega_2}\frac{4\eta\omega_\pm\chi_1 + L\chi_2}{L^2 + 16\eta^2\omega_\pm^2}\,,\quad \chi_1 = -\frac{\Omega_{0z}}{\eta^2 + 4\omega_\pm^2}(\eta k_2'' + 2\omega_\pm k_1'') + k_1'',$$

$$G_3 = \frac{e\omega_{p0}^2}{m_e\omega_\pm\omega_2}\frac{L\chi_2 + 4\eta\chi_1\omega_\pm}{L^2 + 16\eta_2\omega_\pm^2}\,,\quad \chi_2 = \frac{\Omega_{0z}}{\eta^2 + 4\omega_\pm^2}(\eta k_1'' - 2\omega_\pm k_2'') + k_2'',$$

and

$$\Phi_1 = k_1'z - \omega_1 t, \qquad \Phi_2 = k_1''z - \omega_2 t\,, \tag{30}$$

$$\mathbf{E}_2 = \left[-\frac{\omega_\pm^2}{c^2}\left(1 - \frac{2\omega_{p0}^2}{\eta^2 + 4\omega_\pm^2}\right)\right]^{-1}\mathbf{J}_s\,. \tag{31}$$

7. Discussion

In our calculations, different types of second order currents and fields due to interactions among different modes have been evaluated. Appropriate experimental observations may reveal the importance of such interaction.

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REFERENCES

1. N. M. Kroll, A. Ron and N. Rostoker, Phys. Rev. Letters, **13**, 83, 1964.
2. D. Montgomery, Physica, **31**, 693, 1965.
3. B. Blanchier and P. Bonchet, Ann. Radio Elect. (France), **21**, 250, 1966.
4. C. Etievant, S. Ossakow, E. Ozizmir and C. H. Ju, Phys. Fluids, **11**, 1778, 1968.
5. G. S. Bajwa and K. M. Srivastava, Indian J. Phys., **44**, 386, 1970.

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COMMUNICATIO BREVIS

COMPARATIVE STUDIES ON MODEL POTENTIAL CURVES

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As is well-known, the usual "restricted" Hartree—Fock (RHF) method fails to describe correctly the dissociation of a closed-shell system into neutral odd-electron parts but, at large internuclear separations, (if it converges at all) it gives wave functions corresponding to ionic states or their superposition. The RHF method is, therefore, quite inadequate to investigate potential curves and surfaces. This difficulty is first of all due to the use of doubly filled orbitals in constructing the RHF wave functions, which can be avoided within the one-electron approach by introducing DODS ("different orbitals for different spins") schemes. The single DODS determinant wave function of the "unrestricted" Hartree—Fock (UHF) method describes properly the dissociation into neutral parts but, not being an eigenfunction of the total spin operator $\hat{S}^2$, it does not correspond to any definite spin multiplicity. A step further may be made if one considers a pure spin state (e.g. singlet) component of the UHF wave function, selected by using LÖWDIN's spin projection operator [1]. In this case the trial wave function in the variation procedure is just the single determinant (its energy is optimized by solving the UHF equations) and the spin projection is applied only subsequently. This approach may be called, therefore, spin projected UHF or UHF with subsequent spin projection method and it has the disadvantage that the final spin projected wave function, though better, in general, than the non-projected one, is not optimized variationally. If the spin projected determinant itself is used as trial function, i.e., if the orbitals are determined to minimize the energy obtained after the spin projection, one obtains the (spin projected) extended Hartree—Fock (EHF) method [2—11].

The aim of the present note is to present a comparison of the potential curves given by the above methods in the case of some four-electron systems treated at the PPP and CNDO/2 level of integral approximation. We desired to compare the results given by the different one-electron approximations not only with each other but also with the exact eigenvalues and eigenvectors of the corresponding (PPP or CNDO/2) model-Hamiltonians, which can be called

Table I

Comparison of different wave functions for the PPP model of butadiene and cyclo-butadiene

Molecule	Wave function	Total π-electronic energy [eV]	Error of the electronic energy [eV]	Overlap with the exact (full CI) wave function[a]
Butadiene	RHF	−77.660531	1.272469	0.941
	UHF	−77.766680	1.166320	0.856
	UHF with subsequent spin projection	−78.266616	0.666384	0.971
	EHF	−78.759347	0.173653	0.987
	full CI[b]	−78.933000	0	1
Cyclo-butadiene	RHF	−79.350364[c]	2.389109[c]	0.677[c]
	UHF	−81.206897	0.532576	0.683
	UHF with subsequent spin projection	−81.539346	0.200127	0.993
	EHF	−81.739410	0.000063	0.9999986
	full CI[b]	−81.739473	0	1

[a] The projected wave functions are assumed to be renormalized to unity.
[b] Exact for the given PPP model Hamiltonian.
[c] Solution without appropriate spatial symmetry.

the full CI problem. Therefore the size of the full CI problem (increasing in a prohibitive way for the larger systems) strongly motivated the selection of the models investigated. The method of calculations was essentially the same as in [9].

Two systems, (s-trans-)butadiene and cyclo-butadiene have been considered on the PPP level of approximations. The equilibrium geometries and the Mataga—Nishimoto type parametrization of the γ-integrals have been taken the same as in [9, 11], while the β-integrals have been determined to be proportional to the overlap of the $2p_z$ orbitals of the carbon atoms (STO's with orbital exponents 1.625) and by putting $\beta_{ij} = -2.39$ eV for the case of $R_{CC} = 1.39$ Å. This way of determining the β-integrals permitted to consider continuous changes in the bond lengths. The most important results concerning energies and wave functions for the equilibrium configuration of both molecules are collected in Table I*.

Figs 1. and 2 show how the error in the total π-electronic energy (the deviation from the exact full CI value) given by different methods changes

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* Due to the different parametrization used for the β-integrals these results differ numerically (but not in their tendencies) from those in [9, 11].

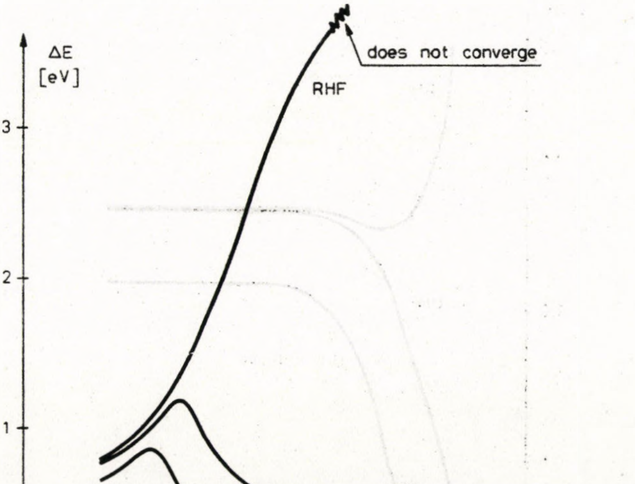

Fig. 1. Error in the total π-electronic energy given by different methods for the PPP model of butadiene as function of the bond length R_{34}

for the case of butadiene when the lengths of the bond $C_3 - C_4$ and $C_2 - C_3$, respectively, are changed within a wide range. $R^0_{34} = 1.34$ Å and $R^0_{23} = 1.47$ Å are the equilibrium bond lengths; accordingly, the scales are selected in such a way that the equilibrium configuration corresponds to the values of the abscissae equal to unity.

As expected, the RHF method gives a rapid increase of the error in the electronic energy with increasing internuclear separation (and then it fails to converge) in the case when a center with a single electron is removed from the system (Fig. 1). It is remarkable that an analogous strong increase of the correlation energy* occurs when the distance between the two closed-shell parts of the system becomes small (Fig. 2). This latter behaviour, however, may be partly due also to the specific model and parametrization (e.g., in the case of the PPP parametrization, the atomic orbitals are assumed to be orthogonal at all distances). It is interesting that the error in the π-electronic energy given by the UHF method decreases significantly just in the directions where the behaviour of the RHF method becomes very bad, while the UHF curves almost coincide with the RHF ones in the opposite limited cases. The

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* The correlation energy is defined as the difference between the RHF and exact energy values, i.e., it is connected with an approximate method of significantly variable quality. Taking into account this fact, one should attribute not too much immediate physical meaning to this quantity.

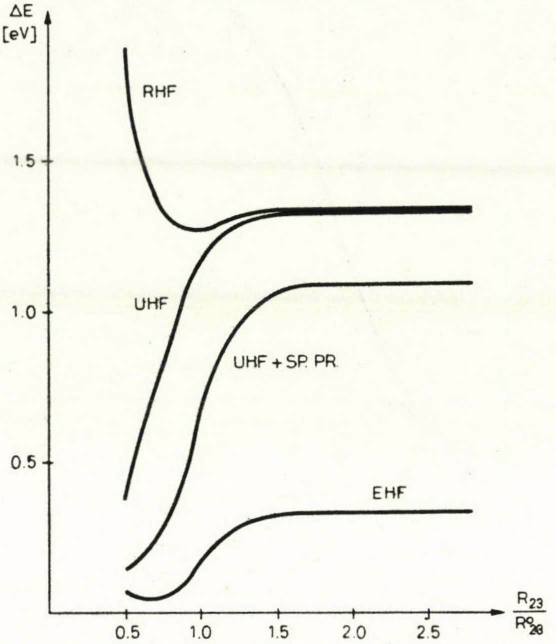

Fig. 2. Error in the total π-electronic energy given by different methods for the PPP model of butadiene as function of the bond length R_{23}

results given by the UHF method with subsequent spin projection are better, of course, than the UHF ones; at the same time the shape of the curves is very similar. The EHF method in all cases gives a significantly smaller error than the other one-electron methods considered.

The results of an analogous calculation for cyclo-butadiene are shown on Fig. 3. The configuration of the regular square with $R_{12}^0 = R_{23}^0 = R_{34}^0 = R_{14}^0 = 1.4$ Å has been taken as the equilibrium one and the lengths of $R_{14} = R_{23}$ have been varied conserving the bond angles to be rectangular.

All the curves exhibit a characteristic behaviour in the vicinity of the point $R_{14}/R_{14}^0 = 1$, where the system becomes most symmetric (regular square). At this point the error in the electronic energy has a maximum in the RHF case and a minimum for the other one-electron methods considered. Moreover, the RHF wave function possesses no correct spatial symmetry properties at this point but corresponds to the lower symmetry of the distorted configurations only. The RHF wave function at all internuclear separations describes one of the "Kekulé structures" with π-electron bond orders 1 and 0 for the case of the smaller and larger bond lengths, respectively. Thus, even the lower symmetry of a rectangle (which we have if $R_{14}/R_{14}^0 \neq 1$) is sufficient to determine uniquely the RHF orbital coefficients for our π-electron model and there

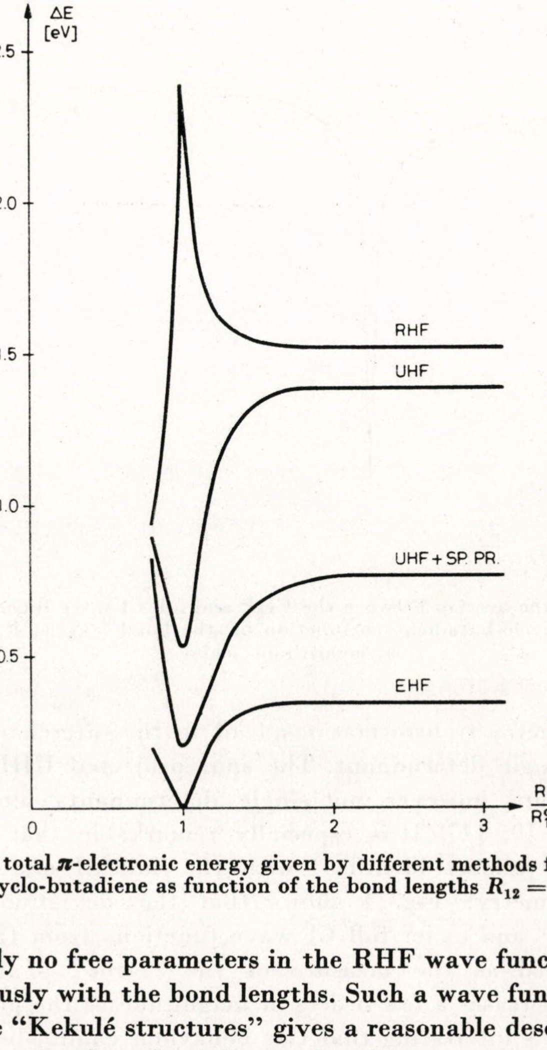

Fig. 3. Error in the total π-electronic energy given by different methods for the PPP model of cyclo-butadiene as function of the bond lengths $R_{12} = R_{34}$

remain effectively no free parameters in the RHF wave function, which could change continuously with the bond lengths. Such a wave function corresponding to one of the "Kekulé structures" gives a reasonable description when the bond lengths are significantly different but becomes very bad if the bond lengths are close to each other. This leads to the maximum of the error obtained for the RHF case* shown in Fig. 3.

We have not found such a simple interpretation for the minima observed for the DODS-type wave functions at the point of the higher symmetry of the system. The UHF wave function has no spatial symmetry in a strict sense

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* Strictly speaking, one may consider the RHF solution with a lower symmetry than that of the system to be incorrect. As discussed e.g., by MUSHER [12], if the RHF wave function is required to correspond to the full symmetry of the system even at the single point of the higher symmetry, then one obtains there a different solution with a different, generally higher, energy ("symmetry dilemma") and the RHF energy curve becomes discontinuous at this point.

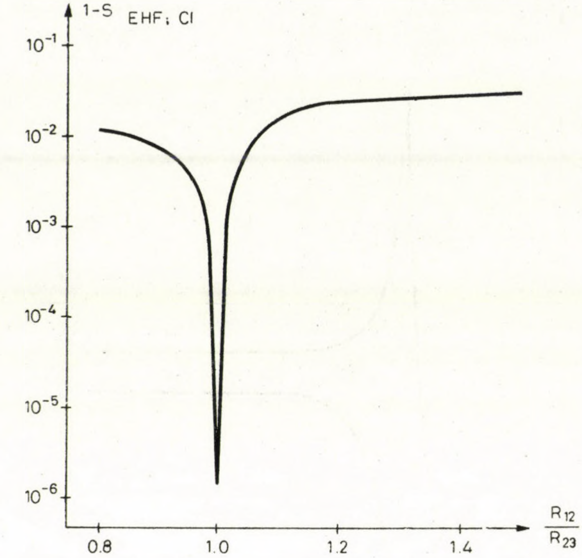

Fig. 4. **Deviation of the overlap between the EHF and full CI wave functions from unity for the PPP model of cyclo-butadiene as function of the bond lengths $R_{12} = R_{34}$. (Note the logarithmic scale)**

since some symmetry transformations lead to the interchange of the spins α and β in the single determinant. The spin projected UHF and the EHF wave functions are, however, not single determinants and have correct spatial symmetry [9, 11]. It is especially remarkable that the EHF wave function becomes almost identical* with the full CI one in the point of the highest symmetry: Fig. 4 shows that the deviation of the overlap between the EHF and exact full CI wave functions from the unity (which may be considered as the measure of the "error" of the EHF wave function itself) decreases a few orders of magnitude as the point $R_{14}/R^0_{14} = 1$ is approached. It is interesting that this behaviour cannot be observed if the system is distorted not into a rectangle but into a rhombus: no such strong extrema appear when the ratio of diagonals becomes unity and the EHF wave function remains of the same excellent quality as for the configuration of a square.

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* The EHF and full CI wave functions are so close to each other at the configuration of the regular square that there appears the question whether their differences could not be attributed to the numerical inaccuracies, only. A specific consideration shows that this is not the case, however. We have expressed the EHF wave function as a linear combination of the full CI eigenvectors and recalculated the EHF energy from this expression, too, in order to check it. It was found that the accuracy of the EHF energy (as follows from the comparison of this value to that calculated originally by using the EHF formalism) is about two orders of magnitude better than the difference between the EHF and full CI energies.

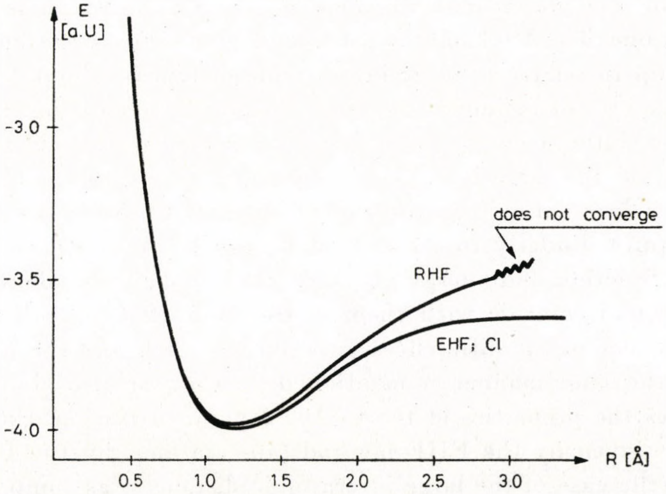

Fig. 5. **Potential curves for the CNDO/2 model of BH molecule (The EHF and full CI curves are undistinguishable)**

The most important conclusion one may draw from these calculations is that investigating potential curves and surfaces with the refined one-electron methods one should pay particular attention to the cases in which the system goes over to a configuration with a higher symmetry. Further considerations of these and related symmetry problems are planned.

We have performed also similar calculations for the BH molecule treated at the CNDO/2 level of the integral approximations. Fig. 5 shows the potential curves of this molecule calculated by the RHF, EHF and full CI methods. Table II contains the most important results concerning energies and wave

Table II

Comparison of different wave functions for the CNDO/2 model of BH molecule ($R_{BH} = 1.2$ Å)

Wave function	Total electronic energy [a. u.]	Overlap with the exact (full CI) wave function[a]	Total energy[b] [a. u.]
RHF	−5.306974	0.99654	−3.984003
EHF	−5.316089	0.999990	−3.993118
full CI[c]	−5.316091	1	−3.993120

[a] The EHF wave function is assumed to be renormalized to unity.
[b] Including the nuclear repulsion energy 1.322971 a. u.
[c] Exact for the given CNDO/2 model-Hamiltonian.

functions for the interatomic distance $R_{BH} = 1.2$ Å, which is close to the equilibrium one. The UHF method does not give solutions differing from the RHF ones up to relatively large interatomic distances (about 1.9 Å) and the UHF results are not included, therefore, in the Table and Figure. As may be seen, the correlation energy is very small for the given parametrization except for the case of the large interatomic distances where the RHF method has the improper dissociation behaviour mentioned above. At all finite interatomic distances (quite similarly to the case of $R_{BH} = 1.2$ Å shown in Table II) the EHF wave function and energy are very close though not identical with the full CI ones and coincide with them in the limit of infinite B—H distance. (The significance of the differences between the RHF and full CI results was checked in the same manner as mentioned for the case of cyclo-butadiene.)

Besides the properties of the CNDO/2 parametrization, the surprisingly good results given by the EHF method (and, in fact, by the RHF method, too, except the case of the large interatomic distances) as compared with the results of the full CI calculations, may be attributed to some specific features of the system considered. We have found that at all interatomic distances and for the case of each ground state wave function considered, including the full CI one, two out of three $2p$ orbitals of the B atom (those which correspond to the directions orthogonal to the B—H bond) are quite empty. This means that the original problem of 4 electrons and 5 atomic orbitals is, in effect, reduced to that of 4 electrons and 3 atomic orbitals, for which the full CI wave function contains a significantly smaller number of free parameters.

The aim of these calculations was not the comparison with experimental results but the comparison of the different one-electron methods with the full CI one the latter being exact for the given CNDO/2 parametrization. It may be mentioned, however, that the equilibrium bond length corresponding to the minimum of the potential curve agrees well with the experimental value 1.23 Å [13], while the depth of the minimum (the dissociation energy) is very large, 238 kcal/mole as compared with the experimental value 70—77 kcal/mole [13, 14], even for the EHF and full CI curves. This is in line with the tendency observed generally for the binding energies calculated by the CNDO/2 method in the RHF approximation. One has to conclude, therefore, that the CNDO/2 parametrization is inadequate for calculating realistic potential curves and surfaces even if the best wave function is used and it is inevitable to apply better schemes of integral determination in such calculations.

REFERENCES

1. P.-O. Löwdin, Phys. Rev., **97,** 1474, 1490, 1509, 1955.
2. P.-O. Löwdin, in Quantum Theory of Atoms, Molecules and Solid State (Academic Press, New York, 1966) p. 601 and references therein.
3. W. A. Goddard III., J. Chem. Phys., **48,** 540, 1967.
4. I. Mayer, Acta Phys. Hung., **34,** 305, 1973.
5. I. Mayer, Chem. Phys. Letters, **11,** 397, 1971.
6. I. Mayer, J. Ladik and G. Biczó, Int. J. Quantum Chem., **7,** 583, 1973.
7. I. Mayer, Int. J. Quantum Chem., **8,** 893, 1974.
8. I. Mayer, Acta Phys. Hung., **37,** 39, 1974.
9. I. Mayer, Int. J. Quant. Chem., **8,** 363, 1974.
10. I. Mayer and J. Kondász, Int. J. Quantum Chem., **9,** 517, 1975.
11. I. Mayer and M. Kertész, Int. J. Quantum Chem., **9,** 527, 1975.
12. J. I. Musher, Chem. Phys. Letters, **7,** 397, 1970.
13. S. Szőke, Acta Chim. Hung., **68,** 345, 1971.
14. B. M. Smirnov, Atomniye Stolknoveniya i Elementarniye Processi v Gazakh. Atomizdat, Moskow, 1968.

RECENSIONES

H. A. ATWATER:

Introduction to General Relativity

Pergamon Press, Oxford 1974

Students may approach the theory of general relativity either from the field of mathematics or from physics. This book contains the answers to many questions which keep querying the *physics-oriented* student while getting a first acquaintance with the subject. All that is required here is some basic notion of classical field theory.

Starting from the fundamentals (coordinates, line element, techniques of tensor analysis etc.) the reader is guided through important chapters of general relativity. The motion of free particles, exact solutions of the gravitational equations, the theory of curved-space electromagnetism, gravitational waves and cosmological models come down to earth in the author's meticulously logical presentation. Beyond the standard theory, a separate chapter outlines and criticises unified field theories and even gives a feeling of the problem of quantization. The last chapter is really a camouflaged appendix devoted to the description of particles and waves in special relativity.

The exercises given at the end of each chapter are not supplied with solution, however, the reader occasionally finds useful hints and suggestions. For constants and numerical data, he may turn to a handy Appendix (a declared one). The student must be warned, however, that reading this textbook alone will not enable him to comprehend the current trend of research in general relativity. He would not find out from here that there exists a modern approach to differential geometry and that significant ideas have been developed about such conspicuous subjects as the singularities or the causal behaviour of the space-time. There are well-known textbooks covering these recent achievements of the theory but one can hope only that filling in the gaps in the student's understanding and answering all his questions in the way this book does will not take another half century.

Z. PERJÉS

A. MÜLLER:

Quantum Mechanics: A Physical World Picture

Akadémiai Kiadó, Budapest, Pergamon Press, Oxford, 1974

The author is an internationally reputed researcher in the field of the problems of the borderland of physics and philosophy. In his work, which was first published in Hungarian in 1967, the problems of the interpretation of quantum mechanics are discussed.

The book first gives a historical review of the various interpretations of quantum mechanics starting with de Broglie, continuing with the so called Copenhagen, the causal interpretation reviewing finally Fok's ideas.

The author's viewpoint apparently represents a further development of Fok's interpretation. The analysis becomes especially convincing since besides confronting the concept of classical physics with the ideas of quantum mechanics the author endeavours to obtain an interpretation of quantum mechanics which facilitates the application of the basic ideas also to the problems of particle physics.

The author's argumentation on the classical and quantum physical probability concepts is in itself remarkable. The central idea of the analysis consists of the classification of the various microphysical interactions which makes it possible to generalize the system of the author's ideas so that it applies not only to quantum mechanics, but also to quantum electrodynamics and microphysics of particles.

In investigating the problem of physical measurement the author develops a most remarkable concept of the relation between the potentially possible and actually realized experiment. Furthermore the objective relation between the dynamical and statistical laws are discussed.

The book may be of considerable interest not only for physicists but also for philosophers and science-philosophers.

G. BIRÓ

G. C. POMRANING:

The Equations of Radiation Hydrodynamics

International Series of Monographs in Natural Philosophy, Volume 54, Pergamon Press, 1973

Radiation hydrodynamics deals with the propagation of radiation through and its interaction with hydrodynamic media. This branch of science is rapidly developing due to the growth of our knowledge pertaining to the nature and interaction of radiation with matter and its importance in understanding processes in astrophysics and other more down-to-earth phenomena where high termperature gas dynamics occurs.

The author presents a systematic treatment of radiative transfer, treating the Compton and inverse Compton scattering, too. His major achievement is — not mentioning here in detail his own contributions to the subject — to succeed in giving a review of the development of the subject since the traditional radiative transfer reasoning transformed to account for the details of the interaction of radiation with matter. His important step is now to collect results cast over a hundred of reports and articles which evaluate and involve the effects of radiations in the equations of motion of the medium. Since the most important aspects of radiation physics (especially those of electromagnetic radiation) require the consistent form of a relativistic formulation, the author presents the relativistic equations of motion of radiation hydrodynamics.

When congratulating to the Author for a very useful and authoritative book facilitating the access for the field of physicists, astrophysicists, reactor engineers and other colleagues, the reviewer cannot avoid mentioning why he is a little bit disappointed about the book.

As mentioned before, the monograph ends with the inclusion of the effects of radiative transfer into the equations of motion. Unfortunately, the author does not quote any example showing the actual modifications of the picture seen by solving these equations. Since this will be one of the most exciting fields in astrophysics and in laser physics as well, we hope that the second edition will contain additional chapters on these questions, too.

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Acta Physica Academiae Scientiarum Hungaricae, Tomus 39 (3), pp. 145—148 (1975)

R-K-R-V POTENTIAL ENERGY CURVE, FRANCK—CONDON FACTORS AND r-CENTROIDS FOR $E^1\Sigma^+ - X^1\Sigma^+$ SYSTEM OF SiS MOLECULE

By

P. H. Katti and V. M. Korwar

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(Received 18. VI. 1975)

The potential energy curve for the $E^1\Sigma^+$ state of SiS molecule has been evaluated by the R—K—R—V method. The Franck—Condon factors are computed by Fraser and Jarmain's method with r_e-shift corrections. r-centroids have been determined by both quadratic equation method and graphical method as suggested by Nicholls and Jarmain. The intensity distribution in the band system under consideration is explained on the basis of F—C factors. Calculation of r-centroids shows that the sequence difference i.e. $\Delta r = \bar{r}_{v'v''} - \bar{r}_{v'+1,v''+1}$ remains constant.

1. Introduction

The representation of the potential energy of a molecule as a function of internuclear distance has vital significance in chemical physics and gas kinetics. With the help of reliable potential energy curves one may proceed to compute Franck—Condon (F—C) factors which have wide applications in astrophysics and physico-chemical problems. The present paper thus deals with the potential energy curve, F—C factors and r-centroids of SiS molecule, which has astrophysical importance.

2. Computational procedure

So far, the R—K—R—V [1—5] method of finding the turning points of the potential energy curve has been preferred to other methods as this potential function makes use of the data on experimental vibrational energy levels. This method is based on W—K—B approximation and yields the expression for the turning points as

$$r_{\text{max, min}} = \left(\frac{f}{g} + f^2\right)^{1/2} \pm f,$$

where

$$f = \left(\frac{8\pi^2 \mu c}{h}\right)^{-1/2} Z_i$$

and

$$g = \frac{(2\pi^2 \mu c)^{1/2}}{h} \sum_{i=1}^{n} \left[2\alpha_i (\omega x)_i^{-1} (U_i^{1/2} - U_{i-1}^{1/2}) + \right.$$

$$\left. + \left\{2B_i - \alpha_i \omega_i (\omega x)_i^{-1}\right\} (Z_i - Z_{i-1})\right],$$

where

$$Z_i = (\omega x)_i^{-1/2}\, |_n \left\{ \frac{\omega_i - 2(\omega x)_i \left(v + \dfrac{1}{2}\right)}{\omega_i - 2(\omega x)_i^{1/2}\, U_i^{1/2}} \right\}.$$

Thus, by using these expressions, the turning points calculated for eighteen vibrational levels of $E^1\Sigma^+$ state of SiS molecule have been presented in Table II. The necessary molecular parameters determined experimentally [6–8] have been tabulated in Table I.

Table I

The molecular parameters of SiS molecule

Molecular state	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	$\alpha_e \cdot 10^{-3}$ (cm^{-1})
$E^1\Sigma^+$	406.83	1.952	0.22137	1.39
$X^1\Sigma^+$	749.69	2.58	0.30363	1.49

Table II

The potential energy curve of $E^1\Sigma^+$ state of SiS molecule

v	U (cm^{-1})	$r_{\min}$ (Å)	$r_{\max}$ (Å)
0	202.927	2.1877	2.3370
1	605.853	2.1397	2.3994
2	1004.875	2.1086	2.4452
3	1399.993	2.0843	2.4842
4	1791.207	2.0640	2.5194
5	2178.517	2.0464	2.5520
6	2561.923	2.0308	2.5827
7	2941.425	2.0167	2.6120
8	3317.023	2.0038	2.6403
9	3688.717	1.9919	2.6677
10	4056.507	1.9809	2.6945
11	4420.393	1.9705	2.7206
12	4780.375	1.9608	2.7463
13	5136.453	1.9516	2.7716
14	5488.627	1.9429	2.7966
15	5836.897	1.9346	2.8213
16	6181.263	1.9267	2.8458
17	6521.725	1.9191	2.8701
18	6858.283	1.9118	2.8943

Table III

F—C factors and r-centroids for $E^1\Sigma^+ - X^1\Sigma^+$ system of SiS molecule

v'	$v''=0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$	$v''=5$
0	—	0.00002	0.00017	0.00079	0.0028	0.0079
	0.0000	2.083	2.099	2.115	2.131	2.148
	2.067	2.084	2.100	2.117	2.133	2.149
	2.068	—	—	2528.70	2576.45	—
1	0.00002	0.0002	0.0013	0.0052	0.0151	0.0334
	2.059	2.075	2.091	2.107	2.123	2.138
	2.059	2.075	2.093	2.108	2.124	2.140
	—	—	2458.06	2503.37	2550.06	2598.02
2	0.0001	0.0010	0.0051	0.0169	0.0391	0.0658
	2.051	2.066	2.082	2.098	2.114	2.130
	2.050	2.066	2.083	2.099	2.115	2.130
	—	2391.36	2434.48	2478.78	2524.27	2571.5
3	0.00034	0.00316	0.01376	0.0364	0.0642	0.0759
	2.042	2.058	2.074	2.089	2.105	2.121
	2.041	2.057	2.074	2.090	2.107	2.122
	—	2369.01	2411.30	2454.75	2499.37	2545.55
4	0.0010	0.0078	0.0277	0.0573	0.0724	0.0517
	2.034	2.050	2.065	2.081	2.097	2.113
	2.032	2.049	2.065	2.082	2.097	2.113
	2306.91	2347.24	2388.78	2431.46	2475.16	—
5	0.00236	0.0156	0.0446	0.0689	0.0559	0.0155
	2.026	2.042	2.057	2.073	2.088	2.104
	2.025	2.040	2.057	2.073	2.089	2.105
	2286.60	2326.11	2366.88	2408.85	—	—

As has been already mentioned above F—C factors can be obtained either from R—K—R—V potential energy curve or may be evaluated by Fraser and Jarmain's method [9, 10] which gives almost the same results as the R—K—R—V method for bands up to $v' + v'' \leq 10$. Since the molecular system under consideration contains most of the bands within this limit, the latter method which is less complicated than the former one, has been employed to calculate F—C factors. Here $|d\alpha/\alpha|$ is greater than 5% so. r_e-shift corrections have been taken into account. The F—C factors have been collected in the first row of Table III.

The r-centroid of a molecule may be defined as

$$\bar{r}_{v',v''} = \frac{\int \psi_{v'}\, r\, \psi_{v''}\, dr}{\int \psi_{v'}\, \psi_{v''}\, dr},$$

where $\psi_{v'}$ and $\psi_{v''}$ represent the wavefunctions of upper and lower vibrational states, respectively, between which the transition takes place. This is a useful factor in the calculation of variation of electron transition moment with internuclear distance if experimental intensity measurements are available. There are two methods proposed by NICHOLLS and JARMAIN [11] to determine r-centroids. One of them is a quadratic equation method and the other a graphical method. We have used both methods in obtaining r-centroids (Å) and the results have been put in the 2nd and 3rd rows of Table III. The last row in Table III gives the wavelengths of the corresponding bands in Å.

3. Conclusions

It can be seen from Table III that there is good agreement between the experimental and theoretical results viz., the absence of 0,0; 1,0; 2,0; 3,0; 0,1; 0,2 and 1,1 bands in the experiments can be attributed to the negligibly small value of F—C factors. But we feel that the bands 0,5; 4,5 and 5,4 may be observable experimentally, as bands 4,0; 5,0 and 4,1 whose F—C factors are of the same order of magnitude as the F—C factors of 0,5; 4,5 and 5,4 bands.

The agreement between the r-centroids calculated by both above mentioned methods is very satisfactory. The sequence difference $\Delta\bar{r} = \bar{r}_{v',v''} - \bar{r}_{v'+1,\, v''+1}$ remains constant. As $r_{e'} + r_{e''}/2\ \Omega\ r_{0,0}$ it is concluded that the potentials are not very anharmonic. Further it is seen that $\bar{r} = 0.01$ Å which suggests that the potential energy curves are not wide.

REFERENCES

1. R. RYDBERG, Z. Physik, **73,** 376, 1931.
2. O. KLEIN, Z. Physik, **76,** 226, 1932.
3. A. L. G. REES, Proc. Phys. Soc. (G. B.), **59,** 998, 1947.
4. J. T. VANDERSLICE, E. A. MAISON, W. G. MAISCH and E. R. LIPPINCOTT, J. Molec. Spectro., **3,** 17, 1959.
5. J. T. VANDERSLICE, E. A. MAISON, W. G. MAISCH and E. R. LIPPINCOTT, J. Molec. Spectro., **5,** 83, 1960.
6. R F. BARROW, J. L. DEVTSCH, A. LAGERQUIST and B. WESTERLUND, Proc. Phys. Soc. (G. B.), **78,** 1307, 1961.
7. D. ANDRICK and H. EHRHARDT, Z. Physik, **192,** 99, 1966.
8. A. LAGERQUIST, G. NILHEDEN and R. F. BARROW, Proc. Phys. Soc., **65,** 419, 1952.
9. P. A. FRASER and W. R. JARMAIN, Proc. Phys. Soc., **A66,** 1153, 1953.
10. P. A. FRASER and W. R. JARMAIN, Proc. Phys. Soc., **A66,** 1145, 1953.
11. R. W. NICHOLS and W. R. JARMAIN, Proc. Phys. Soc., **A69,** 253, 1956.

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SPECTRAL INTENSITIES OF LANTHANIDE PERCHLORATES IN AMIDE SOLVENTS

By

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The absorption spectra of Nd, Ho, Er perchlorates in N-methylformamide and N,N′-dimethylformamide were investigated. Judd—Oefelt method of intensity analysis was applied to determine the symmetry and structure of the lanthanide amide solvates. The lanthanide perchlorates in amide solvents behave as the electrolytes of the 1 : 3 type. In the first coordination sphere of lanthanide ion only amide molecules are present, hence in the first approximation the symmetry factor is responsible for the changes of the intensity of $4f—4f$ transitions. It was found that both for light and heavy lanthanide solvates no difference exists between mono and dimethylformamide. The symmetry for light lanthanide solvates was established as C_{3v} (with possible coordination number 9). For heavy lanthanide solvates however the lower symmetry group of lanthanide ion environment should be expected (C_{2v}).

In our recent papers we have considered the spectral intensities of $f—f$ transitions of lanthanide chlorides in amide solvents [1, 2, 3]. The Judd-Oefelt intensity analysis results enabled us to apply the value of Judd—Oefelt parameter τ_2 experimentally determined from the spectra as an indication of the symmetry of these systems. To eliminate all other influences on the intensity changes we have chosen such systems where the covalency effect was negligible. These investigations, together with the consideration of the nepheloauxetic effect and charge transfer spectra, have been the attempt to determine the structure of lanthanide amide solvates [1, 2, 4, 5]. We have found that amides such as formamide, N-methylformamide, N,N′-dimethylformamide and N,N-diethylformamide form the stable solvates, where no chloride ion is present in the first coordination sphere. It is generally known that in the case of labile systems such as lanthanide solvates, several authors still argue about the presence or absence of chloride ions in the first coordination sphere. The best way to establish firmly the structure of amide solvates was to perform similar investigations for systems where anions cannot compete with the solvent molecules. Such systems are obviously perchlorates, especially in solvents so polar as amides. We have considered perchlorates of Nd, Ho and Er.

Experimental

The lanthanide perchlorates were produced by dissolving lanthanide oxides in 10% perchloric acid, evaporated, crystallized and then recrystallized. The product was dried under vacuum over P_2O_5. The solvents of analytical grade were freshly purified by the method given by DAWSON, GOLBEN and ZIMMERMAN [6] dried over the anhydrous Na_2SO_4, redistilled under vacuum, and this procedure was repeated in average ten times for each solvent. The refractive index of a solvent was used as an purity indication. ($n_D^{20} = 1.4310$ and $n_D^{25} = 1.4294$ for MFA and DMF, respectively). Absorption spectra measurements in the examined range were run on the Cary-14 spectrophotometer taking the respective solvent as a standard solution. All spectra were measured in the wide concentration range of lanthanide ion $C_{Ln^{3+}} = 0.044 - 0.12M$.

Results and calculations

The intensity calculations were performed, taking the complete set of the experimentally available bands into account. The band areas, necessary for the experimental determination of oscillator strengths were calculated numerically on the ODRA 1102 computer. The set of oscillator strengths determined from the spectra was used for the calculation of τ_2 parameters

Table I

The τ_λ parameters calculated from the spectra of Nd perchlorate in DMF and MFA

Solution	Concentration M/1	$\tau_2 \cdot 10^9$	$\tau_4 \cdot 10^9$	$\tau_6 \cdot 10^9$
DMF	0.020	4.65 ± 0.81	8.61 ± 0.75	10.85 ± 1.05
	0.040	4.48 ± 0.71	8.67 ± 0.66	11.26 ± 0.92
	0.080	4.66 ± 0.74	8.65 ± 0.69	11.24 ± 0.96
	0.120	5.01 ± 0.94	10.97 ± 0.94	11.71 ± 1.18
MFA	0.046	4.64 ± 0.69	9.83 ± 0.64	15.63 ± 0.89
	0.100	4.16 ± 0.63	10.33 ± 0.58	15.46 ± 0.81
		$\tau_2^x \cdot 10^9$	$\tau_4^x \cdot 10^9$	$\tau_6^x \cdot 10^9$
DMF	0.020	4.36 ± 0.76	8.07 ± 0.70	10.17 ± 0.98
	0.040	4.20 ± 0.66	8.12 ± 0.62	10.55 ± 0.86
	0.080	4.37 ± 0.69	8.10 ± 0.65	10.53 ± 0.90
	0.120	4.69 ± 0.88	10.28 ± 0.86	10.97 ± 1.10
MFA	0.100	3.88 ± 0.59	9.65 ± 0.56	14.44 ± 0.76
	0.046	4.33 ± 0.64	9.18 ± 0.60	14.60 ± 0.83

from the relation:

$$P = \sum \tau_\lambda \, \sigma\left(f^N \psi_I \,||\, U^{(\lambda)} \,||\, f^N \psi_{I'}\right)^2 / _{2I+1} \, .$$
$$\lambda = 2, 4, 6$$

Parameters were computed by the least square method on the ODRA 1102 computer. The correctness of term assignments was controlled, taking into consideration the different possibilities of this assignment for particular experimental band. The set of parameters was taken for which the smallest mean square error between τ_λ parameters computed from the spectra and that calculated using the Judd—Oefelt relation [1] was found. For a better comparison of τ_λ parameters with the results given for aqueous solutions the correction on the refractive index of solvent was included as for electric dipol transitions [7]:

$$X = \frac{(n^2 + 2)^2}{9n} \, .$$

The results obtained by us for Nd, Ho and Er perchlorates are presented in Tables I and II.

Table II

The τ_λ parameters calculated from the spectra of Ho and Er perchlorates in DMF and MFA

Perchlorate	Solution	Concentration M/1	$\tau_2 \cdot 10^9$	$\tau_4 \cdot 10^9$	$\tau_6 \cdot 10^9$
Ho	DMF	0.110	4.65±0.50	8.61±0.75	6.27±0.30
		0.046	5.49±0.53	8.77±0.77	6.37±0.47
	MFA	0.042	3.25±0.19	7.83±0.29	5.51±0.17
		0.096	3.36±0.31	7.64±0.46	5.73±0.28
Er	DMF	0.100	7.40±0.83	5.39±1.42	3.74±0.79
		0.050	7.69±1.10	5.11±1.81	3.88±1.01
	MFA	0.100	6.94±0.73	4.57±1.20	3.71±0.67
		0.050	7.28±0.70	4.83±1.15	3.55±0.64
			$\tau_2^x \cdot 10^9$	$\tau_4^x \cdot 10^9$	$\tau_6^x \cdot 10^9$
Ho	DMF	0.110	4.36±0.47	8.07±0.70	5.87±0.28
		0.046	5.14±0.50	8.22±0.72	5.97±0.44
	MFA	0.042	3.03±0.18	7.31±0.27	5.15±0.16
		0.096	3.14±0.29	7.13±0.43	5.35±0.26
Er	DMF	0.100	6.93±0.78	5.05±1.33	3.50±0.74
		0.050	7.20±1.03	4.79±1.69	3.63±0.95
	MFA	0.100	6.48±0.68	4.27±1.12	3.47±0.62
		0.050	6.80±0.65	4.51±1.07	3.31±0.60

Table III

Oscillator strengths for different concentrations of $Nd(ClO_4)_3 \cdot xH_2O$ in N,N′-dimethylformamide solutions

Term	Oscillator strengths · 10^8			
	0.0200 M/1	0.0399 M/1	0.0795 M/1	0.1201 M/1
$^4F_{3/2}$	207.34	284.10	280.23	310.56
$^4F_{5/2}$ $^2H_{9/2}$	864.26	954.50	942.50	986.27
$^4S_{3/2}$ $^4F_{7/2}$	1021.70	1024.02	1025.73	1102.22
$^4F_{3/2}$	50.99	58.83	56.18	60.73
$^2G_{5/2}$ $^2G_{7/2}$	1765.23	1753.15	1780.11	2074.66
$^2K_{13/2}$ $^4G_{7/2}$ $^4G_{9/2}$	915.38	921.94	933.34	1086.67
$^2K_{15/2}$ $^2G_{9/2}$ $(^2D^2F)_{3/2}$ $^4G_{11/2}$	250.28	237.60	232.41	278.58
$^2P_{1/2}$ $^2D_{5/2}$	70.51	62.23	61.67	69.83
$^4D_{3/2}$ $^4D_{5/2}$ $^2I_{11/2}$ $^4D_{1/2}$ $^2L_{15/2}$	1407.24	1403.56	1401.41	1588.27

No intensity changes were found for the different concentration of the lanthanide ion (Table III)

The spectra of neodymium perchlorates and chlorides in all amides have similar τ_λ values, so we can assume that there is no difference between the amide solvates. It means, that in the case of neodymium solvates the same symmetry is presented of C_{3v} or C_{2v} type probably with coordination number 9. No difference exists between the perchlorates and chlorides, both anhydrous and hydrated. From this fact it was concluded that pure amide solvates are formed in these systems [1, 2, 8].

The comparison of the data for different Ho and Er amide solvates gives a rather different picture. For Ho and Er both anhydrous and hydrated chlorides in DMF and DEF solution, a distinguished difference appears in comparison with perchlorates in DMF and with chlorides in FA and MFA. The τ_2 parameters for these systems are, however, much higher than for the aqueous solutions. The same solvates are present in mono and dimethylformamide solutions of Nd, Ho and Er perchlorates and in FA and MFA chloride solutions. It was reasonable to assume, taking into account the lanthanide contraction, that solvates of heavy lanthanide ions have probably coordination number 8 [9, 10] and C_{2v} symmetry.

The jump of τ_2 parameter for Ho and Er chlorides in DMF and DEF is caused by the significant symmetry lowering. This can be done either by the lowering of the coordination number to 7, given by the steric effect, or by the nonhomogeneous environment of lanthanide ion. The first possibility has to be excluded, because in such a situation one could expect a significant change of τ_2 parameter for all DMF and DEF solvates, both for chlorides and perchlorates. The second possibility is to assume the preservation of one chloride ion in the direct environment of lanthanide ion in DMF and DEF solution.

That is the good explanation for the fact that DMF and DEF solvates of perchlorates do not differ from MFA solvates. The reported data are part of a larger research performed by us to correlate the intensity of *f*—*f* transitions, in terms of the Judd—Oefelt method with the environment of lanthanide ions [1, 2. 10, 11]. All systems investigated by us [1, 2, 3, 8, 10, 11] in terms of the Judd—Oefelt method of intensity analysis provided the evidence of the forced dipol mechanism and the predominant influence of the symmetry of lanthanide ion on the intensities of *f*—*f* transitions.

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Note added in proof. The computer programme ICh-31 is available from the authors.

REFERENCES

1. K. Bukietyńska and J. Legendziewicz, Roczniki Chemii, **47,** 1809, 1973.
2. J. Legendziewicz, K. Bukietyńska and B. Jeżowska-Trzebiatowska, Acta Phys. Hung., **35,** 167, 1974.
3. B. Jeżowska-Trzebiatowska, J. Legendziewicz and K. Bukietyńska, Proceedings of International Conference on Molecular Spectroscopy, Wroclaw, 1972, p. 142.
4. K. Bukietyńska, B. Jeżowska-Trzebiatowska, B. Keller and J. Legendziewicz, Roczniki Chemii, **42,** 421, 1966.
5. K. Bukietyńska, B. Keller, J. Legendziewicz, and B. Jeżowska-Trzebiatowska, Proceedings of the XIII Inter. Conf. on Coordination Chemistry II, 373 Cracow—Zakopane, 1970.
6. A. Weisberger and P. S. Proskauer, Organic Solvents, Physical Properties and Methods of Purification, New York, 1955, p. 434—436.
7. W. T. Carnall, P. R. Fields and K. Rajnak, Argonne National Laboratory Report ANL—7358—1967; J. Chem. Phys., **49,** 4412, 4421, 4443, 1968.
8. B. Jeżowska-Trzebiatowska, J. Legendziewicz, K. Bukietyńska and Z. Kopaczyńska, Proceedings of the XV-th ICCC Moscow 1973, p. 149.
9. T. Mioduski and S. Siekierski, Proceedings of the XV Inter. Conf. on Coordination Chemistry, Moscow, 1973, II, 514.
10. K. Bukietyńska and R. Vadura, Bull. Acad. Polon. Sci., ser. sci. chim., **22,** 139, 1974.
11. K. Bukietyńska, Acta Univer. Wroclaw, **19,** 174, 1975.

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ZUR NICHTLINEAREN PLASMATHEORIE: OHMSCHES GESETZ DRITTEN GRADES IN DEN FELDSTÄRKEN UND NICHTLINEARE AMPLITUDENGLEICHUNGEN

B. VIERWELLEN-WECHSELWIRKUNG

Von

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In der vorliegenden Arbeit werden drei transversale Plasmawellen, die mit einer longitudinalen Welle wechselwirken, betrachtet, wobei vier Differentialgleichungen für die elektrischen Feldamplituden, über feste Phasen gemittelt, zugrundegelegt werden. Erhaltungssätze und charakteristische Energieübergangszeiten für einige Spezialfälle werden abgeleitet.

I. Das Gleichungssystem

In Teil A dieser Arbeit [1] stellten wir Differentialgleichungen für raumzeitlich langsam veränderliche Feldamplituden von vier wechselwirkenden elektromagnetischen Wellen in einem Plasma auf; von den auf den rechten Seiten auftretenden Wechselwirkungstermen wählen wir folgende aus (wobei wir den Fall dreier transversaler Wellen, die mit einer longitudinalen wechselwirken, betrachten:)

$$\left(\frac{\partial}{\partial t} + \mathbf{v}^l_{gr}\frac{\partial}{\partial \mathbf{r}}\right)\mathbf{E}^l_{\mathbf{k}}(\mathbf{r},t) =$$

$$= -\frac{1}{\left.\left(\frac{\partial}{\partial\omega}(\omega^2\varepsilon^l)\right)\right|_{\omega=\Omega^l(\mathbf{k})}}\,\frac{-4\pi\,\omega_{0e}^4}{32\pi^2\,\pi\,m_e\,n_0}\int d\alpha\,d\tilde{\alpha}\,\frac{\mathbf{k}(\mathbf{k}\cdot\mathbf{k}_2)}{\mathbf{k}^2}\,e^{i\Omega^l(t)}\times$$

$$\times(\mathbf{E}^t_{\mathbf{k}_3}\cdot\mathbf{E}^t_{\mathbf{k}_4})(\mathbf{k}_1\cdot\mathbf{E}^t_{\mathbf{k}_2})\,\frac{e^{-i(\Omega^t_2+\Omega^t_3+\Omega^t_4)t}}{(\Omega^t_3+\Omega^t_4)\,\Omega^t_2\,\Omega^t_3\,\Omega^t_4} \tag{B.1}$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v}^t_{gr}\frac{\partial}{\partial \mathbf{r}}\right)\mathbf{E}^t_{\mathbf{k}}(\mathbf{r},t) = \frac{1}{\left.\left(\frac{\partial}{\partial\omega}\,\omega^2\,\varepsilon^t\right)\right|_{\omega=\Omega^t(\mathbf{k})}}\,\frac{(-4\pi)\,\omega_{0e}^4}{32\pi^2\,m_e\,n_0}\times$$

$$\times\int d\alpha\,d\tilde{\alpha}\left(\mathbf{k}_2-\frac{\mathbf{k}(\mathbf{k}\cdot\mathbf{k}_2)}{\mathbf{k}^2}\right)e^{i\Omega^t t}\,.$$

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$$\cdot \left\{ (\mathbf{E}^t_{\mathbf{k}_3} \cdot \mathbf{E}^t_{\mathbf{k}_4})\, (\mathbf{k}_1 \cdot \mathbf{E}^l_{\mathbf{k}_2}) \frac{e^{i(\Omega^l_2+\Omega^t_3+\Omega_4\;)}}{(\Omega^t_3 + \Omega^t_4)\, \Omega^l_2\, \Omega^t_3\, \Omega^t_4} + \right.$$

$$+ (\mathbf{E}^t_{\mathbf{k}_3} \cdot \mathbf{E}^l_{\mathbf{k}_4})\, (\mathbf{k}_1 \cdot \mathbf{E}^t_{\mathbf{k}_2}) \frac{e^{-i(\Omega^t_2+\Omega^t_3+\Omega_4)t}}{(\Omega^t_3 + \Omega^l_4)\, \Omega^t_2\, \Omega^t_3\, \Omega^l_4} +$$

$$\left. + (\mathbf{E}^l_{\mathbf{k}_3} \cdot \mathbf{E}^t_{\mathbf{k}_4})\, (\mathbf{k}_1 \cdot \mathbf{E}^t_{\mathbf{k}_2}) \frac{e^{-i(\Omega^t_2+\Omega_3+\Omega^t_4)t}}{(\Omega^l_3 + \Omega^t_4)\, \Omega^t_2\, \Omega^l_3\, \Omega^t_4} \right\} \qquad \text{(B.2)}$$

mit den in Teil A [1] eingeführten Bezeichnungen.

Bis jetzt hatten wir ein verschwindendes Dämpfungsdekrement (oder eine verschwindende Anwachsrate) vorausgesetzt; wenn wir diese Bedingung fallenlassen, so fügen wir links $-\gamma_{\mathbf{k}} \mathbf{E}_{\mathbf{k}}$ hinzu, während wir rechts $\mathbf{E}_{\mathbf{k}}$ belassen und einfach als neue, der Dämpfung unterworfene Amplitude uminterpretieren.

Damit bekommen wir für Gleichung (B.1):

$$\left(\frac{\partial}{\partial t} - \gamma^l_{\mathbf{k}} + \mathbf{v}^l_{gr} \frac{\partial}{\partial \mathbf{r}} \right) \mathbf{E}^l_{\mathbf{k}} =$$

$$= \int \frac{4\pi\, \omega^4_{0e}}{32\, \pi^2\, m_e\, n_0} \frac{1}{\left. \left(\dfrac{\partial}{\partial \omega} (\omega^2\, \varepsilon^l) \right) \right|_{\omega=\Omega^l(\mathbf{k})}} d\mathbf{k}_1\, d\mathbf{k}_2\, d\mathbf{k}_3\, d\mathbf{k}_4\, \delta(\mathbf{k} - \mathbf{k}_1 - \mathbf{k}_2) \times$$

$$\times\, \delta(\mathbf{k}_1 - \mathbf{k}_3 - \mathbf{k}_4) \frac{\mathbf{k}(\mathbf{k} \cdot \mathbf{k}_2)}{\mathbf{k}^2} \frac{e^{-i(\Omega^t_2+\Omega_3+\Omega^t_4)t}\, e^{i\Omega^l t}}{(\Omega^t_3 + \Omega^t_4)\, \Omega^t_2\, \Omega^t_3\, \Omega^t_4} \times$$

$$\times\, (E^t_{\mathbf{k}_3}\, \mathbf{e}_{k_3} \cdot E^t_{\mathbf{k}_4}\, \mathbf{e}_{\mathbf{k}_4})\, (\mathbf{k}_1 \cdot E^t_{\mathbf{k}_2}\, \mathbf{e}_{\mathbf{k}_2})$$

wo wir mit

$$\mathbf{E}^t_{\mathbf{k}} = E^t_{\mathbf{k}}\, \mathbf{e}_{\mathbf{k}}\,, \quad \mathbf{E}^t_{\mathbf{k}_1} = E^t_{\mathbf{k}_1}\, \mathbf{e}_{\mathbf{k}_1}\,, \quad \text{etc.} \qquad \text{(B.1a)}$$

Einheitsvektoren in der Polarisationsrichtung eingeführt haben.

Wir können auch (B.1a) in eine skalare Gleichung überführen, wenn wir für die longitudinale Amplitude einführen:

$$\mathbf{E}^l_{\mathbf{k}} = E^l_{\mathbf{k}} \frac{\mathbf{k}}{|\mathbf{k}|}\,.$$

Um die Struktur der Gleichung übersichtlicher zu machen, verwenden wir folgende Abkürzung:

$$C^l(\mathbf{k}, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4) = \frac{4\pi\, \omega^4_{0e}}{32\pi^2\, m_e\, n_0} \frac{\dfrac{(\mathbf{k} \cdot \mathbf{k}_2)}{|\mathbf{k}|}}{\left. \left(\dfrac{\partial}{\partial \omega} (\omega^2\, \varepsilon^l) \right) \right|_{\omega=\Omega^l(\mathbf{k})}} \times$$

$$\times \frac{\delta(\mathbf{k} - \mathbf{k}_1 - \mathbf{k}_2)\, \delta(\mathbf{k}_1 - \mathbf{k}_3 - \mathbf{k}_4)}{(\Omega^t_3 + \Omega^t_4)\, \Omega^t_2\, \Omega^t_3\, \Omega^t_4} (\mathbf{e}_{\mathbf{k}_3} \cdot \mathbf{e}_{\mathbf{k}_4})\, (\mathbf{k}_1 \cdot \mathbf{e}_{\mathbf{k}_2})\,,$$

womit sich für (B.1) ergibt:

$$\left(\frac{\partial}{\partial t} - \gamma_{\mathbf{k}}^{l} + \mathbf{v}_{gr}^{l}\,\frac{\partial}{\partial \mathbf{r}}\right) E_{\mathbf{k}}^{l} =$$

$$= \int C^{l}\,(\mathbf{k}, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4)\, E_{\mathbf{k}_3}^{t}\, E_{\mathbf{k}_4}^{t}\, \mathbf{E}_{\mathbf{k}_2}^{t}\, e^{-i(\Omega_2^{t}+\Omega_3^{t}+\Omega_4^{t})t}\, e^{i\Omega^{l}t}\, d\mathbf{k}_1\, d\mathbf{k}_2\, d\mathbf{k}_3\, d\mathbf{k}_4 \tag{B.1b}$$

oder, wenn wir die Integration über $\mathbf{k}_1$ durchführen ($\mathbf{k}_1 = \mathbf{k}_3 + \mathbf{k}_4$):

$$\left(\frac{\partial}{\partial t} - \gamma_{\mathbf{k}}^{l} + \mathbf{v}_{gr}^{l}\,\frac{\partial}{\partial \mathbf{r}}\right) E_{\mathbf{k}}^{l} =$$

$$= \int \widetilde{C}^{l}\,(\mathbf{k}_1, \mathbf{k}_3 + \mathbf{k}_4, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4)\, E_{\mathbf{k}_3}^{t}\, E_{\mathbf{k}_4}^{t}\, E_{\mathbf{k}_2}^{t}\, e^{-i\Phi t}\, d\mathbf{k}_2\, d\mathbf{k}_3\, d\mathbf{k}_4 \tag{B.1c}$$

mit

$$\Phi \equiv \Omega_2^{t} + \Omega_3^{t} + \Omega_4^{t} - \Omega^{l}\,,$$

$$\widetilde{C}^{l} = \frac{C^{l}}{\delta(\mathbf{k}_1 - \mathbf{k}_3 - \mathbf{k}_4)}\,.$$

Hiemit ist vorgezeichnet, wie wir mit der transversalen Gleichung (B.2) zu verfahren haben. (B.1) enthält die vier Unbekannten $E_{\mathbf{k}}^{l}$, $E_{\mathbf{k}_3}^{t}$, $E_{\mathbf{k}_4}^{t}$, $E_{\mathbf{k}_2}^{t}$; (B.2), geeignet dreimal als Differentialgleichung für $E_{\mathbf{k}_i}^{t}$ angeschrieben, sollte zusammen mit (B.1) ein System von vier Gleichungen für vier Amplituden ergeben.

Zunächst sieht (B.2) mit analog zum Fall (B.1) gewählten Abkürzungen wie folgt aus:

$$\left(\frac{\partial}{\partial t} - \gamma_{\mathbf{k}}^{t} + \mathbf{v}_{gr}^{t}\,\frac{\partial}{\partial \mathbf{r}}\right) E_{\mathbf{k}}^{t}\,(\mathbf{r}, t) =$$

$$= -\int C^{t}\,(\mathbf{k}, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4)\, E_{\mathbf{k}_3}^{t}\, E_{\mathbf{k}_4}^{t}\, E_{\mathbf{k}_2}^{t}\, e^{-i(\Omega_2^{l}+\Omega_3^{t}+\Omega_4^{t})} \times$$

$$\times\, e^{i\Omega^{t}t}\, d\mathbf{k}_1\, d\mathbf{k}_2\, d\mathbf{k}_3\, d\mathbf{k}_4\,,$$

wo

$$C^{t}\,(\mathbf{k}, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4) = \frac{4\pi\,\omega_{0e}^{4}}{32\pi^{2}\, m_e\, n_0}\, \frac{(\mathbf{e}_{\mathbf{k}} \cdot \mathbf{k}_2)}{\left.\left(\dfrac{\partial}{\partial\omega}\,\omega^{2}\,\varepsilon^{t}\right)\right|_{\omega=\Omega^{t}(\mathbf{k})}} \times$$

$$\times\, \frac{\delta(\mathbf{k} - \mathbf{k}_1 - \mathbf{k}_2)\,\delta(\mathbf{k}_1 - \mathbf{k}_3 - \mathbf{k}_4)}{(\Omega_3^{t} + \Omega_4^{t})\,\Omega_2^{l}\,\Omega_3^{t}\,\Omega_4^{t}}\, (\mathbf{e}_{\mathbf{k}_3} \cdot \mathbf{e}_{\mathbf{k}_4}) \left(\mathbf{k}_1 \cdot \frac{\mathbf{k}_2}{|\mathbf{k}_2|}\right),$$

oder nach Durchführung der $\mathbf{k}_1$-Integration:

$$\left(\frac{\partial}{\partial t} - \gamma^t_{\mathbf{k}} + \mathbf{v}^t_{gr}\frac{\partial}{\partial \mathbf{r}}\right) E^t_{\mathbf{k}} =$$

$$= -\int \widetilde{C}^t(\mathbf{k}, \mathbf{k}_3 + \mathbf{k}_3 + \mathbf{k}_4, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4)\, E^t_{\mathbf{k}_3} E^t_{\mathbf{k}_4} E^l_{\mathbf{k}_2} e^{-i\tilde{\Phi}t}\, d\mathbf{k}_2\, d\mathbf{k}_3\, d\mathbf{k}_4$$

mit

$$\tilde{\Phi} = \Omega^l_2 + \Omega^t_3 + \Omega^t_4 - \Omega^t, \qquad \widetilde{C}^t = \frac{C^t}{\delta(\mathbf{k}_1 - \mathbf{k}_3 - \mathbf{k}_4)}\,.$$

Für uns stellt diese Gleichung sozusagen die "abstrakte" Grundform dar, die wir jetzt für $\mathbf{k} \to \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4$ hinzuschreiben haben; dabei machen wir der Reihe nach (jeweils auf die vorausgehende Form bezogen) folgende Übergänge:

$$\begin{aligned} \mathbf{k} &\to \mathbf{k}_2 \\ \mathbf{k}_2 &\to \mathbf{k} \\ \mathbf{k}_3 &\to -\mathbf{k}_3 \\ \mathbf{k}_4 &\to -\mathbf{k}_4 \end{aligned}$$

(aus der abstrakten Form die Gleichung für $\mathbf{k}_2$)

$$\begin{aligned} \mathbf{k} &\to \mathbf{k} \\ \mathbf{k}_2 &\to \mathbf{k}_3 \\ \mathbf{k}_3 &\to \mathbf{k}_4 \\ \mathbf{k}_4 &\to \mathbf{k}_2 \end{aligned}$$

(aus der Gleichung für $\mathbf{k}_2$ die Gleichung für $\mathbf{k}_3$)

$$\begin{aligned} \mathbf{k} &\to \mathbf{k} \\ \mathbf{k}_3 &\to \mathbf{k}_4 \\ \mathbf{k}_2 &\to \mathbf{k}_3 \\ \mathbf{k}_4 &\to \mathbf{k}_2 \end{aligned}$$

(aus der Gleichung für $\mathbf{k}_3$ die Gleichung für $\mathbf{k}_4$)

sodass wir also die folgenden drei transversalen Gleichungen erhalten:

$$\left(\frac{\partial}{\partial t} - \gamma^t_{\mathbf{k}_2} + \mathbf{v}^t_{gr_2}\frac{\partial}{\partial \mathbf{r}}\right) E^t_{\mathbf{k}_2} =$$

$$= -\int \widetilde{C}^t(\mathbf{k}_2, -\mathbf{k}_3 - \mathbf{k}_4, \mathbf{k}, -\mathbf{k}_3, -\mathbf{k}_4)\, E^t_{-\mathbf{k}_3} E^t_{-\mathbf{k}_4} E^l_{\mathbf{k}} \times$$

$$\times\, e^{-i(\Omega^l + \Omega^t_{-3} + \Omega^t_{-4} - \Omega^t_2)t}\, d\mathbf{k}\,(-d\mathbf{k}_3)\,(-d\mathbf{k}_4)\,, \tag{B.1d}$$

$$\left(\frac{\partial}{\partial t} - \gamma^t_{\mathbf{k}_3} + \mathbf{v}^t_{gr_3}\frac{\partial}{\partial \mathbf{r}}\right) E^t_{\mathbf{k}_3} =$$

$$= -\int \widetilde{C}^t(\mathbf{k}_3, -\mathbf{k}_4 - \mathbf{k}_2, \mathbf{k}, -\mathbf{k}_4, -\mathbf{k}_2)\, E^t_{-\mathbf{k}_4} E^t_{-\mathbf{k}_2} E^l_{\mathbf{k}} \times$$

$$\times\, e^{-(\Omega^l + \Omega^t_{-4} + \Omega^l_{-2} - \Omega^t_3)t}\, d\mathbf{k}(-d\mathbf{k}_4)\,(-d\mathbf{k}_2)\,, \tag{B.1e}$$

$$\left(\frac{\partial}{\partial t} - \gamma^t_{\mathbf{k}_4} + \mathbf{v}^t_{gr_4} \frac{\partial}{\partial \mathbf{r}}\right) E^t_{\mathbf{k}_4} =$$

$$= - \int \widetilde{C}^{(t)} (\mathbf{k}_4, - \mathbf{k}_2 - \mathbf{k}_3, \mathbf{k}, - \mathbf{k}_2, - \mathbf{k}_3)\, E^t_{-\mathbf{k}_2} E^t_{-\mathbf{k}_3} E^l_{\mathbf{k}} \times$$

$$\times\, e^{-(\Omega^l + \Omega^t_{-2} + \Omega^t_{-3} - \Omega^t_4)t}\, d\mathbf{k}\, (- d\mathbf{k}_2)(- d\mathbf{k}_3)\,. \tag{B.1f}$$

Wir verwenden nun folgende Eigenschaft der $E^{t,l}_{\mathbf{k}_i}$:

$$E^t_{\mathbf{k}} (\mathbf{r}, t) = E^{t*}_{-\mathbf{k}} (\mathbf{r}, t) \rightarrow \mathbf{e}_{-\mathbf{k}} = e^*_{\mathbf{k}}; \quad E^l_{\mathbf{k}} (\mathbf{r}, t) = - E^{l*}_{-\mathbf{k}} (\mathbf{r}, t)$$

und erhalten damit für die Gleichungen (B.1 d, e, f):

$$\left(\frac{\partial}{\partial t} - \gamma^t_{\mathbf{k}_2} + \mathbf{v}^t_{gr_2} \frac{\partial}{\partial \mathbf{r}}\right) E^t_{\mathbf{k}_2} =$$

$$= - \int \widetilde{C}^t\, E^{t*}_{\mathbf{k}_3} E^{t*}_{\mathbf{k}_4} E^l_{\mathbf{k}}\, e^{-i(\Omega^l - \Omega^t_3 - \Omega^t_4 - \Omega^t_2)t}\, d\mathbf{k}\, d\mathbf{k}_3\, d\mathbf{k}_4\,, \tag{B.1g}$$

$$\left(\frac{\partial}{\partial t} - \gamma^t_{\mathbf{k}_3} + \mathbf{v}^t_{gr_3} \frac{\partial}{\partial \mathbf{r}}\right) E^t_{\mathbf{k}_3} =$$

$$= - \int \overset{\approx}{C}{}^t\, E^{t*}_{\mathbf{k}_4} E^{t*}_{\mathbf{k}_2} E^l_{\mathbf{k}}\, e^{-(\Omega^l - \Omega^t_4 - \Omega^t_2 - \Omega^t_3)t}\, d\mathbf{k}\, d\mathbf{k}_4\, d\mathbf{k}_2\,, \tag{B.1h}$$

$$\left(\frac{\partial}{\partial t} - \gamma^t_{\mathbf{k}_4} + \mathbf{v}^t_{gr_4} \frac{\partial}{\partial \mathbf{r}}\right) \mathbf{E}^t_{\mathbf{k}_4} =$$

$$= - \int \overset{\approx}{\widetilde{C}}{}^{(t)}\, E^{t*}_{\mathbf{k}_2} E^{t*}_{\mathbf{k}_3} E^l_{\mathbf{k}}\, e^{-(\Omega^l - \Omega^t_2 - \Omega^t_3 - \Omega^t_4)t}\, d\mathbf{k}\, d\mathbf{k}_2\, d\mathbf{k}_3\,, \tag{B.1i}$$

wo wir verwendet haben, dass

$$- \Omega(\mathbf{k}) = \Omega(- \mathbf{k})\,.$$

gilt.

II. Wellenpakete mit festen Phasen

Wir betrachten hier Wellenpakete, bei denen innerhalb des Paketes Amplitude und Phase der Wellen:

$$\mathbf{E}_k = |\mathbf{E}_{\mathbf{k}}|\, e^{i\varphi_{\mathbf{k}}}$$

nur schwach veränderlich sind, daher die Einführung mittlerer Amplituden und mittlerer Phasen durch

$$\int |\mathbf{E}_k|\, e^{i\varphi_{\mathbf{k}}}\, d\mathbf{k} = |\overline{\mathbf{E}}_{\mathbf{k}_0}|\, e^{i\varphi_{\mathbf{k}_0}} = \overline{\mathbf{E}}_{\mathbf{k}_0}\,, \quad \overline{E}^{l,t}_{\mathbf{k}_0, \mathbf{k}_{20}, \mathbf{k}_{30}, \mathbf{k}_{40}} \equiv E^{l,t}_{2,34}$$

sinnvoll erscheint.

Zusätzlich nehmen wir vorerst an, dass alle auftretenden Grössen bloss zeitabhängig sind. Wenn wir jetzt das Gleichungssystem (B.1 g, h, i) über $\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4$ integrieren, erhalten wir:

$$\begin{aligned} \dot{E}^l &= c^l E_3^t E_4^t E_2^t , \\ \dot{E}_2^t &= - c_2^t E_3^{*t} E_4^{*t} E^l , \\ \dot{E}_3^t &= - c_3^t E_4^{*t} E_2^{*t} E^l , \\ \dot{E}_4^t &= - c_4^t E_2^{*t} E_3^{*t} E^l , \end{aligned} \tag{B.1j,k,l,m}$$

wo wir $\gamma = 0$ gesetzt und weiters angenommen haben, dass

$$\Phi t \ll 1$$

gilt, d. h. eine Kohärenzbedingung erfüllt ist. — Damit haben wir das gewünschte Gleichungssystem von vier Gleichungen mit vier Unbekannten erreicht.

Daraus lassen sich nun einige Erhaltungssätze ableiten, u. zw. multiplizieren wir nun (B.1 j) mit E^{l*}:

$$E^{l*} \dot{E}^l = c^l E_3^t E_4^t E_2^t E^{l*}$$

bilden das Konjugiert-Komplexe:

$$E^l \dot{E}^{l*} = c^l E_3^{t*} E_4^{t*} E_2^{t*} E^l$$

und addieren:

$$(\partial/\partial t) \left\{ |E^l|^2 / c^2 \right\} = 2 \, Re \, (E_3^t E_4^t E_2^t E^*) \, .$$

Jetzt multiplizieren wir (B.1)k mit E_2^{t*} und addieren es zu seinem Konjugiert-Komplexen:

$$\frac{\partial}{\partial t} \left\{ \frac{|E_2^t|^2}{c_2^t} \right\} = - 2 \, Re \, (E_3^t E_4^t E^{l*} E_2^t) \, .$$

Mit den Abkürzungen

$$\frac{|E_2^t|^2}{c_2^t} \equiv \alpha_2^t , \qquad \frac{|E^l|^2}{c^l} \equiv \alpha^l$$

erhalten wir den Erhaltungssatz:

$$\frac{\partial}{\partial t} \left\{ \alpha^l + \alpha_2^t \right\} = 0 , \quad \rightsquigarrow \quad \alpha^l + \alpha_2^t = \text{const},. \tag{B.2a}$$

sowie, wenn wir weiters einführen:

$$\frac{|E_3^t|^2}{c_3^t} \equiv \alpha_3^t , \qquad \frac{|E_4^t|^2}{c_4^t} \equiv \alpha_4^t ,$$

die Erhaltungssätze

$$\alpha^l + \alpha_3^t = \text{const.}, \quad \alpha^l + \alpha_4^t = \text{const.}, \qquad \text{(B.2b,c)}$$

und daraus

$$\alpha_2^t = \alpha_3^t = \text{const.}, \quad \alpha_2^t - \alpha_4^t = \text{const.}, \quad \alpha_3^t - \alpha_4^t = \text{const.}, \qquad \text{(B.2d,e,f)}$$

also 6, und allgemein bei Vorliegen von n Gleichungen mit n Unbekannten,

$$\binom{n}{2} = \frac{n!}{2!(n-2)!}$$

zweigliedrige Erhaltungssätze.

In die Ableitung ging die Realität der c's ein, was bei Fehlen dissipativer Effekte gerechtfertigt ist [2].

Daneben gibt es einen anderen Typ von Erhaltungssätzen, der mit der Kleinheit von Φ verknüpft ist:

Aus $\Phi \ll 1$, d. h.

$$\Omega^l \approx \Omega_2^t + \Omega_3^t + \Omega_4^t\,,$$

sowie (B.2 a, b, c) haben wir etwa

$$\Omega^l \alpha^l + \sum_{i=2}^{4} \alpha_i^t \Omega_i^t = \text{const.},$$

oder auch

$$\Omega^l \alpha^l + \Omega_2^t \alpha_4^t + \Omega_3^t \alpha_2^t + \Omega_4^t \alpha_3^t = \text{const.},$$

etc.

Wir betrachten nun eine Lösung des Systems (B.1 j, k, l, m) für den Spezialfall verschwindender Phasendifferenz zwischen den Amplituden:

$$\varphi_3^t + \varphi_4^t + \varphi_2^t - \varphi_l^* = 0\,,$$

was den Vorteil hat, dass es die rechten Gleichungsseiten reell macht. Zu diesem Zweck multiplizieren wir (B.1 j) mit E^{l*} und bilden das Konjugiert-Komplexe:

$$E^{l*} \dot{E}^l = c^l E_3^t E_4^t E_2^t E^{l*}, \quad E^l \dot{E}^{l*} = c^l E_3^t E_4^t E_2^t E^{l*}, \quad \dot{\alpha}^l = 2E_3^t E_4^t E_2^t E^{l*} \cdot$$

Wir quadrieren und erhalten:

$$(\dot{\alpha}^l)^2 = 4\,|E_3^t|^2\,|E_4^t|^2\,|E_2^t|^2\,|E^{l*}|^2 \equiv 4c^l c_3^t c_4^t c_2^t \alpha^l \alpha_3^t \alpha_2^t \alpha_4^t\,.$$

Mit Hilfe der Erhaltungssätze drücken wir das nun in α^l aus:

$$(\dot{\alpha})^2 = 4c^l c_2^t c_3^t c_4^t \alpha^l (\alpha_0^l + \alpha_{20}^t - \alpha_l)(\alpha_0^l + \alpha_{30}^t - \alpha_l)(\alpha_0^l + \alpha_{40}^t - \alpha_l)\,,$$

wo wir

$$\alpha^l + \alpha_i^t = \text{const.} = \alpha_0^l + \alpha_{i0}^t\,, \quad \alpha_0 \text{ Anfangswerte}, \ i = 2, 3, 4$$

verwendet haben. Wir führen eine Variablentrennung durch und integrieren:

$$dt\cdot 2\sqrt{c^l c_2^t c_3^t c_4^t}=\frac{d\alpha^l}{\sqrt{\alpha^l(\alpha_0^l+\alpha_{20}^t-\alpha_l)(\alpha_0^l+\alpha_{30}^t-\alpha_l)(\alpha_0^l+\alpha_{40}^t-\alpha_l)}}\,,$$

$$\tau\cdot 2\sqrt{c^l c_2^t c_3^t c_4^t}=\int_{\alpha^l=0}^{\alpha^l=\alpha^l_{\max}}\frac{d\alpha^l}{\sqrt{\alpha^l(\alpha_0^l+\alpha_{20}^t-\alpha_l)(\alpha_0^l+\alpha_{30}^t-\alpha_l)(\alpha_0^l+\alpha_{40}^t-\alpha_l)}}\,, \tag{B.3}$$

wenn wir mit τ die Zeit bezeichnen, die das System braucht, um die Amplitude der longitudinalen Welle von Null auf ihr Maximum anwachsen zu lassen, d. h. also die charakteristische Zeit für den nichtlinearen Energieübergang zwischen zwei Wellentypen.

Der Auswertung des Integrals in (B.3) wenden wir uns nun zu, indem wir vorerst folgende Abkürzungen einführen:

$$A=\frac{\alpha^l}{\alpha_0^l+\alpha_{20}^t}\,,\qquad B=\frac{\alpha_0^l+\alpha_{20}^t}{\alpha_0^l+\alpha_{30}^t}\,,\qquad C=\frac{\alpha_0^l+\alpha_{20}^t}{\alpha_0^l+\alpha_{40}^t}\,,$$

womit wir erhalten:

$$\int_{\alpha^l=0}^{\alpha^l=\alpha^l_{\max}}\frac{d\alpha^l}{\sqrt{\alpha^l(\alpha_0^l+\alpha_{20}^t-\alpha_l)(\alpha_0^l+\alpha_{30}^t-\alpha_l)(\alpha_0^l+\alpha_{40}^t-\alpha_l)}}=$$

$$=\int_0^1\frac{dA}{\sqrt{A(1-A)(1-AB)(1-AC)(\alpha_0^l+\alpha_{30}^t)(\alpha_0^l+\alpha_{40}^t)}}\,.$$

Da die Wurzel nur reelle Werte annehmen soll, ist $\alpha_l<0$ ausgeschlossen, ferner wird für α_l nur Variation zwischen 0 und dem Minimum von $(a_0^l+\alpha_{20}^t,\ \alpha_0^l+\alpha_{30}^t,\ \alpha_0^l+\alpha_{40}^t)$ erlaubt sein. Wir machen o. B. d. A. die Annahme, dass $\alpha_{20}^t<\alpha_{30}^t,\ \alpha_{40}^t$, d. h. α_l variiert zwischen 0 und $\alpha_0^l+\alpha_{20}^t$, A zwischen 0 und 1.

Damit bekommen wir für die charakteristische Zeit τ die Gleichung:

$$\tau=\overbrace{\frac{1}{\sqrt{c^l c_2^t c_3^t c_4^t(\alpha_0^l+\alpha_{30}^t)(\alpha_0^l+\alpha_{40}^t)}}}^{\mathcal{C}}\int_0^1\frac{dA}{\sqrt{A(1-A)(1-AB)(1-AC)}}=$$

$$=\mathcal{C}\cdot\frac{1}{\sqrt{BC}}\int_0^1\frac{dA}{\sqrt{(-1)\,A\,(A-1)\left(A-\frac{1}{B}\right)\left(A-\frac{1}{C}\right)}}\,.$$

Es galt

$$\alpha_{20}^t<\alpha_{30}^t,\ \alpha_{40}^t\,,$$

also

$$B,C<1,\quad 1/B,1/C>1\,.$$

Wenn wir zusätzlich fordern, dass

$$B > C, \quad 1/B < 1/C$$

bekommen wir folgende Ordnung der Nullstellen des Polynoms unter der Wurzel:

$$1/C > 1/B > 1 > 0\,.$$

Hier handelt es sich um ein Polynom vierten Grades, auf das folgende Formel anwendbar ist:

$$p(x) = a_0(x - \alpha_1)(x - \alpha_2)(x - \alpha_3)(x - \alpha_4)\,, \; \alpha_1 > \alpha_2 > \alpha_3 > \alpha_4$$

alle α's reell

$$\int_{\alpha_4}^{\alpha_3} \frac{dx}{\sqrt{p(x)}} = \frac{2}{\sqrt{-a_0(\alpha_1 - \alpha_3)(\alpha_2 - \alpha_4)}}\, \mathcal{K}\left(\sqrt{\frac{(\alpha_1 - \alpha_2)(\alpha_3 - \alpha_4)}{(\alpha_1 - \alpha_3)(\alpha_2 - \alpha_4)}}\right),$$

wo $\mathcal{K}$ ein vollständiges Legendresches Normalintegral erster Gattung ist.

Damit ergibt sich:

$$\tau = \mathcal{C} \cdot \frac{2}{\sqrt{1 - C}}\, \mathcal{K}\left(\sqrt{\frac{B - C}{1 - C}}\right).$$

Jetzt führen wir eine Falldisjunktion durch:

a) C sei nahe bei 0, B nahe bei 1, d. h. die Welle E_4^t übertreffe die anderen auftretenden bei weitem an Intensität: dadurch wird folgende Formel für die Berechnung des Normalintegrals anwendbar:

$$\mathcal{K}\,(k) = \frac{2}{\pi} \ln \frac{4}{k'}\, \mathcal{K}\,(k') - \underbrace{\sum_{\nu=1}^{\infty} c_\nu\, k'^{2\nu}}_{\approx 0}$$

mit

$0 < k < 1$, aber nahe bei 1, $k' = \sqrt{1 - k^2}$

$$\mathcal{K}\left(\sqrt{\frac{B - C}{1 - C}}\right) = \frac{2}{\pi} \ln \frac{4}{\sqrt{\dfrac{1 - B}{1 - C}}}\, \mathcal{K}\left(\sqrt{\frac{1 - B}{1 - C}}\right) \approx$$

$$\approx \frac{2}{\pi}\, \frac{1}{2} \ln \frac{16(1 - C)}{(1 - B)}\, \frac{\pi}{2} \approx \frac{1}{2} \ln \frac{16}{1 - B}\,,$$

wo wir verwendet haben:

$$\mathcal{K}(k) = \frac{\pi}{2} \sum_{\nu=0}^{\infty} \frac{\left(\frac{1}{2};\, 1;\, \nu\right)^2}{(\nu!)^2}\, k^{2\nu}, \quad 0 < k < 1\,,$$

$$(m;\, d;\, \nu) = m(m + d)(m + 2d) \ldots (\mathrm{m} + (\nu - 1)d)$$

sodass wir also für τ haben:

$$\tau = \mathcal{C} \cdot \frac{2}{\sqrt{1-C}} \, \frac{1}{2} \ln \frac{16(\alpha_0^l + \alpha_{30}^t)}{\alpha_{30}^t - \alpha_{20}^t}$$

$$\cong \frac{1}{\sqrt{c^l c_2^t c_3^t c_4^t} \sqrt{\frac{|E_0^l|^4}{c^{l2}} + \frac{|E_{30}^t|^2 |E_0^l|^2}{c_3^t c^l} + \frac{|E_{40}^t|^2 |E^t{}_0|^2}{c_4^t c^l} + \frac{|E_{30}^t|^2 |E_{40}^t|^2}{c_3^t c_4^t}}} \cdot$$

$$\cdot \ln \frac{16\left(\frac{|E_0^l|^2}{c^2} + \frac{|E_{30}^t|^2}{c_3^t}\right)}{\frac{|E_{30}^t|^2}{c_3^t} - \frac{|E_{20}^t|^2}{c_2^t}} \, .$$

Wenn wir jetzt weiters annehmen, dass $\alpha_0^l \ll \alpha_{i0}^t$ sowie $c_3^t \approx c_2^t$ und $|E_{30}^t|^2/c_3^t \equiv \equiv \alpha \approx 2\,|E_{20}^t|/c_2^t$ so erhalten wir für die charakteristische Zeit:

$$\tau \cong \frac{1}{\sqrt{c^l c_2^t}} \, \frac{1}{|E_{30}^t|\,|E_{40}^t|} \ln \frac{16\alpha}{\alpha/2} \cong (2 \div 3) \Big/ |E_{30}^t||E_{40}^t| \sqrt{c^l c_2^t} \, ,$$

d. h. die charakteristische Zeit für den Energieübergang von der und an die longitudinale Welle hängt nicht mehr von der Amplitude dieser Welle ab, sondern nur noch von der der stärksten anderen beteiligten Wellen; die longitudinale Welle selbst geht nur mehr mit dem Kopplungskoeffizienten c^1 ein.

b) Ein überschaubares Ergebnis liefert auch der Fall, dass zwar die Ordnung der Nullstellen beibehalten wird, aber $C \approx B \approx 0$ gilt. Dann gilt

$$\alpha_l^0 + \alpha_{20}^t \ll \alpha_0^l + \alpha_{30}^t, \; \alpha_0^l + \alpha_{20}^t \ll \alpha_0^l + \alpha_{40}^t, \; \alpha_0^l \ll \alpha_{i0}^t, \alpha_{20}^t \ll \alpha_{30}^t, \alpha_{40}^t$$

und für die charakteristische Zeit erhalten wir:

$$\tau \cong \frac{1}{\sqrt{c^l c_2^t}} \, \frac{1}{\sqrt{\alpha_{30}^t \alpha_{40}^t}} \, 2\mathcal{K}(0) = \pi \, \frac{1}{\sqrt{c^l c_2^t} \, |E_{30}^t||E_{40}^t|}$$

d. h. wenn eine der beteiligten transversalen Wellen viel schwächer als die beiden anderen ist, so bestimmen ebenfalls nur die beiden stärksten den zeitlichen Verlauf.

c) Ferner sei $C \approx B \approx 1$, d. h. die longitudinale Welle übertreffe alle anderen bei weitem an Stärke. Dann haben wir für τ:

$$\tau \cong \frac{1}{\sqrt{c^l c_2^t c_3^t c_4^t} \sqrt{|\alpha_0^l|^2}} \, \frac{1}{\sqrt{1 - \frac{\alpha_0^l + \alpha_{20}^t}{\alpha_0^l + \alpha_{40}^t}}} \, \frac{\pi}{2} =$$

$$= \frac{1}{\sqrt{c_2^t c_3^t c_4^t}} \, \frac{1}{|E_0^l|} \, \pi \, \frac{1}{\sqrt{\frac{|E_{40}^t|^2}{c_4^t} - \frac{|E_{20}^t|^2}{c_2^t}}} \, ,$$

d. h. wir haben zwar eine Abhängigkeit verkehrt proportional der Amplitude der stärksten Welle, daneben aber ist die charakteristische Zeit sehr empfindlich für die relative Intensität der schwächsten zur stärksten der transversalen — doch insgesamt sehr schwachen — Wellen. Abhängigkeiten proportional den reziproken Amplituden sind auch für Dreiwellenprozesse berechnet worden [3].

III. Ortsabhängige Systeme

Bis jetzt beschränkten wir uns auf den Fall rein zeitabhängiger Grössen. Wenn wir die Amplitudenmittelwerte, mit denen wir rechnen, auch ortsabhängig machen, erhalten wit folgendes System (weiterhin sei $\gamma = 0$).

$$\left(\frac{\partial}{\partial t} + v_\alpha \frac{\partial}{\partial \mathbf{r}}\right) E^l(\mathbf{r}, t) - c^l E_3^t E_4^t E_2^t ,$$

$$\left(\frac{\partial}{\partial t} + v_\beta \frac{\partial}{\partial \mathbf{r}}\right) E_2^t(\mathbf{r}, t) = - c_2^t E_3^{*t} E_4^{*t} E^l ,$$

$$\left(\frac{\partial}{\partial t} + v_\gamma \frac{\partial}{\partial \mathbf{r}}\right) E_3^t(\mathbf{r}, t) = - c_3^t E_4^{*t} E_2^{*t} E^l ,$$

$$\left(\frac{\partial}{5t} = v_\delta \frac{\partial}{\partial \mathbf{r}}\right) E_4^t(\mathbf{r}, t) = - c_4^t E_2^{*t} E_3^{*t} E^l .$$

Hier ist es schon schwieriger, Erhaltungssätze nach dem Muster des ortsunabhängigen Falles aufzustellen; nur für den Spezialfall, dass die Gruppengeschwindigkeiten $v_\alpha = v_\beta = v_\gamma = v_\delta = d\mathbf{r}/dt$, reduziert sich der Fall auf den früher betrachteten, nur dass sich jetzt das ganze wechselwirkende System mit dieser gemeinsamen Geschwindigkeit — physikalisch realisiert etwa durch Konvektion — durch das Plasma bewegt.

LITERATUR

1. J. W. Weil, Acta Phys. Hung., **38**, 321, 1975.
2. R. C. Davidson, Methods in Non-Linear Plasma Theory, H. S. W. Massey, K. A. Brueckner, Eds., Pure and Applied Physics, **37**, Academic Press, New York (1972).
3. S. Akhmanov, R. V. Khokhlov, VINITI, Moskau (1965): Probleme der nichtlinearen Optik (russisch).

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ANALYTICAL EXPRESSIONS FOR THE DEPENDENCE OF SUPERCONDUCTING PARAMETERS ON ALLOY CONCENTRATION

By

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Analytical expressions are given which describe the dependence of the critical temperature, of the critical magnetic fields and of the GL parameter on the concentration of the alloying material, characterizing the phase transition within the superconducting state in good agreement with the experiments.

In one of our previous papers [1] it was discovered that in superconducting alloys of small GL parameter $\varkappa$ a specific phase transition of new type occurs on the effect of increasing alloy concentration. This means that having reached a certain critical concentration C_c the previous type I superconductivity (Meissner's state) goes over to type II (mixed state).

Our experiments have been carried out with In-Bi specimens containing 0—5 at. % Bi [2].

The evaluation of the experimental results shows that this phase transition occurs at any temperature-dependent $\varkappa(T)$ and at any temperature always whenever the value $\varkappa = 1/\sqrt{2} = \varkappa_c$ has been reached. Therefore this is considered to be the critical value of GL parameter.

The occurring phase transition can be characterized with the following fundamental features:

1. The order parameter describing the superconductivity becomes inhomogeneous as superconductive and normal domains appear. (In the presence of an external current it becomes anisotropic as well). The vector potential has a similar behaviour too.

2. The superconductivity, being previously a surface phenomenon, becomes a volumetric one. (The transport current and the external magnetic field penetrate into the sample).

3. Instead of one critical magnetic field H_c describing the pure superconductivity the critical fields H_{c1} and H_{c2} together determine the magnetic penetration.

4. A sudden change occurs in the value of the thermodynamic entropy matrix [3].

5. A quick change occurs in the macroscopic conductivity matrix. (This registers the superconductive-normal lattice structure).

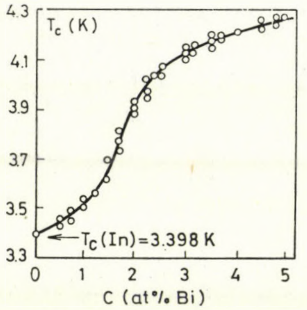

Fig. 1. Dependence of the critical temperature on the alloy concentration

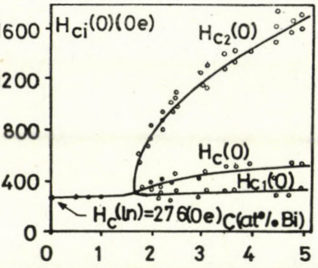

Fig. 2. Dependence of the critical magnetic fields on the alloy concentration

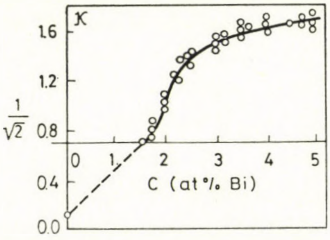

Fig. 3. Dependence of the GL parameter on the alloy concentration

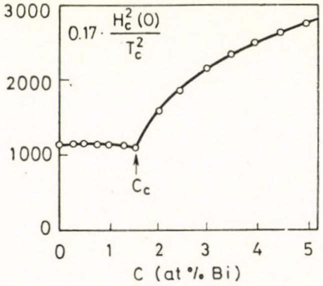

Fig. 4. Dependence of the electron specific heat coefficient on the alloy concentration

The curve $T_c - C$ (Fig. 1) has been determined through direct measurements while the values H_{c1}, H_c and H_{c2} (Fig. 2) have been obtained from the magnetic moment — magnetic field curves in a direct way. For the determination of the function $\varkappa - C$ (Fig. 3) the GOR'KOV—GOODMAN [4, 5] formula further the respective results of the GLAG theory have been used [6, 7, 4].

In our experiments the curve $\varkappa - C$ intersects the value $\varkappa = 1/\sqrt{2}$ at 1.55 at. % alloying material content, consequently in the present case $C_c =$ $= 1.55$ at. % is the critical concentration where the change in type of the superconductivity occurs.

As far as the electron specific heat coefficient formula

$$\gamma = 0{,}17 \frac{H_c(0)^2}{T_c^2} \tag{1}$$

having a part in the BCS theory [8] is valid here, it leads to an interesting result based on our measured data. Namely, the curve $\gamma - C$ obtained from (1) has a sharp break at the critical concentration C_c (Fig. 4) which indicates the occurrence of a second order phase transition. The shape of the curve reflects the presence of single electrons, appearing in the critical point, beside the electron pairs, and their phonon interaction which is different from the pair interaction [9].

The analytical description of the characteristic experimental curves shown in Figs. 1, 2 and 3 was carried out by means of selecting a probe function, taking into consideration the numerical data which characterize the investigated physical quantity in the distinguished point $C = 0$ at. % and $C = C_c$. The determination of the numerical values and the corrections of the probe functions were carried out on a computer type ODRA 1304.

Thus for the concentration dependence of the critical temperature in the range $C < C_c$ under this phase transition the relation

$$T_c = k_1 C^2 + k_2 C + k_3 , \tag{2}$$

$$k_1 = 0.097, \qquad k_2 = 0.015, \qquad k_3 = T_{c\,[\mathrm{In}]} = 3.397,$$

while in the range $C_c < C \leq 5$ at. % the expression

$$T_c = k_4 C^4 + k_5 C^3 + k_6 C^2 + k_7 C + k_8 \tag{3}$$

$$k_4 = -0.021, \quad k_5 = 0.308, \quad k_6 = -1.708, \quad k_7 = 4.246, \quad k_8 = 0.118$$

has been obtained.

According to the measurements the curve $H_{c1}(0) - C$ is nearly linear, i. e. it can be described with the relation

$$H_{c1}(0) = k_9 C + k_{10} , \tag{4}$$

$$k_9 = 10.77, \qquad k_{10} = H_c(0)_{[\mathrm{In}]} = 276.$$

The functional relation $H_c(0) - C$ (naturally in case of $C > C_c$) is characterized by the formula

$$H_c(0) = k_{11} \ln (C - 1.20) + k_{12} , \tag{5}$$

$$k_{11} = 104.4, \qquad k_{12} = 402.6 ,$$

while the $H_{c2}(0) - C$ can be described with

$$H_{c2}(0) = k_{13} \ln (C - 1.16) + k_{14} , \tag{6}$$

$$k_{13} = 594, \qquad k_{14} = 859.$$

For the characterization of the diagram $\varkappa - C$ int the range above C_c the relation

$$\varkappa = \varkappa_c + k_{15}(C - C_c)^{1/5} + k_{16}(C - C_c)^{-4/5} \tag{7}$$

$$k_{15} = 0.811, \qquad k_{16} = -0.151$$

has been applied.

The formulae obtained reflect the experimental result on Figs 1, 2 and 3 with a very good accuracy. The average deviation from them is 0.15% in formula (2), 2.5% in (3), 0.1% in (4), 0.4% in (5), 1.3% in (6) and finally 0.15% in the relation (7).

It is evident that increasing the additive material in the case of other superconducting alloys or compounds of small $\varkappa$ will result in the discovered phase transition. It can be expected that this will be characterized by curves of similar shape and thus the formulae (2)—(7) will be applicable for them too.

REFERENCES

1. I. Kirschner, Phys. Lett., **47*A***, 139, 1974.
2. I. Kirschner, J. Bánkuti, K. Sajó et al., Sov. Phys. JETP, **66,** 2141, 1974.
3. I. Kirschner and K. Martinás, Journ. Low Temp. Phys., **14,** 427, 1974.
4. L. P. Gor'kov, Sov. Phys. JETP, **37,** 833, 1959.
5. B. B. Goodman, IBM J. Res. Develop., **6,** 63, 1961.
6. A. A. Abrikosov, Sov. Phys. JETP, **32,** 1442, 1957.
7. V. L. Ginzburg and L. D. Landau, Sov. Phys. JETP, **20,** 1064, 1950.
8. J. Bardeen, L. N. Cooper and J. W. Schrieffer, Phys. Rev., **108,** 1175, 1957.
9. I. Kirschner, Proc. of 14th Intern. Conf. on Low Temp. Phys. (LT-14), Vol. 2., p. 321., Helsinki, 1975.

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ON THE POSSIBILITY OF PARTICLE CONFINEMENT BY MULTIPOLE FIELDS

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Considerations are given concerning the possible confinement of particles due to their interactions with multipole fields. It is argued that from a certain formal point of view, a properly chosen limit $m \to 0$ for the mass parameter of the multipole fields should be carried out only at the very end of the calculations. The method requires an artificial unitarization.

1. The considerations which follow are connected with some problems of particle confinement via an interaction originating from a Green's function of the $(p^2 + m^2)^{-n}$, $n \geq 1$, integer type. The work was initiated by the article of Kiskis [1]. At the beginning we would like to emphasize that the formulation of the questions, the problems and (partially) the answers are not particularly new. Here we quote Nakanishi's excellent review article [2].

Since the early works of Heisenberg [3] and Froissart [4] we know how to construct automatically a field theory with a propagator of the required type. The construction containing exponents $n > 1$ supposes indefinite metric quantization, leading to multipole ghosts. This can be directly seen from the spectral representation

$$\Delta'(x) = \int \varrho(m^2)\, \Delta(x; m^2) dm^2,$$

where $\partial\Delta/\partial m^2$ implies

$$\varrho(m^2) = -\delta'(m^2).$$

The solution for the value $m \neq 0$ is completely worked out, while the case $m = 0$ leads to some problems. Part of them is connected with the possible non unitary equivalent representations of the zero mass theories and with ultraviolet divergences. Another important point is that the field theory with $m = 0$ possesses no manifestly Lorentz covariant solutions for the free fields [2, 5], (c.f. Eq. (3)) and, therefore, the construction of P_μ and the state vector space, etc., lacks the elegance of the $m \neq 0$ case. These problems are quite transparent in [1].

Therefore we proceed in the following way:

i) First $m \neq 0$ is assumed for the mass of the (scalar) multipole field particles (gluons).

ii) Then the proper limit $m \to 0$ is investigated leading to the confinement of the objects (quarks) which exchange these particles.

We must confess that the following considerations stem mainly from our attraction to field theoretical models of some basic type. Therefore it is quite far from us to suggest, that this is the ultimate solution of the problem of the (possible) quark confinement.

2. The Lagrangian density of the FROISSART model [4] is given by

$$L = -\partial_\mu A \partial_\mu B - m^2 AB - \frac{\lambda}{2} A^2, \tag{1}$$

$m^2 > 0$, λ is real, having a dimension of mass square. The field equations

$$\begin{aligned} (\Box - m^2)A &= 0, \\ (\Box - m^2)B &= \lambda A, \end{aligned} \tag{2}$$

possess the solutions

$$A = A_0, \qquad B = B_0 + \frac{\lambda}{m^2}\left(1 + \frac{1}{2} x_\mu \partial_\mu\right) A_0, \tag{3}$$

where A_0 and B_0 are free fields.

The canonical formalism gives the four-dimensional commutators as

$$\begin{aligned} &[A(x), A(x')] = 0, \\ &[A(x). B(x')] = i\Delta(x - x'; m^2), \\ &[B(x), B(x')] = i\lambda \frac{\partial}{\partial m^2} \Delta(x - x'; m^2). \end{aligned} \tag{4}$$

For the emission and absorption operators of the free fields we have

$$\begin{aligned} &[a, a] = [b. b] = [a. a^+] = [b. b^+] = 0, \\ &[a(\mathbf{k}), b^+(\mathbf{k}')] = [b(\mathbf{k}), a^+(\mathbf{k}')] = \delta(\mathbf{k} - \mathbf{k}'), \end{aligned} \tag{5}$$

and the four momentum operator is

$$P_\mu = \int d\mathbf{k}\, k_\mu \left(a^+(\mathbf{k})\, b(\mathbf{k}) + b^+(\mathbf{k})\, a(\mathbf{k}) + \frac{\lambda}{m^2} a^+(\mathbf{k})\, a(\mathbf{k})\right). \tag{6}$$

The state vector space based on the vacuum state $| 0 >$

$$a \,| 0 > = b \,| 0 > = 0, \qquad < 0 | 0 > = 1 \tag{7}$$

shows that typical dipole field structure: in the one particle sector dipole ghosts; in the many particle sectors multipole ghosts emerge.

Let us consider the interaction of this field with a fixed source ϱ via the interaction

$$L_1 = \varrho(x)\varphi(x)\,, \qquad \varphi(x) = g_1 A(x) + g_2 B(x),$$
$$(H = \Sigma \pi_i(\mathbf{r}) q_i(\mathbf{r}) - L)\,, \tag{8}$$

where g_1 and g_2 are real coupling constants. An exact calculation gives [6] the static interaction potential

$$V = \frac{g_1\, g_2}{4\pi} \frac{e^{-m|\mathbf{r}|}}{|\mathbf{r}|} - \frac{g_2^2\, \lambda}{8\pi m^2} m e^{-m|\mathbf{r}|}\,. \tag{9}$$

This is the same result as is given by the lowest order perturbation calculation with

$$H_1(x) = -L_1(x)\,. \tag{10}$$

This follows from Eq. (4), which yields

$$[\varphi(x), \varphi(x')] = 2\, i g_1 g_2\, \Delta(x - x'; m^2) +$$
$$+ i g_2^2\, \lambda \frac{\partial}{\partial m^2} \Delta(x - x';\; m^2)\,. \tag{11}$$

Thus the vacuum value of the T product is fixed by Eqs. (3), (4), (5), (7) and (11).

In an abbreviated notation Eq. (9) may be written as

$$V(r) = \frac{e^{-mr}}{r} (\alpha + \beta m r)\,, \tag{12}$$

α and β are real dimensionless constants. If $\alpha \ll 0$, $\beta m \gg 0$, m is small, this potential gives rise to a rather strong binding. Expanding $\exp(-mr)$ around $m = 0$ we have

$$V(r) = \frac{\alpha}{r} + m(\beta + \alpha) + m^2 r \left(\frac{\alpha}{2} - \beta\right) + O(m^3).$$

If for m small

$$\frac{\alpha}{2} - \beta = \frac{K}{m^2}\,, \qquad K \text{ finite} \tag{13}$$

$$\lim_{m \to 0} V(r) = \frac{\alpha}{r} + C + Kr\,, \tag{14}$$

but either α, or C diverges.

Considering Eq. (3) or (6) one notices that the limit $m \to 0$ should be carried out with λm^2 fixed.

3. One can get rid quite easily of this problem using the Lagrangian [7]

$$L = -\frac{1}{2}(\partial_\mu B \partial_\mu B + m^2 B^2) - (\partial_\mu A \partial_\mu C + m^2 AC) - \lambda AB \tag{15}$$

instead of (1). Then

$$\begin{aligned} (\Box - m^2)A &= 0\,, \\ (\Box - m^2)B &= \lambda A\,, \\ (\Box - m^2)C &= \lambda B\,. \end{aligned} \tag{16}$$

In an analogous way to Eqs. (3), (4) and (5), one can introduce free fields A_0, B_0 and C_0 with

$$[a(\mathbf{k}), c^+(\mathbf{k}')] = [c^+(\mathbf{k}), a(\mathbf{k}')] = [b(\mathbf{k}), b^+(\mathbf{k}')] = \delta(\mathbf{k} - \mathbf{k}'),$$

other commutators vanish, from which P_μ can be constructed, and the vacuum state can be defined.*

The state vector space corresponds to the situation where in the one particle sector dipole and tripole, in the higher sectors multipole ghost states are present.

Writing

$$\varphi(x) = g_1 A(x) + g_2 B(x) + g_3 C(x),$$

$$[\varphi(x), \varphi(x')] = i\Big(a\, \Delta(x - x'; m^2) + $$

$$+ b\lambda \frac{\partial}{\partial m^2} \Delta(x - x'; m^2) + c\lambda^2 \frac{\partial^2}{\partial (m^2)^2} \Delta(x - x'; m^2)\Big), \tag{17}$$

therefore we have

$$V(r) = \frac{e^{-mr}}{r}(\alpha + \beta mr + \gamma m^2 r^2),$$

$$\alpha,\ \beta,\ \gamma \text{ real dimensionless.} \tag{18}$$

The sign of γ is positive, since it is proportional to $g_3^2 \lambda^2$. The possibility of a strong binding is evident.

Taking the limit $m \to 0$, with λm^{-2} fixed,

$$\lim_{m \to 0} V(r) = \frac{\alpha}{r} + \Delta + Kr, \tag{19}$$

if $\alpha \sim \alpha$, $\beta \sim \Delta/m$, $\gamma \sim K/m^2$ for small m.

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* The identity

$$\frac{\partial \Delta}{\partial m^2} = \frac{1}{2m^2}(2 + x_\mu \partial_\mu)\Delta$$

is erroneously written in [6, 7], therefore there some numerical constants are wrong. Cf. however, [2, 8, 9].

In [8, 9] one can find the form of the Lagrangians which continue the sequence (17) or (18) if required. The next step, in the appropriate limit, gives e.g. an oscillator potential.

4. Although multipole field theories require a quantization with indefinite metric, based mainly on HEISENBERG's suggestion [3] it was thought that such a theory is physically unitary. The proof may be called [2] the ASCOLI—MINARDI theorem [10].*

It turned out [2, 11, 12, 13], however, that the use of multipole ghosts does not guarantee automatically the unitarity of the physical S matrix. General unitarization methods are quoted in [2, 6], for dipole ghosts (see [11, 14, 15, 16]). Therefore, for preventing these types of gluons to emerge in a scattering, some unitarization method must be used. One of them originating from an old treatment of an electrodynamics without photon production (used more recently by SUDARSHAN [17]) seems to be in favour nowadays [18]. This method takes the principal value integral instead of the usual $i\varepsilon$ prescription.

5. Eqs. (13) and (18) require that

$$g^2 \sim \frac{K}{m^2}, \qquad m^2 \text{ small}.$$

Since the other mass dimension parameter is fixed by $\lambda m^{-2} =$ consts. (Cf. Eqs. (4), (6) and (15)), the standard field theoretical treatment gives

$$g \sim \frac{M}{m^2},$$

where M is the mass of the particle (quark) to which the multipole fields are coupled. In the more sophisticated language of the renormalization group method, Eqs. (13) or (19) may reflect only the asymptotical behaviour of g_λ^2.

*

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REFERENCES

1. JOE E. KISKIS, Jr., Phys. Rev. D., **11**, 1178, 1975.
2. N. NAKANISHI, Progr. Theor. Phys. Suppl., **51**, 1, 1972.
3. W. HEISENBERG, Nucl. Phys., **4**, 532, 1957.
4. Introduction to the Field Theory of Elementary Particles, J. Wiley and Sons Ltd., London 1967; M. FROISSART, Nuovo Cim. Suppl., **14**, 197, 1959.
5. J. LUKIERSKI, Acta Phys. Polonica, **33**, 969, 1968.

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* In [7] still this statement stands.

6. K. L. NAGY, State Vector Spaces with Indefinite Metric in Quantum Field Theory, Akadémiai Kiadó, Budapest and Noordhoff Publ. Groningen, Netherlands, 1966.
7. K. L. NAGY, Acta Phys. Hung., **13,** 21, 1961.
8. J. LUKIERSKI, Acta Phys. Polonica, **32,** 551, 771, 1967.
9. K. YOKOYAMA and R. KUBO, Prog. Theor. Phys., **41,** 542, 1969.
10. R. ASCOLI and R. MINARDI, Nuovo Cim., **8,** 951, 1958; **9,** 242, 1958.
11. M. KAROWSKI, Zeitschr. f. Naturforschung, **24**a, 510, 1969.
12. K. L. NAGY, Acta Phys. Hung., **28,** 245, 1970.
13. N. NAKANISHI, Phys. Rev. D, **3** 811, 1971.
14. M. KAROWSKI, Nuovo Cim., **24**A, 126, 1974.
15. K. L. NAGY, Acta Phys. Hung., **32,** 127, 1972.
16. K. SEKINE, Unitarity and Asymptotic Conditions in a Model with Dipole Ghost. Meisei University preprint, 1975.
17. E. C. G. SUDARSHAN, Fields and Quanta, **2,** 175, 1972.
18. S. BLAHA, Towards a Field Theory of Hadron Binding, Cornell University preprint, CLNS-280, 1974.

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PROPAGATION OF A HYDROMAGNETIC SHOCK WAVE IN A STEADY FLOW OF AN IDEAL DISSOCIATING GAS

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The propagation of a hydromagnetic shock wave in steady flow of an ideal dissociating gas is discussed. The variations of flow and field parameters along the direction of propagation of the shock are determined. It is shown that the effects of dissociation on the generation of vorticity and current density vanish, if the magnetic field is applied in the direction of propagation of the shock.

1. Introduction

In dealing with problems of hypersonic flight at high altitude a temperature of many thousand degrees of Kelvin can easily be attained during flight as the kinetic energy of the re-entering craft is dissipated by the atmospheric gas through shock compression and viscous heating. The air molecules, atoms and other species which absorb this kinetic energy may go through a change of chemical composition. In the temperature range from 1000 °K to 7000 °K the only chemical reaction involved is that of dissociation and thus the ionization and electronic excitation may be neglected. The problem of incorporating the effects of the large energy change involved in dissociation into the standard theory of gas flow appears at the same time so important and so formidable that it is worth approaching slowly. One can usefully begin, on both the theoretical and experimental sides, by eliminating the less essential complications which arise from the detailed composition of air, and studying the dynamics of a pure dissociating diatomic gas. Thus, the present work is confined to the study of the effects of non-equilibrium in molecular dissociation and atomic recombination in an inviscid flow problem only. The following assumptions are made:

(i) The molecular transport effects leading to viscosity, diffusion and heat conduction of the gases are neglected;

(ii) A diatomic gas mixture is assumed and each component of the reacting mixture is assumed thermally perfect;

(iii) In the temperature range 1000 °K $\sim$ 7000 °K, for diatomic gases, the contributions of energy from electronic excitation and ionization are both assumed negligible,

(iv) At temperatures where dissociation is important, the radiation heat loss from the gas mixture may not be negligibly small. However, in order to simplify the problem, we exclude such an effect.

LIGHTHILL [1] introduced a new gas model termed as 'ideal dissociating gas' and deduced the oblique shock wave relations in the strong shock approximation. Considering an ideal dissociating gas and a rate equation of his own, FREEMAN [2] studied some of the major features of non-equilibrium flows past a blunt body. EPSTEIN [3] studied the problem of non-equilibrium dissociative flow behind a plane oblique shock. CAPIAUX and WASHINGTON [4] have investigated the non-equilibrium dissociative flow past a wedge by assuming the gas to be LIGHTHILL's dissociating one. HSU [5] determined the flow gradients behind a curved shock in dissociating gases. HSU and ANDERSON [6] obtained the variations of pressure, density, temperature and degree of dissociation along the stream lines in a non-equilibrium flow of a diatomic gas behind a plane oblique shock. In this paper keeping in mind the aforementioned assumptions (i)—(iv), we shall study the down-stream effects of the propagation of a hydromagnetic shock in a steady flow of an ideal dissociating gas. For simplicity we shall assume the upstream flow to be uniform and frozen.

2. Basic equations

For a mixture of perfect gases, the continuity equation of the i^{th} species is [7]

$$\varrho(\mathbf{u} \cdot \nabla)\alpha_i = \sigma_i\,, \tag{2.1}$$

where ϱ and $\mathbf{u}$ denote the density and velocity vector for the mixture. σ_i denotes the mass rate of production of species i per unit volume by chemical reaction and $\alpha_i \overset{\text{def.}}{=} \varrho_i/\varrho$ is the mass fraction of the i^{th} species. The magnetogasdynamic flow equations for the mixture are

$$\varrho(\nabla \cdot \mathbf{u}) + \mathbf{u} \cdot \nabla\varrho = 0\,, \tag{2.2}$$

$$\varrho(\mathbf{u} \cdot \nabla)\mathbf{u} + \nabla p + \frac{1}{4\pi}\mathbf{H} \times (\nabla \times \mathbf{H}) = 0, \tag{2.3}$$

$$(\mathbf{u} \cdot \nabla)\mathbf{H} - (\mathbf{H} \cdot \nabla)\mathbf{u} + \mathbf{H}(\nabla \cdot \mathbf{u}) = 0\,, \tag{2.4}$$

$$\varrho\mathbf{u} \cdot \nabla h - \mathbf{u} \cdot \nabla p = 0, \tag{2.5}$$

where p, H and h are respectively the pressure, magnetic field vector and the enthalpy which for the dissociating gas mixture is given by a functional relation of the form:

$$h = h(p, \varrho, \alpha_i)\,. \tag{2.6}$$

A simple dissociating gas is defined as a gas mixture resulting from a dissociation reaction in a symmetrical diatomic gas A_2, each A_2 molecule being made up from two A_1 atoms. The reaction is

$$A_2 + A_3 \underset{K_r}{\overset{K_f}{\rightleftarrows}} 2A_1 + A_3 \,,$$

where the species A_3 can be either A_2 or A_1 and K_f and K_r are the reaction rate constants for the forward and reverse reactions. The thermal equation of state for a simple dissociating gas is given by [8]

$$p = (1 + \alpha)\varrho RT, \tag{2.7}$$

where T, α and R are respectively the temperature, atom mass fraction or the degree of dissociation and the gas constant for A_2. A flow in which α remains constant, is said to be frozen.

Eq. (2.6) for a simple dissociating gas under our simplifying assumptions, can be written as [9]

$$h = \left\{\frac{7}{2} + \frac{3}{2}\alpha + \frac{T_v}{T}(1-\alpha)\left(\exp\left(\frac{T_v}{T}\right) - 1\right)^{-1}\right\} RT + \alpha D \,,$$

where T_v and D are the characteristic temperature for vibration and dissociation energy per unit mass, respectively. For LIGHTHILL's ideal dissociating gas model the above equation reduces to the form:

$$h = (4 + \alpha)RT + \alpha D \,, \tag{2.8}$$

and the continuity equation (2.1) can be written as [10]

$$\mathbf{u}\cdot\nabla\alpha = \frac{4\varrho D^2 K_r(1+\alpha)}{R^2 T_d^2}\left\{\varrho_d(1-\alpha)\exp\left(-\frac{T_d}{T}\right) - \varrho\alpha^2\right\}, \tag{2.9}$$

where T_d and ϱ_d are respectively the characteristic temperature and characteristic density for dissociation defined by LIGHTHILL [1]. Although ϱ_d is a function of T, it has been seen that the variation of ϱ_d over the temperature range 1000 °K ~ 7000 °K is very slight. Hence for practical purposes the useful simplifications of regarding ϱ_d as a constant should lead to negligible errors. This approximation will be made throughout the whole analysis.

Using (2.2), (2.3), (2.7), (2.8) and (2.9) in (2.5) we get

$$\mathbf{u}\cdot\nabla p + \varrho a_f^2\,\nabla\cdot\mathbf{u} = \frac{4\varrho K_r D^2}{3R^2 T_d^2}\{3p - \varrho D(1+\alpha)^2\}\cdot$$

$$\cdot\left\{\varrho_d(1-\alpha)\exp\left(-\frac{T_d}{T}\right) - \varrho\alpha^2\right\}, \tag{2.10}$$

where a_f is the frozen speed of sound given by

$$a_f^2 = -\varrho\left(\frac{\partial h}{\partial \varrho}\right)_{p,\alpha} \Bigg/ \left\{\varrho\left(\frac{\partial h}{\partial p}\right)_{\varrho,\alpha} - 1\right\}.$$

3. Flow variations behind a shock

We assume that the shock surface is analytic and all the flow variables are continuously differentiable over the shock surface. The orientation of the shock surface is specified at any point by the unit normal vector **n**, which is assumed to be differentiable along the surface. The geometrical configuration of the shock surface can be represented by $\mathbf{r} = \mathbf{r}(y^{\mathrm{I}}, y^{\mathrm{II}})$, where $y^{\beta}(\beta = \mathrm{I}, \mathrm{II})$ are the Gaussian coordinates. We shall now consider all vector quantities decomposed in a form with respect to the shock surface into a normal component and a two dimensional tangential vector. Thus the Eqs. (2.2)—(2.4) and (2.10) can be written in the following forms:

$$\varrho\mathbf{n}\cdot(\mathbf{n}\cdot\nabla)\mathbf{u} + \varrho\nabla_t\cdot\mathbf{u} + u_n(\mathbf{n}\cdot\nabla)\varrho + \mathbf{u}_t\cdot\nabla_t\,\varrho = 0\,, \tag{3.1}$$

$$\varrho u_n\,(\mathbf{n}\cdot\nabla)\mathbf{u} + \varrho(\mathbf{u}_t\cdot\nabla_t)\,\mathbf{u} + \mathbf{n}(\mathbf{n}\cdot\nabla)p + \frac{1}{8\pi}\mathbf{n}(\mathbf{n}\cdot\nabla)H^2 +$$

$$\nabla_t\left(p + \frac{H^2}{8\pi}\right) - \frac{1}{4\pi}\{H_n(\mathbf{n}\cdot\nabla)\mathbf{H} + (\mathbf{H}_t\cdot\nabla_t)\mathbf{H}\} = 0\,, \tag{3.2}$$

$$u_n(\mathbf{n}\cdot\nabla)\mathbf{H} + (\mathbf{u}_t\cdot\nabla_t)\mathbf{H} - H_n(\mathbf{n}\cdot\nabla)\mathbf{u} - (\mathbf{H}_t\cdot\nabla_t)\,\mathbf{u} + \{\mathbf{n}\cdot(\mathbf{n}\cdot\nabla)\mathbf{u} + \nabla_t\cdot\mathbf{u}\}\mathbf{H} = 0, \tag{3.3}$$

$$u_n(n\cdot\nabla)p + \varrho a_f^2\,\mathbf{n}\cdot(\mathbf{n}\cdot\nabla)\mathbf{u} + \varrho a_f^2\,\nabla_t\cdot\mathbf{u} + \mathbf{u}_t\cdot\nabla_t\,p =$$

$$\frac{4\varrho\,D^2\,K_r}{3R^2\,T_d^2}\,\{3p - \varrho D(1+\alpha)^2\}\left\{\varrho_d(1-\alpha)\exp\left(-\frac{T_d}{T}\right) - \varrho\alpha^2\right\}, \tag{3.4}$$

where the subscript t on the nabla operator indicates that only the tangential part of the derivative is included and

$$U_n = \mathbf{u}\cdot\mathbf{n},\quad H_n = \mathbf{H}\cdot\mathbf{n},\quad \mathbf{u}_t = \mathbf{n}\times(\mathbf{u}\times\mathbf{n}),\quad \mathbf{H}_t = \mathbf{n}\times(\mathbf{H}\times\mathbf{n}).$$

The fundamental system of equations for the discontinuity in an ideal dissociating MGD flow is [11]

$$\varrho_1 u_{1n}\left[\left(\frac{4+\alpha}{1+\alpha}\right)\frac{p}{\varrho} + \alpha D + \frac{1}{2}\mathbf{u}^2 + \frac{1}{4\pi\varrho}\mathbf{H}_t^2\right] = H_{1n}[\mathbf{H}_t\cdot\mathbf{u}_t]/4\pi\,, \tag{3.5}$$

$$[p] + \varrho_1\,u_{1n}\,[u_n] + [\mathbf{H}_t^2]/8\pi = 0, \tag{3.6}$$

$$\varrho_1\,u_{1n}\,[\mathbf{u}_t] = H_{1n}\,[\mathbf{H}_t]/4\pi\,, \tag{3.7}$$

$$H_{1n}[\mathbf{u}_t] = [u_n\,\mathbf{H}_t]\,, \tag{3.8}$$

where the square bracket denotes the jump in the quantity enclosed across the discontinuity i.e. $[z] = z - z_1$, where $z(z_1)$ are the values of z evaluated just downstream (upstream) of the discontinuity surface. We define the density strength δ of the discontinuity by the relation $\delta = [\varrho]/\varrho_1$. Then, using the conditions $[\varrho u_n] = 0$ and $[H_n] = 0$ in (3.6)—(3.8) we get

$$\begin{aligned}
[\mathbf{u}_t] &= \delta(4\pi\,\varrho_1\,u_{1n}^2 - \delta H_{1n}^2 - H_{1n}^2)^{-1} H_{1n}\,u_{1n}\,\mathbf{H}_{1t}\,,\\
[\mathbf{H}_t] &= 4\pi\delta(4\pi\varrho_1\,\mathbf{u}_{1n}^2 - \delta H_{1n}^2 - H_{1n}^2)^{-1}\varrho_1\,u_{1n}^2\,\mathbf{H}_{1i}\,,\\
\left[p + \frac{\mathbf{H}_t^2}{8\pi}\right] &= \delta(1+\delta)^{-1}\varrho_1\,\mathbf{u}_{1n}^2\,, \qquad (3.9)\\
[u_n] &= -\,\delta(1+\delta)^{-1}\,u_{1n}\,.
\end{aligned}$$

The strength δ of the shock can be determined either by optical methods such as the Toepler Schlieren technique or in terms of the flow parameters just infront of the shock and the degree of dissociation α by using (3.9) in (3.5). Also, from (3.9), we obtain

$$[\mathbf{u}] = -\,\delta(1+\delta)^{-1}\,u_{1n}\,\mathbf{n} + \delta(4\pi\varrho_1\,u_{1n}^2 + H_{1n}^2 - \delta H_{1n}^2)^{-1}\,u_{1n}\,H_{1n}\,\mathbf{H}_{1t}\,. \qquad (3.10)$$

$$[\mathbf{H}] = 4\pi\varrho_1\,u_{1n}^2\,\delta(4\pi\varrho_1\,u_{1n}^2 - H_{1n}^2 - \delta H_{1n}^2)^{-1}\,\mathbf{H}_{1t}\,. \qquad (3.11)$$

If we suppose that the flow upstream from the shock is uniform and known, we have

$$\nabla_t\,u_{1n} = -\,K\cdot\mathbf{u}_{1t},\quad \nabla_t\,H_{1n} = -\,K\cdot\mathbf{H}_{1t}\,, \qquad (3.12)$$

where K is the curvature tensor of the shock surface. Keeping in view our assumption on the upstream flow and using (3.12) we can easily obtain the ∇_t-derivatives of flow variables at the rear of the shock surface is terms of the known parameters [12].

By virtue of (3.2), (3.3) and (3.4), we obtain

$$\begin{aligned}
\mathbf{n}\cdot\nabla H^2 = {} & \frac{2}{u_n\,M_f^2}\{H_n^2(1 - M_f^2) - M_f^2\,\mathbf{H}_t^2\}\{\mathbf{n}\cdot(\mathbf{n}\cdot\nabla)\,\mathbf{u} + \nabla_t\cdot\mathbf{u}\} + \\
& + \frac{2}{u_n}\{\mathbf{H}\cdot(\mathbf{H}_t\cdot\nabla_t)\,\mathbf{u} - \mathbf{H}\cdot(\mathbf{u}_t\cdot\nabla_t)\,\mathbf{H}\} + \qquad (3.13)\\
& + \frac{2H_n}{\varrho u_n^2}\left\{\frac{H_n}{u_n}(F + \mathbf{u}_t\cdot\nabla_t p)\,\nabla - \varrho\mathbf{H}\cdot(\mathbf{u}_t\cdot\nabla_t)\,\mathbf{u} - \mathbf{H}_t\cdot\nabla_t\,p\right\},\\
& \equiv \nu \text{ (say)},
\end{aligned}$$

where

$$M_f = u_n/a_f$$

and

$$F = \frac{4\varrho D^2\,Kr}{3R^2\,T_d^2}\{\varrho D\,(1+\alpha)^2 - 3p\}\left\{\varrho_d(1-\alpha)\exp\left(-\frac{T_d}{T}\right) - \varrho\alpha^2\right\}.$$

Now, taking dot product of (3.2) with $\mathbf{n}$ and using (3.4) and (3.13), we get

$$\begin{aligned}\mathbf{n}\cdot(\mathbf{n}\cdot\nabla)\mathbf{u} = {} & \frac{1}{4\pi\mu u_n}\left\{\left(H^2+\frac{\lambda}{M_f^2}\right)\nabla_t\cdot\mathbf{u}+\frac{\lambda}{\varrho u_n^2}(F+\mathbf{u}_t\cdot\nabla_t p)+\right.\\ & +\mathbf{H}\cdot(\mathbf{u}_t\cdot\nabla_t)\mathbf{H}-\mathbf{H}\cdot(\mathbf{H}_t\cdot\nabla_t)\mathbf{u}-4\pi\varrho u_n\,\mathbf{n}\cdot(\mathbf{u}_t\cdot\nabla_t)\mathbf{u}+\\ & \left.+\frac{H_n}{\varrho u_n}\mathbf{H}_t\cdot\nabla_t p+\frac{H_n}{u_n}\mathbf{H}\cdot(\mathbf{u}_t\cdot\nabla_t)\mathbf{u}\right\},\\ \equiv {} & \beta \quad \text{(say)},\end{aligned} \tag{3.14}$$

where $\mu=(4\pi u_n M_f^2)^{-1}\,\{\lambda(M_f^2-1)-M_f^2H_t^2\}$

and $\lambda=4\pi\varrho u_n^2-H_n^2\,.$

The equation (3.14) determines the value of $\mathbf{n}\cdot(\mathbf{n}\cdot\nabla)\mathbf{u}$ in terms of the shock geometry and the flow just infront of the shock. The quantities which can be expressed in terms of the shock geometry and the flow parameters just ahead of the shock, will be understood as effectively calculated, because such quantities depend only on the shape and strength of the shock and flow conditions upstream from the shock [13]. If we substitute from (3.14) in (3.13), we get the effective determination of $\mathbf{n}\cdot\nabla H^2(\equiv\nu)$. Using (3.14) in (3.4) and (3.1) we get

$$\mathbf{n}\cdot\nabla p=-\frac{1}{u_n}(\varrho\beta a_f^2+\varrho a_f^2\nabla_t\cdot\mathbf{u}+\mathbf{u}_t\cdot\nabla_t p+F)\,, \tag{3.15}$$

$$\mathbf{n}\cdot\nabla\varrho=-\frac{1}{u_n}(\varrho\beta+\mathbf{u}\cdot\nabla_t\varrho+\varrho\nabla_t\cdot\mathbf{u})\,. \tag{3.16}$$

From (3.2) and (3.3) we get

$$\begin{aligned}(\mathbf{n}\cdot\nabla)\mathbf{u} = {} & \frac{1}{\lambda}\left\{4\pi\left(\varrho\beta a_f^2-\frac{\nu u_n}{8\pi}+\varrho a_f^2\nabla_t\cdot\mathbf{u}+\mathbf{u}_t\cdot\nabla_t p+F\right)\mathbf{n}+H_n(\mathbf{H}_t\cdot\nabla_t\mathbf{u}-\right.\\ & -\mathbf{u}_t\cdot\nabla_t\mathbf{H}-\mathbf{H}\nabla_t\cdot\mathbf{u}-\beta\mathbf{H})+u_n\,\mathbf{H}_t\cdot\nabla_t\mathbf{H}-4\pi\varrho u_n\,\mathbf{u}_t\cdot\nabla_t\mathbf{u}-\\ & \left.-4\pi\,u_n\nabla_t(p+H^2/8\pi)\right\},\end{aligned} \tag{3.17}$$

$$\begin{aligned}(\mathbf{u}\cdot\nabla)\mathbf{H} = {} & \frac{1}{\lambda}\left\{4\pi\varrho u_n(\mathbf{H}_t\cdot\nabla_t\mathbf{u}-\mathbf{u}_t\cdot\nabla_t\mathbf{H}-\mathbf{H}\nabla_t\cdot\mathbf{u}-\beta\mathbf{H})-\right.\\ & -H_n\,\mathbf{H}_t\cdot\nabla_t\mathbf{H}-4\pi H_n\nabla_t\left(p+\frac{H^2}{8\pi}\right)-4\pi\varrho H_n\,\mathbf{u}_t\cdot\nabla_t\mathbf{u}+\\ & \left.+\frac{4\pi H_n}{u_n}\left(\varrho\beta a_f^2+\varrho a_f^2\nabla_t\cdot\mathbf{u}+\mathbf{u}_t\cdot\nabla_t p-\frac{\nu u_n}{8\pi}+F\right)\mathbf{n}\right\}.\end{aligned} \tag{3.18}$$

Thus Eqs. (3.15)—(3.18) determine the variations of flow and field parameters in the direction of propagation of the shock.

4. Determination of the curvature of stream lines

If $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$ are the unit tangent and normal vectors respectively to a stream line, then we have

$$k\boldsymbol{\eta} = \frac{1}{u}(\mathbf{u}\cdot\nabla)\boldsymbol{\xi}, \tag{4.1}$$

where $u^2 = \mathbf{u}\cdot\mathbf{u}$ and $\boldsymbol{\xi} = \mathbf{u}/u$.

In consequence of (4.1), we get

$$k^2 = u^{-4}\{\mathbf{b}^2 - u^{-2}(\mathbf{u}\cdot\mathbf{b})^2\}, \tag{4.2}$$

where $\mathbf{b} = u_n(\mathbf{n}\cdot\nabla)\mathbf{u} + (\mathbf{u}_t\cdot\nabla_t)\mathbf{u}$.

The value of $(\mathbf{n}\cdot\nabla)\mathbf{u}$ in terms of effectively calculated quantities is given by Eq. (3.17) and $(\mathbf{u}_t\cdot\nabla_t)\mathbf{u}$ is obviously an effectively calculated quantity. Thus Eq. (4.2) effectively determines the curvature of a stream line at the rear of the shock surface.

5. Vorticity and current density generated by the shock

The vorticity vector $\boldsymbol{\omega}$ and the current density vector $\mathbf{J}$ can be written as

$$\boldsymbol{\omega} = \mathbf{n}\times(\mathbf{n}\cdot\nabla)\mathbf{u} + \nabla_t\times\mathbf{u};\quad 4\pi\mathbf{J} = \mathbf{n}\times(\mathbf{n}\cdot\nabla)\mathbf{H} + \nabla_t\times\mathbf{H}. \tag{5.1}$$

Taking cross product of (3.17) and (3.18) with $\mathbf{n}$ and using (5.1) we get

$$\begin{aligned}\boldsymbol{\omega} = \mathbf{n}\times\frac{1}{\lambda}\{&H_n(\mathbf{H}_t\cdot\nabla_t\mathbf{u} - \mathbf{u}_t\cdot\nabla_t\mathbf{H} - \mathbf{H}_t\nabla_t\cdot\mathbf{u} - \beta\mathbf{H}_t) + u_n\mathbf{H}_t\cdot\nabla_t\mathbf{H} - \\ &- 4\pi\varrho u_n\mathbf{u}_t\cdot\nabla_t\mathbf{u} - 4\pi u_n\nabla_t(p + H^2/8\pi)\} + \nabla_t\times\mathbf{u},\end{aligned} \tag{5.2}$$

$$\begin{aligned}\mathbf{J} = \nabla_t\times\mathbf{H} + \boldsymbol{\eta}\times\frac{1}{\lambda}\Big\{&H_n\mathbf{H}_t\cdot\nabla_t\mathbf{H} - 4\pi H_n\nabla_t(p + H^2/8\pi) - 4\pi\varrho H_n\mathbf{u}_t\cdot\nabla_t\mathbf{u} + \\ &4\pi\varrho u_n(\mathbf{H}_t\cdot\nabla_t\mathbf{u} - \mathbf{u}_t\cdot\nabla_t\mathbf{H} - \mathbf{H}_t\nabla_t\cdot\mathbf{u} - \beta\mathbf{H}_t)\}.\end{aligned} \tag{5.3}$$

Eqs. (5.2) and (5.3) effectively determine the vorticity and current density generated by an oblique hydromagnetic shock in a steady flow of an ideal dissociating gas. When the magnetic field is acting along the direction of propagation, the derivation of vorticity and current density generated by a shock of given strength is independent of the thermodynamical behaviour of the fluid. Hence, from (5.2) and (5.3) we arrive at the following conclusions:

The generation of vorticity and current density behind a hydromagnetic shock in dissociating gas flows will, in general, depend on the dynamical as well as thermodynamical behaviour of the gas flow. The effects of dissociation on the generation of vorticity and current density vanish, if the magnetic field is acting in the direction of propagation of the shock.

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REFERENCES

1. M. J. LIGHTHILL, J. Fluid Mech., **2,** Pt. 1, 1957.
2. N. C. FREEMAN, J. Fluid Mech., **4,** 405, 1958.
3. M. EPSTEIN, J. Aerospace Sci., **28,** 664, 1961.
4. R. CAPIAUX and W. WASHINGTON, J. AIAA, **1,** 650, 1963.
5. C. T. HSU, J. Aerospace Sci., **27,** 821, 1961.
6. C. T. HSU and J. E. ANDERSON, J. AIAA, **1,** 1789, 1963.
7. S. R. DE GROOT, and P. MAZUR, Non-equilibrium Thermodynamics, North Holland Publishing Company, Amsterdam, 1963.
8. LIEPMANN and ROSKO, Elements of gasdynamics, John Wiley and Sons, Inc, New York, 1960.
9. T. Y. LI, Recent Advances in Non-equilibrium Dissociating Gas Dynamics, ARS Journal, 1961.
10. J. F. CLARKE, J. Fluid Mech., **7,** pt. 4, pp. 577–595, 1960.
11. L. D. LANDAU and E. M. LIFSHITZ, Electrodynamics of Continuous Media, Pergamon Press, New York, 1960.
12. R. RAM, J. Math. Mech. **18,** no. 1, pp. 11–20, 1968.
13. R. RAM and V. D. SHARMA, TENSOR, N. S., **22,** No. 1, pp. 1–5, 1971.

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APPROXIMATIVE METHODS IN THE SEMICLASSICAL THEORY OF MULTIPHOTON PROCESSES

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The present work aims at giving a theoretical background for the several theoretical methods existing in the literature describing multiphoton processes. Within the framework of the semiclassical theory a general expression for the multiphoton transition probability is given — using the formal time-dependent theory of scattering and the general properties of the Schrödinger equation of the problem. The amplitude of the multiphoton transition is a generalisation of the stationary transition operator for the non-stationary case. Using the general expression of the transition probability we compare the different non-perturbative approaches with the perturbation theory and establish the limits of their applicability.

1. In recent years a great theoretical interest has developed in the description of processes involving many photons in one transition in connection with the development of powerful light sources and detection techniques. Although perturbation theory has become fully accepted in semiclassical electrodynamics, its applicability to the non-linear interaction of very intense radiation with matter is doubtful. Due to the known difficulties of perturbation theory some other methods — essentially based on non-perturbative approaches — have been worked out during the development of the theory. The most promising of these methods are the different kinds of quasiclassical (WKB) approximations. In these approximations one must perform a one-step perturbation theoretical calculation for the transition probability between such states that in one of them — under certain conditions — the influence of the external field is properly taken into account. This state may be the initial (bound) as well as the final (free) state. The purpose of the present paper is to provide a general theoretical background for these methods and to make a comparison between their results.

2. In the semiclassical electrodynamics of bound systems the Hamiltonian reads:

$$H = H_0 + H',$$

where

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \tag{1.a}$$

is the atomic Hamiltonian, without external field. $H'(t)$ is the interaction term between the atom and the external field. We always introduce the dipole approximation in this term, i.e. we may always neglect the spatial variation of the field. The form of $H'(t)$ may be further specialized by using either the vector potential (with the gauge div $A = A^0 = 0$) or the scalar potential ($A = 0$). The interaction Hamiltonian in the first case is

$$H_1' = -\frac{e}{mc} Ap + \frac{e^2}{2mc^2} A^2 , \tag{1.b}$$

while in the second case

$$H_2' = -eEx . \tag{1.c}$$

In the dipole approximation (when E and A depend only upon the time) the transition from $H_1'(t)$ to $H_2'(t)$ may be established by a unitary transformation; furthermore, the perturbation series in terms of H_1' transform into the appropriate series of H_2'. We have therefore concluded that the results do not depend on the specific form of the interaction Hamiltonian.

The Schrödinger equation of the field-free problem can be written as

$$i\hbar \frac{\partial \psi_i^{(0)}}{\partial t} = H_0 \psi_i^{(0)} , \tag{2.a}$$

where the subscript i denotes the i-th eigenstate of H_0. For an atom in the presence of an external field

$$i\hbar \frac{\partial \psi_i}{\partial t} = H \psi_i . \tag{2.b}$$

In our case the total Hamiltonian changes periodically in time: $H(t+T) = H(t)$, where $T = 2\pi/\omega$ is the frequency of the external field. From group theoretical considerations [1] we then obtain a general solution of the following form:

$$\psi_i(x, t) = \exp\left\{-\frac{i}{\hbar} \varepsilon_i t\right\} u_i(x, t) , \tag{3.a}$$

where for $u_i(x, t)$ the following relation holds

$$u_i(t) = u_i(t+T) \tag{3.b}$$

and ε_i is the so-called quasi-energy. The initial condition for (3.a) is $\psi_i(t) \to \psi_i^{(0)}(t)$ if $t \to -\infty$. The definition of the quasi-energy is unambiguous up to an additive term of $n\omega\hbar$. If we require $\varepsilon_i \to E_i^0$ (the eigenenergy of (2.a)) when $H' \to 0$, then ε_i is defined unambiguously.

3. The usual way of defining the transition probability between field-free states is related to the expansion of ψ_i given as a power series of H' in terms of $\psi_n^{(0)}$. If our solution of (2.b) together with the proper initial conditions

is non-perturbative we need an extension of the definition of the n-photon transition probability (without referring to the appropriate order of the perturbation series). This extension will be carried out in the following using the language of the time-dependent scattering theory. ψ_i satisfies the following integral equation:

$$\psi_i(t) = \psi_i^{(0)}(t) + \int_{-\infty}^{\infty} dt'\, G_0^+(t-t')\, H'(t')\, \psi_i(t') \,. \qquad (4)$$

Here $G_0^+(t-t')$ is the retarded Green's function of equation (2.a) and the index i refers to the initial condition, i. e. in the limit $t \to -\infty$, $\psi_i(t) \to \to \psi_i^{(0)}(t)$ represents the i-th stationary solution of (2.a). The upper limit of the integration in (4) is clearly t due to retardation. Using adiabatic switching of the perturbation the set of in and out states is the same. By definition the scattering operator S describes all the possible transitions from a given state under the influence of an external field. The matrix element of S between two states i and f gives the transition between these states. On the other hand, this must coincide with the expansion of (4) in terms of the out states [2]:

$$S_{fi} = (\psi_f^{(0)}\, S\psi_i^{(0)}) = \lim_{t\to\infty} \left(\psi_f^{(0)}(t)\, \psi_i(t)\right) = \left(\psi_f^{(0)}(t), \psi_i^{(0)}(t)\right) +$$

$$+ \lim_{t\to\infty} \int_{-\infty}^{\infty} dt' \left(\psi_f^{(0)}(t)\, G_0^+(t-t')\, H'(t')\, \psi_i(t')\right) = \delta_{fi} -$$

$$- \frac{i}{\hbar} \int_{-\infty}^{\infty} dt' \psi_f^{(0)}(t') H'(t')\, \psi_i(t')). \qquad (5)$$

Here we have made use of expression (4) and the connection between the retarded Green's functions and the time development operator. The first term on the right hand side corresponds to the trivial transition. As a consequence we identify the second term with the amplitude of non-trivial transitions:

$$(S-1)_{fi} = -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt' \left(\psi_f^{(0)}(t')\, H'(t')\, \psi_i(t')\right). \qquad (6)$$

Substituting into (6) the expression (3.a) both $u_i(x, t)$ and $H'(t)$ depend periodically on time and the periodically changing part of the integrand can be expanded into Fourier series of $\exp\{in\omega t\}$ and we denote the full coefficient of the individual $\exp\{in\omega t\}$ terms by $T_{ji}^{(n)}$. After performing the time integration in (6) we get the following expression:

$$(\psi_f^{(0)}(S-1)\, \psi_i^{(0)}) = -2\pi i \sum_{n=-\infty}^{\infty} T_{fi}^{(n)}\, \delta(E_f - \varepsilon_i + n\hbar\omega) \,. \qquad (7)$$

The physical meaning of this expression is clear — from a state which develops in time under the influence of an external field the transition into another state is a one step process due to a first-order perturbation. (7) may be regarded as a generalisation of the stationary theory of scattering where $(S-1)_{fi} = -2\pi i T_{fi}\delta(E_f - E_i)$ is the corresponding formula. In the stationary case the following property of the transition operator T is valid:

$$T_{fi} = \begin{cases} (\psi_f^{(0)} H' \psi_i^{(+)}) , \\ (\psi_f^{(-)} H' \psi_i^{(0)}) , \end{cases} \tag{8.a}$$

where $\psi_f^{(+)}$ and $\psi_f^{(-)}$ are exact solutions of Eq. (2.6) with different initial conditions: $\psi_i^{(+)}(t \to -\infty) = \psi_i^{(0)}$ and $\psi_f^{(-)}(t \to \infty) = \psi_f^{(0)}$ [3]. This symmetry property of the transition operator with respect to the initial and final states also holds for the non-stationary case, in addition to all the partial amplitudes (8.a) being fulfilled:

$$T_{fi}^{(n)} = \begin{cases} (\psi_f^{(0)} H' \psi_i^{(+)})^{(n)} , \\ (\psi_f^{(-)} H' \psi_i^{(0)})^{(n)} . \end{cases} \tag{8.b}$$

Finally we give the expression for the multiphoton transition probability per unit time between $\psi_i^{(0)}$ and $\psi_f^{(0)}$

$$w_{fi} = \frac{2\pi}{\hbar} \sum_{n=-\infty}^{\infty} |T_{fi}^{(n)}|^2 \, \delta(E_f - \varepsilon_i + n\hbar\omega) . \tag{9}$$

The term proportional to $\delta(E_f - \varepsilon_i + nhw)$ will then be regarded by definition as the n-photon transition probability. By using the second equation of (8.b) the symmetric counterpart of (9) can be achieved. That is, we have arrived at a simple formal analogue of the perturbation theoretical definition of the transition probability. However, in this expression instead of the intensity of the external field we have an expansion in terms of the number of absorbed or emitted photons, which agrees better with the concept of multiphoton transitions.

4. In this Section we give a short discussion of methods by which one can obtain a solution of Eqs. (2.b) or (4) which is valid at least in a limited range of parameters (intensity and frequency). The best known of these methods is the standard perturbation theory [4]. The word 'standard' is used in the following sense:

a) the basis is the complete set of H_0 eigenfunctions (unperturbed spectrum);

b) the calculation of matrix elements is restricted to the first non-vanishing approximation;

c) the final state is always unperturbed by the external field and it is either a continuum state (in the case of ionization), or a bound state (in the case of excitation). We may assume that at least in the range where the external field intensity is much less than the intra-atomic field the perturbation series converge, apart from the resonances in intermediate states. However, with increasing external field there is a need for solutions other than the perturbation theoretical one. The first of the solutions of this type was given by KELDYSH [5]. In this work the final state problem is solved in the following way. The free state of the electron is described by a plane wave in a homogeneous external electric field and the effect of the atomic Coulomb potential as well as transitions in discrete spectrum are completely ignored. Due to this, the wave function under consideration and the results are appropriate only for the ionization problem of negative and molecular ions in which case the remainder of the target is neutral. The further development of this theory made it possible to consider the effect of the atomic potential [6] and polarizations other than the linear one [7]. The discrete spectrum has an essential influence on the process when intermediate resonances take place i.e. if $E_2(\varepsilon) - E_1(\varepsilon) - n\hbar\omega < \gamma_{1,2}(\varepsilon)$ where $E_{1,2}(\varepsilon)$; $\gamma_{1,2}(\varepsilon)$ are energy and width of the bound levels 1; 2 in the presence of an external field and we assume that $1 \to 2$ is an allowed transition in dipole approximation. Within the framework of the KELDYSH theory the role of resonances is the following [8]: a given final state can be produced from intermediate bound states, this is particularly true if the transitions between bound states are of resonant character.

There is another non-perturbative method existing in the literature: the momentum translation approximation (MTA) of REISS [9]. This is based on an idea similar to that of KELDYSH i.e. one has an approximative solution to the initial state problem in the following from

$$\psi_i^{(+)} \approx \exp\left\{\frac{i}{\hbar}\,\frac{e}{c}\,Ax\right\}\psi_i^{(0)}\,.$$

Taking into consideration (8.b) we can state the principal equivalence of the solutions to the initial and the final state problem. However, as it was pointed out in [10] there are some principal difficulties intrinsic in this last solution because it corresponds to a unitary transformation between two different representations of the external field, i.e. the description with vector and scalar potentials, respectively.

Finally, the present state of the theory enables us to conclude that the KELDYSH theory and its further development seems to be satisfactory at extremely high intensities but there is a lack of theoretical results in the transition range which has been achieved experimentally up to now — where the atomic and external fields are of the same order.

REFERENCES

1. Ja. B. Zel'dovich, Uspekhi Fiz. Nauk, **110,** 139, 1973; A. I. Baz, Ja. B. Zel'dovich and A. M. Perelemov, Scattering, Reaction and Decay in Nonrelativistic Quantum Mechanics, Nauka, Moscow, 1971 (in Russian).
2. R. G. Newton, Scattering Theory of Waves and Particles, McGraw-Hill, New York, 1966.
3. A. S. Davydov, Kvantovaya mekhanika, Fizmatgiz, Moscow, 1974.
4. Y. Gontier and M. Trahin, Phys. Lett., **36**A, 463, 1971.
5. L. V. Keldysh, Zh. Exp. Teor. Fiz., **47,** 1945, 1964.
6. A. M. Perelomov, V. S. Popov and M. V. Terentiev, Zh. Exp. Teor. Fiz., **50,** 1393, 1966; ibid. **51,** 309, 1966; ibid. **52,** 514, 1967.
7. A. I. Nikishov and V. I. Ritus, Zh. Exp. Teor. Fiz., **50,** 255, 1966; ibid. **52,** 233, 1967.
8. L. P. Kotova and M. V. Terentiev, Zh. Exp. Teor. Fiz., **52,** 732, 1967.
9. H. R. Reiss, Phys. Rev., A**1,** 903, 1970; Phys. Rev. Letts., **25,** 1149, 1970; Phys. Rev., D**4,** 3533, 1971.
10. C. Cohen-Tannoudji, J. Dupont-Roc, C. Fabre, G. Grynberg, Phys. Rev., A**8,** 2747, 1973.

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ON THE PREDICTION OF SELFDEPOLARIZATION OF PHOTOLUMINESCENCE IN TWO-DIMENSIONAL SYSTEMS

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Based on the theory of concentrational depolarization of photoluminescence (CDPL) worked out for three-dimensional systems [8] an extension has been made for two-dimensional systems. In the theory the excitation energy remigration and photoluminescence quenching by non-luminescent dimers have been taken into account as well. The expression obtained for emission anisotropy has been compared with the experimental results of Trosper et al. [18] concerning CDPL of chlorophyll-a in two dimensional solutions. Good agreement of theory with experiment has been found for the values of critical distances $\overline{R}_0$ smaller than those obtained in [18] as upper limits.

1. Introduction

The investigation of CDPL in two-dimensional systems is important with regard to the pieces of information available as far as the process of electronic migration of excitation energy in photosynthetic systems is concerned [1—3]. Recently Craver [4] has worked out a CDPL theory for two-dimensional systems. This theory extends those worked out by Förster [5], Ore [6] and Knox [7] to three-dimensional systems. None of the above mentioned theories considers photoluminescence concentrational quenching and for that reason they can be applied merely in such a range of concentration in which PL-quantum yield decrease is not observed.

Not long ago a new theory of CDPL for three-dimensional systems was worked out by one of us [8], taking into account PL quenching by non-luminescent dimers as well as excitation energy remigration.

In the present work theoretical results are presented concerning the CDPL phenomenon in two-dimensional systems as an extension of the above mentioned theory of CDPL for three-dimensional systems. Apart from excitation energy remigration PL concentrational quenching has also been taken into account.

2. Photoluminescence emission anisotropy

Let us assume that: 1. In a two-dimensional non-active medium of a finite surface S only two kinds of active molecules appear: that is monomers D and dimers $D_{||}$ at which the mass action law is satisfied

$$c'' = Kc'^2, \tag{1}$$

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where K is the dimerization constant, c' and c'' are concentrations monomers D and dimers $D_{||}$, respectively. 2. The distribution of D and $D_{||}$ molecules is random with regard to their position and to the orientations of their transition moments. 3. No rotational depolarization occurs. 4. Only monomers D_0 primarily excited by light absorption contribute to the anisotropy of the luminescence observed [9—11]. 5. Molecules D_0 can lose their excitation energy as a result of: a) PL-emission (relative probability P_F), b) inner quenching (P_q), c) non-radiative excitation energy transfer to monomer D (P_{DD}) and d) non radiative excitation transfer to dimer $D_{||}$ ($P_{DD_{||}}$), at which

$$P_F + P_q + P_D + P_{DD_{||}} = 1. \tag{2}$$

Similarly as molecules D_0 also molecules D, excited owing to non-radiative energy transfer, can lose their energy.[1] In order to take into account the effect of energy remigration on emission anisotropy (EA) a model of luminescence centre has been applied — called later on a model of most probable path (MPP) [8, 13]. It has been assumed that the excitation energy located primarily at the molecule D_0 can be transferred in a non-radiative way among molecules D_0, $D_1, \ldots D_n$, where D_1 is the nearest neighbour of D_0 and D_k the nearest neighbour of D_{k-1}, unless molecule D_{k-2} is a still nearer neighbour for D_{k-1}. Molecules D_0 and D_n are the beginning and the end of the group, respectively. They play a role of "reflecting screens" at which molecule D_0 is in our model a totally reflecting screen whereas molecule D_n can be a totally or a partially reflecting one. In the latter case excitation energy can leave the group and pass to molecule D_{n+1} having no way back (D_{n+1} does not belong to the group).[2]

According to assumption 4. the PL-emission anisotropy can be calculated from relation

$$\frac{r}{r_0} = \frac{\eta_{(0)}}{\eta}, \tag{3}$$

where $\eta_{(0)}$ denotes the PL quantum yield of molecules D_0 and

$$\eta = \sum_{m=0} \eta^{(m)} \tag{4}$$

the PL-yield of the whole solution. Yield $\eta_{(0)}$ can be presented in the form [8, 13]:

$$\eta_{(0)} = \eta^{(0)} + \sum_{m=2}^{\infty} h_m \, \eta^{(m)}, \tag{5}$$

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[1] A possibility of the excitation of molecules D as a result of fluorescence light reabsorption is not considered. The effect of reabsorption can be neglected in the case of sufficiently thin layers of the luminescent substance [12]. Thus the neglecting of reabsorption in the case of two-dimensional systems is fully justified.

[2] More information as to the MPP model can be found in [8, 13].

where $\eta^{(m)}$ is the PL-quantum yield of molecules $D^{(m)}$ of order m that is of such which obtained excitation energy after m non-radiative transfers; coefficients h_m determine the contribution of the yield $\eta^{(m)}$ in $\eta_{(0)}$, at which $\eta^{(m)}$ is determined by relation [14]:

$$\eta^{(m)} = P_F[P_{DD}]^m. \tag{6}$$

For a probability of P_F and P_{DD} for two-dimensional systems the expressions given below have been recently obtained:

$$P_F = \eta_0[1 - F(g)], \tag{7}$$

$$P_{DD} = \frac{g_D}{g} F(g), \tag{8}$$

where

$$F(g) = g \int_0^\infty \exp\left[-(z^3 + gz)\right] dz\,, \tag{9}$$

$$\begin{aligned} g = g_D + g_{D_{\parallel}} &= \Gamma\left(\frac{2}{3}\right)(n'_D s_{0D} + n'_{D_{\parallel}} s_{0D_{\parallel}}) = \\ &= \Gamma\left(\frac{2}{3}\right)(Q_D^2 + Q_{D_{\parallel}}^2) = \Gamma\left(\frac{2}{3}\right)\left[\left(\frac{R_{0D}}{\bar{R}}\right)^2 + \left(\frac{R_{0D_{\parallel}}}{\bar{R}}\right)^2\right] \end{aligned} \tag{10}$$

at which η_0 denotes the quantum yield of solution when $n'_{D_{\parallel}} \to 0$, $\Gamma(2/3)$ is the gamma function, $\bar{R}$ the circle radius satisfying relation $n'_D \pi \bar{R}^2 = 1$, where n_D is number of monomer molecules/unit area; $n'_{D_{\parallel}}$ the analogous magnitude for dimers, R_{0D} and $R_{0D_{\parallel}}$ denote critical distances for non-radiative energy transfer from D^* to D and from D^* to $D_{\parallel}$, respectively.

Expressions (7) and (8) describe the concentrational dependences of probabilities P_F and P_{DD} and can be applied to the computation of yields $\eta_{(0)}$ and η. Taking into account relations (3)—(8), we obtain the following expression for emission anisotropy:

$$\frac{r}{r_0} = (1 - \beta F)\left[1 + \sum_{m=2}^{\infty} h_m (\beta F)^m\right], \tag{11}$$

where

$$\beta = \alpha_0 \frac{g_D}{g}\,. \tag{12}$$

Magnitude α_0 denotes the probability of the non-occurrence of excitation energy degradation during its transfer between monomers. Taking into account the excitation energy remigration is reduced to finding[3] coefficients h_m. In [8]

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[3] Assuming that $h_m = 0$ for $m = 2, 3, \ldots$ means a total neglecting of excitation remigration.

the above mentioned MPP model has been applied in order to estimate coefficients h_m. Making use of the same model for a system of three active molecules[4] D_0, D_1, D_2 and applying the same procedure as in [8] the following expression has been obtained for PL-emission anisotropy:

$$^{2}\left(\frac{r}{r_0}\right)'_3 = (1-\beta F)\left\{1+\frac{(\beta F)^2}{4}\left[\frac{Q'_{av}}{1-Q'_{av}(2-Q'_{av})(\beta F)^2}+\right.\right.$$
$$\left.\left.+\frac{1-Q'_{av}}{1-(1-Q'^{2}_{av})(\beta F)^2}+\frac{1}{1-(1-Q'_{av}+Q'^{2}_{av})(\beta F)^2}\right]\right\}, \tag{13}$$

where F and β are determined by Eqs. (9) and (12). Magnitude Q' appearing in (13) expresses the probability that if molecule D_1 is the nearest neighbour of molecule D_0 then simultaneously D_0 is the nearest neighbour of D_1. We assume that there is random distribution of active molecules on the plane at which:

$$Q'_{av} = \frac{P_{av}\left[(a+1)\,g_D\right]}{(a+1)\,P_{av}\,(g_D)}\,, \tag{14}$$

$$a = \frac{1}{3}+\frac{\sqrt{3}}{2\pi}\,, \tag{15}$$

$$P_{av}\,(g_D) = g_D\left[Ci(g_D)\sin g_D - Si\,(g_D)\cos g_D + \frac{\pi}{2}\cos g_D\right]. \tag{16}$$

Function Q'_{av} was obtained in the same way as the analogous function Q_{av} in [17] for three-dimensional systems. Relation (14) was obtained assuming[5]

$$Q' = e^{-a\xi}, \tag{17}$$

where

$$\xi = \pi R^2 n', \tag{18}$$

at which n' is the number of molecules D/unit area, R is the distance between molecules D_0 and D_1. (13) describes the concentrational dependence of PL emission anisotropy of a two-dimensional system within the MPP model of three active molecules and one partially reflecting screen which is D_2 molecule. Molecule D_2 can be a partially or a totally reflecting screen. The "prime" at r/r_0 or its absence will mean that EA concern a group with a partially or totally reflecting screen.

Number 3 on the right side below r/r_0 in (13) means that this group consists of three active molecules and number 2 on the left side above r/r_0 means that the formula refers to a two-dimensional system. Eq. (13) has an analogous

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[4] Schemes of the processes occurring in groups of three active molecules D_0, D_1, D_2 and the distributions of those molecules have been presented in Fig. 1 in [8].

[5] Q' means a probability that there is no molecule D in part $a = 0.608$ of the circle surface of radius R drawn round D_1 and lying outside the corresponding circle drawn round D_0.

form as Eq. (36) in [8] describing the concentrational dependence of PL emission anisotropy of three-dimensional solutions obtained within the same MPP model of three molecules and one partially reflecting screen.

In the place of magnitudes F, β and g there appear the following magnitudes, respectively

$$f = \sqrt{\pi}\,\gamma \exp(\gamma^2)\left[1 - \frac{2}{\sqrt{\pi}}\int_0^{\gamma} \exp(-t^2)\,dt\right], \tag{19}$$

$$\alpha = \alpha_0 \frac{\gamma_0}{\gamma}, \tag{20}$$

$$\gamma = \gamma_D + \gamma_{D\parallel} = \frac{\sqrt{\pi}}{2}(Q_D^3 + Q_{D\parallel}^3). \tag{21}$$

Function Q_{av} replacing function Q'_{av} has an identical form as the latter, however in Q_{av} instead of g_D and $a = 1/3 + \sqrt{3}/2\pi$ the magnitudes γ_D and $a = 11/16$ appear.

In [8] some simpler cases of the MPP model were also considered, namely a group of three molecules and totally reflecting screens as well as groups of two and one molecules and partially or totally reflecting screens. These investigations allowed to obtain some information as to the correctness of the approximation of the MPP-model with three molecules for a description of concentrational changes of emission anisotropy.

Considering some analogous simpler cases for two-dimensional systems leads to expressions:

$${}^2\left(\frac{r}{r_0}\right)_3 = (1-\beta F)\left[1 + \frac{1}{2}\,\frac{(\beta F)^2}{1-(\beta F)^2}\right], \tag{22}$$

$${}^2\left(\frac{r}{r_0}\right)'_2 = \frac{1}{2}\left[\frac{1-\beta F}{1-Q'_{av}(\beta F)^2} + \frac{1-\beta F}{1-(1-Q'_{av})(\beta F)^2}\right], \tag{23}$$

$${}^2\left(\frac{r}{r_0}\right)_2 = \frac{1}{1+\beta F}, \tag{24}$$

$${}^2\left(\frac{r}{r_0}\right)'_1 = 1 - \beta F, \tag{25}$$

$$\left(\frac{r}{r_0}\right)_1 = 1. \tag{26}$$

In Fig. 1 curves r/r_0 are plotted corresponding to MPP model with 1, 2 and 3 active molecules and totally or partially reflecting screens and thus corresponding to different approximations of CDPL theory as to the degree of taking into account excitation energy remigration to molecules D_0.

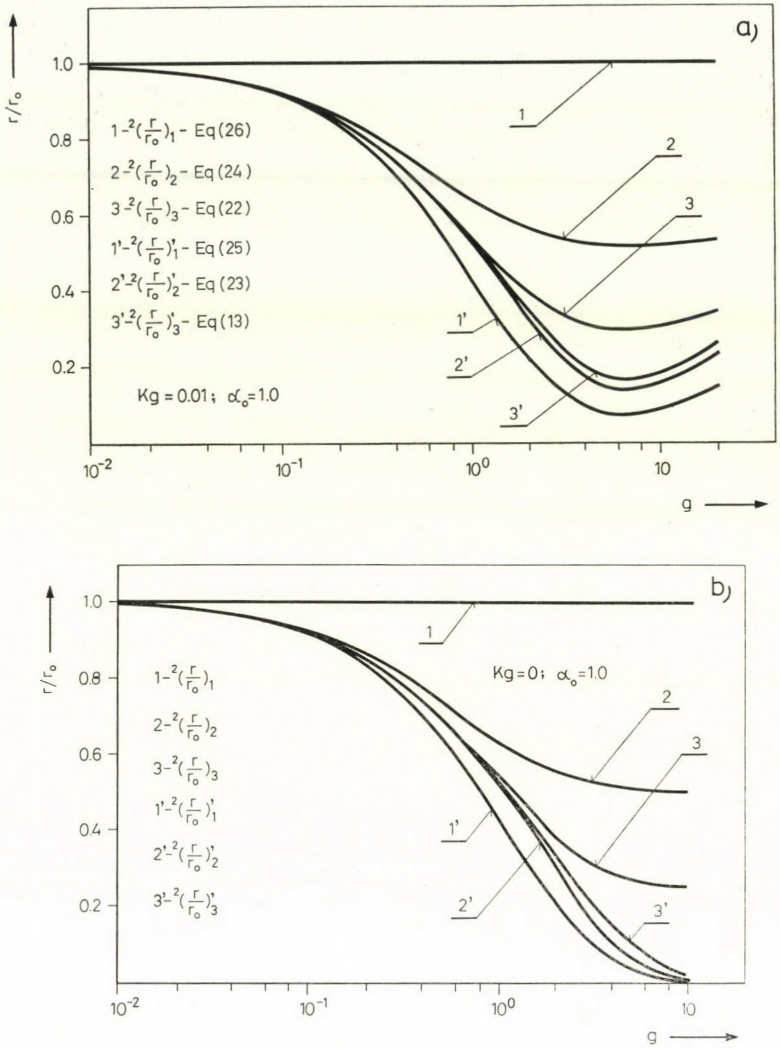

Fig. 1. **PL-emission anisotropy as a function of reduced concentration g computed within MPP model of $n = 1$, 2 and 3 active molecules in the group. Curves 1, 2, 3 refer to the groups of totally reflecting screens, curves 1′, 2′, 3′ refer to the groups of one partially reflecting screen**

The curves in Fig. 1a describe depolarization taking PL concentrational quenching by non-luminescent dimers ($Kg > 0$) also into account; curves in Fig. 1b refer to the case when the quenching of this kind does not occur ($Kg = 0$). Curves 1, 2 and 3 correspond to the groups of totally reflecting screens and thus to the case of total localization of excitation energy within a luminescence centre; curves 1′, 2′ and 3′ refer to the case when excitation energy can leave the group without any possibility of returning. Curves corresponding to each particular approximation of CDPL-theory differ remarkably first of all in

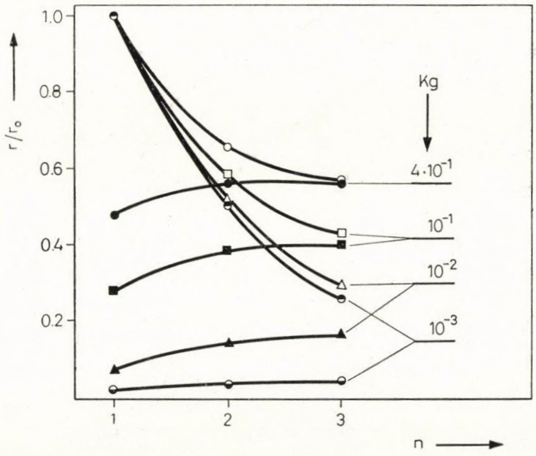

Fig. 2. Values of emission anisotropy obtained for different approximations of CDPL theory and for different values of dimerization constant *Kg*; *n* is the number of active molecules in the group; ◓, △, □, ○ and ◒, ▲, ■, ●- respective values ${}^2(r/r_0)_n$ and ${}^2(r/r_0)'_n$ computed for reduced concentration *g* equal to 10 (◓, ◒), 6 (△, ▲) 3 (□, ■), 3 (○, ●) and $\alpha_0 = 1.0$

the range of high concentrations. In case $Kg > 0$ all the curves (except curve 1) show minima and describe the repolarization process in the range of high concentrations, but in case $Kg = 0$ curves tend to zero for open groups (curves 1′, 2′, 3′) with increasing concentration, and they tend to constant values 1/2 and 1/4 for closed groups (curves 2 and 3). As seen from Fig. 1a differences ${}^2(r/r_0)_n - {}^2(r/r_0)'_n$ decrease with the increasing number of active molecules in the group and we can expect that

$$\lim_{n\to\infty}\left[{}^2\left(\frac{r}{r_0}\right)_n - {}^2\left(\frac{r}{r_0}\right)'_n\right] = 0.$$

Unfortunately, for $n > 3$ we do not obtain expressions in a finite form for r/r_0 as was the case for three dimensional systems [8]. It turns out, however, that the decrease of this difference does not depend merely on the number of molecules in the group but also on the value of the dimerization constant *Kg*.

In Fig. 2 values ${}^2(r/r_0)_n$ and ${}^2(r/r_0)'_n$ are presented for several values *Kg* and for $n = 1, 2, 3$. Values r/r_0 have been computed for such values of *g* at which difference ${}^2(r/r_0)_n - {}^2(r/r_0)'_n$ is maximal. In the case of a group of three molecules the above mentioned difference amounts to 0.03 for $Kg = 0.1$ and to 0.005 for $Kg = 0.4$, that is for $Kg \geq 0.1$ both the open group and the closed one are sufficiently good approximations of CDPL-theory. For smaller values of *Kg* difference ${}^2(r/r_0)_3 - {}^2(r/r_0)'_3$ is rather considerable. Taking into account the rate of change r/r_0 with *n* we should recognize that an open group gives a better

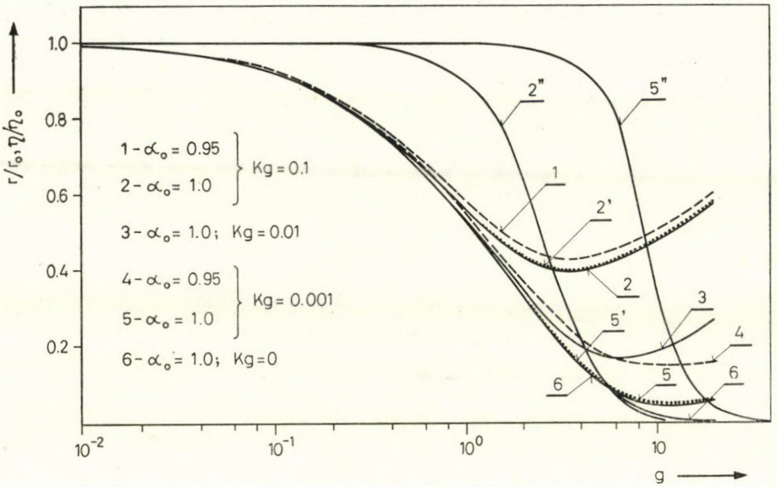

Fig. 3. **Concentrational dependence of emission anisotropy (curves 1—6, 2′ and 5′) and PL-quantum yield (curves 2″ and 5″) of two-dimensional systems for different values of dimerization constant *Kg* and parameter α_0. Curves 1—6 are determined by Eq. (13); curves 2′ and 5′ are determined by Eq. (27); curves 2″ and 5″ taken from [16]; curves 2′, 2″ and 5′, 5″ correspond to the same values *Kg* and α_0 as curves 2 and 5**

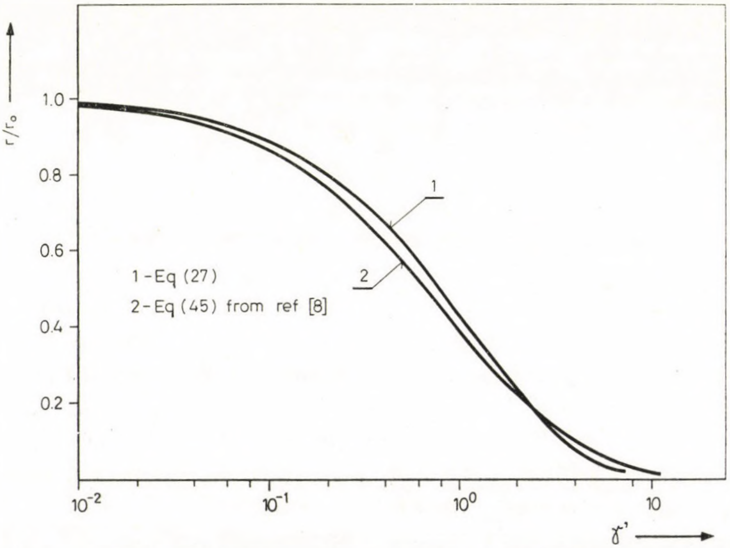

Fig. 4. **Concentrational dependence of emission anisotropy for two-dimensional (curve 1) and three-dimensional solutions (curve 2). Both curves have been plotted for dimerization constant $K = 0$ and $\alpha_0 = 1$. Further explanations in the text**

approximation[6] of the theory than a closed one. For in the latter case values r/r_0 are considerably reduced, first of all in the range of high concentrations, because the assumption of total localization of excitation energy within the group is not correct when PL quenching is insignificant [13]. Fig. 3 presents the dependence (13) for several different values of dimerization constant Kg and parameter α_0. We can see that the effect of value α_0 on the shape of curves r/r_0 is much bigger in the case of small values of Kg (curves 4, 5) than in the case of large Kg (curves 1, 2).

Curves 2 and 5 may be approximated very well by curves 2′ and 5′ plotted with dotted lines and described by the equation

$$ {}^{2}\!\left(\frac{r}{r_0}\right)'_3 = (1-\beta F)\left[1+\frac{1}{2}\,\frac{(\beta F)^2}{1-\frac{3}{4}(\beta F)^2}\right]. \tag{27}$$

This equation was obtained by formally accepting $Q'_{av}=1/2$ in expression (13) (cf. remarks in [8]).

In Fig. 4 the results obtained for a two-dimensional system were compared with those obtained by one of us for three dimensional systems [8]. Dependence AE, ${}^{2}(r/r_0)'$ and ${}^{3}(r/r_0)'$ respectively for a two-(three) dimensional system, (curves 1 and 2) were presented as functions of argument $\gamma'=c/c_0$, where c is concentration per unit area, (unit volume) and c_0 is the inverse of the area (volume) of a circle (sphere) of radius $\bar{R}_0$ in two (three) dimensions. In the range of small and moderate concentrations curves 1 and 2 go very close to each other, then they intersect, similarly as the analogous curves obtained in the Förster—Ore theory (cf. Fig. 1 (a) in [4]).

In Fig. 5 expression (27) is compared with the analogous expressions for two-dimensional systems[7] derived by Craver [4]. Curve 3 illustrates the course of EA obtained in the Knox theory and curve 2 an analogous one obtained in the Förster—Ore theory; curve 1 is described by expression (27). Curve 1 has a similar shape as the other curve shown in Fig. 5; it is shifted towards smaller γ' in relation to the others and in the environment of $\gamma' \approx 1$ the slope of curve 1 is almost identical with that of curve 3. In the range of high concentrations of γ' the shape of EA obtained in the present work (curve 1) is steeper than that predicted by the Craver—Knox theory (curve 3) and is similar to that of the Förster—Ore theory (curve 2).

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[6] As can be seen from Fig. 2 differences ${}^{2}(r/r_0)'_3 - {}^{2}(r/r_0)'_2$ amount to 0.027 and 0.011, respectively for Kg equal to 10^{-2} and 10^{-3}. It results from here that (in the case of small Kg) values ${}^{2}(r/r_0)'_3$ will only be slightly reduced in relation to value

$$\frac{r}{r_0} = \lim_{n\to\infty} {}^{2}\!\left(\frac{r}{r_0}\right)'_n .$$

[7] ${}^{2}(r/r_0)'$ corresponds to P^{2D} in Craver's notation [4].

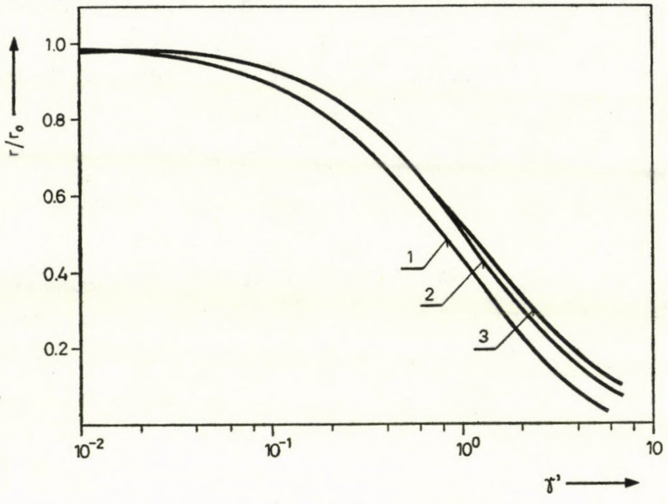

Fig. 5. **Emission anisotropy r/r_0 as a function of reduced concentration $\gamma'=c/c_0$ for two-dimensional systems, 1 — Eq. (27), 2 and 3 — curves obtained by CRAVER [4]**

3. Final remarks

In Fig. 6, expression (27) was compared with the experimental results[8] of TROSPER et al. [18] and referring to the CDPL phenomenon of chlorophyll-a in two-dimensional solutions of castor oil. An agreement of the experimental results with theory for the critical distance $\bar{R}_0 = (53 \pm 4)$ Å was obtained; it is slightly smaller than value (57 ± 4) Å obtained in [18] and estimated there as upper limit of $\bar{R}_0$ assuming that $c = \bar{c}_0$ when $p = p_0/2$ (cf. [19, 20]). CRAVER found a good agreement between the theoretical curve 3 in Fig. 4 with the experimental results for two-dimensional solutions of chlorophyll-a not only in castor oil but in other solvents as well.

As in the range where r/r_0 changes from 1 to ~ 0.2 the shape of EA determined by our Eq. (27) is practically identical (only shifted towards smaller γ') with CRAVER's theoretical curve (curves 1, 4 in Fig. 4), the agreement of curve 1 with the other experimental results of TROSPER et al. is equally good as with curve 3 obtained by CRAVER. On account of this we do not quote any comparisons for the remaining systems. Table I shows the critical distance values $\bar{R}_0$ found by a comparison of the experimental results of TROSPER et al. with theoretical curves 1 and 3.

In the Table the values $\bar{R}_0$ obtained in [18] as "upper" limits are also given.

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[8] Instead of real experimental points we have applied here the least squares straight lines values obtained for these points in [18].

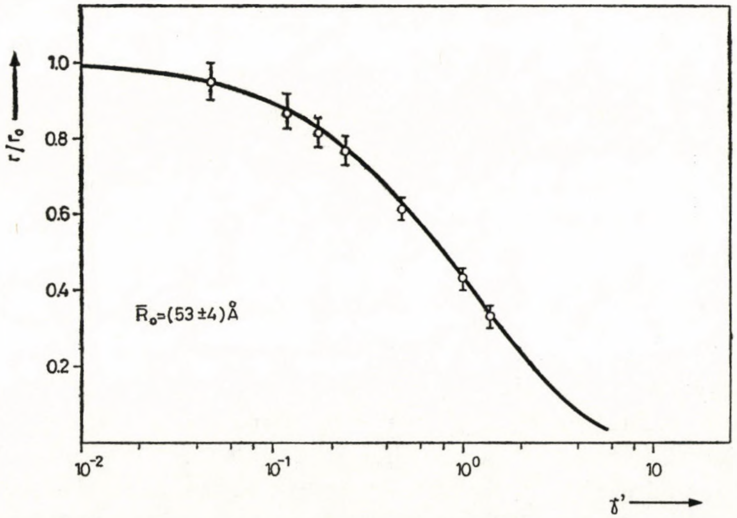

Fig. 6. **Concentrational changes of PL emission anisotropy of chlorophyll-a in two-dimensional solutions of castor oil; Φ—experimental points of Trosper et al. [18]; solid line — theoretical curve (27)**

As can be seen, values $\overline{R}_0$ given in column 4 are smaller for all systems than values $\overline{R}_0$ found as "upper" limits (column 2).

Craver [4] comes to the conclusion that quantum yield concentrational changes observed in the range of high γ' only slightly affect the variation of emission anisotropy. This conclusion clearly contradicts our theoretical and experimental results concerning three-dimensional systems [8, 21]. For two-dimensional systems the theory of PL-concentrational depolarization and PL-concentrational quenching [16] predicts similar results.

In Fig. 3 gives, among others, curves 2″ and 5″ illustrating the variation of quantum yield as function of reduced concentration g. There is an obvious correlation between the quantum yield decrease η/η_0 and stopping the decrease of r/r_0 followed by an increase of r/r_0 together with g. For small values of dime-

Table I

Critical distances $\overline{R}_0$ for chlorophyll-a in two-dimensional solutions

1	2	3	4
Solvent	$\overline{R}_6$ in A		
	Trosper et al.	Craver	Bojarski, Kolka
castor oil	57± 4	62± 3	53± 4
oleyl alcohol	57±11	62±11	53±11
sulpholipid	78± 9	86± 9	74± 9

rization constant Kg (curve 5) the deviation of the shape of r/r_0 curve from curve 6 which corresponds to completely neglecting concentrational quenching in solution is not considerable and appears only in the range of very high concentrations. At a decrease of yield η/η_0 to 1/2, which corresponds to $g = 9.5$, this deviation amounts to 0.02, but for a larger value $Kg = 0.1$ the analogous deviation is much larger and amounts to 0.13 (at $g = 2.5$). The above discussed experimental results cover merely a small range of concentration ($\gamma' = g/\Gamma(2/3) \lesssim 3$) and therefore the decrease of yield η/η_0 cannot change remarkably the shape of the emission anisotropy curve if value Kg is not sufficiently high. **Craver** emphasizes in his work [4] that the values $\bar{R}_0$ for castor oil and oleyl alcohol (see column 3) are in good agreement with value (65 ± 8) Å for $\bar{R}_0$ obtained by **Tweet** et al [22] on the ground of spectral data of chlorophyll-a in monolayers. Still values $(\bar{R}_0)'$ found by a comparison of the experimental results with the theoretical curve differ from values $(\bar{R}_0)''$ computed from spectral data at exciting light frequency $\nu_{exc} = \nu_{0-0}$ where ν_{0-0} is the frequency corresponding to $0-0$ transition; namely at $\nu_{exc} > \nu_{0-0}$ depolarization is larger (particularly in the range of high γ') than at $\nu_{exc} = \nu_{0-0}$ that is relative EA values satisfy the inequality $(r/r_0)_{\nu_{exc}} < (r/r_0)\nu_{0-0}$ [23—25]. In this case $(\bar{R}_0)' < < (\bar{R}_0)''$ which explains a smaller value of $(\bar{R}_0)'$ for chlorophyll-a in castor oil and oleyl alcohol in comparison with value $(\bar{R}_0)''$ found by **Tweet** et al. but does not explain a high value of R_0 for chlorophyll in sulpholipid (see Table I).

In [18] it was suggested that high values of $\bar{R}_0$ for sulpholipid solutions and not reaching zero by emission anisotropy for high γ' might be connected with a local ordering of the pigment molecules. This fact can be as well explained not by partially oriented chlorophyll-a molecules but by concentrational quenching leading to stopping the PL-depolarization (see Fig. 3) and thus to an apparent increase of value $\bar{R}_0$.

To solve this problem requires some further investigations, especially in the range of higher concentrations.

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REFERENCES

1. G. W. **Robinson**, Brookhaven Natl. Lab. Symp., **19**, 16, 1967.
2. R. M. **Pearlstein**, Brookhaven Natl. Lab. Symp., **19**, 8, 1967.
3. K. **Colbow**, Biochim, Biophys. Acta, **314**, 320, 1973.
4. F. W. **Craver**, Mol. Phys., **22**, 403, 1971.
5. Th. **Förster**, Ann. Phys., **2**, 44, 1948.
6. A. **Ore**, J. Chem. Phys., **31**, 442, 1959.
7. R. S. **Knox**, Physica, **39**, 361, 1968.
8. C. **Bojarski**, J. Luminescence, **5**, 413, 1972.
9. M. G. **Galanin**, Trudy Fiz. Instituta im. P. M. Lebediewa, **5**, 341, 1950.
10. I. **Ketskeméty**, Acta Phys. et Chem. Szeged, **1**, 29, 1955.

11. A. Jabłonski, Acta Phys. Polon., A**38**, 453, 1970.
12. I. Ketskeméty, J. Dombi, R. Horvai, J. Hevesi and L. Kozma, Acta Phys. et Chem. Szeged, **7**, 17, 1961.
13. C. Bojarski, Acta Phys. Polon., A **45**, 85, 1974.
14. C. Bojarski and J. Domsta, Acta Phys. Hung., **30**, 145, 1971.
15. C. Bojarski and J. Kusba, II Ogólnopolska Konferencja Luminescencyjna, Toruń 1974, II Luminescencja Substancji Organicznych, pp. 61—66, in Polish.
16. C. Bojarski and J. Kusba, Z. Naturforsch., **30**a, 594, 1975.
17. E. L. Eriksen and A. Ore, Phys. Norveg., **2**, 159, 1967.
18. T. Trosper, R. B. Park and K. Sauer, Photochem. Photobiol., **7**, 451, 1968.
19. C. Bojarski and A. Kawski, Ann. Physik (Leipzig), **7**, 31, 1959.
20. C. Bojarski, Ann. Physik (Leipzig), **12**, 253, 1963.
21. C. Bojarski, A. Bujko, J. Dudkiewicz, J. Kusba and G. Obermueller, Acta Phys. Polon., A **45**, 71, 1974.
22. A. G. Tweet, W. D. Bellamy and G. L. Gaines, J. Chem. Phys., **41**, 2068, 1964.
23. M. Guéron, J. Eisinger and R. G. Schulman, J. Chem. Phys., **47**, 4077, 1967.
24. R. K. Bauer and H. Cherek, Bull. Acad. Polon. Sci., Ser. Sci. Math. Astronom. Phys., **20**, 961, 1972.
25. C. Bojarski, J. Dudkiewicz and A. Bujko, Acta Phys. et. Chem. Szeged, **20**, 267, 1974.

Acta Physica Academiae Scientiarum Hungaricae, Tomus 39 (3), pp. 205—208 (1975)

COMMUNICATIO BREVIS

COMPATIBILITY EQUATION FOR STEADY TRANSVERSE PLANE MHD FLOWS

By

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(Received 26. VIII. 1975)

BERKER [1] has studied the steady flow of a non conducting, inviscid and compressible fluid and obtained compatibility equations. Later these compatibility equations were used by OZOKLAV [2, 3] and CHANDNA [4] to obtain the solutions for plane, anti-symmetric, and three dimensional flow problems. In the present paper the steady MHD flow of an electrically conducting fluid under a uniform magnetic field transverse to the plane of flow is investigated. A compatibility equation is obtained for steady plane transverse MHD flow for viscous compressible fluid. This study is also carried out for incompressible and inviscid plane flows. Compatibility equations are used for obtaining solutions for plane radial flows.

In the absence of external forces and heat conduction, the steady flow of a viscous compressible, perfectly conducting fluid is governed by equations

$$\mathrm{Div}(\varrho \mathbf{V}) = 0, \tag{1}$$

$$\varrho \mathbf{a} + \mathrm{grad}\, p = \mu^{-1} \mathrm{curl}\, \mathbf{B} \times \mathbf{B} + \eta \nabla^2 \mathbf{V} + \frac{\eta}{3} \nabla(\nabla \cdot V), \tag{2}$$

$$\mathrm{curl}\, (\mathbf{V} \times \mathbf{B}) = 0, \tag{3}$$

$$\mathbf{V}\, \mathrm{grad}\, s = 0, \tag{4}$$

$$p = f(\varrho, s), \tag{5}$$

where ϱ is the density, p the pressure, s the specific entropy, **B** the solenoidal magnetic field vector, **V** the velocity vector, $\nu = \eta/\varrho$ the constant kinematic viscosity, μ the constant magnetic permeability and $\mathbf{a} = (\mathbf{V}.\, \mathrm{grad})\, \mathbf{V}$ the acceleration vector of the fluid.

Assuming the flow to be plane and transverse in (x, y) plane, we have

$$\mathbf{B} = (0, 0, B) \quad \text{and} \quad \frac{\partial}{\partial z} \equiv 0 .$$

Therefore (2) and (3) reduce to

$$\varrho\mathbf{a}+\nabla\left(p+\frac{B^2}{2\mu}\right)=\eta\nabla^2\mathbf{V}+\frac{\eta}{3}\nabla(\nabla\cdot\mathbf{V}), \tag{6}$$

$$\mathrm{Div}(B\mathbf{V})=0\,. \tag{7}$$

From (1) and (7) it follows that

$$B=\alpha\varrho, \tag{8}$$

where α is a scalar function satisfying

$$\mathbf{V}\cdot\operatorname{grad}\alpha=0. \tag{9}$$

Eqs. (1), (4), (5), (6) and (7) constitute a system of non-linear partial differential equations composed of six scalar equations containing six unknown scalar functions. Here we will eliminate the four scalar function ϱ, p, s and B among these equations and get a relation containing only **V**, the compatibility equation.

Taking the curl of both sides of (6) and forming the vector product with **V**, it follows that

$$\mathbf{V}\times\operatorname{curl}\mathbf{a}+(\mathbf{V}\cdot\mathbf{a})\operatorname{grad}\log\varrho-(\mathbf{V}\cdot\operatorname{grad}\log\varrho)\,\mathbf{a}=\mathbf{V}\times\nu\Delta^2\boldsymbol{\omega}\,, \tag{10}$$

where $\boldsymbol{\omega}=\nabla\times\mathbf{V}$. Eq. (1) can be written as

$$\mathrm{Div}\,\mathbf{V}+\mathbf{V}.\operatorname{grad}\log\varrho=0. \tag{11}$$

Now eliminating (**V**. grad log ϱ) **a** from (10) and (11), we have

$$(\mathbf{V}\cdot\mathbf{a})\operatorname{grad}\log\varrho=\operatorname{curl}\mathbf{a}\times\mathbf{V}-\mathbf{a}(\operatorname{div}\mathbf{V})+\mathbf{V}\times(\nu\nabla^2\boldsymbol{\omega}). \tag{12}$$

This equation implies the existence of two classes of flow problems according to $\mathbf{V}\cdot\mathbf{a}=0$ (uniform motion) and $\mathbf{V}\cdot\mathbf{a}\neq0$.

For flow problem $\mathbf{V}\cdot\mathbf{a}\neq0$, Eq. (12) gives

$$\operatorname{curl}\left[\frac{\operatorname{curl}a\times\mathbf{V}+\mathbf{V}\times(\nu\nabla^2\boldsymbol{\omega})-\mathbf{a}(\operatorname{div}\mathbf{V})}{\mathbf{V}\cdot\mathbf{a}}\right]=0. \tag{13}$$

This equation is the compatibility equation for flows with $\mathbf{V}\cdot\mathbf{a}\neq0$.

Now we have determined the relation for velocity. The relation for density, the pressure, and the magnetic intensity are determined as follows.

$$\varrho=\exp\int\frac{\operatorname{curl}\mathbf{a}\times\mathbf{V}+\mathbf{V}\times(\mu\nabla^2\boldsymbol{\omega})-\mathbf{a}(\operatorname{div}\mathbf{V})}{\mathbf{V}\cdot\mathbf{a}}\,d\mathbf{r}\,, \tag{14}$$

where $d\mathbf{r}$ is the vector element of arc length for the stream line,

$$p=-\left[\int(\varrho\mathbf{a}-\eta\nabla^2\mathbf{V})d\mathbf{r}+\frac{B^2}{2\mu}-\frac{\eta}{3}(\nabla\cdot\mathbf{V})\right] \tag{15}$$

and $B = \alpha\varrho$, where α is an arbitrary function constant along each stream line.

By removing the viscosity term from the compatibility equation (13), one can obtain directly the compatibility equation for inviscid fluid given by

$$\operatorname{curl}\left[\frac{\operatorname{curl}\mathbf{a}\times\mathbf{V}-\mathbf{a}\operatorname{div}\mathbf{V}}{\mathbf{V}\cdot\mathbf{a}}\right]=0. \tag{16}$$

And hence the relation for density, pressure and magnetic intensity for inviscid fluid are

$$\varrho=\exp\int\frac{\operatorname{curl}\mathbf{a}\times\mathbf{V}-\mathbf{a}\operatorname{div}\mathbf{V}}{\mathbf{V}\cdot\mathbf{a}}\,dr\,, \tag{17}$$

$$p=-\left[\int\varrho\,\mathbf{a}\,dr+\frac{B^2}{2\mu}\right], \tag{18}$$

$$B=\alpha\varrho, \tag{19}$$

The compatibility equation for incompressible viscous fluid is

$$\operatorname{curl}[\nu\nabla\times(\nabla\times\boldsymbol{\omega})-\operatorname{curl}\mathbf{V}\times\boldsymbol{\omega}]=0. \tag{20}$$

The compatibility equations were used by OZOKLAV [2, 3] to determine the velocity field for the steady, rotational plane gas flow problem by inverse method.

It may be of interest to find out relations for velocity field pressure and specific entropy for several problems by using the compatibility equation without using the inverse method used by OZOKLAV [2, 3].

Here we will use the compatibility equation to obtain solution for plane radial flow. We consider the polar coordinate system for which streamlines are given by

$$\theta=\eta=c_1,\quad 0\leq c_1<2\pi \tag{21}$$

and the orthogonal trajectories are given by

$$\gamma=\xi=c_2,\quad 0<c_2<\infty\,. \tag{22}$$

We also know that the square of elemental arc length in this case is given by

$$ds^2=dr^2+r^2d\theta^2. \tag{23}$$

Now taking $\mathbf{e}_1$ as the unit tangent vector to curve $\theta=c_1$ in the direction of r increasing and $\mathbf{e}_2$ as the unit tangent vector to curve $r=c_2$ in the direction of θ increasing, we get

$$\mathbf{V}=V(r,\theta)\mathbf{e}_1. \tag{24}$$

After using (24) in (16) we see that $V(r, \theta)$ satisfies

$$\frac{\partial^2}{\partial r\, \partial\theta} \log \frac{1}{r} \frac{\partial V}{\partial r} = 0. \tag{25}$$

The solution of Eq. (25) is given by

$$V(r, \theta) = l(r) + m(\theta) + \frac{r^2}{2} n(\theta) . \tag{26}$$

This is the desired solution for the velocity field where l, m and n are arbitrary functions of their arguments.

*

The author is indebted to Prof. JAGDISH LAL, D. Sc. Director, Indian Institute of Technology, Kanpur, for his guidance and helpful suggestions.

REFERENCES

1. R. BERKER, C. R. Paris, **242,** 342, 1956.
2. H. OZOKLAV, J. Math. Mech., **8,** 27, 1959.
3. H. OZOKLAV, Arch. Ration, Mech. Anal., **15,** 154, 1964.
4. O. P. CHANDNA, Int. J. Eng. Sci., **9,** 611, 1971.

RECENSIONES

P. W. HAWKES:

Electron Optics and Electron Microscopy

Taylor and Francis, London, 1972, pp. 244, I—XV.

The author, renowned for his numerous works in electron microscopy, has realized a well-planned programme to provide a summary to those who use electron optical equipments as beginners of the fundamentals and performance parameters of these equipments.

After a historical review, the book briefly describes the operating principles of up-to-date types (transmission and scanning microscopes, electron beam microanalysers). The Chapter on the principles of electron lenses begins with the general imaging properties of symmetrical fields and discusses typical lense defects too.

In the Chapter on the construction of electron microscopes the role and technical solutions of the cathode, lenses and apertures are given. Then follows the description of the modes of operation currently used (the bright and dark field technique, the high resolution and selected area diffraction, etc.) and an outline of their technical realization. An extensive chapter analyses the theory of image contrast and the appearance of the amplitude and phase contrast and their role in the imgaging.

The best part of the book is that summarizing, in sufficient detail for the researcher not familiar with electron microscopy, the most effective microscope procedure applied in surface physics: the imaging technique with scanning electron beam. This Chapter also includes different scanning beam electronoptical equipments as well as material research based on the velocity analyses of electrons. Without striving for completeness this Chapter offers a very good selection of important information on this field of electron microscopy.

The description of applications is rather poor, which is obviously due to lack of space. It would have been difficult to review all applications and the necessary preparative techniques in such a short chapter. Those who do not know these, benefit very little from this Chapter, whereas for experts familiar with these techniques it contains nothing new.

Comparing the deficiencies and virtues of this rather short summary of electron microscopy, it can be said that it is a valuable contribution to the extensive literature on this subject.

J. PÓCZA

Planck's Original Papers in Quantum Physics

Classic Papers in Physics, Vol. 1 Hans Kangro, Editor, Taylor & Francis Ltd.
London 1972, 60 pages

In 1970 an International Working Seminar was organized by IUPAP on the Role of the History of Physics in Physics Education where it was agreed that original, classic papers properly annotated and translated would be of great help for teachers of the history of physics. This book is an example of such an attempt. It comprises two basic papers by PLANCK on the spectral energy distribution of electromagnetic radiation (Über die Verbesserung der Wien'-

schen Spektralgleichung, Verhandlungen der Deutschen Physikalischen Gesellschaft Bd. 2 S. 202—204, 1900 and Zur Theorie des Gesetzes der Energieverteilung im Normalspektrum, Verhandlungen der Deutschen Physikalischen Gesellschaft, Bd. 2 S. 237—245, 1900) both in German and English. The notes by HANS KANGRO making up the third chapter serve to help the reader in understanding the original text.

This small volume can be highly recommended to teachers of the history of physics and to all showing an interest in the great epochs of physics.

P. SZÉPFALUSY

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W. H. Freeman and Company, San Francisco

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The purpose of publishing these selected articles is twofold. Today specialization among physicists makes it impossible for a given specialist to be informed about what is being done in fields different even if slightly from his own sphere of interest. At the same time it is well known how fruitful the exchange of ideas in different fields has proven to be in the history of sciences. It is just one of the aims of publishing the Readings in the Physical Sciences and Technology to promote this exchange by presenting to the physicist society the most interesting developments in the physical science. On the other hand, reading these fascinating stories of physics will certainly mean an interesting and exciting excursion into the realm of physics for the layman: for the nonphysicists and among them in particular for young students whose interest is hoped to be aroused and directed toward science in this way.

P. SZÉPFALUSY

J. P. BABUEL-PEYRISSAC:

Equations Cinétiques des Fluides et des Plasmas

(Cours et Documents de Mathématique et de Physique)
Gordon et Breach, Paris—London—New York, 1975, pp. 299.

The book of J. P. BABUEL-PEYRISSAC is the first part of a very useful, interesting and up-to-date series. (Cours et Documents de Mathématique et de Physique, Director: M. LÉVY, Associated Director: E. SCHATZMAN.) The editorial board of the series decided to publish quickly relatively inexpensive works in mathematics, physics and in information theory, which give a concise and modern discussion of these branches of science. Like most of the works in the series, J. P. BABUEL-PEYRISSAC's work is a result of a course organized by the Atomic Energy Agency for young engineers. This circumstance seems to exert a fortunate influence on the style and method of the discussion.

The subject of the book is based on a certain tradition in the French literature. (J. L. Delcroix, R. Jancel, T. Kahan, D. Massiguon, E. Schatzman). The author makes an effort not to be unfaithful to his famous pioneers, his work gives an excellent summary on the classical kinetic theory of fluids and plasmas.

After the discussion of the classical theory of particle collisions the author gives an estimate on the influence of the collisions of third and higher order, treats the Liouville, BBGKY and Boltzmann equations stating clearly the conditions of application of these equations. He derives the equations for the thermal equilibrium of fluids and plasmas from the kinetic equations. In Chapter IV the author deals with Boltzmann's equation and its applications. In the next Chapter he introduces the kinetic theory in a more general form (method of Prigogine-Balescu, BBGKY hierarchy, Sandri's expansion). In the last two Chapters classical hydrodynamics is discussed on the basis of the kinetic theory.

In the Appendix the reader can find useful mathematical and physical relations (integral transforms, expressions for Landau's equation etc.)

M. Dobróka

Printed in Hungary

A kiadásért felel az Akadémiai Kiadó igazgatója
Műszaki szerkesztő: Botyánszky Pál
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Acta Physica Academiae Scientiarum Hungaricae, Tomus 39 (4), pp. 217—226 (1975)

PHASE TRANSITION PHENOMENA AND THE LIPPMANN–SCHWINGER VARIATIONAL PRINCIPLE

By

W. LUCHT

SEKTION MATHEMATIK DER MARTIN-LUTHER-UNIVERSITÄT HALLE, HALLE, GDR

(Received 17. VI. 1975)

It is shown that the partition function need not be determined uniquely if a generalized matrix eigenvalue equation of the type

$$(\mathbf{W}_1 - P\mathbf{W}_2)Y = 0$$

possesses a nontrivial solution Y. The solution may be physically relevant if the parameter P is real. We derive the above eigenvalue equation and discuss its solution. In this context some basic asymptotic considerations are summarized in a theorem.

I. Introduction

In the context of phase transformations (for example: pressure induced transitions) it is known that at transition points (or in their vicinity) ordinary perturbation series may be divergent [1—3]. It is believed that this divergence is coupled to a certain singularity of e.g., the partition function. Influenced by this idea that a certain type of singularities corresponds to the phenomenon of phase transition we use a version of the LIPPMANN—SCHWINGER variational principle [4] to show that such singularities can exist. For the sake of generality we employ a formulation of non-equilibrium statistical mechanics.

II. The physical system and the initial-value problem

We suppose a non-relativistic quantum mechanical spin-independent M-particle system which is enclosed in a sphere of radius L with volume

$$\Omega = \frac{4\pi}{3} L^3 \, .$$

The Hamiltonian shall be of the form [5]

$$\widetilde{H}(P) = H + \sum_{n=1}^{M} \mathfrak{R}_n \mathfrak{r}_n , \tag{1}$$

$$H = \sum_{n=1}^{M} \frac{1}{2m} \mathfrak{p}_n^2 + U(\mathfrak{r}_1, \ldots, \mathfrak{r}_M) , \tag{2}$$

$$(\mathfrak{R}_n)_\alpha = P\Delta^2 \sum_{m(\neq n)} e_{nm}^{(\alpha)} , \quad \alpha = 1, 2, 3. \tag{3}$$

The quantities m, $\mathfrak{r}_n, \mathfrak{p}_n$, P and Δ are, respectively, the mass, the position and impulse vectors of the n-th particle, an external pressure, and the interparticle spacing. U is a potential function (e.g. a superposition of two-body pair potentials) which need not be specified at this point. $e_{nm}^{(\alpha)}$ is the α-component of a unit vector pointing from particle n to the near neighbour particle at m. In the bulk of the system it is $(\mathfrak{R}_n)_\alpha = 0$, since

$$\sum_{m(\neq n)} e_{nm}^{(\alpha)} = 0\,.$$

The forces in Eq. (3) are on the surface. Prescribing

$$\begin{aligned} &L = L' + y,\ 0 < y \ll L,\ 0 < y \ll L'\,, \\ &L' \leq L_0 \leq L,\ 0 \leq n_0 \leq 1 \end{aligned} \tag{4a}$$

we can write

$$\begin{aligned} \sum_n \mathfrak{R}_n \mathfrak{r}_n &= P\Delta^2 \sum_n [-n_0 L_0 \Theta(|\mathfrak{r}_n| - (L-y))] = \\ &= PG \sum_n \Theta(|\mathfrak{r}_n| - L'), \end{aligned}$$

where

$$\Theta(x) = \begin{cases} 1 \text{ for } x \geq 0 \\ 0 \text{ for } x < 0 \end{cases} \quad \text{and } G = -\Delta^2 n_0 L_0. \tag{4b}$$

We introduce the second quantized picture to obtain the representation

$$\widetilde{H}(P) = H + P\int_{\Omega_L} \mathrm{d}\mathfrak{r}\, q(\mathfrak{r}),\ \mathrm{d}\mathfrak{r} = \mathrm{d}x\,\mathrm{d}y\mathrm{d}z \tag{5}$$

with

$$q(\mathfrak{r}) = G\Theta(|\,\mathfrak{r}\,| - L')\psi^+(\mathfrak{r})\psi(\mathfrak{r}). \tag{6}$$

$\psi^+(\mathfrak{r})$ and $\psi(\mathfrak{r})$ are the familiar field creation und destruction operators [6]. H in (5) shall be the second quantized form of the Hamiltonian given in Eq. (2).

Now we use the frame of JAYNES [7, 8] formulation of non-equilibrium statistical mechanics. Suppose that at time $t = 0$ not only the mean energy, $\langle H(0)\rangle$, but also the statistical average values of the observables $Pq(\mathfrak{r})$ are known. Then the average, at time t, of the observable $Pq(\mathfrak{r})$ can be expressed as a functional derivative:

$$\langle Pq(\mathfrak{r}, t)\rangle = \left.\frac{\delta(\beta W)}{\delta\lambda(\mathfrak{r}, t)}\right|_{\lambda(\mathfrak{r},t)=\lambda(\mathfrak{r})\delta(t)}, \tag{7}$$

where we have defined a non-equilibrium partition function Ξ and thermodynamic potential W by (we will use $\hbar = 1$ throughout)

$$\Xi \equiv e^{-\beta W} = Tr\{e^{-\beta(H+P\,K_{\beta_0}}|_{\beta_0=\beta}\}, \tag{8}$$

$$K \equiv K_{\beta_0} = \beta_0^{-1}\int \mathrm{d}x\,\lambda(x)\,q(x),\ q(x) \equiv q(\mathfrak{r}, t) = e^{iHt}q(\mathfrak{r})e^{-iHt}, \tag{9}$$

$$\lambda(x) \equiv \lambda(\mathfrak{r}, t), \int dx \ldots \equiv \int_{-\infty}^{+\infty}\mathrm{d}t\int_{\Omega_L}\mathrm{d}\mathfrak{r} \ldots .$$

The multipliers β and $\lambda(\mathfrak{r})$ are determined from the known initial data $\langle H(0)\rangle$ and $\langle Pq(\mathfrak{r}, 0)\rangle$:

$$\langle H(0)\rangle = \left.\frac{\partial(\beta W)}{\partial\beta}\right|_{\lambda(\mathfrak{r},t)=\lambda(\mathfrak{r})\delta(t)}, \tag{10}$$

$$\langle Pq(\mathfrak{r}, 0)\rangle = \left.\frac{\delta(\beta W)}{\delta\lambda(\mathfrak{r}, 0)}\right|_{\lambda(\mathfrak{r},t)=\lambda(\mathfrak{r})\delta(t)}. \tag{11}$$

The essential physical quantity is the partition function Ξ and we will study ti. Ideally, our aim would be an answer to the question: Do there exist real parameters (β, P) such that Ξ is not or not uniquely determined? If the answer were "yes", then a point would be found at which a phase transition could occur.

III. The variational principle

According to **Isihara** [9] we write in obvious notation (the substitution $\beta_0 = \beta$ is always to be understood)

$$\Xi = Tr\left\{e^{-\beta(H+PK)}\right\} = \Xi_{dq}\cdot\langle U(\beta, 0)\rangle_{dq}, \tag{12}$$

where

$$\Xi_{dq} = Tr\ e^{-\beta H}$$

and

$$\langle\ldots\rangle_{dq} = Tr\{\ldots e^{-\beta H}\}/Tre^{-\beta H} \tag{13}$$

denotes the equilibrium average. The thermal evolution operator $U(.\,,.)$ satisfies the integral equation

$$U(\tau, \tau_0) = 1 - P\int_{\tau_0}^{\tau}\mathrm{d}\tau'\,K(\tau')\,U(\tau', \tau_0). \tag{14}$$

$$K(\tau) = e^{H\tau}Ke^{-H\tau},\ \tau \text{ real}, K^+ = K. \tag{15}$$

This operator is not hermitian: $K^+(\tau) \neq K(\tau)$. However, $K(.)$ is star-hermitian in the sense of **Prigogine** [10]. The star-hermitian conjugation (denoted by *) is defined as the combination of the hermitian conjugation (denoted by $^+$) and the inversion $\tau \to -\tau$:

$$K^*(\tau) = K^+(-\tau) = K(\tau). \tag{16}$$

With this type of conjugation all the nice properties of the familiar time-dependent evolution operator (where $\tau \to it$) are preserved. For example, we have for our operator $U(.\,,.)$

$$\begin{aligned} U(\tau, \tau_2)U^*(\tau, \tau_2) &= U^*(\tau, \tau_2)U(\tau, \tau_2) = 1, \\ U^*(\tau_1, \tau_2) &= U^{-1}(\tau_1, \tau_2) = U(\tau_2, \tau_1). \end{aligned} \tag{17}$$

$U(.\,,.)$ is a star-unitary operator.

As a consequence of this one can use the LIPPMANN—SCHWINGER variational principle with star-hermitian conjugation for the thermal evolution operator. Define the operator-valued functional

$$\begin{aligned} F(V^*, V; \tau_2, \tau_1) = 1 - P\int_{\tau_1}^{\tau_2} \mathrm{d}\tau\, [V^*(\tau, \tau_2)\, K(\tau) + K(\tau)V(\tau,\tau_1)] + \\ + P\int_{\tau_1}^{\tau_2} \mathrm{d}\tau\, V^*(\tau,\tau_2)K(\tau)V(\tau,\tau_1) + P^2\int_{\tau_1}^{\tau_2} \mathrm{d}\tau \int_{\tau_1}^{\tau_2} \mathrm{d}\tau' V^*(\tau,\tau_2)K(\tau) \times \\ \times\, \Theta(\tau - \tau'\, (K(\tau')V(\tau',\tau_1) \end{aligned} \tag{18}$$

with $\Theta(x)$ given in Section II. Then the following theorem is valid:

Theorem: The values of the operators V and V^* for which the functional (18) is stationary, with respect to variations δV and δV^* are the evolution operators of the perturbation Hamiltonian $PK(.)$. Furthermore, the stationary value of the functional itself reduces to the thermal evolution operator for the interval

$$\tau_1 \text{ to } \tau_2.$$

The detailed proof of this theorem follows, e.g., from BESSIS [11] if some obvious modifications concerning the star-hermitian conjugation are performed. We only note that in fact

$$\frac{\delta F}{\delta V^*} = 0 \text{ implies } V(\tau, \tau_1) = 1 - P\int_{\tau_1}^{\tau} \mathrm{d}\tau'\, K(\tau')V(\tau', \tau_1)\,, \tag{19a}$$

and

$$\frac{\delta F}{\delta V} = 0 \text{ implies } V^*(\tau, \tau_1) = 1 + P\int_{\tau_1}^{\tau} \mathrm{d}\tau'\, V^*(\tau',\tau_1)K(\tau'). \tag{19b}$$

(19a) is identical with Eq. (14). On the other hand: Eq. (19b) reduces to (19a) when we take the star-hermitian conjugate of the equation. The stationary value of the functional F reads

$$F(V^* V;\, \tau_2, \tau_1)|_{st} = 1 - P\int_{\tau_1}^{\tau_2} \mathrm{d}\tau V^*(\tau,\tau_2)K(\tau) = V^*(\tau_1, \tau_2) = V(\tau_2, \tau_1). \quad (20)$$

This is the second part of the theorem.

The next step is the Cini—Fubini-Ansatz [12] for the operators V and V^*. Eq. (14), resp. (19a, b), formally generates the Sturm—Liouville expansion

$$U(\tau, \tau_1) = \sum_{k=0}^{\infty} U_k(\tau, \tau_1) \text{ with } U_0(\tau, \tau_1) = 1, \quad (21)$$

$$U_{k+1}(\tau, \tau_1) = - P \int_{\tau_1}^{\tau} \mathrm{d}\tau' K(\tau')U_k(\tau', \tau_1), \quad (22a)$$

$$U^*_{k+1}(\tau, \tau_1) = P \int_{\tau_1}^{\tau} \mathrm{d}\tau' U^*_k(\tau', \tau_1)K(\tau'). \quad (22b)$$

At the N-th order it is chosen

$$U^{(N)}(\tau, \tau_1) = \sum_{k=0}^{N-0} U_k(\tau, \tau_1)\mu_k, \quad (23a)$$

$$U^{(N)*}(\tau, \tau_2) = \sum_{k=0}^{N-1} \lambda_k U^*_k(\tau, \tau_2), \quad (23b)$$

where the μ_i and λ_k are operators to be determined.

Using the same algebra as in Bessis [11] one can derive, with the help of Eqs. (17) and (21) — (23b), the representation of the operator valued functional

$$\begin{aligned} F_z(\lambda_0, \ldots, \lambda_{N-1};\, \mu_0, \ldots, \mu_{N-1};\, \tau_2\,\tau_1) = \\ = 1 + z\Bigg[\sum_{k=0}^{N-1} z^k\{U_{k+1}(\tau_2, \tau_1)\,\mu_k + \lambda_k\, U_{k+1}(\tau_2, \tau_1)\} - \quad (24) \\ - \sum_{j,k=0}^{N-1} z^{k+j}\,\lambda_k\{U_{k+j+1}(\tau_2, \tau_1) - zU_{k+j+2}(\tau_2, \tau_1)\}\,\mu_j\Bigg]. \end{aligned}$$

Here we have introduced an auxiliary variable z. For $z = 1$ one obtains the original functional (18):

$$F = F_z|_{z=1}.$$

The further analysis rests on (24) and the stationarity relation (20).

IV. The problem of the singularities

From (24) we find for $\alpha = 0, 1, \ldots, N-1$

$$\frac{\delta F_z}{\delta \mu_\alpha} = z^{\alpha+1}\left[U_{\alpha+1} - \sum_{k=0}^{N-1} z^k \lambda_k (U_{k+\alpha+1} - zU_{k+\alpha+2})\right] = 0\,, \tag{25}$$

$$\frac{\delta F_z}{\delta \lambda_\alpha} = z^{\alpha+1}\left[U_{\alpha+1} - \sum_{j=0}^{N-1} z^j (U_{j+\alpha+1} - zU_{j+\alpha+2})\,\mu_j\right] = 0\,. \tag{26}$$

This is a system of $2N$ equations for the unknown $2N$ variational operators λ_k and μ_j. Since (25) and (26) are not coupled it is enough for our purposes to consider, say, the Eq. (25). The system (26) can be handled in the same way.

According to Eqs. (22) we replace in (25)

$$z \text{ by } P \text{ and } U_n(\tau_2, \tau_1) \text{ by } w_n = w_n(\beta, 0), \tag{27}$$

where for $n \geq 1$

$$w_n(\beta, 0) = -\int_0^\beta \mathrm{d}\tau' K(\tau') w_{n-1}(\tau', 0);\; w_0 = 1. \tag{28}$$

Furthermore, let us define two $(N, 1)$-column vectors E and R,

$$E = \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \text{ and } R = \begin{bmatrix} \lambda_0 \\ P\lambda_1 \\ \vdots \\ P^{N-1}\lambda_{N-1} \end{bmatrix} \tag{29}$$

and the two (N, N)-matrices $\mathbf{W}_1$ and $\mathbf{W}_2$:

$$\mathbf{W}_i^{(N)} = \begin{bmatrix} w_{0,i} & w_{0,i+1} & \cdots & \cdots & w_{0,N-1+i} \\ \vdots & \vdots & & & \vdots \\ w_{N-1,i} & w_{N-1,i+1} & \cdots & \cdots & w_{N-1.N-1+i} \end{bmatrix};\; i = 1, 2. \tag{30}$$

The matrix elements are operators and are given by (28):

$$w_{j,k} = w_{k,j} = w_{j+k}\,. \tag{31}$$

With these definitions the system(25) can be formally rewritten in the form

$$E^T \mathbf{W}_1^{(N)} = R^T(\mathbf{W}_1^{(N)} - P\mathbf{W}_2^{(N)}). \tag{32}$$

The upper index T means transposition. The task is to find the vector R. This were possible, if the inverse operator $(\mathbf{W}_1^{(N)} - P\mathbf{W}_2^{(N)})^{-1}$ would exist.

If this were not the case, then we would not have a unique solution R (resp. R^T if any). Therefore, we seek real parameters β and P such that the inverse matrix $(\mathbf{W}_1^{(N)} - P\mathbf{W}_2^{(N)})^{-1}$ does not exist. The key suggestion is the following known lemma [13]:

Lemma: If Q denotes an operator, then Q^{-1} is defined if and only if $Qu = 0$ implies $u = 0$ ($u \in D(Q)$, the domain of Q). Thus we should try to solve the following problem: Find a real P and a nontrivial vector Y such that

$$\mathbf{W}_1^{(N)} Y = P\mathbf{W}_2^{(N)} Y \tag{33}$$

is satisfied. This is a well posed generalized eigenvalue problem. Because of Eq. (31) the matrices $\mathbf{W}_i^{(N)}$ are symmetric, but the operators w_n themselves are not hermitian (see (28) in connection with (15)). Hence, in general, real P's are an exception (if a nontrivial solution exists at all).

With Eq. (33) the problem of pressure induced phase transitions is, in principle, reduced to the solution of a non-hermitian eigenvalue problem.

The following question arises: Suppose for fixed N, the number of trial operators, a nontrivial solution of Eq. (33) (with eigenvalue $P_{0,N}$) exists. How is the behaviour of this solution if one adds n further trial operators (on the right of (23))? Especially the case $n \to \infty$ is of basic interest. This question will now be studied.

V. The asymptotic limit

Some notation is needed. Consider the two matrices $\mathbf{W}_i^{(N+n)}$, $i = 1, 2$. These we write for $n \geq 1$ in the form

$$\mathbf{W}_i^{(N+n)} = \begin{bmatrix} \mathbf{W}_i^{11}(0, N-1; i, N-1+i) & \mathbf{W}_i^{12}(0, N-1; N+i, N+n-1+i) \\ \mathbf{W}_i^{21}N, N+n-1; i, N-1+i) & \mathbf{W}_i^{22}(N, N+n-1;\ N+i, N+n-1+i) \end{bmatrix}. \tag{34}$$

The $\mathbf{W}_i^{pq}$ are matrices whose elements are the operators $w_{j,k}$. The first pair of indices in the brackets gives the range of the row indices, the second pair indicates the column indices. For example, in $\mathbf{W}_i^{12}(0, N-1; N+i, N+n-1+i)$ the row index runs from 0 to $N-1$, and the column index runs from $N+i$ to $N+n-1+i$. This rectangular matrix possesses the format (N, n). Corresponding to (34) the vector $Y = Y^{(N+n)}$ is analogous decomposed:

$$Y^{(N+n)} = \begin{bmatrix} Y_a^{(N)} \\ Y_b^{(n)} \end{bmatrix}, \quad Y_a^{(N)} = \begin{bmatrix} | Y_{a1}\rangle \\ \vdots \\ | Y_{aN}\rangle \end{bmatrix}, \quad Y_b^{(n)} = \begin{bmatrix} | Y_{b1}\rangle \\ \vdots \\ | Y_{bn}\rangle \end{bmatrix}. \tag{35}$$

The eigenvalue equation

$$\mathbf{W}_1^{(N+n)}\, Y^{(N+n)} = P\mathbf{W}_2^{(N+n)}\, Y^{(N+n)} \tag{36}$$

yields then under the assumption (for short we suppress the arguments of the matrices)

$$\mathbf{W}_1^{11}\, Y^{(ON)} = P_{0,N}\, \mathbf{W}_2^{11}\, Y^{(ON)},\ P_{0,N} \text{ real}, \tag{37}$$

the inhomogeneous system for $Y_b^{(n)}$:

$$(\mathbf{W}_1^{12} - P_{0,N}\, \mathbf{W}_2^{12})\, Y_b^{(n)} = 0\,, \tag{38a}$$

$$(\mathbf{W}_1^{21} - P_{0,N}\, \mathbf{W}_2^{21})\, Y^{(ON)} + (\mathbf{W}_1^{22} - P_{0,N}\, \mathbf{W}_2^{22})\, Y_b^{(n)} = 0. \tag{38b}$$

Here we have chosen $Y_a^{(N)} = Y^{(ON)}$. The two equations (38) suggest the choice $Y_b^{(n)} \rightarrow 0$. If a suitable norm

$$\|\, (\mathbf{W}_1^{21} - P_{0,N}\, \mathbf{W}_2^{21})\, Y^{(ON)} \,\| \tag{39}$$

would be sufficiently small (ideally, it should go to zero) for suitable N or/and n, then we could consider the solution of Eq. (37) as a solution which makes sense in the asymptotic limit. After these preliminaries we state the following theorem (for some simple functional analytic notions see, e.g., [14]):

Theorem: Suppose that:

(I) For a fixed N with $N \geq 1$ the existence of a nontrivial solution $(P_{0,N},\ Y^{(ON)})$ of the eigenvalue equation (37) in a certain space is known. Let $P_{0,N} \geqq 0$. We write $Y^{(ON)}$ as a column vector

$$Y^{(ON)} = \begin{bmatrix} |\, Y_1^{(ON)} \rangle \\ \vdots \\ |\, Y_N^{(ON)} \rangle \end{bmatrix}.$$

(II) The states $|\, Y_i^{(ON)} >$ are normalized:

$$\|\, |Y_i^{(ON)}> \,\| \equiv (\langle Y_i^{(ON)} \mid Y_i^{(ON)} \rangle)^{1/2} = 1.$$

(III) The following estimates for $1 < m \leq n + 2N$ are valid:

a) $$\left\| \prod_{j=1}^{m} K(\tau_j)\, |\, Y_\nu^{(ON)} > \right\| \leq \xi^m \,\|\, K^m(\beta^*)\, |\, Y_\nu^{(ON)} > \|$$

with $\xi \geq 0$ and $\beta^* \geq 0$.

b) $\|\, K^m(\beta^*) \,\| \leq \delta^{m-1}\, \|K(\beta^*)\|^m$ with $\delta > 0$.

The operator norm is defined by

$$\| A \| = \sup \{ \, \| A \mid Y_\nu^{(ON)} > \| : 1 \leq \nu \leq N \}. \tag{40}$$

Under these assumptions it is for $n \geq 1$ and $x \neq 1$

$$\begin{aligned} \| (\mathbf{W}_1^{21} - P_{0,N} \mathbf{W}_2^{21}) \, Y^{(ON)} \| \leq \frac{\delta^{-1}}{(N+1)!} \left(1 + \frac{x P_{0,N}}{N+2}\right) \times \\ \times \frac{(1-x^N)\, x^{N+1}}{1-x} \left(\frac{1-x^{2n}}{1-x^2}\right)^{1/2}, \end{aligned} \tag{41}$$

where $x = \delta \xi \beta \, \| K(\beta^*) \|$.

Although the proof is not difficult it is somewhat long in detail. We merely give a

Sketch of the proof: The recurrence relation (28), assumptions (II) and (III), the equality

$$\int_0^\beta \mathrm{d}\tau_1 \int_0^{\tau_1} \mathrm{d}\tau_2 \ldots \int_0^{m-1} \mathrm{d}\tau_m = \beta^m / m! \, ,$$

the Schwarz inequality, the triangle inequality and the operator norm (40) yield for $1 < m \leq n + 2N$ the estimate

$$\begin{aligned} \left\| \left\{ w_m(\beta, 0) + P_{0,N} \int_0^\beta \mathrm{d}\tau' K(\tau') w_m(\tau', 0) \right\} \mid Y_\nu^{(ON)} > \right\| \leq \\ \leq \frac{\delta^{-1}}{m!} x^m \left\{ 1 + P_{0,N} \frac{x}{m+1} \right\} \end{aligned} \tag{42}$$

with x given at the end of the theorem. Since by the Schwarz inequality

$$\begin{aligned} \left\| (\mathbf{W}_1^{21} - P_{0,N} \mathbf{W}_2^{21}) \, Y^{(ON)} \right\|^2 \leq \sum_{\nu, \nu' = 1}^{N} \sum_{\mu = 0}^{n-1} \Big\| \Big\{ w_{N+\mu+\nu}(\beta, 0) + \\ + P_{0,N} \int_0^\beta \mathrm{d}\tau' K(\tau') w_{N+\mu+\nu}(\tau', 0) \Big\} \mid Y_\nu^{(ON)} > \Big\| \cdot \Big\| \Big\{ w_{N+\mu+\nu}(\beta, 0) + \\ + P_{0,N} \int_0^\beta \mathrm{d}\tau K(\tau) w_{N+\mu+\nu'}(\tau, 0) \Big\} \mid Y_{\nu'}^{(ON)} > \Big\| \end{aligned}$$

we gain by some elementary manipulations (use of geometric series etc.) with the help of (42) the assertion (41). The theorem shows that for sufficiently large N and $x < 1$ the error can be made arbitrary small, even in the limit $n \to \infty$. For $x > 1$ the right side of (41) diverges in the limit $n \to \infty$.

VI. Summary

Using the notion of star-hermitian conjugation in the LIPPMANN—SCHWINGER variational principle for the thermal evolution operator and the CINI—FUBINI-Ansatz it was shown that the partition function need not be determined uniquely, provided that a nontrivial solution of the eigenvalue equation (37) exists. Assuming the existence of such a solution for a finite number of known trial operators we have formulated a theorem which states the asymptotic properties of this solution. Under certain conditions which are given above such a solution makes sense in the asymptotic limit.

REFERENCES

1. L. D. LANDAU and E. M. LIFSCHITZ, Statistische Physik, Akademie-Verlag, Berlin, 1966.
2. G. A. BAKER and J. KAHANE, Journ. Math. Phys., **10**, 1647, 1969.
3. W. LUCHT, phys. stat. sol. (b), **68**, K 149, 1975.
4. B. A. LIPPMANN and J. SCHWINGER, Phys. Rev., **79**, 469, 1950.
5. R. A. GUYER, Selected Topics in Physics, Astrophysics, and Biophysics, Eds. E. Abecassis de Laredo and N. K. Jurisic, D. Reidel Publ. Co., Dordrecht (Holland)/Boston (USA), 1973.
6. A. L. FETTER and J. D. WALECKA, Quantum Theory of Many-Particle Systems, Mc Graw-Hill Book Co., New York, 1971.
7. E. T. JAYNES, Phys. Rev., **106**, 620, 1957; **108**, 171, 1957.
8. M. D. GIRARDEAU, Journ. Math. Phys., **8**, 389, 1967.
9. A. ISIHARA, Statistical Physics, Academic Press, New York and London, 1971.
10. I. PRIGOGINE and F. MAYNÉ, Transport Phenomena, Eds. G. Kirczenow and J. Marro, Springer Verlag, Berlin, 1974.
11. D. BESSIS, Padé Approximants, Ed. P. R. Graves-Morris, The Institute of Physics London and Bristol, London, 1973.
12. M. CINI and S. FUBINI, Nuovo Cim., **11**, 142, 1954.
13. T. KATO, Perturbation Theory for Linear Operators, Springer Verlag, Berlin 1966 (p. 143).
14. M. REED and B. SIMON, Methods of Modern Mathematical Physics, Vol. I, Functional Analysis, Academic Press, New York and London, 1972.

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THE NATURE OF THE SINGULARITY IN THE GRAVITATIONAL FIELD OF A CHARGED PARTICLE

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On physical grounds, it has been verified that the so called pseudo singularity in the exterior field of a charged particle is irremovable.

I. Introduction

The gravitational field of a charged particle of mass 'm' and charge 'q' is given by the well-known Reissner—Nordström static centro-symmetric metric

$$ds^2 = A^{-1}dr^2 - r^2(d\Theta^2 + \sin^2\Theta d\Phi^2) + Adt^2, \tag{1}$$

where $A = 1 - 2(m/r) + (q/r)^2$. The space-time exhibited by (1) is singular at $r = 0$ and $r = m \pm b$ with $b^2 = m^2 - q^2$.

The question is whether these are real singularities in the geometry of the manifold? If one calculates the Riemann—Christoffel curvature tensor, its non-vanishing components are given by

$$R^{12}_{12} = R^{13}_{13} = R^{24}_{24} = R^{34}_{34} = \frac{mr - q^2}{r^4},$$

$$R^{14}_{14} = R^{23}_{23} = \frac{3q^2 - 2mr}{r^4}. \tag{2}$$

We observe that the components are singular only at $r = 0$ and not at $r = m \pm b$. In the literature the singularity at $r = 0$ is termed as the real one whereas the other two are apparent in the sense that they can be removed by a suitable coordinate transformation. GRAVES and BRILL [1] have obtained a transformation from the coordinates (r, t) to coordinates (u, v) on parallel lines of KRUSKAL's [2] work. They were able to remove the spurious singularity. However, the new coordinate system which they have adopted cooresponds to an accelerated frame of reference and thus the metric has lost its static structure. We maintain the view that if we restrict ourselves to the transformations that preserve the static nature of the space-time given by (1), the singularity therein cannot be removed. ROSEN [3] has stressed the same view in connection with the singularity at $r = 2m$ in the Schwarzschild space-time. HILTON [4] also concluded from her investigations that the nature of the Schwarzschild singularity at $r = 2m$ cannot validly be removed at all; for the surface $r = 2m$ is found to be a physical barrier whose existence is in no way dependent on the coordinate system used to describe the physical situation depicted in Schwarzschild field. We in our earlier work (KARADE and RAO [5]) also arrived at a similar conclusion. We further remarked that no observer confined to the region $r > m + b$ can receive any information through signals from or about the region $r \leq m + b$ in his own finite life time. It is the purpose of this note to establish the above mentioned version on parallel lines of HILTON'S [4] work.

To investigate the physical nature of the singularity at $r \pm m \pm b$, we suppose that an observer, sufficiently away from $r = m + b$, tries to obtain an information from the region $r < m + b$. (Having physical motivation in mind, we have selected the singularity at $r = m + b$.) The most physical way to get an information is through the agency of signalling. There will be no loss of generality if we presume the observer to be an intelligent being well equipped with some technique of remote controlling such that the probe he is sending can be reversed back at his command. To serve the purpose he can select either a material test particle or a photon as a probe which, according to his fancy, may move radially or non-radially in the field of (1). Keeping this in view, the knowledge of the path of the probe becomes a must. In the next Section we obtain the possible paths taken by the probe. The mathematical results thus achieved are interpreted in Section III, on which the nature of the singularity is concluded.

II. Trajectory of a probe

It has already been verified by us (KARADE and RAO [5]) that the particle moving in the field of (1) confines to a plane $\Theta = \pi/2$ under certain initial conditions. The path is given by

$$r^2 \mathrm{d}\Phi/\mathrm{d}s = h, \tag{3a}$$

and

$$\mathrm{d}t/\mathrm{d}s = k/A, \tag{3b}$$

where h and k are constants of integration of physical importance. (It should also be noted that a particle can also carry out a radial motion provided the initial conditions are suitably adjusted.)

(a) *Purely radial motion*

In this case, the equations of motion yield

$$\pm \mathrm{d}r/\mathrm{d}s = (k^2 - A)^{1/2} \tag{4a}$$

and

$$\pm \mathrm{d}r/\mathrm{d}t = (A/k)(k^2 - A)^{1/2}. \tag{4b}$$

In the direction of r increasing, we shall take a positive sign. Integrating Eqs. (4), we obtain

$$\pm s = \alpha_1(r) \qquad \text{for} \qquad |\, k \,| > 1, \tag{5a}$$

$$\pm s = \alpha_2(r) \qquad \text{for} \qquad |\, k \,| = 1, \tag{5b}$$

$$\pm s = \alpha_3(r) \qquad \text{for} \qquad |\, k \,| < 1, \tag{5c}$$

and

$$\pm t = \beta_1(r) \qquad \text{for} \qquad |\, k \,| > 1, \tag{6a}$$

$$\pm t = \beta_2(r) \qquad \text{for} \qquad |\, k \,| = 1, \tag{6b}$$

$$\pm t = \beta_3(r) \qquad \text{for} \qquad |\, k \,| < 1, \tag{6c}$$

where α's and β's are given as below:

$$\begin{aligned} \alpha_1(r) = &-(m/F^3) \log (rF^2 + m + rFy) + \\ &+ (r/F^2)y + \text{const.}, \;\; F^2 = k^2 - 1, \end{aligned} \tag{7a}$$

$$\alpha_2(r) = (1/3m^2)\;(mr + q^2)\quad(2mr - q^2)^{1/2} + \text{const.}, \tag{7b}$$

$$\begin{aligned} \alpha_3(r) = &\,(m/f^3)\text{arc sin}\;[(rf^2 - m)\;(m^2 - q^2f^2)^{-1/2}] - \\ &-(r/f^2)y + \text{const.}, \; f^2 = 1 - k^2, \end{aligned} \tag{7c}$$

$$\begin{aligned} \beta_1 = &\, kr(y/F^2) + (k/F^3)\,(2F^2 - 1) \log\,[m + rF(F + y)] - \\ &-(Q/x_1) \log\,[- b + kx_1 r(k + y)/(r - x_1)] - \\ &-(R/x_2) \log\,[b + kx_2 r(k + y)/(r - x_2)] + \text{const.}, \end{aligned} \tag{8a}$$

$$\begin{aligned} \beta_2 = &\,(1/3m^2)\,(mr + 6m^2 + q^2)\,(2mr - q^2)^{1/2} + \\ &+ \frac{2m^2 - q^2}{2b} \log \frac{(mr - q^2) - b(2mr - q^2)^{1/2}}{(mr - q^2) + b(2mr - q^2)^{1/2}} + \\ &+ m \log \frac{[r - (2mr - q^2)^{1/2}]^2}{(r - x_1)(r - x_2)} + \text{const.}\,, \end{aligned} \tag{8b}$$

$$\begin{aligned} \beta_3 = &\,(km/f^3)(2f^2 + 1)\;\text{arc sin}\;[(rf^2 - m)(m^2 - q^2f^2)^{-1/2}] - \\ &-(Q/x_1) \log\,[-b + kx_1 r(k + y)/(r - x_1)] - kr(y/f^2) - \\ &-(R/x_2) \log\,[b + kx_2 r(k + y)/(r - x_2)] + \text{const.}, \end{aligned} \tag{8c}$$

with
$$x_1 = m + b,\ x_2 = m - b,$$
$$y^2 = k^2 - A,$$
$$Q = (1/2b)[(4m^2 - q^2)x_1 - 2mq^2]$$
and
$$R = (-1/2b)[(4m^2 - q^2)x_2 - 2mq^2].$$

(b) *Photon as a probe*

For a photon trajectory $ds = 0$, and then, we obtain

$$\pm \mathrm{d}r/\mathrm{d}t = A. \tag{9}$$

Integrating Eq. (9), we get

$$\pm t = r + m \log (r^2 - 2mr + q^2) + \frac{2m^2 - q^2}{2b} \log \frac{r - x_1}{r - x_2}. \tag{10}$$

(c) *Non-radial motion of a probe*

In this case
$$kr^2 d\Phi/\mathrm{d}t = hA \tag{11a}$$
and
$$\pm \mathrm{d}r/\mathrm{d}t = A[1 - (A/k^2)(1 + h^2/r^2)]^{1/2}. \tag{11b}$$

III. Interpretation of the results

(a) *The observer at rest*

Here the observer may arrange the probe to move radially or non-radially.

(i) Imagine the probe moving radially towards $r \leq m + b$. This situation is depicted in the structure of the functions α_i and β_i, $i = 1, 2, 3$. The nature of the functions α_i given by the Eqs. (7) along with Eqs. (5) predicts that any signal will take finite proper time (s) to cover the distance between $r > m + b$ and $r = m + b$, whereas from the expressions of the functions β_i given by Eqs. (8) along with (6) imply that the signal takes an infinite coordinate time (t) to travel the same distance.

If the observer uses light as a probe, he will also find that the probe has also taken infinite coordinate time (t) to cover the distance which follows from Eq. (10).

(ii) If the signal is moving non-radially, its path is governed by Eqs. (11). In the neighbourhood of $r = m + b$, the quantity $\pm dr/dt$ given by Eq. (11b) behaves like A, in consequence of which we have the same kind of singularity predicted by Eq. (10) for the radial motion of light, and thus, the argument of HILTON [4] can be applied.

Therefore the observer at rest, using coordinate (t) as the measure of time will not get any information in his finite lifetime from the region $r \leq m + b$ along the radial line of sight.

But the question of finite proper-time (s) still remains to be explained. To measure time in s, the observer must accompany the signal and his velocity at $r = m + b$ becomes infinite. On this ground ROSEN [3] objected the observer's accompanying the signal. This view has been elaborately illustrated in our previous work (KARADE and RAO [5]).

(b) *The observer in motion*

Furthermore if we presume the observer in radial motion or with an arbitrary motion in the field of (1) managing to get an information through signals, it has been found that all the analogous interpretations of HILTON [4] hold good in this situation too.

To put it in a nutshell we conclude that the observer in the region $r > m + b$ and at a larger distance from $r = m + b$ utterly fails to collect the information from the domain $r \leq m + b$ in his own finite lifetime. It is in perspective that we claim that the singularity at $r = m + b$ is irremovable.

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REFERENCES

1. J. C. GRAVES and D. R. BRILL, Phys. Rev., **120**, 1507, 1960.
2. M. D. KRUSKAL, Phys. Rev., **119**, 1743, 1960.
3. N. ROSEN, "Relativity" (Proceedings of the Relativity Conference in the Midwest, 1969) edited by M. Carmeli, et al. Plenum Press, N.-Y. 1970. p. 229.
4. E. HILTON, Proc. Roy. Soc. Lond., *A* **283**, 491, 1965.
5. T. M. KARADE and J. R. RAO, Communicated for publication.

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FREE FALL OF A CHARGED PARTICLE IN CENTRO-SYMMETRIC REISSNER–NORDSTRÖM FIELD

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The motion of a charged particle in a Reissner—Nordström field is discussed and various specific situations are analysed. If the relativistic correction terms are neglected, it has been shown that the particle moves radially under gravitational attraction and electrostatic repulsion.

I. Introduction

The problem of motion in gravitational theory has its own importance. In the Newtonian theory of gravitation, we know that equations of motion are independent of the field equations. Similarly in early days of general relativity the equations of motion of a test particle were postulated as the geodesic equations, which were derived from a variational principle, without recourse to the field equations of the theory. This situation has been changed by EINSTEIN and GROMMER [1] who maintained a view that equations of motion need not be separately postulated whereas they follow as a consequence of the EINSTEIN gravitational field equations. We can think of equations of motion as a condition of integrability for the field equations. INFELD [2] must be highly credited for producing a lot of stimulating literature on this issue. Discussion of motion will be incomplete if we miss to mention the noteworthy and inspiring work of EINSTEIN et al. [5], HAVAS et al. [4], FOCK [5] and CARMELI [6].

Since the motion of a test particle is intrinsically connected with the field equations, its study in some specific physical situation will positively reveal some of the hidden aspects of field we encounter. Recently HILTON [7] and ROSEN [8] have employed the study of the motion of a test particle in the Schwarzschild field to conclude that $r = 2m$ is an irremovable barrier on physical grounds while MARKLEY [9] utilised the analogy of Hamiltonian methods to study the same problem. We, in our work (KARADE and RAO [10], [11], [12]), have studied the behaviour of uncharged test particle in different physical situations. In the present note we have extended the study of the

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motion of the charged particle in the Reissner—Nordström (R—N) field. We have assumed that the moving charge does not disturb the electrogravitational field of the centrally fixed particle and also avoided the controversial problem of radiation from a uniformly accelerated charge (Fulton and Rohrlich [13], Rosen [14] and Rohrlich [15]). The results of Hilton [7], Rosen [8] and Markley [9] come out as consequences of our investigation when the charges on the moving particle and on the fixed particle are made zero. In our case it has been found that if the relativistic corrections are neglected, the particle moves radially under the Newtonian gravitational force of attraction and Coulomb's electrostatic force of repulsion. We have also observed, on physical grounds, that the observer situated sufficiently away from $r = M + B$ is unable to obtain any information about the region $r \leq M + B$ in his finite lifetime.

II. Motion of a charged particle

The gravitational field of a charged particle of mass M and charge Q is given by the well-known R—N static metric

$$ds^2 = A^{-1}\mathrm{d}r^2 - r^2(\mathrm{d}\Theta^2 + \sin^2\Theta\,\mathrm{d}\Phi^2) + A\,\mathrm{d}t^2, \tag{1}$$

where $A = 1 - 2(M/r) + Q^2/r^2$.

The usual units of general relativity are used, with $c = 1$, $G = 1$. If we put $Q = 0$ in (1), we get the Schwarzschild metric as should be expected. Consider a test particle of mass m and and charge q freely moving in the gravitational field given by the metric (1). Its equations of motion are given by Tolman [16]

$$\frac{\mathrm{d}^2x^i}{\mathrm{d}s^2} + \Gamma^i_{jk}\frac{\mathrm{d}x^j}{\mathrm{d}s}\;\frac{\mathrm{d}x^k}{\mathrm{d}s} + \frac{q}{m}\,F^i_j\,\frac{\mathrm{d}x^j}{\mathrm{d}s} = 0 \tag{2}$$

with the convention $F^i_j = g^{ik}F_{kj}$.

If the coordinates r, Θ, Φ are set up about the fixed charge, the surviving components of F_{ij} are

$$F_{41} = -F_{14} = -Q/r^2.$$

Taking the coordinate time $t = x^4$ as the independent variable instead of the proper time s, we get from Eqs. (1) and (2)

$$\dot{s}^2 = -A^{-1}\dot{r}^2 - r^2(\dot{\Theta}^2 + \sin^2\Theta\dot{\Phi}^2) + A, \tag{3a}$$

$$\begin{aligned}\ddot{r} - 3A'\dot{r}^2/2A - rA(\dot{\Theta}^2 + \sin^2\Theta\dot{\Phi}^2) + AA'/2 + \\ + (\dot{r}^2 - A^2)(qQ\dot{s}/Amr^2) = 0,\end{aligned} \tag{3b}$$

$$\ddot{\Theta} + (\dot{r}\dot{\Theta}/A)(2A - rA') - \sin\Theta\cos\Theta\dot{\Phi}^2 - (q/m)\dot{r}\dot{\Theta}\dot{s}F_1^4 = 0, \tag{3c}$$

$$\ddot{\Theta} + (\dot{r}\dot{\Phi}/A)(2A - rA') = 2\cot\Theta\dot{\Theta}\dot{\Phi} - (q/m)\dot{r}\dot{\Phi}\dot{s}F_1^4 = 0, \tag{3d}$$

where a dash and a dot denote respectively differentiation with respect to r and t.

We further assume that initially

$$\Theta = \pi/2,\ \dot{\Theta} = 0 \text{ and } \Phi = 0,\ \dot{\Phi} = 0. \tag{4}$$

From Eqs. (3c, d) and (4), we get

$$\ddot{\Theta} = \ddot{\Phi} = 0.$$

This means that the particle continues to move along the X-axis. We shall replace r by x (and hence current coordinates are x, t) to denote the distance along X-axis. Eqs. (3b) and (4) yield

$$\ddot{x} - (3A'/2A)\dot{x}^2 + (AA'/2) + (qQ\dot{s}/Amx^2)(\dot{x}^2 - A^2) = 0. \tag{5}$$

Also from Eqs. (3a) and (4), we have

$$\dot{s}^2 = A - \dot{x}^2/A. \tag{6}$$

Using Eq. (6), we have from Eq. (5) that

$$\ddot{x} - (3A'/2A)\dot{x}^2 + (AA'/2) - A^{-3/2}(qQ/mx^2)(A^2 - \dot{x}^2)^{3/2} = 0\,. \tag{7}$$

Now dashes denote differentiation with respect to x.

If in addition to Eq. (4) we suppose $\dot{x} = 0$ initially, we conclude from Eq. (7) that $\ddot{x} \neq 0$ and

$$m\ddot{x} \cong -(mM/x^2) + (qQ/x^2) \tag{8}$$

for sufficiently large values of x.

Thus the particle seems to move under the gravitational force of attraction and the electrostatic force of repulsion. In order that the particle remains at rest the Newtonian gravitational attraction must be balanced by the Coulomb's electrostatic repulsion which according to Eq. (8) is possible if

$$mM = qQ \text{ or } (m/q)(M/Q) = 1. \tag{9}$$

It is easily seen that

$$\dot{x} = A \tag{10a}$$

and

$$\dot{x}^2 = A^2[1 - A(1 - qQ/mx)^{-2}] \tag{10b}$$

satisfy Eq. (7).

We find that the trivial solution (10a) corresponds to the trajectory of photon and incidentally we shall examine it. Assuming $M > Q$, Eq. (10a) gives on integration

$$\begin{aligned} x - a + M \log [\{(x - M)^2 - B^2\}/\{(a - M)^2 - B^2\}] + \\ + [(M^2 + B^2)/2B] \log [(x - M - B)/(x - M + B)] = t, \end{aligned} \tag{11a}$$

with the initial conditions

$$\text{at } t = 0,\ \dot{x} = 0 \text{ and } x = a \text{ (very large).} \tag{11b}$$

In Eq. (11a) we have used the result

$$B^2 = M^2 - Q^2. \tag{12}$$

It is further observed that the velocity and acceleration of light vanish at $x = M \pm B$.

(In the following we shall neglect $x = M - B$ because x behaves as a timelike coordinate for $x < M + B$.)

Therefore an observer, equipped with coordinates (x, t) may conclude that light stops at $x = M + B$. But for a proper observer the situation will be different. We, in our earlier work (KARADE et al. [10], [17]) have elaborately discussed this aspect.

Introducing new variables u and v defined by

$$x - (M + B) = u = v^2/4(M + B), \tag{13}$$

the space-time given by (6), in the neighbourhood of $x = M + B$, now be expressed in two forms:

$$\mathrm{d}s^2 = -(2Bu)^{-1}(M + B)^2\mathrm{d}u^2 + 2bu(M + B)^{-2}\mathrm{d}t^2, \tag{14a}$$

$$\mathrm{d}s^2 = -(2B)^{-1}(M + B)dv^2 + (Bv^2/2)(M + B)^{-3}\mathrm{d}t^2. \tag{14b}$$

Using a new parameter p, in place of s, light rays obey

$$\begin{aligned} u &= +\alpha_1 p + \beta_1, \\ v^2 &= +\alpha_2 p + \beta_2, \\ v &= \alpha_3 \exp(-\beta_3 t), \end{aligned} \tag{15}$$

where α's and β's are constants suitably known in terms of M and B. We remark that our results (15) are exactly of the same form as those of ROSEN [8] and hence the trajectories (straight lines and parabolas) are given as in Figs. 4,2 of ROSEN [8]. For light the coordinate time taken to reach the surface $x = M + B$ from any point $x > M + B$ sufficiently large is infinite but the proper time is finite. As a consequence of this an observer, situated at $x > M + B$ sufficiently large and using light as a probe, may fail to get any information about the region $x \leq M + B$ in his lifetime. Finally we would like to point out that our results and their interpretations coincide with those of HILTON [7] and ROSEN [8]. However, the investigations of FINCKELSTEIN [18], FRONSDAL [19] and GRAVES and BRILL [20] hold a contrary view.

For the motion of a charged particle in the neighbourhood of $x = M + B$, from Eqs. (10b) and (14a,b) we get

$$(\mathrm{d}u/\mathrm{d}t)^2 = 4B^2u^2(1 - \alpha u)/(M + B), \tag{16}$$

where $\alpha = 2Bm^2\ (mM + mB - qQ)^{-2}$.

Considering the motion towards $u = 0$, from Eq. (16) we obtain

$$\alpha u = 1 - [k \exp(-2Bt) + 1]^2[k \exp(-2Bt) - 1]^{-2}, \tag{17}$$

with k as a constant of integration. From Eq. (17), we find

$$t \to \infty \text{ as } u \to 0.$$

Therefore the coordinate time elapsed to reach $x = M + B$ is infinite for a charged particle.

We may use $u = 1/\alpha$ at $t = 0$ as the initial condition giving $k = -1$. Then Eq. (17) yields

$$\alpha u = 1 - [1 - \exp(-2Bt)]^2[1 + \exp(-2Bt)]^{-2}. \tag{18}$$

If we suppose $M = Q$, Eq. (16) implies that

$$\mathrm{d}u/\mathrm{d}t = 0 \text{ and also } \mathrm{d}^2u/\mathrm{d}t^2 = 0.$$

Therefore in the neighbourhood of the singularity $r = M + B$ (in fact here $B + =0$) the velocity and acceleration of the charged particle vanish. It is also interesting to note from the expression (10b) that $\dot{x}$ and $\ddot{x}$ both vanish if $M = Q$ and $m = q$. We may conclude, on Newtonian analogue, that the charged particle is permanently at rest and hence in this case the gravitational attraction is completely neutralised by electrostatic repulsion.

Considering the moving particle of unit mass and unit charge and applying the conditions stated in Eq. (11b), its path is given by

$$y^3 - e^3 + C(y - e) + D \log [(y - E)/(y + E)] + \\ + F \log [(y - G)/(y + G)] = Ht\,,$$

where $x = y^2$, $e^2 = a$ and the constants from C to H are known in terms of Q and M.

From the mathematical standpoint, one may also consider the case $M = 0$ (ROSEN [14]). In this case we get

$$\dot{x}^2 = (1 + q^2/x^2)^2[1 - (1 + q^2/x^2)(1 - qQ/mx)^{-2}]\,.$$

From the above expression we find that the velocity of the charged particle vanishes at $x = (Q/2mq)\,(q^2 - m^2)$ but for this value of x acceleration of the particle is nonzero and positive.

The aspects of non-radial motion of a charged particle will be discussed, in a separate paper, by one of the authors (TMK).

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REFERENCES

1. A. EINSTEIN and J. GROMMER, Sitzber. Preuss. Akad. Wiss., **1,** 2, 1927.
2. L. INFELD, and J. PLEBANSKI, Motion and Relativity, Warszawa, 1960.
3. A. EINSTEIN, L. INFELD and HOFFMANN, Ann. Math., **39,** 65, 1938.
4. P. HAVAS, Phys. Rev., **108,** 1351, 1957.
   P. HAVAS and J. N. GOLDBERG, Phys. Rev., **128,** 398, 1962.
   S. F. SMITH and P. HAVAS, Phys. Rev., **138,** B495, 1965.
5. V. FOCK, The theory of space, time and gravitation, Pergamon Press, 1964.
6. M. CARMELI, Il Nuovo Cimento, **37,** 842, 1964; Ann. Phys., **30,** 168, 1964; Phys. Letters., **9,** 124, 1964; Ann. Phys., **34,** 465, 1965; Ann. Phys., **35,** 250, 1965.
7. E. HILTON, Proc. Roy. Soc. Lon., ***A*283,** 491, 1965.
8. N. ROSEN, 'Relativity' (Proceedings of the Relativity Conference in the Midwest, 1969) edited by M. Carmeli et al, Plenum Press, 1970. pp. 229–40.
9. F. L. MARKLEY, Am. J. Phys., **41,** 45, 1973.
10. T. M. KARADE and J. R. RAO, Communicated for publication, 1974.
11. T. M. KARADE and J. R. RAO, Communicated for publication, 1974.
12. T. M. KARADE and J. R. RAO, Communicated for publication, 1975.
13. T. FULTON and F. ROHRLICH, Ann. Phys., **9,** 499, 1960.
14. N. ROSEN, Ann. Phys., **17,** 269, 1962.
15. F. ROHRLICH, Ann. Phys., **22,** 169, 1963.
16. R. C. TOLMAN, Relativity, Thermodynamics and Cosmology, Clarendon Press, Oxford, p. 260, 1934.
17. T. M. KARADE, Communicated to Acta Phys. Hung. 1975.
18. D. FINKELSTEIN, Phys. Rev., **110,** 965, 1958.
19. C. FRONSDAL, Phys. Rev., **116,** 778, 1959.
20. J. C. GRAVES and D. R. BRILL, Phys. Rev., **120,** 1507, 1960.

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EXPLOSION WAVES IN A RADIATIVE GAS

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An analytic solution for propagation of explosion waves in a radiative gas has been obtained. The disturbance is supposed to be headed by a shock surface of variable strength, and the total energy of wave is not constant but varies with time.

1. Introduction

CARRUS et al. [1] studied the propagation of explosion waves in stellar models and took the energy release of the instantaneous centre explosion into account. The disturbance was taken to be headed by a shock surface of constant strength. TAYLOR [2] reduced the equations governing the motion of the fluid to a set of ordinary differential equations, which were integrated by a numerical method. KYNCH [3] and TAYLOR [4] assumed the undisturbed density to vary according to some inverse power of the distance from the centre of explosion and neglected the counter pressure. SEDOV [5] took the counter pressure into account but assumed uniform density in the undisturbed gas. It is now well known that radiation plays an important role in many hydrodynamic processes relevant to strong shocks and explosions. The role of radiation is not merely confined to the luminescence of the heated body but also affects the hydrodynamic movement of matter in form of energy transfer and heat exchange. At very high temperature say one million degrees or even lower, the energy and pressure of radiation become comparable with those of matter and therefore influence the thermodynamic properties of the medium. We have, therefore, in this paper, taken into account radiation effects and attempted to give an analytic solution to the problem of a spherical shock wave produced on account of a central explosion (instantaneous or continuous) in a gravitating mass of equilibrium. The density distribution of the undisturbed gaseous configuration is taken to fall off from the centre as $r^{-\alpha}$, where $1 < \alpha < 3$. The strength of the shock propagated does not remain constant in general, the Mach number of the shock being a function of time. Constancy of the total energy of the wave is not assumed and in fact is not satisfied, except in a particular case. In the actual propagation of explosion waves, the velocity of the shock front is expected to decrease immediately after explosion though more and more energy would be imparted into the wave by the mass of quiescent gaseous matter passing through the shock front. As such, we have taken into account the variation of both the Mach number of the shock as well as the energy of the wave with time.

2. Equations of motion and boundary conditions

The equations of motion, continuity and energy behind a spherical shock surface in a radiative gas are,

$$\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial r}+\frac{1}{\varrho}\frac{\partial p}{\partial t}+\frac{Gm}{r^2}=0\,, \tag{2.1}$$

$$\frac{\partial \varrho}{\partial t}+u\frac{\partial \varrho}{\partial r}+\varrho\frac{\partial u}{\partial r}+\frac{2\varrho u}{r}=0\,, \tag{2.2}$$

$$\frac{\partial E}{\partial t}+u\frac{\partial E}{\partial r}+p\left\{\frac{\partial}{\partial t}\left(\frac{1}{\varrho}\right)+u\frac{\partial}{\partial r}\left(\frac{1}{\varrho}\right)\right\}+\frac{1}{\varrho r^2}\frac{\partial}{\partial r}(Fr^2)=0\,, \tag{2.3}$$

where

$$E=E_M+E_R,\ p=p_M+p_R \text{ and } \frac{\partial m}{\partial r}=4\pi\varrho r^2$$

the suffixes M and R attached to a symbol denote expressions for material and radiative terms, respectively.

Also we have,

$$E_M=\frac{p_M}{\varrho(\gamma-1)}\,,\quad E_R=\frac{3p_R}{\varrho}\,,$$

where γ, as usual, is the ratio of specific heats. The radiation flux F is given by

$$F=-\frac{C}{\varepsilon\varrho}\frac{\mathrm{d}p_R}{\mathrm{d}r}\,, \tag{2.4}$$

where C is the velocity of light and ε is the coefficient of opacity. Also,

$$p_M=zp,\ p_R=(1-z)\,p,\ (0<z<1)$$

so that,

$$E=\frac{p}{\varrho\,(\Gamma-1)} \tag{2.5}$$

where Γ is the Klimshin's coefficient given by

$$\Gamma = \frac{4(\gamma - 1) + z(4 - 3\gamma)}{3(\gamma - 1) + z(4 - 3\gamma)}. \tag{2.6}$$

Now by assuming adiabacy for each element of the fluid, we have,

$$\frac{\partial p}{\partial t} + u \frac{\partial p}{\partial r} = \frac{\Gamma p}{\varrho} \left(\frac{\partial \varrho}{\partial t} + u \frac{\partial \varrho}{\partial r} \right). \tag{2.7}$$

In terms of m, the equation of continuity (2.2) can be expressed as

$$\frac{\partial m}{\partial t} + u \frac{\partial m}{\partial r} = 0. \tag{2.8}$$

The motion is bounded on the outside by a shock surface $r = R(t)$, moving outward with a velocity $V = \frac{\mathrm{d}R}{\mathrm{d}t}$, in terms of which the Rankine—Hugoniot conditions are

$$u_1 = \frac{2V}{\Gamma + 1} \left[1 - \frac{1}{M^2} \right], \tag{2.9}$$

$$p_1 = \frac{p_0}{\Gamma + 1} \left[2\Gamma M^2 - (\Gamma + 1) \right], \tag{2.10}$$

$$\varrho_1 = \frac{\varrho_0 (\Gamma + 1) M^2}{(\Gamma - 1) M^2 + 2}, \tag{2.11}$$

where $M^2 = \frac{V^2 \varrho_0}{\Gamma p_0}$, and p_0, ϱ_0 are pressure and density in the undisturbed region and p_1, ϱ_1 and u_1 are pressure, density and velocity just behind the shock. In front of the shock, in the undisturbed gaseous medium, we have, by assumption $\varrho_0 = \beta r^{-\alpha}$, β being constant. Also, as in SEDOV [5], there is a core round the centre of explosion, which explains for the value $r = 0$. Since the fluid is in hydrostatic equilibrium, we have from (2.1) and the above assumption

$$\frac{\partial p_0}{\partial r} = - \frac{G m_0 \beta r^{-\alpha}}{r^2}, \tag{2.12}$$

where m_0 is the mass within a radius r in the undisturbed state and is given by

$$m_0(r) = 4\pi \int_0^r \varrho_0 r^2 \mathrm{d}r = \frac{4\pi\beta r^{3-\alpha}}{(3 - \alpha)}. \tag{2.13}$$

As a consequence of (2.12) and (2.13) we have

$$p_0 = \frac{2\pi\beta^2 G r^{2-2\alpha}}{(3-\alpha)(\alpha-1)} . \tag{2.14}$$

The physical requirements imposed by the Eqs. (2.14) and (2.13) restrict the value of α so that $1 < \alpha < 3$. The conservation of mass at the shock surface requires

$$m_1 = \int_0^R 4\pi \varrho r^2 \, dr = \frac{4\pi\beta r^{3-\alpha}}{(3-\alpha)} .$$

With the help of Eqs. (2.2) and (2.5), the energy equation (2.3) can be written as

$$\frac{\partial p}{\partial t} + u \frac{\partial p}{\partial r} + \Gamma p \left(\frac{\partial u}{\partial r} + \frac{2u}{r} \right) + \frac{(\Gamma - 1)}{r^2} \frac{\partial}{\partial r} (F r^2) = 0 . \tag{2.15}$$

We now seek a solution of Eq. (2.1), (2.2), (2.7) and (2.15) in the form

$$u = \frac{r}{t} u(\eta) , \tag{2.16}$$

$$p = r^{k+2} t^{\lambda-2} P(\eta) ,$$

$$\varrho = r^k t^\lambda \Omega(\eta) ,$$

$$m = r^{k+3} t^\lambda Z(\eta) ,$$

$$F = r^{k+3} t^{\lambda-3} \bar{F}(\eta) ,$$

where

$$\eta = r^a t^b .$$

The constants K, λ, a and b are for the present kept open and are to be determined from the conditions of the problem.

Let the shock surface be given by

$$\eta_0 = A t^\mu ,$$

where A and μ are constants, so that the velocity of the shock surface is given by

$$V = \frac{\mu - b}{a} \frac{R}{t} .$$

From the equations (2.1), (2.2), (2.7) and (2.15), it can be shown that

$$\frac{\partial E}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} r^2 (uI + F) = 0 , \tag{2.17}$$

where

$$E = \frac{1}{2}\,\varrho u^2 + \frac{p}{(\Gamma - 1)} - \frac{Gm\varrho}{r} \tag{2.18}$$

and

$$I = \frac{1}{2}\,\varrho u^2 + \frac{\Gamma p}{(\Gamma - 1)} - \frac{Gm\varrho}{r}\,. \tag{2.19}$$

Now

$$\frac{p}{\Gamma - 1} = t^{\lambda - 2 - \frac{b}{a}(k+2)}\,\Phi_1(\eta)\,,$$

$$\frac{1}{2}\,\varrho u^2 = t^{\lambda - 2 - \frac{b}{a}(k+2)}\,\Phi_2(\eta)\,,$$

$$\frac{Gm\varrho}{r} = t^{2\lambda - \frac{b}{a}(2k+2)}\,\Phi_3(\eta)$$

so that

$$E = t^{\lambda - 2 - \frac{b}{a}(k+2)}\,\Phi(\eta)\,, \tag{2.20}$$

where we have supposed that

$$\frac{K}{\lambda + 2} = \frac{a}{b}\,. \tag{2.21}$$

From (2.20), it follows that

$$\frac{\partial E}{\partial t} = \left\{\lambda - 2 - \frac{b}{a}(K + 2)\right\}\frac{E}{t} + \frac{b}{a}\,\frac{r}{t}\,\frac{\partial E}{\partial r}\,. \tag{2.22}$$

It is easy to see that in order to get a perfect integral of the combination of Eqs. (2.17) and (2.22) we must have

$$\lambda - 2 - \frac{b}{a}(K + 2) = \frac{3b}{a}\,. \tag{2.23}$$

Without any loss of generality, we may take $\lambda = 2$ in (2.23) so that $K = -5$ and from (2.21) we have, $a = -5$, $b = 4$. Therefore,

$$V = \frac{4 - \mu}{5}\,\frac{R}{t}\,. \tag{2.24}$$

For the disturbance to be characterized by an outgoing shock wave, we should have $\mu < 4$.

Defining the Mach number M at the shock wave by $M^2 = \frac{V^2}{C_0^2}$ we have

$$M^2 = \frac{(4-\mu)^2}{50} \, \frac{(\alpha-1)(3-\alpha)}{\pi \Gamma \beta G} A^{-\frac{\alpha}{5}} t^{\alpha\left(\frac{4-\mu}{5}\right)-2} . \tag{2.25}$$

Now, since

$$C_0{}^2 = \frac{\Gamma p_0}{\varrho_0}, \; \eta_0 = A t^{\mu} = R^{-5} t^4 ,$$

we get

$$R = A^{-\frac{1}{5}} t^{\frac{4-\mu}{5}} .$$

From (2.25) we easily deduce that M is a function of time and will be a decreasing function, if $\alpha < \frac{10}{4-\mu}$.

3. Solution of equations

From (2.16) we have

$$\frac{\partial \varrho}{\partial t} = -\left(\frac{10}{4-\mu}\right) \varrho \frac{V}{R} - \left(\frac{4}{4-\mu}\right) V \frac{r}{R} \frac{\partial \varrho}{\partial r} \tag{3.1}$$

and

$$\frac{\partial p}{\partial t} = -\left(\frac{12}{4-\mu}\right) p \frac{V}{R} - \left(\frac{4}{4-\mu}\right) V \frac{r}{R} \frac{\partial p}{\partial r} . \tag{3.2}$$

Now, from Eqs. (2.17) and (2.22), with values of K, λ, a and b using $K = -5$, $\lambda = 2$, $b = 4$, $a = -5$, determined above we have,

$$r^2 u I + F r^2 - \frac{4}{5} \frac{r^3}{t} E = f(t) . \tag{3.3}$$

The function $f(t)$, when calculated from the conditions at the inner side of the shock surface, is given by,

$$f(t) = \frac{4\pi\beta G(1-z)}{\epsilon(3-\alpha)} A^{\alpha-3} t^{\frac{4-\mu}{5}(3-\alpha)} - \frac{8\pi\beta^2 G A^{\frac{2\alpha-5}{5}} t^{\frac{4-\mu}{5}(5-2\alpha)-1}}{5(\alpha-3)(\Gamma-1)(\alpha-1)} \{2\Gamma(\alpha-1) - 2\alpha + 1\} . \tag{3.4}$$

Now $f(t) = 0$ for a given Γ, if $\alpha = \frac{1}{2}\,\frac{2\Gamma - 1}{\Gamma - 1}$ and $z = 1$, the latter condition corresponds to the non-radiative case. Hence, in the problem under consideration $f(t)$ would not vanish, and increases with time since $\mu < 4$, and $\alpha < 3$.

In equilibrium, the original gravitational and heat energy of the gas enclosed within a radius equal to the radius of the shock, is given by

$$4\pi \int_0^R \left[\frac{p_0}{\Gamma - 1} - \frac{G m_0 \varrho_0}{r}\right] r^2 \mathrm{d}r =$$

$$= - \frac{8\pi^2 \beta^2 G A^{\frac{2\alpha - 5}{5}}\, t^{\frac{4-\mu}{5}(5-2\alpha)}}{(3 - \alpha)(\alpha - 1)(\Gamma - 1)(5 - 2\alpha)} \{2\Gamma(\alpha - 1) - 2\alpha + 1\} \, .$$

When $\alpha = \frac{1}{2}\,\frac{2\Gamma - 1}{\Gamma - 1}$ but not equal to $\frac{5}{2}$, the above expression vanishes showing that the original energy of the gas is zero. Hence we have to make a continuous set of explosions in order that the energy of the wave may vary as it progresses.

In the present problem we imagine the central explosion to be instantaneous so that $f(t)$ is not zero, as deduced earlier.

The values of p, ϱ and u can however be obtained in the case when $f(t)$ is small, its smallness depending not on α or Γ but on the factors β and A. The details follow the same line of procedure as in [6] and are not repeated here.

4. The inner boundary and the energy of the wave

The inner boundary of the wave is obtained as follows.

When

$$r_1 = u_1 \frac{4 - \mu}{4}$$

we have

$$\frac{\mathrm{d}r_1}{\mathrm{d}t} = \frac{4}{5}\,\frac{r_1}{t} \, ,$$

which on integration gives

$$t^4 r_1^{-5} = \text{constant} \, , \tag{4.1}$$

where r_1 is the radius of the inner boundary.

In terms of η we have

$$\eta_1 = r_1^{-5} t^4 = \text{constant}.$$

After the explosion, the total energy $\varphi(t)$ of the configuration is given by

$$\varphi = 4\pi \int_{r_1}^{R} \left[\frac{1}{2} \varrho u^2 + \frac{p}{\Gamma - 1} - \frac{Gm\varrho}{r} \right] r^2 \mathrm{d}r$$

or

$$\varphi = -\frac{4}{5}\pi \int_{\eta_1}^{\eta_0} \left[\frac{1}{2} U^2(\eta)\, \Omega(\eta)\, \eta^{-1} + \frac{P(\eta)}{\Gamma - 1} \eta^{-1}, - GZ(\eta)\, \Omega(\eta) \right] \mathrm{d}\eta \,, \quad (4.2)$$

η_0 and η_1, being the values of η at the shock front and at the surface of the inner boundary, respectively. Since η_1 has been shown to be constant and $\eta_0 = At^{\mu}$, $(\mu \neq 0)$, the equation (4.2) shows that φ is variable depending on time.

REFERENCES

1. P. A. Carrus, P. A. Fox, F. Haas and Z. Kopal, Astrophys. Journ., **113,** 193, 1951.
2. G. I. Taylor, Proc. Roy. Soc. A, **210,** 159, 1950.
3. G. J. Kynch, Modern developments in fluid dynamics, High speed flow ed. L. Howarth 146 (1953).
4. J. L. Taylor, Phil. Mag., **46,** 317, 1955.
5. L. I. Sedov, Similarity and Dimensional Methods in Mechanics, (1959).
6. G. Deb Ray, Proc. National Inst. of Sciences of India. Vol. 35, Supplement 2 (1967).

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AN SU(2) SPIN COEFFICIENT APPROACH TO THE PROBLEM OF RIGIDLY ROTATING FLUID

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This paper deals with the problem of a relativistic stationary, axisymmetric, rigidly rotating fluid by means of Perjés's three-dimensional spin coefficient formalism. The spin coefficient equivalents of the Einstein and Euler equations and those of Weyl and Ricci tensors are calculated. We show that the formalism can be applied even if the cosmological constant Λ is not equal to zero.

1. Introduction

To find the solutions of the Einstein equations is a very difficult problem. If the space-time admits a Killing vector field, the gravitational equations can be reformulated in a 3 dimensional space associated with the trajectories of the Killing motion (background space) [1]. For stationary space-times an SU(2) spin coefficient method has been developed in [1]. The application of this method enables one to find new solutions for the vacuum and electrovac problems [2], [3], [4]. In this paper we show that this method is applicable for the investigation of the stationary, rigidly rotating fluid problem because the spin coefficient form of the field equations is only slightly more complicated than the equations for the vacuum case. The problem of the rigidly rotating fluid is of importance because the final state of a rotating star is such an object.

In Section 2 we investigate the meaning of rigid rotation in general relativity. In Section 2 we apply the method of 3 dimensional relativity for the investigation of the rigidly rotating fluid problem. In this way we get the "3 + 1 decomposed" forms of the Einstein, Euler and material equations. In Section 4 we obtain the spin coefficient forms of these equations, applying the complex triad formalism elaborated in [1]. This Section contains the Weyl and Ricci tensors as well, expressed by the spin coefficients too. The spin coefficient forms of the Einstein equations are simpler than the corresponding equations of the electrovac problem. In Section 4 we prove that there is no rigidly rotating fluid solution with a flat background space. In Section 6 we show that this method can also be applied in the case of a non-zero cosmological constant. We demonstrate that the de Sitter solution can also be simply obtained by this method.

2. The stationary, rigidly rotating fluid

We consider a stationary, axially symmetric metric. The Killing equation has two independent commuting solutions $K^{\mu}_{(\varphi)}$ and $K^{\mu}_{(t)}$, where $t = x^0$, $\varphi = x^3$, $\mu = 0, 1, 2, 3$. The coordinate system can be chosen in such a way that

$$\begin{aligned} K^{\mu}_{(\varphi)} &= \delta^{\varphi}_{3}, \\ K^{\mu}_{(t)} &= \delta^{\mu}_{0}. \end{aligned} \tag{2.1}$$

Condition (2.1) is preserved by the following transformations: (at least for linear combinations of the vectors $K^{\mu}_{(\varphi)}$ and $K^{\mu}_{(t)}$)

$$\begin{aligned} t' &= C_1 t + C_2 \varphi + F(x^A); \\ \varphi' &= C_3 t + C_4 \varphi + G(x^A); \\ x^{A'} &= x^{A'}(x^A). \\ (A &= 1, 2.) \end{aligned} \tag{2.2}$$

Here the C_i-s are constant, $C_1 C_4 - C_2 C_3 = 0$, F and G are arbitrary functions.

The energy-momentum tensor of a perfect fluid has the following form:

$$T_{\mu\nu} = \left(\varrho + \frac{p}{c^2}\right) \mu_{\mu} \mu_{\nu} - p g_{\mu\nu}, \tag{2.3}$$

$$u^{\varphi} u_{\mu} = c^2,$$

Here the scalars φ, p are the mass density and the pressure, respectively, and u is the four-velocity. In the viscous case $T_{\alpha\beta}$ contains further terms. If the fluid is stationary and there is no energy supply these terms must vanish because viscous effects are irreversible. This condition yields equations for u^{α}.

In the rigidly rotating case viscous effects do not play any role, quite independently of the viscosity of the fluid. Namely in this case the distance between two baryons on a $t =$ const. hypersurface is independent of t [5], therefore there is no relative motion. The rotation is rigid when [5]

$$u^{\mu} = u^{\varphi} K^{\mu}_{(\varphi)} + u^{t} K^{\varphi}_{(t)} \tag{2.4}$$

and choosing the coordinate system according to Eq. (2.1)

$$\frac{u^{\varphi}}{u^{t}} = \text{const.} \equiv C. \tag{2.5}$$

We expect that the final state of a rotating star after the gravitational collapse performs rigid rotation because in this case there is no viscous effect.

Now the coordinate system can be chosen so — not violating condition (2.1) — that

$$u^{\varphi} = 0. \tag{2.6}$$

(The transformation (2.2) gives this result when

$$C_4 C = C_3.) \tag{2.7}$$

In the following Sections we shall confine ourselves to the co-ordinate system chosen according to (2.1), (2.6) and we shall investigate only a rigidly rotating fluid.

3. 3-dimensional relativity

Since we have timelike Killing vector, we may apply the method of 3-dimensional relativity [1]. The coordinate system can be chosen in such a way that

$$K^{\mu} = \delta^{\mu}_{0}. \tag{3.1}$$

This condition is preserved by the following transformations:

$$\begin{gathered} t' = t + F^{i}(x)\,, \\ x^{i\,\prime} = x^{i\,\prime}(x^{k})\,, \\ (t = x^{0},\ i = 1, 2, 3). \end{gathered} \tag{3.2}$$

Let us write the line element in the following form:

$$\begin{aligned} \mathrm{d}\tilde{s}^{2} &= -f^{-1}\mathrm{d}s^{2} + f(\mathrm{d}t + \omega_{i}\mathrm{d}x^{i})^{2}\,, \\ \mathrm{d}s^{2} &= g_{ik}\mathrm{d}x^{i}\mathrm{d}x^{k}. \end{aligned} \tag{3.3}$$

(The tilde denotes 4 dimensional quantities.) This form is general because $f = K_{\varrho}K^{\varrho} = 0$. Now we regard g_{ik} as the metric tensor of a 3-dimensional (background) space. The Einstein equations take now the following form:

$$\begin{aligned} &G^{r}{}_{|r} - (G_{r} - \bar{G}_{r})G^{r} = -f^{-2}\tilde{R}_{00}\,, \\ &G_{i|k} - G_{k|i} + G_{i}\bar{G}_{k} - G_{k}\bar{G}_{i} = -i\epsilon_{ikl}\tilde{R}^{l}_{0}f^{-2}\sqrt{g}, \\ &R_{k} + G_{i}\bar{G}_{k} + G_{k}\bar{G}_{i} = f^{-2}(g_{ir}g_{ks}\tilde{R}^{sr} - g_{ik}\tilde{R}_{00}), \end{aligned} \tag{3.4}$$

where

$$G_{i} \equiv \frac{f_{,i} + i\varphi_{i}}{2f}\,;\ \varphi_{i} \equiv \varepsilon_{ikl}\,\omega^{k|l} f^{+2}\sqrt{g}. \tag{3.5}$$

Here $v_{i} = g_{ir}v^{r}$, the stroke denotes 3-dimensional covariant derivation, R_{ik} is the Ricci tensor of the background space. $\tilde{R}^{\alpha\beta}$ can be rewritten by means of $\widetilde{T}^{\alpha\beta}$ taking (3.3) into consideration. Also some further equations exist, e.g. the pressure-density connection.

Let us consider a rigidly rotating fluid. We can perform a coordinate transformation in order to obtain

$$u^{\alpha} = (u^0, 0, 0, 0), \tag{3.6}$$

which preserves conditions (2.1). In this coordinate system we may write the line element in the form (3.2). The form (3.6) is adhered to by the transformations (3.2). Thus the right hand sides of (2.4) assume the following simple forms:

$$\begin{gathered} -f^{-2}\,\widetilde{R}_{00} = A - B; \\ -i\,\epsilon_{ikl}\,\widetilde{R}^{l}_{0} f^{-2}\sqrt{g} = 0 \;\; (\text{and } \varphi_i = \varphi_{,i}); \\ f^{-2}(g_{ir}\,g_{ks}\,\widetilde{R}^{rs} - g_{ik}\,\widetilde{R}_{00}) = g_{ik}(A - 2B); \\ A \equiv -\varkappa c^2 f^{-1}\left(\varrho + \frac{p}{c^2}\right); \\ B \equiv -\frac{1}{2}\varkappa c^2 f^{-1}\left(\varrho - \frac{p}{c^2}\right). \end{gathered} \tag{3.7}$$

The further fluid equations are the following:

a) The pressure—density connection. Making use of (3.7) this is as follows:

$$fB = \psi(fA)\,. \tag{3.8}$$

b) The Euler equations:

$$T^{\alpha\varrho}{}_{;\varrho} = 0. \tag{3.9}$$

Instead of the 4 Euler equations we may use the "continuity equation"

$$T^{\varrho\sigma}{}_{;\sigma}\, u_{\varrho} = 0 \tag{3.10}$$

and the 3-dimensional contracted Bianchi identities

$$\left(R^{ik} - \frac{1}{2} g^{ik} R\right)_{|k} = 0 \tag{3.11}$$

(3 equations). These four equations are equivalent to the Euler equations. It is easy to show that (3.10) is an identity in the case of a rigid rotation. From (3.11) we obtain the following equation:

$$(A - 2B)_{,i} = -2(G_i + \bar{G}_i)(A - B)\,. \tag{3.12}$$

Now we must investigate the quantities A and B. First, from the "energy positivity condition" [6]:

$$A \geq 0, \ A - B \geq 0. \tag{3.13}$$

On the other hand A. R. Curtis has shown that there exists a "causality condition":

$$\frac{\mathrm{d}p}{\mathrm{d}\varrho} \leq c^2. \tag{3.14}$$

Otherwise a "sound" could propagate faster than light in the system. At small densities (according to experience) $p < \varrho c^2$. Thus

$$0 \leq B \leq \frac{A}{2}\,. \tag{3.15}$$

For the simplest cases

$$B = \frac{\alpha}{2} A; \ \alpha = \text{const.} \tag{3.16}$$

The case

$\alpha = 0$ corresponds to a fluid with $p = \varrho c^2$. (Maximally hard matter.) Probably this case is realised in the very dense baryon matter [7].

$\alpha = 1/2$ corresponds to a relativistic degenerate Fermi gas.

$\alpha = 6/7$ corresponds to the equilibrium states of the nucleon-hyperon system [8]

$\alpha = 1$ is the case of the incoherent ($p = 0$) matter.

4. The complex triad formalism

The detailed description of this formalism can be found in [1]. A normalized complex basis vector triad is used in the background space: $z^i_p = l^i$, m^i, $\overline{m}^i$, (l^i is real), $\mathbf{p} = 0, +, -$. The normalization is: $\mathbf{ll} = \mathbf{m\overline{m}} = 1$, $\mathbf{lm} = \mathbf{mm} = 0$. The following scalars are defined:

$$\begin{gathered} \varkappa = -l_{i|k}\, m^i\, l^k\,; \qquad \sigma = -l_{i|k}\, m^i\, m^k\,; \\ \varrho = -l_{i|k}\, m^i\, \overline{m}^k; \ \ \tau = m_{i|k}\, \overline{m}^i\, \overline{m}^k\,; \\ \varepsilon = m_{i|k}\, \overline{m}^i\, l^k\,. \end{gathered} \tag{4.1}$$

ϵ is imaginary, the others are complex. Defining a congruence of curves with tangent $\mathbf{l}$ in the background space, these curves are geodesic if and only if $\varkappa = 0$, and in this case $\mathrm{Re}\varrho$ gives the divergence of the congruence. Similarly, $Im\varrho$ is the rotation and $|\sigma|$ is the shear.

We introduce differential operators as follows:

$$D \equiv l^i \frac{\partial}{\partial x^i}; \quad \delta = m^i \frac{\partial}{\partial x^i} \tag{4.2}$$

with the commutation properties

$$\begin{aligned} D\delta - \delta D &= (\bar{\varrho} + \varepsilon)\delta + \sigma\bar{\delta} + \varkappa D, \\ \delta\bar{\delta} - \bar{\delta}\delta &= -\delta\tau + \bar{\tau}\bar{\delta} - (\varrho - \bar{\varrho})D. \end{aligned} \tag{4.3}$$

The triad can always be chosen in such a manner that

$$\begin{aligned} G_+ = G_i m^i &= 0; \\ \epsilon &= 0, \end{aligned} \tag{4.4}$$

and we have the freedom

$$\begin{aligned} &\mathbf{l}' = \mathbf{l}; \ C^0 \text{ is real and } DC^0 = 0. \\ &\mathbf{m} = \mathbf{m}e^{iC^\circ}; \end{aligned} \tag{4.5}$$

A phase factor χ^0 in one of the quantities ϱ, σ, $\varkappa$, G can be made zero by the transformation (4.5) if $D\chi^0 = 0$. In many cases this choice of the basis vectors is convenient. In the subsequent calculations we will confine our investigations to this choice.

The new form of Eqs. (3.4), (3.7), (3.12) is the following:

$$\begin{aligned} &G_+ = 0, \ \varepsilon = 0, \\ &D\varrho - \bar{\delta}\varkappa = -\tau\varkappa + \varkappa\bar{\varkappa} + \varrho^2 + \sigma\bar{\sigma} + G_0\bar{G}_0 - \frac{1}{2}A + B, \\ &D\sigma - \delta\varkappa = \bar{\tau}\varkappa + \varkappa^2 + (\varrho + \bar{\varrho})\sigma, \\ &D\tau = -\varkappa\bar{\sigma} + \varrho\bar{\varkappa} + \bar{\sigma}\bar{\tau} + \varrho\tau + \bar{G}_0 G_-, \\ &\delta\varrho - \bar{\delta}\sigma = -2\sigma\tau - (\varrho - \bar{\varrho})\varkappa + G_0\bar{G}_+, \\ &\delta\tau + \bar{\delta}\bar{\tau} = 2\tau\bar{\tau} + \varrho\bar{\varrho} - \sigma\bar{\sigma} - G_0\bar{G}_0 + G_+\bar{G}_- - \frac{1}{2}A + B, \\ &DG_0 = (2\varrho + G_0 - \bar{G}_0)G_0 - \varkappa G_- + A - B, \\ &DG_- - \bar{\delta}G_0 = \varrho G_- - \bar{G}_0 G_- + \bar{\varkappa}G_0, \\ &\delta G_0 = -\sigma G_- - \varkappa G_0 - \bar{G}_+ G_0, \\ &\delta G_- = -(\varrho - \bar{\varrho})G_0 + \bar{\tau}G_- - \bar{G}_+ G_-, \\ &D(A - 2B) = -2(G_0 + \bar{G}_0)(A - B), \\ &\delta(A - 2B) = -2\bar{G}_+(A - B), \\ &A \equiv -\frac{kc^2}{f}\left(\varrho + \frac{p}{c^2}\right), \quad B \equiv -\frac{kc^2}{2f}\left(\varrho - \frac{p}{c^2}\right). \end{aligned} \tag{4.6}$$

Now we write down the nonvanishing components of the Weyl and Ricci tensors. These are obtained from the NEWMAN—PENROSE equations [9] substituting the 3 dimensional quantities for the 4 dimensional ones [1]. We get:

$$\begin{aligned}
\psi_0 &\equiv -\tilde{C}_{\alpha\beta\varphi\delta}\,\tilde{l}^\alpha\,\tilde{m}^\beta\,\tilde{l}^\gamma\,\tilde{m}^\delta = -2\sigma G_0\,,\\
\psi_1 &= -\tilde{C}_{\alpha\beta\gamma\delta}\,\tilde{l}^\alpha\,\tilde{n}^\beta\,\tilde{l}^\gamma\,\tilde{m}^\delta = \sqrt{f}\,\varkappa G_0\,,\\
\psi_2 &\equiv -\frac{1}{2}\tilde{C}_{\alpha\beta\gamma\delta}\,(\tilde{l}^\alpha\,\tilde{n}^\beta\,\tilde{l}^\gamma\,\tilde{n}^\delta - \tilde{l}^\beta\,\tilde{n}^\gamma\,\tilde{m}^\gamma\bar{\tilde{m}}^\delta) =\\
&= \frac{f}{2}\left[DG_0 + (G_0+\bar{G}_0)\,G_0 + \varkappa G_- + \frac{1}{3}(A-B)\right],\\
\psi_3 &\equiv \tilde{C}_{\alpha\beta\gamma\delta}\,\tilde{l}^\alpha\,\tilde{n}^\beta\,\tilde{n}^\gamma\,\bar{\tilde{m}}^\delta = \frac{f^{3/2}}{2}[DG_- + (2G_0+\bar{G}_0)G_- - \bar{\varkappa}G_0]\,,\\
\psi_4 &\equiv -\tilde{C}_{\alpha\beta\gamma\delta}\,\tilde{n}^\alpha\,\bar{\tilde{m}}^\beta\,\tilde{n}^\gamma\,\tilde{m}^\delta = \frac{f^2}{2}[\bar{\delta}G_- + (2G_- + \tau)G_- - \bar{\sigma}G_0]\,;
\end{aligned}\tag{4.7}$$

and

$$\begin{aligned}
\Phi_{00} &\equiv -\frac{1}{2}\tilde{R}_{\alpha\beta}\,\tilde{l}^\alpha\,\tilde{l}^\beta = \frac{1}{2}A\,,\\
\Phi_{01} &\equiv \frac{1}{2}\tilde{R}_{\alpha\beta}\,\tilde{l}^\alpha\,\tilde{m}^\beta = 0\,,\\
\Phi_{02} &\equiv -\frac{1}{2}\tilde{R}_{\alpha\beta}\,\tilde{m}^\alpha\,\tilde{m}^\beta = 0\,,\\
\Phi_{10} &\equiv \bar{\Phi}_{01}\,,\\
\Phi_{11} &\equiv \frac{1}{4}\tilde{R}_{\alpha\beta}\,(\tilde{n}^\alpha\,\tilde{l}^\beta + \bar{\tilde{m}}^\alpha\,\tilde{m}^\beta) = \frac{fA}{8}\,,\\
\Phi_{12} &\equiv -\frac{1}{2}\tilde{R}_{\alpha\beta}\,\tilde{m}^\alpha\,\tilde{n}^\beta = 0\,,\\
\Phi_{20} &\equiv \bar{\Phi}_{02}\,,\\
\Phi_{21} &\equiv \bar{\Phi}_{12}\,,\\
\Phi_{22} &\equiv -\frac{1}{2}\tilde{R}_{\alpha\beta}\,\tilde{n}^\alpha\,\tilde{n}^\beta = -\frac{f^2A}{8}\,;\\
\Lambda &\equiv \frac{R}{24} = -\frac{f}{24}(A-4B)\,.
\end{aligned}\tag{4.8}$$

5. The flat background problem

It will be shown that rigidly rotating fluid solutions with flat background space do not exist.

If the background space is flat ($R_{ik} = 0$) we may use Cartesian coordinates. When $i = k$, Eqs. (3.4), (3.7) give

$$| G_1 |^2 = | G_2 |^2 = | G_3 |^2 = \frac{1}{2} A - B . \tag{5.1}$$

On the other hand for $i \neq k$ we get:

$$Re(G_1 \bar{G}_2) = Re(G_1 \bar{G}_3) = Re(G_2 \bar{G}_3) = 0. \tag{5.2}$$

From Eqs. (5.1—2) we obtain: $G_i = 0$, i.e. $f =$ const. and $\omega_i = 0$. This is the Minkowskian space-time, which is empty.

6. Einstein equations with $\lambda \neq 0$

The most general form of the Einstein equations is as follows:

$$R_{\alpha\beta} + \left(\lambda - \frac{1}{2} R\right) g_{\alpha\beta} = \varkappa T_{\alpha\beta} . \tag{6.1}$$

Here λ is the cosmological constant. This equation is equivalent to an Einstein equation with $\lambda = 0$, in which

$$T^{x}_{\alpha\beta} = T_{\alpha\beta} - \frac{\lambda}{\varkappa} g_{\alpha\beta} . \tag{6.2}$$

If the matter is a fluid, $T^{x}_{\alpha\beta}$ is also a fluid energy-momentum tensor, and

$$\begin{aligned} p^x &= p + \frac{\lambda}{\varkappa} ; \\ \varrho^x &= \varrho - \frac{\lambda}{\varkappa c^2} ; \end{aligned} \qquad u^{\alpha x} = u^{\alpha} . \tag{6.3}$$

If the fluid rotates rigidly, the previously described procedure can be used again.

Now we show that the de Sitter vacuum solution can be easily obtained in this way.

We look for vacuum solutions. Consequently:

$$\begin{aligned} A &= 0, \\ B &= \lambda f^{-1}. \end{aligned} \tag{6.4}$$

(The conditions (3.13—15) now cannot be fulfilled.) The velocities do not occur in the equations because $A = 0$, therefore we may treat this problem as a fluid with rigid rotation.

Let us restrict ourselves to the case of geodesic and shearfree eigenrays:

$$\varkappa = \sigma = 0. \tag{6.5}$$

Adding Eqs. (4.6b,g) we obtain:

$$D(\varrho + G) = (\varrho + G)^2. \tag{6.6}$$

The coordinate system can be chosen in the following way:

$$l^i = \delta^i_1;\ m^i = \omega\delta^i_1 + \xi^a\,\delta^i_a;\ a = 2, 3;\ x^1 = r. \tag{6.7}$$

Applying the commutators (4.3) on the quantities r, x^a we obtain equations for the ω and ξ^a:

$$\begin{aligned} D\omega &= \bar{\varrho}\omega + \sigma\bar{\omega} + \varkappa, \\ D\xi^a &= \bar{\varrho}\xi^a + \sigma\bar{\xi}^a, \\ \delta\bar{\omega} - \bar{\delta}\omega &= \bar{\tau}\bar{\omega} - \tau\omega + \bar{\varrho} - \varrho, \\ \delta\bar{\xi}^a - \bar{\delta}\xi^a &= \bar{\tau}\bar{\xi}^a - \tau\xi^a. \end{aligned} \tag{6.8}$$

There remains the following freedom in the choice of the coordinate system:

$$\begin{aligned} r' &= r + r^0(x^a); \\ x^{a'} &= x^{a'}(x^b). \end{aligned} \tag{6.9}$$

The Eq. (6.6) has two solutions:

$$\begin{aligned} \varrho + G_0 &= 0, \\ \varrho + G_0 &= -(r + i\alpha^0)^{-1}, \end{aligned} \tag{6.10}$$

where the upper index ^{0} denotes the quantities independent of r. In the second case we made use of the freedom (6.9a). Now we proceed to the second case.

Looking at the curvanture quantities it can be seen that

$$\psi_0 = \psi_1 = \Phi_{ab} = 0; \quad \Lambda = \frac{\lambda}{6}. \tag{6.11}$$

We will restrict ourselves to the case $\psi_2 = \text{const}$. In this case the algebraic curvature invariants are constant quantities. Assuming this constancy the third of the Eqs. (4.7) can be solved by the help of Eq. (6.10b). If we insert this solution into Eq. (4.6g) and impose the condition $\lim\limits_{r \to 0} f = 1$, we obtain:

$$\begin{aligned} \psi_2 &= -\frac{2}{3}\lambda + \Phi + i\psi; \; \Phi_{,i} = \psi_{,i} = 0; \\ f &= 1 + 2\Phi\alpha^0 r - \psi r^2; \\ \varphi &= \varphi^0 - 2\,\psi\alpha^0\, r - \Phi r^2 . \end{aligned} \tag{6.12}$$

Now we can calculate ϱ and G_0. Afer this the "radial" equations of (6.8) can be solved:

$$\begin{aligned} A &= A^0 f^{-1/2}(r - i\alpha^0)^{-1/2}\, e^{i\Omega}; \; A \equiv (\omega, \xi^a); \\ 2\Omega &\equiv \int f^{-1}\, \varphi_{,r}\, \mathrm{d}r . \end{aligned} \tag{6.13}$$

From the equation $G_+ \; I = 0$ we get:

$$\begin{aligned} \eth\varphi^0 &= 2\alpha^0\omega^0(\psi + i\Phi) ; \\ \omega^0 + i\eth\alpha^0 &= 0 ; \\ \eth &\equiv \xi^{a0}\frac{\partial}{\partial x^a} . \end{aligned} \tag{6.14}$$

Now we can integrate the radial equation of τ:

$$\begin{aligned} \tau &= T f^{-1/2}(r + i\alpha^0)^{-1}\, e^{-i\Omega} , \\ T &\equiv 2\bar{\omega}^0 \int f^{-2}(r - i\alpha^0)[(\Phi^2 + \psi^2) r - \Phi(\psi - i\Phi)]\, \alpha^0 \mathrm{d}r. \end{aligned} \tag{6.15}$$

From the remaining equations (4.6f), (6.8c—d) we get:

$$\begin{aligned} &\alpha = \omega^0 = \Omega = G_- = \psi_3 = \psi_4 = 0 ; \; \Phi = 0, \; \psi = \frac{\lambda}{3} ; \\ &\eth\bar{\xi}^{a0} - \bar{\eth}\xi^{a0} = \bar{\tau}^0\bar{\xi}^{a0} - \tau^a\,\xi^{a0} ; \\ &\eth\tau^0 + \bar{\eth}\bar{\tau} = 2\tau^0\,\bar{\tau}^0 + 1 . \end{aligned} \tag{6.16}$$

It is convenient to introduce the real quantity $P = \xi^{20} = -i\xi^{30}$ and the complex coordinate $z = x^2 + ix^3$ as in [1]. Then the solution of Eq. (6.16) has the following form:

$$P = \frac{1 + z\bar{z}}{2\sqrt{2}} ; \quad \tau^0 = \frac{\bar{z}}{\sqrt{2}} . \tag{6.17}$$

Now the 4-dimensional metric tensor $\tilde{g}_{\alpha\beta}$ can be reconstructed and we get:

$$d\tilde{s}^2 = -\left(1 - \frac{\lambda}{3} r^2\right)^{-1} dr^2 - r^2(d^2\vartheta + \sin^2\vartheta\, d\varphi^2) + \left(1 - \frac{\lambda}{3} r^2\right) dt^2 . \tag{6.18}$$

This is the customary form of the de Sitter solution.

For the sake of completeness we shall investigate also the solution (6.10a). In this case the Eqs. (6.11) are unchanged. From Eqs. (4.6b), (6.10a) we obtain:

$$\begin{aligned} G_0 &= -\varrho = (r + iQ)(r^2 + K)^{-1}; \\ f &= -\lambda(r^2 + K); \\ Q_{,r} &= K_{,r} = 0 . \end{aligned} \tag{6.19}$$

Here we made use of the freedom (6.9a). We impose again the condition $\lim\limits_{r\to 0} f = 1$. As a consequence we have

$$K = -\lambda^{-1}. \tag{6.20}$$

Integrating (6.8a—b) and (4.6a) we get:

$$\begin{aligned} &A = A^0 \mid r^2 - \lambda^{-1} \mid^{-1/2} e^{i\Omega Q}; \quad A \equiv (\omega, \xi^a); \; \Omega \equiv \int \frac{dr}{r^2 - \lambda^{-1}}, \\ &\omega^0 + i\eth Q = 0; \quad 2Q\omega^0 - \eth\varphi^0 = 0. \end{aligned} \tag{6.21}$$

Now the quantities τ, φ can be calculated and the result is the following:

$$\begin{aligned} \tau &= \left[\tau^0 + \bar{\omega}^0 \left(\Omega - \frac{r - iQ}{r^2 - \lambda^{-1}}\right)\right] |r^2 - \lambda^{-1}|^{-1/2} e^{-i\Omega Q}; \\ \varphi &= \varphi^0 \lambda - 2Q\lambda r. \end{aligned} \tag{6.22}$$

Introducing again the quantities P and z we can integrate Eqs. (4.6f), (6.8c—d) and get the following:

$$\text{if } \lambda > 0,\; P = \frac{1 + z\bar{z}}{2\sqrt{2}}; \quad \text{if } \lambda < 0,\; P = -\frac{1 - z\bar{z}}{2\sqrt{2}} \tag{6.23}$$

and, independently of the sign of λ:

$$\begin{aligned} \tau^0 &= \frac{\bar{z}}{\sqrt{2}}; \; \omega^0 = Q = 0; \\ f &= 1 - \lambda r^2; \\ \varphi &= 0. \end{aligned} \tag{6.24}$$

The solutions are static because $\varphi = 0$.

The curvature quantities (4.7—8) vanish except the following two:

$$\psi_2 = -4\,\Lambda = -\frac{2}{3}\lambda\,. \tag{6.25}$$

Reconstructing the 4-dimensional metric tensor we get two solutions:

$$\begin{aligned} &\lambda > 0 \\ &d\tilde{s}^2 = (1-\lambda r^2)dt^2 - \frac{1}{1-\lambda r^2}dr^2 - \lambda^{-1}(d\Theta^2 + \sin^2\Theta\, d\Phi^2); \\ &\lambda < 0 \\ &d\tilde{s}^2 = (1-\lambda r^2)dt^2 - \frac{1}{1-\lambda r^2}dr^2 + \lambda^{-1}(dX^2 + sh^2 X d\Phi^2). \end{aligned} \tag{6.26}$$

The Riemann spaces having a line element of the form (6.26) admit 6 linearly independent Killing vectors. The operators $G_{(i)}$ defined by

$$G_{(i)} = K^{\varrho}_{(i)}\,\partial_{\varrho} \tag{6.27}$$

are the generators of an SU(2) ⊗ SU(1,1) group if λ is positive and an SU(1,1) ⊗ ⊗ SU(1,1) group if λ is negative. Thus the symmetries of these solutions are different from the "hyperspherical" symmetry generally required for the Universe solutions.

7. Conclusion

The Eqs. (4.6) are only slightly more complicated than the corresponding equations of the vacuum problem. In the electrovac problem, which can be conveniently investigated by this method in some cases, 3 complex quantities ($H\mathbf{p}$) appear in addition to the quantities of the vacuum equations. On the other hand, in the rigidly rotating fluid problem only 2 real quantities (A, B) appear. The pressure-density connection (3.8) has an inconvenient form but in the important case when the condition (4.16) is realized its form becomes simple. Thus, in some cases, these equations can be solved. Such solutions will be presented in forthcoming publications.

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REFERENCES

1. Z. Perjés, J. Math. Phys., **11**, 3383, 1970.
2. J. Kóta and Z. Perjés, J. Math. Phys., **13**, 1695, 1972.
3. Z. Perjés, Phys. Rev. Lett., **27**, 1668, 1971.
4. B. Lukács and Z. Perjés, GRG-Journal **4**, 161, 1973.
5. K. S. Thorne, Proc. of the Int. School of Phys. "Enrico Fermi" **47**, 237, 1971.
6. G. F. R. Ellis, Proc. of the Int. School of Phys. "Enrico Fermi" **47**, 104, 1971.
7. J. B. Zel'dovich and I. D. Novikov, Teoriya tyagoteniya i evolyuciya zvezd, Nauka Moscow, 1971.
8. V. A. Ambarcumyan and G. S. Saakyan, Astron. Zh., **37**, 193, 1960.
9. E. T. Newman and R. Penrose, J. Math. Phys., **3**, 566, 1962.

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VARIATIONAL CALCULATION IN THE UNIVERSAL POTENTIAL FIELD WITH EVEN-TEMPERED FUNCTIONS

By

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Atomic one-electron energies and associated radial orthogonalized wavefunctions are calculated with the variational method. The potential field was a universal one and the trial functions were taken as linear combinations of Slater-type orbitals. The exponents were determined by a geometrical series which are sometimes called "even-tempered" exponents [1]. Energies, linear coefficients, exponents are tabulated for Li, O, Cr, Cu atoms, respectively. The agreement with the experimental results and other theoretical ones is good.

1. Introduction

The functional

$$E[\Psi] = \langle \Psi \mid H \mid \Psi \rangle / \langle \Psi \mid \Psi \rangle \tag{1.1}$$

is an extremum for the variational of Ψ if and only if Ψ is equal to an eigenfunction of the Hamiltonian H. In this paper we have used the Rayleigh—Ritz variational principle for the determination of the wavefunction and energy.

The trial function for the k-th energy level is

$$\Psi_k = \sum_{i=1}^{M} C_{ki} \Phi_i \; (k = 1, \ldots M), \tag{1.2}$$

where $\Phi_i (i = 1, \ldots, M)$ is a set of the linearly independent functions and the C_{ki} are the linear coefficients to be determined from the condition

$$\delta E[\Psi] = 0, \tag{1.3}$$

where the variation is with respect to the linear parameters. The nonlinear parameters in Φ_i have been selected by a special procedure (See later).

From Eq. (1.3) one obtains the set of the linear equations,

$$\sum_{i=1}^{M} C_{ki} (H_{ij} - E S_{ij}) = 0 \quad (j = 1, \ldots, M), \tag{1.4}$$

where the overlap integral is

$$S_{ij} = \langle \Phi_i \mid \Phi_j \rangle = \int \Phi_i^* \Phi_j \, d\tau \tag{1.5}$$

and the matrix elements of the energy operator are

$$H_{ij} = \langle \Phi_i \mid H \mid \Phi_j \rangle = \int \Phi_i^* H \Phi_j \, d\tau. \tag{1.6}$$

The Appendix gives details of the algebra for the matrix elements.

The set of Eqs. (1.4) has nontrivial solutions only for those values of E for which

$$\det \| H_{ij} - E S_{ij} \| = 0. \tag{1.7}$$

The M roots E_k of this equation are upper bounds to the M lowest eigenvalues of H [2].

2. Hamiltonian and the trial functions

Consider the following Hamiltonian

$$H = T - eV, \tag{2.1}$$

where $T = -\frac{1}{2} \vec{\nabla}^2 e^2 a_0$ is the kinetic energy operator and

$$V(r) = \frac{Ze}{r} \frac{e^{-\lambda_0 x}}{1 + A_0 x} + C' \frac{e^{-\alpha x}}{1 + Ax} \tag{2.2}$$

is the "universal" potential of a neutral atom with the atomic number Z. The scaled variable is

$$x = \frac{r}{\mu}, \qquad \mu = \frac{0.88534137}{Z^{1/3}} a_0 \tag{2.3}$$

with the constants [3], [4]

$$\begin{array}{ll} \lambda_0 = 0.1837 & \alpha = 0.04 \\ A_0 = 1.05 & A = 9.0 \end{array} \quad C' = \left(\frac{3}{\pi}\right)^{1/3} c Z^{2/3} e a_0^{-1} \tag{2.4}$$

and r is the distance of the electron from the nucleus, a_0 is the radius of Bohr's smallest orbital in the hydrogen atom, and e is the elementary charge.

The parameter c has been determined from the normalization of the charge density [4]. In this mean we get

$$c = 3.266243. \tag{2.5}$$

Because the potential (2.2) is a spherically symmetrical one, we can simplify the Hamiltonian in spherical polar coordinates, so that

$$H \equiv -\frac{1}{2}\,\frac{1}{r}\,\frac{\mathrm{d}^2}{\mathrm{d}r^2}\,r + \frac{1}{2}\,\frac{l(l+1)}{r^2} - V(r)\,, \tag{2.6}$$

where we have introduced atomic units by setting $e = 1$, $a_0 = 1$.

There are two types of possible basis functions ($s = 1$ or 2)

$$\Phi^s(k, n_s) = N_{ns}(\zeta_{ns,\,k})\, r^{n_s}\, e^{-\zeta_{ns,\,k} r}\,, \tag{2.7}$$

where $n_1 = l$ is the azimuthal quantum number for the corresponding orbitals, or $n_1 = \nu - 1$, where ν is the principal quantum number.

The normalization condition gives

$$N_{ns}(\zeta_{ns,\,k}) = \frac{(2\zeta_{ns,\,k})^{n_s + \frac{3}{2}}}{[4\pi(2n_s + 2)!]^{1/2}} \qquad (s = 1 \text{ or } 2). \tag{2.8}$$

The nonlinear parameters are

$$\zeta_{ns,\,k} = a_{ns}(b_{ns})^k, \tag{2.9}$$

where $s_{n_s} > 0$, $b_{n_s} > 1$ for both values of s and $k = 1, \ldots M$, M is the dimension of the basic set. These exponents form a geometrical progression and may be called "even-tempered". According to [1] the original even-tempered atomic orbitals are those with $s = 1$, in which the factor r^l is the same for all of the orbitals with identical l. In the basis of other type, $s = 2$, the factors $r^{\nu - 1}$ are different for orbitals with the same l, but with different principal quantum numbers. We have used these SLATER-type functions as basis set in our calculations. We have determined the a_{n_2} and b_{n_2} for an actual atom by a special procedure based on the SLATER rules [19].

The SLATER exponents are by definition

$$\zeta_{\nu k} = \frac{Z - \sigma(\nu, k)}{\nu}\,, \tag{2.10}$$

where $\sigma(\nu, k)$ are the screening parameters. We have determined the exponents by this method for the orbitals (1s), (2s) resp. (2p), (3p) and so on. From these two values of $\zeta_{\nu k}$ we have determined a_{n_2} and b_{n_2} and with the aid of (2.9) the other exponents. For example the Li atom has the electron configuration: $(1s)^2\,(2s)$. Using the SLATER rules we get the single-ζ exponents

$$\zeta^0_{1s} = 2.7 \quad \text{and} \quad \zeta^{0s}_2 = 0.65\,.$$

The exponents of r are 0 and 1, respectively.

Table I

One-electron energies for the Li, O, Cr, Cu atoms with single-double-triple-zeta approximation (in atomic units)

E, calculated here, E(HFS), Hartree—Fock—Slater [5], E(SL) experimental values revised by Slater [6], E(CL), E(R), E(W), calculated by Clementi, Roothaan, and Watson respectively [7], [8], [9], [10], X, X-ray terms [12].

Z	Shell	$-E$	Single double triple	$-E$(HFS)	$-E$(SL)	$-E$(CL)	$-E$(R)* $-E$(W)	$-E$(X-term)
3	1s	2.11031 2.12212 2.12239		2.199	2.385	—	2.46345*	1.8
	2s	0.07821 0.07836		0.20195	0.2	—	0.07932*	—
8	1s	19.4745 19.4881 19.4888		19.728	19.95	—	—	19.65
	2s	1.09116 1.09503 1.09625		1.072	1.19	—	—	—
	2p	0.46972 0.52097 0.52741		0.52045	0.585	—	—	0.35
24	1s	218.676 218.689 218.689		217.275	220.8	220.591	220.583	220.5
	2s	22.7408 23.8035 23.8055		24.9115	25.95	26.4387	26.4308	25.01
	2p	20.1348 20.2753 20.2803		21.3895	21.5	22.3648	22.3569	21.1683
	3s	2.30297 2.63070 2.63086		2.8557	3.0	3.49901	3.4911	2.62
	3p	1.50621 1.57043 1.61850		1.8455	1.8	2.24828	2.2413	1.51

Table I (continued)

Z	Shell	$-E$ Single double triple	$-E$(HFS)	$-E$(SL)	$-E$(CL)	$-E$(R)* $-E$(W)	$-E$(X-term)
24	$3d$	−0.00863 0.09654 0.10826	0.23945	0.375	0.56886	0.5634	0.075
	$4s$	0.08675 0.15067 0.16251	0.2156	0.285	0.24002	0.2379	—
29	$1s$	328.453 328.466 328.466	324.85	331.0	329.03416	329.0036	330.735
	$2s$	37.2103 39.0196 39.0218	39.075	40.65	41.08504	41.0536	40.585
	$2p$	34.3307 34.4791 34.4837	34.51	34.8	35.87936	35.8483	34.613
	$3s$	3.91148 5.02853 5.02874	4.317	4.8	5.26095	5.2306	4.49
	$3p$	3.21301 3.41866 3.51903	2.8548	3.05	3.55720	3.5287	2.8183
	$3d$	0.289645 0.706316 0.955062	0.37155	0.39	0.74046	0.7155	0.12
	$4s$	0.372103 0.380000 0.392591	0.25455	0.285	0.28486	0.2787	—

Table II

Orbital exponents and linear coefficients for the eigenfunctions of the atomic states. (The last number in the rows for C is an exponent to the base 10.)

$Z = 3$	νl	Exponents	$C(1s)$		$C(2s)$	
single	$1s$	2.7	0.99788562	0	−0.18070473	0
ζ	$2s$	0.65	0.12276234	−1	0.10140410	1
	$1s$	5.502866	0.60592991	−1	−0.47643616	−3
double	$1s'$	2.7	0.92766156	0	0.19288980	0
ζ	$2s$	1.324764	0.51104000	−1	−0.32277556	−1
	$2s'$	0.65	−0.16267865	−1	−0.99218544	0

$Z = 8$	νl	Exponents	$C(1s)$		$C(2s)$	
single	$1s$	7.7	0.99707024	0	−0.25197159	0
ζ	$2s$	2.275	0.12246278	−1	0.10283427	1
	$1s$	14.165940	0.27940000	−1	−0.18387732	−1
double	$1s'$	7.7	0.95675289	0	0.27927300	0
ζ	$2s$	4.185391	0.40704787	−1	−0.27956196	−1
	$2s'$	2.275	−0.12648622	−1	−0.10108471	−1

$Z = 8$	νl	Exponents	$C(2p)$	
single	$2p$	2.45	0.97906870	0
ζ	$3p$	0.583334	0.12423866	0
	$2p$	5.021006	0.87090116	−1
double	$2p'$	2.45	0.77500536	0
ζ	$3p$	1.195478	0.33010809	0
	$3p'$	0.583334	−0.90241496	−1

Table II (continued)

$Z = 24$	νl	Exponents	$C(1s)$		$C(2s)$		$C(3s)$		$C(4s)$	
single ζ	1s	23.7	0.99726747	0	−0.41049474	0	0.18904585	0	−0.12352587	−1
	2s	9.925	0.70691362	−2	0.10367114	1	−0.54216821	0	0.35676694	−1
	3s	4.25	−0.13776498	−2	0.10598709	0	0.10721165	1	−0.74727539	−1
	4s	0.8625	0.51615603	−4	−0.33979232	−2	0.25077044	−1	0.10006782	1
double ζ	1s	36.623282	0.19555740	−1	−0.37752730	−1	−0.10727826	−1	0.65473529	−3
	1s’	23.7	0.96971345	0	0.37007582	0	0.12712990	0	−0.36113620	−1
	2s	15.336965	0.25114313	−1	0.22137806	0	0.13618615	0	−0.63812217	−1
	2s’	9.925	−0.10549719	−1	−0.11963896	1	−0.57293514	0	0.21974334	0
	3s	6.422759	0.38643578	−2	−0.85304755	−1	−0.11743885	−2	−0.64324998	−1
	3s’	4.156355	−0.21890761	−2	0.17232924	−1	0.10011786	1	−0.28200065	0
	4s	2.689670	0.81472923	−3	−0.26936254	−2	−0.20697618	−1	0.11698813	1
	4s’	1.740583	−0.32372715	−3	0.64407804	−3				

For the double-ζ exponents we have (the index n_2 is neglected here)

$$\zeta_{1s} = ab^4, \quad \zeta'_{1s} = ab^3 = 2.7 = \zeta^0_{1s}, \quad \zeta_{2s} = ab^2, \quad \zeta'_{2s} = ab = 0.65 = \zeta^0_{2s}.$$

From these relations one can determine the parameters a and b, then one can get ζ_{1s}, ζ_{2s}.

If $l = 1$ (for example in the case of oxygen) then we take up an electron (ν, p), to the quasi excited orbital $(\nu + 1, p)$ and this configuration will be regarded as in the case of the orbitals (ν, s).

Table II (continued)

$Z = 24$	νl	Exponents	$C(2p)$		$C(3p)$	
single	$2p$	9.925	0.98260505	0	−0.42128671	0
ζ	$3p$	4.25	0.46503687	−1	0.10680976	1
	$2p$	15.167057	0.13430991	0	0.77194025	−1
double	$2p'$	9.925	0.79373519	0	0.23540744	0
ζ	$3p$	6.494709	0.15371002	0	0.26930198	0
	$3p'$	4.25	−0.41814336	−1	−0.12436930	1

$Z = 24$	νl	Exponents	$C(3d)$	
single	$3d$	1.766667	—	
ζ	$4d$	0.25	—	
	$3d$	4.696366	0.37036312	0
double	$3d'$	1.766667	0.72978391	0
ζ	$4d$	0.664580	0.17749335	0
	$4d'$	0.25	−0.34495340	−1

For the other orbitals the procedure is the same (see Table II).

In our case $\nu = n^*$ namely $n^* = 1, 2, 3, \ldots$ It is advantageous that we did not have to carry out a variation of the nonlinear parameters.

We have calculated the one-electron energies by using the above basis sets. There is no significant improvement in going from the double-zeta basis set to the triple-zeta basis set. Therefore we have tabulated only the linear coefficients of calculations with single-zeta and double-zeta sets.

3. Numerical calculations and results

The investigations were performed for the Li atom ($Z = 3$), O ($Z = 8$), Cr ($Z = 24$), Cu ($Z = 29$). The one-electron energies are tabulated in Table I with other theoretical results and experimental data. Comparing our results with the experimental ones, a good agreement is found.

There is small difference between our results and those of the Hartree—Fock—Slater (HFS) calculations, respectively, and the Slater's ionization energies which were determined by the investigations of the optical and X-ray data of the atoms [6]. The linear and non-linear parameters of the one-

Table II (continued)

$Z = 29$	νl	Exponents	$C(1s)$		$C(2s)$		$C(3s)$		$C(4s)$	
single	1*s*	28.7	0.99755501	0	−0.42268654	0	0.23938210	0	−0.83649162	−2
ζ	2*s*	12.425	0.61002517	−2	0.10205207	1	−0.67264012	0	0.23682918	−1
	3*s*	5.916667	−0.12901678	−2	0.13409941	0	0.11094811	1	−0.41137561	−1
	4*s*	0.925	0.20043162	−4	−0.17154587	−2	0.17601009	−1	0.10000345	1
	1*s*	43.618894	0.17416554	−1	−0.40337634	−1	−0.11008711	−1	0.83277058	−3
	1*s*'	28.7	0.97331217	0	0.38127044	0	0.13711095	0	−0.42339911	−1
double	2*s*	18.883789	0.21317796	−1	0.25962044	0	0.17302396	0	−0.80908543	−1
ζ	2*s*'	12.425	−0.87705342	−2	−0.12338155	1	−0.64584956	0	0.25033846	0
	3*s*	8.175299	0.30919984	−2	−0.84466016	−1	−0.10849108	−1	−0.50107250	−1
	3*s*'	5.379116	−0.17304952	−2	0.16979061	−1	0.10469514	1	−0.36264213	0
	4*s*	3.539306	0.62413300	−3	−0.23968075	−2	0.92118738	−1	−0.98102438	−1
	4*s*'	2.328764	−0.24302176	−3	0.49650542	−3	−0.12302227	−1	0.11205654	1

electron wavefunctions are tabulated in Table II. These functions are mutually orthogonal and they have simple analytical forms.

The diamagnetic susceptibility is an efficient check on the accuracy of the wavefunctions for greater values of *r*. The diamagnetic susceptibility has been calculated by the formula [18]

$$-\chi = 0.791987 \times 10^{-6} \sum_k \langle r_k^2 \rangle ,$$

Table II (continued)

$Z = 29$	vl	Exponents	$C(2p)$		$C(3p)$	
single	$2p$	12.425	0.98135763	0	−0.50197706	0
ζ	$3p$	5.916667	0.42542282	−1	0.11014690	1
	$2p$	18.005536	0.14398658	0	0.11414819	0
double	$2p'$	12.425	0.77906960	0	0.20432127	0
ζ	$3p$	8.574065	0.15302140	0	0.46636989	0
	$3p'$	5.916667	−0.40879519	−1	−0.14101632	1

$Z = 29$	vl	Exponents	$C(3d)$	
single	$3d$	2.733334	0.99996848	0
ζ	$4d$*	0.25	0.58127782	−2
	$3d$	9.037928	0.26198798	0
double	$3d'$	2.733334	0.88767601	0
ζ	$4d$*	0.826634	0.38814302	−2
	$4d$*'	0.25	0.12026091	−3

Note: * These orbitals are quasi excited ones.

where the average value $\langle r^2\rangle$ is expressed in atomic units and the sum has to be extended over all electrons of the atom. We have used only double-zeta basis for the wavefunctions.

Table III

Diamagnetic susceptibility $\left(-\chi\times 10^{+6}\,\frac{\text{cm}^3}{\text{mol}}\right)$ of Li, O, Cr and Cu

Z	Slater [21]	Angus [16]	Burns [17]	Clementi [18]	Hartree—Fock non-rel. [20]	Present work
3	14.674	14.674	17.217	15.129	14.7563	14.7186
8	6.949	5.998	8.621	7.211	8.9234	9.3316
24	—	—	—	—	31.5656	33.2774
29	34.588	34.450	17.355	18.883	25.4777	19.603

In Table III we have compared our results with other theoretical ones which were calculated by using SLATER-type functions and parameters by SLATER, ANGUS, BURNS, respectively [16], [17]. The HARTREE—FOCK non-relativistic results are also given [18].

The results clearly show that energy eigenvalues and wave functions calculated by the universal potential field (2.2) have comparable accuracy with the much more laborious HARTREE—FOCK—SLATER (HFS) self-consistent-field values. A further advantage of the wave functions calculated here is that while the HFS results appear in a tabulated form because of the numerical character of the HFS method our wave functions having an analytical form may be used more straightforwardly in molecular calculations.

We have developed a computer program for the calculations. This program consists of different procedures containing the solution of Eq. (1.4) which can be written in the matrix form. We have used Jacobi's method for the calculation of the eigenvalues. The eigenvectors have been determined by the Gauss elimination method. The computer program calculates the values of exponential integral, too.

Appendix

The matrix elements of the Hamiltonian (2.6) with the trial functions (2.7) are

$$H_{ij} = H_{ji} = \frac{N_i N_j}{2} \{[l(l+1) - A_j + B_{ij}] U^2_{ij}\} - \\ - N_i N_j [Z\tilde{a} F(\nu_{ij} - 1, \xi, \tilde{a}) + C' \tilde{b}\, F(\nu_{ij}, \eta, \hat{b})] ,$$

where

$$A_j = \nu_j(\nu_j - 1),$$

$$B_{ij} = \zeta_j \frac{\nu_{ij} - 1}{\zeta_{ij}} \left[2\nu_j - \frac{\zeta_j \nu_{ij}}{\zeta_{ij}} \right].$$

The overlap integrals are given by

$$S_{ij} = S_{ji} = N_i N_j U^0_{ij} ,$$

where

$$\nu_{ij} = \nu_i + \nu_j , \qquad \zeta_{ij} = \zeta_i + \zeta_j , \qquad \tilde{a} = \frac{\mu}{A_0} ,$$

$$\xi = \zeta_{ij} + \frac{\lambda_0}{\mu} , \qquad \eta = \zeta_{ij} + \frac{\alpha}{\mu} , \qquad \tilde{b} = \frac{\mu}{A} .$$

The following integrals occur in the calculations of the matrix elements

$$U^k_{ij} = \int_0^\infty x^{\nu_{ij}-k}\, e^{-\zeta_{ij}x}\, dx = \frac{(\nu_{ij}-k)!}{\zeta_{ij}^{\nu_{ij}-k+1}},$$

if ν_{ij} and k are integers $\zeta_{ij} > 0$ and

$$F(k, l, m) = \int_0^\infty \frac{x^k e^{-lx}}{m+x}\, \mathrm{d}x = (-1)^{k-1} m^k e^{l\cdot m} E_i(-l\cdot m) + \\ + \sum_{s=1}^{k} (s-1)!\,(-m)^{k-s}\, l^{-s}$$

if $|\arg m| < \pi$, $Re\, l > 0$. Because of the potential form (2.2) we had to introduce the exponential integrals

$$E_i(z) = \int_{-\infty}^{z} \frac{e^y}{y}\, \mathrm{d}y.$$

For negative real values

$$E_1(t) = -E_i(-t) = \int_t^\infty \frac{e^{-y}}{y}\, \mathrm{d}y.$$

The power series expansion

$$E_1(t) = -E_c + \log\frac{1}{t} + t - \frac{t^2}{2\,!\,2} + \frac{t^3}{3\,!\,3} - \dots$$

holds with the Euler constant

$$E_c = \int_0^\infty e^{-y}\log\frac{1}{y}\, \mathrm{d}y = 0.577215\dots$$

For $t \gg 1$ the semiconvergent series

$$E_1(t) = \frac{e^{-t}}{t}\left(1 - \frac{1!}{t} + \frac{2!}{t^2} + \dots\right)$$

may be applied.

REFERENCES

1. R. C. Raffanetti, J. Chem. Phys., **59**, 5936, 1973.
2. E. C. Kemble, The Fundamental Principles of Quantum Mechanics. McGraw-Hill, New York, 1937. (Dover, N. Y. 1958.)
3. R. Gáspár, Acta Phys. Hung., **2**, 151, 1952.
4. R. Gáspár, Acta Phys. Hung., **3**, 263, 1954.

5. F. Herman and S. Skillman, Atomic Structure Calculations, Prentice Hall, Inc. Englewood Cliff, New Jersey, 1963.
6. J. C. Slater, Phys. Rev., **98,** 1039, 1955.
7. E. Clementi, J. Chem. Phys., **41,** 295, 1964.
8. E. Clementi, J. Chem. Phys., **41,** 303, 1964.
9. C. C. J. Roothaan, L. M. Sachs and A. W. Weiss, Rev. Mod. Phys., **32,** 186, 1960.
10. R. E. Watson, Phys. Rev., **118,** 1036, 1960.
11. R. E. Watson, Phys. Rev., **119,** 1934, 1960.
12. A. E. Sandström, Encyclopedia of Phys. Edited by S. Flügge. (Springer-Verlag, Berlin 1957) Vol. 30. p. 78.
13. S. Flügge, Practical Quantum Mechanics, II. p. 277. (Springer-Verlag, Berlin—Heidelberg—New York, 1971.)
14. A. Ralston and H. S. Wilf, Mathematical Methods of Digital Computers. p. 84.New York, London, John Wiley Sons, Inc. 1960.
15. S. Gradshteyn and I. M. Ryzhik, Table of Integrals, Series and Products. Academic Press, New York and London 1965.
16. W. R. Angus, Proc. Roy. Soc. (London) *A***136,** 569, 1932.
17. G. Burns, J. Chem. Phys., **41,** 1521, 1964.
18. E. Clementi, D. L. Raimondi and W. P. Rienhardt, J. Chem. Phys., **47,** 1300, 1967.
19. J. C. Slater, Phys. Rev., **36,** 57, 1930.
20. L. B. Mendelsohn and G. Biggs, Phys. Rev. *A***2,** 1130, 1970.
21. J. T. Dehn and L. N. Mulay, J. Chem. Phys., **48,** 4910, 1968.

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COMMUNICATIO BREVIS

P—V DIAGRAM OF QUANTUM CRYSTALS

By

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(Received 22. XII. 1975)

On the basis of the thermodynamic double-time Green's function method a self-consistent dynamical theory of the anharmonic crystals has been recently developed [1] [2]. This theory in a series of previous works [3]—[8] was applied for the investigation of dynamic, thermodynamic and elastic properties of a f.c.c. lattice with nearest neighbour central force interaction. A short summary of the theory and the most interesting results are given in [9].

In this work completing the previous results the equation of state of the quantum crystals at $T = 0\ °K$ is investigated. Using the above mentioned model numerical calculations of $P-V$ diagram have been carried out. In the calculations Morse potential with the choice of the parameters $ar_0 = 6$ was taken as a model potential for the description of the interaction between the neighbouring atoms.

In accordance with [5] the self-consistent equation determining the properties of the crystal in the case of constant pressure at $T = 0$ °K can be written in the form of two coupled equations:

$$\begin{aligned} &\ln \frac{\alpha^2 - (P^*/24)\, x^2}{[\alpha^2 - (P^*/12) x^2]^2} = \left\{ \lambda\alpha - 0.4 \frac{[\alpha^2 - (P^*/36)\, x^2]^2}{\alpha^4} \right\}^{-1}, \\ &x = 1 + (1/12) \ln\, [\alpha^2 - (P^*/24) x^2][\alpha^2 - (P^*/12)\, x^2]^{-4}, \end{aligned} \tag{1}$$

where P^* is the reduced pressure, $x = (l/r_0)$ is the dimensionless atomic distance, λ is the dimensionless coupling constant and α is the pseudoharmonic frequency renormalization. All the notations are the same as in [5]. Solving these equations numerically we can get the $P-V$ diagram of the crystal as the function the parameter λ.

On the other hand considering the crystal at fixed volume at $T = 0$ °K, the self-consistent equation for the dimensionless mean square relative displacement of neighbouring atoms y in accordance with [6] can be written

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in the following form:

$$y\lambda e^{-6(x-1)}\, e^{y}\{2 - e^{6(x-1)}\, e^{-3y/2}\}^{1/2} \times$$
$$\times \left\{1 - \frac{z}{2\lambda}\, \nu_0\, e^{6(x-1)}\, e^{-y}\, \frac{[4 - e^{6(x-1)}\, e^{-3y/2}]^2}{[2 - e^{6(x-1)}\, e^{-3y/2}]^{5/2}}\right\} = 1\,, \qquad (2)$$

where $x = (l/r_0)$ is fixed, $z = 12$ is the number of the nearest neighbour, $\nu_0 = 7{,}3 \cdot 10^{-3}$. Solving this equation numerically for a series of values of λ and using the equation for the reduced pressure in the form

$$P^* = (24/x^2)\, e^{-12(x-1)}\, e^{2y}\, \{1 - e^{6(x-1)}\, e^{-3y/2}\}\ , \qquad (3)$$

we can obtain as in the first case the P—V diagram of the crystal.

Both of these P—V diagrams are of course identical. This is shown in Fig. 1.

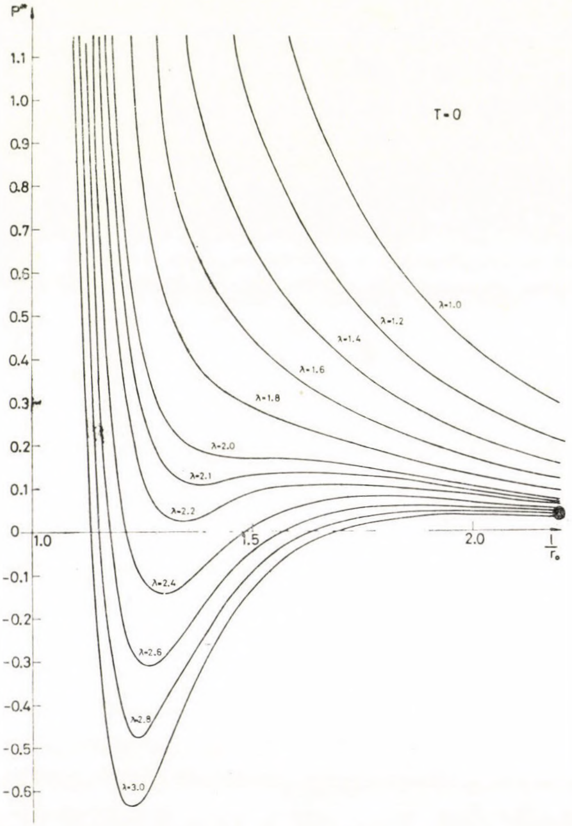

Fig. 1. P—V diagram of quantum crystals at $T = 0$ °K

If the coupling constant of light atoms is small the crystal becomes unstable even at $T = 0\ °K$ as can be expected. In this case the zero-point energy is sufficiently large and the zero-point vibrations destroy the lattice. However, when adequate external pressure is applied, a stable crystal state appears. But if the dimensionless coupling is sufficiently small: $\lambda < \lambda_c \simeq 2.05$, this instability phenomenon disappears.

The results of this work are in accordanc with the results of calculations for the low temperature limit which are given in works [3], [4], [5], [6].

*

We should like to thank Dr. N. M. Plakida for helpful discussions.

REFERENCES

1. N. M. Plakida and T. Siklós, Acta Phys. Hung., **25,** 17, 1968.
2. N. M. Plakida and T. Siklós, phys. stat. sol., **33,** 103, 1969.
3. N. M. Plakida and T. Siklós, phys. stat. sol., **39,** 171, 1970.
4. T. Siklós and V. L. Aksienov, phys. stat. sol. (b) **50,** 171, 1972.
5. T. Siklós and V. L. Aksienov, Acta Phys. Hung., **31,** 335, 345, 1972.
6. N. M. Plakida and T. Siklós, Report JINR, P4-4575, Dubna, 1969 (in Russian).
7. N. M. Plakida and V. L. Aksienov, Fiz. tverd. tela, **15,** 2575, 1973.
8. N. M. Plakida and V. L. Aksienov, phys. stat. sol. (b) **62,** 261, 1974. Fiz. nizk. temp. **1,** 713, 1975.
9. T. Siklós, Acta Phys. Hung., **34,** 327, 1973.

RECENSIONES

IWO BIALYNICKI-BIRULA and ZOFIA BIALYNICKA-BIRULA:

Quantum Electrodynamics

Pergamon Press, Oxford—New York—Toronto, 1975

This book gives a systematical, well constructed building of quantum electrodynamics. Starting from the principles of quantum theory the authors acquaint the reader with different quantum theoretical pictures. In the light of this the S-matrix is introduced, which plays an important role from the point of view of the theory. The next section deals with non-relativistic quantum mechanics, the quantization of Schrödinger field. This is followed by the covariant treatment of classical electromagnetic field. With this knowledge the quantization of the free field is discussed. Afterwards the most classical states of field, the so-called coherent states are treated, and the reader gets acquainted with the coherence of electromagnetic radiation. Also in this chapter the quantum theory of vector field with mass is introduced.

The next section is devoted to the Dirac equation as well as to the Dirac's field quantization, and deals in detail with the Green's functions for the Dirac equation. The coupled Maxwell—Dirac field equations are interpreted in the interaction picture in the next chapter. Here the authors develop correspondence betweens the Feyman diagrams and perturbation theory, and they present the structure of the S-matrix. The section last but one deals with the renormalization, whereas the last one describes certain applications of quantum electrodynamics. At the end of the book useful appendices can be found.

I. PÉCZELI

A. A. SMIRNOW: Metallphysik

Akademie-Verlag, Berlin, 1974.

The book published in the "Wissenschaftliche Taschenbücher" series is a translation of the author's original work published in Ukrainian language in 1966. Its purpose is to in form laymen interested in, or assistants dealing with metal physics. Therefore it does not presume any special knowledge but delivers the qualitative survey of all domains of metal physics.

Starting from the structure of atoms the first chapter makes the reader acquainted with the structure and defects of crystal lattice and the electronic theory of metals, isolators and semi-conductors.

In the second chapter the problems of diffusion, phase transitions, plasticity and the strength of metals are reviewed.

The subjects of the third chapter are the electric and magnetic properties of metals. The problems of electric and thermal conductivity, electronic specific heat, galvanomagnetic effects, optical properties, para, dia ferro and antiferromagnetism, superconductivity, the connection between Mössbauer effect and the plasma oscillation of electrons are discussed.

The book is very suitable for interested laymen to survey the properties of metals and alloys from the point of view of metal physics.

G. GROMA

Irreversible Thermodynamics and the Origin of Life

Edited by G. F. Oster, I. L. Silver, C. A. Tobias;
Gordon and Breach Science Publishers, NewYork, London, Paris, 1974.

This book of 69 pages is divided into two parts. The first one contains the subject of four reports, in which the authors discuss from different aspects the problem of the origin of life by means of the theory of irreversible thermodynamics. The second part consists of the text of an informal session, the participants of which discuss their point of view about the origin of life with respect to the newest results in exobiology.

The report by A. KATCHALSKY ("Chemico-Diffusional Coupling in Heterogeneous Peptide Synthesis") contains important results concerning experimental problems, but the theoretical treatment is rather poor. The report by I. PRIGOGINE ("Symmetry Breaking Chemical Instabilities") represents the unique exact subject, at least as far as physics is concerned. It is another matter to consider how the results attained by PRIGOGINE and his followers contribute to the understanding of the origin of life. The reports by H. J. MOROWITZ ("Energy Flow and Biological Organization") and by H. H. PATTEE ("The Vital Statistics of Quantum Dynamics") are rather qualitative. In our opinion, in the session meeting of the Third International Biophysics Congress, as far as it can be judged from the contents of this book, the solution of the difficult problem of the origin of life has not got too far.

I. GYARMATI

E. C. G. STUECKELBERG DE BREIDENBACH et P. B. SCHEURER:

Thermocinétique Phénoménologique Galiléenne

Birkhäuser Verlag, Basel und Stuttgart, 1974.

Les auteurs présentent dans les sept chapitres de ce livre les fondaments de la théorie de la thermostatique et de la thermodynamique classique. Dans les deux premiers chapitres se trouvent les principes fondamentaux des systèmes discrets et continus, dans une forme concise, axiomatique. Le troisième et le quatrième chapitres décrivent la thermodynamique et la thermostatique des fluides à un seul composant chimique, en les employant aux plus importants problèmes. Le cinquième et le sixième chapitres traitent la thermocinétique et la thermostatique des fluides à plusieurs composants chimiques. Le septième chapitre s'occupe des systèmes solides déformables à un seul composant chimique. Dans l'appendice A se trouevent toutes les précisions mathématiques appliquées dans ce livre, et la description élémentaire de l'espace affine et métrique. L'appendice B présente le troisième pricipe du point de vue de la cinétique relativiste.

Le livre se base sur le cours du professeur STUECKELBERG DE BREIDENBACH, qu'il tient depuis une dizaine d'années aux Universités de Genève et de Lausanne. La manière d'exposition est d'un caractère axiomatique, bien qu'elle est particulière, parce qu'elle diffère si bien de la manière axiomatique de CARATHÉODORY que de l'exposition usuelle de la thermodynamique irréversible. Le livre présente plusieurs nouveaux problèmes et solutions, c'est pourquoi nous le recommandons en premier lieu à ceux qui ont déjà des connaissances dans le domaine de la thermostatique et de la thermodynamique, mais qui s'intéressent à la nouvelle manière d'exposition de cette théorie.

I. GYARMATI

Physics of IV—VI Compounds and Alloys

Edited by Schrab Rabil, Moore School of Electrical Engineering and
Laboratory for Research on the Structure of Matter, University of Pennsylvania,
Philadelphia, Pennsylvania, USA

The book contains the material of the lectures on "Physics of IV—VI Compounds and Alloys" delivered at the Conference of 1972. It gives a wide review of the physical properties of IV—VI compounds and alloys as well as the means made from them and of their characteristics.

In the First Part the transport properties of the epitaxial films of PbTe, PbSe, (PbSn)Te, $PbS_{1-x}Se$ and the properties of the means made by their use are dealt with.

The publications in the Second Part examine the structures of IV—VI compounds and alloys, their bonding conditions, energy band model, defect structures and lattice-dynamical properties.

The Third Part discusses the crystal defects of $Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$ and $PbS_{1-x}Se$, the mobility of charge carriers and the problems of diffusion.

The Fourth Part examines the optical and magneto-optical properties of the material group.

The books has the particular merit of giving detailed information on practical applications of the metals and alloys mentioned. The studies examining the properties of lead-germanium telluride laser-diodes, variable $PbS_{1-x}Se_x$ lasers and hetero-transition lasers are remarkable.

J. GIBER

LJ. NOVAKOVIĆ:

The Pseudo-spin Method in Magnetism and Ferroelectricity

International Series of Monographs in Natural Philosophy Vol. 77, Pergamon Press, 1975

The book contains four large chapters including here 34 separate sections, 5 appendices, and 200 pages. The exposed material is explained by 51 tables, 22 illustrations or pictures, more than 451 equations, 145 references and 355 various notions or expressions.

The first chapter deals with lattice dynamics of KH_2PO_4 structures. Diffuse modes and normal hydrogen vibration modes are evaluated and explained using the pseudo-spin concept. Four normal hydrogen vibration modes are predicted in reciprocal lattice space and the structure and the exact identification of those modes is discussed in detail from a group-theoretical viewpoint. It was concluded that only the lowest-energy vibration mode as associated with one of the antisymmetric representations of the corresponding space point group has explicitly the probability of behaving in the way which is required for a soft ferroelectric mode (also named Cohran mode).

Phase transitions of ferromagnetic and ferroelectric substances are discussed in general in the second chapter. Special attention is paid to the Ising model with a transverse field (also named the "tunneling" model) in order to establish the correct formulation of the isotope effect as observed in all hydrogen-bonded ferroelectrics. The exact solution to this model is still lacking in the international literature, and so the author restricted himself to a self-consistent molecular field approximation. A numerical analysis of the molecular-field equations is given in detail to obtain a satisfactory explanation for a number of observed physical quantities.

Magnetic elementary excitations for Heisenberg ferromagnets and antiferromagnets at low temperatures are formulated in the third chapter using the well-known Holstein—Primakoff and Dyson—Maleev representations. The energy of elementary excitations, order parameter and specified heat are calculated up to the fourth order terms in reciprocal lattice space, thus including the famous spin-wave dynamical interaction. The problem of obtaining a correct boson representation for the spin operators is reviewed in great detail by including a number of genuine papers devoted to spin waves.

Green functions method following the works of Kubo, Zubarev, Tyablikov and Barry is exposed in the last chapter. By developing a suitable decoupling procedure for the double time temperature-dependent Green functions for the Heisenberg ferromagnet at low temperatures the author was able to demonstrate the equivalence existing between the Holstein—Primakoff and Dyson—Maleev representations. Also the kinematical interaction both for ferromagnetic and ferroelectric systems is considered in detail. A particular contribution is given to the exact formulation of the temperature-dependent soft ferroelectric mode in hydrogen-bounded ferroelectrics. Five appendices are added at the end of the book in order to illuminate the mathematical basis, physical constants and energy units used in the preceding text.

T. SIKLÓS

4 S

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