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ON THE ENERGY SPECTRUM OF A MOTT EXCITON IN IONIC CRYSTALS

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A qualitative study of the levels of a Mott exciton in ionic crystals is made from the point of view of a many-electron theory. A many-electron discussion of the exciton reduces to the problem of the motion of two quasi-particles which in the case of triplet states (ortho-exciton) interact through Coulomb forces and in the case of singlet states (para-exciton) through Coulomb and exchange forces. These forces are approximately evaluated using a model in which the electron states at the cation site and the vacant states at the anion site are supposed to be spherically symmetric. The ortho- and para-exciton series of a non-polarizable exciton of large radius are evaluated using a generalized effective mass method. An estimate is given of the influence of the difference from a point charge Coulomb potential on the magnitude of the l-splitting. Using group theory a general level scheme is given for an exciton for the case $\mathbf{K} = 0$ for the O_h group, and the results are compared with the yellow exciton series in a Cu_2O crystal. The properties of an exciton in a magnetic field are discussed.

1. A MANY-ELECTRON DISCUSSION OF THE PROBLEM

A Mott exciton in strongly polar crystals is the result of a transition of an electron from an external, filled p shell of the anion into a vacant state of the s shell of the cation. The extra electron and hole obtained in this way form a system similar to a hydrogen atom. Its states have been considered in many papers.[1–9] In the paper by one of the authors [reference 9, Eq. (8)] the wave function of the exciton in a crystal with undisplaced ions was written as a linear combination of wave functions $C(\mathbf{G}, s, \mathbf{H}, M, S_1, S_2)$ of all electrons in the crystal for which an electron from the external p shell of the anion site **H** with magnetic quantum number M had gone into the s shell of the cation site **G** with spin S_1, while the anion site remained with a spin S_2. These were of the form

$$C(\mathbf{G}, s, \mathbf{H}, M, S_1, S_2) = \sum (-1)^{\nu} P^{\nu} \prod_{\mathbf{h}m\sigma} \Theta_{\mathbf{h}m\sigma}(\mathbf{q}_{\mathbf{h}m\sigma} S_{\mathbf{h}m\sigma})\, \Theta_{\mathbf{G}sS_1}(\mathbf{q}_{\mathbf{G}sS_1} S_1),$$

$$(\mathbf{h}, m, \sigma) \neq (\mathbf{H}, M, -S_2), \qquad (1)$$

where $\Theta_{\ldots}$ are one-electron orthonormal functions, P the electron permutation operator, ν the parity of the permutation, **q** and S_z the coordinate and spin of the electron; **h** numbers the anion sites of the lattice, m and σ number the states in the anion p shell.

It is convenient to choose as the basis functions linear combinations of the C functions which are eigenfunctions of the operator of the square of the total spin of the system. For a singlet state S = 0 and the corresponding function, designated by an index Σ, is equal to

$$\Psi(\mathbf{G}, s, \mathbf{H}, M \,|\, \Sigma) = [C(\mathbf{G}, s, \mathbf{H}, M, {}^1/_2, -{}^1/_2) - C(\mathbf{G}, s, \mathbf{H}, M, -{}^1/_2, {}^1/_2)]/\sqrt{2}. \qquad (2)$$

For S = 1 there are three functions. It is convenient to choose these in such a way that they go over into one another under the action of the O_h group.[10] We distinguish them by indices ξ, η, and ζ:

$$\Psi(\mathbf{G}, s, \mathbf{H}, M \,|\, \xi) = [-C(\mathbf{G}, s, \mathbf{H}, M, {}^1/_2, {}^1/_2) + C(\mathbf{G}, s, \mathbf{H}, M, -{}^1/_2, -{}^1/_2)]/\sqrt{2},$$

$$\Psi(\mathbf{G}, s, \mathbf{H}, M \,|\, \eta) = [C(\mathbf{G}, s, \mathbf{H}, M, {}^1/_2, {}^1/_2) + C(\mathbf{G}, s, \mathbf{H}, M, -{}^1/_2, -{}^1/_2)](i/\sqrt{2}), \qquad (3)$$

$$\Psi(\mathbf{G}, s, \mathbf{H}, M \,|\, \zeta) = [C(\mathbf{G}, s, \mathbf{H}, M, {}^1/_2, -{}^1/_2) + C(\mathbf{G}, s, \mathbf{H}, M, -{}^1/_2, {}^1/_2)]/\sqrt{2}.$$

The wave function of the crystal in the general case will be

$$\Psi = \sum_{\mathbf{GH}MI} \Phi(\mathbf{G}, \mathbf{H}, M \,|\, I)\, \Psi(\mathbf{G}, s, \mathbf{H}, M \,|\, I), \qquad (4)$$

where I takes on four values Σ, ξ, η, and ζ, while M takes on three values. The sum over **G** and **H** extends over the whole of the crystal.

For an exciton moving with wave vector **K**, the function Φ must tend to zero as $|\mathbf{G}-\mathbf{H}|$ increases, and if G and H are translated over a lattice vector distance it must be multiplied by an exponential factor, so that

$$\Phi(\mathbf{G}, \mathbf{H}, M \mid I) = \exp[i\mathbf{K}, \alpha\mathbf{G} + \beta\mathbf{H}]\, \varphi_\nu(\mathbf{G} - \mathbf{H}, M \mid I), \tag{5}$$

where ν denotes all the quantum numbers characterizing the relative motion in the exciton. The average of the crystal Hamiltonian taken over the function $\Psi(4)$ is equal to

$$\begin{aligned} {}^{s}E_\nu(\mathbf{K}) = {} & \frac{1}{N} \sum_{\mathbf{G}\mathbf{G}'\mathbf{H}MI} L_{\mathrm{eff}}(\mathbf{G} - \mathbf{G}', s) \exp[i\mathbf{K}, \alpha(\mathbf{G} - \mathbf{G}')] \\ & \times \varphi_\nu^*(\mathbf{G}' - \mathbf{H}, M \mid I)\, \varphi_\nu(\mathbf{G} - \mathbf{H}, M \mid I) \\ & - \frac{1}{N} \sum_{\mathbf{H}\mathbf{H}'\mathbf{G}MM'I} L_{\mathrm{eff}}(\mathbf{H} - \mathbf{H}', M, M') \exp[i\mathbf{K}, \beta(\mathbf{H} - \mathbf{H}')] \\ & \times \varphi_\nu^*(\mathbf{G} - \mathbf{H}', M' \mid I)\, \varphi_\nu(\mathbf{G} - \mathbf{H}, M \mid I) \\ & + \frac{1}{N} \sum_{\mathbf{G}\mathbf{G}'\mathbf{H}\mathbf{H}'MM'I} \exp[i\mathbf{K}, \alpha(\mathbf{G} - \mathbf{G}') \\ & + \beta(\mathbf{H} - \mathbf{H}')][-F(\mathbf{G}, s, \mathbf{H}', M';\ \mathbf{G}', s, \mathbf{H}, M) \\ & + 2\delta(S) F(\mathbf{G}, s, \mathbf{H}', M'; \mathbf{H}, M, \mathbf{G}', s)] \\ & \times \varphi_\nu^*(\mathbf{G}' - \mathbf{H}', M' \mid I)\, \varphi_\nu(\mathbf{G} - \mathbf{H}, M \mid I) \end{aligned} \tag{6}$$

if we neglect the spin-orbit interaction. This expression separates into two parts corresponding to $S = 0$ when $I = \Sigma$, and $S = 1$ when I takes on the three values ξ, η, ζ. In our approximation the states with $I = \xi$, η, ζ can be also separated, but in the following we shall choose linear combinations of them corresponding to a well determined symmetry. According to reference 9, the coefficients L_{eff} are equal to

$$\begin{aligned} L_{\mathrm{eff}}(\mathbf{G} - \mathbf{G}', s) = {} & L(\mathbf{G}, s,;\ \mathbf{G}', s) \\ & + 2\sum_{\mathbf{h}m} F(\mathbf{G}, s, \mathbf{h}, m;\ \mathbf{G}', s, \mathbf{h}, m) \\ & - \sum_{\mathbf{h}m} F(\mathbf{G}, s, \mathbf{h}, m;\ \mathbf{h}, m, \mathbf{G}', s), \end{aligned} \tag{7}$$

$$\begin{aligned} L_{\mathrm{eff}}(\mathbf{H} - \mathbf{H}', M, M') = {} & L(\mathbf{H}, M; \mathbf{H}', M') \\ & + 2\sum_{\mathbf{h}m} F(\mathbf{h}, m, \mathbf{H}', M';\ \mathbf{h}, m, \mathbf{H}, M) \\ & - \sum_{\mathbf{h}m} F(\mathbf{h}, m, \mathbf{H}', M';\ \mathbf{H}, M, \mathbf{h}, m). \end{aligned}$$

Here

$$L(\mathbf{f}, \lambda;\ \mathbf{f}', \lambda') = \int \Theta_{\mathbf{f}\lambda}^*(\mathbf{q}) \left[-\frac{\hbar^2}{2m} \nabla_{\mathbf{q}}^2 + V(\mathbf{q})\right] \Theta_{\mathbf{f}'\lambda'}(\mathbf{q})\, d\mathbf{q},$$

$$\begin{aligned} & F(\mathbf{f}_1, \lambda_1, \mathbf{f}_2, \lambda_2;\ \mathbf{f}_1', \lambda_1', \mathbf{f}_2', \lambda_2') \\ & = e^2 \int \frac{\Theta_{\mathbf{f}_1\lambda_1}^*(\mathbf{q}_1)\, \Theta_{\mathbf{f}_2\lambda_2}^*(\mathbf{q}_2)\, \Theta_{\mathbf{f}_1'\lambda_1'}(\mathbf{q}_1)\, \Theta_{\mathbf{f}_2'\lambda_2'}(\mathbf{q}_2)\, d\mathbf{q}_1 d\mathbf{q}_2}{|\mathbf{q}_1 - \mathbf{q}_2|}, \end{aligned} \tag{8}$$

where $V(\mathbf{q})$ is the potential produced by the cores of all the ions in the lattice, $\mathbf{f}$ takes on the values $\mathbf{G}$ and $\mathbf{H}$; λ takes on the values M and s. For $\mathbf{G} = \mathbf{G}'$ $L_{\mathrm{eff}}(\mathbf{G} - \mathbf{G}', s)$ can be interpreted as the average kinetic and potential energy (including exchange) of the interaction of an excited electron with the cores of the ions and with all of the 6N valence electrons (the background). For $\mathbf{H} = \mathbf{H}'$ and $M = M'$ $L_{\mathrm{eff}}(\mathbf{H} - \mathbf{H}', M, M')$ plays a similar role for a hole which has, as can be seen from the signs, the opposite mass, charge, and spin. The third sum in (6) can, if $\mathbf{G} = \mathbf{G}'$, $\mathbf{H} = \mathbf{H}'$, $M = M'$, be interpreted as the Coulomb and exchange interaction of the extra electron and the hole. In the triplet states there is no exchange interaction between the hole and the electron. Since the form of the "interaction potential" is different, states with $S = 0$ and $S = 1$ will have different energies. We shall call them para- and ortho-excitons. Since the electron spin can change during a photo-transition due to the spin-orbit interaction, but with a rather small probability, we must expect that the ortho-exciton series will have a very low intensity. Since there are two quasi-particles present, the exciton states will be to some extent similar to the states of the He atom, but since the interaction potential is different for the two series from a point charge Coulomb potential, the l-degeneracy will be lifted.

Overhauser[10] has investigated the lowest states of a Mott exciton for $\mathbf{K} = 0$ in crystals of the NaCl and CsCl type, assuming that the electron goes over from the halide only to the first spherical configuration of Na^+ or Cs^+ ions. He also showed the existence of singlet and triplet states using group theoretical methods and gave the systematics of the lowest exciton terms. However, the restriction to the first spherical configuration is clearly insufficient for a consideration of the excited states. Moreover, Overhauser did not determine the exciton levels. In a recent paper[11] Takeuti considered the exciton in elemental semiconductors with one valence band and one conduction band, using Bloch functions. Restricting himself to a qualitative investigation he also arrived at the result that there are singlet and triplet states present, and concluded that the difference between their levels in the so-called "hydrogen case" are negligible. Ortho- and para-excitons are thus described in his paper by the same equation. Our consideration is more general, and includes, in particular, his scheme and enables us to determine the exciton levels in a well defined approximation. Using the more general description of the wave functions (2) to (5) we shall consider arbitrary exciton states and the case

$\mathbf{K} \neq 0$. For $\mathbf{K} = 0$ we made a group-theoretical analysis of all exciton states for crystals of the group O_h; the result of this analysis is given in the following, but an account of the method is given in a separate paper. In that way a method is found to understand the details of the exciton spectrum which is experimentally observed. Finally, we reduce the determination of the exciton energy (6) to the problem of the motion of two quasi-particles, and in the case of excitons with a sufficiently large radius we shall give a numerical estimate of the Coulomb and exchange integrals and of the energy levels of the para- and ortho-exciton series, taking l-splitting into account.

2. THE REDUCTION OF THE MANY-ELECTRON PROBLEM TO THE EQUATION OF MOTION OF TWO QUASI-PARTICLES

The functional (6) can be rewritten in the form used by Dresselhaus[8] who earlier assumed the presence of two quasi-particles, where one of them is described by the states of a degenerate band. To do this we use the identity

$$\begin{aligned}\frac{1}{N}\sum_{\mathbf{HH'G}} & L_{\mathrm{eff}}(\mathbf{H}-\mathbf{H}', M, M')\exp[i\mathbf{K}, \beta(\mathbf{H}-\mathbf{H}')] \\ & \times \varphi_\nu^*(\mathbf{G}-\mathbf{H}', M'\,|\,I)\,\varphi_\nu(\mathbf{G}-\mathbf{H}, M\,|\,I) \\ = \sum_{\mathbf{ff}_1} & L_{\mathrm{eff}}(\mathbf{f}_1, M, M')\,\varphi_\nu^*(\mathbf{f}, M'\,|\,I)\,\varphi_\nu(\mathbf{f}-\mathbf{f}_1, M\,|\,I) \\ & \times\exp[i\mathbf{K},\beta\mathbf{f}_1] = \sum_{\mathbf{f}}\varphi_\nu^*(\mathbf{f}, M'\,|\,I)\sum_{\mathbf{f}_1}L_{\mathrm{eff}}(\mathbf{f}_1, M, M') \\ & \times\exp[i\mathbf{f}_1, \beta\mathbf{K} + i\nabla_{\mathbf{f}}]\,\varphi_\nu(\mathbf{f}, M\,|\,I) \\ = \sum_{\mathbf{f}} & \varphi_\nu^*(\mathbf{f}, M'\,|\,I)\,E(\beta\mathbf{K} + i\nabla_{\mathbf{f}}, M, M')\,\varphi_\nu(\mathbf{f}, M\,|\,I),\end{aligned} \tag{9}$$

where we have put

$$E(\varkappa, M, M') = \sum_{\mathbf{f}} L_{\mathrm{eff}}(\mathbf{f}, M, M')\exp(i\varkappa\mathbf{f}).$$

The first term in Eq. (6) can be similarly transformed. In the last term we retain only the two-center integrals with $\mathbf{G} = \mathbf{G}'$ and $\mathbf{H} = \mathbf{H}'$. We have then

$$\begin{aligned}{}^{S}E_\nu(\mathbf{K}) = & \sum_{\mathbf{f}MI}\varphi_\nu^*(\mathbf{f}, M\,|\,I)\,E(\alpha\mathbf{K} + i\nabla_{\mathbf{f}}, s)\,\varphi_\nu(\mathbf{f}, M, |\,I) \\ & - \sum_{\mathbf{f}MM'I}\varphi_\nu^*(\mathbf{f}, M'\,|\,I)\,E(\beta\mathbf{K} + i\nabla_{\mathbf{f}}, M, M')\,\varphi_\nu(\mathbf{f}, M\,|\,I) \\ & + \sum_{\mathbf{f}MM'I}[-\mathrm{K}(\mathbf{f}, M, M', s) + 2\delta(S)\,A(\mathbf{f}, M, M', s)] \\ & \times\varphi_\nu^*(\mathbf{f}, M'\,|\,I)\,\varphi_\nu(\mathbf{f}, M\,|\,I),\end{aligned} \tag{10}$$

where

$$E(\varkappa, s) = \sum_{\mathbf{f}} L_{\mathrm{eff}}(\mathbf{f}, s)\exp(i\varkappa\mathbf{f});\quad K(\mathbf{f}, M, M', s) = F(\mathbf{G}, s, \mathbf{H}, M'; \mathbf{G}, s, \mathbf{H}, M);$$

$$A(\mathbf{f}, M, M'\, s) = F(\mathbf{G}, s, \mathbf{H}, M';\ \mathbf{H}, M, \mathbf{G}, s).$$

Minimizing the functional (7) with respect to φ_ν^* leads to a matrix equation for φ_ν which is the same as Eq. (19) of Dresselhaus' paper.[8] The physical meaning of the coefficients $E(\kappa, s)$ and $E(\kappa, M, M')$ is easily ascertained, if we neglect the interaction between the electron and the hole and assume $\varphi_\nu = N^{-1/2}\varphi(M)\exp(i\mathbf{Kf})$, where

$$\sum_{M}|\varphi(M)|^2 = 1. \tag{11}$$

In that case Eq. (10) separates into two parts:

$$E(\alpha\mathbf{K} - \mathbf{k}_1, s) - \sum_{MM'}\varphi_\nu^*(M')\,E(\beta\mathbf{K} - \mathbf{k}_1, M, M')\,\varphi_\nu(M). \tag{12}$$

The first term is the energy of the electron in the band with wave vector $\alpha\mathbf{K} - \mathbf{k}_1$, and the second term gives after diagonalization the energy of the three hole bands corresponding to a wave vector $\beta\mathbf{K} - \mathbf{k}_1$.

The next problem is to find the form of the function $\varphi_\nu(\mathbf{f}_1 M\,|\,I)$. In the general case φ_ν and the exciton levels depend on the exciton wave vector $\mathbf{K}$ which enters as a parameter into the functional (10). The next step in the investigation is performed only for the states with $\mathbf{K} = 0$, into which transitions from the ground state of the crystal are allowed. We can write φ_ν in the form of an expansion in spherical harmonics $Y_{lm}(\theta, \varphi)$ which enables us to classify not only states of small radius, but also states of large radius:

$$\varphi_\nu(\mathbf{f}, M\,|\,I) = \sum_{lm} Y_{lm}(\theta_{\mathbf{f}}\ \phi_{\mathbf{f}})\,R_{\nu lm}(|\mathbf{f}|, M\,|\,I). \tag{13}$$

Here $\theta_{\mathbf{f}}$, $\varphi_{\mathbf{f}}$ are the polar angles which determine the discrete lattice vector $\mathbf{f}$. Using group theory one can show, how, indeed, a combination of spherical harmonics leads to the expansion (13)

3. GROUP THEORETICAL CLASSIFICATION OF EXCITON STATES WITH K = 0

In contradistinction to Overhauser's considerations which assumed to begin with that the electron moved around a fixed hole and along the nearest spherical configuration, and then let the system as a whole be translated, we shall start from the very beginning with arbitrary motion of the electron and the hole.

Substituting the expression for an arbitrary function which possesses translational symmetry (5) and (4) we get for K = 0:

$$\Psi_\nu = \sum_{\mathbf{f}MI} \varphi_\nu(\mathbf{f}, M \mid I)\, \Psi(\mathbf{f}, M \mid I), \tag{14}$$

where

$$\Psi(\mathbf{f}, M \mid I) = \sum_{\mathbf{H}} \Psi(\mathbf{H} + \mathbf{f}, s, \mathbf{H}, M \mid I). \tag{15}$$

We choose to begin with the functions $\Psi(\mathbf{f}, M \mid I)$ as the basis functions for the classification of the states. Since in our approximation the Hamiltonian does not contain the spin variable I, we can at first classify the states only according to the coordinate part of the function $\Psi(\mathbf{f}, M)$. In the case of states of small radius, when we can restrict ourselves to the first spherical configuration, $\mathbf{f}$ will take on, for a lattice of the NaCl type, all six values ($\pm$d, 0, 0), (0, $\pm$d, 0), (0, 0, $\pm$d) which we shall denote by $\pm f_x$, $\pm f_y$, $\pm f_z$. Each value of $\mathbf{f}$ can be combined with one of the three values of M. The indices M_x, M_y, M_z will denote states of an electron in the p-shell of the type xf(r), yf(r), zf(r). The space of the eighteen functions splits up into invariant subspaces corresponding to the irreducible representations:

$$\Gamma^{18} = \Gamma_1 + \Gamma_3 + \Gamma_4 + 2\Gamma_4' + \Gamma_5'. \tag{16}$$

As will become clear in a moment, only transitions into states arising from Γ_4' and Γ_5' are allowed, after multiplication by the spin functions. These irreducible representations correspond to the functions

$$\begin{gathered}
\Gamma_4' \\
[\Psi(f_x, M_x) + \Psi(-f_x, M_x)]/\sqrt{2} \\
[\Psi(f_y, M_y) + \Psi(-f_y, M_y)]/\sqrt{2} \\
[\Psi(f_z, M_z) + \Psi(-f_z, M_z)]/\sqrt{2} \\
\Gamma_4' \\
\tfrac{1}{2}[\Psi(f_y, M_x) + \Psi(-f_y, M_x) + \Psi(f_z, M_x) + \Psi(-f_z, M_x)] \\
\tfrac{1}{2}[\Psi(f_x, M_y) + \Psi(-f_x, M_y) + \Psi(f_z, M_y) + \Psi(-f_z, M_y)] \\
\tfrac{1}{2}[\Psi(f_x, M_z) + \Psi(-f_x, M_z) + \Psi(f_y, M_z) + \Psi(-f_y, M_z)] \\
\Gamma_5' \\
\tfrac{1}{2}[\Psi(f_y, M_x) + \Psi(-f_y, M_x) - \Psi(f_z, M_x) - \Psi(-f_z, M_x)] \\
\tfrac{1}{2}[\Psi(f_x, M_y) + \Psi(-f_x, M_y) - \Psi(f_z, M_y) - \Psi(-f_z, M_y)] \\
\tfrac{1}{2}[\Psi(f_x, M_z) + \Psi(-f_x, M_z) - \Psi(f_y, M_z) - \Psi(-f_y, M_z)]
\end{gathered} \tag{17}$$

Instead of the functions Γ_4' which we have written down we can also take a linear combination of the corresponding lines of the two equivalent representations. In that case we get, in particular, the completely symmetric function $6^{-1/2} \sum_{\mathbf{f}} \Psi(\mathbf{f}, M_x)$, and also the function

$$3^{-1/2}\{\Psi(f_x, M_x) + \Psi(-f_x, M_x) - {}^1/_2[\Psi(f_y, M_x) + \Psi(-f_y, M_x) + \Psi(f_z, M_x) + \Psi(-f_z, M_x)]\}, \tag{18}$$

which occurs in Overhauser's paper.[10]

For states of arbitrary radius we can choose, according to the expansion (13) and Eq. (14) as basis functions

$$\chi_\nu(lm \mid M) = \sum_{\mathbf{f}} \Psi(\mathbf{f}, M)\, Y_{lm}(\theta_{\mathbf{f}} \phi_{\mathbf{f}})\, R_{\nu lm}(|\mathbf{f}| M). \tag{19}$$

One can easily see that now expansion (13) must contain either only even, or only odd l. The allowed transitions correspond to the first states. If we restrict ourselves to only harmonics with $l = 0$ and $l = 2$, the space of the eighteen functions splits into subspaces according to the irreducible representations $\Gamma_2' + \Gamma_3' + 3\Gamma_4' + 2\Gamma_5'$.

The wave functions of the bases of the irreducible representations Γ_4' and Γ_5' will be the following: for the first representation of Γ_4' we have three functions of the kind

$$\sum_{\mathbf{f}} R_{\nu 0}(|\mathbf{f}|)\, Y_{00}(\theta_{\mathbf{f}} \phi_{\mathbf{f}})\, \Psi(\mathbf{f}, M_x), \tag{20}$$

which differ in the index M; similarly for the second representation of Γ_4'

$$\sum_{\mathbf{f}} R_{\nu 20}(|\mathbf{f}|) \tfrac{1}{2}[3\cos^2(\widehat{\mathbf{f}x}) - 1]\, \Psi(\mathbf{f}, M_x); \tag{21}$$

and for the third representation of Γ_4'

$$\sum_{\mathbf{f}} R_{\nu 22}(|\mathbf{f}|)[\cos(\widehat{\mathbf{f}x})\, \Psi(\mathbf{f}, M_x) + \cos(\widehat{\mathbf{f}z})\, \Psi(\mathbf{f}, M_z)] \cos(\widehat{\mathbf{f}y}). \tag{22}$$

For the first representation of Γ_5' we have

$$\sum_{\mathbf{f}} \sin^2(\widehat{\mathbf{f}z}) \cos(2\phi_{xz})\, R_{\nu 22}(|\mathbf{f}|)\, \Psi(\mathbf{f}, M_z), \tag{23}$$

where φ_{xz} is the angle between f and the xz-plane; for the second representation of Γ_5'

$$\sum_{\mathbf{f}} R_{\nu 22}(|\mathbf{f}|)[\cos(\widehat{\mathbf{f}x})\, \Psi(\mathbf{f}, M_x) - \cos(\widehat{\mathbf{f}z})\, \Psi(\mathbf{f}, M_z)] \cos(\widehat{\mathbf{f}y}). \tag{24}$$

If we write down the wave functions of the spin variable I, the basis remains the same for the singlet states, and transitions into Γ_4' states are allowed. For a triplet state the number of basis functions increases by a factor three and the 54 functions fall into groups according to the following irreducible representations:

$$(\Gamma_2' + \Gamma_3' + 3\Gamma_4' + 2\Gamma_5') \times \Gamma_4 = 3\Gamma_1' + 2\Gamma_2' + 5\Gamma_3' + 6\Gamma_4' + 7\Gamma_5'. \tag{25}$$

We shall give one function of each of the irreducible representations of Γ_4'.

The first representation of Γ'_4:

$$\sum_{\mathbf{f}} R_{\nu 20}(|\mathbf{f}|)\, Y_{00}(\theta_{\mathbf{f}}\phi_{\mathbf{f}})\, [-\Psi(\mathbf{f}, M_y|\zeta) + \Psi(\mathbf{f}, M_z|\eta)]/\sqrt{2}, \tag{26}$$

the two other functions are obtained by a cyclic permutation of the variables x, y, z and ξ, η, ζ. The second representation of Γ'_4:

$$\frac{1}{2}\sum_{\mathbf{f}} R_{\nu 20}(|\mathbf{f}|)\, [(3\cos^2(\widehat{\mathbf{f}y}) - 1)\, \Psi(\mathbf{f}, M_y|\zeta) + (3\cos^2(\widehat{\mathbf{f}z}) - 1)\, \Psi(\mathbf{f}, M_z|\eta)]. \tag{27}$$

The third representation of Γ'_4:

$$\sum_{\mathbf{f}} R_{\nu 22}(|\mathbf{f}|)\, [\sin^2(\widehat{\mathbf{f}z}) \cos(2\phi_{xz})\, \Psi(\mathbf{f}, M_z|\eta) + \sin^2(\widehat{\mathbf{f}y}) \cos(2\phi_{xy}) \Psi(\mathbf{f}, M_y|\zeta)]. \tag{28}$$

The fourth representation of Γ'_4:

$$\sum_{\mathbf{f}} R_{\nu 22}(|\mathbf{f}|)\, \{\cos(\widehat{\mathbf{f}x})\, [\cos(\widehat{\mathbf{f}y})\, \Psi(\mathbf{f}, M_y|\zeta) + \cos(\widehat{\mathbf{f}z})\, \Psi(\mathbf{f}, M_z|\zeta)] \tag{29}$$

$$- \cos(\widehat{\mathbf{f}z})[\cos(\widehat{\mathbf{f}x})\, \Psi(\mathbf{f}, M_x|\xi) + \cos(\widehat{\mathbf{f}y})\, \Psi(\mathbf{f}, M_y|\xi)]\}$$

and so on.

The exciton eigenfunctions will be linear combinations of the corresponding lines of these irreducible representations, different for S = 0 and for S = 1. From the point of view of this more general consideration, the level schemes for a NaCl and for a CsCl crystal must be identical, since their lattice symmetry is the same. The different number of states obtained by Overhauser is connected only with the different number of basis functions, he took, since he restricted himself to only one coordination sphere. The differences between the exciton spectra of these crystals must lie only in the individual spacing and intensity of the different lines.

4. EXCITON LEVELS IN THE MACROSCOPIC APPROXIMATION AND A VERY SIMPLE VARIANT OF THE EFFECTIVE MASS METHOD

If the expansion in spherical harmonics contains a limited number of terms, it was shown by the foregoing considerations that the wave functions without spin are not separated as far as the quantum number M is concerned. As a result there will enter into the functional (10) not only diagonal terms in M, and the equation corresponding to this will for $\mathbf{K} = 0$ have the form

$$E(i\nabla_{\mathbf{f}}, s)\, \varphi_\nu(\mathbf{f}, M) - \sum_{M'} E(i\nabla_{\mathbf{f}}, M, M')\, \varphi_\nu(\mathbf{f}, M') + \sum_{M'} [-K(\mathbf{f}, M, M', s) + 2\delta(S)\, A(\mathbf{f}, M, M', s)] \times \varphi_\nu(\mathbf{f}, M') = {}^S E_\nu \varphi_\nu(\mathbf{f}, M). \tag{30}$$

In the present paper we shall, in order to simplify the calculation, neglect the off-diagonal elements in M in Eq. (30). Account will be taken of these terms in a separate calculation. Equation (27) then simplifies to:

$$E(i\nabla_{\mathbf{f}}, s)\, \varphi_\nu(\mathbf{f}) - E(i\nabla_{\mathbf{f}}, M, M')\, \varphi_\nu(\mathbf{f}) + [-K(\mathbf{f}, M, M, s) + 2\delta(S)\, A(\mathbf{f}, M, M, s)]\, \varphi_\nu(\mathbf{f}) = {}^S E_\nu \varphi_\nu(\mathbf{f}). \tag{31}$$

We restrict our considerations to an exciton of large radius. We can then consider **f** to be a continuous variable and go over to the effective mass method (E.M.M.) equation. We shall consider the simplest case when both the electron and the hole band have a unique minimum at K = 0, and, moreover, F(**k**, M, M) does not depend on the value of M. Both bands are then spherically symmetric. It is known that for a number of real crystals the bands have several energy minima and do not possess spherical symmetry, and in the case of degenerate bands one can not expand in powers of K. The corresponding exciton spectra will be much more complicated than the ones obtained in our approximation. We shall concentrate our attention here mainly on ascertaining the role of the exchange potential and an estimate of the magnitude of the *l*-splitting and of the level shift compared to the hydrogen series. As is clear from (6), the many-electron approach to the problem leads to the appearance of another interaction, apart from the Coulomb and exchange potentials namely of each quasi-particle with the background electrons. The influence of the background on the interaction of the electron and the hole was considered by Samoĭlovich and Korenblit.[4] This interaction leads, moreover, to the fact that at large distances the Coulomb interaction is divided by the square of the index of refraction n_0^2. This was in different approximations shown in the papers of Kohn[12] and Liberberg-Kucher.[13] At distances of the order d and $d\sqrt{2}$ (d is the distance between nearest neighbor ions) the error in dividing by n_0^2 is about 10 to 20%. In our considerations this last effect will not enter explicitly, but the final result for both functions will be divided by n_0^2. If $f = |\mathbf{G} - \mathbf{H}| \geq d$ the error is again small and the contribution of this potential at smaller distances is small (especially for a para-exciton). Expanding $E(i\nabla_{\mathbf{f}}, s)$ and $E(i\nabla_{\mathbf{f}}, M, M)$ in powers of $i\nabla_{\mathbf{f}}$ up to $\nabla_{\mathbf{f}}^4$ inclusive, we can write Eq. (31) in the form

$$-\frac{\hbar^2}{2\mu}\nabla^2\varphi_\nu - \frac{\hbar^2 d^2}{\mu c}\nabla^4\varphi_\nu - \frac{e^2}{n_0^2}[K(r) - 2\delta(S)\, A(r)]\, \varphi_\nu = {}^S E_\nu \varphi_\nu. \tag{32}$$

It is different from the equation used by other authors[2–8] through the presence of the exchange potential A(r), the fact that K(r) differs from 1/r and the fact that the following E.M.M. approximations are taken into account. The quantity c depends on the structure of the cation and anion lattices (see Appendix 1). Here $r = |\mathbf{G} - \mathbf{H}|$ is a continuous parameter. The approximate estimate of the integrals K(r) and A(r) is performed with hydrogen-like functions of the 1s type. The equation which is then obtained is quite complicated (see Appendix 2) but can be approximated quite simply:

$$\begin{aligned} -{}^{S}V(r)/(e^2/n_0^2) &= K(r) - 2\delta(S)A(r) \\ &= \frac{1}{r} + \sum_{k=1}^{2} V_k^S \exp(-\gamma_k^S r) + V_3^S \frac{\exp(-\gamma_3^S r)}{r} \end{aligned} \tag{33}$$

through a suitable choice of the parameters V_k^S, γ_k^S for each value of the spin S = 0 and S = 1.

Equation (32) was solved by the variational method using the trial functions

$$\varphi_{nlm}(r) = x_S^{3/2} R_{nl}\left(\frac{x_S r}{na}\right) Y_{lm}(\theta\phi), \tag{34}$$

where $a = a_B n_0^2 m/\mu$ is the effective Bohr radius, $a_B = \hbar^2/me^2$, x_S the variational parameter. The average value of the energy, evaluated by using the functions (34) and taking (A2.8) and (A2.9) into account, is equal to

$$\begin{aligned} {}^{S}E_{nl}(x_S) = \frac{e^2}{2an_0^2 n^2}\Big[x_S^2 - 2x_S \\ - \frac{8}{c}\left(\frac{d}{a}\right)^2 \frac{x_S^4}{n}\left(\frac{1}{l + 1/2} - \frac{3}{4n}\right) - {}^{S}L(x_S \,|\, nl)\Big]. \end{aligned} \tag{35}$$

The first two terms within the brackets correspond purely to the hydrogen problem, the third term is due to the term in ∇^4 and the fourth one to the difference between K(r) − 2δ(S)A(r) and 1/r. $^{S}L(x_S \,|\, nl)$ is given in Appendix 2.

After finding the minimization parameter x_S, the expression (35) for the energy turns out to depend on the orbital quantum number l. One sees easily that the l-splitting between s and p levels varies as $1/n^3$. A numerical estimate will be given for a Cu_2O crystal.

5. THE THEORY OF EXCITONS IN A CRYSTAL OF THE Cu_2O TYPE

Since at the point K = 0 the difference between all groups vanishes, the classification of the states of large radius which was obtained for NaCl remains valid also for Cu_2O. We shall assume that, in accordance with reference 14, the hole can be on one of the O^{--} sites in one of three p states, and the electron on one of the Cu^+ sites in an s state. Such a mechanism of the formation of an exciton is not possible in only one way. At the present time also other possibilities are considered, on which we shall report separately.

In Fig. 1 we have depicted the scheme of those levels of the para-exciton (S = 0) and the ortho-exciton (S = 1) for which transitions from the ground state are possible only through spin-orbit interactions. We have given only S and d states of relative motion, transitions into which are allowed. The distances between the levels are drawn

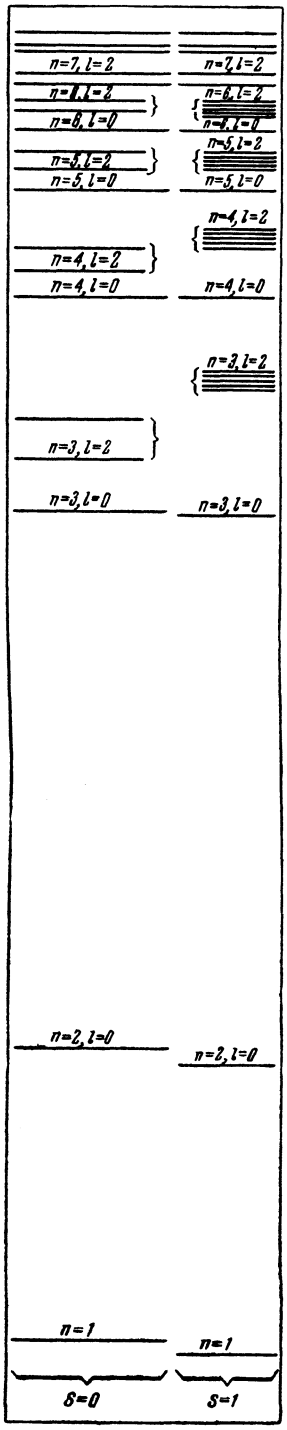

FIG. 1. Scheme of the exciton levels in the crystal, into which a transition from the ground state is allowed.

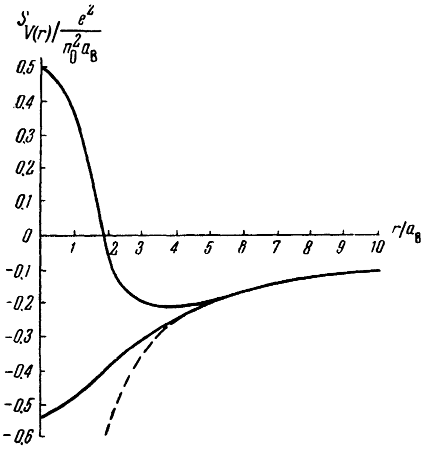

FIG. 2. Potential energy curves for the para- (S = 0) and ortho- (S = 1) exciton in the macroscopic approximation.

arbitrarily. The para-exciton levels must lie somewhat higher, thanks to the presence of the repulsive exchange potential. Pavinskii and Zhilich[15] have shown that due to the presence of two O^{--} ions in the elementary cell of Cu_2O two hole states are possible: even and odd states. Taking this fact into account in our scheme led just to the occurrence of the second exciton series.

Our considerations cannot give us the correct distances between the levels since from the various factors which produce the splitting we have only taken into account the difference in the potentials in their dependence on the total spin. For our numerical calculations we took for the parameters in the atomic functions (A2.1) for Cu $\alpha = 0.743/a_B$ according to Slater[16] and for O^{--} according to the results of Zhilich[14] (for the radial part) $\beta = 1.03/a_B$. As a result of this calculation we obtained an expression for K − 2A (Appendix 2) and found the values of the coefficients in the simplified Eq. (33):

$$S = 0:\quad V_1^0 = -48.47/a_B;\quad V_2^0 = 46.46/a_B;\quad V_3^0 = -1;$$
$$\gamma_1^0 = 1.44/a_B;\quad \gamma_2^0 = 1.503/a_B;\quad \gamma_3^0 = 1.5/a_B. \tag{36}$$
$$S = 1:\quad V_1^1 = -1.554/a_B;\quad V_2^1 = 0;\quad V_3^1 = -1;$$
$$\gamma_1^1 = 1.42/a_B;\quad \gamma_3^1 = 2.1/a_B.$$

For $\beta = 1.18/a_B$ we obtained values close to these. The corresponding curves are given in Fig. 2: −K(r) + 2A(r) for S = 0, and −K(r) for S = 1. The dotted line gives the point charge Coulomb potential. The rest of the evaluation of the exciton energy through Eqs. (35) and (A2.8) was performed for $n_0^2 = 2.5$; $\mu = 0.253\,m$, $a = 24.7\,a_B$.

In Fig. 3 we have given the para-exciton levels taking the exchange potential and the term in ∇^4 into account. We assumed also that the effective masses of the electron and the hole were the same. In that case c = 1/16 according to Appendix 1.

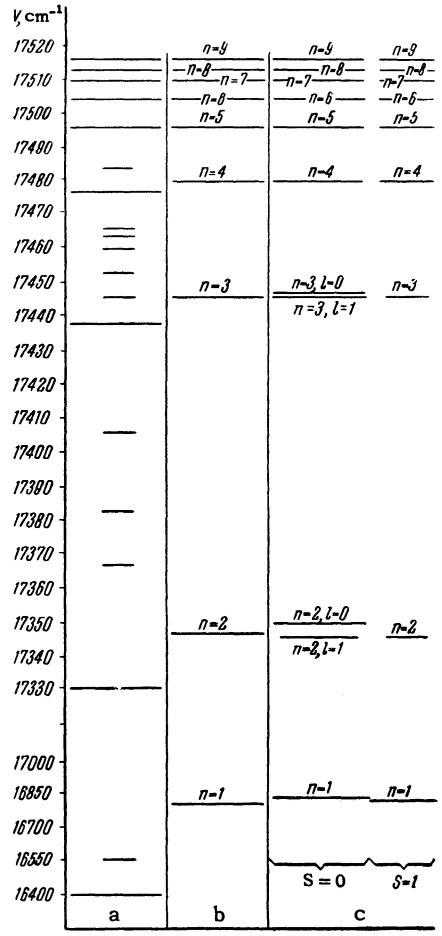

FIG. 3. Comparison of the yellow exciton series observed experimentally with the calculated ones: a – experimental data;[17,18] b – calculated from a hydrogen-like exciton model; c – according to the representation of the present paper.

Side by side we have given for comparison the results of the experiments of Gross and coworkers[17,18] and also the position of the lines for a purely hydrogen series K(r) = 1/r, A(r) = 0.

As can be seen from the figure the shift is appreciable for the s level of the para-exciton series and insignificant for all other levels of the para- and ortho-series. The lines with n = 1 (they are drawn to a different scale) turned out to be very weak experimentally; this cannot be explained in our scheme. The calculations show that the distances between s and p levels of the same n vary for the given values of the parameters as $30/n^3$ cm^{-1} for the para-series and as $1/n^3$ cm^{-1} for the ortho-series. The comparative smallness of the l-splitting produced by the difference of K − 2A from 1/r and by taking the terms in ∇^4 into account is connected with the large radii of the exciton states in Cu_2O.

We also investigated the influence of the difference between K − 2A and 1/r and of the correc-

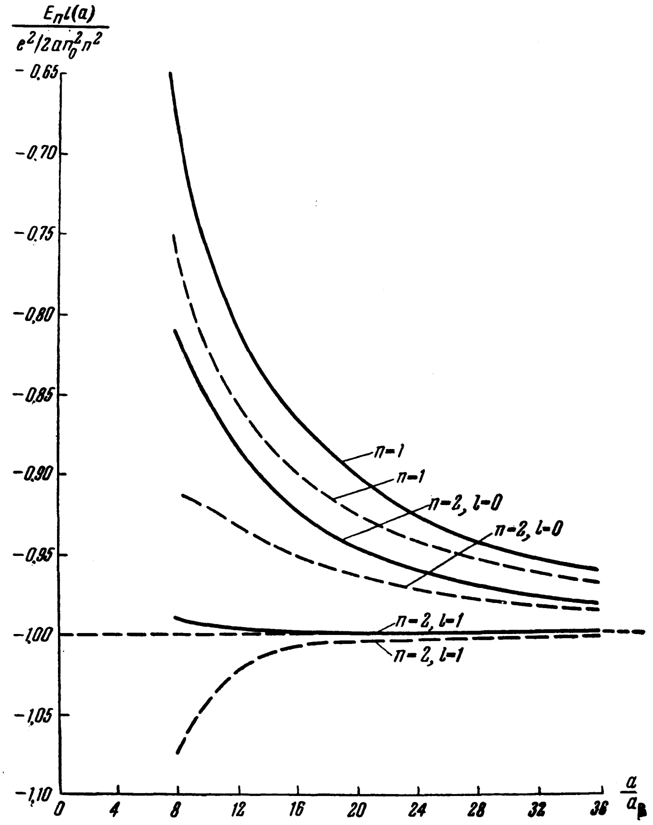

FIG. 4. Shift of the $^0E_{1s}$, $^0E_{2s}$, and $^0E_{2p}$ levels from the usual hydrogen-like position as functions of the magnitude of the effective Bohr radius.

tions to the E.M.M. $\sim\nabla^4$ on the magnitude of the l-splitting for different radii of the state in the simplest case when the effective masses of the electron and hole are assumed to be equal in the correction term $\sim\nabla^4$. The results are given in Fig. 4 for the 1s, 2s, and 2p levels. The solid curves are the ones obtained without taking the term ∇^4 into account, and the dotted lines those with taking this term into account. The horizontal line gives the level of the purely hydrogen problem. The magnitude of the splitting increases steeply with decreasing effective Bohr radius. Simultaneously the role of the corrections to the E.M.M. increases. The exact calculation of the l-splitting and the position of the lowest levels for small radii of the states must thus take into account the discrete structure of the crystal.

In conclusion we note some peculiarities of the behavior of excitons in a magnetic field. The ground state of the crystal in which all spins and orbital momenta are compensated is diamagnetic and its energy in a magnetic field increases as H^2. As a result of the absorption of light due to the presence of the spin-orbit interaction exciton states with $S = 0$ and $S = 1$ are formed. Since their energy levels differ appreciably because of the differences in the interaction potentials and in the character of the orbital motion, the spin-electron resonance in an exciton is essentially different from the spin-electron resonance in polarons and in localized centers with one electron. This difference consists in the fact that the energy necessary for a spin-flip of the exciton electron is equal to the difference between the corresponding levels of the para- and ortho-exciton series. If the levels of the para-exciton series are situated above the corresponding levels of the ortho-exciton series, then the spin-flip of the electron in an external constant magnetic field which leads to the change of an ortho-exciton into a para-exciton, will be accompanied by the absorption of two quanta of energy

$$\hbar\omega = |{}^0E_{nl} - {}^1E_{nl} \pm 2\hbar O_L ,$$

where O_L is the Larmor frequency. In crystals where the levels of the para-exciton series are situated below the corresponding levels of the ortho-exciton series during the same mechanism of transformation of a para-exciton into an ortho-exciton quanta

$$\hbar\omega = |{}^1E_{nl} - {}^0E_{nl} \pm 2\hbar O_L$$

will be absorbed. The absorbed quanta in spin-electron resonance in excitons can correspond to an infrared frequency for some values of the quantity $|{}^0E_{nl} - {}^1E_{nl}|$. This is one of the different peculiarities of exciton spin-resonance absorption. Another property of it is, according to Deĭgen and Pekar[19] the narrowness of the spin-resonance absorption band.

The exciton model considered by us can be generalized both for the case of an exciton in elemental semiconductors and dielectrics and, in particular, for the case of a delta-function form of the function $\varphi_\nu(\mathbf{G}-\mathbf{H})$, that is, for a Frenkel exciton. One needs only let the position vector of the electron **G** take on the same values as the position vector of the hole **H**. The atomic functions in the case **G** = **H** will then be different from the case of differing **G** and **H**.

APPENDIX 1

EXPANSION OF $E(-i\nabla)$ IN POWERS OF $i\nabla$

The behavior of $E_1(\mathbf{k})$ for lattices with identical ions with a face centered cubic cell of edge length $D = 2d$ and an extremum at $\mathbf{k} = 0$ is given in reference 20. Apart from a constant it has for small k the form

$$E_1(\mathrm{k}) = \frac{\hbar^2k^2}{2\mu_1} - \frac{\hbar^2d^2}{16\mu_1}k^4 + \frac{\hbar^2d^2}{48\mu_1}(k_x^4 + k_y^4 + k_z^4). \qquad (1.1)$$

We shall approximate by replacing the cubically symmetric expression by a spherically symmetric one. We perform a similar operation for the expression $E_2(\mathbf{k})$ for a body-centered cubic lattice[20] and replacing $\mathbf{k}$ by $-i\nabla$ we get, apart from a constant

$$E_1(-i\nabla)-E_2(-i\nabla)=-\frac{\hbar^2}{2\mu}\nabla^2-\frac{\hbar^2 d^2}{c\mu}\nabla^4, \qquad (1.2)$$

where

$$c=\frac{40(\mu_1+\mu_2)}{2\mu_2+3\mu_1}, \quad \frac{1}{\mu}=\frac{1}{\mu_1}+\frac{1}{\mu_2},$$

and μ is the reduced effective exciton mass.

APPENDIX 2

EVALUATION OF THE COULOMB AND EXCHANGE INTEGRALS

With the aid of functions of the type

$$\Theta_{\mathbf{G}}(\mathbf{q})=\frac{\alpha^{3/2}}{\sqrt{\pi}}e^{-\alpha|\mathbf{q}-\mathbf{G}|}; \qquad \Theta_{\mathbf{H}}(\mathbf{q})=\frac{\beta^{3/2}}{\sqrt{\pi}}e^{-\beta|\mathbf{q}-\mathbf{H}|} \qquad (2.1)$$

we can write down the Coulomb and exchange integrals. The exchange integral $A(\mathbf{r})$ can be estimated by Hellmann's method[21]

$$A(r)=\frac{\alpha^3\beta^3}{\pi^2}\int\frac{1}{q_{12}}\exp\{-\alpha|\mathbf{q}_1-\mathbf{G}|-\beta|\mathbf{q}_1-\mathbf{H}|-\alpha|\mathbf{q}_2-\mathbf{G}|-\beta|\mathbf{q}_2-\mathbf{H}|\}d\mathbf{q}_1 d\mathbf{q}_2\approx\frac{\alpha^3\beta^3}{\pi^2}\eta(r)\int\left[\frac{1}{|\mathbf{q}_1-\mathbf{G}|}+\frac{1}{|\mathbf{q}_1-\mathbf{H}|}\right]$$

$$\times\exp\{-\alpha|\mathbf{q}_1-\mathbf{G}|-\beta|\mathbf{q}_1-\mathbf{H}|-\alpha|\mathbf{q}_2-\mathbf{G}|-\beta|\mathbf{q}_2-\mathbf{H}|\}\,d\mathbf{q}_1\,d\mathbf{q}_2, \qquad (2.2)$$

with only one difference, namely that we use for $\eta(\mathbf{r})$ a different analytical expression which is more convenient for the integration:

$$\eta(r)=\frac{5}{8}\{1-0.5\exp[-0.11(\beta+0{,}4\alpha)r]\}, \qquad (2.3)$$

where

$$r=|\mathbf{G}-\mathbf{H}|\text{ and }\beta>\alpha.$$

Using the expressions for the two-center integrals[21] we find

$$K(r)-2A(r)$$

$$=\frac{1}{r}+e^{-2\alpha r}\sum_{n=0}^{n=2}\frac{A_n}{r^n}+e^{-2\beta r}\sum_{n=0}^{n=2}\frac{B_n}{r^n}+e^{-(\alpha+\beta)r}\sum_{n=0}^{n=2}\frac{C_n}{r^n}$$

$$+e^{-2\alpha' r}\sum_{n=0}^{n=2}\frac{A_n'}{r^n}+e^{-2\beta' r}\sum_{n=0}^{n=2}\frac{B_n'}{r^n}+e^{-(\alpha'+\beta')r}\sum_{n=0}^{n=2}\frac{C_n'}{r^n}, \qquad (2.4)$$

where

$$A_0=-\frac{\alpha\beta^4}{(\beta^2-\alpha^2)^2}-\frac{40\alpha^3\beta^4}{(\beta^2-\alpha^2)^3}; \qquad A_0'=\frac{20\alpha^3\beta^4}{(\beta^2-\alpha^2)^3};$$

$$B_0=-\frac{\alpha^4\beta}{(\beta^2-\alpha^2)^2}+\frac{40\alpha^4\beta^3}{(\beta^2-\alpha^2)^3}; \qquad B_0'=-\frac{20\alpha^4\beta^3}{(\beta^2-\alpha^2)^3};$$

$$C_0=\frac{40\alpha^3\beta^3(\beta-\alpha)}{(\beta^2-\alpha^2)^3}; \qquad C_0'=-\frac{20\alpha^3\beta^3(\beta-\alpha)}{(\beta^2-\alpha^2)^3};$$

$$A_1=-\frac{(\beta^6-3\alpha^2\beta^4)}{(\beta^2-\alpha^2)^3}+\frac{80\alpha^3\beta^3(3\alpha\beta-\beta^2)}{(\beta^2-\alpha^2)^4}; \qquad (2.5)$$

$$B_1=-\frac{(3\alpha^4\beta^2-\alpha^6)}{(\beta^2-\alpha^2)^3}+\frac{80\alpha^3\beta^3(3\alpha\beta-\alpha^2)}{(\beta^2-\alpha^2)^4};$$

$$C_1=-\frac{80\alpha^3\beta^3[4\alpha\beta-(\beta-\alpha)^2]}{(\beta^2-\alpha^2)^4};$$

$$A_1'=-\frac{40\alpha^3\beta^3(3\alpha\beta-\beta^2)}{(\beta^2-\alpha^2)^4}; \qquad B_1'=-\frac{40\alpha^3\beta^3(3\alpha\beta-\alpha^2)}{(\beta^2-\alpha^2)^4};$$

$$C_1'=\frac{40\alpha^3\beta^3[4\alpha\beta-(\beta-\alpha)^2]}{(\beta^2-\alpha^2)^4};$$

$$A_2=B_2=-\frac{C_2}{2}=\frac{320\alpha^4\beta^4(\beta-\alpha)}{(\beta^2-\alpha^2)^5};$$

$$A_2'=B_2'=-\frac{C_2'}{2}=\frac{160\alpha^4\beta^4(\beta-\alpha)}{(\beta^2-\alpha^2)^5};$$

$$2\alpha'=2\alpha+\delta, \quad 2\beta'=2\beta+\delta, \quad \delta=0.11(\beta+0{,}4\alpha).$$

In evaluating the value of the potential (33) averaged over the functions (34) one comes across integrals of the following form:

$$x^3\int_0^\infty R_{nl}^2(xr/na)\,r^p e^{-\gamma r}r^2\,dr=J_{nl,nl}^{p,\gamma}(x).$$

They are given in a paper by Alder and Winther:[22]

$$J_{nl,nl}^{p,\gamma}(x)=\frac{4(n+l)!\,(2l+p+2)!\,x^{2l+3}2^{2l}}{[(2l+1)!]^2 n^{4+2l}(n-l-1)!\,\gamma^p(\gamma a)^{2l+3}}$$

$$\times F_2\Big(2l+p+3,\ l+1+n,\ l+1-n, \qquad (2.6)$$

$$2l+2,\ 2l+2,\ -\frac{2x}{na\gamma},\ \frac{2x}{na\gamma}\Big),$$

where F_2 is the generalized hypergeometric function with a circle of convergence $4x/\gamma na \leq 1$. The average value of ${}^S V(\mathbf{r})$ is, according to (34) and (2.6), equal to

$$-\frac{e^2}{2an_0^2n^2}[2x_S+{}^S L(x_S|nl)], \qquad (2.7)$$

where

$${}^S L(x_S|nl)=2an^2\left[\sum_{k=1}^{k=2}V_k^S J_{nl,nl}^{0,\gamma_k^S}+V_3^S J_{nl,nl}^{-1,\gamma_3^S}\right]$$

$$=\frac{8(n+l)!\,2^{2l}x_S^{2l+3}}{n^{2l+2}(2l+1)!\,(n-l-1)!\,a^{2l+2}}\Big\{(2l+2)\sum_{k=1}^{k=2}\frac{V_k^S}{(\gamma_k^S)^{2l+3}}$$

$$\times F_2\Big(2l+3,\ l+1+n,\ l+1-n,$$

$$2l+2,\ 2l+2,\ -\frac{2x_S}{na\gamma_k^S},\ \frac{2x_S}{na\gamma_k^S}\Big) \qquad (2.8)$$

$$+\frac{V_3^S}{(\gamma_3^S)^{2l+2}}F_2\Big(2l+2,\ l+1+n,\ l+1-n,$$

$$2l+2,\ 2l+2,\ -\frac{2x_S}{na\gamma_3^S},\ \frac{2x_S}{na\gamma_3^S}\Big)\Big\}.$$

Since the functions (34) are the solutions of the hydrogen problem, the average values of the operators $(-\hbar^2/2\mu)\nabla^2$ and $(-\hbar^2 d^2/\mu c)\nabla^4$ are respectively equal to

$$\frac{e^2 x_S^2}{2an_0^2 n^2} \text{ and } -\frac{8}{c}\left(\frac{d}{a}\right)^2 \frac{e^2}{2an_0^2 n^3}\left[\frac{1}{l + {}^1/_2} - \frac{3}{4n}\right] x_S^4. \quad (2.9)$$

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