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Abstract

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TRANSITION OF SOLID HELIUM TO THE METALLIC STATE AT HIGH PRESSURES

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1. In the present article perturbation theory is applied to the Hartree–Fock equation in finding the energies of states of high symmetry in a helium crystal. The energy gap between the normal and first excited levels of solid helium is calculated. It is found that at a pressure of $3 \cdot 10^7$ atm the energy gap disappears and helium passes into the metallic state. The incorrectness is pointed out of Seldam' s method, which yielded for the transition pressure the value $2 \cdot 10^8$ atm.

2. The Hartree–Fock equations for the crystal have the form

$$\hat{\mathcal{H}}_1\psi_k(r_1)+\frac{4a}{\pi}\int\frac{\rho_1(r_2)}{|r_1-r_2|}\,d\tau_2\cdot\psi_k(r_1)-\frac{2a}{\pi}\int\frac{\rho_2(r_1,r_2)}{|r_1-r_2|}\,\psi_k(r_2)\,d\tau_2=\varepsilon(\mathbf{k})\psi_k(r_1). \tag{1}$$

Here

$$-\hat{\mathcal{H}}_1=\Delta_1+\frac{4a}{\pi}V(r_1),\qquad V(r_1)=\sum_n^N\frac{1}{|r_1-R_n|},\qquad \rho_1(r_2)=\sum_{k'}^N|\psi_{k'}(r_2)|^2,$$

$$\varepsilon(\mathbf{k})=\frac{2a^2}{\pi^2}E(\mathbf{k}),\qquad \rho_2(r_1,r_2)=\sum_{k'}^N\overline{\psi}_{k'}(r_2)\psi_{k'}(r_1); \tag{2}$$

r_1 and R_n are the radius vectors of the electron and of a lattice site, measured in units of a/π. All quantities are expressed in atomic units. $2a$ is the lattice constant, $E(\mathbf{k})$ is the electron energy. The sums over $\mathbf{k}'$ are taken over all points of the Brillouin zone. The functions ψ_k are assumed normalized to a crystal volume equal to $2\pi^3N$.

It is easy to show that for the ground state $\rho_1(r_1)$ and $\rho_2(r_1,r_2)$ in (1) remain invariant under the action of the operations g of the space group of the crystal G.

We shall solve equations (1) for the functions of the ground and weakly excited states. In this case one may assume that ρ_1 and ρ_2 for the excited states remain the same as for the ground state. Thus, for the given problem the Fock equations may be regarded as linear equations with an operator invariant with respect to the group G. The functions ψ_k may therefore be classified according to the irreducible representations of this group τ_{kp} ($\mathbf{k}$ is a vector of the Brillouin zone, p is the number of the representation) ([1]). Therefore the function of a given state may be sought in the form of a series of functions which transform according to the irreducible representation corresponding to the given level. In view of the fact that, for the lattice constants of interest to us, the potential energy is a perturbation, the zeroth approximation is symmetrized plane waves, and the solution can be obtained by expanding the wave functions and the energy levels in a series in powers of a/π.

We shall seek the functions $\psi_k^{(n)}$ in the form of a series in functions transforming according to the representation τ_{kp} (corresponding to the given level), for which we

choose symmetrized combinations of plane waves:

$$\psi_{kp}^{(n)}(r) = \sum_j c_{kpj}^{(n)} f_{kpj}(r), \qquad f_{kpj}(r) = \sum_s b_{kps} e^{i(\mathbf{k}+\mathbf{K}_{js})\mathbf{r}}, \qquad |\mathbf{k}+\mathbf{K}_{js}| = |\mathbf{k}+\mathbf{K}_j|. \tag{3}$$

Here $\mathbf{k}$ is the reduced wave vector; $\mathbf{K}_{js}$ are reciprocal-lattice vectors multiplied by 2π. For nonsymmetric points of the Brillouin zone

$$f_{kpj}(r) = (2\pi^3 N)^{-1/2} e^{i(\mathbf{k}+\mathbf{K}_j)\mathbf{r}}. \tag{4}$$

For symmetric points of the Brillouin zone, the coefficients b_{kps} and the vectors $\mathbf{K}_{js}$ are found with the aid of the theory of group representations. In the zeroth approximation we obtain

$$\psi_{\mathbf{k}}^{(0)}(r) = f_{kp0}(r), \qquad \varepsilon^{(0)}(\mathbf{k}) = k^2. \tag{5}$$

For the functions of the first approximation we have:

$$c_{kpj}^{(1)} = \frac{4\langle f_{kpj}|V|f_{kp0}\rangle}{|\mathbf{k}+\mathbf{K}_j|^2 - k^2}, \qquad c_{kp0}^{(1)} = 0; \tag{6}$$

$$\varepsilon^{(1)}(\mathbf{k}) = -2\int \frac{\rho_2^{(0)}(r_1, r_2)}{|r_1 - r_2|} \overline{f_{kp0}(r_1)}\, f_{kp0}(r_2)\, d\tau_1 d\tau_2 - 4\langle f_{kp0}|V|f_{kp0}\rangle, \tag{7}$$

where here and below it is assumed that the zero Fourier component of $V(r)$ is equal to zero.

Similarly, for the second approximation we find

$$\varepsilon^{(2)}(\mathbf{k}) = -4\sum_j c_{kpj}^{(1)}\langle f_{kp0}|V|f_{kpj}\rangle + 4\int \frac{\rho_1^{(1)}(r_2)}{|r_1-r_2|}|\psi_{\mathbf{k}}^{(0)}(r_1)|^2\,d\tau_1 d\tau_2 - \quad (8)$$

$$-2\int \frac{\rho_2^{(0)}(r_1,r_2)\psi_{\mathbf{k}}^{(1)}(r_2)\overline{\psi_{\mathbf{k}}^{(0)}(r_1)} + \rho_2^{(1)}(r_1,r_2)\overline{\psi_{\mathbf{k}}^{(0)}(r_1)}\psi_{\mathbf{k}}^{(0)}(r_2)}{|r_1-r_2|}\,d\tau_1 d\tau_2.$$

In the expressions for ρ_1 and ρ_2, the symmetrized waves may be replaced by plane waves in view of the relative smallness of the number of symmetric points. Taking this remark into account, it is easy to find ρ_1 and ρ_2:

$$\rho_2^{(0)}(r_1,r_2) = (2\pi^3 N)^{-1}\sum_{\mathbf{k}}^{N} e^{i\mathbf{k}(r_2-r_1)}; \quad (9)$$

$$\rho_2^{(1)}(r_1,r_2) = (2\pi^3 N)^{-1}\sum_{\mathbf{k},j}^{N} c_{kj}^{(1)} e^{i\mathbf{k}(r_2-r_1)}\left[e^{-i\mathbf{K}_j r_1} + e^{i\mathbf{K}_j r_2}\right]. \quad (10)$$

In what follows we shall be interested in the energy levels for symmetric points of the Brillouin zone that correspond to one-dimensional representations with characters $\chi_{kp}(g)$. In these cases the linear combinations will have the form:

$$f_{kpj}(r) = (2\pi^3 N n_{kpj})^{-1/2}\sum_g \chi_{kp}(g)e^{i(\mathbf{k}+\mathbf{K}_j)gr}, \quad (11)$$

where g are the elements of the group of the wave vector $\mathbf{k}$.

Substituting expressions (9), (10), and (11) into (7) and (8), we finally obtain:

$$\varepsilon^{(1)}(\mathbf{k}) = -\frac{4}{\pi^2 N}\sum_{\mathbf{k}'}\frac{1}{(\mathbf{k}+\mathbf{k}')^2} - 4\langle f_{kp0}|V|f_{kp0}\rangle; \quad (12)$$

$$-\varepsilon^{(2)}(\mathbf{k}) = 16\sum_j \frac{|\langle f_{kp0}|V|f_{kpj}\rangle|^2}{|\mathbf{k}+\mathbf{K}_j|^2 - k^2} -$$

$$-\frac{16N_g}{\pi^2 N n_{kp0}}\sum_{g,j,\mathbf{k}'}\frac{c_{kj}^{(1)}\chi_{kp}(g)}{|\mathbf{K}_j|^2}\frac{(\mathbf{k}'-\mathbf{k})^2 - \frac{1}{2}K_j^2}{(\mathbf{k}'-\mathbf{k})^2}\Delta(\mathbf{k}-g\mathbf{k}-\mathbf{K}_j), \quad (13)$$

where N_g is the order of the group of the vector $\mathbf{k}$; n_{kpj} is a normalization factor;

$$\Delta(\mathbf{k}) = \begin{cases} 0, & \text{for } \mathbf{k} \neq 0, \\ 1, & \text{for } \mathbf{k} = 0. \end{cases}$$

In the first term in formula (13), the summation is carried out only over reciprocal-lattice vectors inequivalent for the given representation; moreover,

$$\langle f_{kp0}|V|f_{kpj}\rangle = \frac{2N_g}{\pi^2\sqrt{n_{kp0}n_{kpj}}}\sum_g \frac{\chi_{kp}(g)}{\left|\mathbf{k} - g\mathbf{k} + \mathbf{K}_j\right|^2}. \tag{14}$$

In the second term, the sum over j is taken over all reciprocal-lattice vectors,

$$c^{(1)}_{k'j} = 8\left[\pi^2 K_j^2\left(\left|\mathbf{k}' + \mathbf{K}_j\right|^2 - \left|\mathbf{k}'\right|^2\right)\right]^{-1}. \tag{15}$$

3. As already mentioned, in our approximation the energy gap will be equal to the difference between the highest level of the filled band and the lowest level of the empty band. In view of the smallness of the potential energy it is quite obvious that these levels will correspond to the longest and shortest reduced wave vectors in the Brillouin zone (we shall denote the corresponding points in the Brillouin zone by W and L). Thus, we must find the lowest level at the point W (top of the filled band) and the second level at the point L (bottom of the empty band). It is easy to find that the desired level at the point W corresponds to the unit representation of the group of the wave vector $\mathbf{k}_W$, while at the point L it corresponds to one of the nonunitary one-dimensional representations of the group of the wave vector $\mathbf{k}_L$. The matrices of the irreducible representations of the wave-vector group for the symmetry points of the Brillouin zone of the face-centered cubic lattice have been given more than once in the literature ([2,3]), and we shall not write them out. Using these matrices, from formulas (5), (12), and (13) it is easy to calculate to second order the energy levels $\varepsilon_1(\mathbf{k}_W)$ and $\varepsilon_2(\mathbf{k}_L)$ that are of interest to us. The sums over $\mathbf{k}'$ occurring in these expressions can readily be evaluated with sufficient accuracy by replacing them in the usual way by integrals over the Brillouin zone and then transforming these volume integrals into surface integrals. Omitting the details of the numerical calculations, we give only the final result:

$$\varepsilon_1(\mathbf{k}_W, a) = 1.250 - 0.39a - 0.1a^2,$$

$$\varepsilon_2(\mathbf{k}_L, a) = 0.750 - 0.14a - 0.02a^2.$$

From the equality $\varepsilon_1(\mathbf{k}_W, a) = \varepsilon_2(\mathbf{k}_L, a)$ we find that the energy gap vanishes at $a = 1.4$. Formulas (6), (9), and (10) make it possible to calculate the total energy of the crystal (we again neglect the symmetry points) as a function of

the lattice constant, knowing which one can readily calculate the pressure at the transition point. It turns out to be $p = 3 \cdot 10^7$ atm. In reality the transition will occur at a somewhat different pressure, when the free enthalpies of the ground and excited states of the crystal are compared.

4. The question of the dependence of the energy gap in solid helium on the lattice constant was considered earlier by Seldam ([3]). It is easy to see, however, that for such a small lattice constant ($a \sim 1$) as that used in Seldam' s calculation, the electron density will be almost constant. Therefore it is unreasonable to use, as Seldam does, the atomic approximation for the potential in the crystal.

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Note: Figure translations are in progress. See original paper for figures.