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BOSE EXCITATIONS IN IONIC CRYSTALS

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A study is made of second-quantized elementary Bose excitations of a system of electrons (excitons) interacting with polarization vibrations of a crystal. In the case of weak coupling the interaction leads to a decrease of exciton energy and an increase of effective exciton mass. These effects are estimated quantitatively.

THE interaction between an exciton and lattice oscillations has been considered in a number of papers as a single-particle problem. Exciton energy and the dependence of exciton-phonon interaction on the internal state of the exciton have been investigated for strong coupling by Pekar and Dykman[1] using the methods of polaron theory and by Moskalenko[2] using Bogoliubov's[3] theory of adiabatic perturbations. Ipatova[4] used the method of Lee, Low, and Pines[5] for intermediate coupling and Dykman[6] used the method of traces for weak coupling. In reference 7 Moskalenko regarded the interaction as a small perturbation. Haken[8] has applied the Feynman variational method to the exciton problem.

In the present paper excitons are regarded as elementary excitations in a many-electron system interacting with a lattice. The Hamiltonian of the system is composed of three parts representing electrons, phonons and their interaction:

$$H = H_{\mathrm{el}} + H_{\mathrm{ph}} + H_{\mathrm{int}}. \tag{1}$$

We shall investigate the energy spectrum of weakly excited state of the system assuming that each lattice site holds a single electron, which may exist in either the ground state ($\lambda = 0$) or an excited state ($\lambda = 1$):

$$n_{f0} + n_{f1} = 1; \quad n_{f\lambda} = a_{f\lambda}^{+} a_{f\lambda}, \tag{2}$$

where f is the index of a lattice site and $a_{f\lambda}^{+}$ and $a_{f\lambda}$ are electron creation and destruction operators. The condition for weak excitations is

$$\bar{n}_{f1} \ll \bar{n}_{f0}. \tag{3}$$

In distinction from a real model of ionic crystals such as those of alkali halides we here disregard the two kinds of sites as well as spin closure of the electron states. The present scheme can also be applied to a more real model[9] although such a complication is not required for the investigation of excitons. Indeed, the excited state may represent either an excitation at halide sides f (Dexter's exciton[10]) or electron transfers to neighboring alkali sites g (the usual exciton model). In the latter case there are no valence electrons in the ground state at sites g, which therefore need not be considered explicitly. The homopolar condition (2) will then apply to a pair of neighboring f and g sites. We shall not consider spin closure, which is important for the analysis of singlet and triplet exciton states. We also assume that all electron spins are parallel and that excitations are not accompanied by spin flips. The spin subscript will now be dropped.

The Hamiltonian of a many-electron system subject to the homopolar condition (2) is given by

$$\begin{aligned} H_{\mathrm{el}} = & \sum L(f\lambda f\lambda')\, a_{f\lambda}^{+} a_{f\lambda'} \\ & + \sum F(f_1\lambda_1 f_2\lambda_2 f_1\lambda_1' f_2\lambda_2')\, a_{f_1\lambda_1}^{+} a_{f_2\lambda_2}^{+} a_{f_2\lambda_2'} a_{f_1\lambda_1'} \\ & + \frac{1}{2} \sum F(f_1\lambda_1 f_2\lambda_2 f_2\lambda_2' f_1\lambda_1')\, a_{f_1\lambda_1}^{+} a_{f_2\lambda_2}^{+} a_{f_1\lambda_1'} a_{f_2\lambda_2'}, \end{aligned} \tag{4}$$

where L and F are additive and binary matrix elements, respectively, with summation over all subscripts. This Hamiltonian is diagonalized by neglecting all terms in which more than two operators have the subscript $\lambda = 1$ [weak excitation condition (3)]. After introducing the operators $b_f = a_{f_0}^{+} a_{f_1}$, $b_f^{+} = a_{f_1}^{+} a_{f_0}$, which in approximation (3) obey the commutation relations of Bose statistics, making a linear substitution for operators b_f, b_f^{+} and passing to k-space:

$$b_f = N^{-1/2} \sum_k b_k e^{-i\mathbf{k}\cdot\mathbf{f}}; \quad b_f^{+} = N^{-1/2} \sum_k b_k^{+} e^{i\mathbf{k}\cdot\mathbf{f}}$$

(N is the number of lattice sites in the fundamental crystal region) we obtain[11]

$$H_{\mathrm{el}} = \sum_k v_k b_k^+ b_k + \frac{1}{2} \sum_k u_k b_k b_{-k} + \frac{1}{2} \sum_k u_k^* b_k^+ b_{-k}^+. \quad (5)$$

The energy of elementary excitation (excitons in atomic semiconductors) is then given by $v_k' = \sqrt{v_k^2 - u_k^2}$, where v_k and u_k are certain combinations of Coulomb and exchange integrals. We have analyzed the energy spectrum of these excitations[12] for comparison with single-particle theories, and have found that for a simple cubic lattice with the constant a when k is small v_k and u_k are given by

$$\begin{gathered} v_k = E_1 - E_0 + d - (R - I) - 6|Q| + \hbar^2 k^2/2M, \\ u_k = -6|Q| + |Q| k^2 a^2. \end{gathered} \quad (6)$$

This expression contains the width $E_1 - E_0$ of the forbidden crystal energy band, the Coulomb interaction R and the exchange interaction I between an electron and a hole, the exciton transfer integral Q, the effective exciton mass M and, finally, the quantity d, which is proportional to one-half the sum of the valence and conduction band widths:

$$\begin{gathered} R = \int \theta_0^*(\mathbf{r}_1)\, \theta_1^*(\mathbf{r}_2)\, \Phi(\mathbf{r}_1 \cdot \mathbf{r}_2)\, \theta_0(\mathbf{r}_1)\, \theta_1(\mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2, \\ I = \int \theta_1^*(\mathbf{r}_1)\, \theta_0^*(\mathbf{r}_2)\, \Phi(\mathbf{r}_1 \cdot \mathbf{r}_2)\, \theta_0(\mathbf{r}_1)\, \theta_1(\mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2, \\ Q = \int \theta_1^*(\mathbf{r}_1)\, \theta_0^*(\mathbf{r}_2 - \mathbf{a})\, \Phi(\mathbf{r}_1 \cdot \mathbf{r}_2)\, \theta_0(\mathbf{r}_1)\, \theta_1(\mathbf{r}_2 - \mathbf{a})\, d\mathbf{r}_1 d\mathbf{r}_2, \\ M^{-1} = (m_{\mathrm{el}} + m_{\mathrm{h}})^{-1} + 2|Q| a^2 \hbar^{-2}. \end{gathered} \quad (7)$$

Here $\Phi(r_1 r_2)$ is the interelectron interaction energy and θ_λ are the single-particle basis functions that are used for the transition to the second quantized representation.

The phonon energy operator in terms of the Bose creation and destruction operators $\xi_\varkappa^+$ and $\xi_\varkappa$, respectively, of a phonon with frequency $\omega_\varkappa$ is given by

$$H_{\mathrm{ph}} = \sum_\varkappa \hbar\omega_\varkappa \xi_\varkappa^+ \xi_\varkappa. \quad (8)$$

Finally, the term in (1) which describes the electron-phonon interaction becomes after second quantization

$$H_{\mathrm{int}} = \sum_{f\lambda\lambda'\varkappa} K(f\lambda f\lambda'\varkappa)\, a_{f\lambda}^+ a_{f\lambda'} (\xi_\varkappa + \xi_{-\varkappa}^+), \quad (9)$$

where

$$K(f\lambda f\lambda'\varkappa) = \int \theta_{f\lambda}^*(\mathbf{r})\, A_\varkappa e^{i\varkappa\cdot\mathbf{r}}\, \theta_{f\lambda'}(\mathbf{r})\, d\mathbf{r};$$

$$A_\varkappa = |\varkappa|^{-1} (2\pi e^2 \hbar\omega_\varkappa c_\varkappa/\Omega)^{1/2}.$$

Here Ω is the volume of the fundamental crystal region, $c_\varkappa = 1/n^2 - 1/\epsilon(\omega_\varkappa)$, and n^2 and ϵ are the square of the refractive index and the dielectric constant of the crystal. For a specific calculation this interaction is given the usual form of an interaction between electrons and longitudinal optical lattice vibrations (in the approximation of a dielectric continuum). We shall hereinafter be interested only in the interaction between the lattice and an assumed small number of excited electrons; we shall therefore use the interaction law (9), which is usually employed for the "excess" electrons in the crystal. Any other form of interaction would only change the coefficient K but would not affect the scheme of the calculation. Introducing into (9) the Bose operators b_f and b_f^+ that were defined above and making use of their Fourier components and of (2), we obtain

$$\begin{aligned} H_{\mathrm{int}} &= \sum_{f\lambda\lambda'\varkappa} K(f\lambda f\lambda'\varkappa)\, a_{f\lambda}^+ a_{f\lambda'} (\xi_\varkappa + \xi_{-\varkappa}^+) \\ &= \sum_{f,\varkappa} \{K(f0f0\varkappa)(a_{f0}^+ a_{f0} + a_{f1}^+ a_{f1}) \\ &\quad + [K(f1f1\varkappa) - K(f0f0\varkappa)]\, a_{f1}^+ a_{f1} + K(f1f0\varkappa)\, a_{f1}^+ a_{f0} \\ &\quad + K(f0f1\varkappa)\, a_{f0}^+ a_{f1}\} (\xi_\varkappa + \xi_{-\varkappa}^+) \\ &= \sum_{k,\varkappa} [W(\varkappa)\, b_k^+ b_{k-\varkappa} + \sqrt{N} K_{01} b_{-\varkappa} + \sqrt{N} K_{10} b_\varkappa^+] (\xi_\varkappa + \xi_{-\varkappa}^+), \end{aligned} \quad (10)$$

where

$$\begin{gathered} W(\varkappa) = K(f1f1\varkappa) - K(f0f0\varkappa) = A_\varkappa J_0(\varkappa), \\ K_{01} = K_{10}^* = K(f0f1\varkappa) = A_\varkappa J_1(\varkappa), \\ J_0(\varkappa) = \int e^{i\varkappa\cdot\mathbf{r}} (|\theta_1(\mathbf{r})|^2 - |\theta_0(\mathbf{r})|^2)\, d\mathbf{r}, \\ J_1(\varkappa) = \int e^{i\varkappa\cdot\mathbf{r}} \theta_0^*(\mathbf{r})\, \theta_1(\mathbf{r})\, d\mathbf{r}. \end{gathered} \quad (11)$$

Thus, by means of (5), (8), and (10) the complete Hamiltonian of the system can be put into the form

$$H = H_0 + H_1, \quad (12)$$

$$H_0 = \sum_k v_k b_k^+ b_k + \frac{1}{2} \sum_k u_k b_k b_{-k} + \frac{1}{2} \sum_k u_k^* b_k^+ b_{-k}^+ + \sum_\varkappa \hbar\omega_\varkappa \xi_\varkappa^+ \xi_\varkappa,$$

$$\begin{aligned} H_1 = &\sum_{k,\varkappa} W(\varkappa)\, b_k^+ b_{k-\varkappa} (\xi_\varkappa + \xi_{-\varkappa}^+) + \sqrt{N} \sum_\varkappa K_{10}(\varkappa)\, b_\varkappa^+ (\xi_\varkappa + \xi_{-\varkappa}^+) \\ &+ \sqrt{N} \sum_\varkappa K_{01}(\varkappa)\, b_{-\varkappa} (\xi_\varkappa + \xi_{-\varkappa}^+). \end{aligned}$$

We shall consider weak exciton-phonon coupling so that H_1 is regarded as a perturbation. Before employing perturbation theory it is convenient to renormalize the exciton vacuum in H_0, diagonalizing H_0 in the Bose amplitudes b_k by means of a linear transformation.[13] Following this transformation the Hamiltonian of the system becomes

$$\begin{aligned} H = H_0 + H_1, \quad H_0 &= \sum_k v_k' \beta_k^+ \beta_k + \sum_\varkappa \hbar\omega_\varkappa \xi_\varkappa^+ \xi_\varkappa, \\ H_1 &= \sum_{k\varkappa} [W'(k,\varkappa)\, \beta_k^+ \beta_{k-\varkappa} (\xi_\varkappa + \xi_{-\varkappa}^+) \\ &\quad + W''(k,\varkappa)\, \beta_k^+ \beta_{-k+\varkappa}^+ (\xi_\varkappa + \xi_{-\varkappa}^+) \\ &\quad + K_{01}'(k,\varkappa)\, \beta_\varkappa^+ (\xi_\varkappa + \xi_{-\varkappa}^+) + \text{compl. conj}], \end{aligned} \quad (13)$$

where

$$v'_k = \sqrt{v_k^2 - u_k^2}, \tag{14}$$

$$W'(k, \varkappa) = W(\varkappa)(1 + A_k A_{k-\varkappa})/[(1 - A_k^2)(1 - A_{k-\varkappa}^2)]^{1/2},$$

$$W''(k, \varkappa) = W(\varkappa) A_{k-\varkappa}/[(1 - A_k^2)(1 - A_{k-\varkappa}^2]^{1/2},$$

$$K'_{10}(k, \varkappa) = (K_{10}(\varkappa) + K_{01}(\varkappa) A_k)/[(1 - A_\varkappa^2)(1 - A_{k-\varkappa}^2)]^{1/2},$$

$$A_k = (\sqrt{v_k^2 - u_k^2} - v_k)/u_k.$$

In the first-order perturbation nonvanishing corrections to eigenvalues of the energy are given only by the first term in H_1 while the remaining terms give only second-order corrections due to virtual processes.

We now proceed to use perturbation theory in the form of a canonical transformation to obtain corrections of exciton energy resulting from the exciton's interaction with the phonon field. The canonical transformation of the Hamiltonian (13) is given by

$$\mathcal{H} = e^{-S} H e^{S} = H_0 + H_1$$

$$+ [H_0 + H_1, S] + {}^1/_2 [[H_0 S] S] + \cdots.$$

The generating function S is taken in the form

$$S = \sum_{k,\varkappa} \eta(k, \varkappa) \beta_k^+ \beta_{k-\varkappa} \xi_\varkappa - \sum_{k,\varkappa} \eta^*(k - \varkappa, -\varkappa) \beta_k^+ \beta_{k-\varkappa} \xi_{-\varkappa}^+,$$

and the coefficients $\eta(k, \kappa)$ are obtained from the condition $H_1 + [H_0 S] = 0$. The first-order perturbation gives

$$\mathcal{H} = \sum_k v''_k \beta_k^+ \beta_k + \sum_\varkappa \hbar\omega'_\varkappa \xi_\varkappa^+ \xi_\varkappa, \tag{15}$$

where

$$v''_k = v'_k - \sum_\varkappa |W'(k, \varkappa)|^2 / (v'_{k+\varkappa} - v'_k + \hbar\omega_\varkappa),$$

$$\omega'_\varkappa = \omega_\varkappa + \frac{1}{\hbar} \sum_k \frac{2\,|W'(k, \varkappa)|^2 (v_k - v_{k-\varkappa})}{(v'_k - v'_{k-\varkappa})^2 - \hbar^2\omega_\varkappa^2} \overline{b_k^+ b_k}. \tag{16}$$

Here ω'_K is the renormalized frequency of "free" phonons. If the expressions given above contain divergent denominators the canonical transformation method must be used in the form which Bogoliubov proposed in his papers on the theory of superconductivity.

For the purpose of simplifying the succeeding calculations we shall make the reasonable assumption that the exciton transfer integral is considerably smaller than the width of the energy gap in the crystal:

$$|Q| \ll E_1 - E_0. \tag{17}$$

Then from (14) and (6)

$$W'(k, \varkappa)$$

$$\approx W(\varkappa)\left\{1 + \frac{9\,|Q|^2}{2(E_1 - E_0)^2}\left[1 - \left(\frac{a^2}{6} + \frac{\hbar^2}{2(E_1 - E_0)(m_{\mathrm{el}} + m_{\mathrm{h}})}\right)\right.\right.$$

$$\left.\left. \times (k^2 + (k - \varkappa)^2)\right]\right\} \approx W(\varkappa).$$

By a series expansion of the denominators in the coefficients v''_K of Eq. (15) in terms of exciton momenta, by integrating instead of summing over phonon momenta, and by using (6), (7), (9), and (11), we obtain from (16) the following expressions for the variation of the energy gap width and of the effective exciton mass:

$$\Delta E' = \Delta E - \frac{e^2\hbar}{4\pi^2} \int \frac{|J_0(\varkappa)|^2 \omega_\varkappa c_\varkappa}{\varkappa^2 (\hbar\omega_\varkappa + \hbar^2\varkappa^2/2M)} d\varkappa,$$

$$M^* = M\left[1 + \frac{e^2\hbar^3}{2\pi^2 M k^2} \int \frac{|J_0(\varkappa)|^2 (\mathrm{k}\varkappa)^2 \omega_\varkappa c_\varkappa}{\varkappa^2 (\hbar\omega_\varkappa + \hbar^2\varkappa^2/2M)^3} d\varkappa\right]. \tag{18}$$

Thus the exciton-phonon interaction lowers the energy level of the exciton and increases its effective mass. This result agrees qualitatively with the results of Dykman[6] and Moskalenko[7] for weak exciton-phonon coupling. The shift of the exciton energy level that results from interelectron and electron-phonon interactions may be essential for an examination of certain effects. For example, the character of the field dependence of energy shifts in electric and magnetic fields is changed; specifically linear terms with respect to the field appear.[14] For an electron interacting with the phonon field we must set $\theta_0(r) = 0$ in (11) and pass to the wavelength limit. This gives the energy reduction $\alpha\hbar\omega$ that is known from polaron theory[15] with the dimensionless coupling constant $\alpha = e^2 c (m/2\omega\hbar^3)^{1/2}$.

For numerical estimates it is necessary to adopt a definite form of the second-quantization basis functions $\theta_\lambda(r)$, compute $J_0(\kappa)$ from (11) and calculate the integrals in (18). When expanding the wave function of the system in second-quantization basis functions we use an incomplete set of functions, stopping after the first two terms ($\lambda = 0$ and $\lambda = 1$); the selected functions $\theta_0(r)$ and $\theta_1(r)$ must therefore represent as adequately as possible the real electron states in the crystal. We have performed a calculation for the Cu_2O crystal, where the coupling between excitons and the lattice is apparently weak. We used the Zhilich function[16] $\theta_0(r) = A \exp\{-1.03\, r/a_B\}$ and the Slater function[17] $\theta_1(r) = B \exp\{-0.743\, r/a_B\}$ with values of ω_K and c_K for the wavelength limit. The exciton energy level is reduced by 0.027 ev while its effective mass is increased by 0.4%. No quantitative accuracy can be claimed because of the crude model used and the tentative character of the wave functions. However it should be interesting to develop our many-electron method further by using a specific model and also by considering the behavior of the system in an external field.

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