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Abstract

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PHYSICS

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THE ENERGY OF AN EXCITON IN IONIC CRYSTALS

(Presented by Academician N. N. Bogolyubov, 29 XI 1957)

The energy of an exciton in ionic crystals, taking into account the inertial polarization of the crystal lattice, has been calculated by a number of authors ([1–5]). Haken ([4]) and A. Kasyan made the first attempts to obtain a general expression for the energy of the ground state of an exciton for arbitrary couplings. These works do not completely solve the indicated problem.

In the present note an expression is derived for the energy and effective mass of an exciton, free of restrictions on the magnitude of the coupling constant and on the temperature. This problem for the polaron was solved in ([6]). The Hamiltonian of the system has the form

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} - \frac{e^2}{\varkappa r} +$$

$$+ \sum_f E(f) a_f^+ a_f + \sum_f \left[A_f e^{ifR} \left(e^{i\sigma_2 fr} - e^{-i\sigma_1 fr} \right) + \text{c.c.} \right], \tag{1}$$

where $M = m_1 + m_2$ is the sum of the effective masses of the electron and hole; μ is their reduced mass; $\sigma_i = m_i/M$; R, P are the coordinate and momentum of the center of mass of the exciton; r, p are the coordinate and momentum describing the internal motion of the exciton; a_f^+, a_f are Bose operators for phonons; $E = \hbar\omega$; ω is the limiting frequency of the optical vibrations; $A_f = -\frac{e}{f}\sqrt{\frac{2\pi\hbar\omega c}{V}}$;

$$c = \frac{1}{\varkappa} - \frac{1}{\varepsilon};$$

$\varkappa$ is the square of the refractive index; ε is the dielectric constant. To calculate the statistical sum

$$Z = \operatorname{Sp} e^{-H\beta}, \qquad \beta = \frac{1}{kT}. \tag{2}$$

we shall use its representation by means of the Feynman continual integral

$$Z = \int \cdots \int \delta(R_\beta - R_0)\delta(r_\beta - r_0) \prod_f \delta(q_{f\beta} - q_{f0})\, dR_\beta dR_0 dr_\beta dr_0 \prod_f dq_{f\beta} dq_{f0} \times$$

$$\times \int e^{S'}\, Dr\, DR \prod_f Dq_f. \tag{3}$$

The functional S' can be obtained by making the substitution t by $-i\hbar\beta$ in the expression $iS_H/\hbar$, where S_H is the classical action corresponding to the Hamiltonian (1). From (3) one can eliminate the field oscillators ([7]); as a result we obtain

$$Z = \iint \delta(R_\beta - R_0)\delta(r_\beta - r_0)\, dR_\beta dR_0 dr_\beta dr_0 \int e^{S}\, Dr\, DR\, \chi, \tag{4}$$

where

$$S = -\frac{M}{2\hbar^2}\int_0^\beta \left(\frac{dR}{d\tau}\right)^2 d\tau - \frac{\mu}{2\hbar^2}\int_0^\beta \left(\frac{dr}{d\tau}\right)^2 d\tau + \frac{e^2}{\chi}\int_0^\beta \frac{1}{|r_\tau|}\, d\tau +$$
$$+ \frac{\hbar\omega c e^2}{2}\left[\int_0^\beta d\tau \int_0^\tau d\sigma + \bar{n}\int_0^\beta\int_0^\beta d\tau\, d\sigma\right] e^{-\hbar\omega(\tau-\sigma)} \left[\frac{1}{|R_\tau - R_\sigma + \sigma_2(r_\tau - r_\sigma)|} + \right.$$
$$\left. + \frac{1}{|R_\tau - R_\sigma + \sigma_1(r_\tau - r_\sigma)|} - \frac{1}{|R_\tau - R_\sigma + \sigma_2 r_\tau + \sigma_1 r_\sigma|} - \frac{1}{|R_\tau - R_\sigma - \sigma_1 r_\tau - \sigma_2 r_\sigma|}\right], \tag{5}$$

$$\bar{n} = (e^{\hbar\omega\beta} - 1)^{-1};$$

χ is the statistical sum for the free lattice.

To calculate (4), the variational method is used. S is approximated by the simpler expression S_1, represented in the form of the sum

$$S_1 = S_2 + S_3 \tag{6}$$

and containing free parameters.

Using the representation of an auxiliary particle for S_2, we obtain

$$S_2 = -\frac{M}{2\hbar^2}\int_0^\beta \left(\frac{dR}{d\tau}\right)^2 d\tau - \frac{C_2}{2}\int_0^\beta R_\tau^2\, d\tau + \\ + \frac{\hbar\omega_2 C_2}{2}\left[\int_0^\beta d\tau \int_0^\tau d\sigma + \bar{n}_2 \int_0^\beta \int_0^\beta d\tau\, d\sigma\right] R_\tau R_\sigma e^{-\hbar\omega_2(\tau-\sigma)} - 3\ln\left(2\,\mathrm{sh}\,\hbar\omega_2\frac{\beta}{2}\right), \tag{7}$$

$$\bar{n}_2 = (e^{\hbar\omega_2\beta} - 1)^{-1}.$$

This expression possesses translational invariance.

To approximate the internal motion of the exciton, we choose S_3 in the form

$$S_3 = -\frac{\mu}{2\hbar^2}\int_0^\beta \left(\frac{dr_\tau}{d\tau}\right)^2 d\tau - \frac{C_3}{2}\int_0^\beta r_\tau^2\, d\tau. \tag{8}$$

C_2, ω_2, and C_3 are free parameters, which will be determined from the condition that the right-hand side of the relation

$$Z \geq \exp\left\{\frac{1}{Z_1}\int dr_0\, dR_0 \int (S - S_1) e^{S_1} Dr\, DR\right\} Z_1, \tag{9}$$

be maximal, where

$$Z_1 = \int dr_0\, dR_0 \int e^{S_1} Dr\, DR. \tag{10}$$

The integrals in (9) and (10) are taken over trajectories beginning and ending at one and the same point $r(\beta) = r(0) = r_0$, $R(\beta) = R(0) = R_0$. Owing to the noted invariance property of S_2, for the trajectory $R(\tau)$ one may set $R_0 = 0$. In what follows the notation

$$w = \frac{\omega_2}{\omega}, \qquad v = \frac{\omega_2}{\omega}\left(1 + \frac{C_2}{M\omega_2^2}\right)^{1/2}, \qquad \alpha = \frac{1}{\omega}\left(\frac{C_3}{\mu}\right)^{1/2},$$

$$\lambda = \frac{\hbar\omega\beta}{2}, \qquad g = \frac{ce^2}{\hbar}\left(\frac{M}{2\hbar\omega}\right)^{1/2}. \tag{11}$$

will be used. If we introduce the notation

$$\langle\cdots\rangle = \frac{1}{Z_1}\int dr_0\, dR_0 \int e^{S_1}(\cdots)\, Dr\, DR,$$

then we obtain the results of the calculations:

$$\langle \exp i(\mathbf{f}, \sigma_2 \mathbf{r}_\tau + \sigma_1 \mathbf{r}_\sigma)\rangle == \exp\left\{-\frac{\hbar^2 f^2}{4\mu a \hbar\omega}\left[(\sigma_1^2+\sigma_2^2)\,\mathrm{cth}\, a\lambda + 2\sigma_1\sigma_2 \frac{\mathrm{ch}\, a(\hbar\omega|\sigma-\tau|-\lambda)}{\mathrm{sh}\, a\lambda}\right]\right\}; \tag{12}$$

$$\langle \exp i(\mathbf{f}, \mathbf{R}_\tau - \mathbf{R}_\sigma)\rangle = \exp\left\{-\frac{\hbar^2 f^2}{2M}\left[\frac{\omega^2}{v^2}|\sigma-\tau| - \frac{\hbar\omega}{2}\frac{\omega^2}{v^2}\frac{(\sigma-\tau)^2}{\lambda} + \frac{1}{\hbar\omega}\frac{1}{v}\left(1-\frac{\omega^2}{v^2}\right)\left(\mathrm{cth}\,\lambda v - \frac{\mathrm{ch}\, v(\hbar\omega|\sigma-\tau| - \dots}{\mathrm{sh}\,\lambda v}\right.\right.\right. \tag{13}$$

which form the basis for calculating the right-hand side of (9).

In the calculations a parallel shift was used in the functional integral $x(\tau) = \bar{x}(\tau) + y(\tau)$, where $\bar{x}(\tau)$ is the extremal trajectory satisfying the boundary conditions.

Denote by A the last term of expression (5); then one may write

$$\langle A\rangle = \frac{2\lambda^2 g}{\sqrt{\pi}\,\mathrm{sh}\,\lambda}\int_0^1 ds\ \mathrm{ch}(\lambda s)\times$$

$$\times\left\{\left[\frac{\omega^2}{2v^2}\lambda(1-s^2) + \frac{1}{v}\left(1-\frac{\omega^2}{v^2}\right)\left(\mathrm{cth}\,\lambda v - \frac{\mathrm{ch}\,\lambda v s}{\mathrm{sh}\,\lambda v}\right) + \frac{k}{a}\left(\mathrm{cth}\, a\lambda - \frac{\mathrm{ch}\, a\lambda s}{\mathrm{sh}\, a\lambda}\right)\right]^{-1/2}\right.$$

$$+\left[\frac{\omega^2}{2v^2}\lambda(1-s^2) + \frac{1}{v}\left(1-\frac{\omega^2}{v^2}\right)\left(\mathrm{cth}\,\lambda v - \frac{\mathrm{ch}\,\lambda v s}{\mathrm{sh}\,\lambda v}\right) + \frac{1}{ka}\left(\mathrm{cth}\, a\lambda - \frac{\mathrm{ch}\, a\lambda s}{\mathrm{sh}\, a\lambda}\right)\right]^{-1/2}$$

$$\left.-2\left[\frac{\omega^2}{2v^2}\lambda(1-s^2) + \frac{1}{v}\left(1-\frac{\omega^2}{v^2}\right)\left(\mathrm{cth}\,\lambda v - \frac{\mathrm{ch}\,\lambda v s}{\mathrm{sh}\,\lambda v}\right) + \frac{1}{a}\left(\frac{1+k^2}{2k}\,\mathrm{cth}\, a\lambda + \frac{\mathrm{ch}\, a\lambda s}{\mathrm{sh}\, a\lambda}\right)\right]^{-1/2}\right\}, \tag{14}$$

where $k = m_2/m_1$.

The final expression for $\ln Z$, valid for arbitrary couplings and temperatures, has the form

$$\ln Z \geq \ln Z^{(0)} + 3\ln\frac{v}{\omega} - 3\ln(2\,\mathrm{sh}\,\lambda v) - 3\ln(2\,\mathrm{sh}\,\alpha\lambda)$$

$$-\frac{3}{2}\left(1-\frac{\omega^2}{v^2}\right) + \frac{3}{2}\left(1-\frac{\omega^2}{v^2}\right)\lambda v\ \mathrm{cth}\,\lambda v + \frac{3}{2}\lambda\alpha\ \mathrm{cth}\,\alpha\lambda +$$

$$+3\ln(2\,\mathrm{sh}\,\lambda\omega)+4\lambda\frac{e^2}{\chi\hbar}\sqrt{\frac{\mu a}{\pi\hbar\omega}\,\mathrm{th}\,\alpha\lambda}+\langle A\rangle, \tag{15}$$

where $Z^{(0)}=2V\chi(M/2\pi\beta\hbar^2)^{1/2}$.

We note that for $k=0$ formula (15) reduces to the analogous expression of polaron theory (see [6], (56)). It is important to note that for $k=1$, $\langle A\rangle\neq 0$. For the region of extremely low temperatures, after simplification we obtain the expressions:

$$E_0=E_0^{(0)}+\left\{\frac{3a}{2}-\frac{4e^2}{\chi\hbar}\sqrt{\frac{\mu a}{\pi\hbar\omega}}+\frac{3v}{2}\left(1-\frac{\omega}{v}\right)^2-\frac{\langle A_0\rangle}{\lambda}\right\}\frac{\hbar\omega}{2}, \tag{16}$$

where $E_0^{(0)}$ is the energy of the system in the absence of interaction,

$$\frac{M_{\mathrm{eff}}}{M}=\left(\frac{v}{\omega}\right)^2\exp\left\{-1+\frac{\omega^2}{v^2}+\frac{2}{3}\frac{\langle A_1\rangle}{\lambda}\right\}. \tag{17}$$

Formula (17) was proposed for the polaron in [6]. $\langle A_0\rangle$ and $\langle A_1\rangle/\lambda$ are, respectively, the zeroth and first terms in the expansion of $\langle A\rangle$ in powers of λ^{-1}, and for this temperature range $\langle A\rangle$ has the form

$$\langle A\rangle=\frac{2\lambda g}{\sqrt{\pi}}\int_0^\infty dt\,e^{-t}\left\{\left[\frac{\omega^2}{v^2}\left(1-\frac{t}{2\lambda}\right)t+\right.\right.$$

$$\left.+\frac{1}{v}\left(1-\frac{\omega^2}{v^2}\right)(1-e^{-vt})+\frac{k}{a}(1-e^{-\alpha t})\right]^{-1/2}+$$

$$+\left[\frac{w^2}{v^2}\left(1-\frac{t}{2\lambda}\right)t+\frac{1}{v}\left(1-\frac{w^2}{v^2}\right)(1-e^{-vt})+\frac{1}{k\alpha}(1-e^{-\alpha t})\right]^{-1/2}$$

$$\left.-2\left[\frac{w^2}{v^2}\left(1-\frac{t}{2\lambda}\right)t+\frac{1}{v}\left(1-\frac{w^2}{v^2}\right)(1-e^{-vt})+\frac{1}{\alpha}\left(\frac{1+k^2}{2k}+e^{-\alpha t}\right)\right]^{-1/2}\right\}.$$

In the case of strong coupling of the exciton with the lattice, when a substantial deviation of the parameter k from unity is assumed, one may omit under the integral sign the terms $e^{-\alpha t}$ and e^{-vt} and take $v/w\gg 1$. We denote

$$v=\alpha y,\qquad \alpha=\frac{2}{\pi}\frac{\mu e^4}{\hbar^2\chi^2}\frac{1}{\hbar\omega}\,x. \tag{18}$$

Then for E_0 we obtain the expression

$$E_0 = E_0^{(0)} + I(x, y) + \frac{3}{4}\hbar\omega\left(-1 + \frac{\pi}{4}\frac{(cx)^2}{xy}\frac{(1+k)^2}{k}\frac{1}{g^2}\right), \tag{19}$$

where $I(x, y)$ is the expression known from paper (1). The second term of (19) coincides with the result of (1), where the extremal values of x and y were also determined. The parameter w turned out to be equal to unity. The last term of formula (19) represents a correction to the results of (1).

Under the same simplifying assumptions, an expression was obtained for the effective mass of the exciton

$$M_{\text{eff}} = v^2 M = \frac{4}{\pi^2}\left(\frac{\mu e^4}{\hbar^2\chi^2}\frac{1}{\hbar\omega}\right)^2 x^2 y^2 M. \tag{20}$$

If one uses the definition of the extremal value of the parameter x, it is not difficult to see that (20) coincides with the result of paper ([3]) for the effective mass of the exciton (see also ([5])). In the case of values of k close to unity, the influence on the exciton of inertial polarization may be considered weak, even when the constant g is not small. In this case $v = w(1+\varepsilon)$, where $\varepsilon \ll 1$. The parameter α is close to the corresponding value for a hydrogen-like atom: $\alpha_1 = \frac{16}{9\pi}\frac{\mu e^4}{\hbar^2\chi^2}\frac{1}{\hbar\omega}$. In the calculations it is assumed that $\alpha_1 \gg 1$.

Approximate calculations lead to the following results:

$$E_0 = E_0^{(0)} + E_1 - 1.03\, c\chi\hbar\omega, \qquad M_{\text{eff}} = \left(1 + 0.07\, c\chi\frac{\hbar\omega}{|E_1|}\right)M, \tag{21}$$

where

$$E_1 = -\frac{4}{3\pi}\frac{\mu e^4}{\hbar^2\chi^2}.$$

We note that the corrections to the energy and mass in (21) are smaller than the analogous corrections obtained by perturbation theory ([3]), which is apparently connected with the inexact treatment of the denominators in the formulas of perturbation theory ([3]) and with the special features of the variational method.

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