A generalized functional approach to the polaron problem

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It is well known that two qualitatively different pictures arise in the description of the motion of an electron in an ionic crystal. In the first case, when the electron interacts weakly with the ionic lattice of the crystal, its motion is the same as the motion of a free band electron whose energy is shifted downward with respect to the bottom of the conduction band, and the effective mass is replaced by the renormalized mass[1] (weak-coupling polaron). In the other limiting case, when the electron interacts strongly with the ionic crystal, an entire series of different self-consistent states of the electron and lattice, each of which has its own effective mass and radius[2-4] (strong-coupling polaron), arises.

Although the motion of an electron in an ionic crystal is described in both limiting cases with the help of the Pekar-Frohlich Hamiltonian, each case requires its own special methods of analysis. Thus, for example, in the strong-coupling theory a special form of adiabatic perturbation theory has been developed[2,4] in which the trans-lational degeneracy is removed before the perturbation expansion is made. It has been possible to relate both descriptions within the framework of Feynman's varia-tional approach,[5] in which a smooth upper bound was obtained for the energy of the ground state of the polaron for all values of the electron-phonon coupling constant a (see Fig. 1).

We call attention in this connection to Ref. 6, where the thermodynamic properties are calculated with the help of a special method for performing the calculations and for finding averages of T-products. The approach developed there is more convenient for performing specific calculations than is the use of path integrals.[5] It seems to us that it has definite advantages in the construction of general proofs concerning the choice of the approximating Hamiltonians (this is illustrated in Ref. 6 for the example of the linear Bogolyubov model), in the investigation of the characteristics of the behavior of a polaron in external fields, etc.

1. A generalization of the functional variational approach to the calculation of the energy of the ground state of a polaron is proposed in Ref. 7. The generalization consists in the fact that a model in which the electron interacts with another particle by means of an arbitrary, not necessarily quadratic (as in Feynman's approach[5]) potential v(**r**, **r'**), is used as the trial model in the variationai calculation. The trial action in this case is given by the formula

$$S_0(\mathrm{r},\mathrm{r}') = \frac{1}{2}\int_0^\beta \dot{\mathrm{r}}^2(\tau)d\tau + \frac{m'}{2}\int_0^\beta \dot{\mathrm{r}}'^2(\tau)d\tau + V_0(\mathrm{r},\mathrm{r}'),$$

$$V_0(\mathrm{r},\mathrm{r}') = \int_0^\beta \upsilon[\mathrm{r}(\tau)-\mathrm{r}'(\tau)]d\tau. \qquad (1)$$

The action (1) takes into account the translational in-variance of the initial problem with the Pekar-Frohlich Hamiltonian, in which $\hbar = \omega = m = l$; ω is the frequency of longitudinal optical phonons and m is the electron mass.

As a result, the following inequality for the energy of the ground state of the polaron is obtained[7]:

$$E \le \Phi[\mu, u] = \frac{1}{2\mu}\int |\nabla u|^2 dr - \frac{\alpha}{\sqrt{2}\mu}\iint dr dr' \frac{|u(r)|^2 |u(r')|^2}{|r - r'|}\left(1 - \exp[-C|r - r'|]\right), \quad (2)$$

where $\mu = \frac{m'}{1+m'}$ the reduced mass of the two-particles trial model, and $C = \mu\left(\frac{2}{1-\mu}\right)^{1/2}$; μ is treated, together with the function u(**r**), as the variational parameter. We see that Φ[μ, u] in (2) can be regarded as a modified expression of the Bogolyubov- Pekar- Tyablikov functional,[2-4] into which it goes over when $\mu = 1$ (strong coupling). The main point here is that as $\mu \to 0$, Φ[μ, u] leads to the groundstate energy $E_0 = -\alpha$ of the weak-coupling limit (see below).

In order to obtain the best upper bound for E, it is necessary to minimize the functional Φ[μ, u] with respect to both the variable $\mu \in [0, 1]$ and the function u(**r**) under the condition

$$\int |u(r)|^2 dr = 1 . \quad (3)$$

The condition $\delta[\Phi - e\int |u(r)|^2 d\mathbf{r}] = 0$ leads to the equation

$$\left\{-\frac{1}{2\mu}\nabla^2 - \frac{\alpha\sqrt{2}}{\mu}\int \frac{|u(r')|^2}{|r - r'|}\left(1 - e^{-C|r-r'|}\right)\right\} u(r) = \varepsilon\, u(r), \quad (4)$$

and the conditions $\frac{\varepsilon\Phi}{\delta\mu} = 0$ and $\frac{\partial}{\partial t}\Phi\left[\mu, t^{3/2}u(tr)\right]_{t=1} = 0$

give the following relation for μ:

$$\mu = \frac{4T}{T - \varepsilon},$$

where $T = \frac{1}{2\mu}\int |\nabla u|^2 dr$. The total energy E is related to T and ε by the relation $E = 1/2\,(\varepsilon + T)$.

The solution of this problem for finding the minimum of Φ[μ, u] is given by sets of values of μ, e, and u(**r**) which satisfy Eqs. (3)-(5). It is easy to see that for all α the following exact solutions exist:

a) $\mu_0 = 0$, $\varepsilon_0 = -2\alpha$, $u_0(\mathbf{r}) = $ const; for this solution we have $E_0(\alpha) = -\alpha$;

b) $\mu_n = 1$, $\varepsilon = \varepsilon_n$. u= $u_n(\mathbf{r})$, where ε_n, $u_n(\mathbf{r})$ are solutions of Pekar's equation[3]:

$$\left\{-\frac{1}{2}\nabla^2 - \alpha\sqrt{2}\int dr' \frac{|u_n(r')|^2}{|r - r'|}\right\} u_n(r) = \varepsilon_n u_n(r). \quad (6)$$

Here, as shown in Refs. 2 and 4, Eq. (6) is asymptotically exact in the limit $\alpha \to \infty$

All solutions of (6) satisfy Eq. (5) as a result of the virial theorem: $E = -T$. For the energies of the four lowest states with $\mu = \mu_n = 1$, we have[8, 9]

$$E_1(\alpha) = -0.1085\,\alpha^2,\ E_2(\alpha) = -0.0205\,\alpha^2,\ E_3(\alpha) = -0.0083\,\alpha^2,\ E_4(\alpha) = -0.0045\,\alpha^2. \quad (7)$$

As is well known, $E_0(\alpha)$ and $E_1(\alpha)$ are asymptotically exact expressions for the energy of the ground state of a polaron in the limiting cases $\alpha \to 0$ and $\alpha \to \infty$, respectively. If other solutions of Eqs. (3)-(5) with $\mu \in [0, 1]$ and with energy less than E_0 and E_1 in some range of values of б do not exist, then the energy of the ground state of the polaron, obtained from the variational estimate, will be simply -a for $\alpha < \alpha_1$ and $-0.1085\,\alpha^2$ for $\alpha > \alpha_1$. The value α_1 can be interpreted as the critical value пf б, corresponding to a first-order phase transition from the free ($\alpha < \alpha_1$) into the self-localized state ($\alpha > \alpha_1$); we have $\alpha_1 = 9.21$.

In Ref. 10 these results were obtained when Eq.(4) was solved by the Ritz variational method. Extremely laborious numerical calculations had to be performed. We see here that to obtain there results numerical calculations are not needed. (The other two solutions obtained in Ref. 10 in addition to E_0 and E_1 are not solutions of Eqs. (3)-(5), but are consequences of the use of the Ritz method.)

The existence of a set α_n (n = 2, 3, ...) of "critical" values of a, determined by the equations

$$-\alpha_n = E_n(\alpha_n), \tag{8}$$

also follows from (7). For $\alpha > \alpha_2 = 48.78$ the first excited state is not a free state, but a self-consistent localized state with energy $E_2(\alpha)$; for $\alpha > \alpha_3 = 120.48$, the second excited state with energy $E_3(\alpha)$ becomes the self-consistent localized state, and so on. The complete pattern is illustrated schematically in Fig. 1.

We emphasize that we are discussing here only the picture following from (2), and we ignore the question of how good an approximation to the energy of the polaron it gives. As is well known, Feynman's theorem gives a better numerical estimate of the energy of the ground state of a polaron, with the exception only of very high values of a, and there is no phase transition. Here, we do not even know whether or not there exist other solutions of (3)-(5) with $\mu \in (0, 1)$ and with an energy lower than E_0 and E_1 in some interval of α. These solutions, if they exist, do not appear in the solution of the problem by the Ritz method. The final solution can be obtained only by exact numerical solution of (3)-(5).

2. It follows from the picture described in the preceding section that at the critical transition points such characteristics of the polaron as its mass and radius and the number of excited phonons must change in a jump-like manner. According to Refs. 5 and 11, the following exact path-integral representations exist for the effective mass m^*, the radius R of the ground state of the polaron, and the average number N of phonons in the cloud surrounding the electron:

$$E(\mathrm{v}) = -\lim_{\beta\to\infty}\frac{1}{\beta}\ln \int\limits_{\mathrm{r}(\beta)=\mathrm{r}(0)+\mathrm{v}\beta} e^{-S(\mathrm{r})}D(\mathrm{r}) = E + \frac{m^*\mathrm{v}^2}{2} + \ldots,$$

$$\frac{1}{R} = \frac{4\pi}{V}\sum_{\mathrm{k}}\frac{1}{k^2}\int_0^\infty e^{-r}\mathrm{J}(\mathrm{k},\tau)d\tau, \qquad N = \frac{2\sqrt{2}\pi\alpha}{V}\sum_{\mathrm{k}}\frac{\tau}{k^2}e^{-\tau}\mathrm{J}(\mathrm{k},\tau)d\tau, \tag{9}$$

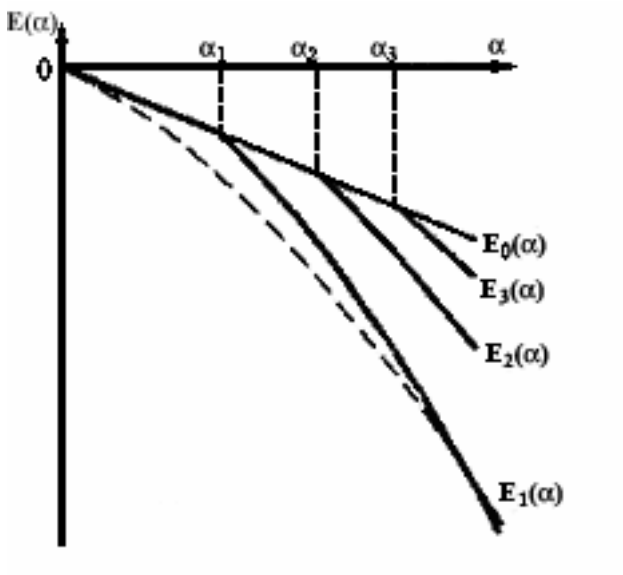

FIG. 1. Upper bound for the energy E of the ground state of a polaron as a function of the coupling constant α; curve 1 shows (schematically) Feynman result,[5] while the curves E_0= -y, E_1 = -0.1085α^2, E_2= -0.0205α^2, and E_3= -0.0083α^2 show the results obtained by solving the problem of the extremum of the functional $\Phi[\mu, u]$ (2): α_1=9.217, α_2=48.78, α_3=120.48.

where S[r] is the action of the polaron, which according to Ref. 5 has the form

$$S(\mathrm{r}) = \frac{1}{2}\int_0^\beta \dot{\mathrm{r}}^2(\tau)d\tau - \frac{\alpha}{2^{3/2}}\int_0^\beta\int_0^\beta d\tau d\sigma \frac{e^{-|\tau-\sigma|}}{|\mathrm{r}(\tau)-\mathrm{r}(\sigma)|},$$

$$\mathrm{J}(\mathrm{k},\tau) = \lim_{\beta\to\infty} \frac{\int_{r(0)=r(\beta)} Dr e^{-S(r)+i\mathrm{k}[r(\tau_1)-r(\tau_2)]}}{\int_{r(0)=r(\beta)} Dr e^{-S(r)}}; \qquad \tau = |\tau_1 - \tau_2|.$$

Within the framework of the approximation (1) of Ref. 7 the function $\mathbf{J}(\mathbf{k},\tau)$ must be replaced by the function $\mathbf{J_0}(\mathbf{k},\tau)$ give by

$$\mathrm{J}_0(\mathrm{k},\tau) = e^{-1/2(1-\mu)k^2\tau}\left|\int |u(\mathrm{r})|^2 e^{i\mu kr} d\mathrm{r}\right|^2.$$

Then the approximate expressions for m^*, R, and N, calculated with the help of (9), assume the form

$$m^* = 1 + \frac{4\sqrt{2}\pi\alpha}{3V}\sum_k \frac{1}{\left[1+1/2(1-\mu)k^2\right]^3}\left|\int |u(\mathrm{r})|^2 e^{i\mu kr} d\mathrm{r}\right|^2,$$

$$\frac{1}{R} = \frac{4\pi}{V}\sum_k \frac{1}{k^2\left[1+1/2(1-\mu)k^2\right]}\left|\int |u(\mathrm{r})|^2 e^{i\mu kr} d\mathrm{r}\right|^2,$$

$$N = \frac{2\sqrt{2}\pi\alpha}{V}\sum_k \frac{1}{k^2\left[1+1/2(1-\mu)k^2\right]^2}\left|\int |u(\mathrm{r})|^2 e^{i\mu kr} d\mathrm{r}\right|^2. \qquad (10)$$

For μ=0, from (10) we obtain: m_0^* =1 + α/6, R_0=1/$\sqrt{2}$ and N_0 = α/2. For μ = 1 and E = $E_1(\alpha)$, we obtain: m_1^* = 1 + 0.0227α^4, R_1 =3.2585/α, N_1 = 0.2170α^2. The corresponding jumps in these quantities at the critical point $б_1$ are. Δm^* =162.3; ΔR = 0.3535; ΔN = 13.82. The jumps at all of the critical points α_n can be calculated analogously with the help of (10).

3. As noted in Sec. 1, the picture obtained is based on the assertion that there are no solutions differing from those indicated in Sec. 1. For μ = 1 ($\alpha \to \infty$), $\Phi[\mu, u]$ coincided with the Bogolyubov-Pekar-Tyablikov functional whose extremals with respect to u(**r**) describe certain states of the electron in the polarization well. The question of the description on the basis of (6) of the electron spectrum in the well formed by the electron upon polarization of the crystal with intermediate coupling remains open. Whether or not it is possible to construct solution of (6) which are close to Pekar's solution with μ< l must be determined by solving the problem (3)-(5) on a computer No significant progress has yet been made along this path and the conclusion arrived at in Ref. 10 and analyzed above that a phase transition is possible from the picture of a weak-coupling polaron to a strong-coupling polaron at some value of α, must be viewed with great caution.

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