

## Ground-state energy of the optical polaron

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The ground-state energy of the optical polaron is calculated by the generalized path-integral formulation. The ground-state approximation is made to simplify the complicated expression, and the Ritz variational and direct integration methods are used to obtain the ground-state energy in the whole range of coupling strength. The results agree with previous work, and it is found that there is a transition for coupling constant  $\alpha_c \approx 9.2$ . The ground-state energy obtained by harmonic approximation, which is equivalent to taking Gaussian-like trial wave functions, is compared with those obtained by Pekar's trial wave function.

### I. INTRODUCTION

The problem of the motion of an electron in ionic crystals or polar semiconductors has been attracting the interest of many solid-state physicists for decades.<sup>1,2</sup> The perturbation<sup>3</sup> and the intermediate-coupling theories<sup>4</sup> are valid when the interaction between the electron and longitudinal-optical phonons is relatively weak and the electron behaves more or less like a free particle dressed with a few phonons. On the other hand, the strong-coupling theory is valid when the interaction is strong enough to make the electron captured in a self-induced potential which is built up by the field of the correlated virtual phonons.<sup>5,6</sup> There are also some theories which interpolate between the weak- and the strong-coupling theories,<sup>7-11</sup> and it is well known that among all the methods, path-integral theory gives the best ground-state energy in the overall range of the coupling strength.<sup>10-12</sup> The Feynman's path-integral formalism was restricted to the harmonic-interaction approximation and it is generalized<sup>11</sup> recently to unspecified general form of interaction potential. In this paper, we try to use the generalized formalism to calculate the optical polaron energy by analytic numerical variational and direct integration methods through a ground-state approximation. It is found, in our ground-state approximation, that the result is better than Feynman's result in an extremely strong-coupling case and agree with that of Pekar's; it also agrees with weak-coupling theories in small-coupling strength; but this result is still inferior to the Feynman's harmonic model in the intermediate range because of the ground-state approximation and one additional use of Jensen's inequality for the generalized formalism.<sup>11</sup> If within this approximation, the harmonic-interaction model, which uses the harmonic

wave function in the generalized formalism with ground-state approximation, will be inferior to the results obtained by analytic numerical variational method with Pekar's-type wave function and direct integration method. And the transition point ( $\alpha_c = 9.2$ ) of the unspecified potential case is lower than that obtained from harmonic-interaction approximation ( $\alpha_c = 9.4$ ).

### II. CALCULATION OF THE OPTICAL POLARON ENERGY

Because the derivation of generalized path-integral formalism is very lengthy and tedious, in the present paper we only briefly write down the results from Ref. 11. The physical motivation of Feynman's theory and Luttinger and Lu's variational method comes from an intuitive belief that in some sense the reaction of the lattice (phonon) system to the motions of an electron might be represented approximately by the reaction of a small number (hopefully, one) of fictitious particles coupled in some simple way to the electron and to one another. In the most simple case, the variational Hamiltonian is chosen as

$$H_v = \frac{\bar{p}^2}{2} + \frac{\bar{P}^2}{2M} + v(\bar{x} - \bar{R}), \quad (1)$$

where  $\bar{p}$ ,  $\bar{x}$  and  $\bar{P}$ ,  $\bar{R}$  are the momentum and coordinate of the electron and the fictitious particle, respectively;  $M$  is the mass of the fictitious particle; and where we use the units  $\hbar = m_e = \omega_0 = 1$ ,  $m_e$  is the effective mass of electron in the conduction band,  $\omega_0$  is the frequency of the optical branch phonon which is taken to be independent of wave vector  $\bar{k}$ .<sup>1</sup>

The optical polaron energy  $E_0$  is a lower bound of the variational energy  $E_v$ ,

$$E_0 \leq E_v = \langle u_0 | p^2 / 2\mu | u_0 \rangle - \frac{\alpha}{\sqrt{2\mu}} \sum_{n=0}^{\infty} \int_{\bar{r}} \int_{\bar{r}'} \frac{u_0^*(\bar{r}') u_0(\bar{r}) u_n^*(\bar{r}) u_n(\bar{r}')}{|\bar{r} - \bar{r}'|} \left( \frac{1 - \exp[-2C(1 + \Delta\epsilon_n)^{1/2} |\bar{r} - \bar{r}'|]}{1 + \Delta\epsilon_n} \right), \quad (2)$$

where  $\mu = M/(M+1)$ ,  $\Delta\epsilon_n = \epsilon_n - \epsilon_0$ , and  $C = M/[2(M+1)]^{1/2}$ , and  $u_n(r)$  and  $\epsilon_n$  are eigenstate and eigenvalue of Schrödinger equation with the undetermined variational potential  $v(\bar{r})$ ,

$$\left[ -\frac{1}{2\mu} \nabla^2 + v(\bar{r}) \right] u_n(\bar{r}) = \epsilon_n u_n(\bar{r}) . \quad (3)$$

Since each term in the summation of Eq. (2) is positive,<sup>11</sup> it is obvious that if we take only the ground-state term ( $n=0$ ) in the summation, then the right-hand side of Eq. (2) is still an upper bound of the polaron energy. Therefore, in this ground-state approximation, we can write

$$E_0 \leq E_v^0 \equiv \int_{\bar{r}} u_0^*(\bar{r}) \frac{\bar{p}^2}{2\mu} u_0(\bar{r}) - \frac{\alpha}{\sqrt{2\mu}} \int_{\bar{r}} \int_{\bar{r}'} \frac{|u_0(\bar{r})u_0(\bar{r}')|^2}{|\bar{r} - \bar{r}'|} [1 - \exp(-2C|\bar{r} - \bar{r}'|)] . \quad (4)$$

Now,  $\mu$  and  $u_0(\bar{r})$  are varied to make  $E_v^0(\mu, u_0)$  as small as possible.

The above energy expression is equal to that of Pekar's theory plus a term

$$\int \int d\bar{r} d\bar{r}' \frac{|u_0(\bar{r})u_0(\bar{r}')|^2}{|\bar{r} - \bar{r}'|} \exp(-2C|\bar{r} - \bar{r}'|) . \quad (5)$$

In the strong-coupling case, we can imagine that the mass of the fictitious particle  $M$  should be large, hence  $C \rightarrow \infty$  to make this additional term extremely small. Since  $\mu$  is less than or equal to one, therefore our result must be better than, at least equal to, that of Pekar's. In the weak-coupling case,  $\mu$  must be small, and the exponent of expression (5) can be expanded, and it is easily seen in this limit that the po-

laron energy is bounded above by  $-\alpha$ , which agrees with that of the second-order perturbation calculations.<sup>3,4</sup>

In order to calculate the polaron energy by Eq. (4) for the overall range of coupling strength, we first apply the Ritz's variational principle with Pekar's-type trial wave function which is shown to be extremely accurate for optical polaron.<sup>13</sup> This trial function is given by

$$u(\bar{r}) = N [1 + b\mu r + a(b\mu r)^2] e^{-b\mu r} , \quad (6)$$

where

$$N^2 = 2(b\mu)^3 / [\pi(14 + 42a + 45a^2)] . \quad (7)$$

$E_v^0(\mu, a, b)$  can be calculated analytically by using the following formulas:

$$\frac{\exp(ik|\bar{r} - \bar{r}'|)}{4\pi|\bar{r} - \bar{r}'|} = ik \sum_{l=0}^{\infty} j_l(kr_<) h_l^{(1)}(kr_>) \sum_{m=-l}^{+1} Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi') , \quad (8)$$

$$\int_x^{\infty} t^n e^{-bt} dt = e^{-bx} \sum_{k=0}^n \frac{n!}{k!} \frac{x^k}{b^{(n-k+1)}} , \quad (9)$$

$$\int_0^{\infty} t^n e^{-bt} dt = \frac{n!}{b^{n+1}} - e^{-bx} \sum_{k=0}^n \frac{n!}{k!} \frac{x^k}{b^{(n-k+1)}} . \quad (10)$$

The expression of  $E_v^0(\mu, a, b)$  is very tedious and complicated. It will be included in the Appendix. We use the direct-search method to find the extremes of the function  $E_v^0(\mu, a, b)$  by adopting the Rosenbrock's rotating-axis algorithm,<sup>14</sup> because it needs only the evaluation of the function. It is found that there are four local minima for given coupling strength  $\alpha$  they are:  $-0.108504\alpha^2$ ,  $-\alpha$ ,  $-0.75\alpha$ , and  $-0.10114\alpha^2$ , and the situations are found in the Pekar theory.<sup>5</sup> The convergence criterion of our computation is set equal to  $10^{-16}$ . Among these local minima, the smallest one is the absolute minimum which should be taken as the upper bound to the polaron energy. Hence for  $\alpha < \alpha_c = 9.21$ , the upper-bound polaron energy is equal to  $-\alpha$ , and for  $\alpha \geq \alpha_c$ , the upper-bound polaron energy is equal to  $-0.108504\alpha^2$ .

If harmonic interaction is assumed, then the wave function is Hermite function and the energy expres-

sion in the ground-state approximation can be calculated analytically, and is given by

$$E(\Omega, \omega) = \frac{3}{4}\Omega - \alpha \frac{\Omega}{\omega} \exp\left(\frac{\Omega}{\omega^2} - \frac{1}{\Omega}\right) \operatorname{erfc}\left(\frac{\Omega}{\omega^2} - \frac{1}{\Omega}\right) , \quad (11)$$

where  $\Omega = (k/\mu)^{1/2}$ ,  $\omega = (k/M)^{1/2}$ , and  $k$  is the Hook's constant of the harmonic potential  $v(\bar{x} - \bar{R}) = \frac{1}{2}k(\bar{x} - \bar{R})^2$ .

The expression (11) has two local minima, one is  $-\alpha$ , the other is  $-0.1061\alpha^2$ , the transition point will be  $\alpha_c' = 9.42$ .

It is seen that the improvement of harmonic potential by the optimum one is about 2% when  $\alpha > 9.21$ . There is no improvement when  $\alpha < 9.21$ , for in weak coupling the Hermite wave function is very similar to that of Pekar's-type wave function in the limit of small  $k$ .

Besides the Ritz's variational method, the direct-integration method is also used to calculate the polaron energy. Since  $E_v^0$  is a function of  $\mu$  and a functional of  $u_0(\vec{r})$ , and the only constraint is that  $u_0$  is normalized, the stationary conditions for the best choice of interaction potential are equivalent to

$$\delta \left( E_v^0 - \lambda \int u_0(\vec{r}')^2 d\vec{r}' \right) / \delta u_0(\vec{r}) = 0, \quad (12)$$

$$\delta E_v^0 / \delta \mu = 0. \quad (13)$$

Therefore we have to solve the self-consistent Hartree-type Schrödinger equation

$$\frac{\bar{p}^2}{2\mu} u_0(\vec{r}) - \frac{\alpha\sqrt{2}}{\mu} \int d\vec{r}' \frac{u_0(\vec{r}')^2}{|\vec{r} - \vec{r}'|} [1 - \exp(-2C|\vec{r} - \vec{r}'|)] u_0(\vec{r}) = \epsilon_0 u_0(\vec{r}) \quad (14)$$

for each  $\mu$ .

This is a prohibitively laborious numerical work, since for each given  $\mu$ , the self-consistent Hartree-type equation needs many iterations to give the polaron energy. Because the second term in the integral of Eq. (14), although the ingenious integration scheme of Miyake is used,<sup>13,15</sup> the iterations are still very time consuming. According to our experience in the Ritz's method, and it is also shown in Miyake's work, Pekar's trial function is an excellent approximation, hence we take  $\mu = 0$  when  $\alpha < \alpha_c$  and  $\mu = 1$  when  $\alpha > \alpha_c$ . By this assumption we can easily find: when  $\alpha < \alpha_c$ , Eq. (14) will be reduced to a particle moving in constant potential of magnitude  $-\alpha$ ; when  $\alpha > \alpha_c$ , Eq. (14) will just be reduced to Pekar's model and can be solved by direct integration to obtain the exact value of the polaron energy.<sup>13</sup> Therefore, by direct integration, the upper-bound polaron energy is equal to  $-0.108513\alpha^2$  for  $\alpha$  larger than  $\alpha_c$ .

### III. DISCUSSION AND CONCLUSION

The optical polaron energy is calculated by the generalized formalism under ground-state approximation, although the energy is higher than harmonic approximation of Feynman's model<sup>7</sup> and Luttinger and Lu's<sup>11</sup> work which include all the excited states; it is shown that the result of the optimum potential approach is better than that of harmonic approximation if they are both under ground-state approximation. We also find a phase-transition-like behavior at  $\alpha_c$  which also occurred, in the work of some other authors, e.g., Gross,<sup>6</sup> Larsen,<sup>16</sup> Luttinger and Lu,<sup>11</sup> Manka,<sup>17</sup> Lepine and Matz,<sup>18</sup> and Shoji and Tokuda.<sup>19</sup> Within our approximation, the mass of the fictitious particle changes abruptly, as coupling increases, from zero to infinity, which shows the abrupt change of

the polaron state from nearly free type to self-trapping type. However, from the work of Sumi and Toyozawa,<sup>20</sup> the conjecture of Peeters and Devresse<sup>21</sup> and the fact that Feynman's polaron theory, which gives a lower upper bound to the ground-state energy than the other approaches in most part range of coupling strength, did not predict a phase transition. Therefore it is still an unanswered theoretical question—whether this feature is a property of general type or if it just comes from approximation. According to the generalized path-integral formalism, we find that if more terms of excited states were included, the lower polaron energy results and the smaller critical transition coupling strength will be, e.g., in harmonic interaction, if only ground state ( $n=0$ ) is included,  $\alpha_c = 9.42$ ; if all the excited states are included,  $\alpha_c$  will be 5.8.<sup>11</sup> We also conjecture the possibility that, by the generalized formalism, if the optimum potential can be determined, and when all the excited states are included, would make the abrupt change disappear, because, in principle, the generalized formalism should give lower energy than Feynman's model.

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### APPENDIX: EXPRESSION OF $E_v(\mu, a, b)$

The trial function  $u(\vec{r}) = N[1 + b\mu r + a(b\mu r)^2]e^{-b\mu r}$  and  $N^2 = 2(b\mu)^3 / [\pi(14 + 42a + 45a^2)]$ , then  $E_v^0$  can be expressed as

$$E_v^0(\mu, a, b) = \frac{b^2\mu A_1(a)}{A_2(a)} - \frac{\alpha b A_3(a)}{1024 A_2^2(a)} + \frac{32b^6\alpha(1-\mu)^{1/2}}{A_2^2(a)} [A_{10}^+(a)A_{10}^-(a) - A_{10}^{+2}(a)] \\ + \frac{\alpha(1-\mu)^{1/2}}{128 A_2^2(a)} \sum_{n=1}^6 \left[ \frac{1}{(b+c)^n} - \frac{1}{(b-c)^n} \right] b^{n+2} A_{n+3}(a),$$

where  $C = \frac{1}{2}(1 - \mu)^{1/2}$  and

$$A_4(a) = 874 + 2622a + 4320a^2 + 4095a^3 + 1771.875a^4 ,$$

$$A_5(a) = A_4(a) ,$$

$$A_6(a) = 616 + 2364a + 3933a^2 + 3690a^3 + 1575a^4 ,$$

$$A_7(a) = 228 + 1848a + 3159a^2 + 2880a^3 + 1181.25a^4 ,$$

$$A_8(a) = 912a + 2136a^2 + 1800a^3 + 675a^4 ,$$

$$A_9(a) = 1140a^2 + 720a^3 + 225a^4 ,$$

$$A_{10}^+(a) = \sum_{n=1}^5 P_n(a) b^{n-1} / (b + C)^{n+1} ,$$

$$A_{10}^-(a) = \sum_{n=1}^5 P_n(a) b^{n-1} / (b - C)^{n+1} ,$$

$$P_1(a) = 0.25 ,$$

$$P_2(a) = 0.5 ,$$

$$P_3(a) = 0.75a + 0.375 ,$$

$$P_4(a) = 1.5a ,$$

$$P_5(a) = 1.875a^2 .$$

<sup>1</sup>C. G. Kuper and G. D. Whitfield; *Polarons and Excitons* (Oliver and Boyd, Edinburgh, 1963).

<sup>2</sup>J. T. Devreese, *Polarons in Ionic Crystals and Polar Semiconductors* (North-Holland, Amsterdam, 1972).

<sup>3</sup>H. Fröhlich, *Adv. Phys.* **3**, 325 (1954).

<sup>4</sup>T. D. Lee, F. E. Low, and D. Pines, *Phys. Rev.* **90**, 297 (1953).

<sup>5</sup>S. Pekar, *J. Phys.* **10**, 347 (1946); *Zh. Eksp. Teor. Fiz.* **19**, 796 (1954).

<sup>6</sup>E. P. Gross, *Ann. Phys. (N.Y.)* **8**, 78 (1959).

<sup>7</sup>R. P. Feynman, *Phys. Rev.* **7**, 660 (1955).

<sup>8</sup>T. D. Schultz, *Phys. Rev.* **116**, 526 (1959).

<sup>9</sup>M. Matsuura, *Can. J. Phys.* **52**, 1 (1974).

<sup>10</sup>W. J. Huybrechts, *J. Phys. C* **2**, L211 (1976); **10**, 3761 (1977).

<sup>11</sup>J. M. Luttinger and C. Y. Lu, *Phys. Rev. B* **21**, 4251 (1980).

<sup>12</sup>J. T. Marshall and L. R. Mills, *Phys. Rev. B* **2**, 3143 (1970).

<sup>13</sup>S. J. Miyake, *J. Phys. Soc. Jpn.* **38**, 181 (1975).

<sup>14</sup>H. H. Rosenbrock, *Comput. J.* **3**, 175 (1960).

<sup>15</sup>S. J. Miyake (private communication).

<sup>16</sup>D. Larsen, *Phys. Rev.* **187**, 1147 (1969).

<sup>17</sup>R. Manka, *Phys. Lett.* **67A**, 311 (1978).

<sup>18</sup>Y. Lepine and D. Matz, *Phys. Status Solidi B* **96**, 797 (1979).

<sup>19</sup>H. Shoji and N. Tokuda, *J. Phys. C* **14**, 1231 (1981).

<sup>20</sup>A. Sumi and Y. Toyozawa, *J. Phys. Soc. Jpn.* **35**, 137 (1973).

<sup>21</sup>F. M. Peeters and J. T. Devreese, *Solid State Commun.* **39**, 445 (1981).