Generalized path-integral formalism of the polaron problem and its second-order semi-invariant correction to the ground-state energy

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Feynman's path-integral formalism of the polaron problem is generalized, by which it is easy and natural to get the second-order perturbation result in the weak-coupling case and the Pekar result in the strong-coupling case, even in the crudest ground-state approximation. With the harmonic approximation, the polaron energy for the whole range of the coupling constant is obtained, but it is found there is a transition at coupling constant $\simeq 5.8$. This generalized formalism is translationally invariant. The best self-consistent variational potential can be determined by a numerical method. Also, in this model it is particularly easy to estimate the second-order semi-invariant correction to the Jensen inequality. This second-order semi-invariant correction explicitly is calculated. It generates the perturbation expansion to fourth order in the weak-coupling case, and it improves Feynman's result by 0.5% for strong coupling. Discussion and suggestions for further study are included.

I. INTRODUCTION

The problem of finding the ground-state energy of the Fröhlich polaron Hamiltonian has a fairly substantial literature. It is well known that among all the methods, Feynman's path-integral theory gives the best ground-state energy in the overall range of the coupling strength.[1] It is our purpose to generalize the Feynman formalism, and we find that in the generalized theory it is much easier to estimate the second-order semi-invariant correction in the harmonic approximation case. In Secs. II and III, we present the generalized formalism of the path-integral theory of the polaron problem.

In Sec. IV, we apply this theory to the ground-state energy in the ground-state approximation and harmonic approximation. In Sec. V, we estimate the energy correction due to the second-order semi-invariant term. Both numerical results and analytic results in the extreme cases are given. In Sec. VI, we summarize the results and some suggestions for further study are made.

II. PATH-INTEGRAL METHOD APPLIED TO THE POLARON PROBLEM

The Hamiltonian of the idealized electron-phonon system by Fröhlich is given by

$$H=\frac{\vec{p}^2}{2}+\sum_j \tfrac{1}{2}(p_j^2+q_j^2)+\sum_j w_j(\vec{x})q_j\,,$$

where we use the units $\hbar=m=\omega=1$. $\vec{p}$, $\vec{x}$ are the momentum and coordinate operators of electron, p_j, q_j are the momentum and coordinate operators of phonons of mode j, and the interaction terms $w_j(\vec{x})q_j$ are $(8\sqrt{2}\pi\alpha/V)^{1/2}[u_{\beta,j}(\vec{x})/k_j]q_j$, where $u_{\beta,j}(\vec{x})$ is given as follows:

$$u_{1,j}(\vec{x})=\cos\vec{k}\cdot\vec{x}\,,\quad u_{2,j}(\vec{x})=\sin\vec{k}\cdot\vec{x}\,.$$

The two real waves $u_{\beta,j}(\vec{x})$, $\beta=1,2$, constitute a complete set when the nonzero values of $\vec{k}$ are restricted to run only over a half-space, that is, a space in which, if a vector $\vec{k}$ occurs, $-\vec{k}$ does not occur.

The partition function of the polaron may be written as

$$z=e^{-\beta F}=\mathrm{Tr}(e^{-\beta H})\,,$$

when $\beta\to\infty$, the leading term is $e^{-\beta E_0}$. Therefore

$$\lim_{\beta\to\infty}[-(1/\beta)\ln z]=E_0\,,$$

where E_0 is the ground-state energy of the polaron. Thus we may calculate the partition function to evaluate E_0. In particular, we would like to know the partition function for large β.

Using the path-integral representation, the partition function is written as

$$e^{-\beta F}=\mathrm{Tr}(e^{-\beta H})=\int_{\{\text{path}\}}\exp\left(-\int_0^\beta H(t)dt\right).$$

Here, let us define our notation clearly as follows: We divided the time axis from 0 to β into $N+1$ subintervals, each of length τ, i.e., $\beta=(N+1)\tau$, and the superscript denotes the time sequence indices.

$$z=\int d\vec{x}^{(0)}\prod_j dq_j^{(0)}\left\{\frac{1}{A}\int\left[\frac{dx}{A}\right]\cdot\frac{1}{B}\int\left[\frac{dq_j}{B}\right]\exp\left(-\int_0^\beta H(t)dt\right)\right]$$

$$=\int d\vec{x}^{(0)}\prod_j dq_j^{(0)}\left[\int d\vec{x}^{(1)}dq_j^{(1)}\cdots d\vec{x}^{(N)}dq_j^{(N)}p_{01}p_{02}\cdots p_{N0}\mathcal{P}_{01,j}\right.$$

$$\left.\times\mathcal{P}_{12,j}\cdots\mathcal{P}_{N0,j}\exp\left(-\sum_j\tau\sum_{l=0}^{N}\left[\tfrac{1}{2}q_j^{(l)^2}+w_j(\vec{x})q_j^{(l)}\right]\right)\right],$$

where the end point coincides with the initial point

$$\vec{x}^{(N+1)}=\vec{x}^{(0)},\quad q_j^{(N+1)}=q_j^{(0)}.$$

We define

$$[d\vec{x}]\equiv d\vec{x}^{(1)}d\vec{x}^{(2)}\cdots d\vec{x}^{(N-1)}d\vec{x}^{(N)},$$

$$\left[\frac{d\vec{x}}{A}\right]\equiv\frac{d\vec{x}^{(1)}}{A}\frac{d\vec{x}^{(2)}}{A}\cdots\frac{d\vec{x}^{(N)}}{A},$$

$$\left[\frac{dq_j}{B}\right]=\frac{dq_j^{(1)}}{B}\frac{dq_j^{(2)}}{B}\cdots\frac{dq_j^{(N)}}{B},$$

$$\{d\vec{x}\}\equiv d\vec{x}^{(0)}[d\vec{x}],$$

$$\{D\vec{x}\}\equiv p_{01}p_{12}\cdots p_{N0}\{d\vec{x}\},$$

similarly for the definition of $\{dq_j\}$ and $\{Dq_j\}$, and

$$A\equiv(2\pi\tau)^{3/2},\quad B\equiv(2\pi\tau)^{1/2},$$

$$p_{12}\equiv\frac{1}{(2\pi\tau)^{3/2}}\exp[-(\vec{x}^{(1)}-\vec{x}^{(2)})^2/2\tau],$$

$$\mathcal{P}_{12,j}\equiv\frac{1}{(2\pi\tau)^{1/2}}\exp[-(q_j^{(1)}-q_j^{(2)})^2/2\tau],\ldots.$$

Now let us define Z' by

$$Z'\equiv\frac{Z}{Z_{\text{ph}}}=\frac{\text{Tr}(e^{-\beta H})}{\text{Tr}(e^{-\beta H_{\text{ph}}})},$$

where

$$H_{\text{ph}}\equiv\tfrac{1}{2}\sum_j(p_j^2+q_j^2).$$

If we integrate out the phonon coordinates (eliminate the phonon oscillators), then we obtain Feynman's result.

$$Z'=\int\{d\vec{x}\}p_{01}p_{12}\cdots p_{N0}e^{W(\vec{x}^{(1)},\vec{x}^{(2)},\vec{x}^{(3)},\ldots,\vec{x}^{(N)})},\quad(1)$$

where

$$W=\tfrac{1}{4}\tau^2\sum_{l,l'=0}^{N}\left(M_{ll'}\sum_j w_j(\vec{x}^{(l)})w_j\vec{x}^{(l')}\right),\qquad(2)$$

with

$$M_{ll'}=e^{-|l\tau-l'\tau|}(\bar{n}+1)+e^{+|l\tau-l'\tau|}\bar{n},$$

$$\bar{n}=1/(e^\beta-1).$$

For $\beta\to\infty$, then $\bar{n}\to 0$, hence we have

$$M_{ll'}\to e^{-|l\tau-l'\tau|}.$$

The physical motivation of our variational method comes from a 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 reactions of a small number (hopefully, one) of particles coupled in some simple way to the electron and to one another. In the most simple case, we choose the variational Hamiltonian as

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

where $\vec{P}$, $\vec{R}$, and M are the momentum, coordinate, and mass of the fictitious particle. We assume the electron couples with the particle by a central force potential $v(\vec{x}-\vec{R})$.

Let us carry out the variational method as follows: by adding and subtracting the term $\int_0^\beta v(\vec{x}(t)-\vec{R}(t))\,dt$ to the exponent of (1), path integrating over the coordinate $\vec{R}$, and dividing by the partition function of a free particle. Also by multiplying and dividing this expression by the path-integral expression of the partition function of a system with Hamiltonian H_v, therefore, we have

$$Z'=\int\{D\vec{x}\}e^W$$

$$=\frac{\int\{D\vec{x}\}\{D\vec{R}\}\exp(W+\int_0^\beta v(\vec{x}-\vec{R})dt-\int_0^\beta v(\vec{x}-\vec{R})dt)}{\int\{D\vec{x}\}\{D\vec{R}\}\exp(-\int_0^\beta v(\vec{x}-\vec{R})dt)}\;\frac{\int\{D\vec{x}\}\{D\vec{R}\}\exp(-\int_0^\beta v(\vec{x}-\vec{R})dt)}{\int\{D\vec{R}\}}$$

$$=\langle e^{V+W}\rangle_v\tilde{Z},$$

where

$$\tilde{Z} \equiv \frac{\int \{D\vec{x}\}\{D\vec{R}\} \exp(-\int_0^\beta v(\vec{x}-\vec{R})dt)}{\int \{D\vec{R}\}} .$$

$\int\{DR\}$ is the path-integral form of the partition function of the free fictitious particle,

$$V \equiv \int_0^\beta v(\vec{x}(t) - \vec{R}(t))dt ,$$

and the average $\langle\cdots\rangle_v$ is defined by

$$\langle A\rangle_v \equiv \frac{\int \{D\vec{x}\}\{D\vec{R}\} A \exp(-\int_0^\beta v(\vec{x}-\vec{R})dt)}{\int \{D\vec{x}\}\{D\vec{R}\} \exp(-\int_0^\beta v(\vec{x}-\vec{R})dt)} .$$

By Jensen's inequality, we have

$$Z' = \langle e^{V+W}\rangle_v \tilde{Z} \geq e^{\langle V+W\rangle_v}\tilde{Z} . \tag{3}$$

The lower bound for Z' is given by the right-hand side of (3), therefore an upper bound for the polaron energy is

$$E_0 \leq E_v \equiv \frac{\ln\tilde{Z}}{\beta} - \frac{\langle V\rangle_v}{\beta} - \frac{\langle W\rangle_v}{\beta} .$$

This variational formulation is different from that of Feynman's[2] which has used a specific form of interaction—"harmonic interaction"—between the electron and the fictitious particle. By that special choice, the form of interaction is given explicity, and fortunately, the exact integration over the $\vec{R}$ variable can be carried out, therefore, in the Feynman's formulation; what remains is the integration over the electron's coordinate $\vec{x}$. In the generalized formulation, we do not specify the form of the interaction which can be varied to make the inequality (3) as strong as possible. The disadvantage of this formulation [as can be seen in (3)] is our use of Jensen's inequality twice, once for the path-integral average over the electron's coordinate $\vec{x}$, and the other for the variable $\vec{R}$. Therefore the lower bound of (3) may be weaker than that of Feynman's method if we also assume the interaction is harmonic. We will show this fact by explicit calculations in a later section. In general, our method can be better, because we can adjust the interaction form self-consistently, as an example, we can obtain the Pekar result (which is better than Feynman's result in the strong coupling limit) very naturally even in the crudest approximation.

III. THE PARTITION FUNCTION OF POLARON FOR AN UNSPECIFIED GENERAL FORM OF VARIATIONAL POTENTIAL

In this section, we formulate the upper bound of the polaron energy for the general form of variational potential $v(\vec{x}-\vec{R})$. If the relative coordinate $\vec{\xi}$ and coordinate of the center of mass $\vec{\eta}$ are used, then the Hamiltonian can be expressed as

$$H_v = -\frac{1}{2}\frac{\nabla_\eta^2}{(M+1)} - \frac{1}{2}\frac{\nabla_\xi^2}{\mu} + v(\vec{\xi}) ,$$

where μ is the reduced mass, $1/\mu = 1 + 1/M$. Therefore, the Schrödinger equation of this system can be separated as follows:

$$\begin{aligned} &-\frac{1}{2}\frac{\nabla_\eta^2}{(M+1)}\left(\frac{1}{\sqrt{V}}e^{i\vec{p}\cdot\vec{\eta}}\right) = E_{\vec{p}}\cdot\left(\frac{1}{\sqrt{V}}e^{i\vec{p}\cdot\vec{\eta}}\right) \\ &\left(-\frac{1}{2\mu}\nabla_\xi^2 + v(\vec{\xi})\right)u_n(\vec{\xi}) = \epsilon_n u_n(\vec{\xi}) , \end{aligned} \tag{4}$$

and the total energy $E(\vec{p}, n)$ is given by

$$E_{(\vec{p},n)} = E_{\vec{p}} + \epsilon_n = \frac{p^2}{2(M+1)} + \epsilon_n .$$

Now, let us calculate $\tilde{Z}$, $\langle V\rangle_v$, and $\langle W\rangle_v$ separately in order to obtain Z'.

First, $\tilde{Z}$ is defined as

$$\tilde{Z} \equiv \frac{\int \{D\vec{x}\}\{D\vec{R}\} \exp(-\int_0^\beta v(\vec{x}-\vec{R})dt)}{\int \{D\vec{R}\}} = \frac{\mathrm{Tr}(e^{-\beta H_v})}{\mathrm{Tr}(e^{-\beta\vec{P}^2/2M})} .$$

The denominator is the partition function of a free particle with mass M; this is well known as

$$\mathrm{Tr}(e^{-\beta\vec{P}^2/2M}) = \int \{D\vec{R}\} = e^{-\beta F_{\mathrm{free}}} = V\left(\frac{M}{2\pi\beta}\right)^{3/2} .$$

The partition function of the system H_v can be expressed in $(\vec{\xi},\vec{\eta})$ representation as (as $\beta\to\infty$)

$$\mathrm{Tr}(e^{-\beta H_v}) = \int d\vec{\xi}\int d\vec{\eta}\,\langle\vec{\xi},\vec{\eta}\,|e^{-\beta H_v}|\,\vec{\xi},\vec{\eta}\rangle \simeq V\left(\frac{M+1}{2\pi\beta}\right)^{3/2} e^{-\beta\epsilon_0} .$$

Therefore we have

$$\tilde{Z} = (1/\mu^{3/2})e^{-\beta\epsilon_0} .$$

Secondly, let us evaluate the $\langle V\rangle_v$ term. There are many ways to do this; the following one is a very simple one:

$$\begin{aligned} \langle V\rangle_v &= \left\langle \int_0^\beta v(\vec{x}-\vec{R})dt \right\rangle_v \\ &= -\frac{\partial}{\partial\lambda}\ln\left[\int \{D\vec{x}\}\{D\vec{R}\} \times \exp\left(-\lambda\int_0^\beta v(\vec{x}-\vec{R})dt\right)\right]_{\lambda=1} \\ &= \int d\vec{x}^{(0)} d\vec{R}^{(0)} \times \left(-\frac{\partial}{\partial\lambda}\left[\ln G_\beta(\vec{x}^{(0)},\vec{R}^{(0)};\ \vec{x}^{(0)},\vec{R}^{(0)}\,|\lambda v)\right]\right)_{\lambda=1} . \end{aligned} \tag{5}$$

$G_\beta(\vec{x}^{(0)},\vec{R}^{(0)};\vec{x}^{(0)},\vec{R}^{(0)}\,|\lambda v) = \langle \vec{x}^{(0)},\vec{R}^{(0)}\,|e^{-\beta H_{\lambda v}}|\vec{x}^{(0)},\vec{R}^{(0)}\rangle$ is the Green's function of the Hamiltonian $(\vec{p}^2/2)+(\vec{P}^2/2M)+\lambda v(\vec{x}-\vec{R})$ beginning at $(\vec{x}^{(0)}, \vec{R}^{(0)})$ and ending at the same position $(\vec{x}^{(0)},\vec{R}^{(0)})$. For β very large,

$$G_\beta(\vec{x}^{(0)},\vec{R}^{(0)};\vec{x}^{(0)},\vec{R}^{(0)}\,|\lambda v)\simeq |\psi_0(\vec{x}^{(0)},\vec{R}^{(0)})|^2 e^{-\beta E_0(\lambda v)}.$$

Therefore the integrand in Eq. (5) can be calculated by using perturbation theory ($\lambda=1+\epsilon$, $\epsilon\to 0$), that is,

$$\begin{aligned}\langle V\rangle_v &= \beta\int d\vec{x}^{(0)}d\vec{R}^{(0)}\frac{\partial E_0(\lambda v)}{\partial\lambda}\\ &=\beta\int d\vec{x}^{(0)}d\vec{R}^{(0)}v(\vec{x}^{(0)}-\vec{R}^{(0)})\,|\psi(\vec{x}^{(0)},\vec{R}^{(0)})|^2\\ &=\beta\int d^3\vec{\xi}\,v(\vec{\xi})\,|u_0(\vec{\xi})|^2. \end{aligned}\tag{6}$$

Last, we evaluate $\langle W\rangle_v$. From Eq. (2), $\langle W\rangle_v$ is written as

$$\langle W\rangle_v=\frac{\tau^2}{4}\sum_j\sum_{l,l'=0}^{N} M_{ll'}\langle w_j(\vec{x}^{(l)})w_j(\vec{x}^{(l')})\rangle_v .$$

Setting $t=(l-l')\tau>0$, we can write this as follows:

$$\langle W\rangle_v \mathrm{Tr}(e^{-\beta H_v}) =\tfrac{1}{2}\int_0^\beta dt(\beta-t)e^t\sum_j \mathrm{Tr}(e^{-(\beta-t)H_v}w_j e^{-tH_v}w_j). \tag{7}$$

As $\beta\to\infty$, we only take the ground state of the discrete level ϵ_n, and sum over the continuous quantum number $\vec{p}$ in the $e^{-(\beta-t)H_v}$ term in calculating the trace. If we also use the fact that

$$\sum_j w_j(\vec{\eta},\vec{\xi})w_j(\vec{\eta}',\vec{\xi}')=\frac{\alpha\sqrt{2}}{|\vec{\eta}-\vec{\eta}'+\vec{\xi}-\vec{\xi}'|}\equiv g(\vec{\eta},\vec{\eta}';\vec{\xi},\vec{\xi}'), \tag{8}$$

the right-hand side of Eq. (7) is given as

$$\frac{\beta}{2}\left(\frac{M+1}{2}\right)^3\int_0^\infty dt\left(\frac{1}{\beta t}\right)^{3/2}e^{-\beta\epsilon_0}\int_{\eta\eta',\xi\xi'} g e^{-[(M+1)/2t](\vec{\eta}-\vec{\eta}')^2}\sum_n u_0^*(\vec{\xi}')u_0(\vec{\xi})u_n^*(\vec{\xi})u_n(\vec{\xi}')e^{-t(\epsilon_n-\epsilon_0)},$$

the $\vec{\eta}$ and $\vec{\eta}'$ integration can be done explicitly,

$$\int_{\eta,\eta'} g e^{-[(M+1)/2t](\vec{\eta}-\vec{\eta}')^2}=\alpha\sqrt{2}V\left(\frac{2\pi}{M+1}\right)^{3/2}\frac{t^{3/2}}{\mu|\vec{\xi}-\vec{\xi}'|}\,\mathrm{erf}\left(\frac{C|\vec{\xi}-\vec{\xi}'|}{\sqrt{t}}\right),$$

where

$$C\equiv\mu\left(\frac{M+1}{2}\right)^{1/2}=\frac{M}{[2(M+1)]^{1/2}},$$

and, because

$$\mathrm{Tr}(e^{-\beta H_v})=V\left(\frac{M+1}{2\pi\beta}\right)^{3/2}e^{-\beta\epsilon_0}.$$

Therefore we have the expression for $\langle W\rangle_v$:

$$\langle W\rangle_v=\frac{\alpha\beta}{\sqrt{2}\mu}\int_{\xi\xi'}\frac{u_0^*(\vec{\xi}')u_0(\vec{\xi})}{|\vec{\xi}'-\vec{\xi}|}\sum_n u_n^*(\vec{\xi})u_n(\vec{\xi}')\int_0^\infty dt\,\mathrm{erf}\left(\frac{C|\vec{\xi}'-\vec{\xi}|}{\sqrt{t}}\right)e^{-t(\Delta\epsilon_n+1)},$$

where

$$\Delta\epsilon_n=\epsilon_n-\epsilon_0.$$

Now the t integration can be done by partial integration, and using the definition of erf function, we have

$$\langle W\rangle_v=\frac{\alpha\beta}{\sqrt{2}\mu}\sum_{n=0}^\infty\int_{\xi\xi'}\frac{u_0^*(\vec{\xi}')u_0(\vec{\xi})u_n^*(\vec{\xi})u_n(\vec{\xi}')}{|\vec{\xi}-\vec{\xi}'|}\left(\frac{1-e^{-2C(\Delta\epsilon_n+1)^{1/2}|\vec{\xi}'-\vec{\xi}|}}{\Delta\epsilon_n+1}\right). \tag{9}$$

If we make use of the Fourier transform

$$\frac{e^{-b|\vec{r}|}}{|\vec{r}|}=\int\frac{d\vec{k}}{(2\pi)^3}\frac{4\pi}{(b^2+k^2)}e^{i\vec{k}\cdot\vec{r}},$$

then $\langle W\rangle_v$ can also be expressed as

$$\langle W\rangle_v=\frac{\alpha\beta}{\sqrt{2}\mu}\sum_{n=0}^\infty 4C^2\int\frac{d\vec{k}}{2\pi^2}\frac{1}{k^2(k^2+b_n^2)}\left|\int d\vec{\xi}\,e^{i\vec{k}\cdot\vec{\xi}}u_0(\vec{\xi})u_n^*(\vec{\xi})\right|^2\equiv\frac{\alpha\beta}{\sqrt{2}\mu}\sum_n G_n, \tag{9'}$$

where we define

$$b_n \equiv 2C(\Delta\epsilon_n + 1)^{1/2},$$

$$G_n \equiv \int \frac{d\vec{k}}{2\pi^2} \frac{4C^2}{k^2(k^2+b_n^2)} \left| \int d\vec{\xi}\, e^{i\vec{k}\cdot\vec{\xi}} u_0(\vec{\xi}) u_n^*(\vec{\xi}) \right|^2 \geq 0.$$

Therefore, it is clear that every G_n term is positive. If we just take any kind of partial sum or a single term, the variational bound still holds true, but makes the inequality weaker.

Let us now summarize the results as follows:

$$\begin{aligned} E_0 \leq E_v &= \epsilon_0 - \langle V \rangle_v/\beta - \langle W \rangle_v/\beta \\ &= \langle u_0 | p^2/2\mu | u_0 \rangle - \frac{\alpha}{\sqrt{2}\mu} \sum_{n=0}^{\infty} \int_{\xi\xi'} \frac{u_0^*(\vec{\xi}') u_0(\vec{\xi}) u_n^*(\vec{\xi}) u_n(\vec{\xi}')}{|\vec{\xi} - \vec{\xi}'|} \left(\frac{1 - \exp[-2C(1+\Delta\epsilon_n)^{1/2} |\vec{\xi} - \vec{\xi}'|]}{\Delta\epsilon_n + 1} \right), \end{aligned} \tag{10}$$

where we combine the first two terms on the right-hand side as

$$\epsilon_0 - \int d\vec{\xi}\, v(\vec{\xi}) |u_0(\vec{\xi})|^2 = \langle u_0 | p^2/2\mu | u_0 \rangle$$

and it is noted $\langle W \rangle_v$ can also be expressed as (9′).

IV. GROUND-STATE APPROXIMATION AND HARMONIC APPROXIMATION FOR THE POLARON ENERGY

From (10) in the last section, it is obvious that if we take only the ground-state term ($n=0$) in the summation of $\langle W \rangle_v$, then the right-hand side of (10) is still an upper bound of the polaron energy. Therefore we can write

$$E_0 \leq E_v^0 = \int u_0^*(\vec{\xi}) \frac{\vec{p}^2}{2\mu} u_0(\vec{\xi}) d\vec{\xi} - \frac{\alpha}{\sqrt{2}\mu} \int \frac{|u_0(\vec{\xi}) u_0(\vec{\xi}')|^2}{|\vec{\xi} - \vec{\xi}'|} (1 - e^{-2C|\vec{\xi}-\vec{\xi}'|}).$$

Since E_v^0 is a functional of u_0 alone and the only constraint is that u_0 is normalized, the stationary condition for the best choice of v, $\delta E_v^0/\delta v(\vec{\xi}) = 0$, is equivalent to

$$\delta\left(E_v^0 - \lambda \int u_0(\vec{\xi}')^2 d\vec{\xi}' \right) \Big/ \delta u_0(\vec{\xi}) = 0.$$

This gives at once

$$\frac{\vec{p}^2}{2\mu} u_0(\vec{\xi}) - \frac{\alpha\sqrt{2}}{\mu} \int d\vec{\xi}' \frac{u_0(\vec{\xi}')^2}{|\vec{\xi} - \vec{\xi}'|} (1 - e^{-2C|\vec{\xi}-\vec{\xi}'|}) u_0(\vec{\xi}) = \epsilon_0 u_0(\vec{\xi}). \tag{11}$$

From the above equation, we see the best self-consistent potential is a Hartree-type potential.

For the strong coupling case, we assume $C \to \infty$,[3] Eq. (11) will just reduce to the semiclassical theory of Pekar.[4] According to the work of Pekar in strong coupling case, the polaron is localized in a Hartree-type potential well, and the polaron energy is then calculated by a variational method. Pekar took the trial function as

$$u_0(r) = N[1 + br + a(br)^2] e^{-br},$$

then obtained the energy

$$E_v^0 = -0.1088\alpha^2.$$

Recently, Miyake[5] recalculated the Pekar energy by both exact numerical integration and Pekar's variational method. It was found that the variational energy is $-0.108504\alpha^2$ which is a little higher than the exact numerical quadrature value ($-0.108513\alpha^2$) as it should be. Therefore, the often quoted result $-0.1088\alpha^2$ of Pekar's variational calculation is not quite accurate. But from Miyake's work, it is found that Pekar's variational calculation gives an excellent approximation; the energy differs by less than 0.01% and the error in the wave function is less than 1% where the value of the wave function is appreciable.

For very small coupling, $\alpha \to 0$, assume $C \to 0$, then by expanding (11), we obtain an equation which describes an electron moving in a constant potential of magnitude $-\alpha$, and from (11), we can easily see in this limit ($\alpha \to 0$) the polaron energy is $-\alpha$, which agrees with that of the second-order perturbation calculation. By this variational method, without any specific form of $v(\vec{x} - \vec{R})$, we can now obtain the correct energy values in both weak and strong limiting cases. In order to find the effects of the inclusion of all the excited states, we take a specific example of interaction potential—harmonic interaction. By this harmonic-interaction approximation, we can get the explicit results which are fairly good for all values coupling constant.

As a matter of fact for this particular choice of interaction,

$$v(\vec{x} - \vec{R}) = \tfrac{1}{2}K(\vec{x} - \vec{R})^2, \tag{12}$$

the $\langle W \rangle_v/\beta$ in our method can be easily shown to be exactly equal to the A which appears in Eqs. (21) and (31) in Feynman's original paper,[2] where

$$A = 2^{-3/2}\alpha \int \left\langle \frac{1}{|\vec{x}(t)-\vec{x}(s)|}\right\rangle_{S_0} e^{-|t-s|}ds$$

$$= \pi^{-1/2}\alpha\Omega \int_0^\infty \{\omega^2\tau + [(\Omega^2-\omega^2)/\Omega] \times (1-e^{-\Omega\tau})\}^{-1/2} e^{-\tau} d\tau\,, \qquad (13)$$

and

$$\omega^2 = K/M\,,\quad \Omega^2 = K/\mu\,.$$

We can also obtain this result by summing up the expression (9′) by taking $u_n(\vec{\xi})$ as the wave functions of harmonic oscillator as an alternative way to obtain the $\langle W\rangle_v$; we include this calculation in the Appendix. For the harmonic approximation,

$$\epsilon_0 - \langle u_0|v(\vec{\xi})|u_0\rangle = \langle u_0|\vec{p}^2/2\mu|u_0\rangle$$

is given by $\frac{3}{4}\Omega$. Therefore the upper bound of the polaron energy is given by

$$E_0 \le E_v = \tfrac{3}{4}\Omega - \alpha\Omega\left(\frac{1}{\sqrt{\pi}}\right)\int_0^\infty \frac{e^{-t}}{\{\omega^2 t + [(\Omega^2-\omega^2)/\Omega](1-e^{-\Omega t})\}^{1/2}}\,dt\,. \qquad (14)$$

Unfortunately, the integral in (14) cannot be evaluated in closed form, so that a complete determination of the polaron energy requires numerical integration.

Equation (14) has two parameters which we varied to give the lowest energy; there we have

$$\partial E_v/\partial\omega = 0,\quad \partial E_v/\partial\Omega = 0\,. \qquad (15)$$

But from (14), we can see that only the integral A contains ω, and A is an even function of ω, so the derivative of A with respect to ω is always zero at $\omega = 0$, and we can see from following this that $\omega = 0$ is a point which makes A maximum.

If we set $\omega = \gamma\Omega$ and $\Omega t = y$,

$$A = \alpha\left(\frac{1}{\pi\Omega}\right)^{1/2}\int_0^\infty dy \frac{e^{-y/\Omega}}{[(1-e^{-y}) + \gamma^2(e^{-y}-1+y)]^{1/2}}\,.$$

From this expression, it is easy to see that $\gamma = 0$ will make A maximum, therefore, the best value of ω is zero. Hence the energy expression (14) can be reduced to

$$E_v = \tfrac{3}{4}\Omega - \frac{\alpha}{\Omega^{1/2}}\frac{\Gamma(1/\Omega)}{\Gamma(\frac{1}{2}+1/\Omega)}\,. \qquad (16)$$

The condition (15), $\partial E_v/\partial\Omega = 0$, yields

$$\frac{3}{4}\frac{1}{z^2}\frac{\Gamma(\frac{1}{2}+z)}{\Gamma(1+z)} = \frac{\alpha}{\sqrt{z}}\left(\frac{1}{2z} - [\psi(1+z) - \psi(\tfrac{1}{2}+z)]\right), \qquad (17)$$

where $z = 1/\Omega$, and $\psi(z) = (d/dz)\ln\Gamma(z)$ when $z\to\infty$ (i.e., $\Omega\to 0$); the condition (17) determining α yields $\alpha\to 5.8$, where we have used the asymptotic relation

$$\frac{\Gamma(1+z)}{\Gamma(\frac{1}{2}+z)} \approx \sqrt{z}\left(1+\frac{1}{8z}+\cdots\right),\quad z\to\infty\,,$$

and

$$\psi(1+z) - \psi(\tfrac{1}{2}+z) \simeq \frac{1}{2z} - \frac{1}{8z^2} + \cdots\,.$$

This means that when $\alpha\to 5.8$, the best value of $\Omega\to 0$. This can also be seen by plotting Eq. (16) directly as a function of Ω for various values of α. It is found that when $\alpha < 5.8$, there is no minimum for E_v but the end point $E_v(\Omega = 0)$ corresponding to the least energy; for $\alpha > 5.8$, there is a minimum for E_v with nonzero Ω (>0). Plotting these E_v as a function of α, we find a transition at $\alpha\simeq 5.8$, that is, $dE_v(\alpha)/d\alpha$ is not continuous at $\alpha\simeq 5.8$.

And for large α we can have large Ω; then

$$A = \alpha\left(\frac{\Omega}{\pi}\right)^{1/2}\frac{1}{\Omega}\frac{\Gamma(\frac{1}{2})\Gamma(1/\Omega)}{\Gamma(\frac{1}{2}+1/\Omega)} \to \alpha\left(\frac{\Omega}{\pi}\right)^{1/2}\left(1+\frac{2\ln 2+\tilde{C}}{\Omega}\right),$$

$\tilde{C}$ is the Euler number here. With this expression of A, we can determine the best choice of Ω as

$$\Omega \simeq 4\alpha^2/9\pi - 4\ln 2 - 2\tilde{C}\,, \qquad (18)$$

and hence the polaron energy

$$E_v = -\frac{\alpha^2}{3\pi} - \tfrac{3}{2}(2\ln 2+\tilde{C}) + O\left(\frac{1}{\alpha^2}\right) \qquad (19)$$

for a large coupling constant.

For α that are small, $\Omega = 0$, then (16) becomes $E_v = -\alpha$. In Table I, a comparison of various previous results about polaron energy in the range of intermediate coupling constant α is given. Here, both Luttinger-Lu and Feynman's results are in the harmonic approximation. From this table, it is found that our result is inferior to that of Feynman's, as it should be, because we have Jensen's inequality one more time than Feynman. But it is known for very strong coupling that Pekar's energy will be lowest, and we have seen that even our result of the ground-state approximation for a general form of potential will approach that of Pekar's result. From this result, we know that in the strong-coupling case, the electron is trapped in a potential which is not like the harmonic potential and the contribution from the states other than ground state is not significant. Those excited states only contribute to the constant term instead of the α^2 term. This can be seen clearly in the following example of harmonic interaction but excluding excited states.

If we take only the ground-state harmonic wave function in the expression (9), instead of taking all the excited states into account, it is trivial to calculate the upper bound of the polaron energy [this result, of course, is worse than (16)], and it is

$$E \leqslant E_v^0 = \tfrac{3}{4}\Omega - \alpha\frac{\Omega}{\omega}\exp\left(\frac{\Omega}{\omega^2} - \frac{1}{\Omega}\right)\operatorname{erfc}\left[\left(\frac{\Omega}{\omega^2} - \frac{1}{\Omega}\right)^{1/2}\right]. \tag{20}$$

For strong coupling, it reduces to

$$E_v^0 \to -(1/3\pi)\alpha^2 \sim -0.106\alpha^2. \tag{21}$$

Comparing (21) with (19), we can see that the excited states contribute only to the "fluctuation energy" (of order α^0). Therefore if we include all the excited states in the calculation of a general potential, the constant "fluctuation-energy" term must come out as it does in the harmonic approximation.

V. ESTIMATION OF THE ENERGY CORRECTION DUE TO THE SECOND-ORDER SEMI-INVARIANT

When we use the path-integral variational method to evaluate the ground-state energy of the polaron, we have assumed the Jensen inequality

$$\langle e^A\rangle \geqslant e^{\langle A\rangle}, \tag{22}$$

where $A = W + V$. However, Jensen's inequality is actually the first term of the exact semi-invariant or cumulant expansion

$$\langle e^A\rangle = \exp\left(\langle A\rangle + \frac{1}{2!}(\langle A^2\rangle - \langle A\rangle^2) + \frac{1}{3!}\times[\langle A^3\rangle - 3\langle A\rangle(\langle A^2\rangle - \langle A\rangle^2) - \langle A\rangle^3] + \cdots\right).$$

Therefore, if the approximation

$$\langle e^A\rangle \simeq e^{\langle A\rangle}$$

is very good, we expect that the fluctuation

$$(1/2!)(\langle A^2\rangle - \langle A\rangle^2)$$

should be a small correction to the inequality (22). With this second cumulant term, we no longer have the Jensen inequality, that is, $\exp[\langle A\rangle + \frac{1}{2}(\langle A^2\rangle - \langle A\rangle^2)]$ may not be a lower bound for $\langle e^A\rangle$.

The second-order semi-invariant is

$$\begin{aligned} F^{(2)} &= [\langle (W+V)^2\rangle - \langle W+V\rangle^2] \\ &= [\langle W^2\rangle - \langle W\rangle^2 + 2(\langle WV\rangle - \langle W\rangle\langle V\rangle) + \langle V^2\rangle - \langle V\rangle^2]. \end{aligned}$$

The second-order semi-invariant correction to the ground-state polaron energy is

$$\begin{aligned} \Delta E &= -(1/2\beta)F^{(2)} \\ &= -(1/2\beta)[(\langle W^2\rangle_v - \langle W\rangle_v^2) + 2(\langle WV\rangle_v - \langle W\rangle_v\langle V\rangle_v) + (\langle V^2\rangle_v - \langle V\rangle_v^2)] \\ &= \Delta E_1 + \Delta E_2 + \Delta E_3. \end{aligned}$$

Therefore, for harmonic interaction, we calculate ΔE_3 first,

$$\begin{aligned} \Delta E_3 &= -\frac{1}{2\beta}(\langle V^2\rangle_v - \langle V\rangle_v^2) \\ &= \frac{1}{2\beta}\frac{\partial}{\partial\mu}\langle V\rangle_{\mu v}\Big|_{\mu=1} = -\tfrac{3}{16}\Omega, \end{aligned} \tag{23}$$

and ΔE_2 is given by

$$\Delta E_2 = -(1/\beta)(\langle WV\rangle_v - \langle W\rangle_v\langle V\rangle_v). \tag{24}$$

To evaluate (24), we replace V by μV in $\langle W\rangle_v$, then

TABLE I. Polaron energy from previous work.

	Coupling constant					
	1	3	5	7	9	11
Fröhlich *et al.* (Ref. 19)	−1.00	−3.00	−5.00			
Gurari (Ref. 20)	−1.00	−3.00	−5.00			
Lee, Low, and Pines (Ref. 21)	−1.00	−3.00	−5.00	−7.00		
Lee and Pines (Ref. 7)	−1.00	−3.00	−5.30	−7.55	−9.95	−12.41
Gross (Ref. 22)	−1.01	−3.09	−5.24	−7.43	−9.65	−11.88
Feynman (Refs. 1 and 2)	−1.01	−3.13	−5.44	−8.11	−11.49	−15.71
Luttinger and Lu (Ref. 23)	−1.00	−3.00	−5.00	−7.36	−10.72	−15.00
Pekar (Ref. 24)				−6.83	−10.31	−14.66
Hohler (Ref. 25)				−6.70	−10.10	−14.33

$$\Delta E_2 = -\frac{1}{\beta}\frac{\partial}{\partial \mu}\langle W\rangle_{\mu v}\Big|_{\mu=1}$$

$$= \frac{\alpha}{4}(\pi\Omega)^{-1/2}\left\{B\left(\frac{1}{\Omega},\frac{1}{2}\right)+B\left(1+\frac{1}{\Omega},-\frac{1}{2}\right)\times\left[\psi\left(1+\frac{1}{\Omega}\right)-\psi\left(\frac{1}{2}+\frac{1}{\Omega}\right)\right]\right\}$$

or

$$= \frac{\alpha}{4}\left(\frac{1}{\Omega}\right)\frac{\Gamma(1/\Omega)}{\Gamma(1/\Omega+\frac{1}{2})}\left[\frac{4}{\Omega}\hat{\beta}\left(\frac{2}{\Omega}\right)-1\right], \tag{25}$$

where $B(x,y)$ is the beta function defined as

$$B(x,y)=\int_0^1 t^{x-1}(1-t)^{y-1}dt=\frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)},$$

and $\hat{\beta}$ is defined by

$$\hat{\beta}(x)=\frac{1}{2}\left[\psi\left(\frac{x+1}{2}\right)-\psi\left(\frac{x}{2}\right)\right] = B(x,\ 1-x)\quad [\mathrm{Re}(x)>0].$$

Now let us concentrate on the expression $\langle W^2\rangle_v - \langle W\rangle_v^2$. From the definition of $\langle W^2\rangle_v$, it can be expressed as

$$\langle W^2\rangle_v=\frac{\alpha^2}{8}\int_0^\beta\cdots\int dt_2ds_2dt_1ds_1e^{-|t_1-s_1|-|t_2-s_2|}\times\left\langle\frac{1}{|\vec{r}_{t_1}-\vec{r}_{s_1}|}\frac{1}{|\vec{r}_{t_2}-\vec{r}_{s_2}|}\right\rangle. \tag{26}$$

Here, we may express $1/|\vec{r}_{t_1}-\vec{r}_{s_1}|$ by a Fourier transform:

$$\frac{1}{|\vec{r}_{t_1}-\vec{r}_{s_1}|}=\int\frac{d\vec{k}}{2\pi^2k^2}\exp[i\vec{k}\cdot(\vec{r}_{t_1}-\vec{r}_{s_1})],$$

and similarly for $1/|\vec{r}_{t_2}-\vec{r}_{s_2}|$. For this reason we need to study

$$I\equiv\langle\exp[i\vec{k}\cdot(\vec{r}_{t_1}-\vec{r}_{s_1})+i\vec{k}'\cdot(\vec{r}_{t_2}-\vec{r}_{s_2})]\rangle_v = \int\{d\vec{r}\}e^{S_0}\exp[i\vec{k}\cdot(\vec{r}_{t_1}-\vec{r}_{s_1})+i\vec{k}'\cdot(\vec{r}_{t_2}-\vec{r}_{s_2})]\Big/\int\{d\vec{r}\}e^{S_0}, \tag{27}$$

where

$$S_0=-\tfrac{1}{2}\int_0^\beta\left(\frac{d\vec{r}}{dt}\right)^2dt-\frac{\omega(\Omega^2-\omega^2)}{8}\iint dt\,ds(\vec{r}_t-\vec{r}_s)^2e^{-\omega|t-s|}.$$

The path integral in the numerator is of the form

$$N=\int\{d\vec{r}\}\exp\left(S_0+\int\vec{f}(t)\cdot\vec{r}(t)dt\right), \tag{28}$$

where specifically

$$\vec{f}(t)=i\vec{k}[\delta(t-t_1)-\delta(t-s_1)]+i\vec{k}'[\delta(t-t_2)-\delta(t-s_2)]. \tag{29}$$

Following Feynman's trick,[2] the exponent of I is obtained by

$$J=-(k^2A+k'^2B+\vec{k}\cdot\vec{k}'D),$$

where

$$A=\frac{\omega^2}{2\Omega^2}|t_1-s_1|+\left(\frac{\Omega^2-\omega^2}{2\Omega^3}\right)(1-e^{-\Omega|t_1-s_1|}),$$

$$B=\frac{\omega^2}{2\Omega^2}|t_2-s_2|+\left(\frac{\Omega^2-\omega^2}{2\Omega^3}\right)(1-e^{-\Omega|t_2-s_2|}),$$

$$D=\left(\frac{\Omega^2-\omega^2}{2\Omega^3}\right)(e^{-\Omega|t_2-s_1|}+e^{-\Omega|s_2-t_1|}-e^{-\Omega|t_2-t_1|}-e^{-\Omega|s_2-s_1|}) -\left(\frac{\omega^2}{2\Omega}\right)(|t_1-t_2|+|s_1-s_2|-|t_1-s_2|-|s_1-t_2|),$$

hence we can write $\langle W^2\rangle_v$ as

$$\langle W^2\rangle_v=\frac{\alpha^2}{8}\int_0^\beta\cdots\int dt_2ds_2dt_1ds_1e^{-|t_1-s_1|-|t_2-s_2|}\frac{1}{4\pi^4}\int\frac{d\vec{k}}{k^2}\int\frac{d\vec{k}'}{k'^2}e^{J(\vec{k},\vec{k}')}.$$

After $\vec{k}$ and $\vec{k}'$ integration, we have

$$\langle W^2\rangle_v = \frac{\alpha^2}{8}\int_0^\beta \cdots \int dt_2 ds_2 dt_1 ds_1 e^{-|t_1-s_1|-|t_2-s_2|}\frac{2}{\pi}\frac{1}{D}\tan^{-1}\left(\frac{D^2}{4AB-D^2}\right)^{1/2}. \tag{30}$$

Recall that best value of ω for minimum energy is always 0, so in our theory the expression for A, B, D is particularly simple,

$$A = \Delta_1 = \Delta(|t_1 - s_1|) = \frac{1}{2\Omega}(1 - e^{-\Omega|t_1-s_1|}),$$

$$B = \Delta_2 = \Delta(|t_2 - s_2|) = \frac{1}{2\Omega}(1 - e^{-\Omega|t_2-s_2|}),$$

$$D = D_{12} = \frac{1}{2\Omega}(e^{-\Omega|t_1-s_2|} + e^{-\Omega|t_2-s_1|} - e^{-\Omega|t_1-t_2|} - e^{-\Omega|s_1-s_2|}),$$

and also, $\langle W\rangle_v$ is given, by the same trick, as

$$\langle W\rangle_v = \frac{\alpha}{\sqrt{8\pi}}\int_0^\beta dt_1 \int_0^\beta ds_1 e^{-|t_1-s_1|}\frac{1}{(\Delta_1)^{1/2}}. \tag{31}$$

This is the expression which appeared in the Eq. (31) of Feynman's paper[2] with $\omega = 0$.

If we define θ by

$$\sin^2\theta = D_{12}^2/4\Delta_1\Delta_2,$$

then we have

$$\langle W^2\rangle_v - \langle W\rangle_v^2 = \frac{\alpha^2}{8\pi}\int_0^\beta \cdots \int dt_2 ds_2 dt_1 ds_1 e^{-|t_1-s_1|-|t_2-s_2|}\frac{1}{(\Delta_1\Delta_2)^{1/2}}\left(\frac{\theta}{\sin\theta} - 1\right). \tag{32}$$

In order to evaluate this expression, we need a theorem on multiple integration; the theorem is:

$$\int_0^\beta dx_n \int_0^\beta dx_{n-1}\int_0^\beta dx_{n-2}\cdots\int_0^\beta dx_1 F(x_1, x_2, \ldots, x_n) = n!\int_0^\beta dx_n \int_0^{x_n} dx_{n-1}\int_0^{x_{n-1}} dx_{n-2}\cdots\int_0^{x_2} dx_1 F_S, \tag{33}$$

where F_s is the symmetrized F, which is defined by

$$F_s = \sum_P F(x_1, x_2, \ldots)/n!,$$

the $\sum_P$ means to sum over all the possible permutations of the arguments of the function F, that is,

$$F_s = \frac{1}{n!}[F(x_1, x_2, x_3, \ldots) + F(x_2, x_1, x_3, \ldots) + F(x_3, x_2, x_1, \ldots) + \cdots].$$

For our case, from Eq. (26), it can be easily found that $\langle W^2\rangle_v$ is symmetric under these interchanges: $s_1 \leftrightarrow t_1$, $s_2 \leftrightarrow t_2$, and $(s_1, t_1) \leftrightarrow (s_2, t_2)$ simultaneously. Therefore we have only three independent expressions in F_s; they are

$$F(s_1t_1s_2t_2),\ F(s_1s_2t_1t_2),\ \text{and}\ F(s_1t_2s_2t_1).$$

Hence we can write $\langle W^2\rangle_v - \langle W\rangle_v^2$ as

$$\langle W^2\rangle_v - \langle W\rangle_v^2 = \frac{\alpha^2}{8\pi}4!\int_0^\beta dt_2 \int_0^{t_2} ds_2 \int_0^{s_2} dt_1 \int_0^{t_1} ds_1 \tfrac{1}{3}[F(s_1t_1s_2t_2) + F(s_1s_2t_1t_2) + F(s_1t_2s_2t_1)], \tag{34}$$

where we assume $t_2 \geq s_2 \geq t_1 \geq s_1$. If we define

$$t_2 - s_2 = \hat{t},\quad s_2 - t_1 = \bar{t},\quad t_1 - s_1 = \tilde{t},$$

we can have $\Delta E_1^{(1)}$ equal to the first term of $(-1/2\beta)(\langle W^2\rangle_v - \langle W\rangle_v^2)$:

$$\Delta E_1^{(1)} = \frac{-\alpha^2}{\pi}\int_0^\infty d\tilde{t}\frac{e^{-\tilde{t}}}{(1-e^{-\Omega\tilde{t}})^{1/2}}\int_0^\infty d\hat{t}\frac{e^{-\hat{t}}}{(1-e^{-\Omega\hat{t}})^{1/2}}\left(1 + \ln 2 - \frac{\theta_0}{\sin\theta_0} - \ln(1+\cos\theta_0)\right), \tag{35}$$

where $\sin\theta_0 = \frac{1}{2}(1-e^{-\Omega\tilde{t}})^{1/2}(1-e^{-\Omega\hat{t}})^{1/2}$. $\Delta E_1^{(2)}$ equals the second term of $(-1/2\beta)(\langle W^2\rangle_v - \langle W\rangle_v^2)$:

$$\Delta E_1^{(2)} = \frac{-\alpha^2}{\pi}\Omega\int_0^\infty d\tilde{t}\, e^{-\tilde{t}}\int_0^\infty d\hat{t}\, e^{-\hat{t}}\int_0^\infty d\bar{t}\, e^{-2\bar{t}}\frac{(\theta_2/\sin\theta_2 - 1)}{(1-e^{-\Omega(\bar{t}+\tilde{t})})^{1/2}(1-e^{-\Omega(\bar{t}+\hat{t})})^{1/2}}. \tag{36}$$

$\Delta E_1^{(3)}$ equals the third term of $(-1/2\beta)(\langle W^2\rangle_v - \langle W\rangle_v^2)$:

$$\Delta E_1^{(3)} = \frac{-\alpha^2}{\pi}\,\Omega \int_0^\infty d\hat{t}\, e^{-\hat{t}} \int_0^\infty d\hat{t}\, e^{-\hat{t}} \int_0^\infty d\bar{t}\, e^{-2\bar{t}} \frac{(\theta_3/\sin\theta_3 - 1)}{[(1-e^{-\Omega(\bar{t}+\hat{t}+\hat{t})})(1-e^{-\Omega\bar{t}})]^{1/2}} \,. \tag{37}$$

Now, we arrive at the final result for second-order semi-invariant correction; the correction is

$$\Delta E = (\Delta E_1^{(1)} + \Delta E_1^{(2)} + \Delta E_1^{(3)}) + \Delta E_2 + \Delta E_3 \,. \tag{38}$$

Recalling that for $\alpha < \alpha_C = 5.8$, $\Omega = 0$ is the best choice. In this case ($\Omega = 0$), we have $\Delta E_1^{(1)} = \Delta E_2 = \Delta E_3 = 0$, and $\Delta E_1^{(2)}$ and $\Delta E_1^{(3)}$ reduce to

$$\Delta E_1^{(2)} = -\frac{\alpha^2}{\pi} \int_0^\infty d\hat{t}\, e^{-\hat{t}} \int_0^\infty d\bar{t}\, e^{-\bar{t}} \int_0^\infty d\bar{t}\, e^{-2\bar{t}} \frac{(\theta_2'/\sin\theta_2' - 1)}{[(\bar{t}+\hat{t})(\bar{t}+\hat{t})]^{1/2}} \,, \tag{39}$$

$$\Delta E_1^{(3)} = -\frac{\alpha^2}{\pi} \int_0^\infty d\hat{t}\, e^{-\hat{t}} \int_0^\infty d\bar{t}\, e^{-\bar{t}} \int_0^\infty d\bar{t}\, e^{-2\bar{t}} \frac{(\theta_3'/\sin\theta_3' - 1)}{[\bar{t}(\bar{t}+\hat{t}+\bar{t})]^{1/2}} \,, \tag{40}$$

where

$$\sin\theta_2' = -\frac{\bar{t}}{[(\bar{t}+\hat{t})(\bar{t}+\hat{t})]^{1/2}} \,,$$

$$\sin\theta_3' = \frac{(\bar{t})^{1/2}}{(\bar{t}+\hat{t}+\bar{t})} \,.$$

Therefore, for $\alpha \leq 5.8$, we have

$$\Delta E = \Delta E_1^{(2)} + \Delta E_1^{(3)} = -\alpha^2 \mathfrak{P} \,,$$

where $\mathfrak{P}$ is a pure number. We can evaluate this pure number by numerical integration, and it is equal to 0.0157. Therefore,

$$\Delta E = -0.0157\,\alpha^2 \,.$$

This result is superior to both that of Haga[6] and Lee and Pine[7]; Haga's result does not reduce to perturbation theory to order α^2 (when α is small). Feynman's result will reduce to that of Haga in the weak-coupling limit. Hohler[8] has done the straightforward fourth-order perturbation calculation, and our result agrees with that of Hohler. Hence in this limit the cumulant series generates the perturbation expansion.

Also for large α, from (18) we know the best choice of Ω is

$$\Omega \sim (4/9\pi)\alpha^2 \,.$$

By this value of Ω, we can obtain the approximate energy corrections: From (35), (36), and (37), we can have

$$\Delta E_1^{(1)} \sim \tfrac{1}{45}\,\alpha^2/\pi, \quad \Delta E_1^{(2)} \sim -\tfrac{1}{24}\,\alpha^2/\pi, \quad \Delta E_1^{(3)} \sim -\tfrac{1}{48}\,\alpha^2/\pi \,,$$

respectively.

Also, from (23) and (25), one can easily obtain

$$\Delta E_2 \sim \alpha^2/6\pi, \quad \Delta E_3 \sim -\tfrac{1}{12}\,\alpha^2/\pi \,.$$

Therefore, in the strong-coupling limit, the energy correction is given by

$$\Delta E = (\Delta E_1^{(1)} + \Delta E_1^{(2)} + \Delta E_1^{(3)}) + \Delta E_2 + \Delta E_3 \simeq -\tfrac{1}{720}\,\alpha^2/\pi \,.$$

This means the coefficient of α^2 is corrected to

$$E + \Delta E = -(\alpha^2/3\pi)(1 + \tfrac{1}{240}) \simeq -0.1066\,\alpha^2 \,.$$

The coefficient of α^2 is 0.4–0.5% lower than that of our previous result. (That is, $-1/3\pi$: This is also Feynman's result.) The ratio of our corrected coefficient to that of Pekar's is 0.980. Comparing with 0.974 which is the ratio of Feynman's to Pekar's, there is a small improvement.

A summary of results of our work and that of other authors is given in Table II (in both the weak- and strong-coupling limits). In Table III, a comparison between our results, with the second order semi-invariant term added, and Feynman's is given. The second-order energy correction was also carried out by Marshall and Mills[9] in Feynman's harmonic model; their sec-

TABLE II. Polaron energy.

For small α:	
$-\alpha$	Lee and Pines; Gurari
$-\alpha$	Fröhlich, Pelzer, and Zierau
$-\alpha - 0.0123\alpha^2$	Feynman
$-\alpha - 0.0126\alpha^2$	Haga
$-\alpha - 0.0140\alpha^2$	Lee *et al.*
$-\alpha - 0.0157\alpha^2$	Hohler
$-\alpha - 0.0157\alpha^2$	Luttinger and Lu
$-\alpha - 0.0159\alpha^2$	Marshall and Mills
For large α:	
$-0.1085\alpha^2$	Pekar
$-0.1085\alpha^2$	Luttinger and Lu (ground-state approx.)
$-0.1085\alpha^2 - \frac{3}{2}$	Pekar, Bogolubov, and Tyablikov
$-0.1061\alpha^2 - \frac{3}{2}(2\ln 2 + \bar{C}) - \frac{3}{4}$	Feynman
$-0.1066\alpha^2 - 3/2(2\ln 2 + \bar{C})$	Luttinger and Lu (harmonic inter. approx.)
$-0.106\alpha^2 - 3/2$	Höhler
$-0.1078\alpha^2$	Marshall and Mills

TABLE III. Plaron energy: Comparison between Feynman's result and Luttinger and Lu's model with second-order semi-invariant term.

α	1	3	5	7	9	11
ν		3.44	4.02	5.81	9.85	15.50
ω		2.55	2.13	1.60	1.28	1.15
E_f	−1.012	−3.13	−5.44	−8.11	−11.48	−15.71
Ω	0.0	0.0	0.0	3.95	8.45	14.30
E_{LL}	−1.00	−3.00	−5.00	−7.36	−10.72	−15.00
ΔE_{LL}	−0.016	−0.14	−0.40	−0.65	−0.84	−1.305
$E_{LL}+\Delta E_{LL}$	−1.016	−3.14	−5.40	−8.01	−11.56	−16.31

ond-order correction is larger than our model of harmonic approximation, as it should be.

VI. DISCUSSION AND SUMMARY

The problem of polaron has received considerable attention in the past years, many authors conjectured that there might be a critical coupling constant α_c (Refs. 10 and 11); when α exceeds this critical value ($\alpha_c \sim 5.8$), the wave function abruptly shrinks (self-traps), and the slope of $E(\alpha)$ changes discontinuously, although E is still a continuous function of the coupling constant α. By the path-integral representation of partition function, the problem of an electron moving in a random system is very similar to the polaron problem. By this close similarity and some other arguments, there is a long-standing conjecture about the possibility of a "phase transition" between localized states and extended states. Our model is very similar to the path-integral method of Feynman which gives nondiscontinuous curve of $E'(\alpha)$, but our method indeed has the discontinuity phenomenon at $\alpha \sim 5.8$. Gross[12] has suggested that the transition between the localized and extended function is abrupt. This abrupt change seems to be a common feature of several approaches. But, because Feynman's treatment is the most successful overall theory of polaron, therefore, it is still an unanswered theoretical question—whether this feature is a property of the general type or if it just comes from approximation.

Our theory is a variational method; hence any choice of trial potential or wave function will give an upper bound of the exact answer. According to the previous work of many other authors and our experience, the harmonic interaction potential seems to be the most reasonable, exactly soluble potential form. Fröhlich[13] has used the wave function appropriate to the lowest-energy state of an electron in a Coulomb potential in Pekar's approximation; the wave function has the form:

$$(\beta^3/8\pi)^{1/2}\exp(-\tfrac{1}{2}\beta|\vec{x}|)\,.$$

It is found the best value is when $\beta=5\alpha/8$ and the corresponding value for energy is

$$E=-0.0977\,\alpha^2\,.$$

In addition, Allcock[14] has shown in ground-state approximation (Pekar's theory), "harmonic oscillator's wave function" or "improved Gaussian wave function" gives a better result than that of the Coulomb potential wave function. Also, Matsuura[15] formulates the problem by path-integral representation with an effective local Hamiltonian (Feynman's model and our model have a two-time-difference retarded effective Hamiltonian) which is not translationally invariant. This effective potential method gives the same result as that obtained from second-order perturbation theory.[16] Matsuura takes his choice of effective potential as Coulomb potential, the results show that the Coulomb potential is inferior to that of harmonic potential. Clearly the calculation based on a harmonic potential will be reasonably satisfactory if the exact potential and harmonic potential agree wherever the electron's wave function is large, and it is indeed so as shown by Allcock.

According to our model, the most general expression of the polaron energy is given by:

$$E_0 \leq \langle u_0|\vec{p}^2/2\mu|u_0\rangle - \langle W\rangle_v/\beta\,,$$

$$[\vec{p}^2/2\mu+v(\vec{\xi})]u_n(\vec{\xi})=\epsilon_n u_n(\vec{\xi})\,,$$

where $\langle W\rangle_v$ is given by Eq. (9) or Eq. (9′). Our formalism is translationally invariant. By ignoring this translational invariance, our formalism can be reduced to the same equation and energy results as that of the Green's-function equation of motion analysis by Matz *et al.*[17] and the effective local Hamiltonian theory of Haken[18] and Matsurra.[15]

Although it is too complicated to get the expression of the self-consistent potential in a closed form, we suggest some iterative procedure, which might be very tedious, but can be done in principle. This work is underway at present; the result will be reported elsewhere.

By the experience from the harmonic interaction potential approximation, it is noticed that the higher excited states contribute only to the constant term (α^0, the fluctuation energy term); it should be a good start by first taking the ground-state approximation. From this approximation, we have the self-consistent potential as the following:

$$v_0(\vec{\xi}) = \frac{-\alpha\sqrt{2}}{\mu} \int d\vec{\xi}' \frac{|u_0(\vec{\xi}')|^2}{|\vec{\xi} - \vec{\xi}'|} (1 - e^{-2C|\vec{\xi}-\vec{\xi}'|}).$$

Using this numerical self-consistent potential as the starting potential, we may calculate the excited wave functions $u_n(\vec{\xi})$ from the Schrödinger equation. By these higher excited states, we can estimate an improved value for $\langle W\rangle_v$ by every given μ. We guess the self-consistent potential appropriate to the polaron problem must be like a Coulomb potential at large distances and like the harmonic potential in the region where the electron wave function is large.

Using our model, it is easy to connect Pekar's result to our theory, which is difficult to see in Feynman's formulation. And it is shown clearly and explicitly that the higher excited states will contribute to the fluctuation energy. This model is not restricted to the harmonic approximation, although it is a pretty good one; in principle, any kind of trial potential is possible, and the best one certainly will be the self-consistent one. In order to see the order of magnitude of the errors which might occur due to the Jensen's inequality, this model is particularly easy to evalute the second-order semi-invariant correction explicitly.

APPENDIX: EVALUATION OF $\langle W\rangle_v$ BY SUMMING OVER COMPLETE STATES OF HARMONIC OSCILLATOR

From Eq. (9′), we write

$$\langle W\rangle_v = \frac{\alpha\beta}{\sqrt{2}\mu} \sum_{n=0}^{\infty} G_n .$$

Because we are dealing with a three-dimensional case, the quantum number n actually is a triplet $(n_1, n_2, n_3) \equiv (\sigma)$, and let us define $n_1 + n_2 + n_3 = N$. Hence

$$G_\sigma = 4C^2 \int \frac{d\vec{k}}{2\pi^2} \frac{1}{k^2(k^2 + b_\sigma^2)} |I_{n_1}|^2 |I_{n_2}|^2 |I_{n_3}|^2 , \qquad \text{(A1)}$$

where we define

$$I_{n_i} = \int_{-\infty}^{+\infty} u_{n_i}(\xi_i) u_0(\xi_i) e^{ik_i\xi_i} d\xi_i , \quad i = 1, 2, 3. \qquad \text{(A2)}$$

If $v(\vec{x} - \vec{R}) = \frac{1}{2}K(\vec{x} - \vec{R})^2$, then

$$u_0(\vec{\xi}) = \left(\frac{\mu\Omega}{\pi}\right)^{3/4} e^{-\mu\Omega\xi^2/2} ,$$

$$u_{(\sigma)} = \left(\frac{\mu\Omega}{\pi}\right)^{3/4} \left(\frac{2^{-(n_1+n_2+n_3)}}{n_1! n_2! n_3!}\right) \times e^{-\mu\Omega\xi^2/2} H_{n_1}(\sqrt{\mu\Omega}\xi_1) H_{n_2}(\sqrt{\mu\Omega}\xi_2) H_{n_3}(\sqrt{\mu\Omega}\xi_3) ,$$

where

$$\omega = \sqrt{K/M} , \text{ and } \Omega = \sqrt{K/\mu} .$$

By the Fourier cosine and sine transform identity, we have

$$\int_{-\infty}^{+\infty} \cos(yx) e^{-x^2} H_{2n}(x) dx = \pi^{1/2} y^{2n} e^{-y^2/4} ,$$

$$\int_{-\infty}^{+\infty} \sin(yx) e^{-x^2} H_{2n+1}(x) dx = (-\pi^{1/2}) y^{2n+1} e^{-y^2/4} ,$$

and

$$I_{n_1} = \begin{cases} \left(\dfrac{1}{2^{n_1} n_1!}\right)^{1/2} (-i) y_1^{n_1} e^{-y_1^2/4} , & n_1 \text{ odd} \\ \left(\dfrac{1}{2^{n_1} n_1!}\right)^{1/2} y_1^{n_1} e^{-y_1^2/4} , & n_1 \text{ even}. \end{cases}$$

Therefore

$$|I_{n_1}|^2 = \frac{1}{2^{n_1} n_1!} y_1^{2n_1} e^{-y_1^2/2}$$

for n_1 even or odd. We have defined $y_i \equiv k_i / \sqrt{\mu\Omega}$. So

$$\begin{aligned} G_{(\sigma)} &= \frac{2^{-N}}{n_1! n_2! n_3!} \left(\frac{4C^2}{2\pi^2}\right) \int d\vec{k} e^{-y^2/2} \frac{y_1^{2n_1} y_2^{2n_2} y_3^{2n_3}}{k^2(k^2 + b_\sigma^2)} , \\ \langle W\rangle_v &= \frac{\alpha\beta}{\sqrt{2}\mu} \sum_\sigma G_\sigma \\ &= \frac{\alpha\beta}{\sqrt{2}\mu} \frac{8C^2}{\pi} \int_0^\infty dk\, e^{-y^2/2} \sum_{n_1 n_2 n_3} \frac{2^{-N}}{n_1! n_2! n_3!} \int_0^\infty dt\, y_1^{2n_1} y_2^{2n_2} y_3^{2n_3} e^{-(b_\sigma^2 + k^2)t} . \end{aligned} \qquad \text{(A3)}$$

Since b_σ^2 is proportional to N, which is the sum of n_1, n_2, n_3, we try to make it as a product of n_1, n_2, n_3, so we use the identity

$$\frac{1}{k^2 + b_\sigma^2} = \int_0^\infty dt\, e^{-(k^2 + b_\sigma^2)t}$$

to separate n_1, n_2, n_3, by writing

$$b_\sigma^2 = 4C^2(\Delta\epsilon_\sigma + 1) = 4C^2\Omega N + 4C^2\,,$$

$$\begin{aligned}\langle W\rangle_v &= \frac{\alpha\beta}{\sqrt{2}\mu}\frac{8C^2}{\pi}\int_0^\infty dt\int_0^\infty dk\, e^{-y^2/2-(4C^2+k^2)t}\prod_{i=1}^{3}\left(\sum_{n_i}\frac{[\frac{1}{2}y_i\exp(-4C^2\Omega n_i t)]^{n_i}}{n_i!}\right)\\ &= \frac{\alpha\beta}{\sqrt{2}\mu}\frac{8C^2}{\pi}\int_0^\infty dt\int_0^\infty dk\, e^{-y^2/2-(4C^2+k^2)t}\prod_{i=1}^{3}[\exp(-y_i^2 e^{-4C^2\Omega t/2})]\\ &= \frac{\alpha\beta}{\sqrt{2}\mu}\frac{8C^2}{\pi}\int_0^\infty e^{-4C^2t}\,dt\int_0^\infty dk\exp\left[-\left(t+\frac{(1-e^{-4C^2\Omega t})}{2\mu\Omega}\right)k^2\right]\\ &= \frac{\alpha\beta}{\sqrt{2}\mu}4C^2\left(\frac{2\mu\Omega}{\pi}\right)^{1/2}\int_0^\infty dt\frac{e^{-4C^2t}}{(1+2\mu\Omega t-e^{-4C^2\Omega t})^{1/2}}\,.\end{aligned} \tag{A4}$$

Therefore,

$$\begin{aligned}\frac{\langle W\rangle_v}{\beta} &= \alpha\Omega\left(\frac{1}{\sqrt{\pi}}\right)\int_0^\infty dt\frac{e^{-t}}{\{\omega^2 t+[(\Omega^2-\omega^2)/\Omega](1-e^{-\Omega t})\}^{1/2}}\\ &= A(\Omega,\ \omega)\,.\end{aligned} \tag{A5}$$

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