Ground-state energy of an exciton-(LO) phonon system in two and three dimensions: General outline and three-dimensional case

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This paper presents a variational study of the ground-state energy of an exciton-phonon system in two or three spatial dimensions. The exciton-phonon interaction is of Fröhlich type. Making use of functional-integral techniques, the phonon part of the problem can be eliminated exactly, leading to an effective two-particle problem, which has the same spectral properties as the original one. Subsequently, we apply Jensen's inequality to obtain upper bounds on the ground-state energy. The paper has two major intentions: First, we demonstrate for the problem under consideration that one can profitably use a nonharmonic trial action within the functional-integral framework. The corresponding variational bounds on the ground-state energy compare favorably with all previous ones. Second, we show that the lowest bound is an analytical function of the electron-phonon coupling parameter and completely smooth throughout the whole parameter region. This is in contrast to previous variational findings, but consistent with rigorous qualitative results for the true ground-state energy. [S0163-1829(96)07942-8]

I. INTRODUCTION

This paper and a following one are concerned with a detailed discussion of the exciton-(LO) phonon problem and, in particular, with the dimensional dependence of the ground-state energy. Because of the enormous amount of literature on this subject (see Sec. VI) there may be some need to clarify the motivation for this new attempt.

To begin with, we mention the controversially discussed question of a delocalization-localization transition in systems of Fröhlich type. Is it possible that energies, wave functions, effective masses, etc., are nonanalytic functions of the electron-phonon coupling parameter? Based on a pioneering paper of Fröhlich,[1] this possibility was excluded for a large class of models: an exciton-(LO) phonon system cannot show phenomenona such as self-trapping or mass stripping. The corresponding proof (see Gerlach and Löwen[2]) is a qualitative one, based on abstract methods of operator analysis. A quantitative calculation of, e.g., the ground-state energy proceeds along different lines; it has to rely on approximation procedures, mostly of variational type. Interestingly enough, many of the corresponding papers do report a phase-transition-like behavior (again, see Sec. VI). In view of the quoted rigorous results one has to conclude that a nonanalytic behavior of an approximate expression for the ground-state energy is an artifact of the approximations made. Without underestimating the merits of the corresponding variational calculations as such, one has to reexamine their results for the critical values of the coupling parameters. In Sec. VI, we present variational results, which are completely smooth and compare favorably with all previous ones.

We shall employ the functional-integral method, combined with a variational ansatz. Functional integration was of particular importance in this field. Haken[3] realized as early as 1957 that Feynman's famous treatment[4] of the polaron problem could be generalized to the case of excitons. The main advantage of this approach is that all exciton observables can be derived from an effective two-particle system, the phonon degrees of freedom being eliminated without any approximation. The corresponding two-particle action is highly suggestive and allows for a direct analysis in limiting cases (see Sec. III). On the other hand, functional integration has an inherent disadvantage: Only very few integrals can be evaluated in closed analytical form; the most important ones are Gaussian integrals for arbitrary spatial dimension. The present functional integral does not admit an analytical solution. It is exactly at this point that variational methods come into the game. At first glance, the flexibility for the choice of variational actions seems to be insufficient—even the constituents of a free exciton are bound within a Coulomb potential, not to mention the phonon-induced interaction. One has to recall, however, that a pure Coulomb action can be transformed into an oscillator action in four dimensions (see, e.g., the work of Duru and Kleinert[5] and Ho and Inomata[6]) — the use of functional-integral methods is compatible with a correct treatment of the Coulomb potential. We shall extensively use this fact in Sec. IV; our ansatz action (17) contains Coulombic terms, too. As for the treatment of electron-phonon interactions, the method of functional integration is known to be ideally suited. Combining these facts, it is not too surprising that we can find an excellent trial action in a variational sense (see Sec. IV below).

II. FORMALIZED STATEMENT OF THE PROBLEM

In the following three sections (II–IV), the spatial dimension D is a parameter; if not explicitly stated otherwise, all equations are valid for $D=2$ and $D=3$.

We start with Fröhlich's Hamiltonian, generalized for the interaction of an electron and a hole with a LO-phonon branch (see, e.g., Haken[3]):

$$H:=\sum_{n=1}^{2}\frac{p_n^2}{2m_n}-\frac{\overline{e^2}}{\epsilon_\infty|\vec{q}_1-\vec{q}_2|}+\sum_{\vec{k}}\hbar\omega a_{\vec{k}}^{\dagger}a_{\vec{k}}+\sum_{n=1}^{2}(-1)^n\sum_{\vec{k}}\left\{\frac{g_{\vec{k}}}{\sqrt{V}}e^{i\vec{k}\vec{q}_n}a_{\vec{k}}+\text{H.c.}\right\}. \tag{1}$$

$n=1,2$ refers to electron and hole, $\vec{p}_n$, $\vec{q}_n$, and m_n are the corresponding momentum and position operators and band masses, and ϵ_0 and ϵ_∞ are the low- and high-frequency limits of the dielectric function. To avoid confusion with electrodynamic units — the permittivity of free space is usually abbreviated as ϵ_0, as well — we absorbed the latter one into our definition of the charge: $\overline{e^2}:=e^2/4\pi\epsilon_0$, e being the hole charge. Furthermore, $a_{\vec{k}}$ and $a_{\vec{k}}^{\dagger}$ are the annihilation and creation operators for phonons with wave vector $\vec{k}$ and dispersion $\omega_{\vec{k}}\equiv\omega$; V is the quantization volume. Finally, the coupling $g_{\vec{k}}$ is connected with $\vec{k}$ and spatial dimension $D=2,3$ as follows:

$$g_{\vec{k}}:=\frac{\sqrt{D-1}g}{k^{\frac{D-1}{2}}},\quad g:=-i\sqrt{\pi\overline{e^2}\hbar\omega\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)}. \tag{2}$$

We remark that the particle-phonon coupling strength can be characterized by the dimensionless parameter

$$\alpha_m:=\frac{\overline{e^2}}{2\hbar\omega}\sqrt{\frac{2m\omega}{\hbar}}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right), \tag{3}$$

m being the particle mass.

The spectral properties of Hamiltonian (1) can conveniently be derived from the diagonal element of the reduced density matrix

$$\rho(\vec{a}_1,\vec{a}_2,\beta):=\text{Tr}_{\text{ph}}\langle\vec{a}_1,\vec{a}_2|e^{-\beta H}|\vec{a}_1,\vec{a}_2\rangle,\quad \beta>0, \tag{4}$$

where $|\vec{a}_1,\vec{a}_2\rangle$ are eigenvectors of $\vec{q}_1$, $\vec{q}_2$ with eigenvalues $\vec{a}_1$, $\vec{a}_2$. The phonon trace can be evaluated (see Feynman and Hibbs[7]). This yields

$$\rho(\vec{a}_1,\vec{a}_2,\beta)=Z_{\text{ph}}\int\int_{\vec{R}_n(0)=\vec{R}_n(\beta)=\vec{a}_n}\delta^D R_1\delta^D R_2\times\exp\{-S[\vec{R}_1,\vec{R}_2]\}. \tag{5}$$

Equation (5) introduces a functional integral. The integration has to be done over all real D-dimensional paths $\vec{R}_n(\tau)$ with fixed end points $\vec{R}_n(0)=\vec{R}_n(\beta)=\vec{a}_n$. Z_{ph} is the partition function for free phonons,

$$Z_{\text{ph}}:=\prod_{\vec{k}}(1-\exp\{-\beta\hbar\omega\})^{-1}, \tag{6}$$

and the action $S[\vec{R}_1,\vec{R}_2]$ reads as follows:

$$\begin{aligned}S[\vec{R}_1,\vec{R}_2]:=&\int_0^\beta d\tau\left\{\sum_{n=1}^{2}\frac{m_n}{2}\dot{\vec{R}}_n^{\,2}(\tau)+U_C(\vec{R}_1(\tau)-\vec{R}_2(\tau))\right\}\\&-\sum_{n,n',\vec{k}}(-1)^{n+n'}\frac{|g_{\vec{k}}|^2}{V}\int_0^\beta\int_0^\beta d\tau d\tau'\\&\times G(\tau-\tau')e^{i\vec{k}\cdot[\vec{R}_n(\tau)-\vec{R}_{n'}(\tau')]}\\&=:S_0[\vec{R}_1,\vec{R}_2]+S_I[\vec{R}_1,\vec{R}_2].\end{aligned} \tag{7}$$

$S_0[\vec{R}_1,\vec{R}_2]$ characterizes a free exciton (first line on the right-hand side), and $S_I[\vec{R}_1,\vec{R}_2]$ contains all phonon-induced modifications (second line on the right-hand side). $G(\tau)$ is defined as

$$G(\tau):=\frac{e^{(\beta-|\tau|)\hbar\omega}+e^{|\tau|\hbar\omega}}{2(e^{\beta\hbar\omega}-1)},\quad \tau\in[-\beta,\beta]. \tag{8}$$

Furthermore, we introduced

$$\dot{\vec{R}}_n(\tau):=\frac{1}{\hbar}\frac{\partial\vec{R}_n(\tau)}{\partial\tau},\quad U_c(\vec{r}):=-\frac{\overline{e^2}}{\epsilon_\infty r}. \tag{9}$$

Because of $G(\tau)=G(\tau-\beta)$ for $0<\tau<\beta$, $G(\tau)$ can be periodically continued with period β and represented as a Fourier series:

$$G(\tau)=\frac{\hbar\omega}{\beta}\sum_n\frac{e^{i\Omega_n\tau}}{\Omega_n^2+\hbar^2\omega^2},\quad \Omega_n=\frac{2\pi n}{\beta}. \tag{10}$$

Equations (5)–(9) clearly state the remaining problem: We have to discuss the density matrix of an effective two-particle system. This exhibits the same spectral properties as the original electron-hole-phonon system. The effects of the particle-phonon interaction are completely incorporated into the additional action S_I, containing self-energy contributions ($n=n'$) as well as corrections to the Coulomb potential between electron and hole ($n\neq n'$). All terms are ''noninstantaneous.''

In the remainder of this article, we shall specifically be concerned with the ground-state energy E_0. Consequently, we have to evaluate

$$\lim_{\beta\to\infty}\left(-\frac{1}{\beta}\ln\rho(\vec{a}_1,\vec{a}_2,\beta)\right)=E_0, \tag{11}$$

the left-hand side being independent of the positions $\vec{a}_n$.

It will prove useful to introduce center-of-mass and relative coordinates $\vec{R}$ and $\vec{r}$ instead of $\vec{R}_1$ and $\vec{R}_2$ in the familiar way. To complete our notational conventions, we add the corresponding formulae; instead of Eqs. (5) and (7) one may use the equivalent expressions

$$\rho(\vec{a},\vec{A},\beta)=Z_{\text{Ph}}\int\int_{\substack{\vec{R}(0)=\vec{R}(\beta)=\vec{A}\\ \vec{r}(0)=\vec{r}(\beta)=\vec{a}}}\delta^D R\,\delta^D r\exp\{-S[\vec{R},\vec{r}]\} \tag{12}$$

and

$$S[\vec{R},\vec{r}]=\int_0^\beta d\tau\left\{\frac{M}{2}\dot{\vec{R}}^2(\tau)+\frac{\mu}{2}\dot{\vec{r}}^2(\tau)+U_c(\vec{r}(\tau))\right\}$$
$$-\sum_{n,n',\vec{k}}(-1)^{n+n'}\frac{|g_{\vec{k}}|^2}{V}\int_0^\beta\int_0^\beta d\tau d\tau'$$
$$\times G(\tau-\tau')e^{i\vec{k}[\vec{R}(\tau)-\vec{R}(\tau')+\gamma_n\vec{r}(\tau)-\gamma_{n'}\vec{r}(\tau')]}$$
$$=S_0[\vec{R},\vec{r}]+S_I[\vec{R},\vec{r}]. \quad (13)$$

In Eq. (13), we defined

$$M:=m_1+m_2,\quad \mu:=\frac{m_1m_2}{M},\quad \gamma_1:=\frac{m_2}{M},\quad \gamma_2:=-\frac{m_1}{M}. \quad (14)$$

III. QUALITATIVE DISCUSSION OF THE PHONON-INDUCED MODIFICATIONS OF THE EXCITON

To begin with, we show that the effective two-particle system, characterized by the action (7), has a lower ground-state energy than a free exciton. To prove this, we insert the Fourier decomposition (10) of the kernel $G(\tau)$ into expression (7) for the action $S_I[\vec{R}_1,\vec{R}_2]$ and find

$$S_I[\vec{R}_1,\vec{R}_2]=-\frac{1}{V}\sum_{k,m}\frac{\hbar\omega}{\beta}\frac{|g_{\vec{k}}|^2}{(\hbar\omega)^2+\Omega_m^2}$$
$$\times\left|\sum_n(-1)^n\int_0^\beta d\tau e^{i[\vec{k}\cdot\vec{R}_n(\tau)+\Omega_m\tau]}\right|^2<0, \quad (15)$$

independently of the detailed functional form of the coupling.

In limiting cases, we can proceed further. Again, we make direct use of formula (7) for $S_I[\vec{R}_1,\vec{R}_2]$. For given values of $\hbar\omega$, β and $R_\infty=\mu\overline{e^2}/2\hbar^2\epsilon_\infty^2$, we consider the following cases.

$\hbar\omega\gg R_\infty,\beta^{-1}$. For a moment, let us concentrate on the nondiagonal terms in S_I. Under the specified conditions, $\hbar\omega G(\tau)$ approaches a delta function $\delta(\tau)$. Inserting this in formula (7) and using the explicit expressions (2) for the coupling, we can perform the $\vec{k}$ integration and find

$$U_{\mathrm{eff}}(\vec{R}_1,\vec{R}_2):=-\frac{\overline{e^2}}{\epsilon_0|\vec{R}_1-\vec{R}_2|} \quad (16)$$

for the total electron-hole interaction. In addition, S_I contains two polaronic self-energy terms. Summarizing, we may view the total system as a two-polaron system, the constituents being bound by a statically screened Coulomb potential. We shall analytically confirm this picture of a so-called ‘‘polaronic exciton’’ in the Appendix.

$R_\infty\gg\hbar\omega,\beta^{-1}$. Under this assumption the Coulomb contribution to the binding energy is the dominant one and neighboring paths $\vec{R}_1(\tau)\sim\vec{R}_2(\tau)$ will be most important for the evaluation of the functional integral. Inspection of Eq. (7) shows that S_I will vanish under these circumstances. We are left with a free, the so-called bare exciton, S being replaceable by S_0. Again, we shall analytically confirm this result in the Appendix.

IV. UPPER BOUNDS FOR THE GROUND-STATE ENERGY

The essential tool to derive lower bounds for the reduced density matrix and, correspondingly, upper bounds for the ground-state energy is Jensen's inequality. As for a general formulation, we refer to the textbook of Reed and Simon;[8] a specialized version will follow below. As in any variational approach, we have to start from a sufficiently flexible trial ansatz. Here, we propose

$$\tilde{S}[\vec{R},\vec{r}]:=\int_0^\beta d\tau\left\{\frac{\mu}{2}\dot{\vec{r}}^2(\tau)+U(\vec{r}(\tau))\right\}+\int_0^\beta d\tau\frac{M}{2}\dot{\vec{R}}^2(\tau)$$
$$+\int_0^\beta\int_0^\beta d\tau d\tau' f(\tau-\tau')\vec{R}(\tau)\vec{R}(\tau')$$
$$=:\tilde{S}_1[\vec{r}]+\tilde{S}_2[\vec{R}], \quad (17)$$

wherein $U(\vec{r})$ and $f(\tau)$ are to be chosen appropriately; $U(\vec{r})$ is to model the relative motion of the phonon-dressed electron and hole, and $f(\tau)$ characterizes the center-of-mass motion. We assume that $U(\vec{r})$ admits of an isolated ground state and stress that there is no restriction to a quadratic form; in fact, we shall finally choose an expression of Coulomb type. The center-of-mass motion, in turn, is modeled by a quadratic action. The reason is that this part of the motion should be free-polaron-like; in this case a quadratic action is known to be an excellent approximation. $f(\tau)$ can be assumed to be a symmetrical function; furthermore, translational invariance must hold. We meet both conditions, if we admit only functions which fulfill

$$f(\tau)=f(-\tau),\quad \int_0^\beta d\tau' f(\tau-\tau')=0 \text{ for any } \tau,\quad 0\leqslant\tau\leqslant\beta. \quad (18)$$

We mention that the latter condition implies that

$$f(\tau)=f(\tau-\beta)\text{ for any }\tau,\quad 0\leqslant\tau\leqslant\beta, \quad (19)$$

is true. To proceed further, let us introduce the abbreviation

$$\langle A\rangle_{\tilde{S}}:=\frac{\int_C\delta^DR\,\delta^Dr\exp\{-\tilde{S}[\vec{R},\vec{r}]\}A[\vec{R},\vec{r}]}{\int_C\delta^DR\,\delta^Dr\exp\{-\tilde{S}[\vec{R},\vec{r}]\}}, \quad (20)$$

where C is a shortcut characterization of the domain of integration [in our case $\vec{R}(0)=\vec{R}(\beta)=\vec{A}$, $\vec{r}(0)=\vec{r}(\beta)=\vec{a}$]. In analogy to Eq. (20) we define expectation values with respect to $\tilde{S}_1$ and $\tilde{S}_2$. Then, we may rewrite

$$\rho(\vec{a},\vec{A},\beta)=Z_{\mathrm{ph}}\langle e^{-(S-\tilde{S})}\rangle_{\tilde{S}}\int_C\delta^DR\,\delta^Dr\exp\{-\tilde{S}[\vec{R},\vec{r}]\}. \quad (21)$$

Let us now apply Jensen's inequality in the specialized version

$$\langle e^{-(S-\tilde{S})}\rangle_{\tilde{S}} \geqslant e^{-\langle S-\tilde{S}\rangle_{\tilde{S}}}. \tag{22}$$

We arrive at the inequality

$$\rho(\vec{a},\vec{A},\beta) \geqslant Z_{\text{ph}} e^{-\langle S-\tilde{S}\rangle_{\tilde{S}}} \int_C \delta^D r\, \delta^D R\, e^{-\tilde{S}_1[\vec{r}]} e^{-\tilde{S}_2[\vec{R}]}. \tag{23}$$

All expressions on the right-hand side can be evaluated in closed form up to normal integrations. To begin with, we consider

$$\begin{aligned}\langle S-\tilde{S}\rangle_{\tilde{S}} &= \int_0^\beta d\tau \langle U_c(\vec{r}(\tau)) - U(\vec{r}(\tau))\rangle_{\tilde{S}_1} \\ &\quad - \int_0^\beta \int_0^\beta d\tau d\tau' f(\tau-\tau') \langle \vec{R}(\tau)\vec{R}(\tau')\rangle_{\tilde{S}_2} \\ &\quad - \sum_{n,n',\vec{k}} (-1)^{n+n'} \frac{|g_{\vec{k}}|^2}{V} \int_0^\beta \int_0^\beta d\tau d\tau' G(\tau-\tau') \\ &\quad \times \langle e^{i\vec{k}\cdot[\vec{R}(\tau)-\vec{R}(\tau')]}\rangle_{\tilde{S}_2} \langle e^{i\vec{k}\cdot[\gamma_n \vec{r}(\tau) - \gamma_{n'}\vec{r}(\tau')]}\rangle_{\tilde{S}_1}.\end{aligned} \tag{24}$$

First, we turn to the two functional integrals with respect to $\vec{R}$. They are both of Gaussian type and can be done according to the recipes given by, e.g., Adamowski, Gerlach, and Leschke.[9] To keep the results as compact as possible, let us introduce the Fourier transform of $f(\tau)$:

$$f(\tau) =: \sum_n f_n e^{i\Omega_n \tau}. \tag{25}$$

Furthermore, define

$$x_n := \frac{\Omega_n}{\hbar\omega} = \frac{2\pi n}{\beta\hbar\omega}, \quad \Delta x_n := \frac{2\pi}{\beta\hbar\omega}, \quad h(x_n) := \frac{2\beta f_n}{\omega^2 M}. \tag{26}$$

Then, one can prove

$$\begin{aligned} I_1 &:= \langle e^{i\vec{k}\cdot[\vec{R}(\tau)-\vec{R}(\tau')]}\rangle_{\tilde{S}_2} \\ &= \exp\left\{ -\frac{\hbar^2 k^2}{\pi M \hbar\omega} \sum_{n=1}^\infty \Delta x_n \frac{1-\cos[\hbar\omega x_n(\tau-\tau')]}{x_n^2 + h(x_n)} \right\}.\end{aligned} \tag{27}$$

The expectation value $\langle [\vec{R}(\tau)-\vec{R}(\tau')]^2\rangle_{\tilde{S}_2}$ can be derived from Eq. (27) as a second derivative with respect to $\vec{k}$ for $\vec{k}=0$. Integration with respect to τ,τ' will finally yield the second integral of interest:

$$\begin{aligned} I_2 &:= \frac{1}{\beta}\int_0^\beta \int_0^\beta d\tau d\tau' f(\tau-\tau') \langle \vec{R}(\tau)\vec{R}(\tau')\rangle_{\tilde{S}_2} \\ &= \left(\frac{D\hbar\omega}{2\pi}\right) \sum_{n=1}^\infty \Delta x_n \frac{h(x_n)}{h(x_n)+x_n^2}.\end{aligned} \tag{28}$$

We notice that one further integral in Eq. (23) can be derived from Eq. (28) by means of a parameter differentiation (for details, we refer again to Ref. 9). One finds

$$\begin{aligned} I_3 &:= -\frac{1}{\beta}\ln \int_{\vec{R}(0)=\vec{R}(\beta)=\vec{A}} \delta^D R \exp\{-\tilde{S}_2[\vec{R}]\} \\ &= \frac{D}{2\beta}\ln\frac{2\pi\beta\hbar^2}{M} + \frac{D\hbar\omega}{2\pi}\sum_{n=1}^\infty \Delta x_n \ln\left(1+\frac{h(x_n)}{x_n^2}\right).\end{aligned} \tag{29}$$

The reader should notice that the right-hand sides of Eqs. (27)–(29) have well-defined limits for $\beta\to\infty$. Then, x_n will turn into a continuous variable x with the domain $0\leqslant x \leqslant \infty$. We note the results for further use:

$$\lim_{\beta\to\infty} I_1 = \exp\left\{ -\frac{\hbar^2 k^2}{\pi M\hbar\omega} P(\hbar\omega(\tau-\tau'))\right\}, \tag{30}$$

where we introduced

$$P(y) := \int_0^\infty dx \frac{1-\cos(xy)}{x^2+h(x)}. \tag{31}$$

Furthermore,

$$\lim_{\beta\to\infty} I_2 = \frac{D\hbar\omega}{2\pi}\int_0^\infty dx \frac{h(x)}{x^2+h(x)} \tag{32}$$

and

$$\lim_{\beta\to\infty} I_3 = \frac{D\hbar\omega}{2\pi}\int_0^\infty dx \ln\left(1+\frac{h(x)}{x^2}\right). \tag{33}$$

Let us finally discuss the functional integrals with respect to $\vec{r}$, which are contained in Eqs. (23) and (24). We mentioned in the Introduction that they can be done directly. It will nevertheless prove useful to make a certain digression. In doing so, we generalize an idea of Haken.[3] The starting point is given by the useful formula[10]

$$\begin{aligned} &\frac{\langle \vec{a}| e^{-\beta H} T_\tau[A_1(\vec{q}(\tau_1))\cdots A_n(\vec{q}(\tau_n))]|\vec{a}\rangle}{\langle \vec{a}|e^{-\beta H}|\vec{a}\rangle} \\ &\quad = \langle A_1(\vec{r}(\tau_1))\cdots A_n(\vec{r}(\tau_n))\rangle_S.\end{aligned} \tag{34}$$

The left-hand side contains standard quantum-mechanical expectation values. H is a certain one-particle Hamiltonian, $A_i(\vec{q})$ a Schrödinger, $A_i(\vec{q}(\tau)) := e^{\tau H} A_i(\vec{q}) e^{-\tau H}$ the corresponding Heisenberg operator, and $\vec{a}$ an arbitrary particle position. The right-hand side is a path-integral expectation value in the sense of Eq. (20). The action S corresponds to H; the paths are closed, the starting and ending point being $\vec{a}$.

We shall now use Eq. (34) to reformulate the path integrals of interest. H is replaced by $\widetilde{H}:=p^2/2\mu+U(\vec{q})$, S by $\widetilde{S}_1$ according to Eq. (17). Let us denote the eigenfunctions and eigenvalues of $\widetilde{H}$ as $\widetilde{\phi}_\mu$ and $\widetilde{E}_\mu$. Restricting ourselves to the case $\beta\rightarrow\infty$, we can derive in a straightforward manner

$$\lim_{\beta\rightarrow\infty}\frac{1}{\beta}\int_0^\beta d\tau\langle U_c(\vec{r}(\tau))-U(\vec{r}(\tau))\rangle_{\widetilde{S}_1}=\langle\widetilde{\phi}_0|U_c-U|\widetilde{\phi}_0\rangle \tag{35}$$

and

$$\lim_{\beta\rightarrow\infty}\frac{1}{\beta}\sum_{n,n',\vec{k}}(-1)^{n+n'}\frac{|g_{\vec{k}}|^2}{V}\int_0^\beta\int_0^\beta d\tau d\tau' G(\tau-\tau')\langle e^{i\vec{k}\cdot[\vec{R}(\tau)-\vec{R}(\tau')]}\rangle_{\widetilde{S}_2}\langle e^{i\vec{k}\cdot[\gamma_n\vec{r}(\tau)-\gamma_{n'}\vec{r}(\tau')]}\rangle_{\widetilde{S}_1}$$
$$=\sum_{\vec{k}}\frac{|g_{\vec{k}}|^2}{V}\int_0^\infty du\ e^{-\hbar\omega u-(\hbar^2k^2/M\hbar\omega\pi)P(\hbar\omega u)}\sum\!\!\!\!\!\!\int_\mu\ e^{u(\widetilde{E}_0-\widetilde{E}_\mu)}\left|\sum_n(-1)^n\langle\widetilde{\phi}_0|e^{i\vec{k}\gamma_n\vec{q}}|\widetilde{\phi}_\mu\rangle\right|^2. \tag{36}$$

In Eq. (36), the combined summation-integration symbol needs a comment: Whenever a part of the spectrum of $\widetilde{H}$ is discrete (continuous), a summation (an integration) has to be done. In addition to Eqs. (35) and (36), we recall the equality

$$\lim_{\beta\rightarrow\infty}\left(-\frac{1}{\beta}\ln\int_{\vec{r}(0)=\vec{r}(\beta)=\vec{a}}\delta^D r\exp\{-\widetilde{S}_1[\vec{r}]\}\right)=\widetilde{E}_0. \tag{37}$$

Combining all results, we can now apply relations (11) and (23) for E_0. Inserting the results (30), (32), (33), and (35)–(37), we arrive at

$$\begin{aligned}E_0\leqslant{}&\widetilde{E}_0+\langle\widetilde{\phi}_0|U_c-U|\widetilde{\phi}_0\rangle\\&+\frac{D\hbar\omega}{2\pi}\int_0^\infty dx\left\{\ln\left(1+\frac{h(x)}{x^2}\right)-\frac{h(x)}{x^2+h(x)}\right\}\\&-\int d^Dk\left\{\frac{|g_{\vec{k}}|^2}{(2\pi)^D}\int_0^\infty du\exp\left\{-\hbar\omega u\right.\right.\\&\left.-\frac{\hbar^2k^2}{M\hbar\omega\pi}P(\hbar\omega u)\right\}\\&\left.\times\sum\!\!\!\!\!\!\int_\mu\ e^{u(\widetilde{E}_0-\widetilde{E}_\mu)}\left|\sum_n(-1)^n\langle\widetilde{\phi}_0|e^{i\vec{k}\gamma_n\vec{q}}|\widetilde{\phi}_\mu\rangle\right|^2\right\}.\end{aligned} \tag{38}$$

Equation (38) is the central result of this article. It is a direct generalization of the corresponding polaron formula, which was derived in Ref. 9.

We add two comments: (1) Setting $h(x)\equiv 0$, one finds a special bound on E_0, which was already published by Haken.[3] This proved to be poor for strong electron-phonon coupling (see our numerical results in Sec. VI). (2) Truncating the μ sum concerning the eigenstates of $\widetilde{H}$, one derives a new class of bounds on E_0, all of them being weaker than the present one. On the other hand, these can readily be evaluated and show a nonanalytical behavior (see Adamowski, Gerlach, and Leschke[11]).

Presently, it seems impossible to find the minimum of the above bound as functional of $f(\tau)$ and $U(\vec{r})$. Instead, we used Feynman's choice

$$h(x):=\frac{(v^2-w^2)x^2}{w^2+x^2} \tag{39}$$

to mimick the center-of-mass motion. Here, v and w ($v\geqslant w$) are variational parameters. We find

$$\int_0^\infty dx\left\{\ln\left(1+\frac{h(x)}{x^2}\right)-\frac{h(x)}{x^2+h(x)}\right\}=\frac{\pi}{2v}(v-w)^2, \tag{40}$$

$$P(y)=\frac{\pi}{2}\left\{\frac{w^2}{v^2}y+\frac{v^2-w^2}{v^3}(1-e^{-vy})\right\}. \tag{41}$$

Inserting Eqs. (40) and (41) into Eq. (38) and expanding the twofold exponential function, caused by the last term of $P(y)$, we arrive at

$$\begin{aligned}E_0\leqslant{}&\widetilde{E}_0+\langle\widetilde{\phi}_0|U_c-U|\widetilde{\phi}_0\rangle+\frac{D\hbar\omega}{4}\frac{(v-w)^2}{v}\\&-\sum_{m=0}^\infty\frac{1}{m!}\left(\frac{\hbar^2}{2M\hbar\omega}\frac{v^2-w^2}{v^3}\right)^m\int d^Dk\left\{\frac{|g_{\vec{k}}|^2}{(2\pi)^D}k^{2m}\right.\\&\times\exp\left\{-\frac{\hbar^2k^2}{2M\hbar\omega}\frac{v^2-w^2}{v^3}\right\}\int_0^\infty du\\&\times\exp\left\{-\left[\hbar\omega(1+mv)+\frac{w^2}{v^2}\frac{\hbar^2k^2}{2M}\right]u\right\}\\&\left.\times\sum\!\!\!\!\!\!\int_\mu\ e^{u(\widetilde{E}_0-\widetilde{E}_\mu)}\left|\sum_n(-1)^n\langle\widetilde{\phi}_0|e^{i\vec{k}\gamma_n\vec{q}}|\widetilde{\phi}_\mu\rangle\right|^2\right\}.\end{aligned} \tag{42}$$

One can verify that a new class of bounds can be found by truncation of the m summation. Inspection of Eq. (42) proves that all of these bounds are weaker than the present one; as for details see the numerical evaluation in the next section. We anticipate the result that every m truncation generates a nonanalytical bound.

Finally, we evaluate the u integration (formally) and find

$$E_0 \leqslant \widetilde{E}_0 + \langle \widetilde{\phi}_0 | U_c - U | \widetilde{\phi}_0 \rangle + \frac{D\hbar\omega}{4} \frac{(v-w)^2}{v}$$
$$- \sum_{m=0}^{\infty} \frac{1}{m!} \left(\frac{\hbar^2}{2M\hbar\omega} \frac{v^2-w^2}{v^3} \right)^m \int d^D k \Bigg\{ \frac{|g_k|^2}{(2\pi)^D} k^{2m}$$
$$\times \exp\left\{ -\frac{\hbar^2 k^2}{2M\hbar\omega} \frac{v^2-w^2}{v^3} \right\}$$
$$\times \sum_{n,n'} (-1)^{n+n'} \langle \widetilde{\phi}_0 | e^{i\vec{k}\gamma_n \vec{q}} (\widetilde{H}-z)^{-1} e^{-i\vec{k}\gamma_{n'}\vec{q}} | \widetilde{\phi}_0 \rangle \Bigg\}, \tag{43}$$

where we defined

$$z := \widetilde{E}_0 - \hbar\omega(1+mv) - \frac{w^2}{v^2} \frac{\hbar^2 k^2}{2M}. \tag{44}$$

Therefore, the remaining task is to specify U (or, equivalently, $\widetilde{H}$) and to calculate the matrix elements in Eq. (43). We choose

$$U(\vec{r}) = -\frac{\lambda \overline{e^2}}{\epsilon_\infty r}, \quad \lambda \geqslant 0. \tag{45}$$

λ is a variational parameter, which measures the effective strength of the potential. Clearly, this ansatz can model the limiting cases, which we discussed in Sec. III. Moreover, it will prove to be very effective for the intermediate-coupling regime.

As the eigenvalue problem of $\widetilde{H}$ is that of a (scaled) hydrogen problem, we can make use of the familiar solution. Concerning Eq. (43), we find

$$\widetilde{E}_0 + \langle \widetilde{\phi}_0 | U_c - U | \widetilde{\phi}_0 \rangle = \frac{4}{(D-1)^2} R_\infty (\lambda^2 - 2\lambda). \tag{46}$$

A much larger effort is needed to evaluate the quantity

$$\frac{64\mu a^2}{\hbar^2} F_m(k) := \sum_{n,n'} (-1)^{n+n'}$$
$$\times \langle \widetilde{\phi}_0 | e^{i\vec{k}\gamma_n \vec{q}} (\widetilde{H}-z)^{-1} e^{-i\vec{k}\gamma_{n'}\vec{q}} | \widetilde{\phi}_0 \rangle$$
$$= \sum_{n,n'} (-1)^{n+n'} \int \int d^D r d^D r' e^{i\vec{k}(\gamma_n \vec{r} - \gamma_{n'} \vec{r}')}$$
$$\times \langle \vec{r} | (\widetilde{H}-z)^{-1} | \vec{r}' \rangle \widetilde{\phi}_0^*(\vec{r}) \widetilde{\phi}_0(\vec{r}'), \tag{47}$$

which is needed in the last term on the right-hand side of Eq. (43). The reader will notice that we have to insert an expression for the Green function $\langle \vec{r} | (\widetilde{H}-z)^{-1} | \vec{r}' \rangle$. It is at this point that we have to distinguish between the cases $D=2$ and $D=3$. We start with the latter one, as we can profitably use important results from the previous literature.

V. THREE-DIMENSIONAL CASE

To the best of our knowledge, the first analytic expression for $\langle \vec{r} | (\widetilde{H}-z)^{-1} | \vec{r}' \rangle$ was given in a paper of Hostler and Pratt,[12] which in turn stimulated many others. Here, we use an expansion due to Zon, Manakov, and Rapoport:[13]

$$\langle \vec{r} | (\widetilde{H}-z)^{-1} | \vec{r}' \rangle = \sum_{l,m} g_l(r,r',z) Y_m^l(\Omega) Y_m^l(\Omega')^*, \tag{48}$$

$$g_l(r,r',z) := \frac{2\mu}{\hbar^2 \sqrt{rr'}} \int_0^\infty \Bigg[e^{[-(r+r')/\kappa a]\cosh(\alpha)}$$
$$\times \coth^{2\kappa}\left(\frac{\alpha}{2}\right) I_{2l+1}\left(\frac{2}{\kappa a} \sqrt{rr'} \sinh(\alpha) \right) \Bigg], \tag{49}$$

where $Y_m^l(\Omega)$ and $I_n(y)$ are spherical harmonics and modified Bessel functions (as for a complete definition of these functions, we quote Edmonds[14] and Erdelyi *et al.*[15]); the scaled Bohr radius a and the quantity κ are defined as

$$a := \frac{\hbar^2 \epsilon_\infty}{\mu \overline{e^2} \lambda} = \frac{a_B}{\lambda}, \quad \kappa := \sqrt{\frac{\widetilde{E}_0}{z}} > 0. \tag{50}$$

Inserting Eq. (49) into Eq. (47), one can perform the $\vec{r}$ and $\vec{r}'$ integrations as well as the l and m summations. The calculation is very lengthy but elementary. Therefore, it seems sufficient to give a precise description of the steps to be done: First, one has to use the familiar expansion of $\exp(i\vec{k}\gamma_n \vec{r})$ as a series of spherical harmonics; then, all angular integrations in Eq. (47) as well as the m summation can be done. One is left with two radial integrations. As the radial part of $\widetilde{\phi}_0(\vec{r})$ is proportional to $\exp(-r/a)$, these integrations turn out to be two Laplace transforms of products of Bessel functions. Having performed one of these,[16] it is useful to evaluate the l summation,[17] before the last integration (a Laplace transform of a Bessel function) is done. Finally, one arrives at

$$4F_m(k) = \sum_{n,n'} \int_0^\infty d\alpha \coth^{2\kappa}\left(\frac{\alpha}{2}\right) \zeta \Bigg\{ \delta_{n,n'} \frac{2\chi^2 + \zeta^2}{I_n^4}$$
$$- (1-\delta_{n,n'}) \left(\frac{2\chi^2+\zeta^2}{J^2} - \frac{4\zeta^2\chi^2 k^2 a^2}{J^3} \right) \Bigg\}, \tag{51}$$

where we introduced the abbreviations

$$\chi := 1 + \frac{\cosh(\alpha)}{\kappa}, \quad \zeta := \frac{\sinh(\alpha)}{\kappa}, \tag{52}$$

$$I_n := (ka\gamma_n)^2 + \chi^2 - \zeta^2,$$
$$J := (\chi^2 - k^2 a^2 |\gamma_1 \gamma_2| - \zeta^2)^2 + \chi^2 k^2 a^2. \tag{53}$$

It is useful to perform a final substitution in expression (51): We set

$$y := \tanh^2\left(\frac{\alpha}{2}\right) \tag{54}$$

and arrive at

$$F_m(k)=\frac{1}{\kappa}\sum_{n,n'}\int_0^1 dy\,y^{-\kappa}\left(\delta_{nn'}\frac{(1+1/\kappa)^2+(2/\kappa^2-1)y+(1/\kappa-1)^2y^2}{\overline{I_n^4}}\right.$$
$$\left.-(1-\delta_{nn'})\left\{\frac{(1+1/\kappa)^2+(2/\kappa^2-1)y+(1/\kappa-1)^2y^2}{\overline{J^2}}-\frac{8k^2a^2y[1/\kappa+1+(1/\kappa-1)y]^2}{\kappa^2\overline{J^3}}\right.\right. . \tag{55}$$

In Eq. (55), we defined

$$\overline{I_n}:=\left(1+\frac{1}{\kappa}\right)^2+k^2a^2\gamma_n^2-\left[\left(\frac{1}{\kappa}-1\right)^2+k^2a^2\gamma_n^2\right]y, \tag{56}$$

$$\overline{J}:=\left\{\left(1+\frac{1}{\kappa}\right)^2-k^2a^2|\gamma_1\gamma_2|-\left[\left(\frac{1}{\kappa}-1\right)^2-k^2a^2|\gamma_1\gamma_2|\right]y\right\}^2$$
$$+k^2a^2\left[\left(1+\frac{1}{\kappa}\right)+\left(\frac{1}{\kappa}-1\right)y\right]^2. \tag{57}$$

Returning to inequality (43), we insert expressions (2), (46), (47), and (55) on the right-hand side and can finally set up the following upper bound on E_0:

$$\frac{E_0}{R_0}\leqslant\frac{1}{(1-\xi)^2}\left\{\lambda^2-2\lambda+\frac{3}{4}\frac{(v-w)^2}{v\eta^2}-\frac{64(\sigma+\sigma^{-1})\xi}{\pi\eta^3\lambda^2}\right.$$
$$\times\sum_{m=0}^{\infty}\frac{1}{m!}\left(\frac{v^2-w^2}{v^3}\right)^m\int_0^\infty dx\,x^{2m}e^{[-(v^2-w^2)/v^3]x^2}$$
$$\left.\times F_m\left(\sqrt{\frac{2M\omega}{\hbar}}x\right)\right\}$$
$$=:B(v,w,\lambda). \tag{58}$$

The reader will notice that we used the static Rydberg unit

$$R_0:=\frac{\mu\overline{e^4}}{2\hbar^2\epsilon_0^2} \tag{59}$$

as the energy scale; in doing so, we follow the convention of most papers to be quoted below. Furthermore, we introduced the three dimensionless material parameters

$$\eta^2:=\frac{R_\infty}{\hbar\omega},\quad \sigma^2:=\frac{m_1}{m_2},\quad \xi:=1-\frac{\epsilon_\infty}{\epsilon_0}. \tag{60}$$

One can easily derive from Eqs. (50) and (44) that

$$\frac{1}{\kappa^2}=1+\frac{1}{\eta^2\lambda^2}\left(1+mv+\frac{w^2}{v^2}x^2\right) \tag{61}$$

is true. Consequently, the bound $B(v,w,\lambda)$ is entirely defined by η, σ, ξ alone.

The remaining task is to minimize $B(v,w,\lambda)$ as a function of the variational parameters v, w, and λ.

VI. NUMERICAL RESULTS AND COMPARISON WITH PREVIOUS WORK

The minimization of $B(v,w,\lambda)$ with respect to v, w, and λ requires a numerical treatment. To achieve a compact presentation of our results, it will prove useful to introduce the notation $B_k(v,w,\lambda)$ for a truncated bound: $B_k(v,w,\lambda)$ is derived from $B(v,w,\lambda)$ by omission of all terms in the m sum, having an m value larger than k. We remind the reader that $B_k(v,w,\lambda)$ is in fact a true upper bound on E_0/R_0 and monotonously decreasing with increasing k, as was remarked in connection with Eq. (42).

It is interesting to begin the discussion by analyzing a restricted class of bounds: Let us consider the case $v=w$. Recalling the definition of the trial action $\widetilde{S}$ [see Eq. (17)] and relations (25), (26), and (39) for the center-of-mass kernel $f(\tau)$, it becomes clear that the equality $v=w$ is equivalent to $f(\tau)=0$: The trial action assumes a free center-of-mass motion. In this case, we find

$$B(v,v,\lambda)=B_0(v,v,\lambda), \tag{62}$$

the right-hand side being independent of v. If we put additionally $\lambda=1$, the trial action is precisely that of an uncoupled exciton-phonon system. Consequently, $B_0(v,v,1)$ reproduces the result of second-order perturbation theory for E_0/R_0. One can easily do better by calculating

TABLE I. Results for the ground-state energy bounds $B_0(v,v,1)$ and $\overline{B_0}$ for specified parameter values $\eta^2=\frac{1}{4}$ and $\zeta=0.5$.

σ^2	$B_0(v,v,1)$	$\overline{B_0}$
0.010	- 44.416	- 45.264
0.020	- 32.832	- 33.664
0.050	- 22.688	- 23.488
0.100	- 17.776	- 18.528
0.200	- 14.544	- 15.264
0.500	- 12.256	- 12.928
1.000	- 11.760	- 12.416

TABLE II. Results for the ground-state energy bounds $B_0(v,v,1)$ and $\overline{B_0}$ for specified parameter values $\eta^2=1$ and $\zeta=0.5$.

σ^2	$B_0(v,v,1)$	$\overline{B_0}$
0.010	-22.544	-23.224
0.020	-16.824	-17.432
0.050	-11.840	-12.376
0.100	- 9.484	- 9.928
0.200	- 7.980	- 8.340
0.500	- 6.948	- 7.228
1.000	- 6.732	- 6.992

TABLE III. Results for the ground-state energy bounds $B_0(v,v,1)$, $\overline{B_0}$, and B_0 for specified parameter values $\eta^2=4$ and $\zeta=0.5$.

σ^2	$B_0(v,v,1)$	$\overline{B_0}$	B_0
0.010	- 11.927	- 12.341	-13.408
0.020	- 9.178	- 9.497	– $v=w$ –
0.050	- 6.900	- 7.093	———–
0.100	- 5.884	- 6.001	———–
0.200	- 5.275	- 5.345	———–
0.500	- 4.884	- 4.925	———–
1.000	- 4.805	- 4.840	– $v=w$ –

$$\overline{B_0}:=\inf_\lambda B_0(v,v,\lambda). \tag{63}$$

Tables I–III contain a collection of results for $B_0(v,v,1)$ as well as $\overline{B_0}$. B_0 will be explained below.

What about the quality of these bounds? As $\widetilde{S}$ assumes the center-of-mass motion to be free, the corresponding electron-phonon coupling constant

$$\alpha_M=\frac{\overline{e^2}}{2\hbar\omega}\sqrt{\frac{2M\omega}{\hbar}}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)=\eta\xi\left(\sigma+\frac{1}{\sigma}\right) \tag{64}$$

should be sufficiently small. Interestingly enough, we can demonstrate (numerically) that α_M may be of the order 10, before the bound $\overline{B_0}$ becomes poor. To do so, we consider the more general bounds

$$B_k:=\inf_{v,w,\lambda}B_k(v,w,\lambda). \tag{65}$$

In principle, these bounds admit an infimum for $v\neq w$. This is equivalent to a nonfree center-of-mass motion. In any case, $B_k\leq\overline{B_0}$ and in particular $B_0\leq\overline{B_0}$ is guaranteed. Comparing B_0 with $\overline{B_0}$, we find a remarkable behavior: If η and ξ are fixed, there may exist a critical value of α_M (or, equivalently, σ) in the following sense: If $\alpha_M<\alpha_M^c$, $B_0=\overline{B_0}$ is true, v and w being equal. If $\alpha_M>\alpha_M^c$, $B_0<\overline{B_0}$ will be found, the minimizing values of v and w being not equal. For $\alpha_M=\alpha_M^c$, B_0 is a nonanalytic function of α_M.

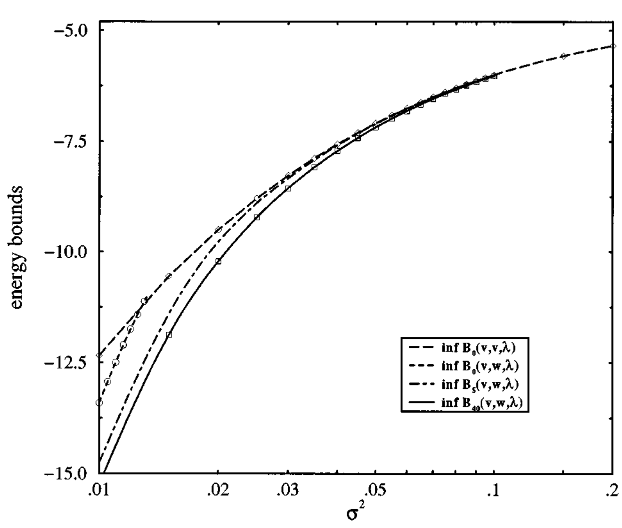

FIG. 1. Comparison of separate upper bounds to the ground-state energy as gained by minimization of the corresponding $B_k(v,w,\lambda)$.

Having in mind that E_0/R_0 is an analytical function of α_M (or, equivalently, σ) for all possible values of α_M (or, equivalently, σ), we evaluated B_k for larger values of k. In Fig. 1, we show typical graphs for $\overline{B_0}$, B_0, B_5, and B_{40} as functions of σ^2 (η^2 and ξ being fixed). The conclusion is obvious: For $k\to\infty$, no critical value of σ^2 exists. So far, our numerical findings are consistent with the analytical results, which were quoted in the Introduction.

In Tables IV–VI we list our results for B_{40} and $\overline{B_0}$. The corresponding η^2 values are changing from 4 to 40. For smaller values of η, one may use $\overline{B_0}$ from the preceding Tables I–III. In this parameter region, B_{40} and $\overline{B_0}$ differ from each other by less than 1%. Furthermore, we quoted two previous bounds B_{ABS} and B_{AGL}, which are due to Adamowski, Bednarek, and Suffczynski[18] and Adamowski, Gerlach, and Leschke.[19] To the best of our knowledge, these compare favorably with all previous ones, but in separate σ regions: The former one is excellent for small or intermediate, the latter one for large electron-phonon coupling parameters α_M. Moreover, we added two columns for the continuum edge Σ/R_0 and our prediction for the binding energy $\Delta E/R_0$. Σ is the sum of the polaronic self-energies of electron and hole. It is important to treat Σ on the same level of accuracy as E_0. In general, it is not sufficient to use the second-order perturbation result $-\hbar\omega(\alpha_1+\alpha_2)$ for Σ, as

TABLE IV. Comparison of the ground-state energy bounds $\overline{B_0}$ and B_{40} with previous ones by Adamowski, Bednarek, and Suffczynski (B_{ABS}) and Adamowski, Gerlach, and Leschke (B_{AGL}) for $\eta^2=4$, $\zeta=0.5$. In addition, the continuum edge Σ/R_0 and the binding energy $\Delta E/R_0$ are presented.

σ^2	$\overline{B_0}$	B_{40}	B_{ABS}	B_{AGL}	Σ/R_0	$\Delta E/R_0$
0.010	-12.341	-15.241	- 12.185	- 15.395	-14.70	-0.5
0.020	-9.497	-10.212	- 9.364	- 10.311	-9.38	-0.83
0.050	-7.093	-7.185	- 6.994	- 7.028	-5.99	-1.19
0.100	-6.001	-6.024	- 5.926	- 5.678	-4.557	-1.467
0.200	-5.345	– $v=w$ –	- 5.287	- 4.893	-3.660	-1.685
0.500	-4.925	———-	- 4.879	- 4.407	-3.029	-1.896
1.000	-4.840	– $v=w$ –	- 4.797	- 4.311	-2.892	-1.948

TABLE V. Comparison of the ground-state energy bounds $\overline{B_0}$ and B_{40} with previous ones by Adamowski, Bednarek, and Suffczynski (B_{ABS}) and Adamowski, Gerlach, and Leschke (B_{AGL}) for $\eta^2=8$, $\zeta=0.5$. In addition, the continuum edge Σ/R_0 and the binding energy $\Delta E/R_0$ are presented.

σ^2	$\overline{B_0}$	B_{40}	B_{ABS}	B_{AGL}	Σ/R_0	$\Delta E/R_0$
0.010	-9.262	-13.603	- 9.096	- 13.626	-13.0	-0.6
0.020	-7.326	-8.578	- 7.201	- 8.552	-7.62	-0.96
0.050	-5.758	-5.822	- 5.682	- 5.566	-4.36	-1.46
0.100	-5.089	-5.096	- 5.038	- 4.634	-3.300	-1.796
0.200	-4.707	– $v=w$ –	- 4.671	- 4.173	-2.621	-2.086
0.500	-4.474	———-	- 4.446	- 3.906	-2.163	-2.311
1.000	-4.428	– $v=w$ –	- 4.402	- 3.855	-2.064	-2.364

TABLE VI. Comparison of the ground-state energy bounds $\overline{B_0}$ and B_{40} with previous ones by Adamowski, Bednarek, and Suffczynski (B_{ABS}) and Adamowski, Gerlach, and Leschke (B_{AGL}) for $\eta^2=40$, $\zeta=0.5$. In addition, the continuum edge Σ/R_0 and the binding energy $\Delta E/R_0$ are presented.

σ^2	$\overline{B_0}$	B_{40}	B_{ABS}	B_{AGL}	Σ/R_0	$\Delta E/R_0$
0.010	-5.556	-12.275	- 5.473	- 12.201	-11.4	-0.9
0.020	-4.889	-7.260	- 4.843	- 7.124	-6.0	-1.3
0.050	-4.418	-4.432	- 4.398	- 4.134	-2.88	-1.55
0.100	-4.242	– $v=w$ –	- 4.230	- 3.661	-1.81	-2.43
0.200	-4.150	———	- 4.142	- 3.556	-1.296	2.854
0.500	-4.097	———	- 4.091	- 3.498	-1.013	-3.084
1.000	-4.087	– $v=w$ –	- 4.081	- 3.487	-0.964	-3.123

was frequently done. One will systematically overestimate the binding energy that way, the mistake growing with α. Here, we used the involved variational results from Ref. 9. In any case, ΔE is not necessarily an upper bound on the binding energy. Based on our extensive numerical studies, we estimate the error of ΔE to be in the order of 1%.

Table VII provides a comparison of ground-state energies, presented in various papers (ours included) and for various materials of interest. The data are based on the material parameters, given in Table VIII; for a more complete compilation, we refer to the work of Iadonisi and Bassani.[36] Going through the experimental literature, the reader will realize that some parameters, in particular masses, have changed considerably over the years, in some cases up to a factor of 2. Therefore, it is impossible to perform a direct comparison with most of the papers, to be quoted below. To compare even so, we used their input parameters in our bound. Proceeding this way, we realized that our bound compared favorably with all previous ones, which we are aware of. We found no use in publishing these data, as they are based on parameters which had to be revised because of improved experimental findings. Instead, we refer to Tables I–VI, which cover a relevant parameter regime. Concerning binding energies ΔE, we recall the remarks from the last section. To establish a well-defined basis for a comparison, we included our values for the continuum edge Σ. The lower the ground-state energy and Σ are, the higher is the *a priori* reliability of the theory with respect to the predicted value of ΔE.

Finally, we comment on related publications. We apologize in advance for being incomplete, but we hope to be representative.

TABLE VII. Absolute ground-state energy bounds in meV as derived by Iadonisi and Bassani E_{IB} (Ref. 36), Pollmann E_P (Ref. 29), and the present authors $\overline{B_0}$. Σ denotes the continuum edge.

	E_{IB}	E_P	$\overline{B_0}$	Σ
GaAs	9.56	—	9.62	6.04
GaP	25.70	—	25.78	14.13
ZnS	110.02	—	110.14	68.41
CuCl	443.22	440.5	443.91	226.51
TlCl	127.85	125.8	128.05	115.31
TlBr	80.86	79.94	80.75	71.94

TABLE VIII. Material parameters as employed to obtain the ground-state energy bounds in Table VII.

	ϵ_0	ϵ_∞	$m_1[m_e]$	$m_2[m_e]$	α_e	α_h	$\hbar\omega$ [meV]
GaAs	13.1	11.1	0.0665	0.131	0.0682	0.0957	36.8
GaP	11.0	9.1	0.17	0.238	0.129	0.153	50.0
ZnS	8.6	5.2	0.28	0.394	0.712	0.845	43.4
CuCl	7.4	3.7	0.44	3.60	2.005	5.735	27.2
TlCl	37.6	5.1	0.37	0.36	2.594	2.558	21.5
TlBr	35.1	5.4	0.18	0.38	2.051	2.980	14.3

Perturbation theory of second order with respect to the exciton-phonon coupling was performed by Mahanti and Varma,[20] Sak,[21] and Wang and Matsuura.[22] The corresponding results have to be compared with our bound $B_0(v,v,1)$. We mention that there was a controversial discussion concerning the correct weak-coupling limit of the polaronic exciton. After all, Sak's results were confirmed. A brief discussion of this limit is contained in the Appendix.

Most of the previous variational calculations were particularly influenced by the Lee-Low-Pines[23] approach to the free polaron. Early papers are due to Haken[24] and Meyer.[25] Based on these, refined calculations were performed by Mahler and Schröder,[26] Barentzen,[27] Fock, Kramer, and Büttner,[28] Pollmann and Büttner,[29] Bednarek and Suffczynski,[30] Hattori,[31] Adamowski, Bednarek and Suffczynski,[18] Behnke and Büttner,[32] Kane,[33] Bednarek,[34] Matsuura and Büttner,[35] and Iadonisi and Bassani.[36]

Functional-integral methods were used by Haken,[3] Moskalenko,[37] Matsuura and Mavroyannis[38] and Adamowski, Gerlach, and Leschke.[19] The corresponding papers can directly be related to the present one. The bound of Matsuura and Mavroyannis, based on Haken's early work, coincides with our bound $\overline{B_0}$. Their trial action can be derived from ours in Eq. (17), if one puts $f(\tau)=0$; no phonon-induced center-of-mass term appears. The work of Moskalenko and Adamowski, and Gerlach and Leschke, on the other hand, concentrates on the phonon-induced center-of-mass effects. Their trial actions contain at most bilinear expressions of the center-of-mass and relative coordinates. There is a clear indication that the coupling of both coordinates is of minor importance, whereas both self-interactions have to be kept. Concerning quantitative bounds on the ground-state energy, a center-of-mass term is important in the strong-coupling regime; this is in agreement with the present results (see Fig. 1 and Tables I–VI) and was mentioned above. Concerning qualitative properties of the bounds such as analyticity, a center-of-mass term is indispensable, as was shown above (again, see Fig. 1).

The discussion of analytical properties leads us back to the controversy concerning an eventual delocalization-localization transition in exciton-phonon systems. Direct references are Sumi,[39] Pekar, Rashba, and Sheka[40] as well as Shimamura and Matsuura.[41] In all these papers indications for a transition were deduced from the behavior of variational bounds. These bounds are as interesting as any involved variational study of the ground-state energy; their analytical behavior, however, is not that of the exact (but unknown) eigenvalue.

VII. CONCLUSION

This paper is concerned with a qualitative and quantitative discussion of an exciton-(LO) phonon system. To the best of our knowledge, we obtain the lowest upper bound on the ground-state energy known so far. The interesting point about this bound is its smoothness as a function of the particle-phonon coupling for the whole parameter region of electron and hole. This is in agreement with rigorous qualitative results for the true ground-state energy and disproves once more, now quantitatively, previous assertions of a phase-transition-like behavior of the system for certain coupling parameters.

Concerning the methodological part of this work, we make use of a nonharmonic trial action within the functional-integral approach: Besides an ansatz of Feynman type for the center-of-mass motion, we choose a scaled Coulomb potential for the relative motion of the exciton. All functional integrals of interest can be reduced to normal integrals, containing the Green function of hydrogen. It is crucial that these can once more be simplified by means of a decomposition of the Green function as a series of spherical harmonics. We shall demonstrate in a forthcoming paper that the corresponding procedure can be generalized.

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APPENDIX

In this appendix we discuss two limiting cases of the exciton-phonon system. The so-called polaronic limit is defined by $\eta \ll 1$, the opposite case of a bare exciton by $\eta \gg 1$. Alternatively, one may contrast the effective radii: The Bohr radius of a polaronic (bare) exciton is large (small) in comparison with the polaron radius.

To render an analytical discussion, we restrict ourselves to the weak-coupling case $\alpha_M \ll 1$. A convenient starting point is given by Eq. (43), evaluated for $v=w$ and $U=U_c$. In addition, we make use of the relation

$$e^{i\vec{k}\gamma_n\vec{q}}\widetilde{H}(\vec{p},\vec{q})e^{-i\vec{k}\gamma_{n'}\vec{q}}=e^{i\vec{k}(\gamma_n-\gamma_{n'}\vec{q})}\widetilde{H}(\vec{p}-\hbar\gamma_{n'}\vec{k},\vec{q}). \qquad \text{(A1)}$$

We find for the second-order expression $E^{(2)}$ of the ground-state energy

$$E^{(2)}=-\frac{4R_\infty}{(D-1)^2}-\frac{(D-1)|g|^2}{2\pi^{D-1}}\int_0^\infty dk\sum_n \langle\widetilde{\phi}_0|(1-e^{-i\vec{k}\cdot\vec{q}}) \times\left(\widetilde{H}+R_\infty+\hbar\omega+\frac{\hbar^2k^2}{2m_n}-\frac{\hbar\vec{k}\vec{p}}{m_n}\right)^{-1}|\widetilde{\phi}_0\rangle. \qquad \text{(A2)}$$

At this point it proves useful to define dimensionless variables $\vec{k}'$, $\vec{q}'$, and $\vec{p}'$ as follows: $\vec{k}=:(\sqrt{2\mu\omega/\hbar})\vec{k}'$, $\vec{q}=:a_B\vec{q}'$, and $\vec{p}=:\hbar(a_B)^{-1}\vec{p}'$. One finds

$$E^{(2)}=-\frac{4R_\infty}{(D-1)^2}-\frac{(D-1)\hbar\omega\xi\eta}{\pi^{D-2}}\int_0^\infty dk'\sum_n \langle\widetilde{\psi}_0|(1-e^{-i\vec{k}'\cdot\vec{q}'/\eta})[\eta^2(1+\widetilde{h})+1+|\gamma_n|(k')^2-\widetilde{v}_{\vec{k}}]^{-1}|\widetilde{\psi}_0\rangle, \qquad \text{(A3)}$$

where we introduced

$$\widetilde{h}:=(p')^2-\frac{2}{q'},\quad \widetilde{v}_{\vec{k}}:=2|\gamma_n|\eta\vec{k}'\cdot\vec{p}'. \qquad \text{(A4)}$$

The scaled ground-state wave function $\widetilde{\Psi}_0$ is found from $\widetilde{\phi}_0$, if a_B is replaced by 1. Formula (A3) allows for a simple discussion of the two limiting cases, which are of interest here. One finds by direct inspection that no phonon-induced contribution survives for $\eta\to\infty$. The opposite limit $\eta\to 0$ needs some more analysis: Expanding the propagator $[\eta^2(1+\widetilde{h})+1+|\gamma_n|(k')^2-\widetilde{v}_{\vec{k}}]^{-1}$ with respect to $\widetilde{v}_{\vec{k}}$, the remaining integrations can be done term by term. Up to corrections of the order $\hbar\omega\eta^2$, the result is

$$E^{(2)}=-\frac{D-1}{2}\pi^{(3-D)}(\alpha_1+\alpha_2)\hbar\omega-\frac{4R_0}{(D-1)^2}\frac{\mu_P}{\mu}. \qquad \text{(A5)}$$

Here, μ_P is the reduced mass of the two constituting polarons. These, in turn, have individual masses $m(1+x\alpha)$, where x is $\frac{1}{6}$ in three and $\pi/8$ in two dimensions.

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