Treatment of the exciton-phonon interaction via functional integration. I. Harmonic trial actions

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We consider an exciton-LO-phonon system described by Fröhlich's Hamiltonian. Making use of the functional-integration technique one can eliminate the phonon terms exactly leading to an effective two-particle system with the same spectral properties as the original one. The action functional of this effective system is approximated by a general isotropic harmonic trial action. Using Jensen's inequality we obtain an upper bound on the ground-state energy in analytical form. Expressed in excitonic rydberg units, this bound is calculated as a function of three variables: the ratios of electron and hole (band) mass σ, excitonic rydberg and LO-phonon energy, and the static and high-frequency dielectric constant. For a given value of the electron-phonon coupling constant this bound is rapidly decreasing if σ tends to zero, leading us to an upper limit for the total ground-state energy which is considerably lower than that given by other authors using, e.g., effective Hamiltonians. The same holds true for the corresponding estimate of the self-energy of the system. If electron and hole mass are comparable, our bound is worse than that derived from effective Hamiltonians. The reason for this behavior is that the contribution of the electron-hole Coulomb potential to the total energy becomes more important. In this case a harmonic approximation is too poor. We include an analytical discussion of limiting cases, which adds nicely to the numerical results.

I. INTRODUCTION

This paper is concerned with a treatment of the exciton-phonon problem by means of functional-integration techniques. In view of the enormous literature on the subject there may be a need to clarify the motivations for such an approach. They can be summarized as follows. Firstly, the effects of exciton-phonon interactions can be discussed in a highly transparent manner. In particular, it is possible to reduce the original electron-hole-field problem to an effective two-particle problem without need of any approximation. Secondly, the functional-integral approach provides us with analytical results which are difficult to prove otherwise. We mention the explicit formulas for binding energies in limiting cases, which are given in Sec. III. Thirdly, the numerical results complete nicely those found by other authors.

We start with Fröhlich's Hamiltonian for the interaction of an electron and a hole with a branch of longitudinal-optical lattice vibrations. It reads

$$H=\sum_{j=1}^{2}\frac{\vec{p}_j^2}{2m_j}-\frac{e^2}{\epsilon_\infty|\vec{q}_1-\vec{q}_2|}+\sum_{\vec{k}}\hbar\,\omega\,a_{\vec{k}}^*a_{\vec{k}}+\frac{1}{\sqrt{V}}\sum_{\vec{k}}\sum_{j=1}^{2}\left[g_j(\vec{k})e^{i\vec{k}\cdot\vec{q}_j}a_{\vec{k}}+\text{H.c.}\right]. \tag{1}$$

Here $\{\vec{p}_j,\vec{q}_j\}$ are momentum and position operators of electron and hole, $\{m_j\}$ their band masses. $a_{\vec{k}}$, $a_{\vec{k}}^*$ are annihilation and creation operators for phonons with frequency ω and wave vector $\vec{k}$; the quantization volume is V. Finally, the electron-(hole-) phonon coupling is given by

$$g_j(\vec{k})=\frac{g}{k}\delta_j\,,\quad \delta_j=\begin{cases}1, & j=1\text{ (electron)}\\ -1, & j=2\text{ (hole)}\end{cases} \tag{2}$$

where

$$g=-i\,(2\pi e^2\hbar\omega/\epsilon^*)^{1/2},\quad \epsilon^{*-1}=\epsilon_\infty^{-1}-\epsilon_0^{-1}\ . \tag{3}$$

ϵ_∞ and ϵ_0 are the high- and low-frequency limits of the dielectric function. Spectral properties of Hamiltonian (1) can conveniently be deduced from

$$\rho_\beta(\vec{r}_1\vec{r}_2,\ \vec{r}_1'\vec{r}_2')=\mathrm{Tr}_{\text{ph}}\,\langle\vec{r}_1\vec{r}_2|\,e^{-\beta H}|\vec{r}_1'\vec{r}_2'\rangle\ . \tag{4}$$

Here $|\vec{r}_1\vec{r}_2\rangle$ is an eigenstate of the operators $\vec{q}_1,\vec{q}_2$. ρ_β may be viewed as a reduced density matrix, $(k_B\beta)^{-1}$ as a (formal) temperature. It is well known that the phonon trace in expressions of type (4) can be evaluated if H is quadratic in the phonon operators (see Feynman and Hibbs[1]). The result is

$$\rho_\beta(\vec{r}_1\vec{r}_2,\ \vec{r}_1'\vec{r}_2')=Z_{\text{ph}}\int_{\vec{r}_1\vec{r}_2,\,\vec{r}_1'\vec{r}_2'}\delta^3R_1\delta^3R_2\,e^{-S[\vec{R}_1,\vec{R}_2]}\ . \tag{5}$$

Equation (5) introduces a functional integral. In particular, $\int_{\vec{r}_1\vec{r}_2,\vec{r}_1'\vec{r}_2'}\delta^3R_1\delta^3R_2\times\cdots$ is to indicate Wiener integration over all real, three-dimensional paths with fixed endpoints $\vec{R}_i(0)=\vec{r}_i'$, $\vec{R}_i(\beta)=\vec{r}_i$. The action $S[\vec{R}_1,\vec{R}_2]$ reads as follows (see Schultz[2]):

$$S[\vec{R}_1,\vec{R}_2]=\int_0^\beta d\tau\left(\sum_j \frac{m_j}{2}\dot{\vec{R}}_j^2(\tau)-\frac{e^2}{\epsilon_\infty|\vec{R}_1(\tau)-\vec{R}_2(\tau)|}\right)-\frac{|g|^2}{4\pi}\sum_{j,j'}\delta_j\delta_{j'}\int_0^\beta d\tau d\tau'\frac{G(\tau-\tau')}{|\vec{R}_j(\tau)-\vec{R}_{j'}(\tau')|}\ . \quad (6)$$

Finally, $\dot{\vec{R}}(\tau)=(1/\hbar)(d\vec{R}/d\tau)$, Z_{ph} denotes the free phonons partition function, and

$$G(\tau)=\cosh[\hbar\omega(\beta/2-|\tau|)]/[2\sinh\hbar\omega(\beta/2)] \quad (7)$$

is the temperature-dependent oscillator Green's function. Equation (6) clearly shows the effect of the exciton-phonon interaction: It is described by the second part of the formula and consists of two self-interaction terms ($j=j'$) and two corrections to the Coulomb potential ($j\neq j'$), both of equal size. All terms are "noninstantaneous," the overall contribution is negative; the latter can be shown by using the Fourier decompositions of $G(\tau-\tau')$ and $|\vec{R}(\tau)-\vec{R}(\tau')|^{-1}$. Therefore the ground-state energy is lowered in comparison with the free-exciton case. It should be noted that Eqs. (5) and (6) describe an effective two-particle system. Its spectral properties are exactly those of the original one. To get a first impression of what is going on in such a system let us qualitatively discuss (5) and (6): Dominant contributions to the functional integral are due to paths at equal "time" $\tau=\tau'$ and paths $\vec{R}_i(\tau)$ with considerable overlap. We are to clarify the relative weight of such contributions.

(1) Let $\hbar\omega\gg\mathcal{R}_\infty,\beta^{-1}(\mathcal{R}_\infty=\mu e^4/2\hbar^2\epsilon_\infty^2)$. Because of $\beta\hbar\omega\gg1$, $G(\tau-\tau')$ is strongly peaked for $\tau=\tau'$. Moreover, $\int_0^\beta d\tau'\ \hbar\omega G(\tau-\tau')=1$. Therefore $\hbar\omega G(x)$ approaches a δ function in $0\leq x\leq\beta$. This fact in addition to $\hbar\omega\gg\mathcal{R}_\infty$ assures us that the self-interaction terms are dominant. The effective two-particle interaction takes the form

$$-e^2(\epsilon_\infty^{-1}-\epsilon^{*-1})\int_0^\beta d\tau\frac{1}{|\vec{R}_1(\tau)-\vec{R}_2(\tau)|}$$

$$=-\frac{e^2}{\epsilon_0}\int_0^\beta d\tau\frac{1}{|\vec{R}_1(\tau)-\vec{R}_2(\tau)|}\ . \quad (8)$$

Therefore the system may be viewed as containing two polarons embedded in a Coulomb potential screened with ϵ_0 ("polaronic exciton"). This is exactly the result of Sak's perturbation approach.[3]

(2) Let $\beta^{-1}\ll\hbar\omega\ll\mathcal{R}_\infty$. Now paths with $\vec{R}_1(\tau)\approx\vec{R}_2(\tau)$ give leading contributions to the functional integral. However, then

$$\sum_{jj'}\delta_j\delta_{j'}\int_0^\beta d\tau d\tau'\frac{G(\tau-\tau')}{|\vec{R}_j(\tau)-\vec{R}_{j'}(\tau')|}\approx0\ . \quad (9)$$

This is the well known cancellation of phonon effects which characterizes a "small" or "bare" exciton; the system may be viewed as containing two bare particles embedded in a Coulomb potential screened with ϵ_∞.

Unfortunately it seems impossible at the present time to evaluate the functional integral (5) exactly. To proceed further we follow ideas of Feynman,[4] Haken,[5] and Moskalenko[6] and construct an upper bound on the ground-state energy.

II. UPPER BOUND ON THE GROUND-STATE ENERGY

To begin with, let us define the expectation value of a quantity A with respect to an arbitrary trial action $\tilde{S}$:

$$\langle A\rangle_{\tilde{S}}=\frac{\oint\delta^3R_1\delta^3R_2e^{-\tilde{S}[\vec{R}_1,\vec{R}_2]}A[\vec{R}_1,\vec{R}_2]}{\oint\delta^3R_1\delta^3R_2e^{-\tilde{S}[\vec{R}_1,\vec{R}_2]}}\ . \quad (10)$$

Here we introduced the abbreviation

$$\oint\delta^3R_1\,\delta^3R_2f[\vec{R}_1,\vec{R}_2]$$

$$=\int d^3r_1d^3r_2\int_{\vec{r}_1\vec{r}_2,\vec{r}_1\vec{r}_2}\delta^3R_1\,\delta^3R_2f[\vec{R}_1,\vec{R}_2]\ . \quad (11)$$

Now all following considerations rely on Jensen's inequality: Let $\tilde{S}$ be a trial action such that

$$\tilde{E}_0=-\lim_{\beta\to\infty}\beta^{-1}\ln\oint\delta^3R_1\delta^3R_2e^{-\tilde{S}[\vec{R}_1,\vec{R}_2]} \quad (12)$$

and

$$\Delta E=\lim_{\beta\to\infty}\beta^{-1}\langle S-\tilde{S}\rangle_{\tilde{S}} \quad (13)$$

exist. Then $\tilde{E}_0+\Delta E$ is an upper bound on the ground-state energy E_0:

$$E_0\leq\tilde{E}_0+\Delta E\ . \quad (14)$$

In this paper we choose as trial action

$$\tilde{S}[\vec{R},\vec{r}]=\int_0^\beta d\tau\left(\frac{M}{2}\dot{\vec{R}}^2(\tau)+\frac{\mu}{2}\dot{\vec{r}}^2(\tau)\right)$$

$$+\int_0^\beta d\tau d\tau'[f_1(\tau-\tau')\vec{R}(\tau)\cdot\vec{R}(\tau')+f_2(\tau-\tau')\vec{r}(\tau)\cdot\vec{r}(\tau')+f_3(\tau-\tau')\vec{R}(\tau)\cdot\vec{r}(\tau')]\ . \quad (15)$$

Notice that we introduced center-of-mass and relative coordinates $\vec{R}$ and $\vec{r}$; furthermore, $M=m_1+m_2$, $\mu^{-1}=m_1^{-1}+m_2^{-1}$. $f_i(\tau-\tau')$, $i=1, 2, 3$, are continuous functions which serve to minimize the upper bound (14); without loss of generality we may assume $f_i(\tau-\tau')=f_i(\tau'-\tau)$.

$\tilde{S}[\vec{R},\vec{r}]$ is a general isotropic harmonic trial action. To have it translation invariant, the equations

$$0=\int_0^\beta d\tau' f_1(\tau-\tau')=\int_0^\beta d\tau' f_3(\tau-\tau'),\quad 0\leq\tau\leq\beta \tag{16}$$

must be fulfilled. To evaluate (12), (13), and (14) we make use of an idea due to Feynman[4]: Suppose we knew the generating functional

$$I[\vec{\eta}_1,\vec{\eta}_2]=\left\langle \exp\left\{\int_0^\beta d\tau[\vec{\eta}_1(\tau)\cdot\vec{R}(\tau)+\vec{\eta}_2(\tau)\cdot\vec{r}(\tau)]\right\}\right\rangle_{\tilde{S}} \tag{17}$$

wherein $\{\vec{\eta}_i(\tau)\}$ are two integrable functions and $0=\int_0^\infty d\tau\,\vec{\eta}_1(\tau)$; the latter is to hold true because of translation invariance. Then $\tilde{E}_0$, ΔE can immediately be deduced. To prove this we proceed as follows: From (13) we have

$$\Delta E=\lim_{\beta\to\infty}\Delta E_\beta\ , \tag{18}$$

where

$$\Delta E_\beta=\beta^{-1}\langle S-\tilde{S}\rangle_{\tilde{S}}=-e^2/(\beta\epsilon_\infty)\int_0^\beta d\tau\,\langle r(\tau)^{-1}\rangle_{\tilde{S}}$$
$$-\beta^{-1}\int_0^\beta d\tau d\tau'\left(\frac{|g|^2}{4\pi}G(\tau-\tau')\sum_{jj'}\delta_j\delta_{j'}\langle|\vec{R}(\tau)-\vec{R}(\tau')+\rho_j\vec{r}(\tau)-\rho_{j'}\vec{r}(\tau')|^{-1}\rangle_{\tilde{S}}\right.$$
$$\left.+f_1(\tau-\tau')\langle\vec{R}(\tau)\cdot\vec{R}(\tau')\rangle_{\tilde{S}}+f_2(\tau-\tau')\langle\vec{r}(\tau)\cdot\vec{r}(\tau')\rangle_{\tilde{S}}+f_3(\tau-\tau')\langle\vec{R}(\tau)\cdot\vec{r}(\tau')\rangle_{\tilde{S}}\right) \tag{19}$$

and

$$\rho_1=m_2/M\ ,\ \rho_2=-m_1/M\ . \tag{20}$$

All expectation values in (19) can be derived from (17). For example, choose

$$\vec{\eta}_1(\tau)=i\vec{k}[\delta(\tau-\tau_1)-\delta(\tau-\tau_2)]\ ,$$

$$\vec{\eta}_2(\tau)=i\vec{k}[\rho_j\delta(\tau-\tau_1)-\rho_{j'}\delta(\tau-\tau_2)] \tag{21}$$

and let $I(\vec{k},\tau_1,\tau_2)=I[\vec{\eta}_1,\vec{\eta}_2]$; then

$$\langle|\vec{R}(\tau_1)-\vec{R}(\tau_2)+\rho_j\vec{r}(\tau_1)-\rho_{j'}\vec{r}(\tau_2)|^{-1}\rangle_{\tilde{S}}$$
$$=\frac{1}{2\pi^2}\int\frac{d^3k}{k^2}\,I(\vec{k},\tau_1,\tau_2)\ . \tag{22}$$

The remaining quadratic terms in (19) are obtained as functional derivatives of $I[\vec{\eta}_1,\vec{\eta}_2]$ with respect to $\vec{\eta}_1$, $\vec{\eta}_2$. As for $\tilde{E}_0$, let us replace f_3 by λf_3, accordingly $\tilde{S}$ by $\tilde{S}_\lambda$. λ is a positive number. Moreover, we define a "free energy" $\tilde{F}_\lambda$ by

$$\tilde{F}_\lambda=-\frac{1}{\beta}\ln\oint\delta^3r\,e^{-\tilde{S}_\lambda[\vec{R},\vec{r}]}\ . \tag{23}$$

Consequently,

$$\tilde{E}_0=\lim_{\beta\to\infty}\tilde{F}_{\lambda=1}\ . \tag{24}$$

Now consider

$$\frac{\partial\tilde{F}_\lambda}{\partial\lambda}=\frac{\beta^{-1}}{e^{-\beta\tilde{F}_\lambda}}\oint\delta^3R\,\delta^3r\,e^{-\tilde{S}_\lambda[\vec{R},\vec{r}]}\frac{\partial}{\partial\lambda}\tilde{S}_\lambda[\vec{R},\vec{r}]$$
$$=\beta^{-1}\int_0^\beta d\tau d\tau' f_3(\tau-\tau')\langle\vec{R}(\tau)\cdot\vec{r}(\tau')\rangle_{\tilde{S}_\lambda}\ . \tag{25}$$

Consequently, this derivative is known from the results above. Moreover, $\tilde{F}_{\lambda=0}$ is a free energy of two decoupled particles with quadratic actions and may be taken from.[7] Hence, $\tilde{E}_0$ can explicitly be computed from (24) and (25) and

$$\tilde{F}_{\lambda=1}=\tilde{F}_{\lambda=0}+\int_0^1 d\lambda\,\frac{\partial\tilde{F}_\lambda}{\partial\lambda}\ . \tag{26}$$

The remaining task is to find $I[\vec{\eta}_1,\vec{\eta}_2]$. This can be done in analogy to Ref. 7 or according to the recipe we give in Ref. 8. The result is

$$I[\vec{\eta}_1,\vec{\eta}_2]=\exp\left[\frac{\beta}{2}\left(\frac{\vec{\eta}_{2,0}^{\,2}}{2\beta f_{2,0}}+\sum_{n\neq0}\frac{C_n\vec{\eta}_{1,n}\cdot\vec{\eta}_{1,-n}-2B_n\vec{\eta}_{1,n}\cdot\vec{\eta}_{2,-n}+A_n\vec{\eta}_{2,n}\cdot\vec{\eta}_{2,-n}}{A_nC_n-B_n^2}\right)\right]\ , \tag{27}$$

where

$$\vec{\eta}_{i,n}=\beta^{-1}\int_0^\beta d\tau\, e^{-i\nu_n\tau}\vec{\eta}_i(\tau),\quad f_{i,n}=\beta^{-1}\int_0^\beta d\tau\, e^{-i\nu_n\tau}f_i(\tau)\,,$$

$$A_n=M\nu_n^2/\hbar^2+2\beta f_{1,n},\quad C_n=\mu\nu_n^2/\hbar^2+2\beta f_{2,n}\,, \tag{28}$$

$$B_n=\beta f_{3,n},\quad \nu_n=2\pi n/\beta\ .$$

Now it is an easy task to calculate the upper bound on E_0 according to (14). Introducing dimensionless variables

$$t=\hbar\omega\tau,\quad x_n=\frac{1}{\hbar\omega}\nu_n\,, \tag{29}$$

and letting $\beta\to\infty$ (compare Ref. 7), we arrive at

$$E_0\leq B[h_1,h_2,h_3]\,, \tag{30}$$

where

$$B[h_1,h_2,h_3]/\hbar\omega=\frac{3}{2\pi}\int_0^\infty dx\left[\ln\left(\frac{N(x)}{x^4}\right)-\frac{A_2(x)h_1(x)+A_1(x)h_2(x)-2h_3^2(x)}{N(x)}\right]$$
$$-\frac{e^2}{\epsilon_\infty\hbar}\left(\frac{2\mu}{\hbar\omega}\right)^{1/2}\left[\left(\int_0^\infty dx\,\frac{A_1(x)}{N(x)}\right)^{-1/2}+\frac{\epsilon_\infty}{2\sqrt{2}\epsilon^*}\sum_{jj'}\delta_j\delta_{j'}\int_0^\infty dt\,\frac{e^{-t}}{\sqrt{P_{jj'}(t)}}\right]. \tag{31}$$

Here $h_i(x)$, $i=1, 2, 3$, is proportional to the Fourier transform of $f_i(z)$ in $0\leq z\leq\infty$ and therefore may be chosen to minimize (31). Furthermore,

$$A_i(x)=x^2+h_i(x),\quad i=1,2 \tag{32}$$

$$N(x)=A_1(x)A_2(x)-[h_3(x)]^2\,, \tag{33}$$

$$P_{jj'}(t)=\int_0^\infty dx\,\frac{1}{N(x)}\left(\frac{\mu}{M}A_2(x)[1-\cos(xt)]+\tfrac{1}{2}A_1(x)[\rho_j^2+\rho_{j'}^2-2\rho_j\rho_{j'}\cos(xt)]\right.$$
$$\left.-\sqrt{(\mu/M)}(\rho_j+\rho_{j'})h_3(x)[1-\cos(xt)]\right) \tag{34}$$

III. EVALUATION OF THE UPPER BOUND

Every set of functions $h_i(x)$, $i=1, 2, 3$, generates an upper bound on E_0 via Eq. (31). For a given set the actual value of this bound depends on the interplay of three dimensionless physical parameters which we choose as follows:

$$\eta=\frac{e^2}{\epsilon_\infty\hbar}\sqrt{\mu/2\hbar\omega}=\sqrt{\mathcal{R}_\infty/\hbar\omega}\ , \tag{35}$$

$$\alpha=\frac{\epsilon_\infty}{\epsilon^*}\eta<\eta\,, \tag{36}$$

$$\sigma=m_1/m_2\,. \tag{37}$$

E_0 and B are invariant against interchange $m_1 \leftrightarrow m_2$ or equivalently $\sigma\leftrightarrow\sigma^{-1}$ [see Hamiltonian (1) and Eq. (31)]. Therefore we may assume $\sigma\leq 1$. A particular consequence of this symmetry is that the partial derivatives of E_0 and B with respect to σ vanish for $\sigma=1$.

η, α, σ are well suited for analytical investigations of (31); this will be shown in the sequel. As far as numerical calculation and the comparison with previous work is concerned, we shall later use a different set of parameters which was introduced by other authors. Necessary conditions for $B[h_1, h_2, h_3]$ to take a minimum are

$$\frac{\delta B[h_1,h_2,h_3]}{\delta h_i(x)}=0,\quad i=1,\ 2,\ 3. \tag{38}$$

These equations can be discussed well in limiting cases: Let $\alpha\ll 1$. It is easy to show [use (38), $i=3$] that $h_3(x)=O(\alpha)$ for all η, σ, x. Furthermore, this minimizing solution contributes a term $O(\alpha^2)$ to the bound. If we are for terms of order α^0 and α^1, we may put $h_3(x)\equiv 0$. As for $h_2(x)$ we find from (38), $i=2$, that up to contributions of order α, $h_2(x)=s^2$, where s is positive and independent of α. So we get from (31)

$$B[h_1, h_2=s^2,\ h_3=0]/\hbar\omega = \tfrac{3}{4}s - \frac{2\sqrt{2}\,\eta}{\sqrt{\pi}}\sqrt{s} + \frac{3}{2\pi}\int_0^\infty dx\left[\ln\left(1+\frac{h_1(x)}{x^2}\right) - \frac{h_1(x)}{x^2+h_1(x)}\right]$$

$$-\frac{\alpha}{\sqrt{2}}\sum_{jj'}\delta_j\delta_{j'}\int_0^\infty dt\,\frac{e^{-t}}{\sqrt{P_{jj'}(t)}}\ , \tag{39}$$

where $P_{jj'}(t)$ now takes the simplified form

$$P_{jj'}(t) = \frac{\mu}{M}\int_0^\infty dx\,\frac{1-\cos(xt)}{x^2+h_1(x)} + \frac{\pi}{4s}(\rho_j^2+\rho_{j'}^2 - 2\rho_j\rho_{j'}e^{-st})\ . \tag{40}$$

It should be noted that (39) is an upper bound on $E_0/\hbar\omega$ under all circumstances though in general not the lowest one, if $\alpha \not\ll 1$. We discuss three cases.

(*A*) $\eta\sqrt{\sigma} \gg 1$: *Bare exciton.* The minimizing value of s has the property $s \propto \eta^2 \gg 1$. As a consequence the leading terms in $\sum_{jj'}\cdots$ cancel; $h_1(x)$ is zero. We obtain

$$\frac{B}{\hbar\omega} = -\frac{8}{3\pi}\eta^2[1+O(\eta^{-3}\sigma^{-3/2})]$$

$$= -\frac{8}{3\pi}\frac{\mathcal{R}_\infty}{\hbar\omega}[1+O(\eta^{-3}\sigma^{-3/2})]\ . \tag{41}$$

Apart from the "wrong" factor, $8/3\pi$ instead of 1, this is exactly the result which was to be expected from the qualitative discussion in the Introduction. The discrepancy in the numerical factors is due to the harmonic approximation of the instantaneous Coulomb interaction in (15). Nevertheless, phonon influences are excellently described within the Gaussian approximation. This is suggested by polaron theory; further support comes from a subsequent paper (II), in which we will discuss a Coulombic term in the trial action.

(*B*) $\eta \ll 1$, $\sigma = O(1)$: *Polaronic exciton, comparable masses of electron and hole.* Now the minimizing value of s has the property $s \ll 1$. Expanding $P_{jj'}(t)$ up to second order in s and setting $h_1(x) \equiv 0$, we arrive at

$$\frac{B}{\hbar\omega} = -\sum_j \frac{\alpha}{\sqrt{|\rho_j|}} - \frac{8}{3\pi}(\eta-\alpha)^2\left(1+\sum_j\frac{\alpha}{\sqrt{|\rho_j|}}\,\frac{|\rho_j|}{6}\right) + O(\alpha\eta^3)$$

$$= -\sum_j \alpha_j - \frac{8}{3\pi}\,\frac{\mu_p e^4}{2\epsilon_0^2\hbar^2}\Big/\hbar\omega + O(\alpha\eta^3)\ . \tag{42}$$

Here we introduced the usual electron-phonon and hole-phonon coupling constants $\alpha_j = \alpha/\sqrt{|\rho_j|}$ and the "reduced polaron mass"

$$\frac{1}{\mu_P} = \sum_j [m_j(1+\alpha_j/6)]^{-1}\ . \tag{43}$$

We stress that in comparison with a free exciton the two simultaneous changes $m_j \to m_j(1+\alpha_j/6)$ and $\epsilon_\infty \to \epsilon_0$ occur. As for the "wrong" factor $8/3\pi$ in (42), see Sec. III (A).

(*C*) $\eta \ll 1$, $\alpha/\sqrt{\sigma} \gg 1$: *Polaronic exciton, small electron-hole mass ratio.* Expressing ρ_j, μ/M by σ and collecting leading terms in $\sqrt{\sigma}$ we obtain from (39) and (40)

$$\frac{B}{\hbar\omega} = \min_{h_1}\left\{\frac{3}{2\pi}\int_0^\infty dx\left[\ln\left(1+\frac{h_1(x)}{x^2}\right) - \frac{h_1(x)}{x^2+h_1(x)}\right] - \frac{\alpha}{2\sqrt{\sigma}}\int_0^\infty dt\,\frac{e^{-t}}{\sqrt{P(t)}}\right\}$$

$$-\alpha - \frac{8}{3\pi}\,\frac{\mu(1+\frac{1}{6}\alpha)e^4}{2\epsilon_0^2\hbar^2}\Big/\hbar\omega + O(\alpha\eta^3) + O(\alpha\sqrt{\sigma})\ , \tag{44}$$

where

$$P(t) = \int_0^\infty dx\,\frac{1-\cos(xt)}{x^2+h_1(x)}\ . \tag{45}$$

Interestingly enough, the first part in (44) is exactly the expression for a general Gaussian bound on the self-energy of a free polaron with coupling constant $\alpha/\sqrt{\sigma}$, which was studied recently.[7] For large $\alpha/\sqrt{\sigma}$ this polaron bound approaches $-(3\pi)^{-1}(\alpha/\sqrt{\sigma})^2$. Consequently, a dramatic lowering of the ground-state energy occurs. The second part in (44) contains the self-energy ($-\alpha$) and the "polaronic" Coulomb term of the relative motion. As $\alpha < \eta \ll 1$, the appearance of the weak-coupling result for the (polaronic) self-energy was to be expected.

We close this section with a compilation of our numerical results. Starting from expression (31) for the bound on E_0 we performed two calculations. In a first example we used

$$h_i(x)=\gamma_i\,,\quad x>0,\quad i=1,\ 2,\ 3 \tag{46}$$

$\{\gamma_i\}$ being real variational parameters which serve to minimize (31). The corresponding trial action $\tilde{S}$ may be characterized as harmonic and instantaneous. In the following table and the figures this is indicated by "H.O."

Our second example is

$$h_i(x)=(B_i x^2+C_i)/(x^2+D_i),\quad x\geq 0,\quad i=1,2$$
$$h_3(x)\equiv 0,\quad C_1=0\ . \tag{47}$$

B_i, C_i, D_i are real variational parameters. Now the trial action $\tilde{S}$ is a two-particle generalization of Feynman's[4] trial action; in particular, it is noninstantaneous. The corresponding results are characterized by an index "FE." As was indicated earlier, we parametrize our numerical results in a way that differs from that which we took for the analytical investigation—a comparison with previous work is easier this way. The energy unit is the excitonic Rydberg

$$\mathcal{R}_0=\mu e^4/(2\hbar^2\epsilon_0^2)\ . \tag{48}$$

Instead of (35)–(37) we use additionally the parameters

$$\mathcal{R}_0/\hbar\omega,\quad \epsilon_0/\epsilon_\infty,\quad m_1/m_2\ . \tag{49}$$

Table I and the Figs. 1 and 2 contain our results.

IV. DISCUSSION AND COMPARISON WITH PREVIOUS WORK

An interesting aspect of our results is the rapid lowering of the total energy bound if $\sigma=m_1/m_2$ tends to zero. As was shown in the preceding part, the reason for this behavior is strong hole-phonon coupling, which has to be treated adequately. The same strong-coupling effect shows up for the bound Σ on the self-energy which is additionally given in the Table and in Fig. 1. Σ was calculated as a sum of two one-polaron bounds on the corresponding ground-state energy according to Feynman's theory.[4,7]

As far as a comparison with previous work is concerned, we have already mentioned the early pioneering papers of Haken[5] and Moskalenko[6]; they introduced the functional-integration method to exciton theory. In his first paper Haken investigated harmonic and nonharmonic trial actions, the latter being of Coulomb type. Here we are concerned with the harmonic case. Haken's example can be derived from (15) by taking $f_1(\tau)=f_3(\tau)=0$, $f_2(\tau)=C_2\delta(\tau)$. In a second paper he admitted additionally a harmonic coupling of m_1, m_2 to two fictitious particles, which is equivalent to having contributions to $f_i(\tau)$ of the form $p_j[\delta(\tau-\tau')-w_j G_{w_j}(\tau-\tau')]$, $j=1,2$ [as for $G_w(\tau-\tau')$ see Eq. (7); $\hbar\omega$ has to be replaced by w]. Moskalenko used $f_1(\tau)=C_1[\delta(\tau)-wG_w(\tau)]$, $f_2(\tau)=C_2\delta(\tau)$, $f_3(\tau)=0$. In both cases a numerical evaluation is missing. Recently Atzmüller[9] reinvestigated Haken's examples for special material parameters in the region $m_1/m_2>0.12$. His results are in good agreement with ours.

TABLE I. Upper bounds on the ground-state energy (B) and self-energy (Σ) of the exciton in units of $\mathcal{R}_0=\mu e^4/2\hbar^2\epsilon_0^2$ as a function of the mass ratio m_1/m_2 and the energy ratio $\mathcal{R}_0/\hbar\omega$. The value of $\epsilon_0/\epsilon_\infty$ is fixed as 2. $B_{\rm H.O.}$, $B_{\rm FE}$, and $B_{\rm BAS}$ correspond to Eqs. (46) and (47) and Ref. 12, respectively.

Energy bounds	m_1/m_2 0.01	0.02	0.05	0.1	0.2	0.5	1.0	$\frac{\mathcal{R}_0}{\hbar\omega}$
$-B_{\rm H.O.}$	12.201	7.1242	4.1337	3.6606	3.5563	3.4980	3.4870	
$-B_{\rm FE}$	12.534	7.2482	4.1358	3.6539	3.5521	3.4943	3.4837	10
$-\Sigma$	11.333	6.0299	2.8534	1.8030	1.2922	1.0144	0.9613	
$-B_{\rm BAS}$	5.4726	4.8432	4.3977	4.2303	4.1418	4.0907	4.0810	
$-B_{\rm H.O.}$	13.626	8.5519	5.5661	4.6340	4.1726	3.9058	3.8546	
$-B_{\rm FE}$	13.587	8.3032	5.3113	4.5807	4.1597	3.9019	3.8514	2
$-\Sigma$	12.870	7.5786	4.4212	3.2893	2.6149	2.1539	2.0554	
$-B_{\rm BAS}$	9.0961	7.2005	5.6818	5.0380	4.6709	4.4464	4.4024	
$-B_{\rm H.O.}$	15.395	10.311	7.0275	5.6775	4.8928	4.4069	4.3111	
$-B_{\rm FE}$	14.866	9.6183	6.7388	5.5745	4.8576	4.3935	4.3000	1
$-\Sigma$	14.614	9.3479	5.9757	4.5467	3.6462	3.0174	2.8818	
$-B_{\rm BAS}$	12.185	9.3639	6.9935	5.9258	5.2865	4.8789	4.7972	

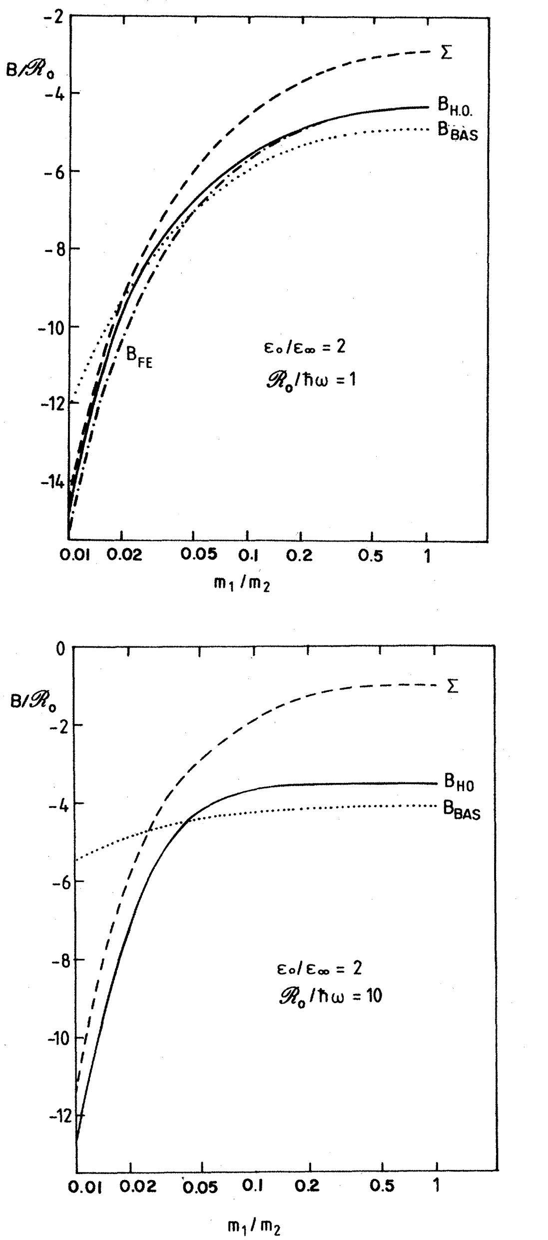

FIG. 1. Upper bounds on the ground-state energy (B) and self-energy (Σ) of the exciton in units of $\mathcal{R}_0$ as a function of the mass ratio m_1/m_2. $\epsilon_0/\epsilon_\infty$ and $\mathcal{R}_0/\hbar\omega$ are fixed as indicated. In the case $\mathcal{R}_0/\hbar\omega = 10$ the deviation of $B_{\text{H.O.}}$ and B_{FE} is within 2%; therefore only $B_{\text{H.O.}}$ appears in the figure.

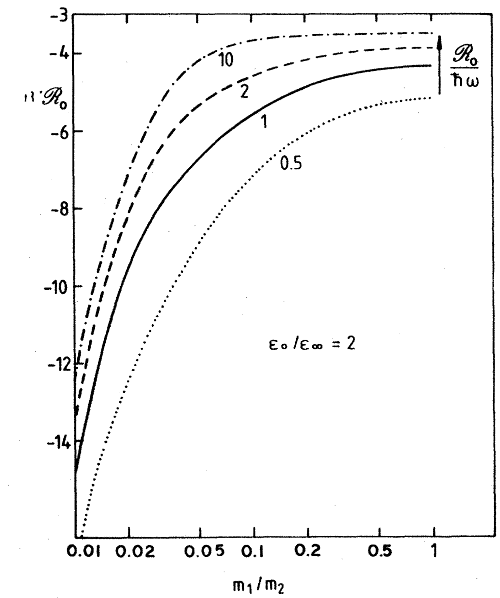

FIG. 2. Upper bounds on the ground-state energy (B) of the exciton in units of $\mathcal{R}_0$ as a function of m_1/m_2 and $\mathcal{R}_0/\hbar\omega$. $\epsilon_0/\epsilon_\infty$ is fixed as indicated.

A host of theoretical predictions comes from the discussion of so-called "effective Hamiltonians." An outline of this concept can be found, e.g., in Refs. 11 and 12; mostly the authors use normal variational methods. Recent publications are due to Kane,[10] Pollmann and Büttner,[11] Bednarek, Adamowski, and Suffczynski,[12] Aldrich and Bajaj,[13] Hattori,[14] and Mahler and Schröder.[15] In Table I and in Fig. 1 we show the result of the involved variational calculations in Ref. 12; the energy bound B_{BAS} compares favorably with those which can be found in Refs. 10, 11, and 13–15.

Obviously B_{BAS} is superior to $B_{\text{H.O.}}$ and B_{FE} in the region $\sigma > 0.05$. The main reason for the discrepancy was given in Sec. III A: The harmonic approximation of the instantaneous Coulomb potential underestimates the corresponding contribution to the total energy by a factor $8/3\pi$. For $\sigma < 0.05$, however, things change drastically: Now $B_{\text{H.O.}}$ and B_{FE} are superior to B_{BAS}. It is interesting to notice that even our upper bound Σ on the self-energy is lower than B_{BAS}, if σ is sufficiently small. This has an important consequence: $B - \Sigma$ is an estimate for the binding energy of the ground state. $B - \Sigma > 0$ indicates "no binding"; actually this is what happens in the case of effective-Hamiltonian theories of type[10–15], if (as in our case) a better approximation for the self-energy is used than that, which derives from the polaron theory of Lee, Low, and Pines.[16] In particular, the result of the extrapolation $\sigma \to 0$ must be doubted; nevertheless, this limit is physically relevant; it applies to the case of a bound polaron.

Usually bound polarons are described by a Hamiltonian which can be derived from (1)—choose $\rho_1 = 1$, $\rho_2 = 0$—by a unitary transformation which subtracts automatically the infinite self-energy of the static charge (see the work of Platzmann,[17] Matsuura[18]). We compared our results with those of Refs. 17 and 18. Taking care of the relation $\sqrt{\mathcal{R}_0/\hbar\omega}\,(\epsilon_0/\epsilon_\infty - 1) = \alpha$ and choosing realistic values for the parameters, we found good agreement.

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