

Concise calculations of the ground-state energy for the strongly bound exciton-phonon system

Chen Qinghu, Wang Kelin, and Wan Shaolong

Center for Fundamental Physics, University of Science and Technology of China, Hefei 230026, China

(Received 20 June 1994)

A concise variational approach is presented for the calculation of the ground-state energy of the strongly bound exciton-phonon system. By using the phonon coherent state to represent the phonon wave function, which depends on the wave function of the relative motion $\phi(\mathbf{r})$, a nonlinear integrodifferential equation satisfied by $\phi(\mathbf{r})$ is derived. Numerical calculations are carried out for a few polar materials and the upper bounds to the true ground-state energy of corresponding excitons are obtained. It is found that our method is especially suitable for the case of the strong binding.

The problem of a Wannier exciton interacting with an LO-phonon field has been the subject of an enormous number of investigations since the pioneering study by Haken¹ in 1956. One reason is that it provides a significant example for two interacting fermions in a boson field. Another more serious one is that the obtained energies can be used to explain the optical spectra near the absorption edge of semiconductors. The main approaches applied to this problem can be divided into three types: variational calculations¹⁻⁶ including the path-integral method,⁶ the perturbation theory,^{7,8} and Green's-function methods.⁹⁻¹¹ But this problem is still far away from an exact solution up to now. Therefore it is also necessary to develop new methods to this problem. On the other hand, in our opinion, it is important to study the exciton-phonon problem for the strong binding, such as that in some polar materials.

The purpose of this paper is to present a variational approach to the calculation of the exciton ground-state energy for the strong binding. We start with the well-known exciton-phonon Hamiltonian for an isotropic system in a nondegenerate two-band model,

$$H = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} - \frac{e^2}{\epsilon_\infty r} + \sum_{\mathbf{k}} \hbar\omega_0 a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \sum_{\mathbf{k}} [v_{\mathbf{k}} \rho_{\mathbf{k}}(\mathbf{r}) a_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} + \text{H.c.}], \quad (1)$$

where M and μ are the total and reduced band masses, \mathbf{P}, \mathbf{p} , and \mathbf{R}, \mathbf{r} are center-of-mass and relative momenta and coordinates, respectively, $a_{\mathbf{k}}^\dagger$ and $a_{\mathbf{k}}$ are, respectively, the creation and annihilation operators of the LO phonons with the wave vector \mathbf{k} , and $\hbar\omega_0$ is the LO-phonon energy,

$$\rho_{\mathbf{k}}(\mathbf{r}) = e^{is_2 \mathbf{k}\cdot\mathbf{r}} - e^{-is_1 \mathbf{k}\cdot\mathbf{r}}, \quad s_i = m_i/M \quad (i=1,2), \quad (2)$$

$$v_{\mathbf{k}} = -i \left[\frac{2\pi e^2 \hbar\omega_0}{\epsilon^* \nu} \right]^{1/2} \frac{1}{|\mathbf{k}|}, \quad \frac{1}{\epsilon^*} = \frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty}, \quad (3)$$

with ϵ_∞ and ϵ_0 the high-frequency and static dielectric constants, respectively. As usual, we eliminate the center-of-mass coordinate \mathbf{R} from Eq. (1) by the unitary transformation

$$U_1 = \exp[i(\mathbf{Q} - \sum_{\mathbf{k}} \hbar\mathbf{k} a_{\mathbf{k}}^\dagger a_{\mathbf{k}}) \cdot \mathbf{R}], \quad (4)$$

where the total linear momentum of the system \mathbf{Q} is a constant of motion. Set $\mathbf{Q}=0$ for when only the ground state is concerned, then the Hamiltonian (1) can be written as follows:

$$H = \frac{\mathbf{p}^2}{2\mu} - \frac{e^2}{\epsilon_\infty r} + \sum_{\mathbf{k}} \left[\hbar\omega_0 + \frac{\hbar^2 \mathbf{k}^2}{2M} \right] a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \sum_{\mathbf{k}} [v_{\mathbf{k}} \rho_{\mathbf{k}}(\mathbf{r}) a_{\mathbf{k}} + \text{H.c.}] + \sum_{\mathbf{k}, \mathbf{k}'} \hbar^2 \frac{\mathbf{k}\cdot\mathbf{k}'}{2M} a_{\mathbf{k}}^\dagger a_{\mathbf{k}'}^\dagger a_{\mathbf{k}} a_{\mathbf{k}'}, \quad (5)$$

where the last term is referred to as the recoil term.

It is noted that the Hamiltonian (5) does not conserve the total number of phonons, so a reasonable approximate choice of the wave function of the phonon part is a coherent state of phonons. The next step in almost all previous variational calculations was to factorize the total wave function by using the phonon coherent state and the wave function of the relative motion

$$|\dots\rangle = \exp \left[\sum_{\mathbf{k}} [F_{\mathbf{k}}(\mathbf{r}) a_{\mathbf{k}} - F_{\mathbf{k}}(\mathbf{r}) a_{\mathbf{k}}^\dagger] \right] |0\rangle \phi(\mathbf{r}), \quad (6)$$

where the ket $|0\rangle$ denotes the phonon vacuum state.

Until now almost all authors have chosen the amplitudes $F_{\mathbf{k}}(\mathbf{r})$ to be functions of the relative coordinate \mathbf{r} . It should be admitted that these treatments contain the underlying physics. But it results in some mathematical difficulties. To overcome these difficulties, two approximations had been introduced in Refs. 1-5. First, the forms of $F_{\mathbf{k}}(\mathbf{r})$ were chosen physically. For detailed knowledge of these choices, one can refer to the literature. Particularly in Ref. 5, Iadonisi, Bassani, and Strinati introduced a rather complicated technique of an expansion of $F_{\mathbf{k}}(\mathbf{r})$ in partial waves in correspondence to the different angular momentum values. Second, all authors assumed $\phi(\mathbf{r})$ to take the hydrogenlike form,

$$\phi(\mathbf{r}) = \left[\frac{\lambda^3}{\pi} \right]^{1/2} e^{-\lambda r}, \quad (7)$$

where λ is a variational parameter. Indeed, some variational approaches can give good bounds to the true

ground-state energy of excitons for some parameter values due to successful choices of $F_{\mathbf{k}}(\mathbf{r})$.

In this paper, different from all previous variational approaches, the total wave-function solution to the Hamiltonian (5) is assumed to take the following form:

$$\begin{aligned} |\cdots\rangle &= \phi(\mathbf{r}) |A\rangle, \\ |A\rangle &= \exp \left[\sum_{\mathbf{k}} [\alpha^*(\mathbf{k}) a_{\mathbf{k}} - \alpha(\mathbf{k}) a_{\mathbf{k}}^\dagger] \right] |0\rangle, \end{aligned} \quad (8)$$

where $\alpha(\mathbf{k})$ is a variational function and will be determined consistently from the wave function of the relative motion $\phi(\mathbf{r})$. The key difference between Eqs. (6) and (8)

is that $F_{\mathbf{k}}(\mathbf{r})$ is replaced by $\alpha(\mathbf{k})$. Obviously, the previous wave function (6) is more universal than ours. But it is very difficult to determine $F_{\mathbf{k}}(\mathbf{r})$ from the relative motion, so some approximations were introduced as stated before. Based on Eq. (8), we will develop a more rigorous variational approach where no approximation is made. On the other hand, in the strong-coupling theory of single polarons,^{13,14} it has been proved that Eq. (8) is really a quite good variational wave function. Therefore, as far as the strong-binding case is concerned, we expect our approach is superior to the existing methods.

In the next step, we average the Hamiltonian (5) over the wave function (8) and have the energy expectation

$$E[\alpha^*(\mathbf{k}), \alpha(\mathbf{k})] = E_r + \sum_{\mathbf{k}} \left[\hbar\omega_0 + \frac{\hbar^2 \mathbf{k}^2}{2M} \right] \alpha^*(\mathbf{k}) \alpha(\mathbf{k}) + \sum_{\mathbf{k}} [v_{\mathbf{k}} \langle \rho_{\mathbf{k}}(\mathbf{r}) \rangle \alpha(\mathbf{k}) + \text{H.c.}] + \sum_{\mathbf{k}, \mathbf{k}'} \hbar^2 \frac{\mathbf{k} \cdot \mathbf{k}'}{2M} \alpha^*(\mathbf{k}) \alpha^*(\mathbf{k}') \alpha(\mathbf{k}) \alpha(\mathbf{k}'), \quad (9)$$

where

$$E_r = \int d\mathbf{r} \phi^*(\mathbf{r}) \left[-\frac{\nabla_{\mathbf{r}}^2}{2\mu} - \frac{e^2}{\epsilon_{\infty} r} \right] \phi(\mathbf{r})$$

is independent of $\alpha(\mathbf{k})$ and $\alpha^*(\mathbf{k})$,

$$\begin{aligned} \langle \rho_{\mathbf{k}}(\mathbf{r}) \rangle &= 4\pi \int_0^\infty dr r \phi^2(r) \\ &\times \left[\frac{\sin(s_2 kr)}{s_2 k} - \frac{\sin(s_1 kr)}{s_1 k} \right]. \end{aligned} \quad (10)$$

In the following we will neglect the last term, which comes from the recoil term, in the energy expectation. We will prove that this term vanishes exactly in our approach subsequently. Then, minimizing the energy expectation with respect to $\alpha(\mathbf{k})$ and $\alpha^*(\mathbf{k})$ results in

$$\begin{aligned} \alpha(\mathbf{k}) &= -\frac{V_{\mathbf{k}} \langle \rho_{\mathbf{k}}^*(\mathbf{r}) \rangle}{\hbar\omega_0 + \frac{\hbar^2 \mathbf{k}^2}{2M}}, \\ \alpha^*(\mathbf{k}) &= -\frac{V_{\mathbf{k}} \langle \rho_{\mathbf{k}}(\mathbf{r}) \rangle}{\hbar\omega_0 + \frac{\hbar^2 \mathbf{k}^2}{2M}}. \end{aligned} \quad (11)$$

According to Eqs. (3), (10), and (11), we know that both $\alpha^*(\mathbf{k})$ and $\alpha(\mathbf{k})$ are only related to the module of the vector \mathbf{k} , namely, $\alpha^*(\mathbf{k}) = \alpha^*(k)$, $\alpha(\mathbf{k}) = \alpha(k)$. Therefore

if we perform the angular integration first, there must be an angular integral in the last term of the energy expectation (9) which gives

$$\int_0^\pi d\theta \sin\theta \cos\theta = 0. \quad (12)$$

Such a term really vanishes exactly. In our opinion, for the variational wave function Eq. (8) where $\alpha^*(\mathbf{k})$ and $\alpha(\mathbf{k})$ are determined by Eq. (11), the neglect of the recoil term in the Hamiltonian (5) does not violate the variational principle.

If averaging the Hamiltonian (5) over the phonon coherent state $|A\rangle$, we have the following effective Hamiltonian in the representation of the relative coordinate:

$$\begin{aligned} H_{\text{eff}} &= \frac{\mathbf{p}^2}{2\mu} - \frac{e^2}{\epsilon_{\infty} r} + \sum_{\mathbf{k}} \left[\hbar\omega_0 + \frac{\hbar^2 \mathbf{k}^2}{2M} \right] \alpha^*(\mathbf{k}) \alpha(\mathbf{k}) \\ &+ \sum_{\mathbf{k}} [v_{\mathbf{k}} \rho_{\mathbf{k}}(\mathbf{r}) \alpha(\mathbf{k}) + \text{H.c.}]. \end{aligned} \quad (13)$$

It is of some interest to note that the effective Hamiltonian contains the wave function of relative motion $\phi(\mathbf{r})$. Substituting Eq. (11) into Eq. (13), transforming the summation $\sum_{\mathbf{k}}$ into an integral $v/(2\pi)^3 \int d\mathbf{k}$, and performing all angular integrals analytically, the Schrödinger equation for $\phi(\mathbf{r})$ is finally obtained as follows:

$$\begin{aligned} E\phi(\mathbf{r}) &= \left[-\frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2\mu} - \frac{e^2}{\epsilon_{\infty} r} \right] \phi(\mathbf{r}) + \frac{\omega_0}{\pi \epsilon^*} \int_0^\infty dk \frac{|\langle \rho_{\mathbf{k}}(\mathbf{r}) \rangle|^2}{\hbar\omega_0 + \frac{\pi^2 \mathbf{k}^2}{2M}} \phi(\mathbf{r}) \\ &- \frac{2\omega_0}{\pi \epsilon^*} \int_0^\infty dk \left[\frac{\sin(s_2 kr)}{s_2 kr} - \frac{\sin(s_1 kr)}{s_1 kr} \right] \frac{\langle \rho_{\mathbf{k}}(\mathbf{r}) \rangle}{\hbar\omega_0 + \frac{h^2 \mathbf{k}^2}{2M}} \phi(\mathbf{r}). \end{aligned} \quad (14)$$

This is a nonlinear integrodifferential equation satisfied by the wave function of the relative motion $\phi(\mathbf{r})$. It is easily found that the hydrogenlike form wave function is not an exact solution to this equation. It is noticed that

Eq. (14) cannot be solved analytically. Therefore a numerical solution is clearly called for.

Given the values of the material parameters, in principle, the upper bounds to the true ground-state energy can

TABLE I. Some parameters of LiF, CuCl, and Cu₂O (notations are shown in the text).

Material	m_1	m_2	ϵ_0	ϵ_∞	$\hbar\omega_0$	R_1	R_2	R_y^0
LiF	0.78	10.0	9.3	2.9	56.4	17.59	4.91	113.8
CuCl	0.44	3.60	7.4	3.7	27.2	33.72	11.79	97.4
Cu ₂ O	0.61	0.84	7.1	6.2	75.1	17.23	14.69	95.4

be evaluated by solving the Schrödinger equation numerically. Here we briefly describe the numerical procedures. Choosing an initial wave function, substituting it into Eq. (10), Eq. (14) is then reduced to a two-point boundary value problem. The boundary conditions are $\phi'(0)=0$ and $\phi(\infty)=0$. For each iteration, by the shooting method, we can get a new solution for the wave function. In general, it is not the true solution of the Schrödinger equation (14), because they are different from that in $\langle\rho_{\mathbf{k}}(\mathbf{r})\rangle$ according to Eq. (10). But it is believed that after sufficient time iterations the obtained solution is brought into close agreement with the true one. In the following calculations, based on our extensive tests, we believe that our results for the energy are very accurate.

In order to test our approach, we will apply it to the problem of excitons in some polar materials with a variety of parameters. In Table I we list the parameters of these materials, which are directly cited from Ref. 5. In columns 7 and 8 the single polaron radii R_1 and R_2 for the electron and the hole are given, which are calculated from $R_i=(\hbar/2m_i\omega_0)^{1/2}$, $i=1,2$. In the last column, we present the exciton Rydberg $R_y^0=\mu e^4/2\hbar^2c_0^2$. In our paper energies are in meV, masses and lengths are in atom units.

Our numerical results are reported in Table II. In the first column, our variational results for the total exciton energy are given. Because the actual exciton radius has not been obtained so far, we will calculate it from the obtained wave function for the relative motion by fitting it with a hydrogenlike form (7), as shown in column 7. For obtaining the binding energy, we also list the sum of two polaron energies Σ of the free electron-hole pair in column 4, which results from the Feynman theory.¹² Hence we can easily get the exciton binding energy in column 5. For comparison, in columns 3 and 8 we list the more recent variational results for the total exciton energy and the exciton radius obtained by Iadonisi, Basani, and Strinati.⁵ Besides, the experimental values for the exciton binding energy are listed in column 6.

It can be seen from Table II that, in LiF, our result for the total exciton energy is considerably lower than the recent well-known one E_T^{IBS} ,⁵ the binding energy is much closer to the experimental data. In addition, our result

for the exciton radius is nearly equal to the previous one $a_{\text{ex}}^{\text{IBS}}$.⁵ In CuCl, our results for the total exciton energy, the binding energy, and the exciton radius agree with the previous variational ones. Also, like previous variational approaches, our exciton binding energy E_b in CuCl is larger than the corresponding experimental data E_b^{exp} . This is perhaps partially due to the neglect of central cell corrections which increase the total energy by enlarging the exciton radius. Unfortunately, in Cu₂O, our method yields worse results for excitons.

As is well known, the larger the values of $R_y^0/\hbar\omega$ and R_1/a_{ex} , the stronger the exciton-phonon binding in the system should be. It is very interesting to note from Table II that exciton-phonon binding in LiF is the strongest among the materials listed, because of the largest values of $R_y^0/\hbar\omega=2.02$ and $R_1/a_{\text{ex}}=6.49$. As a result, we get very good results for the excitons. In CuCl, the exciton-phonon binding is the next stronger, due to ratios $R_y^0/\hbar\omega=3.58$ and $R_1/a_{\text{ex}}=3.47$. We obtain as good results as those in the recent variational ones.⁵ But in Cu₂O, the exciton-phonon binding is not strong enough, for the reason that the values of $R_y^0/\hbar\omega=1.27$ and $R_1/a_{\text{ex}}=0.98$ are relatively smaller than those in LiF and CuCl. Consequently, we got unsatisfactory results. It follows that as the exciton-phonon binding become stronger, our method becomes more useful.

In summary, we have presented a variational approach to the strong-binding exciton-phonon problem. The wave function of the phonon part is assumed to take the form related to the wave function of the relative motion, which is intrinsically different from those taken by all previous authors. Moreover, the wave function for the relative motion is numerically calculated from the derived integrodifferential equation rather than select a hydrogenlike form to minimize the energy expectation, which is also different, to the best of our knowledge, from all previous approaches. Most importantly, compared to previous rather involved methods, although our approach is very simple, to the best of our knowledge, in some strong binding materials, our variational approach can give the best results for excitons. We admit that for the weak-binding case, our approach is inferior to some previous ones. It is also possible that a more general

TABLE II. Some results for excitons in LiF, CuCl, and Cu₂O (notations are shown in the text).

Material	E_T	E_T^{IBS}	Σ	E_b	E_b^{exp}	a_{ex}	$a_{\text{ex}}^{\text{IBS}}$	R_1/a_{ex}	$R_y^0/\hbar\omega$
LiF	-2922	-2816	-1282	1640	1800	2.70	2.7	6.49	2.02
CuCl	-424	-428	-195	229	194	9.73	10.1	3.47	3.58
Cu ₂ O	-129	-136	-32	97		17.6	18.4	0.98	1.27

form of $\alpha(\mathbf{k})$, leading to a finite recoil term, could improve the result for the weak-coupling limit. We will discuss this problem elsewhere.

Finally, we would like to point out that the variational method developed in this paper is also suited for the treatment of bipolarons, because bipolarons are known to

exist in the strong-coupling range.¹⁵ These calculations are in progress.

This research was supported by the Nonlinear Science Foundation of China.

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