PHYSICAL REVIEW B VOLUME 10, NUMBER 8 15 OCTOBER 1974

Wannier exciton in a polarizable field*

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(Received 12 September 1973; revised manuscript received 19 February 1974)

An expression for calculating the state energies of a Wannier exciton, interacting with a crystalline polarization field, is derived. The derived expression is applicable for arbitrary values of the electron-hole binding. This expression is applied to calculate the binding energy of a Wannier exciton in the ionic polarization field for a number of polar semiconductors. The results obtained are discussed in relation to experimental results and some comments on the previous calculations of other authors and the present authors are drawn.

I. INTRODUCTION

The problem of an electron and a hole interacting with each other through a Coulomb law as a Wannier exciton, and with a crystalline polarization field (ionic or electronic polarization field), has been of considerable interest. In order to see the effect of the interaction between the electron-hole pair and the crystalline polarization field on the binding energies of excitons, theoretical studies have been carried out for quite some time. However, most of the work has been done in two limiting cases, namely, the strong-binding case[1,2] and the weak-binding case.[3-7] Recently Mahanti and Varma[8] used a many-body approach to solve the problem in both the weak- and strong-binding limits within the effective mass theory; they then introduced an interpolation scheme to calculate the binding energy of a Wannier exciton of aribtrary binding. However, from the discrepancy between the Mahanti-Varma result and that of Sak derived later[7] in the weak-binding limit, the accuracy of this interpolation scheme is now in question. More recently, Vooght and Bajaj[9] extended the method used in Ref. 10 to the calculation of the ground state of a Wannier exciton in a polar crystal. As can be seen clearly in the work of Wang, Woo and Matsuura[11] (referred to as WWM hereafter), such a method is applicable only to the case where the unperturbed energy of the hydrogenic Hamiltonian is not greater than the virtual-particle energy. This is due to the omission of one term (which is important for large binding) in their evaluation of second-order perturbation correction of the energy.

In this paper we use a second-order perturbation theory in which the interaction between a source particle and virtual particle can be reduced to a small perturbation even for the strong coupling, as in the work of WWM, to derive directly a reasonable expression for computing the binding energy of a Wannier exciton in a polarizable field for arbitrary binding. The derivation is given in Sec. II. Then the derived result is applied to calculate the binding energies of excitons for a number of polar semiconductors in Sec. III. The results obtained are discussed in relation to experimental values and Mahanti-Varma's results in Sec. IV. Further, we comment on the calculation of Vooght and Bajaj.

II. CALCULATION

A. Formulation

The total Hamiltonian of a Wannier exciton consisting of an electron and a hole in a crystalline polarization field may be written[5]

$$H=\frac{P^2}{2M}+\frac{p^2}{2\mu}-\frac{A}{r}+\sum_{\vec{k}}\epsilon\, a^\dagger_{\vec{k}} a_{\vec{k}} + \sum_{\vec{k}}\left[V_{\vec{k}} a_{\vec{k}} e^{i\vec{k}\cdot\vec{R}}\left(e^{-i\mu_1\vec{k}\cdot\vec{r}}-e^{i\mu_2\vec{k}\cdot\vec{r}}\right)+\text{c. c.}\right], \quad (1)$$

using the coordinates of the center of mass in which the position vector of the center of mass of the electron at $\vec{r}_1$ and the hole at $\vec{r}_2$ is $\vec{R}=(m_1\vec{r}_1+m_2\vec{r}_2)M^{-1}$, where M is the total mass of the electron-band mass m_1 and the hole-band mass m_2. Here $\vec{P}=-i\hbar(\partial/\partial\vec{R})$ is the momentum operator of the center of mass. $\vec{p}$ and $\vec{r}$ are, respectively, the relative momentum operator and coordinate of the electron and hole. μ is the reduced mass given by $m_1\, m_2\, M^{-1}$ and $\mu_j=\mu/m_j$ for $j=1,2$. A equals e^2 for electronic polarization and e^2/ϵ_∞ for ionic polarization, ϵ_∞ being the usual high-frequency dielectric constant. ϵ is the energy of a virtual particle (a phonon energy for ionic polarization and a longitudinal exciton energy for electronic polarization) and is considered as wave-vector independent as in the polaron problem. The meanings of the remaining symbols are the same as in Ref. 5. The last term in Eq. (1) is the interaction between a Wannier exciton (described by the Hamiltonian consisting of the first three terms) and the crystalline polarization field (described by the fourth term) under consideration in the center-of-mass representation.

In order to eliminate $\vec{R}$ from Eq. (1), we introduce a unitary transformation similar to that in Ref. 12, i.e.,

$$\Phi = U\Psi , \tag{2}$$

where Φ is an eigenfunction of H in Eq. (1) and U takes the form

$$U = \exp\left[\frac{i}{\hbar}\left(\hbar\vec{Q} - \sum_{\vec{k}} \hbar\, \vec{k}\, a^\dagger_{\vec{k}} a_{\vec{k}}\right)\cdot \vec{R}\right] . \tag{3}$$

Here $\hbar\vec{Q}$ is the sum of $\vec{P}$ and the exciton recoil momentum operator, i.e.,

$$\hbar\vec{Q} = \vec{P} + \sum_{\vec{k}} \hbar\vec{k}\, a^\dagger_{\vec{k}} a_{\vec{k}} , \tag{4}$$

and is a constant of the motion due to its commutation with the total Hamiltonian H. Application of this transformation to the eigenequation of H, i.e., $H\Phi = E\Phi$, yields

$$\mathcal{H}\Psi = E\Psi , \tag{5}$$

with $\mathcal{H}$ given by

$$\mathcal{H} \equiv U^{-1} H U = \frac{\hbar^2}{2M}\left(\vec{Q} - \sum_{\vec{k}} \vec{k}\, a^\dagger_{\vec{k}} a_{\vec{k}}\right)^2 + \frac{p^2}{2\mu} - \frac{A}{r} + \sum_{\vec{k}} \epsilon\, a^\dagger_{\vec{k}} a_{\vec{k}} + H_I , \tag{6}$$

in which H_I takes the form

$$H_I = \sum_{\vec{k}} \left[V_{\vec{k}} a_{\vec{k}} \left(e^{-i\mu_1 \vec{k}\cdot\vec{r}} - e^{i\mu_2 \vec{k}\cdot\vec{r}}\right) + \text{c.c.} \right] . \tag{7}$$

In this work we are essentially interested in calculating the binding energies for states in which the center of mass of the electron-hole pair is at rest and hence we set $\vec{Q} = 0$. For this case, with the use of the commutation relation $[a_{\vec{k}}, a^\dagger_{\vec{k}'}] = \delta_{\vec{k},\vec{k}'}$, the first term in Eq. (6) can be written

$$\sum_{\vec{k}} \frac{\hbar^2 k^2}{2M}\, a^\dagger_{\vec{k}} a_{\vec{k}} + H' ,$$

where

$$H' = \frac{\hbar^2}{2M} \sum_{\vec{k}} \sum_{\vec{k}'} \vec{k}\circ \vec{k}'\, a^\dagger_{\vec{k}} a^\dagger_{\vec{k}'} a_{\vec{k}} a_{\vec{k}'} , \; .$$

Hence $\mathcal{H}$ can be written

$$\mathcal{H} = \frac{p^2}{2\mu} - \frac{A}{r} + \sum_{\vec{k}} E_{\vec{k}}\, a^\dagger_{\vec{k}} a_{\vec{k}} + H' + H_I , \tag{8}$$

where $E_{\vec{k}} = \epsilon + \hbar^2 k^2 / 2M$.

We shall use a perturbation method, in which the perturbation involved can be reduced to one weaker than the original interaction H_I given in Eq. (7), to treat the problem considered in this work. Therefore, we now introduce a simple canonical transformation in which the annihilation operator for phonons $a_{\vec{k}}$ transforms to

$$\alpha_{\vec{k}} = a_{\vec{k}} + V^*_{\vec{k}} \sigma^*_{\vec{k}} / E_{\vec{k}} , \tag{9}$$

where the quantity $\sigma^*_{\vec{k}}$ is completely arbitrary under the condition that $\alpha_{\vec{k}}$ should act as an annihilation operator for bosons. Really, such a transformation amounts to nothing but the change of the reference system of virtual particles. With the use of Eq. (9) and its complex conjugate, Eq. (8) can be rewritten

$$\mathcal{H} = H_e + \sum_{\vec{k}} E_{\vec{k}}\, \alpha^\dagger_{\vec{k}} \alpha_{\vec{k}} + H'_I + H'_\alpha . \tag{10}$$

Here H_e is given by

$$H_e = p^2/2\mu + V_{\text{eff}}(\vec{r}) , \tag{11}$$

with $V_{\text{eff}}(\vec{r})$ having the form

$$V_{\text{eff}}(\vec{r}) = -\frac{A}{r} - \sum_{\vec{k}} \frac{|V_{\vec{k}}|^2}{E_{\vec{k}}} \times \left[\sigma^*_{\vec{k}}\left(e^{-i\mu_1 \vec{k}\cdot\vec{r}} - e^{i\mu_2 \vec{k}\cdot\vec{r}}\right) + \text{c.c.}\right] + \sum_{\vec{k}} \frac{|V_{\vec{k}}|^2 |\sigma_{\vec{k}}|^2}{E_{\vec{k}}} , \tag{12}$$

which is an effective interaction between the electron and the hole resulting from the above canonical transformation. H'_I in Eq. (10) is of the form

$$H'_I = \sum_{\vec{k}} \left[V_{\vec{k}}\, \alpha_{\vec{k}} X(\vec{r}) + \text{c.c.} \right] , \tag{13}$$

where

$$X(\vec{r}) = \left(e^{-i\mu_1 \vec{k}\cdot\vec{r}} - e^{i\mu_2 \vec{k}\cdot\vec{r}}\right) - \sigma_{\vec{k}} . \tag{14}$$

This H'_I is the interaction between the exciton and the polarizational field in the $\alpha_{\vec{k}}$ representation. It amounts to an interaction like the above H_I minus the interaction $\sum_{\vec{k}} (V_{\vec{k}} \alpha_{\vec{k}} \sigma_{\vec{k}} + \text{c.c.})$ resulting from the above canonical transformation. Here $\sigma_{\vec{k}}$ is arbitrary and can be chosen to make H'_I a small perturbation even in the strong-coupling case. H'_α in Eq. (10) is the $\alpha_{\vec{k}}$ representation of H', i.e., H' written in terms of the boson operators $\alpha_{\vec{k}}$ and $\alpha^\dagger_{\vec{k}}$.

Now, we take the last two terms in Eq. (10) as perturbations and the sum of the remaining two terms as an unperturbed Hamiltonian. From the eigenequation of this unperturbed Hamiltonian we obtain

$$H_e |m\rangle = \epsilon^0_m |m\rangle \tag{15}$$

and

$$\left(\sum_{\vec{k}} E_{\vec{k}}\, \alpha^\dagger_{\vec{k}} \alpha_{\vec{k}}\right) |n_{\vec{k}}\rangle = \epsilon_\nu |n_{\vec{k}}\rangle . \tag{16}$$

Here $|m\rangle$ is an eigenfunction of H_e in Eq. (11) and ϵ^0_m is the corresponding eigenenergy given by

$$\epsilon^0_m = \langle m | \left(\frac{p^2}{2\mu} - \frac{A}{r}\right) | m \rangle$$

$$+\sum_{\vec{k}} \frac{|V_{\vec{k}}|^2}{E_{\vec{k}}} \left[|\sigma_{\vec{k}}|^2 - (\sigma_{\vec{k}}^* \rho_{\vec{k},m} + \text{c.c.}) \right] , \tag{17}$$

with $\rho_{\vec{k},m}$ defined by

$$\rho_{\vec{k},m} = \langle m | (e^{-i\mu_1 \vec{k}\cdot\vec{r}} - e^{i\mu_2 \vec{k}\cdot\vec{r}}) | m \rangle . \tag{18}$$

$|n_{\vec{k}}\rangle \equiv |n_{\vec{k}_1}, n_{\vec{k}_2}, \ldots\rangle$ denotes an eigenstate of the second term of $\mathcal{H}$ in Eq. (10) and ϵ_v is the corresponding eigenvalues. Thus the eigenenergy of an unperturbed state $|m\rangle|n_{\vec{k}}\rangle$ is $\epsilon_m^0 + \sum_{\vec{k}} E_{\vec{k}} n_{\vec{k}}$, where $n_{\vec{k}}$ is the number of virtual particles of wave vector $\vec{k}$. Then, for the initial state $|n\rangle|0\rangle$ in which $|m\rangle$ is $|n\rangle$ and no virtual particles are present, the energy correction due to H_I' is given in second-order perturbation theory by

$$\Delta E_n^{(2)} = \sum_{m,\vec{k}} \frac{|V_{\vec{k}}|^2 |\langle n | X(\vec{r}) | m \rangle|^2}{\epsilon_n^0 - \epsilon_m^0 - E_{\vec{k}}} . \tag{19}$$

Thus, in second-order perturbation theory the total energy for the state under consideration is the energy given by Eq. (17) for $m = n$ plus $\Delta E_n^{(2)}$ given by Eq. (19). After substituting $X(\vec{r})$ given in Eq. (14) into Eq. (19) this total energy, E_n, can also be written

$$E_n = \langle n | (p^2/2\mu - A/r) | n \rangle + \Delta E_n , \tag{20}$$

with ΔE_n given by

$$\Delta E_n = \sum_{m,\vec{k}} \frac{|V_{\vec{k}}|^2 |\langle n | (e^{-i\mu_1 \vec{k}\cdot\vec{r}} - e^{i\mu_2 \vec{k}\cdot\vec{r}}) | m \rangle|^2}{\epsilon_n^0 - \epsilon_m^0 - E_{\vec{k}}} . \tag{21}$$

This expression has the same form as that obtained in the usual second-order perturbation theory, which treats H_I as a perturbation on the Hamiltonian consisting of the first three terms in Eq. (8).[6,9] However, it should be noted that $|m\rangle$ and ϵ_m^0 in Eq. (19) are the eigenfunctions and eigenenergies of the unperturbed Hamiltonian H_e in Eq. (11), not those of $p^2/2\mu - A/r$ as in the usual second-order perturbation theory.

As is shown in Appendix A the last term in Eq. (20) gives the correct results for the energy of the electron-hole pair due to its interaction with the polarization field in the strong- and weak-binding cases regardless of the omission of the other perturbation H_α'. Thus the energy correction due to H_α', which for spherical symmetric $\sigma_{\vec{k}}$ is given in second-order perturbation theory by

$$-\sum_{\vec{k},\vec{k}'} \left(\frac{\hbar^2}{2M}\right)^2 (\vec{k}\cdot\vec{k}')^2 |V_{\vec{k}}|^2 |\sigma_{\vec{k}}|^2 |V_{\vec{k}'}|^2 |\sigma_{\vec{k}'}|^2 \times \left[E_{\vec{k}}^2 E_{\vec{k}'}^2 \left(2\epsilon + \frac{\hbar^2 k^2}{2M} + \frac{\hbar^2 k'^2}{2M} \right) \right]^{-1} ,$$

is negligible as compared with ΔE_n given by Eq. (21). Hereafter we omit the energy correction due to H_α' and take Eq. (20) as the energy expression for a Wannier exciton in the polarization field under consideration. Note that this omission does not amount to dropping the first term in Eq. (6). If this term was completely omitted as in the work of Vooght and Bajaj,[9] then the corresponding ΔE_n does not give the correct result in the weak-binding limit (cf. Appendix A).

B. Comparison with Haken's result

Haken[13] has obtained an expression for the upper bound of the true exciton ground-state energy E_T using the path-integral method. For the state in which the center of mass of the electron-hole pair is at rest as considered in this work, it is given by

$$E_T \le E_g = \langle 1 | \frac{p^2}{2\mu} - \frac{A}{r} | 1 \rangle + \sum_{m,\vec{k}} \frac{|V_{\vec{k}}|^2 |\langle 1 | (e^{-i\mu_1 \vec{k}\cdot\vec{r}} - e^{i\mu_2 \vec{k}\cdot\vec{r}}) | m \rangle|^2}{\epsilon_1 - \epsilon_m - E_{\vec{k}}} . \tag{22}$$

Here ϵ_m and $|m\rangle$ are, respectively, the mth eigenenergy and eigenfunction of the Hamiltonian

$$H = p^2/2\mu + W_{\text{eff}}(r) , \tag{23}$$

where $W_{\text{eff}}(r)$ is an arbitrary effective interaction between the electron and the hole. The ground-state energy given by Eq. (22) has the same form as Eq. (20) for the ground state. Further, the eigenfunctions and eigenenergies of the Hamiltonian given by Eq. (23), appearing in Eq. (22), are essentially the same as those of the Hamiltonian given in Eq. (11), though it is treated as an unperturbed Hamiltonian in the present work. This is because, like $W_{\text{eff}}(r)$ is Eq. (23), the effective interaction $V_{\text{eff}}(\vec{r})$ in Eq. (11) is arbitrary as a result of the arbitrariness of $\sigma_{\vec{k}}$ in $V_{\text{eff}}(\vec{r})$ [cf. Eq. (12)]. Accordingly, the result of Haken, E_g given by Eq. (22), amounts to the second-order result of the perturbation theory as described in the present work. Then, we may apply Eq. (22) to conclude that the ground-state energy calculated by the presently proposed second-order perturbation approach should be above the true ground-state energy of the total Hamiltonian used.

C. Evaluation of ΔE_n

The sum over m and k in Eq. (21) for ΔE_n is too complex to evaluate exactly in general. We shall adopt an approximate method suggested by WWM for this evaluation and write this ΔE_n in the form

$$\Delta E_n = \sum_{i=1}^{2} S_{ni} + S_{n12} + S_{n21} - \sum_{\vec{k}} \frac{|V_{\vec{k}}|^2 |\rho_{\vec{k},n}|^2}{E_{\vec{k}}} , \tag{24a}$$

$$S_{ni} = \sum_{m,\vec{k}} \frac{|V_{\vec{k}}|^2 |\langle n | X_i(\vec{r}) | m \rangle|^2}{\epsilon_n^0 - \epsilon_m^0 - E_{\vec{k}}} , \tag{24b}$$

$$S_{n12} = -\sum_{m,\vec{k}} \frac{|V_{\vec{k}}|^2 \langle n | X_1(\vec{r}) | m \rangle \langle m | X_2^*(\vec{r}) | n \rangle}{\epsilon_n^0 - \epsilon_m^0 - E_{\vec{k}}} , \tag{24c}$$

and S_{n21} is given by Eq. (24c) with X_1 replaced by X_2 and X_2^* by X_1^*. Here $X_1 = e^{-i\mu_1\vec{k}\cdot\vec{r}} - \rho_{\vec{k},n1}$ and $X_2 = e^{i\mu_2\vec{k}\cdot\vec{r}} - \rho_{\vec{k},n2}$, where $\rho_{\vec{k},n1} = \langle n|e^{-i\mu_1\vec{k}\cdot\vec{r}}|n\rangle$ and $\rho_{\vec{k},n2} = \langle n|e^{i\mu_2\vec{k}\cdot\vec{r}}|n\rangle$. $\rho_{\vec{k},n}$ in Eq. (24a) is equal to $\rho_{\vec{k},n1} - \rho_{\vec{k},n2}$.

To calculate S_{ni}, for example, we introduce an operator F_i satisfying the equation

$$([F_i, H_e] - E_{\vec{k}}F_i)|n\rangle = X_i^*|n\rangle \ . \tag{25}$$

In terms of F_i thus defined, the matrix element $\langle m|X_i^*|n\rangle$ in Eq. (24b) is equal to $(\epsilon_n^0 - \epsilon_m^0 - E_{\vec{k}}) \times\langle m|F_i|n\rangle$ so that (24b) can be reduced to

$$S_{ni} = \sum_{\vec{k}} |V_{\vec{k}}|^2 \langle n|X_i F_i|n\rangle \ , \tag{26}$$

making use of the completeness of the eigenfunctions of H_e. Expanding $|n\rangle$ in terms of the complete set of the plane waves as

$$|n\rangle = \sum_{\vec{q}''} \langle\vec{q}''|n\rangle|\vec{q}''\rangle \ , \tag{27}$$

and inserting $\sum_{\vec{q}}|\vec{q}\rangle\langle\vec{q}|$ and $\sum_{\vec{q}'}|\vec{q}'\rangle\langle\vec{q}'|$ in Eq. (26) as in Ref. 9, we have

$$S_{ni} = \sum_{\vec{k}} |V_{\vec{k}}|^2 \sum_{\vec{q},\vec{q}',\vec{q}''} \langle n|\vec{q}\rangle\langle\vec{q}|X_i|\vec{q}'\rangle \times\langle\vec{q}'|F_i|\vec{q}''\rangle\langle\vec{q}''|n\rangle \ . \tag{28}$$

Substituting the matrix element $\langle\vec{q}'|F_i|\vec{q}''\rangle$ obtained from Eq. (25) and then taking the summations over $\vec{q}'$ and $\vec{q}''$, we obtain

$$S_{ni} = S_{ni1} + S_{ni2} + S_{ni3} + S_{ni4} \ , \tag{29a}$$

with

$$S_{ni1} = \frac{2m_i}{\hbar^2} \sum_{\vec{k},\vec{q}} \frac{|V_{\vec{k}}|^2 |\langle n|\vec{q}\rangle|^2}{2\vec{q}\cdot\vec{k} - k^2 - \chi_i} \ , \tag{29b}$$

$$S_{ni2} = -\frac{2m_i}{\hbar^2} \sum_{\vec{k},\vec{q}} \frac{|V_{\vec{k}}|^2 \rho_{\vec{k},ni}^* \langle n|\vec{q}\rangle\langle\vec{q} + \mu_i\vec{k}|n\rangle}{2\vec{q}\cdot\vec{k} + u_i k^2 - \chi_i} \ , \tag{29c}$$

$$S_{ni3} = \frac{2\mu}{\hbar^2} \sum_{\vec{k}} \sum_{\vec{q},\vec{q}'} \frac{|V_{\vec{k}}|^2 R_{\vec{q}-\mu_i\vec{k},\vec{q}'} \langle\vec{q}'|n\rangle\langle n|\vec{q}\rangle}{\vec{q}'^2 - |\vec{q} - \mu_i\vec{k}|^2 - \chi_{\vec{k}}^2} \ , \tag{29d}$$

and S_{ni4} is given by Eq. (29d) with $\langle n|\vec{q}\rangle$ replaced by $-\rho_{\vec{k},ni}^*\langle n|\vec{q} - \mu_i\vec{k}\rangle$. Here $\chi_i = (2m_i\epsilon/\hbar^2)^{1/2}$, $\chi_{\vec{k}} = (2\mu E_{\vec{k}}/\hbar^2)^{1/2}$, u_i is equal to $(m_2 - m_1)M^{-1}$ for $i = 1$, and $(m_1 - m_2)\,M^{-1}$ for $i = 2$, and $R_{\vec{q}-\mu_i\vec{k},\vec{q}'}$ is given by[11]

$$R_{\vec{q}-\mu_i\vec{k},\vec{q}'} = -\langle\vec{q} - \mu_i\vec{k}|\,[F_i, V_{\text{eff}}(\vec{r})]\,|\vec{q}'\rangle \ . \tag{30}$$

S_{n12} and S_{n21} in Eq. (24a) can also be evaluated in a way similar to the above calculation for S_{ni}. S_{n12} thus evaluated is given by

$$S_{n12} = S_{n12a} + S_{n12b} + S_{n12c} + S_{n12d} \ , \tag{31a}$$

where

$$S_{n12a} = -\frac{2m_2}{\hbar^2} \sum_{\vec{k},\vec{q}} \frac{|V_{\vec{k}}|^2 \langle n|\vec{q}\rangle\langle\vec{q} + \vec{k}|n\rangle}{2\vec{q}\cdot\vec{k} + k^2 - \chi_2} \ , \tag{31b}$$

$$S_{n12b} = \frac{2m_2}{\hbar^2} \sum_{\vec{k},\vec{q}} \frac{|V_{\vec{k}}|^2 \rho_{\vec{k},n1} \langle n|\vec{q}\rangle\langle\vec{q} + \mu_2\vec{k}|n\rangle}{2\vec{q}\cdot\vec{k} + u_2 k^2 - \chi_2} \ , \tag{31c}$$

$$S_{n12c} = -\frac{2\mu}{\hbar^2} \sum_{\vec{k}} \sum_{\vec{q},\vec{q}'} \frac{|V_{\vec{k}}|^2 R_{\vec{q}+\mu_1\vec{k},\vec{q}'} \langle\vec{q}'|n\rangle\langle n|\vec{q}\rangle}{\vec{q}'^2 - |\vec{q} + \mu_1\vec{k}|^2 - \chi_{\vec{k}}^2} \ , \tag{31d}$$

and S_{n12d} is given by Eq. (31d) with $\langle n|\vec{q}\rangle$ replaced by $-\rho_{\vec{k},n1}\langle n|\vec{q} + \mu_1\vec{k}\rangle$. S_{n21} is given by Eq. (31a) with an interchange of 1 and 2.

Now, let us discuss the relation between the terms S_{ni3} and S_{ni4} in Eq. (29a). These terms vanish separately in the weak-binding limit where the effective potential $V_{\text{eff}}(\vec{r})$ is effectively zero, because in such a limit $R_{\vec{q}-\mu_i\vec{k},\vec{q}'}$ becomes zero. In going from the weak-binding limit to the strong-binding limit, the factor $\langle n|\vec{q}\rangle - \rho_{\vec{k},ni}^*\langle n|\vec{q} - \mu_i\vec{k}\rangle$, which characterizes the difference between S_{ni3} and S_{ni4}, tends to zero ($\langle n|\vec{q}\rangle$ and $\langle n|\vec{q} - \mu_i\vec{k}\rangle$ approach each other and $\rho_{\vec{k},ni}^*$ tends to unity because $|n\rangle$ is a localized function) and these two terms cancel exactly in the strong-binding limit. Consequently, a good cancellation between S_{ni3} and S_{ni4} will occur even in the intermediate region of binding just as in the case of bound polarons.[11] The same is true for the cancellation between the corresponding terms in S_{n12} or S_{n21}. Therefore, to a good approximation, S_{ni3} and S_{ni4} in S_{ni} and the corresponding terms in S_{n12} and S_{n21} can be omitted in computing ΔE_n given by Eq. (24a). Hence

$$\Delta E_n \simeq \sum_{i=1}^{2} (S_{ni1} + S_{ni2}) + S_{n12a} + S_{n12b} + S_{n21a} + S_{n21b} - \sum_{\vec{k}} \frac{|V_{\vec{k}}|^2 |\rho_{\vec{k},n}|^2}{E_{\vec{k}}} \ . \tag{32}$$

ΔE_n thus evaluated can be shown to give the correct results in the weak- and strong-binding limits (see the Appendix A for results in these limits). Because of this and because small error from the omission of S_{ni3} and S_{ni4} will be canceled to some extent by another small error from the omission of S_{n12c} and S_{n12d}, ΔE_n as given by Eq. (32) is probably valid to a good approximation for arbitrary binding.

III. BINDING ENERGY OF AN EXCITON IN A POLAR SEMICONDUCTOR

The binding energy of an exciton in the ground state is given as the difference in energy between the ground state and the state corresponding to $n = \infty$. For the limit of $n = \infty$ in which $|n\rangle$ is completely diffused, the unperturbed energy and the terms in the energy correction given by Eq. (32) all vanish except S_{ni1} which is the self-energy of the electron or hole in this limit. Therefore, the total energy of the electron-hole pair for the state with $n=\infty$, E_∞ is just the sum of the self-energies of the electron and the hole. Consequently, we need only a detailed calculation for the ground state in calculating the binding energy of interest.

A. Ground states

In the calculation of ground states we consider two cases, i.e., $\sigma_{\vec{k}}$ equal to $aE_{\vec{k}}/\epsilon$, where a is an arbitrary real constant and $\sigma_{\vec{k}}$ equal to $\rho_{\vec{k},1}$.

1. $\sigma_{\vec{k}}=aE_{\vec{k}}/\epsilon$

In the case of $\sigma_{\vec{k}}$ equal to $aE_{\vec{k}}/\epsilon$, the effective interaction defined by Eq. (12) can be reduced to

$$V_{\text{eff}}(\vec{r})=-\gamma/r \tag{33}$$

after replacing the summation over $\vec{k}$ by the $\vec{k}$ integration as in the usual procedure. γ in this equation is given by $\gamma=A-(ae^2/\epsilon^*\mu)\,(m_2-m_1)$ and is essentially arbitrary due to the arbitrariness of the constant a. Note that a constant potential $\sum_{\vec{k}}|V_{\vec{k}}|^2a^2E_{\vec{k}}/\epsilon^2$ was omitted in Eq. (33).

Consequently, the electronic part of the unperturbed Hamiltonian, H_e given by Eq. (11), becomes hydrogenic and its eigensolutions appearing in Eq. (19) are exactly hydrogen like. Hence the lowest state of H_e, which appears in Eq. (20) with ΔE_n given by Eq. (32) for the calculation of the ground state, is of the form

$$|1\rangle=(\lambda^3/\pi)^{1/2}e^{-\lambda r}\,. \tag{34}$$

For $V_{\text{eff}}(\vec{r})$ given by Eq. (33), λ in Eq. (34) is given by $\lambda=\mu\gamma/\hbar^2$.

We now come to the choice of γ in the unperturbed Hamiltonian. Theoretically, γ is arbitrary. However, for the calculation of the ground state, since the true ground-state energy is always below that calculated by the present second-order perturbation theory for arbitrary γ (cf. Sec. IIB), γ may be determined such that the ground-state energy obtained finally is the lowest one within the present case.

2 $\sigma_{\vec{k}}=\rho_{\vec{k},1}$

If $\sigma_{\vec{k}}$ is chosen as $\rho_{\vec{k},1}\equiv\langle 1|(e^{-i\mu_1\vec{k}\cdot\vec{r}}-e^{i\mu_2\vec{k}\cdot\vec{r}})|1\rangle$, then the effective interaction defined by Eq. (12) becomes

$$\begin{aligned}V_{\text{eff}}(\vec{r})=-\frac{A}{r}-\sum_{\vec{k}}\frac{|V_{\vec{k}}|^2}{E_{\vec{k}}}\\ \times[\rho^*_{\vec{k},1}(e^{-i\mu_1\vec{k}\cdot\vec{r}}-e^{i\mu_2\vec{k}\cdot\vec{r}})+\text{c.c.}]\\ +\sum_{\vec{k}}\frac{|V_{\vec{k}}|^2|\rho_{\vec{k},1}|^2}{E_{\vec{k}}}\,.\end{aligned} \tag{35}$$

The corresponding unperturbed Hamiltonian H_e given by Eq. (11) is thus not hydrogenic.

Consequently, in this case the lowest state of H_e, $|1\rangle$ which appears in $\rho_{\vec{k},1}$ and also in Eq. (20) with ΔE_n given by Eq. (32) for the calculation of the ground state, should be written as a linear combination of a complete set of hydrogenic eigenfunctions (or other type eigenfunctions) in a rigorous scheme. Nevertheless, in a numerical calculation we may take the hydrogen like 1*s* function as a trial function of $|1\rangle$, because the mixing between the 1*s* state and higher hydrogenic states due to the interaction given by the second term in Eq. (35) is not large in general. This trial function, which has the same form as Eq. (34), and the corresponding energy ϵ_1^0 can be determined by the usual variational procedure from the equation

$$\epsilon_1^0=\langle 1|\left(\frac{p^2}{2\mu}-\frac{A}{r}\right)|1\rangle-\sum_{\vec{k}}\frac{|V_{\vec{k}}|^2|\rho_{\vec{k},1}|^2}{E_{\vec{k}}}\,, \tag{36}$$

which is obtained from Eq. (17) for the effective interaction given in Eq. (35). We note that the energy expression as given by Eq. (36) has the form of that obtained by the adiabatic approach (or Hartree approach) in the strong-coupling theory of polarons. Therefore, in the present case, the zero-order perturbation results in the presently used perturbation theory are adiabatic-type results and the corresponding corrections from Eq. (19) are the corrections to the adiabatic-type results. We also note that it may appear from first sight that Haken's inequality given by Eq. (22) cannot be directly applied in general when the variation method with a rather simple trial function is used to determine the unperturbed solutions. However, as can be seen later from calculated ground-state energies, the use of the simple trial function in the present case does not affect the applicability of the Haken's inequality.

Having determined the lowest state of H_e, $|1\rangle$, the corresponding ΔE_1 can be calculated from Eq. (32) straightforwardly after replacing the summations over wave vectors $\vec{k}$ and $\vec{q}$ by the corresponding integrations as in the usual procedure.

B. Numerical results

We apply the calculation as presented above to the binding energy of an exciton for polar semiconductors. In this case the interaction is one between the electron-hole pair and the ionic polarization. Therefore, for this calculation, A and $V_{\vec{k}}$ in the energy expression derived above are, respectively, e^2/ϵ_∞ and $-i(2\pi e^2\epsilon/k^2V\epsilon^*)^{1/2}$. Here $\epsilon(\equiv\hbar\omega)$ is the energy of a longitudinal optical phonon, V is the volume of the crystal under consideration, and $\epsilon^{*-1}=\epsilon_\infty^{-1}-\epsilon_s^{-1}$, ϵ_s being the static dielectric constant. The values adopted for dielectric constants, ϵ, and the electron-phonon coupling constant $\alpha[=e^2(m_e/2\epsilon)^{1/2}/\epsilon^*\hbar$, where m_e is the free-electron mass] are given in Table I. Among the crys-

TABLE I. Electron mass m_1, hole mass m_2, high-frequency dielectric constant ϵ_∞, static dielectric constant ϵ_s, longitudinal optical-phonon energy ϵ, and the electron-phonon coupling constant α. Masses are in the free-electron mass and energies in meV.

		m_1	m_2	ϵ_∞	ϵ_s	ϵ	α
TlBr	(*A*)	0.20[a]	0.40[a]	5.41[b]	35.1[b]	14.3[b]	4.82
	(*B*)	0.18[c]	0.38[c]				
TlCl	(*A*)	0.30[a]	0.50[a]	5.10[b]	37.6[b]	21.5[b]	4.26
	(*B*)	0.37[c]	0.36[c]				
CdTe	(*A*)	0.105[d]	0.36[d]	7.05[e]	10.0[e]	21.3[e]	1.06
	(*B*)	0.11[c]	0.35[c]				
CdS	(*A*)	0.178[d]	0.383[d]	5.10[f]	8.87[f]	38.0[f]	1.58
	(*B*)	0.18[c]	0.57[c]				
ZnS	(*A*)	0.248[d]	0.894[d]	5.20[f]	8.77[f]	43.7[f]	1.38
	(*B*)	0.19[c]	0.94[c]				
GaAs	(*A*)	0.066[d]	0.389[d]	10.9[g]	12.9[g]	36.2[g]	0.28
	(*B*)	0.09[c]	0.52[c]				

[a] H. Overhof and J. Treusch, Solid State Commun. 9, 53 (1971).

[b] Reference 14.

[c] Masses used in the work of Mahanti and Varma.

[d] See text for details.

[e] Reference 15.

[f] Reference 16.

[g] Reference 17.

tal parameters the band masses, especially the hole band masses, are rather uncertain. Thus we use two sets of mass parameters for each material as seen in Table I. Note that one of the two sets is essentially that used by Mahanti and Varma[8] as indicated in Table I. Also note that the values of masses with the superscript d in Table I are calculated from $m_i^* = m_i/(1 - \frac{1}{6}\alpha_i)$, where m_i^* is the polaron mass [for CdTe, $m_1^* = 0.11m$ and $m_2^* = 0.40m$ from Ref. 15, where m is the free-electron mass; for CdS, $m_1^* = 0.20m$ from Ref. 16 and $m_2^* = 0.458m$ from $\mu^* = m_1^* m_2^*/(m_1^* + m_2^*) = 0.139m$ which is obtained from 3*s* and 4*s* levels in Ref. 18 by assuming the simple hydrogenic formula with $\epsilon_s = 8.87$; for ZnS, $m_1^* = 0.28m$ and $m_2^* = 1.571m$ from Ref. 19, assuming $m_2^* = \frac{1}{3}(2/m_{2\perp}^* + 1/m_{2\parallel}^*)$; for GaAs, $m_1^* = 0.0665m$ from Ref. 20 and $m_2^* = 0.40m$ is the average value of the light-hole mass $0.12m$ and heavy-hole mass $0.68m$ in Ref. 21]. The numerical results thus calculated for the ground-state energy $E_g (\equiv E_1)$ for $\sigma_{\vec{k}} = aE_{\vec{k}}/\epsilon$ and that for $\sigma_{\vec{k}} = \rho_{\vec{k},1}$, and the corresponding binding energies E_B are summarized in Table II. In this table $E_g^{(1a)}$ and $E_g^{(10)}$ are, respectively, the lowest value of E_g which we can get for $a \neq 0$ and E_g for $a = 0$, which is nothing but that of the usual second-order perturbation theory. $E_g^{(2)}$ in the same table denotes the calculated E_g for $\sigma_{\vec{k}} = \rho_{\vec{k},1}$. For a comparison, the binding energy obtained by Mahanti and Varma[8] and that obtained from an effective Hamiltonian as given in Ref. 6,[25] denoted, respectively, by E_B^{MV} and E_B^{MW}, are also given in Table II. In order to see how the ionic polarization affects the exciton binding energy, in Table II the binding energy calculated by dropping all the ionic polarization effects, E_B^∞ is also given. Also, the value of the correction obtained from Eq. (19) for the case of $\sigma_{\vec{k}} = \rho_{\vec{k},1}$, denoted by $\Delta E_1^{(2)}$, is given in Table II, showing the order of a correction to the adiabatic or Hartree-type calculation.

IV. DISCUSSION

As shown in Table II, the ground-state energy E_g calculated for $\sigma_{\vec{k}} = 0$, corresponding to the usual second-order perturbation theory, is about the same as those calculated for the cases of $\sigma_{\vec{k}} \neq 0$ for materials considered. The same is true even in the the case where the transformed interaction H_I' is significantly reduced such as in ZnS.[26] This is obviously due to a large cancellation between the direct interaction energy like S_{ni} and the exchange interaction energy like S_{n12}. Note that such a cancellation becomes worse as the difference between the electron mass and the hole mass increases. At any rate, as far as the total ground-state energy is concerned the usual second-order perturbation theory works well for materials like those listed in Table II. Thus, the extreme approach such as the adiabatic or Hartree-type approach is inappropriate, as indicated by the correction of such an approach in Table II.

From the binding-energy results in Table II we see immediately that for the materials with the coupling constant $\alpha \lesssim 2$ such as CdTe, CdS, ZnS, and GaAs, the results of the present calculation are about the same as the other two and all are in fairly good agreement with experimental values. However, for TlCl and TlBr for which $\alpha \approx 4-5$ the results of the present calculation are quite different from the other two and also from experimental results as shown in Table II. In fact, our calculated ground-state energy, which can be concluded to be above the true ground-state energy of the exciton Hamiltonian given by Eq. (1) in Sec. II if the evaluation of ΔE_n is accurate, is very much below the really true ground-state energy for TlCl and TlBr, as indicated by the difference between the presently calculated binding energy and experimentally observed binding energy in Table II. This big discrepancy cannot be entirely attributed to the method to evaluate ΔE_n, since, according to Ref. 11, this method overestimates the magnitude of the energy correction only by a small percentage (less than 10% in any case). Then a large portion of the above discrepancy may have to be attributed to the values of masses used for the electron and hole in TlCl and TlBr,[27] or to the omission of a (central-cell) correction to the exciton Hamiltonian used in this work,[28,29] or to both.

The masses used for the electron and hole in TlCl and TlBr in Mahanti-Varma's work[8] are the

TABLE II. 1*s* exciton binding energy without ionic polarization $E_B^\infty = \mu e^4/2\epsilon_\infty^2\hbar^2$, the sum of the energy shifts of the bottom of conduction band and top of the valence band $E_\infty = -(\alpha_1+\alpha_2)\hbar\omega$, the present theoretical ground-state energies $E_g^{(10)}$, $E_g^{(1a)}$, $E_g^{(2)}$, and the corresponding 1*s* exciton binding energies $E_B^{(10)} = |E_g^{(10)} - E_\infty|$, $E_B^{(1a)} = |E_g^{(1a)} - E_\infty|$, $E_B^{(2)} = |E_g^{(2)} - E_\infty|$, the correction to the Hartree-type calculation $\Delta E_1^{(2)}$, the theoretical results by Mahanti and Varma E_B^{MV}, and theoretical results by Matsuura and Wang E_B^{MW}, and the experimental binding energy E_B^{expt}. All energies are in meV.

		E_B^∞	E_∞	$E_g^{(10)}$	$E_B^{(10)}$	$E_g^{(1a)}$	$E_B^{(1a)}$	$E_g^{(2)}$	$E_B^{(2)}$	$\Delta E_1^{(2)}$	E_B^{MV}	E_B^{MW}	$E_B^{\mathrm{expt.}}$
TlBr	(*A*)	62.0	−74.5	−94.9	20.4	−94.9	20.4	−94.9	20.4	−30.9	···	3.4	9.8[a]
	(*B*)	56.8	−71.8	−88.2	16.4	−88.2	16.4	−88.3	16.5	−29.2	8.0	2.8	
TlCl	(*A*)	98.1	−115.0	−150.4	35.4	−150.4	35.4	−150.4	35.4	−50.7	···	4.4	11.7[a]
	(*B*)	95.4	−110.8	−148.2	37.4	−148.3	37.5	−148.3	37.5	−52.8	9.0	4.3	
CdTe	(*A*)	22.3	−20.8	−32.9	12.1	−33.3	12.5	−32.9	12.1	−8.5	···	11.2	11 ± 1[b]
	(*B*)	22.9	−20.8	−33.4	12.6	−33.8	13.0	−33.5	12.7	−8.6	12.0	12.5	
CdS	(*A*)	63.6	−62.4	−92.4	30.0	−92.8	30.4	−92.5	30.1	−26.3	···	25.6	26[c]
	(*B*)	71.6	−70.7	−103.1	32.4	−103.8	33.1	−103.3	32.6	−25.4	28.0	29.2	
ZnS	(*A*)	97.7	−87.1	−135.3	48.2	−135.9	48.8	−135.5	48.4	−28.8	···	42.9	37[c]
	(*B*)	79.5	−84.8	−118.6	33.8	−120.4	35.6	−119.1	34.3	−26.1	41.0	33.8	
GaAs	(*A*)	6.4	−8.8	−13.4	4.6	−13.5	4.7	−13.3	4.5	−5.2	···	4.7	4.2[d]
	(*B*)	8.8	−10.2	−16.5	6.3	−16.6	6.4	−16.4	6.2	−5.7	6.0	6.4	

[a] Reference 22. [b] Reference 23. [c] Reference 16. [d] Reference 24.

same as the set labeled *B* in Table II. Also, the exciton Hamiltonian used is the same in their work and the present work. Nevertheless, their calculated binding energy for an exciton in TlCl or TlBr is in fairly good agreement with the experimental value. However, the reason for such good agreement is not at all clear to us.

Our results also prompt us to discuss the calculation of Vooght and Bajaj.[9] In their calculation, with the neglect of the quantities like $R_{\vec q-\mu_i\vec k,\vec q}$ given in Eq. (30), terms like S_{ni3} given in Eq. (29d) are omitted (which should be present in their calculation). S_{ni3} is zero when the unperturbed energy vanishes as mentioned previously and becomes more and more important as the unperturbed energy increases.[11] Thus, the omission of the S_{ni3} itself may cause a large error in the calculation of ΔE due to the direct interaction of the electron or hole with the polarization field for all materials listed in Table II except GaAs. However, in their calculation of the ground-state energy this error (from the omission of S_{ni3}) plus an error from the omission of the first term in Eq. (6) will be canceled to some extent by similar errors in their calculation of ΔE due to the exchange interaction between the electron and hole. Accordingly, the net error involved in their ground-state calculation may not be serious for materials such as those listed in Table II.

In summary, we would conclude from above that the present and other previous calculations all are reasonable for materials with $\alpha \lesssim 2$ and not clear for materials with large α. For the latter materials, a central-cell-type correction is probably needed if the presently available band masses are believed to be reasonable for both electron and hole.

APPENDIX A: ΔE_n IN TWO EXTREME CASES

Here we consider ΔE_n given by Eq. (21) for the two extreme cases (a) $|\epsilon_n^0| \gg \epsilon$ and (b) $|\epsilon_n^0| \ll \epsilon$. In case (a) the terms in Eq. (21) all vanish except the term with $m=n$, because the energy denominator becomes very large for the terms with $m \neq n$. Therefore, for $|\epsilon_n^0| \gg \epsilon$,

$$\Delta E_n = -\sum_{\vec k} \frac{|V_{\vec k}|^2 |\rho_{\vec k,n}|^2}{E_{\vec k}} . \tag{A1}$$

The wave function $|n\rangle$ in $\rho_{\vec k,n}$ is a solution determined from Eq. (15) for $m=n$, i.e., a solution in the adiabatic or Hartree-type approximation. Hence, ΔE_n given by Eq. (A1) is a result for the energy of the electron-hole pair due to its interaction with the polarization field in the strong-binding case.[2]

On the other hand, in case (b) ΔE_n can be calculated by the method used in Ref. 5. The result thus calculated is

$$\Delta E_n = \sum_{j=1}^{2} E_{Dj} + E_E , \tag{A2}$$

with E_{Dj} given by

$$E_{Dj} = -\sum_{\vec k} \frac{|V_{\vec k}|^2}{\epsilon + \hbar^2 k^2/2m_j} - \sum_{\vec k} \frac{|V_{\vec k}|^2}{(\epsilon + \hbar^2 k^2/2m_j)^3} \times \langle n| \left(\frac{\hbar \vec k \cdot \vec p}{m_j}\right)^2 |n\rangle + \cdots , \tag{A3}$$

and E_E given by

$$E_E = \sum_{\vec{k}} |V_k|^2 \left(\frac{1}{\epsilon + \hbar^2 k^2/2m_1} + \frac{1}{\epsilon + \hbar^2 k^2/2m_2} \right) \times \langle n | e^{i\vec{k}\cdot\vec{r}} | n \rangle + \cdots \, . \tag{A4}$$

E_{Dj} has the same form as the energy of a bound electron due to its direct interaction with the polarization field in the weak-binding case. Therefore it is the energy of the jth source particle (electron or hole) due to its interaction with its own polarization field in the weak-binding case. E_E is the energy due to the interaction between the electron and hole via the polarization field (see Ref. 5 for details) and is an exchange energy in the weak-binding case. Note that the effective Hamiltonian appearing in the first term in E_E is just the basic expression of the well-known Haken-Schottky potential[3] in the weak-binding case.

Accordingly, we may conclude that the energy correction ΔE_n given by Eq. (21) gives the correct results for the energy of the electron-hole pair due to its interaction with the polarization field in the strong- and weak-binding cases.

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[*] Work supported in part by the National Research Council of Canada.

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[25] The effective Hamiltonian used is essentially the one at $T = 0\,°\mathrm{K}$ in Ref. 6, which consists of terms up to first order in α and $E_B^\infty/\hbar\omega$ in Ref. 5. The inclusion of higher-order terms in α and $E_B^\infty/\hbar\omega$ is too comples to perform straightforwardly.

[26] For ZnS, according to the theoretical results of Table II, the unperturbed energy and the second-order energy correction are, respectively, -79.5 meV $(= -E_B^\infty)$ and -39.1 meV $(= E_g^{(10)} + B_B^\infty)$ for $\sigma_{\vec{k}} = 0$, and -93.0 meV $(= E_g^{(2)} - \Delta E_1^{(2)})$ and -26.1 meV $(= \Delta E_1^{(2)})$ for $\sigma_{\vec{k}} = \rho_{\vec{k},1}$ when using the B set of mass parameters.

[27] Masses to be used in the calculation of the exciton binding energy for TlCl and TlBr seem rather uncertain [see Ref. 22 and J. W. Hodby, G. T. Jenkin, K. Kobayashi and H. Tamura, Solid State Commun. 10, 1017 (1972)].

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