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BINDING ENERGY OF A MOTT–WANNIER EXCITON IN A POLARIZABLE MEDIUM

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A new effective interaction potential between an electron and a hole of a Mott–Wannier exciton in a polarizable medium is derived following a procedure similar to that of Haken. The variational polaron wave functions used are those first proposed by Haga. Using this effective interaction potential the values of the binding energy of an exciton are calculated variationally in several polar crystals. The values thus obtained agree very well with those derived from experimental measurements and are always considerably smaller than those calculated using Haken's potential.

THERE HAS BEEN a great deal of interest in theoretical and experimental investigations of the behaviour of Mott–Wannier excitons in polar crystals in recent years. These studies have yielded important information about the band parameters of these materials. Some time ago, Haken[1] derived an effective interaction potential between an electron and a hole of a Mott–Wannier exciton in a polarizable medium using a two-particle generalization of the Fröhlich[2] Hamiltonian. Towards this end he used a wave function for the exciton which was expressed in terms of products of free electron polaron and free hole polaron wave functions of Lee, Low and Pines.[3] This procedure neglects the correlation effects between the electron polaron and the hole polaron. As the Mott–Wannier excitons in most polar materials are rather shallow, this was considered a reasonable assumption. Recently, Bachrach and Brown[4] have determined experimentally the binding energies of Mott–Wannier excitons in thallous halides. They found values of 6.5 ± 1 and 11 ± 2 meV in TlBr and TlCl respectively. Using the best known values of the electron polaron masses and the hole polaron masses in these materials they calculated the binding energies using a simple hydrogenic formula with a static dielectric constant. The values of the binding energy they obtained were much too small. The use of the latest cyclotron resonance masses[5] does not change the situation significantly.[6] As thallous halides are polar crystals, the effective interaction between the electron and the hole may not be purely Coulombic. Using Haken's potential,[1] they then calculated variationally the binding energies of excitons in these materials using a hydrogenic wave function as a trial function. The values they calculated turned out to be about an order of magnitude larger than those obtained experimentally. This circumstance led to several theoretical attempts[7–11] to calculate the binding energy of a Wannier exciton in a polarizable medium.

In this note we calculate the effective interaction potential between an electron and a hole of a Mott–Wannier exciton in a polar crystal following a procedure similar to that of Haken but using the variational free polaron wave functions first proposed by Haga.[12] Using the effective potential thus derived, we calculate variationally the binding energy of a Mott–Wannier exciton in several polar crystal using a hydrogenic trial wave function. This work was motivated by our desire to find out how the use of different free polaron wave functions in Haken's procedure will modify the potential he derived using Lee, Low and Pines wave functions. As shown in Table 2, the values of the binding energy we calculate are significantly lower than those obtained by using Haken's potential and are in good agreement with those obtained experimentally.

The Hamiltonian of our system, which consists of a conduction electron and a hole coupled together by an attractive screened Coulomb potential, both interacting with the longitudinal-optical phonon field of the crystal lattice can be written as[1]

$$H_0 = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} - \frac{e^2}{\epsilon_\infty |\mathbf{r}_1 - \mathbf{r}_2|} + \sum_{\mathbf{q}} \hbar\omega b_q^+ b_q$$
$$+ \sum_{\mathbf{q}} [\gamma_q (e^{+i\mathbf{q}\cdot\mathbf{r}_1} + e^{i\mathbf{q}\cdot\mathbf{r}_2}) b_q + \text{c.c.}] \qquad (1)$$

where b_q and b_q^+ are the annihilation and creation operators for a longitudinal optical phonon of wave vector **q**. The optical phonon frequency is ω and is assumed to be independent of **q**. The momentum, position coordinate and the band mass are denoted by $\mathbf{p}_i$, $\mathbf{r}_i$ and m_i where $i = 1$ for the electron and $i = 2$ for the hole.

The quantity γ_q is defined as

$$\gamma_q = -\frac{i\hbar\omega}{q}\left(\frac{4\pi\alpha_i}{\beta_i V}\right)^{1/2} \qquad (2)$$

$$\alpha_i = \frac{1}{2\bar{\epsilon}}\left(\frac{e^2\beta_i}{\hbar\omega}\right), \tag{3}$$

$$\beta_i = \left(\frac{2m_i\omega}{\hbar}\right)^{1/2}, \tag{4}$$

$$\frac{1}{\bar{\epsilon}} = \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right), \tag{5}$$

V is the volume of the crystal and ϵ_∞ and ϵ_0 denote the high frequency and the static dielectric constants respectively. Note that the parameter γ_q is the same for both an electron and a hole.

To derive an effective interaction potential between an electron and a hole of a Mott–Wannier exciton we use the following product wave function for the exciton

$$\psi = \sum_{\mathbf{k}_1,\mathbf{k}_2} C_{\mathbf{k}_1,\mathbf{k}_2}\phi^{(1)}_{\mathbf{k}_1}(\mathbf{r}_1, b_q^+)\phi^{(2)}_{\mathbf{k}_2}(\mathbf{r}_2, b_q^+) \tag{6}$$

where $\phi^{(1)}_{\mathbf{k}_1}(\mathbf{r}_1, \mathbf{b}_q^+)$ is a free electron polaron wave function and $\phi^{(2)}_{\mathbf{k}_2}(\mathbf{r}_2, \mathbf{b}_q^+)$ is a free hole polaron wave function. For these wave functions we use the following form as first derived by Haga.[12]

$$\phi^{(i)}_{\mathbf{k}_i}(\mathbf{r}_i, b_q^+) = \mathrm{e}^{i\mathbf{k}_i\cdot\mathbf{r}_i}\, U^{(i)}\left(1 + \sum_{\mathbf{q}} c^{(i)}_{\mathbf{q}} b_q^+\right)|\phi_0\rangle \tag{6}$$

where $|\phi_0\rangle$ is the phonon vacuum state and $U^{(i)}$ is the canonical transformation first used by Lee, Low and pines.[3] For small values of k_i we have[3]

$$U^{(i)} = \exp\left[\sum_{\mathbf{q}} (f^{(i)}_{\mathbf{q}} b_q^+ - f^{(i)*}_{\mathbf{q}} b_q\right] \tag{7}$$

where

$$f^{(i)}_{\mathbf{q}} = \mp 2i\left(\frac{\pi\alpha_i\beta_i^3}{V}\right)^{1/2}\frac{\mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}_i}}{q(q^2+\beta_i^2)} \tag{8}$$

$$c^{(i)}_{\mathbf{q}} = \frac{2f^{(i)}_{\mathbf{q}}q^2}{(1+\alpha_i/12)(q^2+\beta_i^2)}. \tag{9}$$

In equation (8) (—) sign corresponds to the electron and (+) corresponds to the hole. As Wannier excitons are rather shallow in most semiconductors we have used free polaron wave functions for small values of $\mathbf{k}_i$. Following a method similar to that used by Haken[1] we find, using Haga's free polaron wave functions,[12] that the effective Hamiltonian can be written as

$$H = -\alpha_1\,\hbar\omega - \alpha_2\,\hbar\omega + \frac{p^2}{2\mu^*} + V(r). \tag{10}$$

Here **p** and **r** are relative momentum and position coordinates respectively and μ^* is defined as

$$\frac{1}{\mu^*} = \frac{1}{m_1^*} + \frac{1}{m_2^*} \tag{11}$$

where the polaron masses m_1^* are related to the band masses m_i

$$m_i^* = \frac{m_i(1+\alpha_i/12)}{(1-\alpha_i/12)} \tag{12}$$

as first calculated by Haga.[12]

The effective interaction potential $V(r)$ can be written as

$$V(r) = -\frac{e^2}{\epsilon_\infty r} + \frac{n(r)V_H(r) + V'(r)}{n} \tag{13}$$

where

$$V_H(r) = \frac{e^2}{\bar{\epsilon}_r}\left[1 - \frac{\mathrm{e}^{-\beta_1 r} + \mathrm{e}^{-\beta_2 r}}{2}\right] \tag{14}$$

is the expression first derived by Haken.[1] The other symbols in equation (13) are defined as

$$V'(r) = \sum_{\mathbf{q}}\left[\gamma_q\left(\mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}_1}c^{(2)}_{\mathbf{q}}\left\{1 + \sum_{\mathbf{k}} c^{(1)*}_{\mathbf{k}}c^{(1)}_{\mathbf{k}} + \sum_{\mathbf{k}} c^{(2)*}_{\mathbf{k}}c^{(2)}_{\mathbf{k}}\right\}\right) - \gamma_q\left(\mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}_2}c^{(1)}_{\mathbf{q}}\left\{1 + \sum_{\mathbf{k}} c^{(1)*}_{\mathbf{k}}c^{(2)}_{\mathbf{k}} + \sum_{\mathbf{k}} c^{(1)}_{\mathbf{k}}c^{(2)*}_{\mathbf{k}}\right\}\right)\right] \tag{15}$$

$$n(r) = \left(1 + \sum_{\mathbf{k}} c^{(1)*}_{\mathbf{k}}c^{(1)}_{\mathbf{k}}\right)\left(1 + \sum_{\mathbf{k}} c^{(2)*}_{\mathbf{k}}c^{(2)}_{\mathbf{k}}\right) + \left(1 + \sum_{\mathbf{k}} c^{(1)*}_{\mathbf{k}}c^{(2)}_{\mathbf{k}}\right)\left(1 + \sum_{\mathbf{k}} c^{(2)*}_{\mathbf{k}}c^{(1)}_{\mathbf{k}}\right) - 1, \tag{16}$$

and n stands for the quantity obtained by integrating $(\psi^*\psi)$ over all the electron, hole and phonon variables. When we put $c_{\mathbf{q}} = 0$ the Haga's wave functions go over to Lee, Low and Pines[3] wave functions and equation (13) reduces to the effective interaction potential obtained by Haken.

It is possible to evaluate $V'(r)$, $n(r)$ and n analytically using methods of complex integration. The expression for $V(r)$ thus obtained is rather complicated. However, terms containing products like $c^{(1)}_{\mathbf{q}}c^{(2)*}_{\mathbf{q}}$ and $c^{(2)}_{\mathbf{q}}c^{(1)*}_{\mathbf{q}}$ when summed over the wave vectors make a relatively small contribution to the binding energy of an exciton in most materials. For the purpose of exhibiting the general form of the effective interaction potential we neglect these terms and write $V(r)$ as

$$V(r) \approx -\frac{e^2}{\epsilon_\infty r} + V_H(r) + \frac{e^2\beta_1}{2\bar{\epsilon}}\,\frac{\mathrm{e}^{-\beta_1 r}}{\{1+\alpha_1/[4(1+\alpha_1/12)^2]\}(1+\alpha_{1/12})} + \frac{e^2\beta_2}{2\bar{\epsilon}}\,\frac{\mathrm{e}^{-\beta_2 r}}{\{1+\alpha_2/[4(1+\alpha_2/12)^2]\}(1+\alpha_{2/12})} \tag{17}$$

Table 1. Values of the electron band mass (m_1), *electron polaron mass* (m_1^*), *hole band mass* (m_2), *hole polaron mass* (m_2^*), *all expressed in terms of free electron mass, static dielectric constant* (ϵ_0), *optical dielectric constant* (ϵ_∞) *and longitudinal optical phonon energy* ($\hbar\omega$) *expressed in meV in several polar crystals. The electron band masses and the hole band masses are determined from their respective polaron masses using equation (12)*

Material	m_1	m_1^*	m_2	m_2^*	ϵ_0	ϵ_∞	$\hbar\omega$
CdTe (6)	0.0917	0.0965	0.32	0.35	10.23	7.21	21.3
CdS (6)	0.158	0.179	0.57	0.7	9.68	5.24	38
ZnO (13)	0.235	0.271	0.78	0.95	8.15	4.0	72
TlCl (6)	0.355	0.55	0.49	0.82	37.6	5.1	21.5

Table 2. Values of the binding energies calculated using Haken's potential (E_H), *using our potential* (E_p), *using simple hydrogenic formula* (ϵ_{1s}) *and measured experimentally* (E^{expt}) *in several polar crystals. All energies are expressed in units of meV. The values of* E_H *are calculated using band masses determined from the polaron masses using Lee, Low and Pines*[3] *formula i.e.* $m_i^* = m_i(1 + \alpha_i/6)$

Material	E_H	E_p	ϵ_{1s}	E^{expt}
CdTe	12.2	10.2	9.8	10 (14)
CdS	34.1	24.8	20.8	28 (15)
ZnO	88.0	58.7	43.8	59 (11)
TlCl	79.4	46	3.17	11 + 2 (4)

To obtain the ground-state energy of our system described by equation (10), we follow a variational approach since it is obviously not possible to solve for the eigenfunctions and eigenvalues of this Hamiltonian in an analytic form. We choose the following hydrogenic wave function as our trial function

$$|i\rangle = \left(\frac{\beta^3}{\pi a^3}\right)^{1/2} e^{-\beta r/a} \tag{18}$$

where β is a variational parameter and a is the effective Bohr radius

$$a = \frac{\epsilon_0\hbar^2}{\mu^* e^2} \tag{19}$$

Using this wave function we calculate the expectation value of the Hamiltonian given by equation (10) in a closed form. This expression is then minimized numerically with respect to β for several polar crystals. The value of the binding energy of an exciton is then obtained by subtracting this expression from the sum of the electron polaron self energy ($-\alpha_1\hbar\omega$) and the hole polaron self energy ($-\alpha_2\hbar\omega$) as the latter are the energies of the electron polaron and the hole polaron respectively at a very large distance. The results are shown in Table 2. The values of the various physical parameters used are given in Table 1. In Table 2, we also give the values of the binding energy obtained by using Haken's potential (E_H), the hydrogenic expression ($\epsilon_{1s} = \mu^* e^4/2\epsilon_0^2\hbar^2$) and those obtained from experimental measurements. We find that the values of the binding energy we calculate are in good agreement with the experimental values (except for TlCl) whereas those obtained by using Haken's potential show a considerable disagreement. Even in the case of TlCl the use of our effective interaction potential reduces the binding energy to about half the value obtained from Haken's potential. We find that except in the case of TlCl, the values of the binding energy we calculate are somewhat smaller than the experimental values. In these materials the polaron hole masses are known only approximately as no cyclotron resonance measurements have been done for the holes. Our calculation of the binding energy does not include the contributions of exchange interaction and the central cell effects. The central cell effects make a positive contribution and the exchange interaction makes a negative contribution to the binding energy thus partially cancelling each other.

We have also calculated the energies of several low-lying excited states of a Mott–Wannier exciton in polar crystals. This along with the details of our calculations and a comparison between our results and those obtained by others will be published elsewhere.

To conclude, we have derived an effective interaction potential between an electron and a hole of a Mott–Wannier exciton in a polarizable medium, using Haga's free polaron wave functions and following a procedure similar to that of Haken. Using this potential we have calculated variationally the values of the binding energy of an exciton in several polar crystals. We find that the values thus obtained are considerably smaller than those obtained by using Haken's potential and are in better agreement with the experimental values.

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