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Wannier excitons in a thin crystal film

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Energy levels and wave functions of Wannier excitons in a crystal film whose thickness is smaller than the size of the exciton are calculated. The exciton is found to behave like a two-dimensional hydrogenic atom when projected onto a plane parallel to the film surface; it behaves like an independent particle and hole in a potential well in the direction normal to the film. The effect of the finite thickness of the film is calculated perturbatively. The energy-level scheme is plotted for a numerical example.

I. INTRODUCTION

Surface excitons and polaritons have been the subject of a wide range of both experimental and theoretical investigations[1-17] in recent years. Most of these works were concerned with what happens locally near the surface of a semi-infinite crystal. However, the study of excitons in crystal slabs of finite thickness has not received as much attention so far. Of particular interest is the case of Wannier excitons in a thin semiconductor film. Owing to the large static dielectric constant ϵ and small effective electron and hole masses in some semiconductors the radius of the hydrogenlike Wannier exciton can be as large as a few hundred angstroms. If the thickness d of the film is comparable or less than the exciton diameter, it is clear that the structure of the exciton itself will be strongly affected by the finite geometry of the film. One might ask: Will the exciton be constructed like an oblately deformed hydrogen atom or will the two surfaces exert such a destructive influence that a hydrogen-atom-like exciton state can no longer be formed? How does the finite but small thickness affect the exciton energy levels?

We also recall that in a bulk crystal the exciton combines with a photon of the same momentum to form a polariton,[18,19] an excited eigenstate of the crystal. A finite geometry such as that of a thin film breaks the crystal symmetry, rendering it possible for the exciton to decay radiatively. The decay of the Frenkel exciton under such circumstances was treated recently.[20] Interestingly, the decay rate was found to be super-radiative. It would be of great interest to study the corresponding problem for the Wannier exciton. However, before we can investigate the coupling with photons, the study of the exciton itself, the object which undergoes radiative decay, must be completed.

In this paper we shall solve for the energy levels and the associated wave functions of Wannier excitons in a thin-crystal film. One might wonder how such information about the exciton in a restricted geometry can be found if one already has difficulty trying to find the states of just a single electron in such geometry. The answer is, of course, that we are not starting from the basic Hamiltonian for electrons in a finite lattice with surfaces. We shall assume that the properties of the Bloch electron in the bulk, including the band energies, are known. The properties of the exciton in thin films will ultimately be expressed in terms of these bulk properties as well as a parameter related to the work function associated with the surfaces. The parameter represents the height of the potential barrier that an electron from within the film has to climb before it can leak out. However, for simplicity, we shall neglect the distortion of the electron potential at the unit cells near the surface barrier. This implies that the possibility of Tamm-type electron surface states[21,22] and their effect on the exciton will be excluded.

The method of the equivalent Hamiltonian will be used. The basic idea in treating our problem with finite geometry is to represent the effect of the broken crystal symmetry introduced by the surfaces by an appropriate external potential in the equivalent Hamiltonian, while the "kinetic-energy" term is still characterized by the band energy of the electron in the bulk. Our calculation is facilitated by the assumption of small film thickness d which renders a perturbation calculation possible. Qualitatively, our result shows that the exciton levels are divided into separate bands with band spacing essentially determined by the small thickness d. The levels in each band are like those of two-dimensional hydrogen atoms, but modified by the finite film thickness. Although the actual calculation is carried out for a simple cubic lattice, the method employed in reaching the solution and the qualitative results are expected to be valid for other types of lattice.

II. FORMULATION OF THE EXCITON PROBLEM

For simplicity we consider a semiconductor crystal with two nondegenerate energy bands. The valence band is denoted by v and the conduction band by c. The ground state is the state in which the v band is fully occupied and the c band completely empty. The one-electron–one-hole excited state of the bulk crystal can be written

$$|c\vec{\mathrm{j}};\, v\vec{\mathrm{l}}\rangle = (C^{c}_{\vec{\mathrm{j}}})^{\dagger} C^{v}_{\vec{\mathrm{l}}} |\Psi_{\mathrm{grd}}\rangle , \tag{1}$$

where $(C^{c}_{\vec{\mathrm{j}}})^{\dagger}$ creates an electron described by the Wannier function of band c and lattice site $\vec{\mathrm{j}}$, and $C^{v}_{\vec{\mathrm{l}}}$ annihilates an electron of band v and site $\vec{\mathrm{l}}$. The relations between the Wannier function $a_n(\vec{\mathrm{R}} - \vec{\mathrm{R}}_i)$ and the Bloch function $\psi_{n\vec{\mathrm{k}}}(\vec{\mathrm{R}})$ are given by

$$a_n(\vec{\mathrm{R}} - \vec{\mathrm{R}}_i) = \frac{1}{\sqrt{N}} \sum_{\vec{\mathrm{k}}} e^{-i\vec{\mathrm{k}}\cdot\vec{\mathrm{R}}_i} \psi_{n\vec{\mathrm{k}}}(\vec{\mathrm{R}}) \tag{2}$$

and

$$\Psi_{n\vec{\mathrm{k}}}(\vec{\mathrm{R}}) = \frac{1}{\sqrt{N}} \sum_{i} e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{R}}_i} a_n(\vec{\mathrm{R}} - \vec{\mathrm{R}}_i) . \tag{3}$$

Let the z axis be in the direction normal to the film surfaces. To avoid complications we assume the x-y plane to be parallel to the crystal planes, for example, of a cubic crystal.

The crystal-film potential U_{film} acting on an electron is then periodic in the x-y plane but is cut off in the z direction near the surfaces at $|z| = \frac{1}{2}d$, where potential barriers rise instead. Within the film where $|z| < \frac{1}{2}d$, U_{film} is assumed to be periodic also along the z direction, without any distortion even near the surfaces. Thus, electron surface states of the Tamm type[21,22] do not exist in our model. Of course, the potential along a line parallel to the z axis still depends on the distance of the line from the z axis.

We are now going to represent the effect of the potential barrier by superimposing a finite attractive square well

$$V(z) = \begin{cases} 0, & |z| < \frac{1}{2}d \\ V_0, & |z| > \frac{1}{2}d \end{cases} \tag{4}$$

on the film potential described above. Note that the total potential outside the film is just a constant. However, to make use of the bulk parameters we define $U_{\mathrm{bulk}}(\vec{\mathrm{R}})$ to be the fully periodic potential of the bulk crystal with no boundaries. This $U_{\mathrm{bulk}}(\vec{\mathrm{R}})$ coincides with the film potential $U_{\mathrm{film}}(\vec{\mathrm{R}})$ for $|z| < \frac{1}{2}d$, but differs from it for $|z| > \frac{1}{2}d$ where the potential becomes constant for the film. Therefore, along a line parallel to the z axis, the actual single-particle potential $U_{\mathrm{film}}(\vec{\mathrm{R}}) + V(z)$ as seen by an electron in the film is as plotted in Fig. 1. This same potential can be considered as a superposition of the bulk potential $U_{\mathrm{bulk}}(\vec{\mathrm{R}})$ and $V'(\vec{\mathrm{R}})$, the variations of which along the line parallel to the z axis is plotted in Fig. 2.

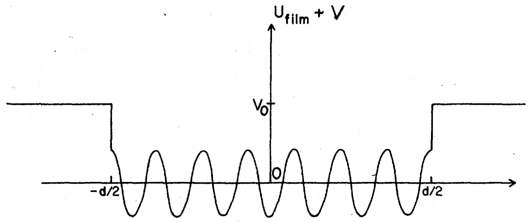

FIG. 1. Periodic potential and the potential barrier for the film as seen along a line parallel to the z axis.

According to Fig. 2 we can look upon the crystal film as a bulk crystal with no boundary, but acted on by an external potential $V'(\vec{\mathrm{R}})$. The Hamiltonian for electrons can thus be written

$$H = \sum_i \Big(h_i + \sum_{j>i} \sum V_{ij} \Big) , \tag{5}$$

where

$$\begin{aligned} h &= \frac{\hbar^2}{2m} \nabla^2 + U_{\mathrm{bulk}}(\vec{\mathrm{R}}) + V'(\vec{\mathrm{R}}) \\ &= h_0 + V'(\vec{\mathrm{R}}) \end{aligned} \tag{6}$$

and V_{ij} is the Coulomb repulsion among electrons.

We can expand the excitonic eigenstates of H in terms of the particle-hole states of Eq. (1) as

$$|E\rangle = \sum_{\vec{\mathrm{j}}} \sum_{\vec{\mathrm{l}}} C(\vec{\mathrm{j}}, \vec{\mathrm{l}}) |c\vec{\mathrm{j}}, v\vec{\mathrm{l}}\rangle . \tag{7}$$

The expansion coefficients $C(\vec{\mathrm{j}}, \vec{\mathrm{l}})$ satisfy the Schrödinger equation

$$\sum_{\vec{\mathrm{j}}'\vec{\mathrm{l}}'} \Big\langle c\vec{\mathrm{j}}; v\vec{\mathrm{l}} \Big| \sum_i h_i + \sum_{j>i}\sum V_{ij} \Big| c\vec{\mathrm{j}}'; v\vec{\mathrm{l}}' \Big\rangle C(\vec{\mathrm{j}}', \vec{\mathrm{l}}') = EC(\vec{\mathrm{j}}, \vec{\mathrm{l}}) . \tag{8}$$

The evaluation of the matrix elements is tedious but standard.[19] The important point to note is that

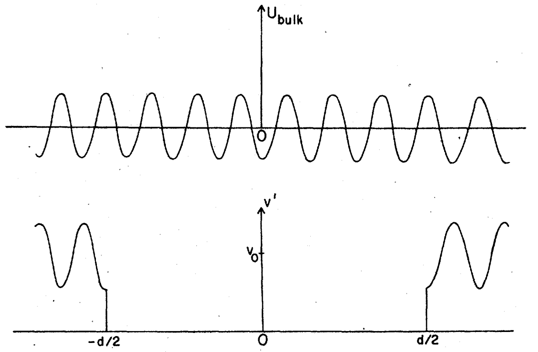

FIG. 2. Potential $U_{\mathrm{film}} + V(z)$ decomposed into $U_{\mathrm{bulk}} + V'$ as seen along a line parallel to the z axis.

now the term h_0 in Eq. (6) is diagonal with respect to the Bloch states of the bulk crystal given by Eq. (3). This is why we purposely extracted h_0 from the actual Hamiltonian. Other terms in the Hamiltonian such as the potential barriers at the surfaces are then treated as external potentials acting on the electrons and can be conveniently expressed in the representation of the Bloch states or, via Eq. (3), of the Wannier states.

The matrix elements[19] of the Coulombic $\sum\sum_{j>i} V_{ij}$ give rise to, in particular, the interaction between the particle $c\,\vec{j}$ and the hole $v\,\vec{l}$. First consider the exchange matrix elements

$$V^{v\vec{l},\,c\vec{j}'}_{c\vec{j},\,v\vec{l}'} = \int a_c^*(\vec{r}_1 - \vec{j}')a_v(\vec{r}_1 - \vec{l}')V(\vec{r}_1 - \vec{r}_2)$$
$$\times\, a_v^*(\vec{r}_2 - \vec{l})a_c(\vec{r}_2 - \vec{j})\,d\vec{r}_1\,d\vec{r}_2\,.$$

In the limit of a large exciton, the exciton radius a_0 is much greater than the spatial spread of any individual Wannier function. This means that in the above integral the variation of $V(\vec{r}_1 - \vec{r}_2)$, which is on a length scale of a_0, may be neglected in the length scale of the Wannier functions, leading to the vanishing of the above exchange matrix element on account of the orthogonality of the Wannier functions for different bands. This result is true regardless of the thickness of the film. Similarly the direct matrix elements

$$V^{c\vec{j}',\,v\vec{l}}_{c\vec{j},\,v\vec{l}'} = \int a_c^*(\vec{r}_1 - \vec{j}')a_c(\vec{r}_1 - \vec{j})V(\vec{r}_1 - \vec{r}_2)$$
$$\times\, a_v^*(\vec{r}_2 - \vec{l})a_v(\vec{r}_2 - \vec{l}')\,d\vec{r}_1\,d\vec{r}_2$$

are vanishingly small in the same limit of $a_0 \gg a$ (lattice spacing) due to the orthogonality of Wannier functions referring to different lattice sites when $(\vec{j},\vec{l}) \neq (\vec{j}',\vec{l}')$. Thus we have to take into account only the diagonal element $V^{c\vec{j},\,v\vec{l}}_{c\vec{j},\,v\vec{l}}$ which can be approximated as $e^2/\epsilon\,|\vec{j} - \vec{l}\,|$, considering the large separation $|\vec{j} - \vec{l}\,|$ as compared to the spread of a Wannier function. The above approximations, usually made in the study of Wannier excitons in the bulk crystal, are valid also in the present case of a thin film since they are based just on the fact that $a_0 \gg a$, which is true for both cases. Other matrix elements of V_{ij} can be incorporated into the single-particle band energy or into the ground-state energy. These terms can be ignored if we assume that our Bloch states satisfy a Hartree-Fock-type equation with the average effect of the two-particle interaction V_{ij} already taken into account and if we are only interested in excited levels as measured from the true ground state.

The matrix elements of h_0 in the Wannier representation lead to the usual hopping intergrals. Eventually, Eq. (8) can be reduced to

$$\sum_{\vec{j}'}[\mathcal{E}_c^0(\vec{j} - \vec{j}') + \langle c\,\vec{j}\,|V'|\,c\,\vec{j}'\rangle]C(\vec{j}',\vec{l}\,)$$
$$-\sum_{\vec{l}'}[\mathcal{E}_v^0(\vec{l}' - \vec{l}\,) + \langle v\,\vec{l}'|V'|v\,\vec{l}\,\rangle]C(\vec{j},\vec{l}')$$
$$-(e^2/\epsilon\,|\vec{j} - \vec{l}\,|)C(\vec{j},\vec{l}\,) = (E - E_{\text{grd}})C(\vec{j},\vec{l}\,)\,, \quad (9)$$

where ϵ is the dielectric constant, E_{grd} is the true ground-state energy of the thin film, and

$$\mathcal{E}_c^0(\vec{j} - \vec{j}') = \langle c\,\vec{j}\,|h_0|\,c\,\vec{j}'\rangle\,, \quad (10\text{a})$$

$$\mathcal{E}_v^0(\vec{l}' - \vec{l}\,) = \langle v\,\vec{l}'|h_0|v\,\vec{l}\,\rangle\,. \quad (10\text{b})$$

We remind ourselves that, on the left-hand side of Eq. (9), the minus sign of the second term indicates that it is associated with the hole and that of the third term shows that it is a particle-hole interaction, always opposite in sign to the particle-particle interaction. The hopping integrals of Eq. (10) are, as usual, related to the band energies $E_c(\vec{k}\,)$ and $E_v(\vec{k}\,)$ by

$$\mathcal{E}_c^0(\vec{j} - \vec{j}') = \frac{1}{N}\sum_{\vec{k}} E_c(\vec{k}\,)e^{i\vec{k}\cdot(\vec{j}-\vec{j}')}\,, \quad (11\text{a})$$

$$\mathcal{E}_v^0(\vec{l}' - \vec{l}\,) = \frac{1}{N}\sum_{\vec{k}} E_v(\vec{k}\,)e^{i\vec{k}\cdot(\vec{l}'-\vec{l})}\,. \quad (11\text{b})$$

Conversely, we have

$$E_c(\vec{k}\,) = \sum_{\vec{j}} \mathcal{E}_c^0(\vec{j}\,)e^{-i\vec{k}\cdot\vec{j}}\,, \quad (11\text{c})$$

$$E_v(\vec{k}) = \sum_{\vec{l}} \mathcal{E}_v^0(\vec{l}\,)e^{-i\vec{k}\cdot\vec{l}}\,. \quad (11\text{d})$$

Using Eq. (11) one can immediately show, as usual,[19]

$$\sum_{\vec{j}'} \mathcal{E}_c^0(\vec{j} - \vec{j}')C(\vec{j}',\vec{l}\,) = E_c(-i\nabla_{\vec{j}})C(\vec{j},\vec{l}\,) \quad (12\text{a})$$

and

$$\sum_{\vec{l}'} \mathcal{E}_v^0(\vec{l} - \vec{l}')C(\vec{j},\vec{l}') = E_v(i\nabla_{\vec{l}})C(\vec{j},\vec{l}\,) \quad (12\text{b})$$

and substitute them into Eq. (9) to obtain

$$\left(E_c(-i\nabla_{\vec{j}}) - E_v(i\nabla_{\vec{l}}) - \frac{e^2}{\epsilon\,|\vec{j} - \vec{l}\,|}\right)C(\vec{j},\vec{l}\,)$$
$$+\sum_{\vec{j}'}\langle c\,\vec{j}\,|V'|\,c\,\vec{j}'\rangle C(\vec{j}',\vec{l}\,)$$
$$-\sum_{\vec{l}'}\langle v\,\vec{l}'|V'|v\,\vec{l}\,\rangle C(\vec{j},\vec{l}') = (E - E_{\text{grd}})C(\vec{j},\vec{l}\,)\,, \quad (13)$$

where

$$\langle v\,\vec{l}'|V'|v\,\vec{l}\,\rangle = \int a_v^*(\vec{R} - \vec{l}')V'(\vec{R})a_v(\vec{R} - \vec{l}\,)\,d\vec{R}\,,$$

etc. We shall now make the approximation that, for region within the film,

$$\langle c\vec{\mathrm{j}}\,|V'|\,c\vec{\mathrm{j}}'\rangle = V_c(z_{\vec{\mathrm{j}}})\delta_{\vec{\mathrm{j}},\vec{\mathrm{j}}'}\,, \tag{14a}$$

$$\langle v\vec{\mathrm{l}}'\,|V'|\,v\vec{\mathrm{l}}\rangle = V_v(z_{\vec{\mathrm{l}}})\delta_{\vec{\mathrm{l}},\vec{\mathrm{l}}'}\,. \tag{14b}$$

This approximation will be valid for any $V'(\vec{\mathrm{R}})$ which varies slowly in the scale of the Wannier functions such as the square-well potential of Eq. (4) in the present case. For regions outside the film $V'(R)$ varies rapidly and the local approximation breaks down. The Schrödinger equation (13) reduces, inside the film region, to

$$\left(E_c(-i\nabla_{\vec{\mathrm{j}}}) + V(z_{\vec{\mathrm{j}}}) - E_v(i\nabla_{\vec{\mathrm{l}}}) - V(z_{\vec{\mathrm{l}}}) - \frac{e^2}{\epsilon\,|\vec{\mathrm{j}}-\vec{\mathrm{l}}|}\right)C(\vec{\mathrm{j}},\vec{\mathrm{l}}) = (E - E_{\mathrm{grd}})C(\vec{\mathrm{j}},\vec{\mathrm{l}})\,, \tag{15}$$

where $V(z)$ is given by Eq. (4) since V' is the same as $V(z)$ for $|z|<\frac{1}{2}d$. Equation (13) is valid, of course, for both the regions outside and inside the film.

For simplicity we assume simple cubic lattice and energy bands of the tight-binding form

$$E_c(\vec{\mathrm{k}}) = E_0 + E_{\mathrm{gap}} + 6\gamma_c - 2\gamma_c(\cos k_x a + \cos k_y a + \cos k_z a)\,, \tag{16a}$$

$$E_v(\vec{\mathrm{k}}) = E_0 - 6\gamma_v + 2\gamma_v(\cos k_x a + \cos k_y a + \cos k_z a)\,, \tag{16b}$$

where a is the lattice spacing and E_0 is the energy at the top of the valance band. When an electron is in an empty lattice with no kinetic energy, its energy is defined to be zero. Since the square well $V(z)$ in Eq. (15) affects only the motion in z direction we may expand E_v and E_c to second order in k_x and k_y in the effective-mass approximation. Thus Eq. (15) becomes

$$\left\{\frac{\hbar^2}{m_e^* a^2}\left[1-\cos\left(-ia\frac{\partial}{\partial z_e}\right)\right] + V(z_e) + \frac{\hbar^2}{m_h^* a^2}\left[1-\cos\left(ia\frac{\partial}{\partial z_h}\right)\right] - V(z_h) - \frac{\hbar^2}{2m_e^*}\frac{\partial^2}{\partial\vec{\mathrm{r}}_e^2} - \frac{\hbar^2}{2m_h^*}\frac{\partial^2}{\partial\vec{\mathrm{r}}_h^2} - \frac{e^2}{\epsilon}(r^2+z^2)^{-1/2}\right\}\Psi(\vec{\mathrm{r}}_e, z_e; \vec{\mathrm{r}}_h, z_h) = \mathcal{E}\Psi(\vec{\mathrm{r}}_e, z_e; \vec{\mathrm{r}}_h, z_h) \tag{17}$$

where we introduced the notations

$$\gamma_c = \hbar^2/2m_e^* a^2\,,\quad \gamma_v = \hbar^2/2m_h^* a^2$$
$$\mathcal{E} = E - E_{\mathrm{grd}} - E_{\mathrm{gap}}$$
$$\vec{\mathrm{j}} = (\vec{\mathrm{r}}_e, z_e),\quad \vec{\mathrm{l}} = (\vec{\mathrm{r}}_h, z_h),\quad \vec{\mathrm{r}} = \vec{\mathrm{r}}_e - \vec{\mathrm{r}}_h,\quad z = z_e - z_h\,, \tag{18}$$
$$\Psi(\vec{\mathrm{r}}_e, z_e; \vec{\mathrm{r}}_h, z_h) = C(\vec{\mathrm{j}},\vec{\mathrm{l}})\,.$$

Note that $\vec{\mathrm{r}}_e$, $\vec{\mathrm{r}}_h$, and $\vec{\mathrm{r}}$ are two-dimensional position vectors.

III. EXCITON IN THE LIMIT OF SMALL FILM THICKNESS

To solve Eq. (17) for $|z|<\frac{1}{2}d$ and Eq. (13) for $|z|>\frac{1}{2}d$, we first separate the Hamiltonian into three parts

$$H = H_z + H_{xy} + H'\,, \tag{19}$$

where

$$H_z = h_c(z_e) - h_r(z_h)\,, \tag{20a}$$

$$h_c(z) = \begin{cases} \dfrac{\hbar^2}{m_e^* a^2}\left[1-\cos\left(-ia\dfrac{\partial}{\partial z}\right)\right] + E_0 + E_{\mathrm{gap}} + V(z), & |z|<\frac{1}{2}d \quad (20\mathrm{b}) \\ -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial z^2} + V(z)\,, & |z|>\frac{1}{2}d \quad (20\mathrm{c}) \end{cases}$$

$$h_v(z) = \begin{cases} \dfrac{-\hbar^2}{m_h^* a^2}\left[1-\cos\left(ia\dfrac{\partial}{\partial z}\right)\right] + E_0 + V(z), & |z|<\frac{1}{2}d \quad (20\mathrm{d}) \\ -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial z^2} + V(z)\,, & |z|>\frac{1}{2}d \quad (20\mathrm{e}) \end{cases}$$

$$H_{xy} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial\vec{\mathrm{R}}_{\mathrm{c.m.}}} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\vec{\mathrm{r}}^2} - \frac{e^2}{\epsilon r}\,, \tag{21}$$

$$H' = \frac{e^2}{\epsilon}\left(\frac{1}{r} - \frac{1}{(r^2+z^2)^{1/2}}\right)\,, \tag{22}$$

where M and μ are the total mass and the reduced mass of the electron hole system, respectively. $\vec{\mathrm{R}}_{\mathrm{c.m.}}$ is the two-dimensional position vector of the center of mass of the system in the x-y plane. In Eq. (20), the Hamiltonian H_z of the electron and hole is written as the energy of the z-directional motion of the single electron in the c band minus that of the single electron in the v band. For $|z|<\frac{1}{2}d$, $h_c(z)$ and $h_v(z)$ given by Eqs. (20b) and (20d) are written according to Eq. (17) except for the explicit appearance of E_0 and E_{gap}. For the region $|z|>\frac{1}{2}d$ we recall that the single-particle Hamiltonian h of Eq. (6) is that of a free electron in potential $V(z)$ outside the film (see Fig. 1) while the same h is responsible for Eqs. (20b) and (20d) inside the film.

In the limit of small film thickness, i.e., d is small compared to the radius a_0 of exciton, we can treat H' of Eq. (22) as a perturbation, for we can then roughly expand H' about $z=0$ so that

$$\langle H'\rangle \sim \left\langle\frac{e^2 z^2}{2\epsilon r^3}\right\rangle \sim \frac{e^2}{2\epsilon a_0}\,\frac{d^2}{a_0^2}\,.$$

Then, according to Eqs. (19)–(21) the motion in the x-y plane is separable from that in the z direction. The unperturbed wave function is in product form

$$\Psi_0(\vec{j},\vec{l}) = \varphi_{k_e}(z_e)\tilde{\varphi}_{k_h}(z_h)\psi(\vec{r})\chi(\vec{R}_{\text{c.m.}}) . \tag{23}$$

The wave equations satisfied by these functions are

$$h_c(z_e)\varphi_{k_e}(z_e) = E_z^{(e)}\varphi_{k_e}(z_e) , \tag{24}$$

$$-h_v(z_h)\tilde{\varphi}_{k_h}(z_h) = E_z^{(h)}\tilde{\varphi}_{k_h}(z_h) , \tag{25}$$

$$\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial\vec{r}^2} - \frac{e^2}{\epsilon r}\right)\psi(\vec{r}) = E_r\psi(\vec{r}) , \tag{26}$$

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial\vec{R}^2_{\text{c.m.}}}\chi(\vec{R}_{\text{c.m.}}) = E_R\chi(\vec{R}_{\text{c.m.}}) , \tag{27}$$

with

$$\mathcal{E}^{(0)} = E_z^{(e)} + E_z^{(h)} + E_r + E_R .$$

The solution to the square-well problem of Eq. (24) are

$$\varphi_{k_e}(z_e) = \begin{cases} A_+\cos k_+ z_e , & |z_e| < \frac{1}{2}d \\ B_+ e^{-\kappa_+|z_e|} , & |z_e| > \frac{1}{2}d \end{cases} \tag{28a}$$

for even-parity states, and

$$\varphi_{k_e}(z_e) = \begin{cases} A_-\sin k_- z_e , & |z_e| < \frac{1}{2}d \\ \pm B_- e^{-\kappa_-|z_e|} , & |z_e| > \frac{1}{2}d \end{cases} \tag{28b}$$

for odd-parity states. Substitution of Eq. (28) into Eq. (24) yields the energy relation

$$E_z^{(e)} = E_0 + E_{\text{gap}} + \frac{\hbar^2}{m_e^* a}(1 - \cos\xi_\pm) = -\frac{\hbar^2\eta_\pm^2}{2ma^2} + V_0 , \tag{29}$$

where we have defined $\xi_\pm = k_\pm a$ and $\eta_\pm = K_\pm a$. Matching of the logarithmic derivatives at $|z| = \frac{1}{2}d$ yields

$$\xi_+\tan(\xi_+ d/2a) = \eta_+ , \tag{30a}$$

$$-\xi_-\cot(\xi_- d/2a) = \eta_- . \tag{30b}$$

Similarly, the solutions to Eq. (25) are

$$\tilde{\varphi}_{k_h}(z_h) = \begin{cases} A'_+\cos k'_+ z_h , & |z_h| < \frac{1}{2}d \\ B'_+ e^{-\kappa'_+|z_h|} , & |z_h| > \frac{1}{2}d \end{cases} \tag{31a}$$

for even-parity states, and

$$\tilde{\varphi}_{k_h}(z_h) = \begin{cases} A'_-\sin k'_- z_h , & |z_h| < \frac{1}{2}d \\ \pm B'_- e^{-\kappa'_-|z_h|} , & |z_h| > \frac{1}{2}d \end{cases} \tag{31b}$$

for odd-parity states. The corresponding energy relation is

$$-E_z^{(h)} = E_0 - \frac{\hbar^2}{m_h^* a^2}(1 - \cos\xi'_\pm) = -\frac{\hbar^2\eta'^2_\pm}{2ma^2} + V_0 \tag{32}$$

and the condition resulting from matching of logarithmic derivatives is

$$\xi'_+\tan(\xi'_+ d/2a) = \eta'_+ , \tag{33a}$$

$$-\xi'_-\cot(\xi'_- d/2a) = \eta'_- . \tag{33b}$$

Note that E_0 and E_{gap} appear explicitly in Eqs. (29) and (32) because we match the energies within and without the film. The relevant quantity is actually $V_0 - E_0$ or $V_0 - E_0 - E_{\text{gap}}$ which provides a measure of the work function. The Eqs. (29) and (30) can be solved numerically or graphically for the electron energy levels associated with the z-directional motion; Eqs. (32) and (33) can be similarly solved for the hole.

The relative motion of the electron and the hole in the x-y plane is described by Eq. (26). It is just like that of a two-dimensional hydrogen atom. It can be solved exactly to give

$$E(n) = -\mu e^4/2\epsilon^2\hbar^2(n+\tfrac{1}{2})^2 , \quad n = 0,1,2,\ldots \tag{34}$$

$$\begin{aligned} \psi_{n,m}(\vec{r}) &= \frac{1}{\sqrt{2\pi}} e^{im\phi} R_{n,m}[2r/(n+\tfrac{1}{2})a_0] \\ &= \frac{1}{\sqrt{2\pi}} e^{im\phi}\left[\frac{[(n+m)!]^3(2n+1)}{(n-m)!}\left(\frac{(n+\frac{1}{2})a_0}{2}\right)^2\right]^{-1/2} \\ &\quad\times\left(\frac{2r}{(n+\frac{1}{2})a_0}\right)^{|m|} e^{-r/(n+1/2)a_0} L_{n+|m|}^{2|m|}\left(\frac{2r}{(n+\frac{1}{2})a_0}\right) \end{aligned} \tag{35}$$

where $L_p^q(\rho)$ is the Laguerre polynomial,[23] and $a_0 = \epsilon\hbar^2/\mu e^2$. The principal quantum number n can take any positive integral values including zero. The angular momentum quantum number $m = 0, \pm 1, \pm 2, \ldots$, with $|m| \leq n$ for a given n.

Equation (27) describes the free motion of the center of mass of the exciton in the x-y plane. We shall simply assume zero momentum for this motion.

From Eqs. (23)–(27), (29), (30), and (32)–(35) we see that in the zeroth-order solution the Wannier exciton is structured like a two-dimensional hydrogen atom in the plane parallel to the film surface; but, in the normal direction it behaves like independent electron and hole trapped in the potential well characterized by the work function of the crystal.

IV. PERTURBATIVE EFFECT OF FINITE THICKNESS ON THE EXCITON

As we saw in Sec. III, the assumption of small thickness of the crystal film enables us to separate the motion of the electron and hole in z direction from that in the x-y plane. In fact, the energy-level scheme is such that level spacings associated with the z motion are comparatively the largest; the hydrogen-atom-like motion in the x-y plane will then split each of these levels into a set of sublevels. However, the nonzero thickness will modify these sublevels associated strictly with the two-dimensional hydrogen-atom-like states. This modification can be calculated by treating H' given by Eq. (22) perturbatively.

The perturbation energy is given by

$$E'=\frac{e^2}{\epsilon}\int_{-\infty}^{\infty}dz_e\int_{-\infty}^{\infty}dz_h|\varphi_{k_e}(z_e)\tilde{\varphi}_{k_h}(z_h)|^2 I(Z)\,, \tag{36}$$

where

$$I(Z)=\frac{(n+\frac{1}{2})a_0}{2}\int_0^{\infty}|R_{n,m}(\rho)|^2\left(\frac{1}{\rho}-\frac{1}{(\rho^2+Z^2)^{1/2}}\right)\rho\,d\rho \tag{37}$$

and

$$\rho\equiv\frac{2r}{(n+\frac{1}{2})a_0}\,,\quad |Z|\equiv\frac{2|z_e-z_h|}{a_0(n+\frac{1}{2})}\,.$$

Basically, the dimensionless perturbation parameter is d^2/a_0^2. However, one should not try to approximate H' by expanding about $z=0$, or the integral in Eq. (37) would diverge on account of the lower limit for levels with $m=0$. We shall now calculate E' for the most important level with $n=m=0$ and even parity $\phi(z)$. Since the Laguerre polynomial $L_0^0=1$, we have

$$\begin{aligned}I(Z)&=\frac{4}{a_0}\int_0^{\infty}e^{-\rho}[1-\rho/(\rho^2+Z^2)^{1/2}]\,d\rho\\&=\frac{4}{a_0}\left(1+|Z|-\frac{\pi|Z|}{2}[H_1(|Z|)-N_1(|Z|)]\right),\end{aligned} \tag{38}$$

where $H_1(|Z|)$ is the Struve function of order 1 and $N_1(|Z|)$ is the Neuman function of order 1. Since $I(Z)$ is obviously an even function of Z, we can obtain E' by using Eqs. (28a), (31a), (36), and (37)

$$E'=\frac{4e^2}{\epsilon}\left[A_+^2\int_0^{d/2}dz_e\cos^2(k_+z_e)+B_+^2\int_{d/2}^{\infty}dz_e\,e^{-2\kappa_+z_e}\right]\left[A_+'^2\int_0^{d/2}dz_h\cos^2(k_+'z_h)+B_+'^2\int_{d/2}^{\infty}dz_h\,e^{-2\kappa_+'z_h}\right]I(Z)\,, \tag{39}$$

where the two bracketed terms should be understood as integral operators acting on $I(Z)$. Exact evaluation of the integral has to be done on a computer. To a high degree of accuracy, however, it can be evaluated analytically if one notes that the function

$$\begin{aligned}f(Z)&=1+|Z|-\tfrac{1}{2}\pi|Z|[H_1(|Z|)-N_1(|Z|)]\\&\approx|Z|\ \text{ for } |Z|<1\\&\simeq1\ \text{ for } |Z|>1\end{aligned} \tag{40}$$

or equivalently,

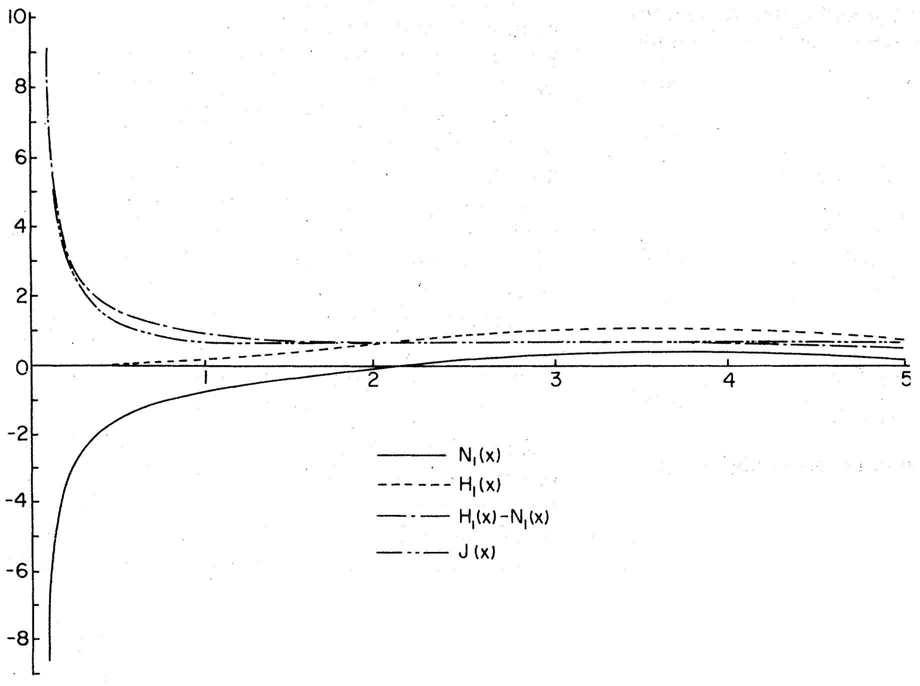

FIG. 3. Approximate representation of the difference of the Struve function $H_1(Z)$ and the Neuman function $N_1(Z)$.

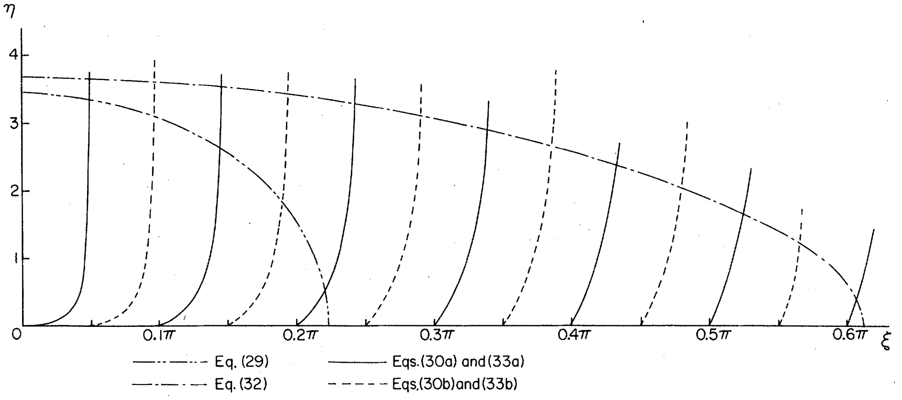

FIG. 4. Graphical solutions of the energy eigenvalues $E_z^{(e)}$ and $E_z^{(h)}$.

$$H_1(|Z|) - N_1(|Z|) \approx J(|Z|),$$

where

$$J(|Z|) = \begin{cases} 2/\pi |Z| & \text{for } |Z| < 1, \\ 2/\pi & \text{for } |Z| > 1. \end{cases} \tag{41}$$

A comparison of $H_1 - N_1$ with J is plotted in Fig. 3. After $I(Z)$ is replaced by $4f(Z)/a_0$ in Eq. (39), the integration becomes straightforward but very tedious. We shall present the numerical results for a slab with several different values for the thickness d.

We consider a semiconductor with $V_0 - E_0 = 6$ eV, $\epsilon = 15$, $a = 3$ Å, $E_{\text{gap}} = 0.7$ eV, $m_e^* = 0.04$ m, and $m_h^* = 0.2$ m. The values of the parameters correspond roughly to those of Ge. Figure 4 shows the graphical solutions to Eqs. (29)–(30) and to Eqs. (32)–(33) for $d = 60$ Å as an example. The computed level schemes for $E_z^{(e)}$, $E_z^{(h)}$ and the lowest E_z levels are shown in Fig. 5. Each of these E_z levels splits into a band of sub levels due to the two-dimensional hydrogenic motion according to Eq. (34) and is shown schematically in Fig. 6. Then, each sublevel is perturbed by H' to give an energy correction E'. The lowest two sublevels in each band are $E_r(n=0) = -7.58 \times 10^{-3}$ eV and $E_r(n=1) = -0.84 \times 10^{-3}$ eV relative to the original level before splitting. The first-order perturbation energy calculated from Eq. (39) is $E' = 2.42 \times 10^{-3}$ eV for $d = 60$ Å, or about 36% of the spacing between the sublevels. Therefore, treating H' of Eq. (22) as a perturbation is justified for d small compared with a_0, which is approximately 260 Å in the present numerical example. In fact, a very rough estimate of the various terms in H of Eqs. (19)–(22) could have been made before we launched into the actual computation. Clearly, the level spacing associated

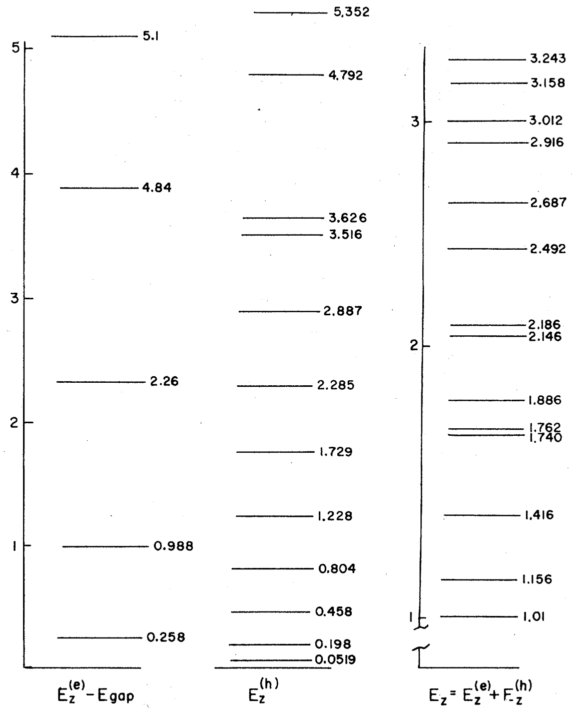

FIG. 5. Spectra $E_z^{(e)}$, $E_z^{(h)}$ and the lowest levels $E_z = E_z^{(e)} + E_z^{(h)}$. All energies are in eV.

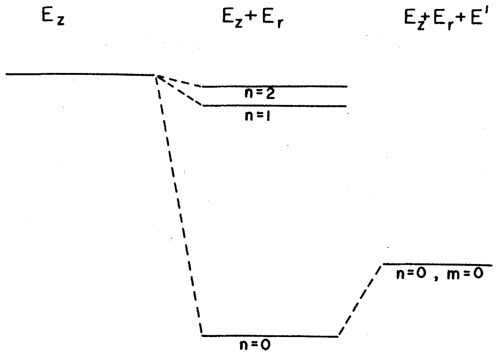

FIG. 6. Splitting of each E_z level into a band of hydrogenic sublevels with each corrected further by perturbation energy E'.

with $E_z^{(e)}$ or $E_z^{(h)}$ is of the order of $\hbar^2/m_e^* d$ or $\hbar^2/m_h^* d$ according to the uncertainty principle. The energy spacing between the sublevels is of the order of

$$\frac{e^2}{\epsilon a_0} = \frac{\hbar^2}{\mu d^2}\,\frac{d^2}{a_0^2}\,,$$

appropriate for hydrogenic states. If we expanded H' of Eq. (22) about $z=0$ we would have obtained

$$E' = \langle H' \rangle \simeq \left\langle \frac{e^2 z^2}{2\epsilon r^3} \right\rangle \simeq \frac{e^2}{2\epsilon a_0}\,\frac{d^2}{a_0^2}\,.$$

Then,

$$\frac{\Delta E_r}{\Delta E_z} \sim \frac{d^2}{a_0^2} \quad \text{and} \quad \frac{E'}{\Delta E_r} \sim \frac{d^2}{a_0^2}\,.$$

However, the estimate of E' using an H' expanded about $z=0$ is not accurate for the two-dimensional hydrogenic states with zero angular momentum (i.e., the $m=0$ states), for such states have nonvanishing probability at $r=0$ according to Eq. (35), causing a divergent result for $\langle 1/r^3 \rangle$. This is why our E' computed from Eq. (36) or Eq. (39) is considerably larger than the above estimate. On the other hand, the estimate can indeed be used for other $m \neq 0$ states for which $\langle 1/r^3 \rangle$ is finite.

Calculations for $d = 120$ Å yield $E' = 4.77 \times 10^{-3}$ eV, which is almost comparable to ΔE_r and, therefore, cannot be trusted as a perturbation. This shows that our present microscopic analysis, which depends on the method of perturbation in an essential way, is valid for film thickness less than 40 layers or so. For much thicker films, approaches using the concept of dielectric constant to treat the polarization involving the electrons and the holes together with the corresponding macroscopic boundary conditions at the surfaces should be valid.[24]

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