Eigenstates of excitons near a surface

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The exact eigenstates and energies of an electron and a hole of equal effective masses, with an attractive δ-function interaction and hard-wall repulsion at the surfaces of a solid, are classified and obtained explicitly for a solid of arbitrary thickness. Both bound and scattering states of the exciton are significantly quantized for thin films.

I. INTRODUCTION

The present study concerns the effects of collisions, with the confining walls of a solid, on a Wannier exciton. This is a special case of the three-body problem: a composite particle, the exciton (an electron and a hole bound by mutual attraction) reflected by the one-body forces at a surface. Such problems are generally insoluble. We obtain an exact solution only for impenetrable surfaces, an attractive one-dimensional δ-function two-body interaction and equal masses $m_e = m_h$. Nevertheless, our solution gives insight into the physical properties to be expected. We indicate the (variational) extension of our results to three-dimensions, enabling the more realistic Coulomb interaction to be considered; at the same time the boundary conditions are respected. With applications, calculations, and comparison with experiments deferred to a companion paper,[1] the present work consists of the construction of solutions for two important cases: the semi-infinite solid and the finite-thickness film bounded by two parallel surfaces.

The Wannier exciton is described by a Hamiltonian:

$$H=-\frac{1}{2m_e}\nabla_e^2-\frac{1}{2m_h}\nabla_h^2+V(r_e-r_h)+E_g \quad (\hbar=1)\,. \qquad (1)$$

Instead of the familiar periodic boundary conditions, two-particle eigenstates are now subject to the boundary conditions $\Psi=0$ when either electron or hole is at the surface. The energy gap separating conduction-band electrons from valence-band holes is E_g, such that eigenvalues of (1) less than E_g are stable (bound) exciton states, those greater than E_g are the scattering (unbound) states which we do not approximate by plane waves, as usual, but we calculate exactly. If either of the masses is significantly greater than the other, then the adiabatic method may be used to obtain the eigenstates subject to an error of $O(m_</m_>)^{1/2}$. This well-known procedure starts by fixing the more massive particle (say 1) and computing the eigenstates $\phi_n(r_2)$ and eigenvalues E_n, with the distance z_1 from the bounding surface being a parameter in both [owing to the effects of the boundary condition $\phi_n(r_2)=0$ at $z_2=0$]. The composite wave functions obtained by Pekar[2] in his original work on the excitons are of the form

$$\Psi\sim\sin q_z z_1 e^{i(q_x x_1+q_y y_1)}\phi_n(\vec{r}_2)\,. \qquad (2)$$

These vanish at $z_1=0$ but neglect the repulsion, prior to impacting the wall, caused by the rise in the "effective potential" $E_n(z_1)$. The introduction of a 90° phase shift into the solution by Ting *et al.*[3]

$$\Psi\sim\cos q_z z_1 e^{i(q_x x_1+q_y y_1)}\phi_n(\vec{r}_2) \qquad (3)$$

probably overcompensates for this effect. As we shall see, far from the surface our exact solution satisfies Pekar's ansatz near optical threshold, and approaches that of Ref. 3 at higher energies. Near the surface, however, it is more complex than either.

We now turn to the one-dimensional model. Assuming an attractive two-body potential $-2^{1/2}\lambda\delta(z_e-z_h)$, the Hamiltonian in the z direction takes the form

$$H_z=-\frac{1}{2m_e}\frac{\partial^2}{\partial z_e{}^2}-\frac{1}{2m_h}\frac{\partial^2}{\partial z_h{}^2}-2^{1/2}\lambda\delta(z_e-z_h)+E_g\,. \qquad (4)$$

When m_e and m_h are comparable in magnitude, as is generally the case in solids,[4] an expansion in the ratio of the masses must converge slowly if at all, so we examine directly the limiting case $m_e=m_h$ (denoted m henceforth, for simplicity). One then rotates by 45° in the z_e-z_h plane to a new set of coordinates, shown in Fig. 1:

$$\zeta_1\equiv 2^{-1/2}(z_h+z_e) \text{ and } \zeta_2\equiv 2^{-1/2}(z_h-z_e)\,, \qquad (5)$$

The physically allowed space occupies the first quadrant in the z_e, z_h plane or, equivalently, the

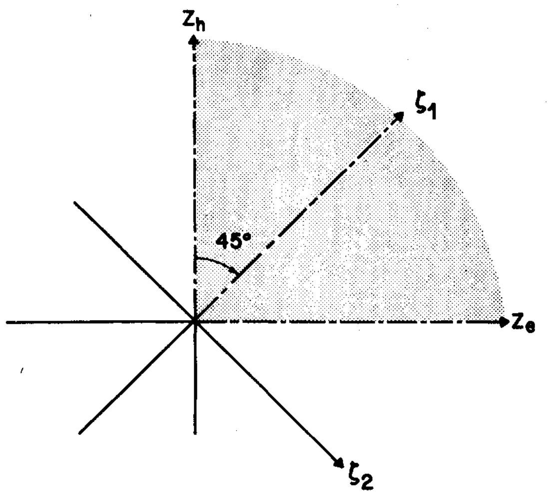

FIG. 1. z_e-z_h plane. Physical interactions occur along the straight-line segments indicated by dash-dot-line, attractive two-body interaction along 45° line and infinitely repulsive one-body forces along horizontal and vertical axes. Wave-function differs from zero only in first quadrant (shaded ragion). Introduction of potentials along straight-line segments in other quadrants, indicated by solid line, symmetrizes the Hamiltonian without affecting eigenstates

sectors within ±45° of the ζ_1 axis. Thus if we introduce an "image" interaction $-\lambda 2^{1/2}\delta(z_h+z_e)$ which vanishes everywhere within the allowed region, there can be no effect on the eigenstates except to render the Hamiltonian more symmetrical in the new variables and the solution more obvious. The suitably augmented H is

$$H_\zeta = -\frac{-1}{2m}\left(\frac{\partial^2}{\partial\zeta_1^2}+\frac{\partial^2}{\partial\zeta_2^2}\right) - \lambda[\delta(\zeta_1)+\delta(\zeta_2)] + E_g . \tag{6}$$

This is separable into two identical Hamiltonians each of the form

$$h_\zeta \equiv \frac{1}{2m}\frac{\partial^2}{\partial\zeta^2} - \lambda\delta(\zeta) . \tag{7}$$

We classify the eigenstates of (7) according to parity. The odd states, $u_q(\zeta)$ unaffected by the interaction, are

$$u_q(\zeta) = \sin q\zeta , \quad \text{with energy } \epsilon_q = q^2/2m \tag{8}$$

(unnormalized). The even-parity states include the ground state,

$$g_0(\zeta) = e^{-\lambda m|\zeta|} , \quad \text{with energy } \epsilon_0 = -\tfrac{1}{2}m\lambda^2 , \tag{9a}$$

and the scattering states,

$$g_q(\zeta) = \cos(q\,|\zeta| + \theta_q), \quad \text{with } \epsilon_q = q^2/2m , \tag{9b}$$

the phase shifts θ_q being given by

$$\theta_q = \tan^{-1}(m\lambda/q) , \tag{10}$$

limited to the interval $-\frac{1}{2}\pi \leqslant \theta_q \leqslant +\frac{1}{2}\pi$. Note the limiting behavior, $g \sim \sin q\zeta$ at small q, and $\sim\cos q\zeta$ at large q in conformity with one or the other ansatz of Eqs. (2) and (3).

II. ONE SURFACE AT $z = 0$

In the ζ coordinates, the single surface is located at $\zeta_2 = \pm\zeta_1$ (see Fig. 1). The obvious choice of Ψ as a Slater determinant forces the wave function to vanish along $\zeta_2 = \zeta_1$. The second boundary condition can be satisfied only if the one-particle functions chosen to make up the determinantal function are *both even* or *both odd*. Thus the bound-state excitons belong to the even-even family:

$$\Psi_{0q} = (2\lambda m/L)^{1/2}[g_0(\zeta_1)g_q(\zeta_2) - g_0(\zeta_2)g_q(\zeta_1)] , \tag{11}$$

with energy $E_{0q} = \epsilon_0 + \epsilon_q + E_g$. The scattering states belong either to the odd-odd family

$$\Psi_{u,qq'} = (2/L^2)^{1/2}[u_q(\zeta_1)u_{q'}(\zeta_2) - u_q(\zeta_2)u_{q'}(\zeta_1)] ; \tag{12a}$$

or to the even evens family

$$\Psi_{g,qq'} = (2/L^2)^{1/2}[g_q(\zeta_1)g_{q'}(\zeta_2) - g_q(\zeta_2)g_{q'}(\zeta_1)] , \tag{12b}$$

both having energy $E_{qq'} = \epsilon_q + \epsilon_{q'} + E_g \geqslant E_g$; the normalization constants were obtained assuming the length of the solid $L \to \infty$.

The continuum of states (11) overlaps the scattering states continuum (12) for $\epsilon_0 + \epsilon_q > 0$, i.e., for $q^2 > (m\lambda)^2$. In this high-energy range the bound states are unstable against decomposition into a free electron-hole pair by any perturbation such as an impurity atom or lattice vibration. This threshold also yields a unit of distance $L_0 = 2^{1/2}/m\lambda$. A traveling-wave exciton will not measure less than $O(L_0)$, therefore if the length L of the solid is comparable to L_0, interference between scattering at the front and back surfaces can not be neglected. This is an important consideration in the study of the recently developed heterostructures[5] consisting of layered films 50–100 Å in thickness, and we therefore turn now to this quantum interference effect.

III. TWO SURFACES AT $z = 0$ AND $z = L$

In the z_e-z_h plane the physically admissable coordinates lie within the square $0 < z_e < L$ and $0 < z_h < L$, with $\Psi = 0$ on the four sides of this square. It is therefore permissible to augment the interactions in (6) by periodic extensions lying outside this region, creating what is in effect a two-dimensional Kronig-Penney model, illustrated in Fig. 2. In the ζ_1-ζ_2 plane the interactions are along the lines of a grid $2^{1/2}L$ apart. The eigen-

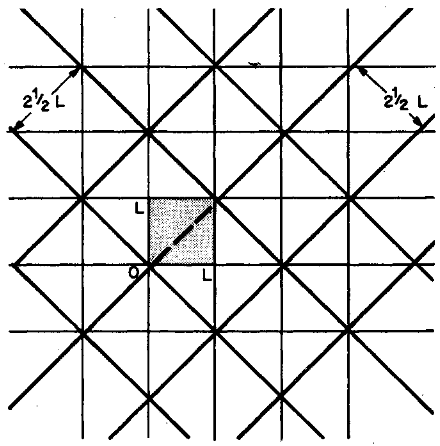

FIG. 2. For a finite thickness film with z_e or z_h extending over the interval 0–L the physical space is the shaded area indicated. Extensions of the interactions to the solid lines at 9 ± 45° creates a two-dimensional Kronig-Penney model. The boundary conditions in the text are designed to make the determinantal wave functions vanish along the $z_e = 0$ and L lines and along the $z_h = 0$ and L lines (and on their periodic extensions), thus maintaining the exciton within the physical square.

functions of the suitable augmented Eq. (6) still factor, and in either variable ζ_i are eigenfunctions of

$$h_\zeta = -\frac{1}{2m}\frac{\partial^2}{\partial\zeta^2} - \lambda\sum_{n=-\infty}^{+\infty}\delta(\zeta - n\sqrt{2}L). \qquad (13)$$

Let the Bloch function solutions $\phi(\zeta)$ of (13) be labeled according to inversion symmetry $s=\pm$ (corresponding to g or u of the preceding analysis) and lattice-translational symmetry t, $\phi(\zeta + 2^{1/2}L) = t\phi(\zeta)$, as well as the energy eigenvalue, thus $\phi_{\epsilon,s,t}(\zeta)$. Because the translation and inversion operators do not commute, they can not share a complete set of states. One easily verifies that the general eigenvalues $t = e^{i\alpha}$ are incompatible with inversion symmetry unless $\alpha = 0$ or π.

We next construct the Slater determinants as in Eqs. (11) and (12), ensuring that $\Psi = 0$ on the $z_h = 0$ boundary. Imposition of the requirement $s_1 = s_2 = \pm 1$ (denoted gg or uu in Sec. II) ensures the vanishing on the $z_e = 0$ boundary. A requirement $t_1 = t_2 = \pm 1$ for the translational quantum numbers allows Ψ to vanish on the remaining two edges of the square. Thus the allowed states of the exciton, both bound ($E < E_g$) and unbound ($E > E_g$), are quantized according to the following set of rules: the eigenstates are

$$\Psi_{\epsilon_1,\epsilon_2,s,t} = C_{\epsilon_1,\epsilon_2,s,t}[\phi_{\epsilon_1,s,t}(\zeta_1)\phi_{\epsilon_2,s,t}(\zeta_2) - \phi_{\epsilon_1,s,t}(\zeta_2)\phi_{\epsilon_2,s,t}(\zeta_1)] \quad (s=\pm 1, t=\pm 1) \qquad (14)$$

having energies $E = \epsilon_1 + \epsilon_2 + E_g$, with C a suitable normalization constant. Aside from normalization, the individual functions ϕ_i and energies ϵ_i are given as follows: the odd functions are

$$\phi_{q,-1,t}(\zeta) = \sin(\zeta n\pi/2^{1/2}L), \qquad (15)$$

where $q = n\pi/2^{1/2}L$, $t = (-1)^n$ and $\epsilon_q = q^2/2m$. The even functions belong to two distinct categories: those with $t = +1$ have an extremum at $\zeta = \pm 2^{-1/2}L$, those with $t = -1$ vanish at those points. Either t labels one bound state and a complementary set of scattering states, viz.:

$$\phi_{\epsilon_0,+1,+1}(\zeta) = \cosh\left(\frac{|\zeta| - 2^{-1/2}L}{a_+}\right), \quad \epsilon_{0,+1} = -\tfrac{1}{2}ma_+^2,$$

where

$$(1/a_+)\tanh(2^{-1/2}L/a_+) = m\lambda \qquad (16a)$$

gives the bound state for $t = +1$ as a function of L, and

$$\phi_{q,+1,+1}(\zeta) = \cos q(|\zeta| - 2^{-1/2}L), \quad \epsilon_{q,+1} = q^2/2m,$$

where

$$q\tan(q2^{-1/2}L) = -m\lambda \qquad (16b)$$

yields the allowed values of q for the scattering states of $t = +1$.

For $t = -1$, the equations for the bound state are

$$\phi_{\epsilon_0,+1,-1}(\zeta) = \sinh\left(\frac{|\zeta| - 2^{-1/2}L}{a_-}\right); \quad \epsilon_{0,-1} = -\tfrac{1}{2}ma_-^2,$$

where

$$(1/a_-)\coth(2^{-1/2}L/a_-) = m\lambda \qquad (17a)$$

have a solution only for $L > 2^{1/2}/m\lambda$; but for all values of L there is always a full complement of $t = -1$ scattering solutions:

$$\phi_{q,+1,-1}(\zeta) = \sin q(|\zeta| - 2^{-1/2}L), \quad \epsilon_{q,-1} = q^2/2m,$$

where

$$q\cot(q2^{-1/2}L) = m\lambda. \qquad (17b)$$

The spectra of exciton energies, both bound and unbound, is calculated using the above equations. Numerical results are given in the companion paper.[1]

IV. SOME APPLICATIONS

We have verified that a product function,

$$\Phi = \Psi(z_e, z_h)e^{iK(r_e+r_h)/2}R(r_e - r_h), \qquad (18)$$

where $r = (x, y)$ and $K = (K_x, K_y)$ is the center of mass wave vector, with Ψ given by (11) or (14), a function of λ, can reproduce the ground-state energy for the Coulomb potential numerically to satisfactory accuracy. Such functions may be viewed as trial functions in the variational solution of Eq.

(1) which satisfy the appropriate boundary conditions, with λ, i.e., the size of the orbit, the variational parameter. The two-dimensional function $R(r_e - r_h)$ may be obtained either as a solution of the effective Schrödinger equation, or more simply, may be taken as Gaussian or exponential functions with a characteristic length to be optimized.

The theory of size effects in excitons has important applications to the optical properties of semiconducting thin films and heterostructures. Conservation of momentum would ascribe to the optical spectrum associated with the exciton bound states extremely narrow linewidths, therefore explanations of the observed linewidths have invoked such momentum relaxing processes as scattering by impurities and phonons, or the decay of the electromagnetic intensity within the sample. We find that the effects of the boundary conditions alone are sufficient to produce a substantial linewidth. In the companion paper,[1] we compute these various applications, and compare with several approximate methods in the literature.[6]

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