Generalized spheroidal wave equations from an image-potential method for surface effects on impurity states

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Based on the hydrogenic effective-mass approximation, an image-potential method is developed for the treatment of impurities in semiconductors with a boundary surface. The Schrödinger equation is separable in prolate spheroidal coordinates (ξ, η, ϕ). Generalized spheroidal wave equations of ξ and η resulting from the separation constitute the basic equations for the study of surface effects on impurity states.

In the case when the effective-mass approximation is valid, the shallow impurity levels of a substitutional impurity differing by one unit of valence from atoms of the pure material are merely the hydrogenic levels.[1] This is true only if the impurity is located in an infinite bulk crystal. In actual practice, often an impurity is on or near the surface of a crystal. Many workers have studied surface effects on impurity levels using variational method or perturbation theory.[2-9] In this Brief Report we present a set of generalized spheroidal wave equations which can serve as the basic equations for the treatment of surface effects on impurity states along a somewhat different line of approach. Our purpose here is to give solely the derivation of these equations but not their applications.

Consider a semi-infinite isotropic semiconductor occupying the $z \geq 0$ half-space and having a surface coincident with the x-y plane. The $z < 0$ half-space is a vacuum. Let a donor impurity be at $(x,y,z) = (0, 0, d)$ with an extra positive charge in the nucleus. An extra electron with effective mass m^* is at an arbitrary point $P = (x,y,z)$ in the $z \geq 0$ half-space. In GaAs, one of the As atoms replaced by a Te or Se atom serves as a real example of such a system.[1] Now the problem is to find the solution of the following Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m^*}\nabla^2 + V(x,y,z) \right]\psi(x,y,z) = E\psi(x,y,z) \ , \quad (1)$$

where the potential $V(x,y,z)$ is chosen to be[2,3]

$$V(x,y,z) = \begin{cases} -\dfrac{e^2}{\epsilon[x^2+y^2+(z-d)^2]^{1/2}}, & z > 0 \ , \\ \infty, & z = 0, \end{cases} \quad (2)$$

where ϵ is the dielectric constant of the crystal and E is measured from the conduction-band edge. For simplicity, we use units such that length and energy are expressed in the effective first Bohr radius $a_e \equiv \hbar^2\epsilon/m^*e^2$ and the effective Rydberg $R_e \equiv e^4m^*/2\epsilon^2\hbar^2$, respectively. Equation (1) becomes

$$\left[\nabla^2 + E + \frac{2}{[x^2+y^2+(z-d)^2]^{1/2}} \right]\psi(x,y,z) = 0 \ , \quad (3)$$

with the boundary condition

$$\psi(x,y,0) = 0. \quad (4)$$

It is convenient to change this one-center problem into a two-center one by considering the following potential:

$$\tilde{V}(x,y,z) = -\frac{e^2}{\epsilon[x^2+y^2+(z+d)^2]^{1/2}}\theta(-z)$$
$$-\frac{e^2}{\epsilon[x^2+y^2+(z-d)^2]^{1/2}}\theta(z)$$
$$\equiv V_i(x,y,z) + V_r(x,y,z) \ ,$$

where V_i and V_r are the "image potential" and real potential, respectively; $\theta(z)$ is the Heaviside step function

$$\theta(z) = \begin{cases} 1, & z > 0 \ , \\ \frac{1}{2}, & z = 0 \ , \\ 0, & z < 0. \end{cases}$$

By image potential we mean the virtual image of the Coulombic part of potential (2) produced by the x-y plane, which is to be visualized for this purpose as if it were a plane mirror. Our image potential is invented merely as a mathematical aid and is entirely different from the potential of image charge commonly encountered in interface problems. This potential of image charge is in some instances also called "image potential" and must not be confused with what we call an image potential. Let $r_a = [x^2+y^2+(z+d)^2]^{1/2}$ and $r_b = [x^2+y^2+(z-d)^2]^{1/2}$, as shown in Fig. 1. The Schrödinger equation with $\tilde{V}(x,y,z)$ as
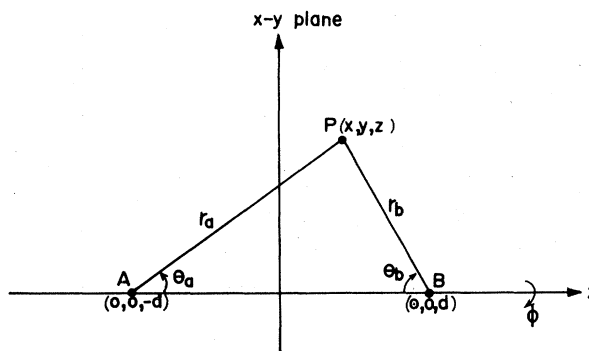

FIG. 1. Coordinates used in the potential functions.

the potential is

$$\left[\nabla^2 + E + \frac{2}{r_a}\theta(-z) + \frac{2}{r_b}\theta(z)\right]\tilde{\psi}(x,y,z) = 0 \ . \tag{5}$$

The most appropriate coordinate system for this equation is the prolate spheroidal one in which the variables are

$$\xi = \frac{r_a + r_b}{R}, \quad \eta = \frac{r_a - r_b}{R}, \quad \phi \ ,$$

where $R = 2d$ and ϕ is the azimuthal angle. Their ranges are $1 \leq \xi < \infty$, $-1 \leq \eta \leq 1$, and $0 \leq \phi \leq 2\pi$. (x,y,z) and

(ξ, η, ϕ) are related by the equations

$$x = \frac{R}{2}[(\xi^2 - 1)(1 - \eta^2)]^{1/2}\cos\phi \ ,$$

$$y = \frac{R}{2}[(\xi^2 - 1)(1 - \eta^2)]^{1/2}\sin\phi \ ,$$

$$z = \frac{R}{2}\xi\eta \ .$$

It can be shown that Eq. (5) is now separable. Let $\tilde{\psi} = M(\xi)N(\eta)\Phi(\phi)$; then

$$\frac{d}{d\xi}\left[(\xi^2 - 1)\frac{d}{d\xi}M(\xi)\right] + \left[A - \frac{m^2}{\xi^2 - 1} + \frac{R^2 E}{4}\xi^2 + R\,\xi\right]M(\xi) = 0 \ , \tag{6}$$

$$\frac{d}{d\eta}\left[(1 - \eta^2)\frac{d}{d\eta}N(\eta)\right] + \left[-A - \frac{m^2}{1 - \eta^2} - \frac{R^2 E}{4}\eta^2 + R\,|\eta|\right]N(\eta) = 0 \ , \tag{7}$$

$$\left[\frac{d^2}{d\phi^2} + m^2\right]\Phi(\phi) = 0 \ , \tag{8}$$

where A and m^2 are separation constants. E is negative for the bound-state solution. $\Phi(\phi)$ has the usual form $e^{\pm im\phi}$ with m equal to zero or a positive integer. Apart from the absolute value of η in the last term of Eq. (7), Eqs. (6) and (7) are very nearly the same as the equations that have appeared in the theory of the hydrogen atom,[10] in one-electron diatomic molecular ions,[11-24] in the application of diatomic orbitals to multiple-electron diatomic molecules,[25-28] and, in general, in two-center problems.[18, 23, 29-32] Equations (6) and (7) are called "generalized spheroidal wave equations."[29] Since Eq. (7) is even in η and since there is only one solution which is finite in $-1 \leq \eta \leq 1$,[30] $N(-\eta) = \pm N(\eta)$. Those $N(\eta)$ that have odd η parity have odd z parity too. The odd-parity solution has the property

$$N_{\text{odd}}(\eta) = 0 \quad \text{at } \eta = 0 \ (z = 0) \ . \tag{9}$$

In the $\eta > 0$ $(z > 0)$ region, $N_{\text{odd}}(\eta)$ satisfies the Schrödinger equation with (2) as the potential. Hence the solution of Eq. (3) is

$$\psi = M(\xi)N_{\text{odd}}(\eta)\Phi(\phi), \quad \eta \geq 0 \ . \tag{10}$$

The associated eigenvalue can be obtained from Eqs. (6)

and (7) with odd η parity.

Results in limiting cases can be drawn immediately from these basic equations. It can be shown that when $d = 0$, the ψ of Eq. (10) reduces to the hydrogenic eigenfunction in spherical polar coordinates with the restrictions $\cos\theta \geq 0$ and $l + m = $ odd integer. The latter is called customarily the "surface selection rule." This result is exactly the same as that obtained by others with the conventional method.[2] In the opposite case $d \rightarrow \infty$, it can be proved by following a procedure similar to Ref. 31 that the eigenstates are the hydrogenic levels in parabolic coordinates. Hence the ground state at $d = 0$ is a $2p_0$ state, while at $d \rightarrow \infty$ it is a $1s$ state.[1]

For given d, Eqs. (6) and (7) must be solved explicitly. The eigenvalue E can be obtained as a function of d by eliminating the separation constant A from the simultaneous solutions. The solution of (6) can be either Jaffé's[14] or Hylleraas's[13] solution. The former solution is

$$M(\xi) = (\xi^2 - 1)^{m/2}(\xi + 1)^\sigma e^{-p\xi} \sum_{s=0}^{\infty} a_s\left[\frac{\xi - 1}{\xi + 1}\right] \ ,$$

where $p^2 = -\frac{1}{4}R^2 E$ and $\sigma = R/2p - m - 1$. The coefficient a_s satisfies the following relation:

$$(s + 1)(s + m + 1)a_{s+1} - [2s^2 + (4p - 2\sigma)s - A' - 2p\sigma - (m + 1)(m + \sigma)]a_s + (s - 1 - \sigma)(s - 1 - \sigma - m)a_{s-1} = 0 \ , \tag{11}$$

where $A' = A - p^2$. Hylleraas's solution is expanded into associated Laguerre polynomials

$$M(\xi) = (\xi^2 - 1)^{m/2}e^{-u/2} \sum_{t=0}^{\infty} \frac{b_t}{(m + t)!}L_{m+t}^m(u) \ ,$$

with $\xi = 1 + u/2p$. The coefficient b_t satisfies the relation

$$(t + m + 1)(t - m - \sigma)b_{t+1} + t(t - 1 - \sigma)b_{t-1} + \{2t^2 + 2t(2p - \sigma) - [A' + 2p\sigma + (m + 1)(m + \sigma)]\}b_t = 0 \ . \tag{12}$$

The absolute value of η in the last term of Eq. (7) makes this equation less familiar to us. A similar situation occurs in the Schrödinger equation for a double oscillator.[33] We assume $N(\eta)$ to be expanded in the following form:[30]

$$N_{\text{odd}}(\eta) = \begin{cases} e^{p\eta} \displaystyle\sum_{r=0}^{\infty} c_r P_{r+m}^m(\eta), & 0 \leq \eta \leq 1 \ , \\[3mm] -e^{-p\eta} \displaystyle\sum_{s=0}^{\infty} c_s P_{s+m}^m(-\eta), & -1 \leq \eta \leq 0. \end{cases}$$

c_r satisfies the following relation:

$$\frac{(r+2m+1)(R+2p+2pr+2pm)}{2r+2m+3}c_{r+1}$$

$$-[A'+(r+m)(r+m-1)]c_r$$

$$+\frac{r(R-2pr-2pm)}{2r+2m-1}c_{r-1}=0 \quad . \quad (13)$$

$N(\eta)$ can be equally well written as

$$N_{\text{odd}}(\eta)=\begin{cases} e^{-p\eta}\sum_{r=0}^{\infty}\bar{c}_r P_{r+m}^m(\eta), & 0\leq\eta\leq 1, \\ \\ -e^{p\eta}\sum_{s=0}^{\infty}\bar{c}_s P_{s+m}^m(-\eta), & -1\leq\eta\leq 0. \end{cases}$$

Then $\bar{c}_r$ satisfies a relation obtained from (13) by changing the sign of p. $N(\eta)$ may also have the alternative expansion[30]

$$N_{\text{odd}}(\eta)=\begin{cases} (1-\eta^2)^{m/2}e^{p\eta}\sum_{r=0}^{\infty}d_r(1-\eta)^r, & 0\leq\eta\leq 1, \\ \\ -(1-\eta^2)^{m/2}e^{-p\eta}\sum_{s=0}^{\infty}d_s(1+\eta)^s, & -1\leq\eta\leq 0. \end{cases}$$

d_r satisfies the relation

$$2(r+1)(r+m+1)d_{r+1}+(2pm+2pr-R)d_{r-1}$$

$$-[r(r+1)+2r(2p+m)+A'-R$$

$$+(m+2p)(m+1)]d_r=0 \quad . \quad (14)$$

This $N_{\text{odd}}(\eta)$ and relation (14) can be changed slightly with

p replaced by $-p$. To get the ψ of (10), we must solve either Eq. (11) or Eq. (12) simultaneously with either Eq. (13) or Eq. (14) combined with condition (9). The difference equations constructed from these recurrence relations can be written in the form of infinite-dimensional matrix equations. For practical purposes, they can be truncated to finite but sufficiently large dimension so that good convergence of $M(\xi)$ and $N_{\text{odd}}(\eta)$ is guaranteed. To solve the simultaneous matrix equations, the Newton-Raphson method[34] may be employed in actual numerial computation.[25,31,35] The solution so obtained is exact.

The potential function (2) is slightly crude because the effect of image charges of the ion and the electron is omitted. With this effect taken into account,[4,9] the Schrödinger equation is no longer separable. An appropriate way of treating this problem is the incorporation of a perturbative-variational approach[36] in the image-potential method.

Applicability of the image-potential method is not restricted solely to isotropic semiconductors and can be extended to anisotropic materials, e.g., Si or Ge, by approximating the transverse and longitudinal electron effective masses to a scalar effective mass by the method of Ref. 7.

A similar application of Eqs. (6)–(8) to the study of surface effects on the Wannier exciton is also possible. In this case, m^* in Eq. (1) is replaced by the reduced mass calculated from the effective masses of the electron and the hole, and d is now the distance between the center of mass of the electron-hole system and the boundary surface in the z direction. Satpathy has independently observed the separability of the Schrödinger equation for Wannier excitons near a semiconductor surface.[37]

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