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Strong-perturbation theory for impurities in semiconductors

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An improved version of the perturbation theory has been proposed. Expressions for the wave functions and energies of both degenerate and nondegenerate cases are derived. This method provides a simple way to treat problems involving more than one potential in the Hamiltonian and the case when the perturbations are comparable with or larger than the unperturbed Hamiltonian. We use this method to study the ground state of a hydrogenic atom in a uniform magnetic field of arbitrary strength in which the usual perturbation treatment is limited for most semiconductors to a small range of magnetic field.

I. INTRODUCTION

There are only a few types of problems which can be solved exactly by using the Schrödinger equation. Usually many approximation methods are introduced to solve appropriate problems. The most common methods are perturbation and variational methods. Perturbation theory is applicable when the perturbation is small compared to the unperturbed Hamiltonian and in general it is hard to find a proper variational trial wave function for use in the variational method.

More generally, if we consider a system involving more than one potential in the Hamiltonian (or the case where the perturbations are comparable with or larger than the unperturbed Hamiltonian), the problem becomes very complicated. First, it is hard to find proper approximation methods and second, even if one does find approximate solutions, it is difficult to justify the physical results. It is always possible to find solutions using numerical methods for such problems, but usually it is not possible to provide a good physical perspective especially for the wave functions.

Recently, the problem of a shallow impurity in a quantum well has been intensively investigated. There are two potentials involved in such problems; one is the Coulomb potential and the other is the quantum-well potential. The variational method has been widely used[1–5] to treat these problems. For the variational wave function, one takes the product of the wave functions corresponding to the quantum-well and Coulomb potentials, and treats this as a trial wave function. The variational method has been also used to treat more complex problems, such as a shallow impurity in a quantum well or in a superlattice in the presence of an electric or magnetic field.[6–9] It has also been used by Liu and Lin[10] to solve the hydrogenic atom in a semi-infinite space.

In this paper, we propose a new approximation method to deal with the above problems. Many of these can be solved simply to a certain degree of accuracy. Expressions for the wave functions and energies of both degenerate and nondegenerate cases are derived. We only discuss the case of two potentials here. The same method can easily be applied to other problems. As an example, we use this method to solve the ground state of the hydrogenic atom in a uniform magnetic field of arbitrary strength. This problem is of interest in semiconductor physics where typical values of the effective mass m^* and dielectric constant ϵ make the effective rydberg, R^* about 10^4 times smaller than for the free hydrogen atom. In particular, the magnetoabsorption of semiconductors has received great attention because it can provide important information about the electronic band structure of these materials. Our solutions, to the first-order approximation, are in good agreement with those obtained in Refs. 11 and 12 where very complicated methods have been used.

II. THE FORMALISM

Consider the Hamiltonian

$$H = H_0 + V' , \tag{1}$$

where

$$H_0 = -\nabla^2 + V_0 . \tag{2}$$

V' is a perturbation of another potential which is comparable to H_0. We want to solve the Schrödinger equation

$$H\psi = E\psi . \tag{3}$$

Assume that H_0 has an exact solution

$$H_0\phi = E_0\phi . \tag{4}$$

We introduce a factor $f = e^{-g}$ in the wave function ψ and write ψ as

$$\psi = f\phi . \tag{5}$$

Substituting Eq. (5) into (3), we get

$$H\psi = f[H_0\phi + \phi(V' - |\nabla g|^2 + \nabla^2 g) + 2\nabla g\cdot\nabla\phi] . \tag{6}$$

We chose g in such way that

$$|\nabla g|^2 - \nabla^2 g = V' , \tag{7}$$

then from Eqs. (3), (5), and (6), we have

$$f\tilde{H}\phi=Ef\phi\ , \tag{8}$$

where

$$\tilde{H}=H_0+H' \tag{9}$$

and

$$H'=2\nabla g\cdot\nabla\ . \tag{10}$$

Notice that H' only operates on ϕ. The function g can be solved from Eq. (7) with the initial conditions

$$V'=0,\quad g=0,\quad \text{and } \nabla g=0\ . \tag{11}$$

The Eq. (11) is deduced from the condition that $H\psi=H_0\phi$ when $V'=0$. From Eqs. (7) and (11), we have two independent solutions, and we can always determine which one is suitable for the real problems.

A few remarks should be made here. First, the wave function ψ already includes the term $f=e^{-g}$, which connects V' through Eq. (7); after this transformation, the perturbation theory is applicable even if the perturbation is very large. Second, we can treat H' either by the perturbation or the variational method. In this paper, we treat H' as a perturbation. Third, if Eq. (7) cannot be solved analytically, we can always take

$$H'=2\nabla g\cdot\nabla+V'-|\nabla g|^2-\nabla^2 g$$

as a perturbation, but one must choose the function g such that $V'-|\nabla g|^2-\nabla^2 g$ is minimum. Fourth, the wave functions for different excited states are not orthogonal as is the case for the usual perturbation method.[13] Nevertheless, it still gives good results as we will see.

Before we give a detailed discussion, let us examine which kinds of common and useful potential forms of V' ensure that g can be solved exactly and analytically. Writing $g=r^m$ and substituting g into Eq. (7), we find for three dimensions

(a) $m=2,\quad V'=r^2,\quad g=r^2\ ,$

(b) $m=1,\quad V'=r^{-1},\quad g=r\ ,$

(c) $m=-1,\quad V'=r^{-4},\quad g=r^{-1}\ .$

This method provides most accurate solutions if it is used to solve problems involving more than one potential with one of the potentials being of Coulomb, harmonic-oscillator, or r^{-4} form. We now derive the wave functions and energies for both degenerate and nondegenerate cases.

A. Nondegenerate case

Starting from Eq. (8), following the usual perturbation procedure,[13] we get

$$f(H_0-E_n^{(0)})\phi_n^{(1)}=-f(H'-E_n^{(1)})\phi_n^{(0)}\ . \tag{12}$$

Because H is Hermitian, we have

$$\int \psi_1(H\psi_2)^* d\mathbf{r}=\int \psi_2^* H\psi_1 d\mathbf{r}\ , \tag{13}$$

where $\psi_i=f\phi_i$ $(i=1,2)$. From Eqs. (5), (8), (9), and (13), we get

$$\int (f\phi_2)^* fH_0\phi_1 d\mathbf{r}=\int |f|^2\phi_1(H_0\phi_2)^* d\mathbf{r}+\int |f|^2[\phi_1(H'\phi_2)^*-\phi_2^* H'\phi_1]d\mathbf{r}\ . \tag{14}$$

Multiplying both sides of Eq. (12) by $(f\phi_n^{(0)})^*$, integrating over the whole space and using Eq. (14), we have

$$E_n^{(1)}\int |f|^2|\phi_n^{(0)}|^2 d\mathbf{r}=\int |f|^2\phi_n^{(0)*}H'\phi_n^{(0)}d\mathbf{r}+\int |f|^2[\phi_n^{(1)}(H'\phi_n^{(0)})^*-\phi_n^{(0)*}(H'\phi_n^{(1)})]d\mathbf{r}\ . \tag{15}$$

For the first-order approximation to the energy, we can neglect the second term on the right-hand side of the above equation. So we have

$$E_n^{(1)}=\frac{\int |f|^2\phi_n^{(0)*}H'\phi_n^{(0)}d\mathbf{r}}{\int |f|^2|\phi_n^{(0)}|^2 d\mathbf{r}}\ . \tag{16}$$

For the first-order wave function, we write

$$\phi_n^{(1)}=\sum_l{}' a_l^{(1)}\phi_l^{(0)},\quad (l\neq n) \tag{17}$$

substituting Eq. (17) into Eq. (12), and using the same procedure for obtaining Eq. (15), we have

$$\sum_l{}'(E_l^{(0)}-E_n^{(0)})\langle m\,|\,l\rangle a_l^{(1)} =E_n^{(1)}\langle m\,|\,n\rangle-H'_{mn},\quad (m\neq n)\ , \tag{18}$$

where

$$H'_{mn}=\int (f\phi_m^{(0)})^* fH'\phi_n^{(0)}d\mathbf{r}\ ,$$

$$\langle m\,|\,n\rangle=\int (f\phi_m^{(0)})^* f\phi_n^{(0)}d\mathbf{r}\ .$$

We can always solve Eq. (18) be choosing a finite set of l depending on the accuracy we desire. Combining Eq. (18) with Eq. (15), the wave function to the first order can be determined.

For the second-order energy of the nondegenerate case, we have

$$f(H_0-E_n^{(0)})\phi_n^{(2)}+f(H'-E_n^{(1)})\phi_n^{(1)}=fE_n^{(2)}\phi_n^{(0)}\ . \tag{19}$$

Multiply the above equation by $(f\phi_n^{(0)})^*$ on both sides and integrating, from Eq. (14) we have

$$\int (f\phi_n^{(0)})^* fH'\phi_n^{(1)}d\mathbf{r}-E_n^{(1)}\int (f\phi_n^{(0)})^* f\phi_n^{(1)}d\mathbf{r}+\int |f|^2[\phi_n^{(2)}(H'\phi_n^{(0)})^*-\phi_n^{(0)*}(H'\phi_n^{(2)})]d\mathbf{r}=E_n^{(2)}\langle n\,|\,n\rangle\ .$$

For the energy to the second order, the third term on the left-hand side of the above equation can be neglected and we have

$$E_n^{(2)}=(\langle n\,|\,n\rangle)^{-1}\left[\int (f\phi_n^{(0)})^* fH'\phi_n^{(1)}d\mathbf{r}-E_n^{(1)}\int (f\phi_n^{(0)})^* f\phi_n^{(1)}d\mathbf{r}\right] , \tag{20}$$

where $\phi_n^{(1)}$ and $E_n^{(1)}$ can be obtained from Eqs. (15) and (18).

B. Degenerate case

Suppose there are k degenerate wave functions for energy E_n given by $\phi_{n,i}$ $(i=1,\ldots,k)$. We write the wave functions $\phi_n^{(0)}$ as the linear combinations of $\phi_{n,i}^{(0)}$ $(i=1,\ldots,k)$, i.e.,

$$\phi_n^{(0)}=\sum_{i=1}^{k} C_i^{(0)}\phi_{n,i}^{(0)} . \tag{21}$$

Substituting Eq. (21) into Eq. (12), and multiplying both sides by $(f\phi_{n,l}^{(0)})^*$ and integrating, we get

$$\int (f\phi_{n,l}^{(0)})^* f(H_0-E_n^{(0)})\phi_n^{(1)}d\mathbf{r} = -\int (f\phi_{n,l}^{(0)})^*(H'-E_n^{(1)})\sum_{i=1}^{k} C_i^{(0)}\phi_{n,i}^{(0)}d\mathbf{r} .$$

Using Eq. (14), and retaining only the first-order term, i.e., neglecting the term

$$\int |f|^2[\phi_{n,l}^{(0)}(H'\phi_n^{(1)})^*-\phi_n^{(1)*}(H'\phi_{n,l}^{(0)})]d\mathbf{r} ,$$

we get

$$\sum_{i=1}^{k}(H'_{li}-E_n^{(1)}\langle l\,|\,i\rangle)C_i^{(0)}=0, \quad (l=1,2,\ldots,k) . \tag{22}$$

Here

$$H'_{li}=\int |f|^2\phi_{n,l}^{(0)*}H'\phi_{n,i}^{(0)}d\mathbf{r} ,$$

$$\langle l\,|\,i\rangle=\int |f|^2\phi_{n,l}^{(0)*}\phi_{n,i}^{(0)}d\mathbf{r} .$$

The first-order energies $E_n^{(1)}$, $E_{n,i}^{(1)}$ $(i=1,2,\ldots,k)$ can be obtained by solving Eq. (22), or equivalently the matrix

$$\begin{vmatrix} H'_{11}-E_n^{(1)}\langle 1\,|\,1\rangle & H'_{12}-E_n^{(1)}\langle 1\,|\,2\rangle & \cdots & H'_{1k}-E_n^{(1)}\langle 1\,|\,k\rangle \\ H'_{21}-E_n^{(1)}\langle 2\,|\,1\rangle & H'_{22}-E_n^{(1)}\langle 2\,|\,2\rangle & \cdots & H'_{2k}-E_n^{(1)}\langle 2\,|\,k\rangle \\ \vdots & \vdots & & \vdots \\ H'_{k1}-E_n^{(1)}\langle k\,|\,1\rangle & H'_{k2}-E_n^{(1)}\langle k\,|\,2\rangle & \cdots & H'_{kk}-E_n^{(1)}\langle k\,|\,k\rangle \end{vmatrix}=0 . \tag{23}$$

The wave functions $\phi_n^{(0)}$ can also be determined from Eq. (23) in combination with the normalization condition.

III. APPLICATIONS TO A PHYSICAL PROBLEM

Now we apply the above method to the problem of a hydrogenic atom in a uniform magnetic field of arbitrary strength. Using the effective-mass approximation, the Hamiltonian in cylindrical coordinates can be written as[14]

$$H=H_0+V' , \tag{24}$$

where

$$H_0=-\nabla^2-2/r-i\frac{\partial}{\partial\phi} ,$$

$$V'=\eta^2\rho^2/4 ,$$

and $r=(\rho^2+z^2)^{1/2}$, $\rho=(x^2+y^2)^{1/2}$. The units of energy and length here are R^*, the effective rydberg, a^* the effective Bohr radius. $R^*=R_0m^*/m_0\epsilon^2$ and $a^*=a_0\epsilon m_0/m^*$, where ϵ is the static dielectric constant, m^* and m_0 are the effective mass of the electron and the free-electron mass, respectively; R_0 and a_0 are the hydrogen rydberg and Bohr radius, respectively. η is a parameter which represents a measure of the effect of the magnetic field on a particular substance. Also $\eta=\hbar\omega_c/2R^*$ and $\omega_c=Be/m^*$. It is obvious that H_0 has an exact solution, that for the hydrogen atom in the free space, $\phi_{nlm}(\mathbf{r})$. From Eq. (7), we have

$$|\nabla g|^2-\nabla^2 g=\eta^2\rho^2/4 ,$$

and, combining this with the initial conditions, $\eta=0$, $g=0$, and $\nabla g=0$, we have $g=\eta\rho^2/4$. Note that a constant η also contributes to H_0. The wave function ψ and

TABLE I. Energies of hydrogenic atom in a uniform magnetic field.

η	E^{a}	E^{b}	E^{c}
0.1	-0.995		-1.000
0.3	-0.958		-1.000
0.5	-0.894		-0.862
0.7	-0.811		-0.761
0.9	-0.714		-0.666
1.0	-0.662		-0.605
2.0	-0.0438		0.005
3.0	0.672		0.787
4.0	1.439		1.572
5.0	2.240		2.392
10	6.506		6.741
20		15.70	15.95
30		25.03	25.48
40		34.51	35.00
50		44.07	44.72
100		92.51	93.65

[a]Reference 11.
[b]Reference 12.
[c]Present results.

H' [see Eqs. (5) and (10)] are given by

$$\psi = e^{-\eta\rho^2/4}\phi$$

and

$$H' = 2\nabla g \cdot \nabla = \eta\rho\frac{\partial}{\partial\rho} \ .$$

We will now treat H' as a perturbation. The zeroth-order wave function is $\phi^{(0)} = \phi_{nlm}(r,\theta,\varphi)$, the wave function of a hydrogen atom in free space. So we have

$$E^{(0)}_{nlm} = -\frac{1}{n^2} + \eta + m\eta \ , \qquad (25)$$

$$\psi^{(0)}_{nlm} = N\exp(-\eta\rho^2/4)\phi_{nlm}(r,\theta,\varphi) \ , \qquad (26)$$

where N is a normalization constant. We only discuss the results of the ground state here. The results for the excited states will be discussed elsewhere.[15] For the ground state, $\phi^{(0)}_{100} = (1/\sqrt{\pi})e^{-r}$, the normalization condition is

$$N^{-2} = \frac{1}{\pi}\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-\eta\rho^2/2}e^{-2r}r^2\sin\theta\, dr\, d\theta\, d\varphi \ .$$

To perform the integration, we change to the parabolic coordinate[16] α_1 and α_2, we have

$$\begin{aligned} N^{-2} &= (\tfrac{1}{2})\int_0^\infty\int_0^\infty e^{-\eta\alpha_1\alpha_2/2-\alpha_1-\alpha_2}(\alpha_1+\alpha_2)d\alpha_1 d\alpha_2 \\ &= \eta'[1+\eta' e^{\eta'}\mathrm{Ei}(-\eta')] \ , \end{aligned} \qquad (27)$$

where $\eta' = 2/\eta$ and $\mathrm{Ei}(-x)$ is the exponential integral.[17] The energy to first order in H' can be calculated as follows:

$$\begin{aligned} H'\phi^{(0)}_{100} &= -N\eta\frac{\rho^2}{r}\frac{1}{\sqrt{\pi}}e^{-r} \ , \\ E^{(1)}_{100} &= -N^2\frac{\eta}{\pi}\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-\eta\rho^2/2-2r}\frac{\rho^2}{r}r^2\sin\theta\, dr\, d\theta\, d\phi \\ &= -N^2\eta\int_0^\infty\int_0^\infty e^{-\eta\alpha_1\alpha_2/2-\alpha_1-\alpha_2}\alpha_1\alpha_2 d\alpha_1 d\alpha_2 \\ &= 2+2e^{\eta'}\mathrm{Ei}(-\eta')[1+\eta' e^{\eta'}\mathrm{Ei}(-\eta')]^{-1} \ , \\ E_{100} &= E^{(0)}_{100}+E^{(1)}_{100} = -1+\eta+2+2e^{\eta'}\mathrm{Ei}(-\eta')[1+\eta' e^{\eta'}\mathrm{Ei}(-\eta')]^{-1} \ . \end{aligned} \qquad (28)$$

In Table I, we list the results of our calculation and others, all of which have been rounded to three decimals.

Notice that very complicated calculations have been performed in order to get the results in Refs. 11 and 12. Here we used a very simple calculation, only to the first order of energy, and nevertheless the results are in very good agreement with those in Refs. 11 and 12.

In conclusion, we have proposed an improved version of the perturbation theory. It provides a method to treat the problems involving more than one potential, or a very large "perturbation" term in the Hamiltonian. The expressions for energies and wave functions for both degenerate and nondegenerate cases have been derived. This method was used to study the ground state of a hydrogenic atom in a uniform magnetic field of arbitrary strength. The results for the ground-state energies, to the first-order approximation, are in quantitative agreement with other more elaborate calculations, which is quite encouraging, thus pointing out the effectiveness of the present method. Applications of this method to the problem of a shallow impurity in the presence of both electric and magnetic fields is under investigation.

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[1] G. Bastard, Phys. Rev. B **24**, 4714 (1981).

[2] Wen-ming Liu and J. J. Quinn, Phys. Rev. B **31**, 2348 (1985).

[3] S. Chaudhuri, Phys. Rev. B **28**, 4480 (1983).

[4] K. Jayakumar and S. Balasubramanian, Phys. Rev. B **32**, 6904 (1985).

[5] J. W. Brown and H. N. Spector, J. Appl. Phys. **59**, 1179 (1986).

[6] Mitsuru Matsurra and Tsuneo Kamizato, Phys. Rev. B **33**, 8385 (1986).

[7] J. A. Brum, C. Priester, and G. Allan, Phys. Rev. B **32**, 2378 (1985).

[8] K. Jayakumar, S. Balasubramanian, and M. Tomak, Phys. Rev. B **33**, 4402 (1986).

[9] H. X. Jiang (unpublished).

[10] Zhengpeng Li and D. L. Lin, Phys. Rev. B **28**, 4413 (1983).

[11] P. C. Makado and N. C. Mcgill, J. Phys. C **19**, 873 (1986).

[12] M. Altarelli and N. O. Lipari, Phys. Rev. B **9**, 1733 (1974).

[13] E. Merzbacher, *Quantum Mechanics,* 2nd ed. (Wiley, New York, 1970), pp. 413—420.

[14] P. C. Makado, Physica **132B**, 7 (1985).

[15] H. X. Jiang (unpublished).

[16] L. D. Landau and E. M. Lifschitz, *Quantum Mechanics,* 3rd ed. (Pergamon, Oxford, 1977), p. 132.

[17] Milton Abramowitz and Irene A. Stegun, *Handbook of Mathematic Functions with Formula, Graphs, and Mathematical Table,* in *National Bureau of Standards Applied Mathematics Series* (Natl. Bur. Stand., Washington, D.C., 1964), p. 228.