Shallow-impurity states in semiconductor quantum-well structures

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The ground-state energy of a shallow impurity in a semiconductor quantum well of finite barrier height is calculated using a variational method. The binding energy U is obtained as a function of the well width L, the impurity position z_i, and the height of the potential barrier V_0. The behavior of the variational parameter λ, which determines the extension of the wave function around the impurity, is also studied. The maximum binding energy corresponds to the minimum value of λ. Larger values of V_0 result in faster variation of U with z_i. Our results agree very well with published experimental data.

I. INTRODUCTION

The development of molecular beam epitaxy (MBE) in the last few years has made it possible to fabricate systems consisting of alternate layers of two different semiconductors with similar lattice structure and matching lattice parameters. These new periodic structures, which can have spatial periods considerably greater than the lattice constants, are referred to as superlattices.[1] Two types of superlattices have so far been studied in great detail. One of these (referred to as type I) is exemplified by the GaAs-$Al_xGa_{1-x}As$ system in which the band gap of GaAs is contained entirely within the band gap of $Al_xGa_{1-x}As$. The discontinuities of both the conduction- and valence-band edges at the interfaces give rise to potential wells for both electrons and holes in the GaAs layers. These potential wells are separated by potential barriers in the $Al_xGa_{1-x}As$ layers, whose height depends on the Al concentration (x value). The other type of superlattice system (referred to as type II) is typified by an InAs-GaSb system. Here the band match is such that the conduction-band minimum of InAs is below the valence-band maximum of GaSb. Thus, in this case, a spatial separation of electrons and holes takes place due to the transfer of electrons ($\sim 10^{17}$ cm^{-3}) from GaSb to InAs.

This investigation of shallow impurity states in the superlattice has recently attracted considerable attention. Bastard[2] has calculated the binding energy of the ground impurity state as a function of the layer thickness and the impurity position assuming an infinitely deep potential well. Mailhiot *et al.*[3] have studied the energy spectrum of shallow donor states in a quantum well. They considered two cases, the donor at the center and at the edge of the quantum well. Greene and Bajaj[4] have reported a calculation of the binding energy of the ground donor state as a function of the potential barrier height and of the width of the quantum well under the assumption that the positive ion is located at the center of the well.

In this paper we report a calculation of the binding energy of the ground state of an impurity in a potential well of finite depth as a function of the well width, the impurity position within the well, and the potential barrier height. We also study the behavior of the variational parameter λ, which determines the extent of the wave function around the impurity, with well width for different values of the barrier height when the impurity is located at the center of the well. We find an interesting relation between the variation of the binding energy and the variation of the parameter λ with the well width; namely, the maximum value of binding energy corresponds to the minimum value of λ. Its physical meaning is clear; the more tightly bound the electron, the smaller its extension about the impurity. In addition, we find that the larger the barrier height V_0, the more rapid the variation of the binding energy U with position z_i, as would be suspected intuitively. Our results agree very well with the experimental data of Miller *et al.*[5]

II. THEORY

We will consider only those superlattices whose barrier layers are sufficiently wide that the quantum wells can be treated as independent potential wells. For the sake of definiteness, we assume the impurity is donor, although it is clear that our results also apply to the acceptor sites provided the parameters of the electron are replaced by ones of a hole. Within the framework of the effective-mass approximation, the Hamiltonian H of an electron around the hydrogenic donor attached to the first conduction subband in the quantum well can be written as

$$H=\frac{\hbar^2}{2m^*}\nabla^2-\frac{e^2}{\epsilon[\rho^2+(z-z_i)^2]^{1/2}}+V(z)\ . \tag{1}$$

Here $V(z)$ is the potential-energy barrier which confines the carrier in the well of height V_0 and width L; we assume that

$$V(z)=\begin{cases}0 & \text{if } |z|<\dfrac{L}{2},\\ V_0 & \text{if } |z|>\dfrac{L}{2}\end{cases}\ . \tag{2}$$

The origin of a Cartesian coordinate system is chosen at the center of the well, $\rho^2=x^2+y^2$ is the distance in the layer plane measured from impurity site, and z_i is the coordinate of the impurity site along the superlattice axis.

The effective mass m^* and dielectric constant ϵ vary across the interface between the semiconductors. For the GaAs-$Al_xGa_{1-x}As$ ($x \leq 0.4$) superlattice, the differences between the values of m^* and ϵ in the well material and the corresponding values in the barrier material are very small. Because the electron is largely confined to the well, it should be a reasonably good approximation to use the values of m^* and ϵ in the well.

The wave functions associated with Hamiltonian (1) are a solution of the Schrödinger equation

$$H\psi(\vec{r})=E\psi(\vec{r}) . \tag{3}$$

Equation (3) probably cannot be solved exactly, because the transverse and longitudinal variables (ρ,z) do not separate. We use the variational method to obtain an approximate solution to the problem, taking the electron wave function as the product of two factors

$$\psi(\vec{r})=f(z)g(\rho,z) . \tag{4}$$

The function

$$f(z)=\begin{cases} A\cos(\alpha z), & |z|<\dfrac{L}{2} \\ Be^{-\beta|z|}, & |z|>\dfrac{L}{2} \end{cases} \tag{5}$$

is the ground-state wave function of the electron in the one-dimensional square well potential in the absence of the impurity.[6] The parameters α and β are defined by the following equations:

$$\alpha=\frac{(2m^*E_0)^{1/2}}{\hbar}, \quad \beta=\frac{[2m^*(V_0-E_0)]^{1/2}}{\hbar} , \tag{6}$$

where E_0 is the electron energy in this state. The boundary conditions that f and df/dz be continuous at $z=\pm L/2$ require that $E_0(V_0,L)$ and the coefficients A and B satisfy the equations

$$\left[\frac{V_0-E_0}{E_0}\right]^{1/2}=\tan\left[\frac{(2m^*E_0)^{1/2}}{\hbar}\frac{L}{2}\right] \tag{7}$$

and

$$B/A=\cos\left[\alpha\frac{L}{2}\right]e^{\beta L/2} . \tag{8}$$

We make the assumption that the function $g(\rho,z)$ can be expressed as a simple one-parameter exponential

$$g(\rho,z)=\exp\left[-\frac{1}{\lambda}[\rho^2+(z-z_i)^2]^{1/2}\right] . \tag{9}$$

Here λ is the single variational parameter which determines the extent of $g(\rho,z)$ around the impurity. The coefficient A is determined by the normalization condition $\langle\psi|\psi\rangle=1$. This condition gives the complicated relation

$$\begin{aligned} A^2=\frac{2}{\pi\lambda^3}\Bigg\{ & 1-\cosh\left[\frac{2z_i}{\lambda}\right]\exp\left[-\frac{L}{\lambda}\right]+\frac{1}{(1+\alpha^2\lambda^2)^2}\cos(2\alpha z_i) \\ & +\left[\left[\frac{1}{(1+\alpha^2\lambda^2)^2}+\frac{L}{2\lambda}\frac{1}{1+\alpha^2\lambda^2}\right][\alpha\lambda\sin(\alpha L)-\cos(\alpha L)]+\frac{\alpha\lambda}{2(1+\alpha^2\lambda^2)}\sin(\alpha L)-\frac{L}{2\lambda}\right] \\ & \times\cosh\left[\frac{2z_i}{\lambda}\right]\exp\left[-\frac{L}{\lambda}\right]+\left[\frac{1}{1+\alpha^2\lambda^2}[\cos(\alpha L)-\lambda L\sin(\alpha L)]+1\right]\frac{z_i}{\lambda}\sinh\left[\frac{2z_i}{\lambda}\right]\exp\left[-\frac{L}{\lambda}\right] \\ & +\left[\frac{B}{A}\right]^2\frac{1}{1+\lambda\beta}\left[\left[1+\frac{L}{\lambda}+\frac{1}{1+\lambda\beta}\right]\cosh\left[\frac{2z_i}{\lambda}\right]-\frac{2z_i}{\lambda}\sinh\left[\frac{2z_i}{\lambda}\right]\right]\exp\left[-\left[\frac{1}{\lambda}+\beta\right]L\right]\Bigg\}^{-1} . \end{aligned} \tag{10}$$

The ground-state energy E of a hydrogenic donor in the quantum well is $E=\langle\psi|H|\psi\rangle$, and the binding energy U is equal to E_0-E, where E_0 is the solution of (7). With the trial wave function (4), U can be obtained in a closed form

$$\begin{aligned} U=A^2\frac{\pi\lambda^2e^2}{2\epsilon}\Bigg\{ & 1+\frac{\cos(2\alpha z_i)}{1+\alpha^2\lambda^2}-\left[1+\frac{1}{1+\alpha^2\lambda^2}[\cos(\alpha L)-\alpha\lambda\sin(\alpha L)]\right]\cosh\left[\frac{2z_i}{\lambda}\right]\exp\left[-\frac{L}{\lambda}\right] \\ & +\left[\frac{B}{A}\right]^2\frac{2}{1+\lambda\beta}\cosh\left[\frac{2z_i}{\lambda}\right]\exp\left[-\left[\frac{1}{\lambda}+\beta\right]L\right]\Bigg\}-\frac{\hbar^2}{2m^*}\frac{1}{\lambda^2} . \end{aligned} \tag{11}$$

Maximizing U (i.e., minimizing E) with respect to λ, we obtain the binding energy $U(V_0,L,z_i)$ as a function of the barrier potential V_0, the well width L, and the impurity position z_i along the superlattice axis.

With $L=\infty$ and $z_i=0$, the wave function (4) becomes the ground state of three-dimensional hydrogen impurity (bulk donor) with $\lambda=a^*$ and $U=R^*$, where a^* is the effective Bohr radius and R^* is the effective Rydberg, namely

$$a^*=\epsilon\hbar^2/m^*e^2\,, \tag{12}$$

$$R^*=e^2/2\epsilon a^*\,. \tag{13}$$

For the limiting case, $V_0=\infty$, we have $\alpha=\pi/L$ and $\beta=\infty$; our Eqs. (10) and (11) reduce to those of Bastard.[2] E_0 decreases as L is increased. When $L\gg a^*$, then $E_0\ll V_0$ and Eq. (7) reduces to that of Greene.[4]

III. RESULTS AND DISCUSSIONS

The GaAs-$Al_xGa_{1-x}As$ structure is one of the most extensively studied superlattices. The band-gap difference ΔE_g between GaAs and $Al_xGa_{1-x}As$ is a function[7] of Al concentration x, which is reasonably well approximated by the relation

$$\Delta E_g=(1.155x+0.37x^2)\,, \tag{14}$$

in units of eV.

For Al concentration less than about 40 at. % ($x=0.4$), $Al_xGa_{1-x}As$ has a direct band gap at the Γ point. The conduction-band offset is about 85% of the band-gap difference between the two semiconductors; the valence-band offset is about 15%.[8] With GaAs as the quantum-well material, the effective mass of the electron in the conduction band and the dielectric constant are $m^*=0.067m_0$ and $\epsilon=13.1$, respectively.[8] Then for the donor in the GaAs well, the effective Bohr radius and the Rydberg value are $a^*=103.4$ Å and $R^*=5.29$ meV, respectively.

We first study the case in which the impurity is at the center of the quantum well ($z_i=0$). Figure 1 shows the variation of reduced binding energy $U(V_0,L,0)/R^*$ with the reduced well width (L/a^*) for several different barrier heights, namely $V_0=10R^*$, $30R^*$, and $50R^*$. For GaAs-$Al_xGa_{1-x}As$ structure, these barriers correspond to $V_0=52.9$, 158.7, and 264.5 meV, respectively. For a given value of V_0, the binding energy U increases as L is reduced until it reaches a maximum, whose value depends on the V_0. Figure 2 shows the variation of the reduced variational parameter λ/a^* with L/a^* for different values of V_0. This curve has a minimum at small but finite values of L/a^*. Comparing Fig. 1 with Fig. 2 it is quite clear why a maximum of binding energy occurs for finite potential barrier. As the well size L is reduced, λ decreases, and the electron wave function is compressed nearer to the donor. The stronger Coulomb attraction leads to stronger binding of the electron to the donor ion. When L/a^* becomes smaller than a certain value, which varies with barrier height V_0, λ increases, and more and more wave function leaks out of the well, so U decreases. The minimum of λ/a^* corresponds to the maximum confinement of the wave function and therefore to the maximum of the binding energy. For instance, for $V_0=30R^*$, when $L=0.035a^*$, λ and U reach minimum $\lambda_{\min}=0.79a^*$ and maximum $U_{\max}=2.27R^*$, respectively. Figures 1 and 2 also present the effect of the barrier height. Greater V_0 results in the smaller λ and therefore in greater U. With the increasing of V_0, the well size L for which the maximum of U occurs decreases. When V_0 tends to infinite, this well size tends to zero. Because the electron around a donor in the center of the quantum well is far away from the barrier, for very large values of L, the effect of V_0 is greatly reduced; the curves for different values of V_0 cannot be distinguished. λ and U tend to a^* and R^*, respectively, corresponding to the values for a bulk donor. In Fig. 3 we display the dependence of $U(V_0,L,0)$ upon V_0 for a given L ($L=a^*$). U/R^* varies linearly with $(V_0/R^*)^{-1/2}$ in agreement with the result of Greene.[4] We extrapolate U to $V_0\to\infty$ and find it to be about $2.25R^*$, agreeing with Bastard's value for infinite barrier.[2]

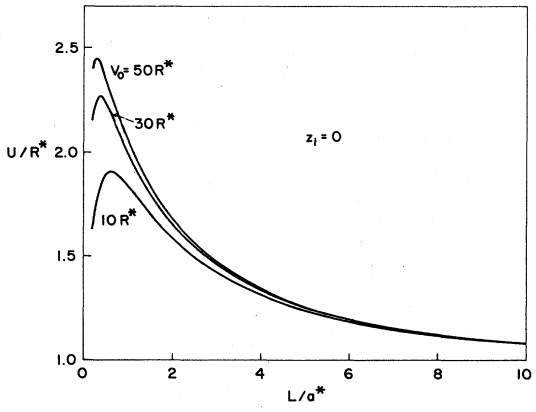

FIG. 1. The variation of the reduced binding energy U/R^* of the impurity state as a function of the reduced well width L/a^* for several values of the barrier height V_0. The impurity is at the center of the well.

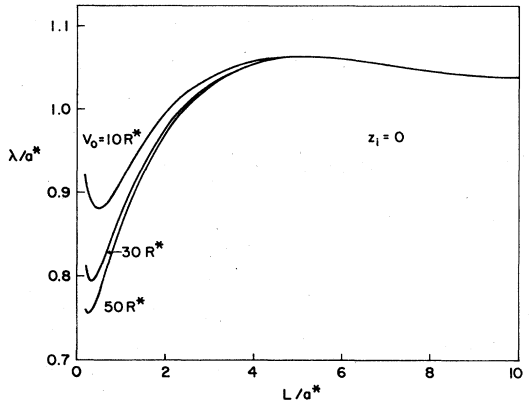

FIG. 2. The variation of the reduced variational parameter λ/a^* as a function of the reduced well width L/a^* for several values of V_0. The impurity is at the center of the well.

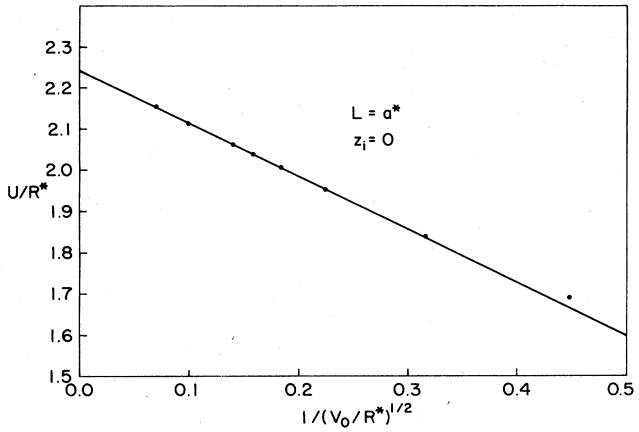

FIG. 3. The variation of the reduced binding energy U/R^* of the impurity state as a function of the inverse of the square root of the reduced barrier potential V_0/R^* for a well width $L=a^*$. The impurity is at the center of the well.

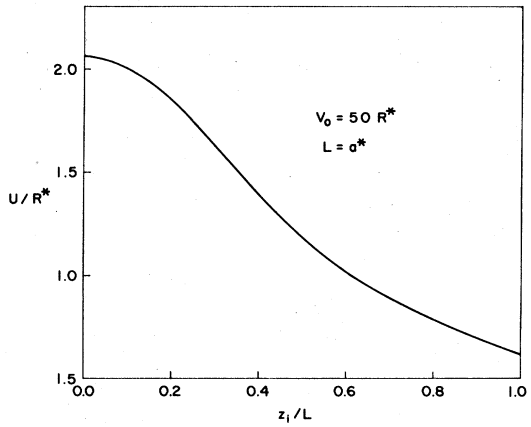

FIG. 5. The variation of the reduced binding energy U/R^* of the impurity state as a function of the impurity position along the z axis ($0 \leq z_i/L \leq 1$) for a potential barrier $V_0=50R^*$ for a well width $L=a^*$.

We have also calculated the binding energy $U(V_0,L,z_i)$ as a function of the position z_i of the impurity along the z axis for $L=a^*$ for several different values of V_0. As shown in Fig. 4, U/R^* has a maximum at $z_i=0$, and decreases as the impurity moves from the center to the edge of the well. This is due to the repulsive barrier potential which tends to push the electronic charge distributions away from the donor, thereby leading to a reduced Coulomb attraction. The larger the barrier height V_0 is, the more rapid the variation of the binding energy U with impurity position z_i. If the impurities are randomly distributed within the quantum well the confinement effect results in a spreading of the donor levels which depends upon the donor position. Figure 5 shows the variation of U/R^* with z_i/L in the range where donor position varies from the center to a position outside of the well ($z_i/L=0\rightarrow 1$) for $V_0=50R^*$ for $L=a^*$. For large values of V_0 the situation for ($z_i/L>0.5$) corresponds to that of a donor in the barrier material binding an electron which is mainly in the quantum well, a problem of some importance for modulation-doped materials.

Miller *et al.*[5] have used extrinsic photoluminescence spectroscopy to estimate the variation of the binding ener-

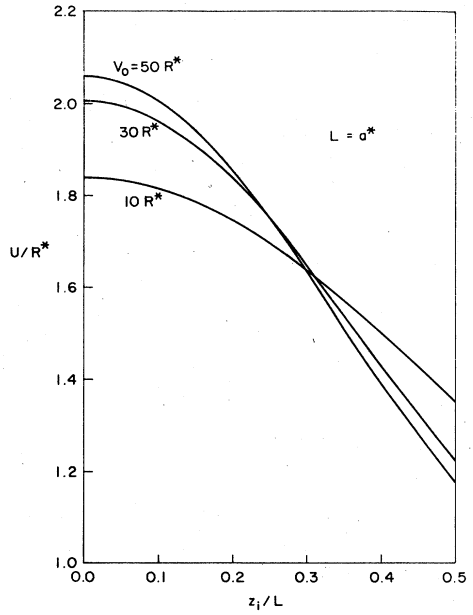

FIG. 4. The variation of the reduced binding energy U/R^* of the impurity state as a function of the impurity position along the z axis ($0 \leq z_i/L \leq 0.5$) for several different values of V_0 and a well width $L=a^*$.

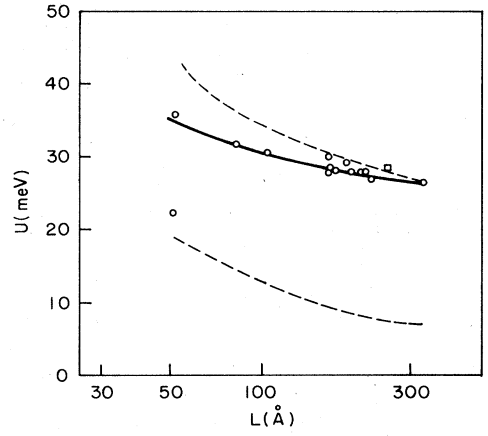

FIG. 6. The variation of the binding energy of acceptors with the well width for GaAs-$Al_xGa_{1-x}As$ superlattices. The experimental values are measured by Miller *et al.* The lowest single circle corresponds to the binding energy determined from a second shoulder of photoluminescent spectrum. The upper and lower dashed curves represent the theoretical prediction of Bastard for the binding energy of carbon acceptors in the center of the well and at the interface, respectively. The solid curve is what we calculate theoretically.

gy of acceptors, presumably carbon, with the well size for GaAs-$Al_xGa_{1-x}As$ superlattices. The Al concentration in their samples is about 30%. They find that U increases as L is reduced from 300 to 50 Å. The valence band of GaAs is complicated, so the hole effective mass must be expressed with a tensor. However, we can use a scalar m^* to approximate it. From the experimental value of binding energy of a carbon acceptor in bulk GaAs

$$U=R^*=m^*e^4/2\epsilon^2\hbar^2=26.0\ ,$$

in units of meV, and $\epsilon=13.1$, we obtain the hole effective mass $m^*=0.33m_0$ and $a^*=\epsilon\hbar^2/m^*e^2=21.1$ Å. This value of m^* is very near the heavy-hole effective mass $m_H^*=0.35m_0$.[9] For $x=0.3$, the barrier height is

$$V_0=0.15\Delta E_g=56.97\ \text{meV}=2.19R^*\ .$$

We have calculated U as a function of L for $V_0=2.19R^*$ for $z_i=0$. As shown in Fig. 6, the curve we calculate agrees very well with the data determined experimentally over the range of L used in these measurements. The theoretical results of binding energy calculated with infinite potential barrier by Bastard[2] are considerably larger than those measured.[5] Since $L/a^*>2$, the effect on binding energy for impurities at the interface is small.[2]

IV. CONCLUSION

The binding energy $U(V_0,L,z_i)$ of the impurity states in the quantum well is a function of the barrier height V_0, the well width L and the impurity position z_i. For a given value of V_0, as L is reduced, U increases and the variational parameter λ decreases until they reach a maximum and a minimum, respectively. The maximum of U corresponds to the minimum of λ. Larger values of V_0 result in the smaller λ and, therefore, in the greater U. With the increasing of V_0, the well size L for which the maximum of U occurs decreases. When $V_0=\infty$, this well size tends to zero so that no maximum occurs. For a given L, U varies linearly with $(V_0)^{-1/2}$. U has a maximum at $z_i=0$ and decreases as the impurity moves from the center to the edge of the well. The larger V_0 is, the faster the variation of U with z_i. The results we calculate agree very well with the experimental data of Miller *et al.*[5]

After this paper was submitted for publication, the recent work of Tanaka *et al.*[10] was brought to our attention. Like us, these authors have used a very simple variational function to study the donor binding energy as a function of donor position relative to the center of a quantum well of finite depth. Our investigation of the dependence of the donor energy on the depth and width of the quantum well shows that the simple variational wave function gives results which are in good agreement with the more elaborate functions used by other authors.[3,4] Our result for the binding energy versus donor position for $V_0=50R^*=0.265$ eV (in Figs. 4 and 5) is in good agreement with the results of Tanaka *et al.*[10] for $V_0=0.318$ eV (their Fig. 3). In addition, the curves in their Fig. 10 corresponding to type-I and type-IV barriers (the symmetric barriers) are qualitatively similar to the set of curves for binding energy versus position in the quantum well shown in our Fig. 4. However, we have demonstrated explicitly that the simple variational wave function gives results for the binding energy which are well fit by $U=A+BV_0^{-1/2}$ (Fig. 3) for the case in which $L\simeq a^*$. We have also shown that the experimental results of Miller *et al.* can be well described by our simple model if the parameters appropriate to acceptors in $GaAs/Ga_{0.7}Al_{0.3}As$ are used.

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[1]L. Esaki and R. Tsu, IBM J. Res. Dev. **14**, 61 (1970).
[2]G. Bastard, Phys. Rev. B **24**, 4714 (1981).
[3]C. Mailhiot, Yia-Chung Chang, and T. C. McGill, Phys. Rev. B **26**, 4449 (1982).
[4]Ronald L. Greene and K. K. Bajaj, Solid State Commun. **45**, 825 (1983).
[5]R. C. Miller, A. C. Gossard, W. T. Tsang, and O. Munteanu, Phys. Rev. B **25**, 3871 (1981).
[6]Leonard I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968), Chap. 2.
[7]H. J. Lee, L. Y. Juravel, J. C. Wolley, and A. J. Springthorpe, Phys. Rev. B **21**, 659 (1980).
[8]H. C. Casey and M. B. Panish, *Heterostructure Lasers* (Academic, New York, 1978), Pt. A, Chap. 4.
[9]P. Lawaetz, Phys. Rev. B **4**, 3460 (1971).
[10]K. Tanaka, M. Nagaoka, and T. Yamabe, Phys. Rev. B **28**, 7068 (1983).