PHYSICAL REVIEW B VOLUME 52, NUMBER 4 15 JULY 1995-II

Strong-confinement approach for impurities in quantum dots

J.M. Ferreyra and C.R. Proetto
Comisión Nacional de Energía Atómica, Centro Atómico Bariloche and Instituto Balseiro, 8400 San Carlos de Bariloche, Río Negro, Argentina

(Received 20 March 1995; revised manuscript received 4 May 1995)

The problem of a donor impurity in a confined geometry with dielectric mismatch at the boundaries has been studied. It is shown that in the limit of dot size smaller than the effective Bohr radius, the problem admits an extremely simple perturbative solution for arbitrary impurity locations. The first-order energy corrections ("binding" energy) are obtained analytically for the s- and p-like states, and with a minimal numerical effort for the $d,f,g,\ldots$ states. Important charge-induced polarization effects are found for the particular case of a silicon dot embedded in an amorphous silicon dioxide (a-SiO_2) matrix.

One of the main motivations behind the widespread interest in the physics of semiconductor heterostructures lies in the feasibility of producing quantum confined systems, where carriers are restricted to move in two, one, or zero dimensions (quantum wells, wires, and dots, respectively).[1] Recently, much attention has been given to the electronic structure of quantum-dot structures owing to their potential application in electronic devices. For instance, confined donors,[2–5] acceptors,[6] and excitons[7,8] in quantum dots have been studied.

A common theme in all these studies is the problem of a hydrogen atom in a confined geometry. While this problem admits in principle an exact solution,[2] this is rather cumbersome and restricted to on-center impurities in spherical quantum dots. Generalizations of these results for the interesting case of off-center impurities leads to variational calculations.[9] The aim of this work is to point out that in the strong-confinement limit (dot dimension smaller than the effective Bohr radius) an extremely simple method can be applied to these problems.[10] The utility of the technique is illustrated for the simplest case: a donor impurity located anywhere in an infinite barrier spherical quantum dot of dielectric constant ε_1 immersed in a matrix of dielectric constant ε_2.

Within the envelope function approach to the effective mass approximation, the Hamiltonian for this problem can be written as[5]

$$H=-\frac{1}{\lambda^2}\nabla^2+\frac{1}{\lambda}V_s(r)-\frac{1}{\lambda}V_c(\mathbf{r},\mathbf{r}_i), \tag{1}$$

where $\mathbf{r}$ ($\mathbf{r}_i$) is the electron (impurity) coordinate, ∇^2 is a three-dimensional (3D) Laplacian, V_c is the effective Coulomb interaction between electron and donor (including the induced polarization charges)

$$V_c(\mathbf{r},\mathbf{r}_i)=2\sum_{\ell=0}^{\infty}P_\ell(\cos\xi)\left\{\eta(1-r_i)\left[\frac{r_<^\ell}{r_>^{\ell+1}}+\frac{(\ell+1)(\varepsilon_1-\varepsilon_2)}{\varepsilon_2+\ell(\varepsilon_1+\varepsilon_2)}r_<^\ell r_>^\ell\right]+\eta(r_i-1)\frac{\varepsilon_1(2\ell+1)}{\varepsilon_2+\ell(\varepsilon_1+\varepsilon_2)}\frac{r^\ell}{r_i^{\ell+1}}\right\}, \tag{2}$$

and V_s corresponds to the self-polarization interaction between the electron and the bound surface charge density that it induces at the spherical boundary,

$$V_s(r)=\sum_{\ell=0}^{\infty}\frac{(\ell+1)(\varepsilon_1-\varepsilon_2)}{\varepsilon_2+\ell(\varepsilon_1+\varepsilon_2)}r^{2\ell}. \tag{3}$$

In writing Eqs. (1)–(3), we use the effective Rydberg $\mathrm{Ry}^*=m^*e^4/2\hbar^2\varepsilon_1^2$ as the unit of energy (with m^* the effective mass of the semiconductor well acting material), the dot radius R as the unit of length, and $\lambda=R/a_0^*$ ($a_0^*=\varepsilon_1\hbar^2/m^*e^2$ being the effective Bohr radius). Besides, in Eq. (2) $P_\ell(\cos\xi)$ are the Legendre polynomials of order ℓ, ξ the angle between electron and donor (measured from an origin at the dot center), $r_<$ ($r_>$) the smaller (greater) between r and r_i, and $\eta(x)$ is the step function. It is easy to check that when $\varepsilon_1=\varepsilon_2$, V_c reduces to the usual Coulomb interaction $2/|\mathbf{r}-\mathbf{r}_i|$, while $V_s=0$.

The important point to note from (1) is that the kinetic energy scales as $1/\lambda^2$, while Coulomb and self-polarization contributions scale as $1/\lambda$. Thus the former dominates at small λ. In this strong-confinement limit, V_c and V_s can be treated by standard perturbation theory. The same technique has been applied in Refs. 11–13 to study the stability of biexcitons in semiconductor quantum dots.

The zero-order wave functions are just the one-particle kinetic energy eigenfunctions in the sphere $-\nabla^2\psi(\mathbf{r})=E\psi(\mathbf{r})$ with the boundary condition $\psi(r=1)=0$. The solutions which are finite at the origin are $\psi_{n\ell m}(\mathbf{r})=N_{n\ell}j_\ell(kr)Y_{\ell m}(\theta,\phi)$ with energy $E=k^2$; $N_{n\ell}$ is a normalization constant, $j_\ell(kr)$ are the spherical Bessel functions, and $Y_{\ell m}$ the spherical harmonics. The wave function must vanish at the boundary $j_\ell(k)=0$, giving the eigenvalue spectrum $k_{n\ell}=x_{n\ell}$, where $x_{n\ell}$ is the nth zero of the ℓth spherical Bessel function.[14] The normalization integral can be evaluated explicitly to give $N_{n\ell}^2=2/j_{\ell+1}^2(x_{n\ell})$.

Application of standard perturbation theory up to second order in λ yields the following expansion for the total energy:

$$E_\alpha=\frac{1}{\lambda^2}E_\alpha^{(0)}+\frac{1}{\lambda}E_{s\alpha}^{(1)}-\frac{1}{\lambda}E_{c\alpha}^{(1)}-E_\alpha^{(2)}+\cdots, \tag{4}$$

with $E_\alpha^{(0)}=x_\alpha^2$, $E_{i\alpha}^{(1)}=\langle\alpha|V_i|\alpha\rangle$ $(i=s,c)$, and $E_\alpha^{(2)}=\Sigma'_\beta[(|\langle\alpha|V_s+V_c|\beta\rangle|^2)/(E_\beta^{(0)}-E_\alpha^{(0)})]$; α (or β) stands for a given set of one-particle quantum numbers (n,ℓ,m). Since the first two terms on the right-hand side of Eq. (4) are constants independent of the presence of impurities, we will concentrate our attention on the impurity dependent remaining terms. The difference $E_\alpha-E_\alpha^{(0)}/\lambda^2-E_{s\alpha}^{(1)}/\lambda$ is also known as the "binding energy" of the hydrogenlike confined system, by analogy with higher dimensionality cases. This terminology, however, must be used with caution, as for the particular case of quantum dots no truly unbound configuration exists, because the electrons are always constrained to remain inside the dot.

We start our analysis with the simplest case $\ell=m=0$ (s states). Explicit calculation of matrix element $\langle n00|V_c|n00\rangle$ yields the following analytic expression for the first-order perturbed energy:

$$E_{c,n00}^{(1)}(r_i)=2\left[\frac{\varepsilon_1}{\varepsilon_2}-\frac{\sin(2\pi n r_i)}{2\pi n r_i}+\mathrm{Cin}(2n\pi)-\mathrm{Cin}(2n\pi r_i)\right] \tag{5a}$$

if $r_i\leq 1$, and

$$E_{c,n00}^{(1)}(r_i)=\frac{2}{r_i}\frac{\varepsilon_1}{\varepsilon_2} \tag{5b}$$

if $r_i\geq 1$, with Cin being the cosine integral function.[14] Only the term $\ell=0$ of the sum in Eq. (2) gives a contribution for these s-like states.

A graphical representation of Eq. (5) is given in Fig. 1, the lower set corresponding to the case $\varepsilon_1=\varepsilon_2$ of no dielectric mismatch between dot and matrix (this could apply to GaAs/Al_xGa_{1-x}As quantum dots), the upper set corresponding to a situation with a large dielectric mismatch $\varepsilon_1=12$, $\varepsilon_2=4$ (this could apply to Si/a-SiO_2 quantum dots[15]). As is evident from Eq. (5), the first-order energy correction is an increasing function of the dielectric mismatch ($\varepsilon_1>\varepsilon_2$), resulting in an enhancement of about 100% for the particular case displayed in Fig. 1. Physically, this arises from the fact that the induced charge of the donor is positive if $\varepsilon_1>\varepsilon_2$ [see Eq. (2)]; consequently, as the electron interacts both with the donor and its induced charge, this results in a large increment of the "binding" energy. Also, it is interesting to note that as $E_{c,n00}^{(1)}(0)=2[(\varepsilon_1-\varepsilon_2)/\varepsilon_2+\mathrm{Cin}(2\pi n)]$, with $\mathrm{Cin}(x)$ an increasing function of its argument, the first-order correction increases with n, for the case of the on-center impurity. This is due to the fact that the zero-order electronic density, which is proportional to $|j_0(k_{n0}r)|^2$, has a maximum at $r=0$; this becomes higher and narrower when n increases. The first feature explains the large binding with increasing n, while the second is associated with the reverse situation found when $r_i\gtrsim 0.4$. For $r_i\geq 1$, the result $E_{c,n00}^{(1)}(r_i)=2\varepsilon_1/r_i\varepsilon_2$, independent of n, is understood as a consequence of an electrostatic Coulomb interaction between two nonoverlapping charge distributions: the point impurity and the spherically symmetric electronic density.

In order to test the accuracy of our strong-confinement approach, we have performed a second-order calculation for the ground $\alpha=100$ state ($\varepsilon_1=\varepsilon_2$); the correction to the first-order result is given by the dashed line in Fig. 1. The correction is seen to have a maximum when $r_i\approx 0$, but even for this case and in the worst situation $\lambda=1$, it amounts to just a few percent of the first-order contribution. The same conclusion applies qualitatively to all the remaining excited states studied in this work.

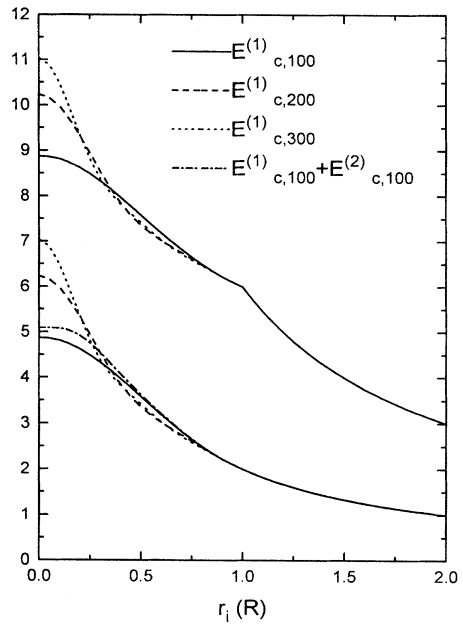

FIG. 1. First-order Coulomb energy corrections (in units of Ry*) versus impurity location for the three lowest s-like states; lower (upper) set, $\varepsilon_1=\varepsilon_2$ ($\varepsilon_1=12,\varepsilon_2=4$). The slope discontinuity at $r_i=1$ for the upper set is due to the boundary dielectric discontinuity. Second-order corrections are also included for the ground $n=1$ state and $\varepsilon_1=\varepsilon_2$.

We proceed now to discuss the next case: $\ell=1$ or p-like states. The main difference with the previous calculations for the $\ell=0$ states is that the zero-order energies, being independent of m, are the same for the $\ell=1,m=0,\pm 1$ states. According to degenerate perturbation theory, the first-order correction to the energy is given by the diagonalization of the 3×3 matrix of the perturbation (2) in the zero-order basis of the $\ell=1,m=0,\pm 1$ states. The explicit expression for the matrix elements is as follows:

$$V_{-1,-1}=V_{1,1}=F(r_i)-\frac{1}{10}(3\cos^2\theta_i-1)G(r_i), \tag{6a}$$

$$V_{0,0}=F(r_i)+\frac{1}{5}(3\cos^2\theta_i-1)G(r_i), \tag{6b}$$

$$V_{-1,0}=-V_{0,1}=\frac{3}{5\sqrt{2}}\sin\theta_i\cos\theta_i e^{i\phi_i}G(r_i), \tag{6c}$$

$$V_{-1,1}=V_{1,-1}^*=-\frac{3}{10}\sin^2\theta_i e^{2i\phi_i}G(r_i), \tag{6d}$$

with $V_{m,m'} \equiv \langle \psi_{n1m} | V_c | \psi_{n1m'} \rangle$, $F(r_i) = (\varepsilon_1 - \varepsilon_2)/\varepsilon_2 + \alpha(r_i)/r_i + \beta(r_i)$, $G(r_i) = 3r_i^2 \gamma(1)(\varepsilon_1 - \varepsilon_2)/(2\varepsilon_1 + 3\varepsilon_2) + \gamma(r_i)/r_i^3 + r_i^2 \delta(r_i)$, and

$$\alpha(r_i) = \frac{2r_i(1+k_{n1}^2)}{k_{n1}^2}\left[1 + \frac{\sin(2\bar{r}_i)}{2\bar{r}_i} - \frac{2\sin^2(\bar{r}_i)}{\bar{r}_i^2}\right], \quad (7a)$$

$$\beta(r_i) = \frac{2(1+k_{n1}^2)}{k_{n1}^2}\left[1 + \mathrm{Cin}(2k_{n1}) - \mathrm{Cin}(2\bar{r}_i) - \sin^2(k_{n1}) - \frac{\sin(2\bar{r}_i)}{\bar{r}_i} + \frac{\sin^2(\bar{r}_i)}{\bar{r}_i^2}\right], \quad (7b)$$

$$\gamma(r_i) = \frac{2(1+k_{n1}^2)}{k_{n1}^5}\left[\bar{r}_i + \frac{\bar{r}_i^3}{3} + \left(\frac{\bar{r}_i^2}{2} - \frac{5}{4}\right)\sin(2\bar{r}_i) + \frac{3\bar{r}_i}{2}\cos(2\bar{r}_i)\right], \quad (7c)$$

$$\delta(r_i) = (1+k_{n1}^2)\left[\frac{1}{\bar{r}_i^4}\sin^2(\bar{r}_i) - \frac{1}{k_{n1}^2}\sin^2(k_{n1}) + \frac{1}{\bar{r}_i^2} - \frac{\sin(2\bar{r}_i)}{\bar{r}_i^3}\right], \quad (7d)$$

where $\bar{r}_i = r_i k_{n1}$. These expressions are valid if $0 \leq r_i \leq 1$; taking the appropriate limit in the equations above, it is easy to see that only the contribution proportional to $\beta(r_i)$ remains finite for the $r_i = 0$ on-center impurity case. When $r_i \geq 1$, $F(r_i) = \varepsilon_1/\varepsilon_2 r_i$, $G(r_i) = 5\varepsilon_2\gamma(1)/(2\varepsilon_1 + 3\varepsilon_2) r_i^3$. For these p-like states, only terms with $\ell = 0$ and 2 from Eq. (2) give a nonzero contribution.

The diagonalization of matrix (6) yields a set of three eigenvalues (for each n), which as a result of the inherent spherical symmetry of the system are independent of the angular impurity coordinates θ_i and ϕ_i. Given this fact, we have at our disposal the choice of the impurity angular coordinates: inspection of (6) reveals the obvious choice $\theta_i = 0$ (corresponding to the impurity moving along the z axis), as this choice renders matrix (6) automatically diagonal. Accordingly, the eigenvalues are given directly by the diagonal elements (6a) and (6b) with $\theta_i = 0$,

$$E^{(1)}_{c,n11} = E^{(1)}_{c,n1-1} = F(r_i) - G(r_i)/5, \quad (8a)$$

$$E^{(1)}_{c,n10} = F(r_i) + 2G(r_i)/5. \quad (8b)$$

A plot of these solutions is given in Fig. 2 for the two lowest values of the principal quantum number n; again the lower (upper) set corresponding to the $\varepsilon_1 = \varepsilon_2$ ($\varepsilon_1 = 12, \varepsilon_2 = 4$) case. Clearly, induced polarization effects are as important as for the previous case; besides, its contribution is impurity position dependent, which explains why the upper set is not merely the lower set plus a rigid shift (as is the case in Fig. 1). Similar to the results for the $\ell = 0$ s-like states, we found that the first-order correction to the energy of the $\ell = 1$ p-like states increases with n, for on-center impurities. However, the $\ell = 1, m = 0$ state shows a nonmonotonic dependence on r_i, presenting a maximum

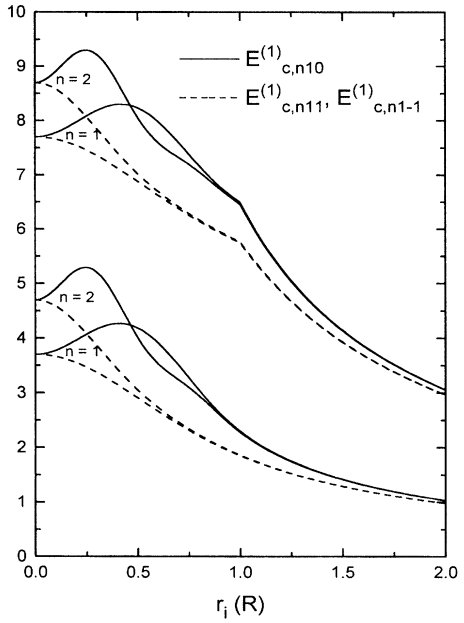

FIG. 2. First-order Coulomb energy corrections (in units of Ry*) as a function of impurity location for the two lowest p-like states; lower (upper) set, $\varepsilon_1 = \varepsilon_2$ ($\varepsilon_1 = 12, \varepsilon_2 = 4$). The degeneracy of $m = \pm 1$ states is not lifted when $r_i \neq 0$.

binding energy at some finite value of r_i inside the quantum dot. Both features are easy to understand by recalling that the zero-order electronic density, which is proportional to $|j_1(k_{n1}r)|^2$ in this case, is zero at the origin and shows a maximum that approaches the origin gradually with increasing n. Therefore, the donor ion at the origin influences the states with larger n more strongly. The nonmonotonic behavior of $E^{(1)}_{c,n10}$ is explained by the angular dependence of the zero-order electronic density, which gives rise to an accumulation of negative charge along the z axis, the same axis where the impurity is moving radially. On the contrary, p-like states with $m = \pm 1$ present an accumulation of negative charge in the x-y plane, and consequently $E^{(1)}_{c,n1\pm1}$ always decreases when the impurity goes away along z. It is interesting to note that for $r_i \geq 1$, Eqs. (7a) and (7b) correspond exactly to the electrostatic interaction energy between a point charge and a charge distribution with a net charge and quadrupolar moments. The first interaction contributes with the term $F(r_i)$ and decays as $1/r_i$, while the second gives rise to the term $G(r_i)$, which decays as $1/r_i^3$.

It should be emphasized that while the results presented for p-like states correspond to the particular case $\theta_i = \phi_i = 0$ (impurity moving along the z axis), they are actually valid for arbitrary values of the angular impurity coordinates.

To illustrate the versatility of our approach, we present in Fig. 3 the first-order energy corrections for the ground and first nine excited states of our quantum-dot hydrogen atom; for simplicity, we present only results corresponding to no dielectric mismatch ($\varepsilon_1 = \varepsilon_2$). The displayed results are for the impurity moving along the z axis and $m = 0$. Similar to the $\ell = 1$ case, this choice of the impurity position renders

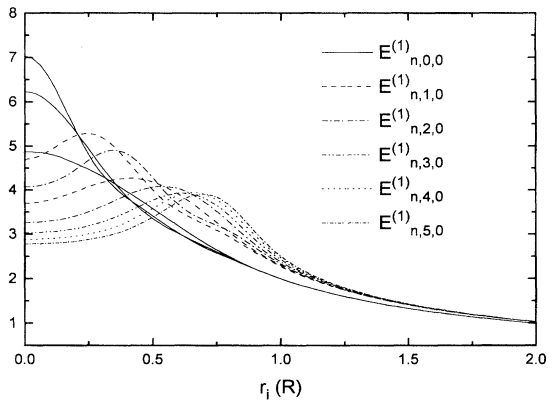

FIG. 3. Behavior of the first-order energy corrections (in units of Ry*) for the ten lowest states in the absence of a dielectric constant mismatch at the boundary. The value of $m=0$ and the principal quantum number n runs from 1 to 3 for s-like states, from 1 to 2 for p- and d-like states, and $n=1$ for the remaining $l=3$, 4, and 5 states.

the $(2\ell+1)\times(2\ell+1)$ Hamiltonian matrix of the angular momentum ℓ states automatically diagonal; as seen previously, no generality is lost with this choice. After this simplification, the only calculation necessary to obtain an output like Fig. 3 is the numerical integration of a few one-dimensional radial integrals (as the angular integrations can be carried out analytically).

Several features should be noted from this figure.

(i) While it is possible to give a defined ordering for the zero-order energy contributions $(E^{(0)}_{c,100}<E^{(0)}_{c,110}<E^{(0)}_{c,120}<E^{(0)}_{c,200}<\cdots)$, the ordering of the first-order corrections is impurity position dependent. For instance, the ordering at $r_i=0$ $(E^{(1)}_{c,300}>E^{(1)}_{c,200}>E^{(1)}_{c,100}>E^{(1)}_{c,210}>\cdots)$ is completely reversed when $r_i\simeq 0.75$.

(ii) All the $m=0$ states with $\ell\neq 0$ have a maximum contribution when $r_i\neq 0$; the reason for this behavior is the same as that explained above for the $\ell=1$ states.

(iii) While the electronic charge distributions associated with the $\ell=0,1,2,3,\ldots$ angular momentum quantum numbers are quite different from a multipole expansion analysis, already for $r_i\simeq 2$ the only sizable interaction which remains is between the impurity and the point charge electronic contribution.

(iv) Finally, a comparison between our results and Fig. 3(b) of Ref. 9(b) reveals a good qualitative agreement between the two approaches. This is not surprising, as the latter results were obtained for a quantum dot with $\lambda=1$ and barrier height $V_0=80$ Ry*, which is inside the regime of validity of our perturbative approach.

In summary, in the present work we have demonstrated that for quantum dots of typical size smaller than the effective Bohr radius, an extremely simple perturbative approach can be used to study the problem of a confined donor impurity located anywhere. We believe this to be the most natural approach for small quantum-dot structures. The technique is so simple that it is possible to obtain analytic expressions for the s-like and p-like states; analogous results for higher excited states only requires a minimal numerical effort. It should be pointed out that since the results presented in this work are absolutely rigorous in the limit of small dot sizes, they can be used as a test in the study of more complicated problems. A number of possible extensions seems feasible owing to the simplicity of the strong-confinement approach: the equivalent but more intricate problem of acceptor impurities in quantum dots, the shape dependence of the present results, and the possible generalization to the more realistic case of parabolic confinement.

One of us (J.M.F.) is indebted to the CONICET of Argentina for financial support. The authors wish to thank V. Grunfeld for a careful reading of the manuscript.

[1] G. Bastard, J.A. Brum, and R. Ferreira, Solid State Phys. **44**, 229 (1991).
[2] J.L. Zhu, Phys. Rev. B **39**, 8780 (1989).
[3] D.S. Chuu, C.M. Hsiao, and W.N. Mei, Phys. Rev. B **46**, 3898 (1992).
[4] K.R. Brownstein, Phys. Rev. Lett. **71**, 1427 (1993).
[5] R. Tsu and D. Babić, Appl. Phys. Lett. **64**, 1806 (1994).
[6] G.T. Einevoll and Y.C. Chang, Phys. Rev. B **40**, 9683 (1989).
[7] Y. Kayanuma and H. Momiji, Phys. Rev. B **41**, 10 261 (1990).
[8] G.T. Einevoll, Phys. Rev. B **45**, 3410 (1992).
[9] (a) J.L. Zhu and X. Chen, J. Phys. Condens. Matter **6**, L123 (1994); (b) Phys Rev. B **50**, 4497 (1994).
[10] L.E. Brus, J. Chem. Phys. **80**, 4403 (1984); IEEE J. Quantum Electron. **22**, 1909 (1986).
[11] L. Bányai, Phys. Rev. B **39**, 8022 (1989).
[12] G.W. Bryant, Phys. Rev. B **41**, 1243 (1990).
[13] Y.Z. Hu, M. Lindberg, and S.W. Koch, Phys. Rev. B **42**, 1713 (1990).
[14] M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1970).
[15] Q.Y. Ye, R. Tsu, and E.H. Nicollian, Phys. Rev. B **44**, 1806 (1991).