D^- centers in spherical quantum dots

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A negatively charged donor center D^- (i.e., a neutral shallow donor D^0 that binds a second electron) in a spherical quantum dot is studied by use of a variational approach. A trial function which includes electron-correlation effects and approaches the Chandrasekhar-type function in the limit of zero barrier height is used. The well-radius and barrier-height dependence of the "binding energy" of the D^- center is obtained. The dimensional characteristics are clearly demonstrated not only for the "binding energy" and its maximum of the D^- center but also for the ratio of D^- to D^0 "binding energy" and the electron-correlation effect.

Recently, shallow donors in various quantum-well structures, such as two-dimensional quantum wells (2DQW's) and quantum-well wires and dots (QWW's and QD's) have been the subject of considerable study. Attention has been mainly focused on the neutral shallow donors D^0. Very recently, D^- centers (i.e., a D^0 center that binds a second electron) have been shown to form readily in selectively doped multiple quantum wells because of the electron transfer from the weakly bound barrier donors to the low-potential quantum wells.[1,2] Though the effort has been directed toward understanding the behavior of D^- centers in bulk semiconductors[3–9] and 2DQW's,[1,2,10] no information seems to be available concerning the properties of D^- ions in QWW's and QD's. The fundamental study of the properties of such systems in low dimensions is important in its own right, as reducing the dimensionality often introduces unexpected physical phenomena.

Our interest in the study of the D^- ion in low dimensions is motivated by the following reasons. With the advances in the epitaxial crystal growth techniques and the intensive work done on the fabrication of QWW's and QD's in a number of laboratories, the optical and electronic properties of these structures have been the subject of both theoretical and experimental investigations. For instance, Bryant[11] and Lee and Spector[12] have studied the D^0 states in QWW's, and Zhu, Xiong, and Gu,[13] and Einevoll and Chang[14] have studied D^0 and acceptor states in QD's, respectively. Asada, Miyamoto, and Suematsu[15] have shown that the linear gain of quantum boxes is much larger than that of bulk crystals at fixed carrier density, and that the laser threshold can be reduced by use of the box structures. Schmitt-Rink, Miller, and Chemla[16] have published a theory of the linear and nonlinear optical properties of semiconductor microcrystallites. Based on the study of the behavior of D^- centers in doped multiple quantum wells, Huant and coworkers[1,2] have shown quite recently that it has become possible to control the D^- concentration in the structures with increased accuracy and pointed out that having a well-controlled D^- population under equilibrium conditions opens the possibility of studying many phenomena related to negatively charged donors in semiconductors. Pang and Louie[10] have predicted that for D^- in a $[(100\ \text{Å}\ \text{GaAs})/(100\ \text{Å}\ \text{Ga}_{0.75}\text{Al}_{0.25}\text{As})]_{150}$ multiple quantum well, there is a sevenfold increase in binding energy over that of the bulk case. Therefore it is interesting to study electronic properties of D^- centers in QWW's and QD's for understanding the dimensionality dependence of the binding energies of D^- ground states and the possibility of some future device applications (D^- population control). In addition, many calculations of the correlation effect in multielectron states in quantum dots have been done. For example, multielectron systems with and without a magnetic field,[17–19] and biexcitons in dots[20–23] have been studied. However, since no work mentioned above treated positive-ion centers in multielectron systems, the study of two electrons in a dot with a positive-ion center is therefore useful for achieving a better understanding of the effect of positive-ion centers on low-dimensional electron correlations.

In this paper, we report a calculation of the ground-state energy and "binding energy" of a D^- ion in a quantum dot, using a variational approach. The effective-mass model is applied to the D^- ion and a trial function is introduced. Then, the well-radius and barrier-height dependence of the binding energy of the D^- ion is obtained. The electron correlation in confinement conditions is also considered.

For definiteness let us consider a D^- ion at the center of a spherical quantum dot of radius R_0. The potential due to the discontinuity of the band edges at the GaAs-$Ga_{1-x}Al_xAs$ interface $r=R_0$ is as follows:

$$V(r)=\begin{cases} V_0 & \text{if } r \geq R_0 \\ 0 & \text{if } r < R_0 \end{cases}, \tag{1}$$

where r is the electron-donor distance. According to the hydrogenic-effective-mass theory, the Hamiltonian for the D^- in a spherical QD is given by

$$H = H(1,W) + H(2,W) + \frac{2}{r_{12}} , \tag{2}$$

with

$$H(i,W) = -\nabla_i^2 - \frac{2W}{r_i} + V(r_i) , \tag{3}$$

where $H(i,W)$ and $2/r_{12}$ are, respectively, the Hamiltonian of a donor in the spherical QD and the interaction between the two electrons. It is written in a dimensionless form so that all energies are measured in units of the effective Rydberg Ry* and all distances are measured in units of effective Bohr radius a^*. W is set equal to 1. In order to show the dimension features of Coulomb interactions in D^- states clearly, we have neglected the differences of the electronic effective masses and the dielectric constants between the quantum dot and the surrounding material in the Hamiltonian. It is reasonable for the case of the strong confinement and small dielectric-constant difference. However, we should point out that if there is significant penetration into the barrier, the effect of the electronic effective masses can be important, and that the effect of the discontinuity of the dielectric constants on the D^- states should be considered for large differences.

For determining the electronic structure and the "binding energy" of the ground state (spin singlet state) in a spherical QD, we use a trial function which includes electron-correlation effect and approaches the Chandrasekhar-type trial function[24] at $V_0=0$. It is as follows:

$$\Psi = A(1+Cr_{12})\{\Psi(\lambda_1,r_1)\Psi(\lambda_2,r_2)+\Psi(\lambda_2,r_1)\Psi(\lambda_1,r_2)\} , \tag{4}$$

where C and λ_1 and λ_2 are variational parameters, and A is the normalization constant. $\Psi(\lambda_i,r_i)$ are the ground-state eigenfunctions of $H(i,\lambda_i)$ which is equal to $H(i,W)$ of Eq. (3) as $W=\lambda_i$. We should point out that $\Psi(\lambda_i,r_i)$ can be exactly obtained with the use of different series forms in different regions of the radial equation.[13] It is interesting to note that $\Psi(\lambda_1,r)$ and $\Psi(\lambda_2,r)$ approach $\exp(-\lambda_1 r)$ and $\exp(-\lambda_2 r)$ within a normalization constant as R_0 approaches infinity. In the limiting case, it is clearly seen that the electrons are in ground-state hydrogenic orbitals; they tend to stay apart, keeping down their repulsive interaction energy, as indicated by the correlation factor $(1+Cr_{12})$, which becomes relatively small as $r_{12}\to 0$. Using the variation method for the limiting case, Chandrasekhar[24] found $\lambda_1=1.075$, $\lambda_2=0.478$, $C=0.312$, and the corresponding binding energy $E_B=0.0518$ Ry* which is very close to the "exact" value of 0.0555 Ry*.[25] However, with the polarization term in r_{12} omitted ($C=0$), the variation method gave $\lambda_1=1.039$, $\lambda_2=0.283$, and $E_B=0.027$ Ry*, which is only about half of the "exact" value. It is the reason why the correlation factor is included in the trial function of Eq. (4). It is also interesting to point out that the dimensional characteristic of the electron-correlation effect can be studied by using the trial function with the correlation factor. Using the trial function, the variational energy $E(D^-)$ is given by

$$E(D^-) = \min_{\lambda_1,\lambda_2,c} \langle \Psi|H|\Psi\rangle , \tag{5}$$

where

$$\langle \Psi|H|\Psi\rangle = \langle \Psi|H(1,\lambda_1)|\Psi\rangle + \langle \Psi|H(2,\lambda_2)|\Psi\rangle + \langle \Psi|[1/r_{12}-(2-2\lambda_1)/r_1-(2-2\lambda_2)/r_2]|\Psi\rangle . \tag{6}$$

The first and second terms are calculated partly analytically and partly numerically. The third term can be calculated numerically. Compared with the binding energy of a D^- center in a three-, two-, or one-dimensional system, the "binding energy" of the D^- ground state in the dot is defined as follows:

$$\begin{aligned} E_B(D^-) &= E(D^0)+E_0-E(D^-) \\ &= 2E_0 - E_B(D^0) - E(D^-) , \end{aligned} \tag{7}$$

where $E(D^0)$ is the lowest level of the Hamiltonian of Eq. (3), i.e., the D^0 ground-state energy in the spherical QD, which can be solved exactly as mentioned above, and E_0 and $E_B(D^0)$ are, respectively, the lowest level of an electron in the spherical QD without the Coulomb potential and the "binding energy" of the neutral donor, which is equal to $E_0-E(D^0)$.

In order to check the calculation method, the ground state of a D^- ion in a spherical QD with $V_0=0$ has been calculated. Calculated results have shown that the best values of λ_1, λ_2, and C are 1.075, 0.478, and 0.312, respectively. With these values the binding energy obtained is 0.0518 Ry*. It is exactly the same as that obtained by Chandrasekhar.[24]

In order to study the well-radius and barrier-height dependence of the "binding energy" of a D^- ion in a spherical QD, a numerical calculation has been performed for the spherical QD of R_0 between 0 and $10a^*$ with different V_0. In Fig. 1, we have plotted the "binding energies" of a D^- center in spherical QD's of $V_0=40$ Ry* and ∞ Ry* as a function of R_0. It is readily seen that the binding energy of $V_0=\infty$ Ry* increases more rapidly than that of $V_0=40$ Ry* with decreasing R_0. For a finite barrier height, it increases monotonically until it reaches a maximum and then decreases rapidly with decreasing R_0. The "binding energies" are much larger than those (0.0555 and 0.480 Ry*) of three-dimensional (3D) D^-[25] and two-dimensional (2D) D^-[26] centers as R_0 is smaller. The maximum of the D^- center in the spherical QD with $V_0=40$ Ry* is equal to 2.41 Ry* at $R_0=0.340a^*$ [much the same as the position of the max-

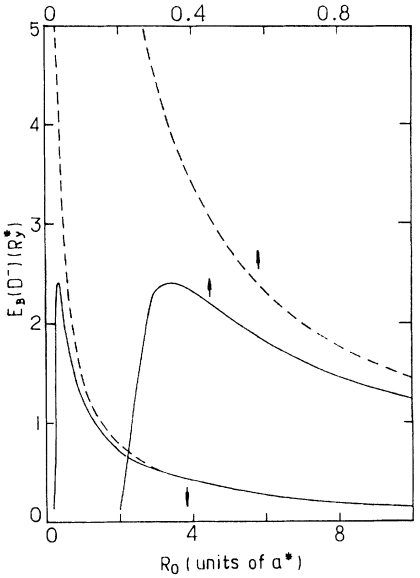

FIG. 1. "Binding energy" $E_B(D^-)$ of D^- ground states in spherical QD's of $V_0=40$ Ry* (solid curves) and ∞ Ry* (dashed curves) vs the well radius R_0. Arrows indicate relevant transverse scales. Effective atomic units are used. The same units are used in all of the following figures.

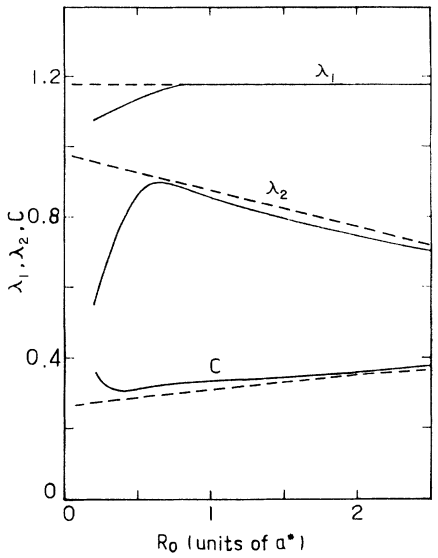

FIG. 2. Variational parameters λ_1, λ_2, and C vs the well radius R_0. Solid and dashed curves represent the parameters of $V_0=40$ and ∞ Ry*, respectively.

imum of $E_B(D^0)$] (Ref. 13) and 43.4 and 5.00 times as large as those of 3D D^- and 2D D^- centers,[25,26] respectively. Furthermore, it is interesting to study the variational approach and the dimension features as R_0 approaches zero. We have performed a variational calculation for small R_0 with $V_0=40$ Ry*. The "binding energies" have been obtained to be equal to 2.36, 2.15, 1.17, 0.70, 0.343, 0.128, 0.0526, and 0.0518 Ry* for $R_0/a^*=0.3$, 0.28, 0.25, 0.24, 0.22, 0.2, 0.1, and 0, respectively. The data show that the variation of the "binding energies" with $R_0<0.2a^*$ (not shown in Fig. 1) is much slower than that with $R_0>0.2a^*$. This can be understood as we note that there is no bound state for an electron in the dot with $R_0<R_c=0.5\pi/(V_0)^{1/2}$ and without the positive-ion center.[27] It is also interesting to note that the "binding energy" is almost independent of V_0 as R_0 is large, and that its value (0.143 Ry*) of $R_0=10a^*$, however, is still much larger than that of a 3D D^- center while the "binding energy" of the corresponding D^0 center approaches that of a 3D D^0 center. We have also calculated the "binding energy" at $R_0=15a^*$ which is equal to 0.0520 Ry* and very close to the bulk limit (0.0518 Ry*).[24]

In Fig. 2, we have shown the variational parameters as a function of R_0. As seen in the figure, the λ_1, λ_2, and C are almost independent of V_0 as R_0 is large. In the region, λ_1 is almost a constant, λ_2 increases and approaches λ_1, and C decreases slightly as R_0 decreases. However, this is not the case of small R_0. As R_0 decreases from some small R_0, both λ_1 and λ_2 of $V_0=40$ Ry* decrease and λ_2 of $V_0=\infty$ Ry* still increases and approaches λ_1 which is almost a constant in the region. The λ_2 of $V_0=40$ Ry* decreases quicker than the λ_1. In the smaller R_0 region, C, as shown, increases for $V_0=40$ Ry* and still decreases for $V_0=\infty$ Ry* as R_0 decreases. It is interesting to point out that for infinite barrier dots, the electron-correlation effect becomes small and the variational energy is not very sensitive to the variational parameter C as R_0 approaches zero and Coulomb effects are frozen out. At a given small R_0, however, the difference between λ_1 and λ_2 is larger for a small fixed C than that for a large fixed C. In Fig. 2, we have shown that λ_1, λ_2, and C approaches 1.18, 0.99, and 0.27 as R_0 approaches zero. In order to study the electron-correlation effect, we have performed the variational calculation without the polarization term Cr_{12} in Eq. (4). It has been found that the λ_1 and λ_2 are less than those obtained by the variational method with $C\neq 0$, and that the difference between λ_1 and λ_2 is larger than that with $C\neq 0$. It means that with the help of the polarization term Cr_{12}, one can make a single-electron orbital $\Psi(\lambda_1,r_1)$ close to the other $\Psi(\lambda_2,r_2)$ in a D^- center. The ratio of the "binding energy" difference due to omitting the term Cr_{12} to the "binding energy" is also calculated. For the dot with infinite barrier height, the ratio is equal to 0.007, 0.0216, 0.0648, 0.139, 0.210, and 0.514 for $R_0/a^*=0.1$, 0.3, 1, 3, 10, and ∞, respectively. What we have mentioned above shows that as an increasing confinement (reducing the dimensionality) makes one electron with a spin close to the other with the opposite spin and have less room to avoid the other in a D^- center, the electron-correlation effect on the wave function and "binding energy" can become weak.

In Fig. 3, the ratio σ of $E_B(D^-)$ to $E_B(D^0)$ has been plotted as a function of $1/R_0$. The enhanced confinement freeze-out effect for the D^- states in a spherical QD of $V_0=\infty$ Ry* is clearly seen from this figure. The effect is very similar to that of the D^- states in a magnetic field.[9] This has been understood from the fact that the extension of the outer orbital in a D^- center

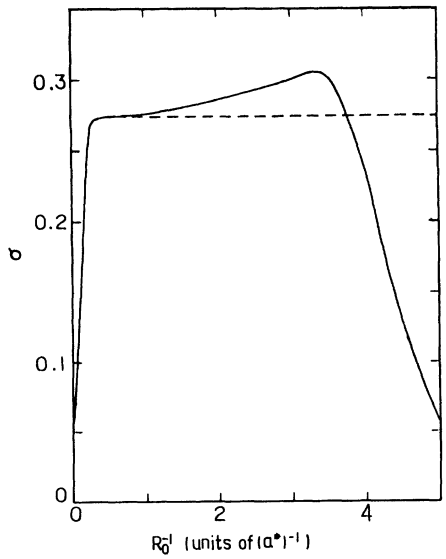

FIG. 3. Ratio σ of $E_B(D^-)$ to $E_B(D^0)$ vs one over the well radius R_0. Solid and dashed curves represent the σ of $V_0=40$ and ∞ Ry*, respectively.

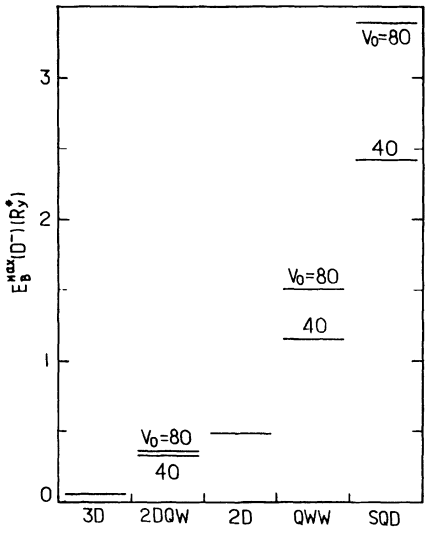

FIG. 4. Maximum "binding energy" $E_B^{max}(D^-)$ of D^- ground states vs the well dimensionality and barrier height V_0 (see the text). 2DQW, QWW, and SQD stand for two-dimensional quantum well, quantum-well wire, and spherical quantum dot, respectively.

sharply decreases with increasing the confinement even in a large R_0 regime or a weak field regime, compared with the extension of a neutral donor orbital which decreases rather slowly. However, the σ of $V_0=40$ Ry* increases quickly, approaches its maximum, and, then, decreases quickly as $1/R_0$ increases from zero. The maximum can be slightly different between different barrier heights. It is interesting to note that the limit value or maximum of σ, shown in Fig. 3, is larger than that of 3D D^- states in a magnetic field[9] and about the same as that of 2D D^- states in a magnetic field.[28] It, in fact, means that the limit or maximum value of σ, i.e., the freeze-out effect, is strongly dependent on the confined dimensionality and weakly dependent on the barrier height and the well shape.[28] Then, we can conclude that "binding energies" and their maxima of D^- ground states increase with the confined dimensionality more rapidly than those of D^0 ground states since the maximum or limit value of σ increases with increasing dimensionality.

According to the confined dimensionality dependence of the freeze-out effect mentioned above and using the maxima[13] of "binding energies" of D^0 states in 2DQW's, QWW's, and QD's with different well shapes and barrier heights, we can correctly estimate the maxima of D^- states in the corresponding structures. In Fig. 4, we have shown that the "binding-energy" maxima of D^- states in various dimensions. The values of 2DQW's (Ref. 28) and spherical QD's are obtained by variational approaches while the values of QWW's are estimated by using the binding-energy maxima of D^0 states in QWW's (Refs. 11 and 12) and the σ limit value of 3D D^- states in a magnetic field.[9,10] They are, respectively, 0.326, 1.15, and 2.41 Ry* for the 2DQW, QWW, and spherical QD with $V_0=40$ Ry* and 0.355, 1.50, and 3.38 Ry* for these structures with $V_0=80$ Ry*. The binding energies of 3D and 2D D^- states are also shown in Fig. 4 and are equal to 0.0555 (Ref. 25) and 0.480 Ry*,[26] respectively.

It is well known that the D^- ion has one and only one bound state in three-dimensional systems. Phelps and Bajaj[26] have shown that it is not bound for a zero-orbital angular-momentum triplet state of a D^- ion in two dimensions. The corresponding triplet state of a D^- ion in spherical QD's can be easily constructed within the framework of our trial function by antisymmetrizing it relative to the interchange of electron spatial coordinates. Using this trial function, we have calculated the variation energy $E(D^-)$ of the zero-orbital angular-momentum triplet state and obtained a negative "binding energy" defined as Eq. (7), i.e., an "unbound" state, even though the triplet state is really bound in the dot and including the impurity potential should lower the energy of the state without the potential. It should be interesting to know whether there are positive binding energies for higher angular-momentum triplet states in spherical QD's. This work is in progress.

In conclusion, it is worthwhile to point out that we have obtained the magnitude of "binding energy" of the D^- ground state in spherical QD's and its well-radius and barrier-height dependence. Then, the electron-correlation effect of the D^- center in spherical QD's and the dimensionality dependence of the σ and $E_B(D^-)$ have been clearly demonstrated. It will be useful for understanding the electronic properties in low-dimensionality systems and for designing future devices. Speaking of the variational calculation, we believe that the kind of trial function used consisting of the exact solutions of single-electron states of an appropriate Hamiltonian is more powerful and suitable for application to D^- ions not only in spherical QD's with $R_0>R_c$ (Ref. 27) but also in QWW's and 2DQW's with and without external fields. Using this kind of trial function, we are studying the behavior of D^- centers in 2DQW's and QWW's in a magnetic field. This will be reported else-

where.[28] Finally, we should point out that D^- centers could be located anywhere in a spherical QD and that the "binding energy" will decrease as the D^- location shifts to the edge of the spherical QD. The quantum dots cannot be spherical. It should be interesting therefore to extend the present work to a systematic investigation of the positional dependence of D^- "binding energies" in spherical QD's and other kinds of quantum dot.

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