Vol 13 No 6, June 2004
1009-1963/2004/13(06)/0942-06

Chinese Physics

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Effects of a donor on the bond property of quantum-dot molecules*

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(Received 16 October 2003; revised manuscript received 3 February 2004)

Within the framework of effective mass approximation, we have calculated the electronic structure of the two laterally coupled quantum dots with a donor by the finite element method. The calculated results show that the bond states of quantum-dot molecules are quite sensitive to the donor positions. By varying the donor position, the transition from covalent to ionic bond state is realized for some electronic states. Some extreme cases are also discussed for comparison.

Keywords: covalent bond, ionic bond, wave function, energy level
PACC: 7320D, 7125W, 7155H

1. Introduction

In recent years much attention has been devoted to the electronic properties of semiconductor quantum dots (QDs). Many authors have also studied the impurity states in QDs, especially the theoretical works on hydrogenic impurity states. Most of them focus on the binding energies of donors and acceptors in a QD. When the donor is localized at the centre of a spherical QD, its calculated ground-state energy approaches the correct limit of the three-dimensional (3D) hydrogen atom as the radius of the QD becomes very large,[1] without considering the spatially dependent screening of an impurity ion caused by the valence electrons, and the dielectric mismatch between the well and barrier materials.[2] For the hydrogenic impurities at different positions in spherical QDs,[3,4] the methods of treatment are usually the variational procedure under the effective mass approximation. Zhu *et al*[4] found that the donor position heavily affects the level ordering of single-electron spectra in the QD.

Since the covalent bonds and ionic bonds in double dots were observed in the experiment,[5] the QD molecules[6] have attracted increasing attention because of the potential application in quantum computing.[7]

The electronic structure of the QD molecules without impurities were investigated by many authors.[8,9] Coherent bonding and antibonding states are formed in the QD molecules in the strong coupling case.[10] By varying the distance between the centres of the coupled QDs, a transition from weak- to strong-coupling situation is realized.[11,12] Conditions for the formation of covalent bonds have been discussed in our previous paper.[12] However, to our knowledge, there has not been any systematic investigation related to the donors effects on the electronic structure of QD molecules yet. It is worthwhile to perform theoretical study on this interesting subject.

There are two interesting relative problems in the QD molecules. The first is how to place an atom (impurity) into a QD molecule. The second is how the single electron spectrum of QD molecules is changed by the atom (impurity). In this paper, we will focus on the second problem. The discussion is based on the calculated donor spectra in semiconductor QD molecules. Our calculation is carried out using the

*Project supported in part by the National Natural Science Foundation of China (Grant Nos 10274007 and 90103027), and in part by the Doctoral Research Fund of Hebei Normal University.
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finite element method [13] within the effective-mass approximation. This method is a powerful tool in dealing with the eigenvalue problem of an asymmetric system, so it is also suitable for investigating the effects of the donor on the electronic structure of QD molecules.

2. Theoretical model

Within the framework of effective mass approximation, the Hamiltonian of a hydrogenic donor type of impurity located in a double-QD molecule is written as

$$H = \frac{p^2}{2m^*} + V(\boldsymbol{r}) - \frac{e^2}{4\pi\varepsilon\left|\boldsymbol{r} - \boldsymbol{r}_i\right|}. \tag{1}$$

The first term is the kinetic energy of the electron, $V(\boldsymbol{r})$ is the confining potential of the QD molecule, and the third term is the impurity potential. Here, $\boldsymbol{r}_i$ is the position vector of the donor, $\boldsymbol{r}$ is the position vector of the electron, m^* is the electron effective mass. However, the effect of spin is neglected. We assume that the effective mass of the electron inside the QD is the same as that outside it. The polarization and image charge effects have been ignored because of the smaller difference of the dielectric constant between the two materials.[4]

The electronic structure of the QD molecules is the solution to the Schrödinger equation $H\Psi = E\Psi$. For semiconductor QDs, two idealistic models are the spherical QDs in 3D space with a rectangular potential and the circular QD in two-dimensional (2D) space with a parabolic potential, which have been used by a number of authors because of the high symmetry.

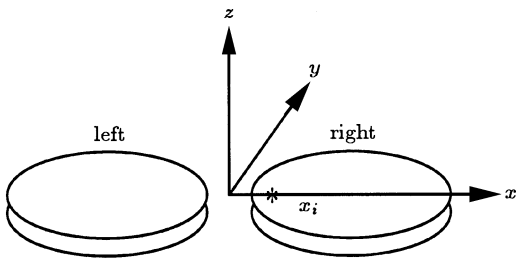


Fig.1. Sketch of a laterally coupled double-dot molecule with a donor located in the x axis.

For the two disc-shaped QDs (see Fig.1),[5] the component z of the electron position vector $\boldsymbol{r}$ is almost the same as that of the donor position vector $\boldsymbol{r}_i$ because the thickness of the dots is very small. So the z-dependence of the impurity potential is regarded as a constant. The problem turns into $H = H_{//} + H_z$.[14] The wavefunction of the electron can be written as

$$\Psi(x, y, z) = \phi(x, y)\psi(z), \tag{2}$$

where $\phi(x, y)$ and $\psi(z)$ are the wavefunctions in the xy plane and in the z direction respectively. The corresponding eigen-energy of the electron in QDs is

$$E = E_{//} + E_z. \tag{3}$$

For circular QDs, the dimension in the z direction is much smaller than that in the xy plane. The energy level interval of E_z is much larger than that of $E_{//}$. So it is reasonable to set $E_z = E_{z0}$, the energy of the ground state. Hence the laterally coupled QDs are simplified to a 2D problem. The Schrödinger equation in the xy plane is written as

$$\begin{aligned} &-\frac{\hbar^2}{2m^*}\left\{\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2}\right\} \\ &-\frac{e^2}{4\pi\varepsilon\sqrt{(x - x_i)^2 + (y - y_i)^2}}\phi \\ &+ V(x, y)\phi = (E - E_{z0})\,\phi \end{aligned} \tag{4}$$

in rectangular coordinates. By adopting reduced atomic units (a.u.*), which correspond to a length unit of one effective Bohr radius $a^* = \hbar^2\varepsilon/m^*e^2$, and an energy unit of one effective Rydberg $R^* = m^*e^4/2\hbar^2\varepsilon^2$, Eq.(4) becomes

$$\begin{aligned} &-\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2}\right) - \frac{2}{\sqrt{(x - x_i)^2 + (y - y_i)^2}}\phi \\ &+ V(x, y)\phi = E\phi. \end{aligned} \tag{5}$$

The eigenstates of a donor are then obtained by solving the Schrödinger equation (5) with the finite element method.[13] By varying the donor-position (x_i, y_i), we can study the effects of the donor-position on the bond property of the double-QD molecules.

3. Numerical results and discussion

In order to investigate the effects of a donor on the valence-bond of QD molecules, we assume that the radii of two circular QDs are both $1a^*$ and the confining potentials are square-well potentials with a height of $40R^*$.[15] In order to obtain sufficient coupling, the distance between the two dot centres is set to be $2.2a^*$. If the origin of the coordinates is chosen at the midpoint between the centres of the two dots, then the centres of the dots are respectively at $(-1.1a^*, 0)$ and $(1.1a^*, 0)$. So the confining potential $V(x, y)$ of the QD molecule in Eq.(5) is written as

$$V(x,y)=\begin{cases} 0, & \text{if } \sqrt{(x+1.1)^2+y^2}\le 1 \text{ or } \sqrt{(x-1.1)^2+y^2}\le 1; \\ 40R^*, & \text{if } \sqrt{(x+1.1)^2+y^2}>1 \text{ and } \sqrt{(x-1.1)^2+y^2}>1. \end{cases} \tag{6}$$

Substituting $V(x,y)$ of Eq.(6) into Eq.(5) and giving the value of donor-position (x_i,y_i), we can obtain the eigenstates of the hydrogenic donor impurity in the QD molecule by numerically solving the Schrödinger equation (5) with the finite element method.

Suppose the donor position is $(x_i,0)$, and that the energy levels of impurity states vary with impurity position x_i. Figure 2 shows the 12 lowest energy eigenvalues from E_1 to E_{12} of the system as functions of donor-position x_i. Note that some energy levels change dramatically, while others change slightly.

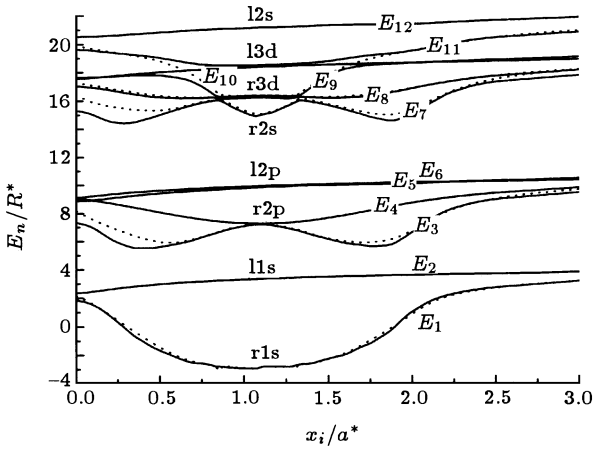


Fig.2. The energy eigenvalues of bound states in QDs as functions of the donor-position x_i. The solid lines denote the 12 lowest energy levels of the QD molecule. The dashed lines denote the six lowest energy levels of bound states 1s, 2p, 2s, 3d in the isolated right QD with the donor impurity.

When the donor impurity is at the origin, i.e. $x_i=0$, all the eigenstates are delocalized states over both QDs according to the corresponding eigenfunctions. They are covalent bond states just as Oosterkamp *et al* observed.[5] When the donor impurity is at the centre of the right dot, i.e. $x_i=1.1a^*$, all the eigenstates are localized in one of the two QDs according to the eigenfunctions, just as the electronic states in two isolated QDs. The states of E_1, E_3, E_4, E_7, E_8 and E_9 correspond to the electronic states (orbits) 1s, 2p, 3d and 2s in the isolated right QD with a donor located at the dot centre. The states of E_2, E_5, E_6, E_{10}, E_{11} and E_{12} correspond to the electronic states (orbits) 1s, 2p, 3d and 2s in the isolated left QD with a donor out of the left dot. We use r1s, r2p, r3d, r2s and l1s, l2p, l3d, l2s respectively to denote the orbits in the isolated right and left QDs in Fig.2 at $x_i=1.1a^*$. Here the notation of the states (orbits) in a QD are similar to the spherical case in Refs.[4,15]. They are all ionic bond states described by Oosterkamp *et al.*[5] So we find that the donor-position dramatically affects the bond property of the QD molecules.

In order to describe clearly, we plot the electronic energy levels of states (orbits) 1s, 2p, 3d and 2s in the isolated right QD as functions of donor-position x_i in Fig.2 (dashed lines). This agrees with Zhu *et al*'s results.[4] Notice the intersections of 2s level with 3d level at $x_i=0.6a^*$ and $1.6a^*$, which alter the sequence of the energy levels. This feature is the main reason for the appearing of covalent bond states E_9 and E_{11} in the QD molecules near $x_i=0.6a^*$ and $1.6a^*$ in Fig.2. The detailed variations of these eigenstates are described as follows.

The energy eigenvalue E_1 of the molecule changes dramatically with increasing x_i just like the level 1s in the isolated right dot shown by the lowest dashed line in Fig.2. The lowest energy is around $x_i=1.1a^*$. With increasing x_i from zero, its eigenfunction changes from a delocalized state over the both dots (see Fig.3 (a)) to a localized state in the right dot (see Fig.3 (b)). In other words, with increasing x_i this molecular bond gradually changes from a covalent bond (bonding) consisting of two 1s orbits in both dots to an ionic bond (1s orbit in the isolated right-hand dot).

The energy E_2 of the second eigenstate increases slightly with increasing x_i, as shown in Fig.2. The reason is that the donor out of the left hand dot has a little effect on the electronic energy of the left dot. With increasing x_i, the eigenfunction of E_2 also changes from a delocalized state over both dots to a localized state in the left dot. The delocalized state is a covalent bond (anti-bonding) state consisting of two 1s orbits in both dots, and the localized state is an ionic bond state (1s orbit in the left dot).

Just like the variations of E_1 and E_2, with increasing x_i the eigenstates E_3, E_4, E_5, E_6, E_7, E_8, E_{10} and E_{12} gradually change from covalent bond states consisting of 2p, 3d, 2s orbits in both dots to ionic bond states (2p, 3d, 2s orbits in one dot). Here the 2p and 3d orbits respectively include two orbits with different symmetry to axis x, i.e. p, p′ and d, d′.[12]

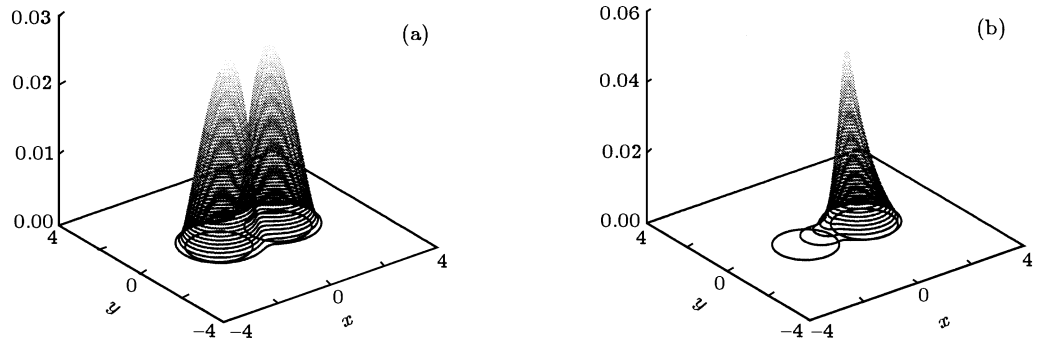


Fig.3. The electronic eigenfunctions of E_1 in the double-QD molecules. (a) When $x_i = 0$, it is a covalent bond state consisting of 1s orbits in the two dots. We use r1s+l1s to denote this kind of wavefunction. (b) When $x_i \geq 0.3a^*$, it is an ionic bond state (1s orbit in the right QD). We use r1s to denote this kind of wavefunction.

The variations of the eigenstates E_9 and E_{11} are different from other energy levels. According to the 11th eigenfunction in Fig.4, we know this eigenstate gradually changes first from a covalent bond state (see Fig.4(a)) to an ionic bond state (see Fig.4(b)), then gradually changes into a covalent bond state (see Fig.4(c)) again around $x_i = 0.63a^*$. With further increasing x_i, it gradually changes into an ionic bond state (orbit 3d in the isolated left dot) again. After $x_i = 1.1a^*$, it does the reverse. Similarly, the variation of the ninth eigenfunction with increasing x_i is covalent bond (antibonding of orbits 3d in the two dots) $\rightarrow$ ionic bond (orbit 3d in the isolated left dot) $\rightarrow$ covalent bond (bonding of orbits 3d in left dot and orbits 2s in right dot) $\rightarrow$ ionic bond (orbits 2s in right dot) $\rightarrow$ ionic bond (orbits 3d in right dot) $\rightarrow$ ionic bond (orbits 2s in right dot) $\rightarrow$ covalent bond (bonding of orbits 3d in left dot and orbits 2s in right dot) $\rightarrow$ ionic bond (orbits 3d in left dot).

Comparing the energy variation of level 2s in the

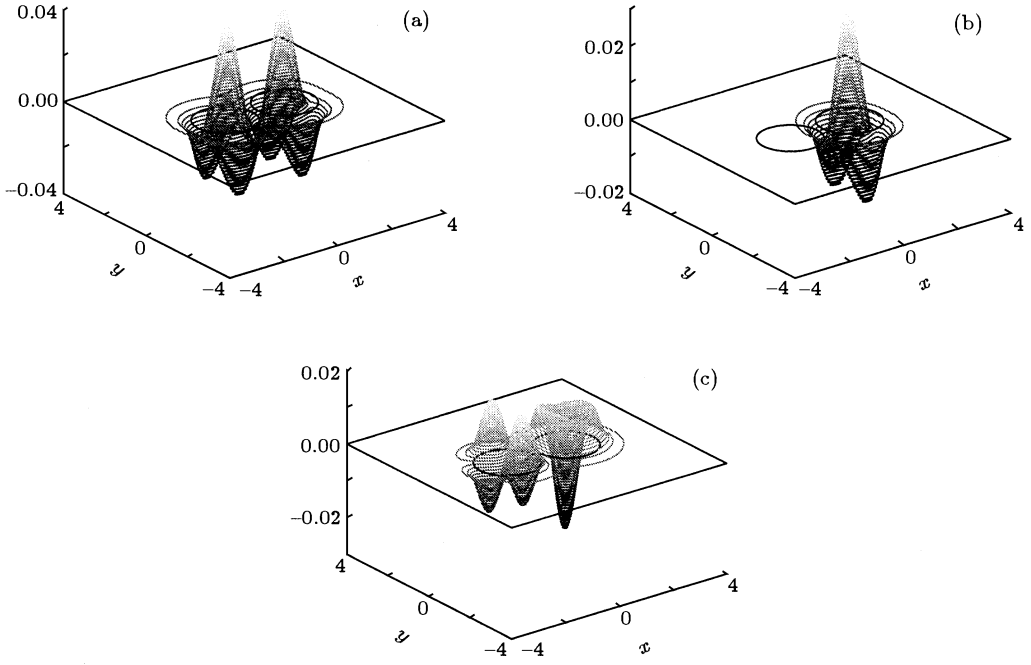


Fig.4. The electronic wavefunctions of E_{11} in the double-QD molecules. (a) When $x_i = 0$, it is a covalent bond state. In very concrete terms, it is a bonding state of 2s orbits in the two dots. (b) When $x_i = 0.3a^*$, it is an ionic bond state (2s orbits in the right dot). (c) When $x_i = 0.63a^*$, it is a covalent bond state. In very concrete terms, it is the antibonding state of 2s orbit in the right dot and 3d orbit in the left dot.

isolated right dot with that of the level 3d in the isolated left dot, we find that there is a crossing between the dashed line of r2s and the solid line of E_{10}. So the 2s orbit in the right-hand dot and 3d orbit in the left-hand dot satisfy the conditions [12] of forming covalent bonds around $x_i = 0.6a^*$ and $x_i = 1.6a^*$. Thus, the eigenstates E_9 and E_{11} are covalent bond states around $x_i = 0.6a^*$ and $x_i = 1.6a^*$, and they correspond respectively to the bonding state and antibonding state consisting of orbits 2s in the right dot and 3d orbit in the left dot.

From the above discussions, we know that donor-position makes the valence-bond of the double-dot molecule alternate between the covalent bond and ionic bond states. According to the experimental results,[5] the covalent bond corresponds to a strong coupling between the two QDs, and the ionic bond corresponding to a weak coupling between the two QDs. So the donor position makes the coupling between the two dots alternate between strong coupling and weak coupling. When the donor is at the origin, the coupling between the two dots is the strongest. When the donor is off the centre, the coupling becomes weaker. Our conclusions are instructive in practical experiments.

According to the above conclusions, we can also deduce the following extreme cases. When the donor is far away from the QD molecule, all the eigenstates are covalent bond states, just as the case without donor.[13] In this case, the coupling between the two dots is weaker than the case that the donor is at the origin, but it is stronger than the case that each dot has a donor at its centre. The reason is that the Coulomb potential of donor ion attracts a large proportion of the electron wave function around the ion. All the eigenstates in the above three cases are covalent bond states. When the donor moves along the y axis, the eigenstates keep the covalent bond states with a slight variation of the eigen-energy value.

Figure 5 shows some electronic energy levels in the double-dot molecules, with a donor impurity at the origin and with one donor impurity at the centre of each dot, in comparison with the case without donor. The notations of the levels in the figure denote the combination of orbits of single QD,[4] which also denote the bond property of the level. Note that all the eigenstates are covalent bond states for these cases. And the coupling strength has a close relationship with the energy splitting between bonding state and corresponding antibonding state, and a wider energy splitting relates to a stronger coupling between the QDs.

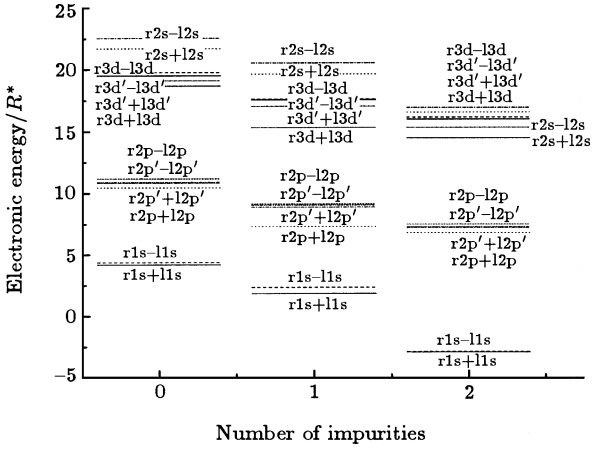


Fig.5. The comparison among the eigen-energies of double-QD molecules: without impurity, one impurity at the origin, two donors, each of which lies at the centre of each dot. s, p, d denote the electronic orbits in a single dot, and '+' denotes the bonding state, while '–' denotes the antibonding state.

4. Conclusion

Within the framework of effective mass approximation, we have calculated the electronic structure of the two laterally coupled QDs with a donor by the finite element method, which has not received any systematic investigation yet in both experiment and theory. Numerical results show that the change of the donor position affects effectively the electronic states in the QD molecule. It not only makes the covalent bond states change into ionic bond states, but also can change the latter into the former. As different electronic states correspond to different strengths of the coupling between the two QDs, the coupling between QDs can be adjusted by changing the donor position. The strength of the coupling in covalent bond states has a close relationship with the energy splitting between bonding state and corresponding antibonding state, a wider energy splitting relates to a stronger coupling between the QDs. The effects of donors on the bond property, which is a special phenomenon in the artificial molecule, are instructive in fabricating desired QD molecules and designing quantum function devices.

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