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The study of the valence bond property in a two-different-quantum-dot molecule*

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The electronic energy spectrum and wavefunction of a quantum-dot molecule are studied by means of the finite-element solution of the single electron Schrödinger equation. We find that the nature of the coupling can be covalent, ionic, or "intermediate" new mixed states, depending on various parameters such as the separation distance between two dots, the height of potential barrier, matching of the energies and parities of the orbital localized on each dot. The bond property can be used to explain the experimental result obtained by Oosterkamp *et al.* (1998 *Nature* **395** 873).

Keywords: electronic structure, symmetry, covalent bond, ionic bond, mixed state
PACC: 7155, 7135

1. Introduction

In recent years, much attention has been devoted to the properties of semiconductor quantum dots (QDs). In these systems, carriers (electron, hole) are subjected to a confining potential in all spatial directions, which gives rise to a discrete energy spectrum and novel phenomena of interest in fundamental physics as well as in applications to electronic and optoelectronic devices.[1,2] If one QD is an artificial atom,[3] then multiple coupled QDs can be considered to be artificial molecules.[4] Combining the concepts from chemistry with artificial molecules, new investigations are possible. These range from studies of the "chemical bond" between two coupled dots, to zero-dimension-state spectroscopy, to possible new applications, such as quantum devices, including the proposed quantum computers.[5−7]

A considerable body of experimental and theoretical work has led to a detailed quantitative understanding of QD molecules.[8−16] The type of coupling (including purely electrostatic coupling and tunnelling coupling) between QDs determines the character of the electronic states and the nature of transport through the artificial molecules. When electrons tunnel at appreciable rates between QDs in a coupled dot system, the system forms an artificial molecule with "molecular" electronic states which can extend across the entire system. Analogies with chemistry and biochemistry may permit the design of new types of quantum devices and circuits based on tunnel-coupled QDs. Perhaps the most adventurous of these would be a quantum computer with electronic states which coherently extend across the entire system.[6] The coherence of electronic states becomes an important issue whenever wave-like aspects of electrons are important. Currently, the issue of the coherence of electron states inside QDs and the coherence of tunnelling processes is actively discussed, but relatively few data are available.[17,18] The experimental result of Oosterkamp *et al.*[11] has shown that two QDs could be connected to form an "artificial molecule". Depending on the strength of the inter-dot coupling, an 'ionic' or 'covalent' bond can be formed between the two dots. In the former case the electrons are mainly localized in either individual dots, while in the latter case the electrons are delocalized over both dots. The covalent binding leads to bonding and anti-bonding states, whose energy difference is proportional to the degree of tunnelling. Their results demonstrate the controllable quantum coherence in single-electron devices—an essential requirement for practical applications of QD circuitry.

One of the important challenges at this point is to understand the fundamental properties of QD molecules. Here the inter-dot coupling can be tuned through external parameters, far out of the regimes known in 'natural molecules' where the ground-state interatomic distance is dictated by the nature of bond-

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ing. Some new phenomena will occur in these "artificial molecules" when the external parameters are varied. Through the study of such phenomena, coupled dots may become a unique laboratory to explore electronic states and new features. The conditions of forming covalent bond QD molecules have not been investigated in detail yet, so we aim to study these conditions in this paper.

2.Theoretical model and numerical calculation

In this paper, we investigate the electronic structure of two laterally coupled cylindrical QDs, using the effective mass approximation. The single-particle states of the system are expressed by the eigenfunctions of the Hamiltonian $H = -\hbar^2\nabla^2/2m^* + V$, where m^* is the electron effective mass, and V is the confining potential of the QD molecule, which consists of two different QDs. When the size in the z-direction is much smaller than that in the x- and y-direction, the vertical and lateral motions of a single electron are decoupled. Thus the confinement potential V of the QD molecule splits into $V_z + V_{xy}$.[19] The eigenvalues and eigenfunctions of the single electron Schrödinger equation are $E = E_z + E_{xy}$ and $\psi(x, y, z) = \varphi(x, y)\phi(z)$, where $\varphi(x, y)$ and $\phi(z)$ denote the solutions for the lateral and vertical motions, respectively. The effect of the dot–dot interaction appears only in the energy levels (E_{xy}) associated with the xy motion because of the lateral coupling. Since the energy difference between the first and second lowest states for the z motion is larger than that for the xy motion, the lowest-energy states mainly result from the hybridization of the xy-plane motions. So most works about the laterally coupled double QDs system choose the two-dimensional electron gas as a model. In contrast to previous works, in this paper we study the chemical bond property of the QD molecule consisting of two QDs of different sizes coupled in plane by a tunnelling barrier. 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 energy Ry*=$m^*e^4/2\hbar^2\varepsilon^2$, the Schrödinger equation of the QD molecule in rectangular coordinates can be rewritten as

$$-\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2}\right) + V_1(x, y)\phi + V_2(x, y)\phi = E\phi. \quad (1)$$

By solving the Schrödinger equation (1) with different coefficients by means of the finite-element method,[16] we can study the property of the coupling between two different QDs. Some cases of coupling between two different QDs have been investigated in our previous paper.[16] A special case is re-investigated here to perfect the conditions for forming a covalent bond in view of linear combination of atomic orbits (LCAO). Figure 1 shows an illustration of this special QD molecule. In this case, the confining potentials V_1 and V_2 in Eq.(1) are

$$V_1 = \begin{cases} 0 & \sqrt{(x - x_{\rm l})^2 + y^2} < 1; \\ 40 & \sqrt{(x - x_{\rm l})^2 + y^2} \geq 1, \end{cases} \quad (2)$$

$$V_2 = \begin{cases} 0 & \sqrt{(x - x_{\rm r})^2 + y^2} < 0.565; \\ 40 & \sqrt{(x - x_{\rm r})^2 + y^2} \geq 0.565. \end{cases} \quad (3)$$

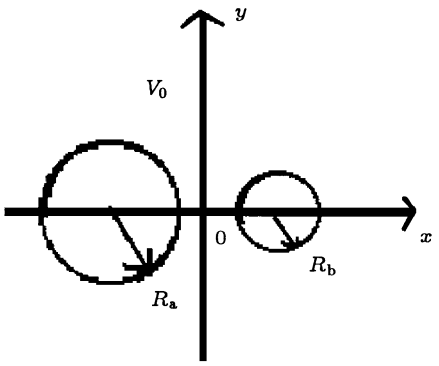


Fig.1. Illustration of a coupled QD molecule. The radii of the left and right dots are, respectively, $1a^*$ and $0.565a^*$. The confining potentials are 40Ry* outside the dots and zero within the dots.

We solve the Schrödinger equation (1) for different separation distances ($d = x_{\rm r} - x_{\rm l}$) between the centres of the two QDs by the finite-element method. The four lowest eigenenergies as functions of d are plotted in Fig.2. According to the Pauli exclusion principle, the first four energy levels have a capacity for eight electrons. Assuming that there is no splitting of energy level degeneracy in multi-electron atoms, the aufbau principle would give the following structure for the molecule made up of such two "pancake" atoms.

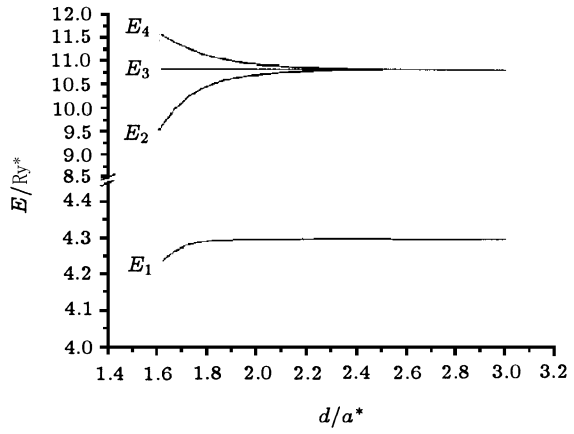


Fig.2. The four lowest eigenenergies of the molecule as functions of d.

When an electron is in the eigenstate E_1, the probability of electronic spatial distribution is almost localized in the left dot according to the wavefunction of E_1 (see Fig.3(a)). The wavefunction of eigenstate E_1 is almost the orbit $\varphi_{\rm s}$ in the left dot, and its leakage into the adjacent dot is small even with a very thin potential barrier. Thus, the ground state E_1 is an ionic bond state. The major reason for E_1 being an ionic bond state lies in the fact that the energies of the two discrete states in the two isolated QDs do not match. This restriction to form a covalent bond is well known from most papers in the literature.

When an electron is in the eigenstate E_2 with a small distance between the two dots, the electron extends over both dots, as shown in Fig.3(b). The wavefunction of this state is of the bonding state as a linear combination of the orbit $\varphi_{\rm s}$ in the left dot and the orbit $\varphi_{\rm p^+}$ in the right dot. Here $\varphi_{\rm p^+}$ presents the orbit p with symmetry about the x-axis, i.e. $\varphi_{\rm p^+}(x,-y)=\varphi_{\rm p^+}(x,y)$. One reason for E_2 being a covalent bond state is that the energies of the orbit $\varphi_{\rm s}$ in the isolated right QD and the orbit $\varphi_{\rm p^+}$ in the isolated left QD are equal, as shown in Fig.2 at large d, i.e. the energies between the two orbits match.

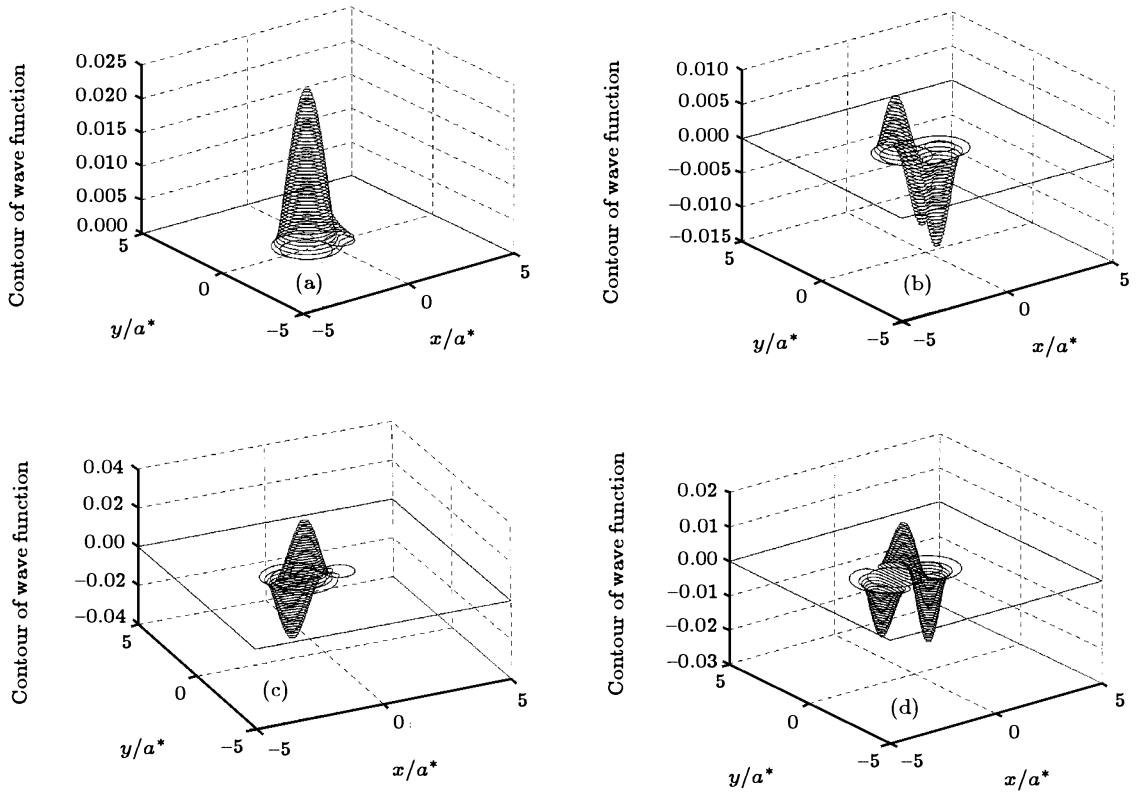


Fig.3. The wavefunctions of the four lowest eigenstates of the QD molecule with $d=1.6a^*$. The thickness of the potential barrier is $t=d-R_{\rm r}-R_{\rm l}=0.035a^*$. (a) The ionic bond state E_1; (b) the covalent bond state E_2; (c) the ionic bond state E_3; (d) the anti-bonding state E_4.

When an electron is in the state E_3, the electronic spatial distribution probability is completely localized in the left QD, as shown in Fig.3(c). Hence the state E_3 is an ionic bond state. The wavefunction of state E_3 represents the orbit φ_{p^-} in the isolated left QD, and its leakage into the adjacent dot is zero. Here φ_{p^-} presents one orbit of the twofold degenerate state 1p in the isolated left dot with $\varphi_{\mathrm{p}^-}(x,-y) = -\varphi_{\mathrm{p}^-}(x,y)$. The fact that the overlap between the orbits φ_{p^-} and φ_{s} is zero is the main reason that the eigenstate E_3 is an ionic bond state even when the energies of the two orbits match. The reason for overlap being zero lies in the fact that the QD molecule is symmetric about the x-axis. The symmetry of orbit φ_{p^-} is different from that of orbit φ_{s} with respect to the x-axis, with $\varphi_{\mathrm{p}^-}(x,-y) = -\varphi_{\mathrm{p}^-}(x,y)$ and $\varphi_{\mathrm{s}}(x,-y) = -\varphi_{\mathrm{s}}(x,y)$. Even the energy of the orbit φ_{p^-} in the left isolated QD matches with that of the 1s orbit in the right isolated QD; the zero overlap between the two orbits shows that there is no interaction between the two QDs even with a small distance. The orbits φ_{p^-} and φ_{s} cannot form a covalent bond because of their different symmetries. The symmetry of the orbital also restricts the tunnelling of electrons from left to right dots even with a very thin potential barrier. So the energy of state E_3 does not change with d. The restriction of wavefunction symmetry plays an important role in the coupling between the two QDs.

When an electron fills the energy level E_4 for the two dots with a small distance, the electron is in a covalent bond state as shown in Fig.3(d). This covalent bond is the anti-bonding state consisting of orbit φ_{p^+} in the left dot and orbit φ_{s} in the right dot. The eigenstate E_4 is a covalent bond state due to the following factors: (1) the energy of orbit φ_{p^+} in the isolated left QD is equal to that of orbit φ_{s} in the isolated right QD; (2) the symmetry of orbit φ_{p^+} is same as that of orbit φ_{s}, i.e. $\varphi_{\mathrm{p}^+}(x,-y) = \varphi_{\mathrm{p}^+}(x,y)$ and $\varphi_{\mathrm{s}}(x,-y) = \varphi_{\mathrm{s}}(x,y)$; (3) the potential barrier between the two dots is neither thick nor high. These three factors are the criteria for the covalent bond state between two QDs. These are similar to the criteria for natural molecules.[20]

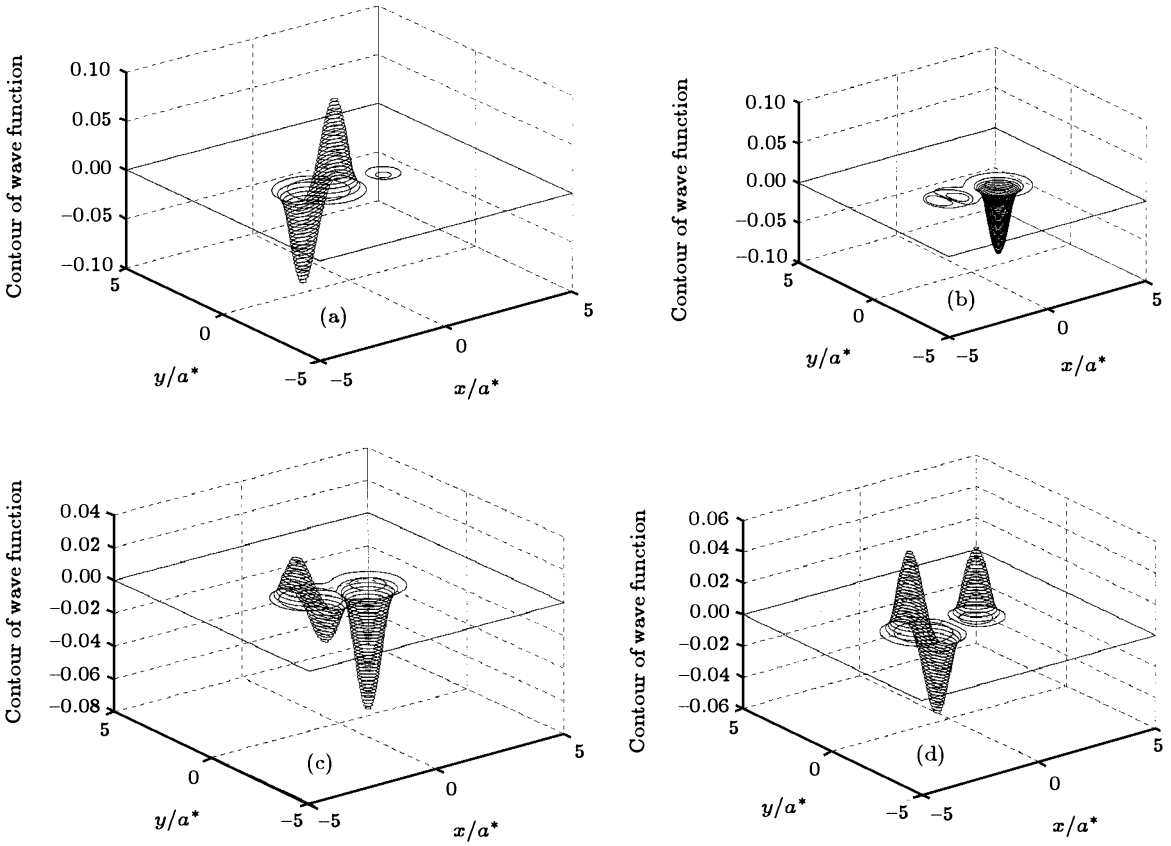


Fig.4. Wavefunctions of states E_2 and E_4 with large $d = 2.4a^*$ (a) and (b), and with intermediate values of $d = 1.85a^*$ (c) and (d), respectively.

When d is very large, the wavefunction overlap between the two dots is zero, and the system behaves as two isolated QDs (see Figs.4(a), and 4(b)). Therefore, there is no coupling between the two QDs. This type of QD molecule is the ionic bond molecule observed by Oosterkamp *et al.*[11] Note that the energies of orbit $\varphi_{\rm s}$ in the right isolated dot and orbits $\varphi_{\rm p+}$ and $\varphi_{\rm p-}$ in the left isolated dot are equal, as shown in Fig.2 with large d. This is one reason that the states E_2 and E_4 are covalent bond states when d is small. When the distance changes from small to large, the energy of state E_2 becomes higher, in contrast to that of state E_4. The energies of states E_2 and E_4 vary just like those of two identical QDs in a previous work.[16] The wavefunctions of states E_2 and E_4 change from covalent to ionic bond. During the change of states E_2 and E_4 with increasing d, the electron in the QD molecule can be at a somewhat mixed state that possesses properties of both covalent bond and ionic bond, as shown in Figs.4(c) and 4(d); this is what natural molecules cannot realize. These mixed states interpret the measured pumped current through the coupled double-dot,[11] predicted by Rontani *et al.*[12] to be observable in the addition spectra and in the magnetization changes.

In order to investigate the effects of the potential barrier height on the coupling between two dots, we replace the confining potential 40Ry* in Eqs.(2) and (3) with V_0 and vary it from 30 to 200Ry*, while keeping $d = 1.7a^*$. Then we calculate the electronic structure of the molecule. The numerical results are shown in Fig.5. Note that eigenenergies of the molecule increase as the potential barrier height increases in Fig.5 (a). The reason for this is that the confining potentials are simultaneously hoisted. The covalent bond states E_2 and E_4 gradually change into mixed states (as in Figs.4(c) and 4(d)) when the height of the potential barrier increases. When the height of the potential barrier is very large, there is almost no coupling between the two QDs, and both states E_2 and E_4 become ionic bond states (see Fig.6) just like that of two isolated QDs. So the potential barrier plays an important role in the QD coupling.

To compare with the experiment,[11] we study further the above results. Figure 5(b) shows the energy difference $\Delta E = E_{\rm right} - E_{\rm left} = E_{\rm s} - E_{\rm p}$, where $E_{\rm s}$ and $E_{\rm p}$ are the energies of the uncoupled states in the right and left dots, as a function of the energy splitting of $\Delta E^* = E_{\rm anti-bond} - E_{\rm bond} = E_4 - E_2$. This function illustrates the effects of the energy difference on the coupling between the two dots. The curve basically agrees with that in Ref.[11]. This reveals that the energy difference of the uncoupled states of the two dots plays an important role in the coupling between them. In other words, the smaller the energy difference, the stronger the QD coupling.

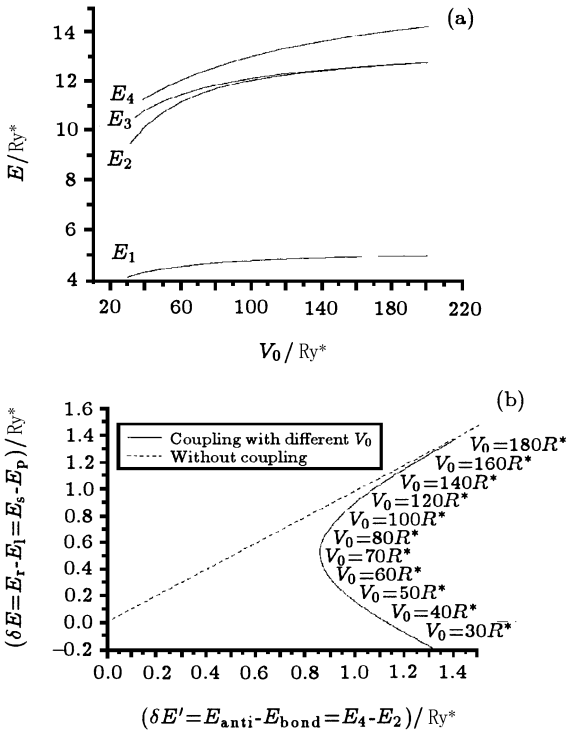


Fig.5. The effects of the potential barrier height on the valence bond property of the QD molecule: (a) the four lowest eigenenergies as functions of V_0; (b) the effects of the energy difference between orbits s and p on the valence bond property. The solid line indicates the coupling strength, which is proportional to the energy splitting of the anti-bonding state E_4 and bonding state E_2, changes with the energy difference between orbits s and p respectively in the two uncoupled dots due to V_0. The dashed line corresponds to the uncoupled two QDs. The solid line is asymptotic to the dashed line, indicating that the coupling between the dots is weaker.

We have also investigated the effects of the confining potential shape, QD shape,[21,22] and QD layout on the coupling between the two dots. All these effects can be attributed to three factors: the thickness and height of potential barrier; the matching of the energy levels; and the parity of the wavefunction. All these features are tunable in the QD molecules, while they are untunable in the natural molecules.

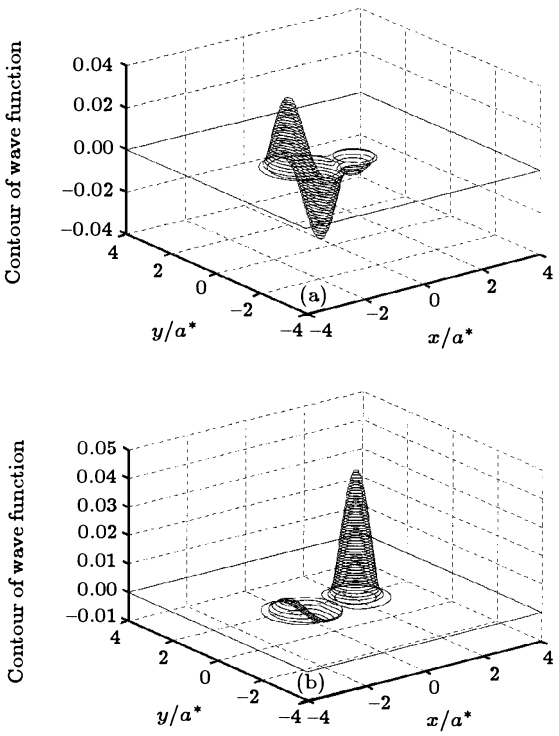


Fig.6. Wavefunctions of the ionic bond states E_2 and E_4 when the potential barrier is 120Ry*, with $d = 1.7a^*$.

3. Conclusions

From the above results, we conclude that both ionic bonds and covalent bonds can exist in the two-QD molecules under different conditions. These conditions of forming ionic bond, covalent bond, and mixed states in the QD molecules are summarized as follows:

1. There will be an ionic bond state in QD molecules under one of the following conditions:

(a) energy levels in different QDs do not match;

(b) the symmetry of the wavefunction in QDs is different from that in the proximate dots;

(c) the height or thickness of the potential barrier between two dots is very large.

2. There will be a covalent bond state in QD molecules as the energy levels in the different QDs match, and the symmetries of the wavefunctions corresponding to the matching energy levels are identical, and the potential barrier between QDs is neither thick nor high.

3. The mixed state, which possesses the properties of both covalent and ionic bonds, can be formed in QD molecules at intermediate potential barrier between QDs, when the energy levels of the two QDs match and their parities of corresponding wavefunctions are identical.

Our results show the multiformity (covalent, ionic, or "intermediate" states) and controllability (various parameters) of the QD molecules. These features cannot be realized in the natural molecule, and are instructive to fabricate desired QD molecules and to design quantum function devices.

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