Eur. Phys. J. B **29**, 141–145 (2002)
DOI: 10.1140/epjb/e2002-00272-0

**THE EUROPEAN
PHYSICAL JOURNAL B**

# Spin configuration transformation in laterally coupled few-electron artificial molecules

Zhenhong Dai[1,2,a], Jinzuo Sun[2], Lide Zhang[1], Maowang Lu[1], Zuohong Li[2], and Shiyong Huang[2]

[1] Institute of Solid State Physics, Chinese Academy of Science, PO Box 1129, Hefei, 230031, PR China
[2] CCAST(World Laboratory), PO Box 8730, Beijing 100080, PR China
Institute of Opto-Electronic Information Technology, YanTai University, 264005, PR China

Received 8 March 2002 / Received in final form 29 May 2002

**Abstract.** Artificial molecules, namely laterally coupled quantum dots with a three-dimensional spherical confinement potential well of radius $R$ and depth $V_0$ , were studied by the unrestricted Hartree-Fock-Roothaan (UHFR) method. By varying the distance $d$ between the centers of the two coupled quantum dots, the transition from the strong coupling situation to the weak one is realized. Hund's rule, suitable for a single quantum dot is destroyed in certain conditions in the artificial molecule. For example, in the few-electron system of the strongly coupled quantum-dot molecule, a transformation of spin configuration has been found.

**PACS.** 73.23.Hk Coulomb blockade; single-electron tunneling – 73.40.Gk Tunneling – 73.50.-h Electronic transport phenomena in thin films

Recent advances in nano-technologies have made it feasible to fabricate zero-dimensional structures called quantum dots(QDs) [1,2]. As quantum dots reveal atomic properties such as discrete energy levels and shell structures, they are often referred to as artificial atoms [3–5]. In contrast to natural atoms, the number of excess electrons $N$ embedded in these QDs are tunable. Therefore, these systems are ideal to study few-electron interaction effects, such as the shell effect [3] as a function of the QD radius and transformations in the ground-state spin configuration as a function of an external magnetic field [4]. Recently, quantum dots have been the subject of extensive experimental [5–8] and theoretical investigations [9–12].

Considering single quantum dots to now represent well understood systems [3-5], some more complex systems have been studied and it is conceivable and likely that these studies will be of use in future applications [8,13,14]. There have been extensive experimental studies about transport properties in multiple-dot systems [15,16], also known as artificial quantum-dot molecules (QDM) [14,17]. The advantages of QDM are the tunability of both the electron number and the coupling strength by appropriate design. The latter allows the investigation of transformations of electron spin configurations. A simple example of artificial molecules is analogous to a two-atom molecule, consisting of two coupled quantum dots side by side in a plane or on top of each other (lateral [16–18] or vertical [19–21] quantum-dot molecules, respectively). The increased interest in coupled quantum dots is indicated by the growing number of papers on this topic [13–21]. Experimentally, Austing *et al.* have measured addition spectra of vertical QDM in different coupling regimes [20]. Waugh *et al.* have studied the Coulomb blockade effects in lateral QDM [16] and found a conductance pattern similar to that of single quantum dots for strong coupling systems, whereas the weakly coupled systems showed a pair structure of conductance peaks. Theoretically, Rontani *et al.* have applied the exact diagonalization technique [18] and Andreas *et al.* have used the spin-density function theory (SDFT) to study coupled quantum dots [17]. Quantum-dot molecules with a harmonic confinement potential have also been studied by Yakimenko *et al.* [22] and Yannouleas *et al.* [23], and some valuable results have been obtained.

In this paper, we have investigated the excess electron ground-state filling structure of two laterally coupled (identical) quantum dots with a finite three-dimensional confinement potential using the unrestricted Hartree-Fock-Roothaan (UHFR) method. This method has been previously used to calculate the ground-state energy of single quantum dots [10–12], and in this case we applied it to the artificial molecule with a potential well of finite depth. We consider a system of excess electrons, which are confined in two laterally coupled spherical semiconductor QDs embedded in a matrix, as shown in the inset of Figure 1. The potential profile for this quantum-dot molecule is given by the following: the potential-well

---

[a] *Permanent address*: Department of Physics, Yantai University, 264005 PR China
e-mail: `zhdai@ytu.edu.cn`

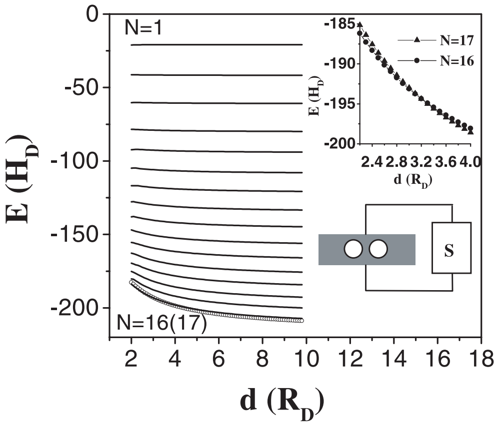

**Fig. 1.** Energy $E$ of the ground state corresponding to the artificial double-dot molecule for $V_0 = 25H_D$ as function of double quantum dot center distance $d$ for excess electron filling number $N = 1 - 17$. The radius of each single quantum dot is $1.0R_D$. The donor Hartree $H_D$ is the unit of energy, and the donor Bohr radius $R_D$ is the unit of distance. The upper inset on the right is the ground-state energy *vs.* $d$ for excess electron numbers $N = 16, 17$. The lower inset on the right is the two-dimensional schematic of a double quantum-dot molecule with a source of electrons S.

region inside the QD and the potential-barrier region in the surrounding matrix. The effective-mass Hamiltonian of $N$ excess electrons confined in the double quantum-dot molecule has the form

$$H = \sum_{i=1}^{N} h(\mathbf{r}_i) + \frac{1}{4\pi\varepsilon\varepsilon_0}\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}, \tag{1}$$

here, $\mathbf{r}_i$ is the position vector of $i$th electron, $r_{ij}$ is the electron-electron distance, $h(\mathbf{r}) = -(\hbar^2/2m^*)\nabla^2 + V(\mathbf{r})$ is the one-electron Hamiltonian with the confinement potential

$$V(\mathbf{r}) = \begin{cases} -V_0 \text{ if } |\mathbf{r}| < R \text{ or } |\mathbf{r}-\mathbf{d}| < R \\ 0 \qquad\qquad \text{otherwise.} \end{cases} \tag{2}$$

The origin of coordinates is in the center of the left quantum dot, the direction of vector $\mathbf{d}$ is from the center of the left quantum dot to that of the right one, and $|\mathbf{d}| = d$ is the center distance of two quantum dots, reflecting the coupling strength of QDM. $V_0 > 0$ represents the conduction-band discontinuity at the quantum well/barrier interface. The conduction-band minimum of the barrier material is set to zero and taken as a reference energy level. We neglect the change of effective mass and dielectric constant at the well/barrier interface.

The schrödinger equation for the $N$-electron system has been solved using the UHFR method. The $N$-electron wave function was taken as a single Slater determinant constructed from the one-electron spinorbitals of QDM

$$\varphi_i(\eta_j) = \psi_{\mu s}(\mathbf{r}_j)\chi_s(\sigma_j). \tag{3}$$

Here, $i, j = 1, \cdots, N$, $\eta = (\mathbf{r}, \sigma)$, $\sigma$ is the spin variable. Normally, in the Slater determinant, the artificial molecular orbital is a linear combination of single quantum-dot orbitals which are usually the spherical Bessel functions. However in order to solve expediently the many-center problem of electrons in the QDM, the spatial wave functions $\psi_{\mu s}$ of one-electron spinorbitals of QDM have been expanded into the Gaussian variational basis as follows:

$$\psi_{\mu s}(x, y, z) = \sum_{l_k m_k n_k k} C^{\mu s}_{l_k m_k n_k \xi} x^{l_k} y^{m_k} z^{n_k} \exp\left(-\xi_{lmnk} r_k^2\right), \tag{4}$$

where coefficients $C^{\mu s}_{l_k m_k n_k \xi}$ and exponential factors $\xi_{lmnk}$ are the variational parameters, and $r_k$ is the distance between an electron and the center of the $k$th quantum dot. This method is the famous Gauss basis simplification in quantum chemistry. Using the appropriate combinations of parameters $(lmnk)$, we can construct the quantum-dot molecule orbitals. The nonlinear parameters $\xi_{lmnk}$ ($l_k + m_k + n_k \leqslant 2$, $k = 1, 2$) account for the electron localization in the $k$th spherical quantum dot, and were determined by optimizing the ground-state energy to the minimum values in the single quantum dot. However, the linear variational parameters $C^{\mu s}_{l_k m_k n_k \xi}$ for all the occupied spin molecular orbitals were re-selected by the self-consistent iterative diagonalization of the UHFR equations in the whole artificial molecule system.

Throughout the present paper, the following units are used: the donor Hartree $H_D = (m_e H_y)/(m_{e0}\varepsilon_s^2)$ is the energy unit, and the donor Bohr radius $R_D = (m_{e0}/m_e)\varepsilon_s a_D$ is the length unit (where the hydrogen Hartree $H_y = 27.2107$ eV, the hydrogen Bohr radius $a_D = 0.0529$ nm, $\varepsilon_s$ is the static dielectric constant, $m_e$ is the electron conduction-band mass, and $m_{e0}$ is the free-electron rest mass). We neglect the difference in the dielectric constants of the quantum dot and matrix. For InAs/GaAs or AlGaAs/GaAs quantum dots, it is a reasonable approximation.

One of the important results obtained using the UHFR method is that, with the decrease in interdot distance $d$, the largest number of electrons filled in the two laterally coupled quantum dots is less than that filled in the uncouple case. According to our calculation results [10] and that of other authors [11,12], a spherical quantum dot with radius $R = 1.0R_D$ and $V_0 = 25H_D$ can contain at most 10 electrons, and therefore, it was estimated that the double quantum-dot molecule could contain up to 20 electrons. In order to study the characteristics of excess electron filling with the change of coupling strength between the two QDs, The radius of the quantum dots was fixed and the variation of the ground-state energy of the artificial molecule with the distance $d$ between the centers of two quantum dots was examined. The results are shown in Figure 1. The $N$-electron system confined in the QDM can form a bound state if the condition of binding $E_N < E_{N-1}$ is fulfilled, where $E_N$ and $E_{N-1}$ are the ground-state energies of the artificial molecule consisting of $N$ and $N-1$ excess electrons. With the increase of excess filling electron number $N$ from 1 to 17, the ground-state energies of electrons in the QDM are shown by the curves 1–17, respectively. From Figure 1 it can be seen that, for $N = 1 - 16$,

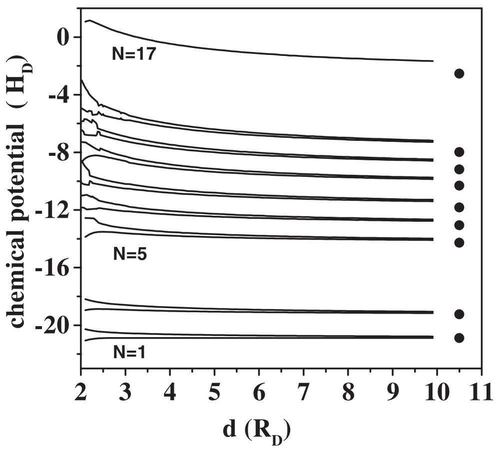

**Fig. 2.** Chemical potential of an $N$-electron artificial QDM as a function of the quantum-dot center distance $d$. All parameters of the molecule are the same as those used in Figure 1. The black circle dots on the right of the figure are the corresponding chemical potentials of a single quantum dot under the same conditions.

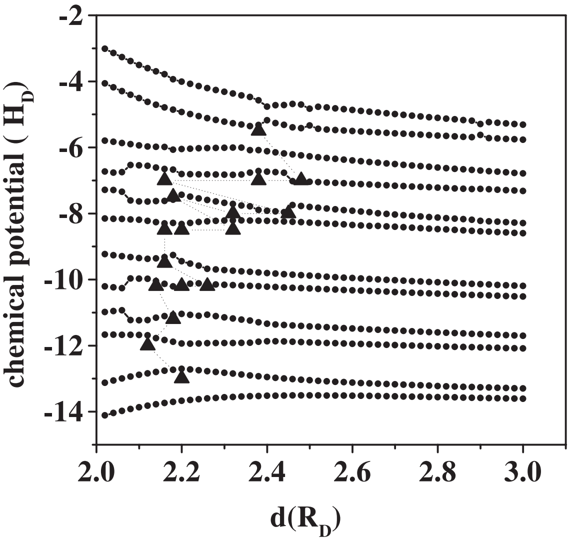

**Fig. 3.** Chemical potential of electrons in the second shell of the QDM as a function of the center distance $d$ of two quantum dots. All parameters of the QDM are the same as those of Figure 2. The sign $\Delta$ indicates the position of the spin configuration transformation.

the artificial molecule is stable. However, in the case of $N = 17$, when the center distance of the two quantum dots is approximately less than $3.0R_D$, the ground-state energy of the molecule is larger than that for $N = 16$. The subsequent addition of excess electrons is difficult. So, for excess electron number $N = 17$, a stable state of the system is unattainable for small values of d. In the strong coupling situation the greatest number of excess electrons filled in the two coupled quantum dots is sixteen.

The characteristic behavior associated with excess electron shell filling is also visible if we calculate the chemical potentials for the artificial molecules. The chemical potential of $N$-electron system is defined as $\mu_N = E_N - E_{N-1}$, where $|\mu_N|$ represents the amount of energy released when this N-electron artificial molecule is created, and where $E_N$ is the ground-state energy of the $N$-electron QDM. The $N$-electron artificial molecule is stable if the corresponding chemical potential is negative. The difference $\Delta E = \mu_{N+1} - \mu_N$, a quantity of experimental interest, represents the addition energy [4,11,12], which is the external energy required to add an excess electron to the $N$-electron artificial molecule system. $\Delta E$ is larger than the first excitation energy of the $N$-electron system, and is characteristic of excess electron filling. According to the normal electron filling rule for a single quantum dot, we calculated the chemical potentials of the double-dot molecule, and the results are shown in Figure 2. It can be seen that, in the weak coupling region, $d$ ranges from approximately $2.5R_D$ to $6.5R_D$. With the increase of excess electron numbers $N$, from $N = 5$ to 4 and from $N = 17$ to 16, the significant decrease of the chemical potential corresponds to the full electron filling of the first and the second shells, respectively. That is to say that there are four electrons in the first shell, twelve electrons in the second shell and the last one electron is added to the third shell. Also, from $N = 11$ to 10, the small decrease of $\mu_N$ corresponds to the electron half-filling of the second shell. On the other hand, the chemical potential curves display obvious pair form, which has been observed experimentally [16]. With the increase of $d$, the pair structure of the chemical potential curves in the molecule disappears gradually and spin close degenerate states appear. In the strongly coupled situation, that is where $d$ was a value in the range of approximately $2.0R_D$ to $2.5R_D$, even if the electron filling shows a shell structure, the half-filling of shells disappears, and the distribution of the chemical potential curves is irregular. Obviously, this is due to the strong electron interaction between the two quantum dots.

The important difference between artificial molecules and natural molecules is that, for an artificial molecule, as the shells are filled, it appears as if each single artificial atom is filled in turn. In the weak coupling situation, the first two filled electrons are polarized, which is opposite to the case of the unpolarized hydrogen molecule. The reason for this may be due to the essentially different physical properties between the confinement potential of the artificial atom and coulomb attractive potential of natural atom nucleus. In the artificial molecule, when coupling between the two QDs of the QDM, the first two electrons prefer to locate in different dots in order to maximize the system stabilities, and their spin is parallel.

The results shown in Figure 2 are based on Hund's rule, The breakdown of Hund's rule has not been considered, but in fact, in the strongly coupled situation, Hund's role governing the electron spin configuration is destroyed. Our results show, commencing with the second shell, when the center distance between the two quantum dots is less than certain values, the electron spin configurations of the molecule do not exactly obey the normal Hund's rule. In Figure 3, the detailed calculation results of the chemical potentials for the excess electrons of the second shell are presented. In generating the chemical

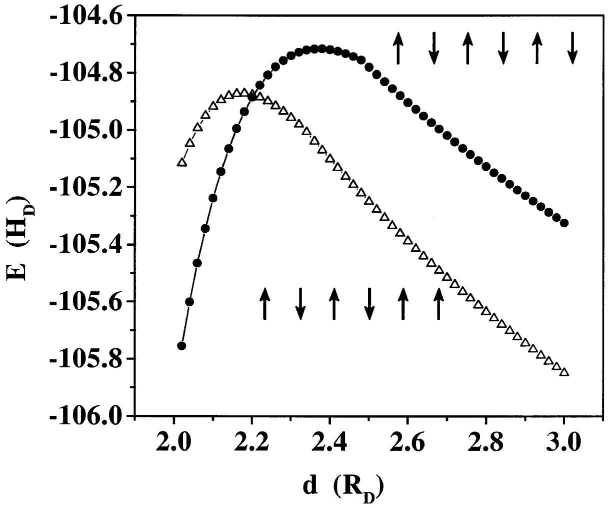

**Fig. 4.** The ground-state energy $E$ for excess electron filling number $N = 6$ in the QDM *vs.* the distance $d$ of double quantum dot centers. Two curves correspond to the two different electron spin configurations indicated. The parameters of the QDM are the same as those of Figure 1.

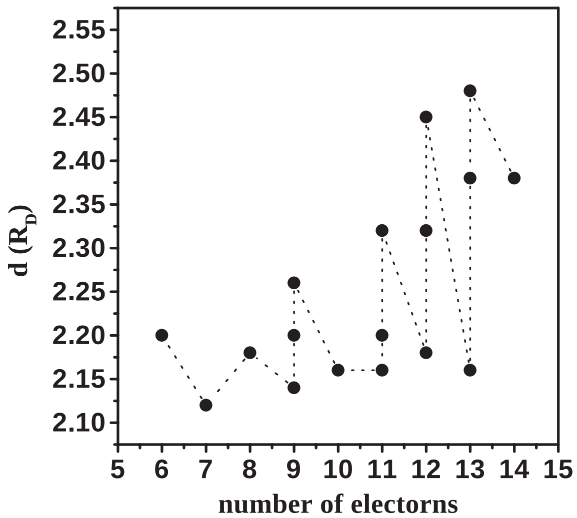

**Fig. 5.** The center distance $d$ of the two quantum dots of the QDM, where spin configuration transformation occurs, as a function of the number of excess filling electrons, where $d$ is the distance between the two quantum dot centers. All parameters of the QDM are the same as those of Figure 1.

potential values for the center distances of the quantum dots considered, the electrons have been added while ensuring that the ground-state energy of the spin configuration has a minimum value. In the strong coupling region, Hund's rule has been destroyed due to composite influence of a) the strong interdot electron interaction, b) the small spacing between discrete energy levels arising from the confining potential, and c) the electron exchange interaction, as shown in Figure 3. We use $\Delta E$ to represent the energy reduction due to the exchange interaction between electrons with parallel spins. The ground-state energy of the artificial molecule can be lowered by $\Delta E$ if the electrons of the second shell have parallel spins with different angular momenta rather than anti-parallel spins with the same angular momentum. However, in the strong coupling case, when the energy difference of two electrons with parallel spins and different angular momenta in the molecule is larger than their exchange energy, the above exchanging effect is negated. In this case, the two electrons tend to place themselves at the lowest energy with antiparallel spins and the same angular momentum. In Figure 4, the ground-state energy of the molecule consisting of six excess electrons is shown. At the crossing point of the two curves, the transformation of the electron spin configuration occurs in order to obtain the most stable, few-electron artificial molecule system.

The transformation of the spin configuration is dependent on the number of the electrons and the center distance of two quantum dots. In Figure 5, we show the distance of the two quantum dots at the point where the electron spin configuration is changed, as a function of the number of electrons. From Figure 5, it is clear that the transformation of spin configuration is not pronounced when the shell is half-filled, such as in the case of excess electron number $N = 9, 12$ and $13$. Where the shell is fully filled, there is no spin configuration transformation.

In conclusion, our results may be summarized as follows. Hund's rule applies when the interaction-induced exchange energy is larger than the splitting of the energy levels in the left and right dot, since the latter decays exponentially and the former only algebraically with increasing $d$. So it is clear that Hund's rule applies for large $d$ but does not hold when d becomes small. On the other hand, the situation in artificial molecules is very different from that in natural molecules. In the weak coupling situation, it seems certain that the electronic filling pattern of the double-dot artificial molecule is best represented by alternate electron filling into the two different single quantum dots. As a result of the electron interaction between the quantum dots, the chemical potential of each single quantum dot splits into two in the molecule and the excess electron fillings follows Hund's rule, the chemical potential curves display pair form, and finally evolve to a narrow, nearly degenerate state, which indicates that, in the very weakly coupled molecules, the interdot electron interaction is negligible. In the case of strong coupling, we have discovered the transformation of electron spin configuration, and while the shell structure is retained, the sub-shell structure disappears. It should be noted that, in Figure 3, at a certain d values, there exists sudden variations in the chemical potential curves. It is natural to consider the occurrence of a spin configuration transformation at these points, but in fact, according to our calculation results, the spin configuration transition occur elsewhere. In this case, the effect of the distance $d$ of the two quantum dots is similar to that of the radius $R$ in single quantum dot, and of course this effect will require further study.

This work was supported by the National Foundation of Natural Science in China Grants No 10074064.

## References

1. M.A. Kastner, Rev. Mod. Phys. **64**, 849 (1992)
2. N.F. Johnson, J. Phys. Cond. Matt. **7**, 965 (1995)
3. S. Tarucha, D.G. Austing, T. Honda, Phys. Rev. Lett. **77**, 3613 (1996)
4. L.P. Kouwenhoven, T.H. Oosterkamp, M.W.S. Danoesastro, M. Eto, D.G. Austing, T. Honda, S. Tarucha, Science **278**, 1788 (1997)
5. U. Banin, Yunwei Cao, D. Katz, O. Millo, Nature **400**, 542 (1999)
6. B.T. Miller, W. Hansen, S. Manus, R.J. Luyken, *et al.*, Phys. Rev. B **56**, 6764 (1997)
7. D.M.T. Kuo, Yia-Chung Chang, Phys. Rev. B **61**, 11051 (2000)
8. N. Takahashi, H. Ishikuro, T. Hiramoto, Appl. Phys. Lett. **76**, 209 (2000)
9. D. Giuliano, A. Tagliacozzo, Phys. Rev. Lett. **84**, 4677 (2000)
10. Zhenhong Dai, Jinzuo Sun, Lide Zhang, *et al.*, Chin. Phys. Lett. **19**, 117 (2002)
11. S. Bednarek, B. Szafran, J.A. Damowski, Phys. Rev. B **59**, 13036 (1999)
12. B. Szafran, J.A. Damowski, S. Bednarek, Phys. Rev. B **61**, 1971 (2000)
13. C.T. Black, C.B. Marray, R.L. Sandstrom, Shouheng Sun, Science **290**, 1131 (2000)
14. J.P. Mccaffrey, M.D. Robertson, S. Fafard, Z.R. Wasilewski, E.M. Griswold, L.D. Madsen, J. Appl. Phys. **85**, 2272 (2000)
15. R. Ziegler, C. Bruder, H. Schoeller, Phys. Rev. B **62**, 1961 (2000)
16. F.R. Waugh, M.J. Berry, D.J. Mor, R.M. Westervelt, K.L. Campman, A.C. Gossard, Phys. Rev. Lett. **75**, 705 (1995)
17. A. Wensouer, O. Steffens, M. Suhrke, U. Rossler, Phy. Rev. B **62**, 2605 (2000)
18. M. Rontani, R. Rossi, F. Manghi, E. Molinari, Solid State Commun. **112**, 151 (1999)
19. H. Imamura, P.A. Maksym, H. Aoki, Phys. Rev. B **59**, 5817 (1999)
20. D.G. Austing, S. Tarucha, Physica B **151**, 249 (1998)
21. B. Partoens, F.M. Peeters, Phys. Rev. Lett. **84**, 4433 (2000)
22. I.I. Yakimenko, A.M. Bychkov, K.F. Berggren, Phy. Rev. B **63**, 165309 (2001)
23. C. Yannouleas, U. Landman, Phys. Rev. Lett. **82**, 5325 (1999)