

Singlet-triplet splitting, correlation, and entanglement of two electrons in quantum dot molecules

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Starting with an accurate pseudopotential description of the single-particle states, and following by configuration-interaction treatment of correlated electrons in vertically coupled, self-assembled InAs/GaAs quantum dot molecules, we show how simpler, popularly practiced approximations, depict the basic physical characteristics including the singlet-triplet splitting, degree of entanglement (DOE), and correlation. The mean-field-like single-configuration approaches such as Hartree-Fock and local spin density, lacking correlation, incorrectly identify the ground-state symmetry and give inaccurate values for the singlet-triplet splitting and the DOE. The Hubbard model gives qualitatively correct results for the ground-state symmetry and singlet-triplet splitting, but produces significant errors in the DOE because it ignores the fact that the strain is asymmetric even if the dots within a molecule are identical. Finally, the Heisenberg model gives qualitatively correct ground-state symmetry and singlet-triplet splitting only for rather large interdot separations, but it greatly overestimates the DOE as a consequence of ignoring the electron double occupancy effect.

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I. INTRODUCTION

Two vertically^{1,2} or laterally³ coupled quantum dots containing electrons, holes, or an exciton constitute the simplest solid structure proposed for the basic gate operations of quantum computing.^{4,5} The operating principle is as follows: when two dots couple to each other, bonding and antibonding “molecular orbitals” (MOs) ensue from the single-dot orbitals $\{i_j\}$ of the top (T) and bottom (B) dots: $\psi(\sigma_g) = \psi_T(s) + \psi_B(s)$ is the σ -type bonding and $\psi(\sigma_u) = \psi_T(s) - \psi_B(s)$ is the σ -type antibonding state. Similarly, $\psi(\pi_u) = \psi_T(p) + \psi_B(p)$ and $\psi(\pi_g) = \psi_T(p) - \psi_B(p)$ are the “ π ” bonding

interdot separation. The unrestricted (U) HF (Ref. 11) corrects some of the problems of RHF by relaxing the requirement of (i) two electrons of different spins occupying the same spatial orbital, and (ii) the single-particle wave functions have the symmetry of the external confining potential. The UHF-EMA correctly give the singlet lower in energy than the triplet,¹² and can also predict Mott localization of the electrons in the dot molecule, which breaks the many-particle symmetry.¹¹ However, since in UHF, the symmetry-broken wave functions are only the eigenstates of the z component of total spin $S=s_1+s_2$, but not of S^2 , the UHF-EMA incorrectly mixes the singlet and triplet.^{11,12} For the simple case of dot molecules having inversion symmetry, (e.g., molecules made of spherical dots but not of vertical lens-shaped dots), assuming EMA and neglecting spin-orbit coupling, there is an *exact* symmetry. For this case, Refs. 16 and 17 indeed were able to project out the eigenstates of S^2 , yielding good spin quantum numbers and lower energy. However, for vertically coupled lens shaped quantum dots (i.e., realistic self-assembled systems) ~~even for spherical dots, but in the~~

$V_{\text{ps}}(\mathbf{r}) = \sum_{n,\alpha} v_{\alpha}(\mathbf{r} - \mathbf{R}_{n,\alpha})$. The pseudopotentials used for InAs/GaAs are identical to those used in Ref. 27 and were tested for different systems.^{23,27,28} We ignored spin-orbit coupling in the InAs/GaAs quantum dots, since it is extremely small for electrons treated here (but not for holes which we do not discuss in the present work). Without spin-orbit coupling, the states of two electrons are either pure singlet or pure triplet. However, if a spin-orbit coupling is introduced, the singlet state would mix with triplet state.

Equation (1) is solved using the “linear combination of Bloch bands” (LCBB) method,²⁹ where the wave functions ψ_i are expanded as

$$\psi_i(\mathbf{r}) = \sum_{n,\mathbf{k}} \sum_{\lambda} C_{n,\mathbf{k}}^{(\lambda)} \phi_{n,\mathbf{k},\vec{\epsilon}}^{(\lambda)}(\mathbf{r}). \quad (2)$$

In the above equation, $\{\phi_{n,\mathbf{k},\vec{\epsilon}}^{(\lambda)}(\mathbf{r})\}$ are the bulk Bloch orbitals of band index n and wave vector \mathbf{k} of material λ (=InAs, GaAs), strained uniformly to strain $\vec{\epsilon}$. The dependence of the basis functions on strain makes them variationally efficient. (Note that the potential V

A. Level-1 theory: All-bound-state configuration interaction

where ϵ_g and ϵ_u are the single-particle energy levels for the MOs $|\sigma_g\rangle$ and $|\sigma_u\rangle$, respectively. In the absence of spin-orbit coupling, the triplet states $|a\rangle$ and $|b\rangle$ are not coupled to *any* other states, as required by the total spin conservation, and thus they are already eigenstates. The rest of the matrix can be solved using the integrals calculated from Eq. (4). The results of the 6×6 problem were compared (not shown) to the all-bound-state CI results: We find that the Σ states of level-2 theory are very close to those of the all-bound-state CI calculations, indicating a small coupling between σ and π orbitals in the *strong confinement* region. We thus do not show graphically the results of level 2. However, since we use only σ orbitals, the Π states of level 1 [Fig. 5(a)] are absent in level-2 theory. Especially, the important feature of crossover between Σ and Π_u states at 4 and 4.5 nm is missing.

C. Level-3 theory: Single-configuration in the molecular basis

As is well known, mean-field-like treatments such as RHF and LSD usually give incorrect dissociation behavior of molecules, as the correlation effects are not adequately treated. Given that RHF and LSD are widely used in studying QMDs,^{10,13,14} it is important to understand under which circumstance the methods will succeed and under which cir-

$$e_\eta = \langle \eta | \hat{T} | \eta \rangle = \sum_i U_{\eta,i}^* U_{\eta,i} \epsilon_i, \quad (15)$$

$$t_{\eta_1 \eta_2} = \langle \eta_1 | \hat{T} | \eta_2 \rangle = \sum_i U_{\eta_1,i}^* U_{\eta_2,i} \epsilon_i, \quad (16)$$

where ϵ_i is the single-particle level of the i th *molecular* orbital, and \hat{T} is kinetic energy operator. Using the transformation of Eq. (15), Eq. (16), and Eq. (B2), we calculate all parameters of Eq. (13). Figure 7(a) shows the effective single-dot energy of the “ s ” orbitals obtained in the Wannier representation for both top and bottom dots. We see that the effective single-dot energy levels increase rapidly for small d . Furthermore, the energy levels for the top and bottom orbitals are split due to the strain asymmetry between the two dots. We compute the Coulomb energies J_{TT} , J_{BB} of the “ s ” orbitals on both top and bottom dots, and the interdot Coulomb and exchange energies J_{TB} and K_{TB} and plot these quantities in Fig. 7(b). Since J_{TT} and J_{BB} are very similar, we plot only J_{TT} . As we can see, the Coulomb energies of the dot-centered orbitals are very close to the Coulomb energy of the s orbitals of an *isolated* single dot (dashed line). The interdot Coulomb energy J_{TB} has comparable amplitude to J_{TT} and decays slowly with distance, and remain very significant, even at large separations. However, the exchange energy between the orbitals localized on the top and bottom dot K_{TB} is extremely small even when the dots are very close.

2. “First-principles” Hubbard model and Heisenberg model: Level 4

In level-4 approximation, we use only the “ s ” orbital in each dot. Figure 1(b) shows all possible many-body basis functions of two electrons, where the top and bottom dots are denoted by “ T ” and “ B ,” respectively. The Hamiltonian in this basis set is

Coulomb integrals in the new basis set are given by Eq. (B2), while other quantities including the effective single-particle levels e_η for the η th dot-centered orbital, and the coupling between the η_1 th and η_2 th orbitals $t_{\eta_1 \eta_2}$ can be obtained from

$$H = \begin{pmatrix} e_T + e_B + J_{\text{TB}} - K_{\text{TB}} & 0 & 0 & 0 & 0 & 0 \\ 0 & e_T + e_B + J_{\text{TB}} - K_{\text{TB}} & 0 & 0 & 0 & 0 \\ 0 & 0 & e_T + e_B + J_{\text{TB}} & -K_{\text{TB}} & t - \tilde{\Gamma}_{\text{BB}}^{\text{TB}} & t - \tilde{\Gamma}_{\text{TT}}^{\text{TB}} \\ 0 & 0 & -K_{\text{TB}} & e_T + e_B + J_{\text{TB}} & -t + \tilde{\Gamma}_{\text{BB}}^{\text{TB}} & -t + \tilde{\Gamma}_{\text{TT}}^{\text{TB}} \\ 0 & 0 & t - \tilde{\Gamma}_{\text{TB}}^{\text{BB}} & -t + \tilde{\Gamma}_{\text{TB}}^{\text{BB}} & 2e_B + J_{\text{BB}} & 0 \\ 0 & 0 & t - \tilde{\Gamma}_{\text{TB}}^{\text{TT}} & -t + \tilde{\Gamma}_{\text{TB}}^{\text{TT}} & 0 & 2e_T + J_{\text{TT}} \end{pmatrix}, \quad (17)$$

where $t = t_{\text{TB}}$ and to simplify the notation, we ignore the orbital index “ s ”

model by assuming $e_T=e_B=\epsilon$; $J_{TT}=J_{BB}=U$; and let $J_{TB}=V$, $K_{TB}=K$. We can then solve the simplified eigenvalue equation analytically. The eigenvalues of the above Hamiltonian are (in order of increasing energy):

(i) ground-state singlet $^1\Sigma_g^{(a)}$,

$$E = 2\epsilon + \frac{1}{2}[U + V + K - \sqrt{16t^2 + (U - V - K)^2}]; \quad (18)$$

(ii) triplet states (threefold degenerate) $^3\Sigma_u$,

$$E = 2\epsilon + V - K; \quad (19)$$

(iii) singlet $^1\Sigma_u$,

$$E = 2\epsilon + U; \quad (20)$$

(iv) singlet $^1\Sigma_g^{(b)}$,

$$E = 2\epsilon + \frac{1}{2}[U + V + K + \sqrt{16t^2 + (U - V - K)^2}]. \quad (21)$$

In the Hubbard limit where Coulomb energy $U \gg t$, the singlet-triplet splitting $J_{S-T} = E(^3\Sigma) - E(^1\Sigma_g) \sim 4t^2/(U - V)$, which reduces the model to the Heisenberg model

$$H = \frac{4t^2}{U - V} \vec{S}_T \cdot \vec{S}_B, \quad (22)$$

where \vec{S}_T and \vec{S}_B are the spin vectors on the top and bottom dots. The Heisenberg model gives the correct order for singlet and triplet states. The singlet-triplet splitting $J_{S-T} = 4t^2/(U - V)$ is plotted in Fig. 5(c) and compared to the results from all-bound-state CI calculations (level 1), and single-configuration approximations (level 3). As we can see, at $d > 6.5$ nm, the agreement between the Heisenberg model with CI is good, but the Heisenberg model greatly overestimates J_{S-T} at $d < 6$ nm.

E. Comparison of pair-correlation functions for level-1 to 4 theories

In the previous sections, we compared the energy levels of two-electron states in several levels of approximations to all-bound-state CI results (level 1). We now provide further comparison of level-1–4 theories by analyzing the pair-correlation functions and calculating the electron-electron entanglement at different levels of approximations.

In Fig. 8 we show the pair-correlation functions of Eq. (6) for the $^1\Sigma_g^{(a)}$ and $^1\Sigma_g^{(b)}$ states at $d \sim 7$ nm for level-1 and level-3 theories. The correlation functions give the probability of finding the second electron when the first electron is fixed at the position shown by the arrows at the center of the bottom dot (left-hand side of Fig. 8) or the top dot (right-hand side of Fig. 8). Level-1 and level-2 theories give correlation-induced electron localization at large d : for the $^1\Sigma_g^{(a)}$ state, the two electrons are localized on different dots, while for the $^1\Sigma_g^{(b)}$ state, both electrons are localized on the same dot.²⁴ In contrast, level-3 theory shows delocalized states because of the lack of configuration mixing. This problem is shared by RHF and LSD approximations.

F. Comparison of the degree of entanglement for levels-1 to 4 theories

The DOE of the four “ Σ ” states are plotted in Fig. 9 for level-1, level-3, and level-4 theories; the DOEs of level-2 theory are virtually identical to those of level-1 theory, and are therefore not plotted. We see that the Hubbard model has generally reasonable agreement with level-1 theory while the DOEs calculated from level-3 and level-4 (Heisenberg model) theories deviate significantly from the level-1 theory, which is addressed below.

(i) *The $^1\Sigma_g^{(a)}$ state:* The level-1 theory [culated dThec.3548Q0.315.3]

of the $^1\Sigma_g^{(a)}$ state in RHF and LSD approximations are also zero as a consequence of lack of correlation. In contrast, the Heisenberg model of level-4 theory gives $\mathcal{S}(^1\Sigma_g^{(a)})=1$. This is because the Heisenberg model assumes that the both electrons are localized on different dots with zero double occupancy, and thus overestimates the DOE.^{24,45}

(ii) *The $^1\Sigma_g^{(b)}$ state:* The Hubbard model gives the DOE of the $^1\Sigma_g^{(b)}$ state identical to that of $^1\Sigma_g^{(a)}$ state. This is different from the result of level-1 theory, especially at large inter-dot separations. The difference comes from the assumption in the Hubbard model that the energy levels and wave functions on the top dot and on the bottom dot are identical while as discussed in Ref. 24, the wave functions are actually asymmetric due to inhomogeneous strain in the real system. At $d > 8$ nm, the $^1\Sigma_g^{(b)}$

product of single-particle wave functions. An entangled system displays nonlocality which is one of the properties that distinguishes it from classic systems. So far, the only well established theory of entanglement pertains to two *distinguishable* particles,^{32,34} (e.g., electron and hole). For a system made of two distinguishable particles (A, B), the entanglement can be quantified by von Neumann entropy of the partial density matrix of either A or B ,³¹⁻³³

=0. In our approach, the maximum entanglement that a state can have is $\mathcal{S}=\log_2 N$, where N is the number of single-particle states.

(ii) The DOE measure of Eq. (A9)

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