Molecular Quantum Entanglement in Functionalized Semiconductor Nanostructures

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The feasibility of creating molecular quantum entanglement in functionalized semiconductor nanostructures is computationally demonstrated. Entangled hole states, localized deep in the semiconductor band gap, are generated by electron-hole pair separation after photoexcitation of molecular surface complexes. The approach is illustrated for model arrays of catechol molecules anchored to small TiO$_2$-anatase nanostructures. It is shown that molecular quantum entanglement can persist for hundreds of picoseconds in spite of thermal motion and surface disorder, under cryogenic and vacuum conditions. Moreover, it is shown that the relaxation dynamics of the entangled states can be coherently controlled by a sequence of ultrashort 2π pulses.

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A general model of a quantum computer can be envisioned as an array of two-level systems, representing quantum bits (qubits), where quantum computations are implemented according to one- and two-qubit unitary transformations [1]. Entanglement of such qubits is, however, crucial to achieve the desired exponential speedup of quantum algorithms relative to their corresponding classical analogs [2]. Therefore, the problem of creating and manipulating entangled states in real application devices is an important scientific and technological challenge.

The feasibility of creating and coherently controlling molecular quantum entanglement in model arrays of catechol molecules, anchored to TiO$_2$-anatase nanostructures (see Fig. 1) is computationally demonstrated in this Letter. Such functionalized semiconductors are inexpensive and readily available materials, already implemented in a wide range of technological applications (e.g., Grätzel solar cells [3]). Moreover, the present model system has been investigated both theoretically [4] and experimentally [5, 6] and serves as a prototype of aromatic anchoring ligands, upon which a wide range of molecular structures can be attached for specific applications [7].

Semiconductor functionalization involves the adsorption of molecules on a semiconductor surface and the formation of surface complexes. The complexes usually introduce electronic states in the semiconductor band gap that sensitize the host material for photo-absorption at frequencies characteristic of the molecular adsorbates (see Fig. 2). Photoexcitation of a surface complex results in interfacial electron transfer, through sub-picosecond electron-hole pair separation (see Fig. 2), when there is

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suitable energy match between the photoexcited molecular state in the adsorbate and the electronic states in the conduction band of the semiconductor material [4, 8, 9]. The injected electron then thermalizes in the conduction band, leaving a hole in the surface complex. Under off-resonance conditions relative to the semiconductor energy bands, the hole state can relax only to near-resonant states in impurities or neighboring adsorbate molecules coupled by the common host substrate. Therefore, the off-resonance condition hinders electron-hole recombination and stabilizes the hole within the monolayer of adsorbate molecules. This Letter investigates the relaxation dynamics of hole states, after electron-hole separation, in a realistic model of functionalized semiconductor nanostructures under cryogenic and vacuum conditions.

The model system is constructed by extending three identical supercell units along the [-101] direction of the TiO$_2$-anatase structure (see Fig. 1). The model system contains a total of 372 atoms, including 96 [TiO$_2$] units and three catechol molecules adsorbed on the (101) surface of a TiO$_2$-anatase nanostructure. The nanostructure extends over 30.66 Å × 15.13 Å × 30.95 Å along the [-101], [010] and [101] directions, respectively. For further reference, the central adsorbate molecule is labeled C while the adsorbate molecules on the left and right are labeled L and R, respectively.

Adjacent adsorbate molecules are 10.23 Å apart from each other, modeling a typical monolayer density of approximately 1 catechol molecule per 155 Å$^2$ (i.e., ∼1 µmol m$^{-2}$). The model system is initially prepared, as described in Ref.[4], by geometry optimization using the Vienna Ab-initio Simulation Package (VASP/VAMP) [10]. The package implements the Density Functional Theory (DFT) in a plane wave basis set, making use of the Perdew-Wang [11] generalized gradient approximation (GGA) for the exchange-correlation functional and ultrasoft Vanderbilt pseudopotentials for modeling the core electrons [12].

In order to investigate the relaxation dynamics after photoexcitation of the system, representative nuclear trajectories are obtained by carrying out ab initio-DFT molecular dynamics simulations at 100 K. The electronic relaxation is described according to a tight-binding model Hamiltonian gained from the Extended Hückel (EH) approach [13, 14], in the basis of Slater type orbitals for the radial part of the atomic orbital (AO) wavefunctions. The basis set includes the 4s, 3p and 3d atomic orbitals of Ti$^{4+}$ ions, the 2s and 2p atomic orbitals of O$^{2-}$ ions, the 2s and 2p atomic orbitals of C atoms and the 1s atomic orbitals of H atoms. Due to thermal nuclear motion, the AOs \( \{|k_i(t)\} \) form a time-dependent nonorthogonal basis set, with \( S_{ij}(t) = \langle k_i(t)|k_j(t) \rangle \) as the time-dependent overlap matrix elements.

The time-dependent electronic wavefunction

\[
|\Psi(t)\rangle = \sum_q B_q(t)|\phi_q(t)\rangle,
\]

is propagated in the representation of molecular orbitals (MOs) \( |\phi_q(t)\rangle = \sum_i C_{i,q}(t)|k_i(t)\rangle \) — i.e., the instantaneous eigenstates of the generalized eigenvalue equation \( H(t)C(t) = S(t)C(t)E(t) \), with instantaneous eigenvalues \( E_q(t) \). The propagation scheme recursively applies the time evolution operator as defined by the short-time approximation,

\[
|\Psi(t + \tau/2)\rangle \approx \sum_q B_q(t)e^{-\frac{i}{\hbar}E_q(t)\tau/2}|\phi_q(t)\rangle,
\]

where the expansion coefficients

\[
B_q(t + \tau) = \sum_p B_p(t)e^{-\frac{i}{\hbar}[E_p(t)+E_q(t+\tau)]\tau/2}
\]

\times|\phi_q(t+\tau)\rangle|\phi_p(t)\rangle,
\]

are approximated as follows,

\[
B_q(t + \tau) \approx B_q(t)e^{-\frac{i}{\hbar}[E_q(t)+E_q(t+\tau)]\tau/2},
\]

for sufficiently small propagation time slices \( \tau \).

The initial hole state, after photoexcitation of the central (C) surface-complex, is predominantly the Highest Occupied Molecular Orbital (HOMO) of the adsorbate molecule in C. Its subsequent relaxation dynamics is quantitatively described in terms of the time-dependent hole populations \( \rho_\alpha(t) \) of molecular adsorbates \( \alpha = (L,C,R) \). The time-dependent hole populations \( \rho_\alpha(t) \) are computed by projecting the time-evolved wavefunction onto the atomic orbitals of \( \alpha \)

\[
\rho_\alpha(t) = |\sum_{i\in\alpha} \sum_j A_i(t)^* S_{ij}(t) A_j(t)|,
\]

where the sum over \( j \) includes all atomic orbitals in the nanostructure, whereas the sum over \( i \) includes only the atomic orbitals of \( \alpha \). The coefficients \( A_i(t) \), introduced by Eq. (6), are the expansion coefficients of the time-evolved wavefunction in the AO representation \( \{|k_i(t)\} \)

\[
A_i(t + \tau) = \sum_q C_{i,q}(t + \tau) B_q(t + \tau).
\]

Figure 3 shows the evolution of the time-dependent populations \( \rho_\alpha(t) \), with \( \alpha = (L,C,R) \), during the first 50 ps of dynamics. Thin lines in Fig. 3 report results for a representative nuclear trajectory and thick lines represent averages over initial conditions. Note that, according to the results reported in Fig. 3, the hole tunnels from one adsorbate molecule to the other and remains localized in the monolayer of adsorbate molecules throughout the whole simulation time. Therefore, Fig. 3 indicates that the relaxation dynamics of the hole is significantly different from the relaxation dynamics of the photoexcited electron which is rapidly injected into the semiconductor material (see inset in Fig. 2). The calculated hole-tunneling period, obtained from Fig. 3, is \( T \approx 42 \) ps and has an exponential dependence with the separation between molecular adsorbates. These results
are consistent with a super-exchange hole transfer mechanism mediated by the semiconductor host substrate. Note that there is negligible overlap between the AOs of nearby adsorbate molecules, since the adsorbates are anchored to the semiconductor surface more than 10 Å away from each other. Therefore, (near-resonant) electronic states localized in different adsorbate molecules are only indirectly coupled by the common semiconductor host-structure. It is important to mention that the asymmetric nature of the underlying relaxation dynamics (as evidenced by the asymmetric population of the R and L adsorbates) is primarily due to the intrinsic asymmetry of the substrate environments that interact with the adsorbates. Such small differences in local environments determine asymmetric couplings between molecular adsorbates and a preferential direction for the hole motion.

An approximate description of the underlying hole-tunneling dynamics, for a pair of adsorbate molecules \( j \) and \( k \), coupled by the host substrate, can be given in terms of the Rabi formulae: 
\[
\rho_j(t) = \frac{\gamma_{jk}}{2\pi} \sin^2 \left( \Gamma_{jk} t \right)
\]
and 
\[
\rho_k(t) = 1 - \rho_j(t).
\]

The parameter \( \Gamma_{jk} = \left[ (\gamma_{jk}^2/\hbar^2) + (\omega_{jk}/2)^2 \right]^{1/2} \) is the Rabi frequency, \( \gamma_{jk} \) is the effective quantum coupling between resonant states and \( \omega_{jk} \) is the corresponding Bohr frequency. The parameters computed from Fig. 3 are \( \omega_{LC} \approx 4.5 \omega_{RC} \) and \( \gamma_{RC} \approx 1.12 \gamma_{LC} \).

Fig. 4 shows a detailed analysis of the early time relaxation dynamics for a representative nuclear trajectory. Most importantly, it is evidenced that the time-dependent hole populations \( \rho_\alpha(t) \) with \( \alpha = \{ C, R, L \} \) (top panel) are correlated with the motion of the molecular adsorbates (middle panel). That is, the adsorbate-semiconductor separation strongly modulates the electronic states responsible for relaxation of the initial excitation, since the adsorbate-semiconductor separation affects the time-dependent energy differences \( \varepsilon_{RC} \) and \( \varepsilon_{LC} \) between the initially populated state \( C \) and the near-resonant electronic states in the \( R \) and \( L \) adsorbates, respectively (bottom panel). The maximum population exchange, during the first 1ps of dynamics, is observed at approximately \( t=0.42 \) ps when the adsorbate-semiconductor separation reaches a maximum value. Therefore, moderate thermal fluctuations exert a strong influence on the hole relaxation by modulating the electronic couplings responsible for quantum dynamics.

The extent to which these results are significant is associated with the feasibility of manipulating the underlying coherent-quantum dynamics by implementing readily available femtosecond laser techniques. To this end, we examine coherent-control of the super-exchange hole tunneling dynamics by implementing a train of optical 2\( \pi \) pulses that successively generate a phase-shift of \( \pi \) in the initially populated state relative to an auxiliary state [15]. Considering that the pulses are much shorter than the time interval \( \tau_p \) between consecutive pulses, such a coherent-control scenario can be explicitly implemented by transforming the time-evolved wavefunction according to the unitary operation
\[
|\Psi(t)\rangle \longrightarrow |\Psi(t)\rangle - 2 \frac{\langle \Psi(0) | \Psi(t) \rangle^{\dagger} |\Psi(0)\rangle}{\langle \Psi(0) | \Psi(0) \rangle} |\Psi(0)\rangle,
\]
when a 2\( \pi \) pulse is applied at time \( t \).

Figure 5 shows the influence of such a coherent-control scheme on the underlying relaxation dynamics. The 2\( \pi \) pulses are applied at intervals \( \tau_p = 0.6 \) ps in the 20—60 ps time range. Notice that the intervals \( \tau_p \) are much shorter than the tunneling period \( T \approx 42 \) ps. The net effect of the pulses is to affect the interference phenomena responsible for the mechanism of super-exchange hole transfer, coherently keeping the populations of adsorbate molecules at approximately constant values. The tunneling process is, however, re-established at the end of
the coherent-control process. Therefore, this calculation demonstrates that coherences are preserved during the overall relaxation dynamics in spite of the nuclear thermal motion and the covalent coupling between the catechol adsorbate molecules and the semiconductor host substrate.

In summary, this Letter demonstrates the feasibility of creating and coherently controlling molecular quantum entanglement in a realistic model of functionalized semiconductor nanostructures. It is shown that entanglement of hole states, localized deep in the semiconductor band gap, can be created by photoexcitation of surface complexes and is preserved for long times despite the thermal nuclear motion and the intrinsic surface disorder, providing results of broad theoretical and experimental interest. Besides the direct implications on a general model of a quantum computer, the fundamental physics discussed in this Letter is central in a wide range of existing technological applications. In particular, it is predicted that super-exchange hole tunneling dynamics on a surface monolayer of adsorbate molecules significantly contributes to the overall photo-conductivity of TiO$_2$ at typical surface coverage levels under cryogenic and vacuum conditions.

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