

Modelling chemical reactions using semiconductor quantum dots

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Abstract – We propose the use of semiconductor quantum dots for simulating chemical reactions, as electrons are redistributed among such artificial atoms. We show that it is possible to achieve various reaction regimes and obtain different reaction products by varying the speed of voltage changes applied to the gates forming quantum dots. Considering the simplest possible reaction, $H_2 + H \rightarrow H + H_2$, we show how the necessary initial state can be obtained and what voltage pulses should be applied to achieve a desirable final product. Our calculations have been performed using the Pechukas gas approach, which can be extended for more complicated reactions.

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Detailed simulations of chemical and biological processes can provide crucial insight on these and help determining optimal experimental regimes and conditions. However, the high-accuracy modelling, at the quantum level, of even the simplest chemical reactions represents a significant challenge because it encompasses changes that involve the motion of electrons in the forming and breaking of chemical bonds. On classical computers, the resource requirements for the complete simulation of the time-dependent Schrödinger equation scale exponentially with the number of atoms in a molecule, imposing very severe limitations in the systems that can be modelled. However, recent developments of novel quantum computation schemes allow a polynomial scale of required resources. Via these approaches, a quantum system can simulate the behavior of another quantum system of interest (see, *e.g.*, [1–3]).

Semiconductor quantum dots can be described as artificial atoms (see, *e.g.*, [4]). These have discrete electron spectra revealing a shell structure and exchange corrections to the electron energies according to Hund's rules. In this sense, *coupled quantum dots* can be regarded as *artificial molecules* [5]. Depending on the tunnel coupling

strengths, electron distribution, and shell structure, the dots can form both ionic- and covalent-like bonds. Manifestations of these molecular states in double-dot structures were observed by numerous groups [6]. The idea of using the charge degrees of freedom in double-dot systems as a qubit has been proposed theoretically [7] and implemented experimentally [8].

Recent achievements in nanotechnology facilitate the precise control of the number of electrons in quantum dots and the tunnel energy splittings, by tuning the voltages applied to the gates [9]. Measuring the current through a quantum point contact in the vicinity of the structure allows the determination of the exact charge locations [10]. Moreover, structures with *three* coupled quantum dots have been recently fabricated and characterized [11,12] with the potential to easily increase the number of dots, as needed.

Based on these developments, we propose to employ the electron redistribution in coupled quantum dot systems for chemical reaction modelling. The number of electrons in the first and second quantum dot shells are 2 and 4, respectively. Accordingly, a quantum dot with one electron can be considered as an *artificial hydrogen atom*

(one electron vacancy in the outer shell) and a quantum dot containing four electrons can be viewed as an *artificial oxygen atom* (two electron vacancies in the outer shell). Consequently, the coupling of these three dots (which can be easily controlled by changing the gates' potentials) can model the covalent molecular bond formation between the four-electron dot and each of the one-electron dots. This would represent the hydrogen oxidation reaction, with the formation of an *artificial water molecule*. Increasing the number of dots would allow the modelling of more complicated reactions. Moreover, such *artificial chemical reactions* can be done under conditions (such as the presence of an external magnetic field) not readily accessible in all real molecules. Furthermore, the speed of the reactions could be easily varied in a very wide range. In quantum chemistry, calculations of chemical reactions usually employ the molecular Hamiltonian written in the second-quantized form [3],

$$H = \sum_{pq} \langle p|H_0|q \rangle a_p^\dagger a_q - \frac{1}{2} \sum_{pqrs} \langle pq|V_e|rs \rangle a_p^\dagger a_q^\dagger a_r a_s. \quad (1)$$

Here $a_p^\dagger(a_p)$ are Fermi operators responsible for a creation (annihilation) of an electron in a single-particle orbital $|p\rangle$, $|pq\rangle = |p\rangle \otimes |q\rangle$ is a two-electron state, H_0 is a single-particle Hamiltonian consisting of kinetic and nuclear attraction operators, and V_e is a term related to the electron-electron repulsion. The system of coupled quantum dots is characterized by a similar Hamiltonian. In the first step of the modelling, each single-particle atomic orbital of the molecules should be mapped into a single-particle orbital of the quantum dot system. Only the active states participating in the reaction must be selected. Afterwards we have to carefully choose control parameters for the dots (gate voltages, barriers heights, distances between dots, magnetic fields, etc.) with the aim of mapping the energy spectrum of the real molecules to the spectrum of the dots (with a fixed scale coefficient). The possibility to do this efficiently is supported by recent experiments [12] where four quantum states of three dissimilar semiconductor quantum dots were tuned in resonance to form multiple quadruple points on the stability diagram, thus demonstrating the fine tunability that quantum dot structures can achieve. Therefore, even though, contrary to three-dimensional atoms, the dots are quasi-two-dimensional objects, we believe that the proposed approach can qualitatively and sometimes quantitatively describe the outcome of real chemical reactions.

The Hamiltonian of the system under study can be separated into two parts

$$H(t) = H_0 + \lambda(t)V \quad (2)$$

where H_0 describes the invariant part and $\lambda(t)V$ is responsible for the reaction. The time dependence of the parameter $\lambda(t)$ can be chosen specifically for various reaction regimes. For small $\dot{\lambda} \equiv d\lambda/dt$ we have an adiabatic evolution, with the system following its

ground state during the reaction. For extremely large λ , the system's state remains unchanged; and for the intermediate case, several Landau-Zener transitions may occur at the avoided crossing points, with various states being populated after the reaction. It should be noted that even the "slow" evolution mentioned above must be faster than the decoherence time for the coupled quantum dots system, which is about 1 ns according to ref. [8]. In contrast to adiabatic quantum computing [13,14], where the aim is to keep the system either at or near its ground state, here we focus on a completely different issue: *how to control the population of desirable (not necessarily ground) states by changing the speed of evolution and the shape of $\lambda(t)$* . Harnessing the constructive features of the Landau-Zener effect allows us to travel more effectively in the whole Hilbert space, not only near its bottom part. From this point of view, the proposed approach can be considered as a step towards a better control of the quantum-mechanical state of the system, which is one of the broad objectives of quantum information processing.

The evolution of the instantaneous energy levels $E_n(\lambda)$ and eigenfunctions $|n\rangle$ of the Hamiltonian (2) can be exactly mapped [14] on the classical Hamiltonian dynamics of a 1D gas of fictitious particles (Pechukas gas [15]), with positions $x_n(\lambda) = E_n(\lambda)$ and momenta $v_n(\lambda) = V_{nn}(\lambda)$. The "particle repulsion" is determined by the additional set of variables, the "angular moments" $l_{mn}(\lambda) = [E_m(\lambda) - E_n(\lambda)]V_{mn}(\lambda)$:

$$\begin{aligned} \frac{d}{d\lambda} x_m &= v_m, \\ \frac{d}{d\lambda} v_m &= 2 \sum_{m \neq n} \frac{|l_{mn}|^2}{(x_m - x_n)^3}, \\ \frac{d}{d\lambda} l_{mn} &= \sum_{k \neq m,n} l_{mk} l_{kn} \left(\frac{1}{(x_m - x_k)^2} - \frac{1}{(x_k - x_n)^2} \right). \end{aligned} \quad (3)$$

Note that all the matrix elements in eq. (3) are taken between the instantaneous eigenstates of the Hamiltonian (2). The probabilities of the Landau-Zener transitions between states $m \leftrightarrow n$ is given by

$$p_{m,n} = \exp \left(- \frac{(\Delta_{\min}^{m,n})^3}{4\pi\hbar l_{mn} |\dot{\lambda}|} \right), \quad (4)$$

where $\Delta_{\min}^{m,n}$ is the minimal separation of levels at avoided crossing. We chose to use the Pechukas gas approach because of its potential scalability for systems with a large number of elements [14].

Here, we examine the simplest possible chemical reaction: the scattering of a hydrogen atom from a hydrogen molecule ($\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$), see fig. 1. Even though this reaction was performed and theoretically described for nearly a century, some details (not understandable without accurate modelling at the quantum level) were observed recently [16] (where the slightly different reaction, $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$, was studied). Although the reaction was dominated by a direct recoil mechanism

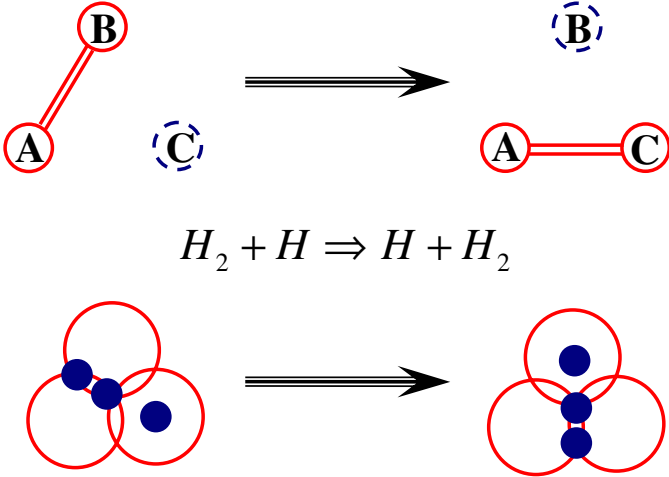


Fig. 1: (Color online) Schematic diagram of the $H_2 + H \rightarrow H + H_2$ reaction showing the bonds (upper panel) and the electron redistribution in the coupled quantum dot system (lower panel).

(when the incident hydrogen atom recoils along its original path after removing a deuterium atom to form a HD molecule), a second slower reaction mechanism occurs with a time delay of 25 fs. One of the possible explanations of such time delay is the formation of a metastable “quasi-bound” quantum state decaying into the reaction products. Such a system, with three nuclei and three electrons, can be mapped onto the triple-quantum-dot system with the Hamiltonian

$$H = H_{3D} + H_C + H_{\text{tun}}, \quad (5)$$

where

$$\begin{aligned} H_{3D} &= \sum_{S=1,2} (E_{AS}N_{AS} + E_{BS}N_{BS} + E_{CS}N_{CS}), \\ H_C &= U_A N_{A1} N_{A2} + U_B N_{B1} N_{B2} + U_C N_{C1} N_{C2} \\ &\quad + U_{AB} N_A N_B + U_{BC} N_B N_C + U_{AC} N_A N_C, \\ H_{\text{tun}} &= - \sum_{S=1,2} \left(\Delta_{AB} a_{AS}^\dagger a_{BS} + \Delta_{BC} a_{BS}^\dagger a_{CS} \right. \\ &\quad \left. + \Delta_{AC} a_{AS}^\dagger a_{CS} + \text{h.c.} \right), \end{aligned} \quad (6)$$

$S=1(2)$ for spin-up(-down) electrons, A, B, C are the dot indices and $N_{A,B,C}$ are the total populations of the corresponding dots. The Hamiltonian, eqs. (5), (6), has 20 eigenfunctions and eigenvalues for the three-electron case, which can be determined from the solution of the corresponding Schrödinger equation for specific values of the system parameters. It should be noted that these parameters can be controlled by the gates’ voltages applied to the triple-dot system. We will use the following pulse sequence: in the first stage, the desired initial state is formed; in the second stage, an extremely fast restoring pulse is used to return the gates into their initial conditions while simultaneously preserving the system state; finally, in the third stage, the desired final state is obtained.

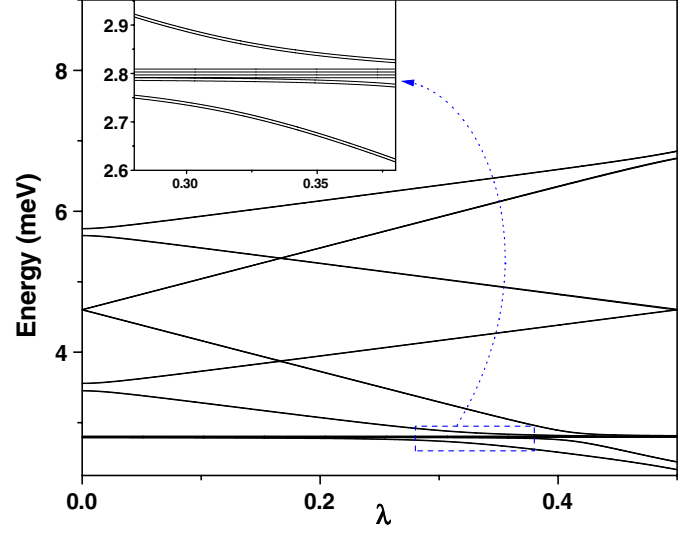


Fig. 2: (Color online) Energies of the three-electron states in the triple-dot structure *vs.* the parameter λ representing different gate voltages. Inset: magnified region with several avoided level crossings.

To better link to experiments, we choose the intradot Coulomb energies $U_A = U_B = U_C = 2$ meV, the interdot Coulomb energies $U_{AB} = U_{BC} = U_{AC} = 0.2$ meV, and the tunnel matrix elements $\Delta_{AB} = \Delta_{BC} = \Delta_{AC} = 0.05$ meV. We also introduce a small Zeeman energy $E_1 - E_2 = 0.003$ meV for all three dots, to lift the spin degeneracy. The dot energies before reaction ($\lambda = 0$) are chosen as $E_B = E_C = E_A + 0.5E_P$ with $E_P = 2.2$ meV. In this case, the ground state for the Hamiltonian, eq. (5), is given by

$$\begin{aligned} \Psi_1(\lambda = 0) &= \sqrt{\frac{2}{3}} a_{A1}^\dagger a_{B2}^\dagger a_{C2}^\dagger |0\rangle \\ &\quad - \sqrt{\frac{1}{3}} \frac{a_{B1}^\dagger a_{C2}^\dagger + a_{B2}^\dagger a_{C1}^\dagger}{\sqrt{2}} \times a_{A2}^\dagger |0\rangle, \end{aligned} \quad (7)$$

i.e., it is a superposition of the state $a_{A1}^\dagger a_{B2}^\dagger a_{C2}^\dagger |0\rangle$, where a single electron is located in each dot (no bonds, with a probability $2/3$), and the state, a spin-triplet T_0 , formed in the dots B and C , plus one electron located on the dot A (with a probability $1/3$). It should be noted that the real chemical bond is formed by the spin-singlet state only. The first excited state is the spin-singlet formed in the dots B and C , plus one electron located in dot A

$$\Psi_2(\lambda = 0) = \frac{a_{C2}^\dagger a_{B1}^\dagger - a_{C1}^\dagger a_{B2}^\dagger}{\sqrt{2}} \times a_{A2}^\dagger |0\rangle. \quad (8)$$

In the first stage, it is necessary to form an initial state, the spin singlet, describing a chemical bond between dots A and B (see fig. 1). We can do it starting at $\lambda = 0$ from the ground state (7) and proceeding to the excited state $\Psi_7(\lambda = 0.5)$. We start with examining the response of the system to the sweep $V = E_P(N_C - N_B)$ where λ is changed linearly from 0 to 0.5 with various speed. The variations of the state energies with λ are shown in fig. 2.

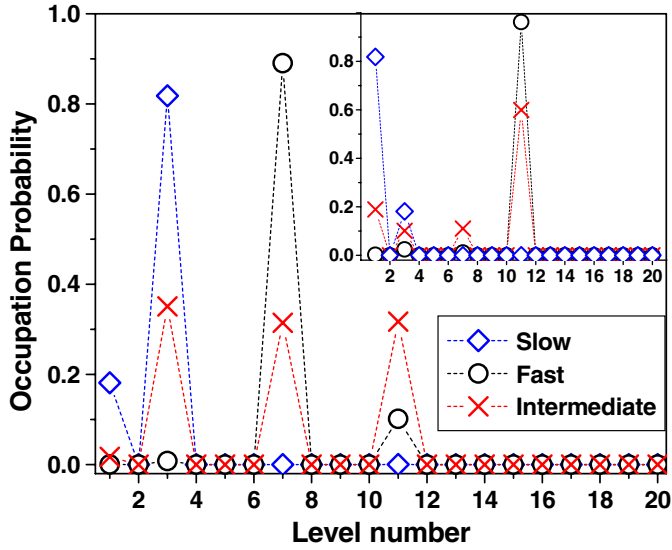


Fig. 3: (Color online) Level populations at the end of the parametric evolution of the Hamiltonian (2) when starting from the ground (main panel) and the first excited (inset) states for different reaction speeds (in units of meV/\hbar): $\lambda = 10^{-3}$ (blue diamonds), 10^{-2} (red crosses in the main panel), $7.5 \cdot 10^{-2}$ (red crosses in the inset), 10^{-1} (black circles in the main panel), 1 (black circles in the inset). The dashed lines connecting the symbols are added as a guide to the eye.

Several avoided level crossings can be clearly seen in this figure, and in the inset magnifying the region with many possible Landau-Zener transitions. The reaction products are shown in fig. 3 for various speeds of change. In the main panel, the initial state is the ground one; while in the inset we start from the first excited state. At low speeds only the states near the ground state can be occupied at the end of the evolution (adiabatic sweep). When λ increases, certain states can be populated while most other states are almost empty. This subset of occupied states is controlled by the sequence of the avoided crossings and is unique for a chosen parametric evolution (*i.e.*, a chosen H_0 and V). Thus, one can simulate a desirable chemical/nuclear reaction by changing H_0 and/or V , *i.e.*, by changing the device architecture and gate structure, as well as by occupying certain initial states. However, for chemical reactions with complicated potential energy surfaces the possible outcomes are numerous, and we can adjust the function $\lambda(t)$ to follow a specific reaction pathway. Even for a fixed pathway, a variation of the speed $\dot{\lambda}$ allows us to switch with a definite probability between the output states (*i.e.*, output products). In particular, it is evident from fig. 3 that at the relatively fast sweep with almost 0.9 probability the final state of our reaction becomes

$$\Psi_7(\lambda = 0.5) = \frac{a_{A2}^\dagger a_{B1}^\dagger - a_{A1}^\dagger a_{B2}^\dagger}{\sqrt{2}} \times a_{C2}^\dagger |0\rangle, \quad (9)$$

which is the spin-singlet in the dots A and B , plus one electron located in dot C . It should be noted that this is

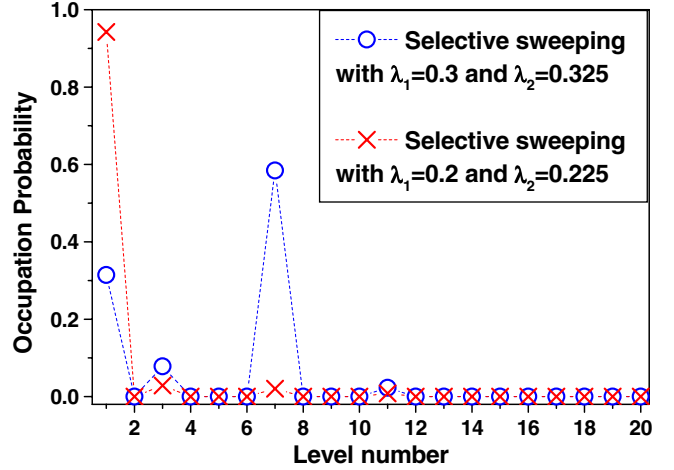


Fig. 4: (Color online) Occupation of states at the end of the parametric evolution when the step-like signal $\lambda(t)$, described in the text, is applied with $\lambda_1 = 0.2$, $\lambda_2 = 0.225$ (red crosses) and $\lambda_1 = 0.3$, $\lambda_2 = 0.325$ (blue circles). Note that output products corresponding to red crosses were found for almost all values of λ_1 and λ_2 , while output products shown by blue circles are unique and can be achieved only for a specific values of λ_1 and λ_2 .

essentially the same state as $\Psi_2(\lambda = 0)$, besides a change of the dot numeration.

In the second stage, we apply a very fast pulse, $V_{\text{restore}} = 0.5E_P(N_A + N_B) - E_P N_C$, to restore the initial gate potentials corresponding to the value $\lambda = 0$. After this pulse, the state of the system remains unchanged and the initial state of the reaction $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ is formed, as shown on the left side of fig. 1.

In the third stage, we apply a pulse $V' = E_P(N_B - N_A)$, changing λ from 0 to 0.5, to achieve the configuration shown on the right side of fig. 1. However, this state,

$$\Psi'_7(\lambda = 0.5) = \frac{a_{C2}^\dagger a_{A1}^\dagger - a_{A2}^\dagger a_{C1}^\dagger}{\sqrt{2}} \times a_{B2}^\dagger |0\rangle, \quad (10)$$

can only be achieved with small probability $P = 0.1$, even after a fast enough sweep (see inset of fig. 3). To overcome this, we apply the following *selective* sweep, using a step-like signal, $\lambda(t) = \lambda_1 t$ for $0 < \lambda_1 < \lambda < \lambda_2$ and $\lambda(t) = \lambda_2 t$ otherwise, with $\lambda_1 \gg \lambda_2$. In this case, we can activate Landau-Zener transitions at avoided crossings within a desirable interval $\lambda_1 < \lambda < \lambda_2$. Based on this technique we can mainly achieve a unique output quantum state (or product) 10 as shown in fig. 4 for $\lambda_1 = 0.3$ and $\lambda_2 = 0.325$ (blue online circles). It is evident that the desired final state has a sufficiently large probability $P = 0.6$. However, this large probability cannot be reached without carefully choosing λ_1 and λ_2 . Indeed, the red online crosses in fig. 4 show the standard final occupation probability.

In summary, we propose to model chemical reactions via electron redistributions between coupled semiconductor quantum dots. As an example, the simplest chemical reaction, $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ is examined here with the three

nuclei and three electrons being simulated by the three-electron states in the triple-dot structure. We achieve the following bond redistribution between the three dots after the following procedure: i) starting from the ground state of the three-dot system which contains (with $P=1/3$) a spin-triplet of the electron pair $B=C$, a fast adiabatic sweep is used to obtain the spin-singlet state for electrons between dots A and B ($A=B$ covalent bonding) with $P=0.9$; ii) applying a sharp restoring pulse we return to the initial Hamiltonian, without changing the state of the system; iii) we apply a selective adiabatic sweep to the dots B and A and transfer the bond to the covalent coupling between dots C and A , $C=A$ (with $P=0.1$ with fast, but not selective sweep, and with $P=0.6$ with a slow but selective sweep), which is described by the spin-singlet state of the electron pair which is shared by the dots A and C . In stages i) and ii), the initial state (left side of fig. 1) is formed and in the stage iii) it is transferred to the final state (right side of fig. 1). It should be emphasized that the final state is obtained with non-unit probability, indicating possible different reaction outcomes, as it is the case with real experiments [16]. Complex chemical reactions are usually characterized by a sophisticated potential energy surface. A fraction of this surface, containing a targeted simulation pathway, can be mapped (after rescaling) into the energy landscape of a quantum dot structure. Then, a fine-tuning of the function $\lambda(t)$ can direct the artificial reaction along a certain chosen pathway on the potential energy surface, with a distribution of the possible outcomes which reflects the results of real chemical transformations. We believe that the direct emulation of chemical reactions with quantum electronic devices provides a new way in analogous quantum information processing which complements standard schemes of quantum state control and manipulation.

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