Programming quantum systems: modelling chemical reactions using semiconductor quantum dots

A. Yu. Smirnov[1,2,3], S. Savel'ev[1,4], L. G. Mourokh[1,3,5], and Franco Nori[1,6]

[1] *Frontier Research System, The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama, 351-0198, Japan*

[2] *CREST, Japan Science and Technology Agency, Kawaguchi, Saitama, 332-0012, Japan*

[3] *Quantum Cat Analytics, 1751 67 St. E11, Brooklyn, New York 11204, USA*

[4] *Department of Physics, Loughborough University, Loughborough LE11 3TU, UK*

[5] *Department of Physics, Queens College, The City University of New York, Flushing, New York 11367, USA*

[6] *Center for Theoretical Physics, Physics Department, The University of Michigan, Ann Arbor, MI 48109, USA*

Abstract

We propose using semiconductor quantum dots for a simulation of 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.

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, *quantum systems can be programmed* to 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 of precise control of the number of electrons in quantum dots and the tunnel energy splittings by 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] with the potential to easily increase the number of the dots, as needed.

Based on these developments, we propose to employ the electron redistribution in coupled quantum dot systems for *chemical reaction modelling*. In particular, the number of electrons in the first and second quantum dot shells are 2 and 4, respectively. Accordingly, the quantum dot with one electron can be considered as an *artificial hydrogen atom* (one electron vacancy in the outer shell) and the 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 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 reactions can be done under conditions (such as a presence of an external magnetic field) not readily accessible in all real molecules and the speed of the reaction could be easily varied in a very wide range.

The Hamiltonian of the system can be separated into two parts

$$H(t) = H_0 + \lambda(t)V \tag{1}$$

where the first term describes the invariant part and the second term is responsible for the reaction. It should be noted that the time dependence of the parameter λ 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 $\dot{\lambda}$, the system's state remains unchanged; and for the intermediate case, several Landau-Zenner transitions may occur at the avoided crossing points, with various states being populated after the reaction. In contrast to adiabatic quantum computing [12, 13], 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 $\lambda(t)$.

The evolution of the instant energy levels $E_n(\lambda)$ and eigenfunctions $|n\rangle$ of Hamiltonian (1) can be exactly mapped [13] on the classical Hamiltonian dynamics of 1D gas of fictitious particles (Pechukas gas [14]), 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" $l_{mn}(\lambda) = (E_m(\lambda) - E_n(\lambda))V_{mn}(\lambda)$:

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

Note that all the matrix elements in Eq. (2) are taken between the instantaneous eigenstates of the Hamiltonian (1). The probabilities of the Landau-Zenner transitions between states

3

$m \leftrightarrow n$ is given by

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

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 in a system with large number of elements [13].

Here, we examine the simplest possible chemical reaction: the scattering of a hydrogen atom from a hydrogen molecule ($H+H_2 \rightarrow H_2+H$), 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 [15] (where the slightly different reaction, $H + D_2 \rightarrow HD + D$, was studied). Although the reaction was dominated by a direct recoil mechanism 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

$$H = H_{3D} + H_C + H_{\text{tun}}, \tag{4}$$

where

$$\begin{aligned}
H_{3D} &= \sum_{S=1,2} (E_{AS}N_{AS} + E_{BS}N_{BS} + E_{CS}N_{C1S}), \\
H_C &= U_A N_{A1}N_{A2} + U_B N_{B1}N_{B2} + U_C N_{C1}N_{C2} + U_{AB}N_A N_B + U_{BC}N_B N_C + U_{AC}N_A N_C, \\
H_{\text{tun}} &= -\sum_{S=1,2} \left(\Delta_{AB}a_{AS}^+ a_{BS} + \Delta_{BC}a_{BS}^+ a_{CS} + \Delta_{AC}a_{AS}^+ a_{CS} + h.c.\right),
\end{aligned} \tag{5}$$

$S = 1(2)$ 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. (4,5), has 20 eigenfunction 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 restoration pulse is used to return the gates into their initial conditions preserving the system state; finally, in the third stage, the desired final state is obtained.

To 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. (4), is given by

$$\Psi_1(\lambda = 0) = \sqrt{\frac{2}{3}}\, a_{A1}^+ a_{B2}^+ a_{C2}^+ |0\rangle - \sqrt{\frac{1}{3}}\, \frac{a_{B1}^+ a_{C2}^+ + a_{B2}^+ a_{C1}^+}{\sqrt{2}} \times a_{A2}^+ |0\rangle\,, \tag{6}$$

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

$$\Psi_2(\lambda = 0) = \frac{a_{C2}^+ a_{B1}^+ - a_{C1}^+ a_{B2}^+}{\sqrt{2}} \times a_{A2}^+ |0\rangle\,. \tag{7}$$

In the first stage, we examine the response of this system to the sweep $V = E_P(N_C - N_B)$ with λ changed linearly from 0 to 0.5 with various speed. The variations of the state energies with λ are shown in Fig. 2. 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 $\dot{\lambda}$ 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., changing the device architecture and gate structure, as well as by occupying certain initial states. If the speed, $\dot{\lambda}$, is high enough, well defined final states can be reached, and the population of other output states (i.e., output products) can be suppressed. In particular, it is evident from Fig. 3 that with almost 0.9 probability the final state becomes

$$\Psi_7(\lambda = 0.5) = \frac{a_{A2}^+ a_{B1}^+ - a_{A1}^+ a_{B2}^+}{\sqrt{2}} \times a_{C2}^+ |0\rangle\,, \tag{8}$$

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 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, $V_{\text{restore}} = 0.5E_s(N_A + N_B) - E_sN_C$, to restore the initial gate potentials. After this pulse the state of the system remains unchanged and the initial state of the $H + H_2 \rightarrow H_2 + H$ is formed, as shown in the left panel 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 in Fig. 1, right panel. However, this state,

$$\Psi_7(\lambda = 0.5) = \frac{a_{C2}^+a_{A1}^+ - a_{A2}^+a_{C1}^+}{\sqrt{2}} \times a_{B2}^+|0\rangle \,, \tag{9}$$

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, $\lambda(t) = \dot{\lambda}_1 t$ for $0 < \lambda_1 < \lambda < \lambda_2 < 0$ and $\lambda(t) = \dot{\lambda}_2 t$ overwise, with $\dot{\lambda}_1 \gg \dot{\lambda}_2$. 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) as shown in Fig. 4 for $\lambda_1 = 0.3$ and $\lambda_2 = 0.325$ (black circles). It is evident that the desired final state has sufficiently large probability $P = 0.6$.

In summary, we propose to model chemical reactions via electron redistributions between coupled semiconductor quantum dots. As an example, the simplest chemical reaction, $H + H_2 \rightarrow H_2 + H$ 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 panel of Fig. 1) is formed and in stage (iii) it is transferred to the final state (right panel 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 [15].

---

[1] R.P. Feynman, Int. J. Theor. Phys. **21**, 467 (1982); S. Lloyd, Science **273**, 1073 (1996).

[2] E. Manousakis, J. Low Temp. Phys. **126**, 1501 (2002).

[3] A. Aspuru-Guzik, A.D. Dutoi, P.J. Love, and M. Head-Gordon, Science **309**, 1704 (2005).

[4] M. Kastner, Physics Today **46**, 24 (1993).; S. Tarucha, D.G. Austing, T. Honda, R.J. van der Hage and L.P. Kouwenhoven, Phys. Rev. Lett. **77**, 3613 (1996); M. Stopa, Phys. Rev. B **54**, 13767 (1996); L.P. Kouwenhoven, T.H. Oosterkamp, M.W.S. Danoesastro, M. Eto, D.G. Austing, T. Honda, and S. Tarucha, Science **278**, 1788 (1997).

[5] W.G. van der Wiel, S. De Franceschi, J.M. Elzerman, T. Fujisawa, S. Tarucha, and L.P. Kouwenhoven, Rev. Mod. Phys. **75**, 1 (2003).

[6] See, e.g., A.W. Holleitner, R.H. Blick, A.K. Hüttel, K. Eberl, and J.P. Kotthaus, Science **297**, 70 (2002); M. Pioro-Ladriere, M. Ciorga, J. Lapointe, P. Zavadzki, M. Korkusinski, P. Hawrylak, and A.S. Sachrajda, Phys. Rev. Lett. **91**, 026803 (2003); M. Rontani, S. Amaha, K. Muraki, F. Manghi, E. Molinari, S. Tarucha, and D.G. Austing, Phys. Rev. B **67**, 085327 (2004).

[7] A. Barenco, D. Deutsch, A. Ekert, and R. Jozsa, Phys. Rev. Lett. **74**, 4083 (1995).

[8] T. Hayashi, T. Fujisawa, H.D. Cheong, Y.H. Jeong, and Y. Hirayama, Phys. Rev. Lett. **91**, 226804 (2003); T. Fujisawa, T. Hayashi, H.D. Cheong, Y.H. Jeong, and Y. Hirayama, Physica E **21**, 1046 (2004).

[9] See, e.g., M. Ciorga, A.S. Sachrajda, P. Hawrylak, C. Gould, P. Zawadzki, S. Jullian, Y. Feng, and Z. Wasilewski, Phys. Rev. B **61**, R16315 (2000); A.C. Johnson, J.R. Petta, J.M. Taylor, A. Yacoby, M.D. Lukin, C.M. Marcus, M.P. Hanson, A.C. Gossard, Nature **435**, 925 (2005); A.K. Hüttel, S. Ludwig, H. Lorenz, K. Eberl, and J.P. Kotthaus, Phys. Rev. B **72**, 081310(R) (2005).

[10] M. Field, C.G. Smith, M. Pepper, D.A. Ritchie, J.E.F. Frost, G.A.C. Jones, and D.G. Hasko,

Phys. Rev. Lett. **70**, 1311 (1993).

[11] A. Vidan, R.M. Westervelt, M. Stopa, M. Hanson, and A.C. Gossard, Appl. Phys. Lett. 85, 3602 (2004); L. Gaudreau, S.A. Studenikin, A.S. Sachrajda, P. Zawadzki, A. Kam, J. Lapointe, M. Korkusinski, and P. Hawrylak, Phys. Rev. Lett. **97**, 036807 (2006).

[12] E. Farhi et al., Science **292**, 472 (2001).

[13] A.M. Zagoskin et al., Phys. Rev. Lett. **98**, 120503 (2007).

[14] P. Pechukas, Phys. Rev. Lett. **51**, 943 (1983).

[15] S.C. Althorpe, F. Fernandes-Alonso, B.D. Bean, J.D. Ayers, A.E. Pomerantz, R.N. Zare, and E. Wrede, Nature **416**, 67 (2002); D.E. Manolopoulos, Nature **419**, 266 (2002); S.A. Harich, D. Dal, C.C. Wang, X. Yang, S.D. Chao, and R.T. Skodje, Nature **419**, 281 (2002).
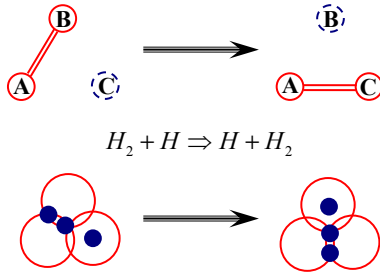
FIG. 1: (Color online) Schematic diagram of the $H_2 + H \rightarrow H + H_2$ reaction showing the bonds (upper panel) and the electron redistribution in the coupled quantum dot system (lower panel).
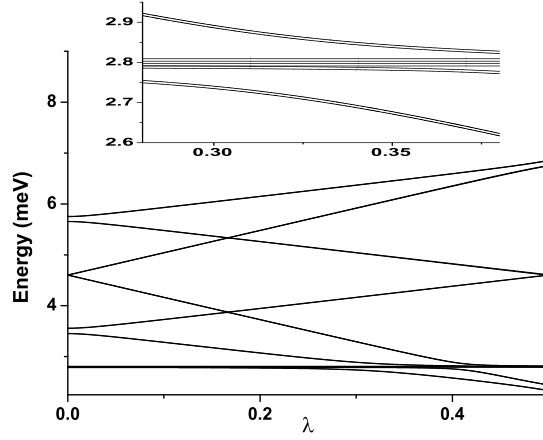
FIG. 2: Energies of the three-electron states in the triple-dot structure versus parameter λ representing different gate voltages. Inset: Magnified region with several avoided level crossings.
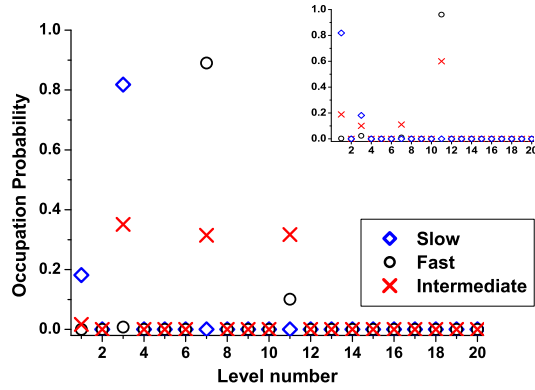

FIG. 3: (Color online) Level populations at the end of the parametric evolution of the Hamiltonian (1) when starting from the ground (main panel) and the first excited (inset) states for different reaction speeds $\dot{\lambda} = 10^{-3}$ (blue diamonds), 10^{-2} (red crosses in the main panel), $7.5 \cdot 10^{-2}$ (red crosses in the inset), 10^{-1} (black circles in the main panel), 1 (black circles in the inset).
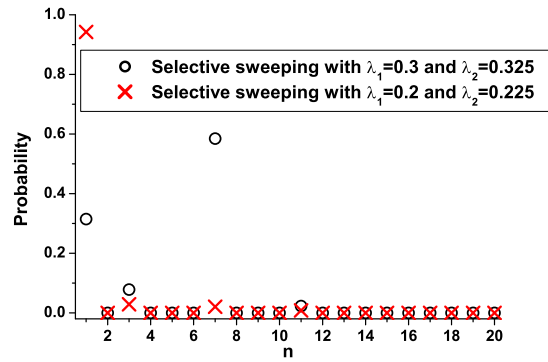
10

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 $\lambda_1 = 0.3$, $\lambda_2 = 0.325$ (black circles). Note that output products corresponding to red up triangles was found for almost all positions of the step in $\lambda(t)$, while output products shown by black down triangles are unique and can be achieved only for a specific position of the step in $\lambda(t)$.