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Intramolecular Hamiltonian logic gates

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Abstract

An intramolecular computing model is presented that is based on the quantum time evolution of a single molecule driven by the preparation of a non-stationary single-electron state. In our scheme, the input bits are encoded into the coupling constants of the Hamiltonian that governs the molecular quantum dynamics. The results of the computation are obtained by carrying out a quantum measurement on the molecule. We design reliable AND, XOR, and HALF-ADDER logic gates. This opens new avenues for the design of more complex logic circuits at a single-molecular scale.

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1. Introduction

Recent remarkable experimental advances in the field of atomic scale technology [1,2] have opened a way to the design of novel devices at the scale of a single molecule. Particular attention has been paid to the possibility to integrate inside a single molecule the logic gates and circuits that could provide an interesting alternative to the currently used microelectronic devices based on silicon technology [3]. The molecular logic gates could offer an unprecedented miniaturization [4] and may be also superior in terms of energy consumption [5]. So far, the attempts to build molecular logic gates have been mostly based on the direct analogue with the standard electronic circuitry where the input and output signals are voltages and/or currents in some circuit that involves the molecule [6]. It was shown that it is indeed possible to design molecules that could mimic the behavior of the electronic logic gates [7]. However, this approach currently suffers form the disadvantage that the predicted resulting signal current or voltage is usually very small [8].

In this paper we propose a novel design of the intramolecular logic gates in which the computation is driven by the quantum evolution of a non-stationary state of the molecule. In practice, this may involve, for example, the tunneling of electrons through the molecule. In addition, the encoding of the input and output bits significantly differs from the previous proposals. We suggest to

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encode the values of the input bits into the coupling constants of the Hamiltonian that governs the molecular quantum dynamics. This can be achieved, for example, by switching between several conformations of the molecule with the use of a scanning tunneling microscope (STM) [9]. We consider two alternative readouts of the output of the computation. One option is to read the population of some molecular quantum levels at some predetermined time T after the computation start. Thus, the calculation result is obtained by carrying out a quantum measurement on the molecular system. An alternative option consists in coupling the molecule to an auxiliary system (e.g., a reservoir), and looking at the populations of the auxiliary quantum levels in order to read out the calculation result.

In short, the main idea behind the present proposal is to explore the rich and complex structure of the Hilbert space of the molecular states. This makes it possible to implement rather complicated logical gates such as the HALF-ADDER gate without needing to increase the spatial size of the molecule. We also emphasize from the outset that our goal is to design classical logic gates driven by quantum evolution, not quantum gates.

The present paper is organized as follows. The model of the Hamiltonian intra-molecular logic gate is described in Section 2. In Section 3 we derive extremal equations for the interaction Hamiltonian that describes (in the tight-binding approximation) the molecular logic gate. The tools developed in Section 3 are employed to design the XOR gate, AND gate, and HALF-ADDER gate. The corresponding results are reported in Section 4, where the readout of the computational result is performed on the molecule. A more realistic model where the readout is performed by measuring the state of some auxiliary systems attached to the main molecule is considered in Section 5. Finally, the conclusions are drawn in Section 6.

2. Model of the intramolecular logic gate

In this paper, the molecule is described in the tight-binding approximation by several effective quantum levels that are mutually coupled. The abstract model system is depicted in Fig. 1. To provide enough flexibility for a logic-gate design we consider a six-level system, initially prepared in a (non-stationary) state $|1\rangle$. In what follows, we design logic gates with two input bits and one or two output bits. We shall assume that the input bits are encoded into the values of the coupling constants α_{12} and α_{13}. By selectively switching between two values $\alpha_{nn'}^{(0)}$ and $\alpha_{nn'}^{(1)}$ that correspond to the logical values 0 and 1, respectively, we can encode a single input bit into the interaction between states $|n\rangle$ and $|n'\rangle$. In practice, the coupling strength can be modified e.g. by changing the conformation of the molecule, which can be accomplished with the tip of an STM [9].

More generally, we can switch between N different global settings of the coupling constants, which means that the computation can have N different inputs. The computation is driven by the temporal evolution of the quantum system induced by the total Hamiltonian $H_{\rm tot}$. To make our model sufficiently general we assume that $H_{\rm tot}$ consists of three different contributions:

$$H_{j,\rm tot} = H_j + H_c + H_0. \tag{1}$$

Here j labels all possible inputs and the part H_j contains the encoded input bits. For the system depicted in Fig. 1, we have

$$H_j = \alpha_{12}^{(j)}(|1\rangle\langle 2| + |2\rangle\langle 1|) + \alpha_{13}^{(j)}(|1\rangle\langle 3| + |3\rangle\langle 1|). \tag{2}$$

In contrast, H_0 is a fixed Hamiltonian, which cannot be modified or changed at will. This Hamiltonian describes the part of the system that cannot be freely designed, so it imposes constraints on the design of the gate. In our particular model, we assume that the molecule is partially symmetric in a sense that the levels $|4\rangle$ and $|5\rangle$ are coupled to the level $|6\rangle$ similarly as $|2\rangle$ and $|3\rangle$ are

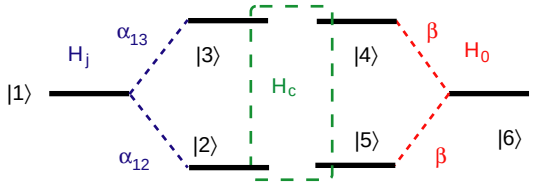

Fig. 1. Schematic model of the six-level system that represents the Hamiltonian intra-molecular logic gate.

coupled to $|1\rangle$,

$$H_0 = \beta(|4\rangle\langle 6| + |6\rangle\langle 4|) + \beta(|5\rangle\langle 6| + |6\rangle\langle 5|). \quad (3)$$

Finally, H_c is also a fixed Hamiltonian that does not depend on the values of the input bits. However, in contrast to H_0, H_c can be chosen freely in order to tune the desired logic gate operation. In our case, H_c couples the "central" levels $|2\rangle$, $|3\rangle$, $|4\rangle$, and $|5\rangle$.

In our simplified model, the result of the computation is read out at a time T after the beginning of the computation by performing a quantum measurement on the system. The measurement is described by a positive operator valued measure (POVM) that is characterized with M operators $\Pi_k \geqslant 0$ ($k = 1, \ldots, M$) which sum up to the identity operator

$$\sum_{k=1}^{M} \Pi_k = I. \quad (4)$$

If the Hamiltonian of the system is set to H_j, then we should, ideally, observe the outcome $\Pi_{k(j)}$ where the functional dependence $k(j)$ specifies the computational task to be performed by the system. Consider, as an illustrative example, the XOR gate. In this case, the computation should yield two outcomes 0 or 1, hence the measurement on the system is a two-component POVM $\{\Pi_0, \Pi_1\}$. The ideal functional dependence is $k = 0$ for $j = 00$ or 11, and $k = 1$ for $j = 01$ or 10. We will see that, by choosing H_c appropriately, this functional dependence can be achieved in the molecule with a very high fidelity.

Consider now the gate operation. At time $t = 0$ the system is prepared in the input state ρ_{in} and evolves for time T according to the Hamiltonian $H_{j,\text{tot}}$ to the output state (we work in units $\hbar = 1$)

$$\rho_{j,\text{out}} = \mathrm{e}^{-\mathrm{i}H_{j,\text{tot}}T}\rho_{\text{in}}\mathrm{e}^{\mathrm{i}H_{j,\text{tot}}T}. \quad (5)$$

The probability to obtain the correct measurement outcome $\Pi_{k(j)}$ is given by the trace,

$$P(k(j)|j) = \mathrm{Tr}[\Pi_{k(j)}\rho_{j,\text{out}}]. \quad (6)$$

In order to design the Hamiltonian logical gate, we must first define a figure of merit that quantifies its performance. In the following, we use as a figure of merit the average probability of success:

$$F = \frac{1}{N}\sum_{j=1}^{N} P(k(j)|j) = \frac{1}{N}\sum_{j=1}^{N} \mathrm{Tr}[\Pi_{k(j)}\rho_{j,\text{out}}], \quad (7)$$

where the average is taken over all N possible values of the input bits. It holds that $0 \leqslant F \leqslant 1$ and the gate is perfect if $F = 1$.

The measurement at time T should, in fact, discriminate some subsets of the states $\rho_{j,\text{out}}$ that are generated from the input state ρ_{in} via N different evolutions governed by Hamiltonians $H_{j,\text{tot}}$. We can thus say that the purpose of the measurement is effectively to discriminate some subsets of the N different unitary evolutions [10,11]. This is, for instance, the case of the XOR gate, where we only need to distinguish whether the Hamiltonian of the system belongs to the subset $\{H_{00}, H_{11}\}$ (the output should be 0) or to the subset $\{H_{10}, H_{01}\}$ (the output should be 1), but we need not to distinguish between the Hamiltonians in each subset.

3. Design of the optimal intramolecular Hamiltonian

We now proceed to the determination of the intramolecular coupling Hamiltonian H_c that maximizes the fidelity of the molecular logic gate at a given fixed time T. This is certainly a nontrivial optimization problem, which generally cannot be solved analytically. We therefore resort to a numerical optimization procedure. We first derive a variation δF of the gate fidelity F that corresponds to a small change δH_c of the Hamiltonian H_c. From the variation, we will be able to extract δH_c that increases the value of F. This permits an easy numerical optimization based on a steepest ascend algorithm.

The variation of F is most easily derived within the framework of the time-dependent first-order perturbation theory. Let us focus on a single term $P(k|j)$ of the gate fidelity. For the sake of notation simplicity, we do not explicitly write the dependence of k on j in what follows. Let $|\phi_{jl}\rangle$ and λ_{jl} denote the eigenstates and eigenvalues of the unperturbed Hamiltonian $H_{j,\text{tot}}$. We can expand

an arbitrary pure input state $|\psi\rangle$ in the basis $|\phi_{jl}\rangle$,

$$|\psi(0)\rangle = \sum_l c_l(0)|\phi_{jl}\rangle. \tag{8}$$

In the Schrödinger picture, this state evolves in time according to

$$|\psi(t)\rangle = \sum_l c_l(t)\mathrm{e}^{-\mathrm{i}\lambda_{jl}t}|\phi_{jl}\rangle, \tag{9}$$

where the time dependence of $c_l(t)$ is due to the perturbation term δH_c. In the first order approximation, we obtain from the Schrödinger equation

$$i\frac{\mathrm{d}}{\mathrm{d}t}c_l = \sum_m \langle\phi_{jl}|\delta H_c|\phi_{jm}\rangle \mathrm{e}^{-\mathrm{i}(\lambda_{jm}-\lambda_{jl})t}c_m(0). \tag{10}$$

A straightforward integration yields

$$c_l(t) = c_l(0) + \sum_m \delta H^{(j)}_{c,lm}\frac{\mathrm{e}^{-\mathrm{i}(\lambda_{jm}-\lambda_{jl})t}-1}{\lambda_{jm}-\lambda_{jl}}c_m(0), \tag{11}$$

where $\delta H^{(j)}_{c,lm} = \langle\phi_{jl}|\delta H_c|\phi_{jm}\rangle$. We can now determine the variation of the unitary transformation δU_j defined as

$$\delta U_j = \mathrm{e}^{-\mathrm{i}(H_{j,\mathrm{tot}}+\delta H_c)t} - \mathrm{e}^{-\mathrm{i}H_{j,\mathrm{tot}}t}. \tag{12}$$

If we compare the left- and right-hand sides of the formula

$$\delta U_j|\psi(0)\rangle = \sum_l [c_l(t)-c_l(0)]\mathrm{e}^{-\mathrm{i}\lambda_{jl}t}|\phi_{jl}\rangle, \tag{13}$$

then we immediately find that

$$\delta U_j \approx \sum_{l,m} \delta H^{(j)}_{c,lm}\frac{\mathrm{e}^{-\mathrm{i}\lambda_{jm}t}-\mathrm{e}^{-\mathrm{i}\lambda_{jl}t}}{\lambda_{jm}-\lambda_{jl}}|\phi_{jl}\rangle\langle\phi_{jm}|. \tag{14}$$

Since we are interested in small variation, we have only kept the terms linear in δH_c.

The calculation of the variation $\delta P(k|j)$ is now straightforward. On combining Eqs. (5) and (6), we have

$$\begin{aligned}\delta P(k,j) &= \delta\mathrm{Tr}[U_j\rho_{\mathrm{in}}U_j^\dagger \Pi_k] \\ &= \mathrm{Tr}[\delta U\rho_{\mathrm{in}}U_j^\dagger\Pi_k + U_j\rho_{\mathrm{in}}\delta U_j^\dagger\Pi_k] \\ &= \mathrm{Tr}[\delta H_c X_j + \delta H_c^\dagger X_j^\dagger].\end{aligned} \tag{15}$$

Here we have used

$$\delta H_c = \sum_{l,m}\delta H^{(j)}_{c,lm}|\phi_{jl}\rangle\langle\phi_{jm}| \tag{16}$$

and we have defined the operators

$$X_j = \sum_{lm}\langle\phi_{jm}|\rho_{\mathrm{in}}U_j^\dagger\Pi_{k(j)}|\phi_{jl}\rangle \times\frac{\mathrm{e}^{-\mathrm{i}\lambda_{jm}t}-\mathrm{e}^{-\mathrm{i}\lambda_{jl}t}}{\lambda_{jm}-\lambda_{jl}}|\phi_{jm}\rangle\langle\phi_{jl}|. \tag{17}$$

The total variation of the gate fidelity can then be expressed as a sum of N variations, namely

$$\delta F = \frac{1}{N}\sum_{j=1}^{N}\mathrm{Tr}[\delta H_c(X_j + X_j^\dagger)], \tag{18}$$

where X_j is evaluated at $t = T$ and we have taken into account that H_c is Hermitian operator (hence, the variation δH_c should also be Hermitian). We can see from Eq. (18) that the value of fidelity will increase if we change the intramolecular Hamiltonian H_c according to

$$H_c \to H_c + \varepsilon\sum_{j=1}^{N}(X_j + X_j^\dagger). \tag{19}$$

The value of ε can be optimized at each iteration step to maximize the increase of F. Therefore, Eq. (19) gives a prescription for a simple iterative algorithm that finds the optimal H_c that maximizes the gate fidelity. Note that this method only yields a local maximum. The determination of the global maximum of F (which is a complicated non-linear function of H_c) is a very hard problem which cannot be easily solved even numerically. In our numerical experiments, we started the iterations from many randomly chosen initial H_c's, and selected the best among the solution Hamiltonians.

So far, we have not placed any constraints on the Hamiltonian H_c. However, according to the scheme shown in Fig. 1, H_c should couple only certain subsets of the levels. This constraint can be easily incorporated into the present formalism. Suppose that the Hamiltonian H_c is of the form

$$H_c = \sum_{(n,n')\in M} H_{c,nn'}|n\rangle\langle n'|, \tag{20}$$

where M is a set of the ordered pairs (n,n'). To preserve this structure during the iterations, we replace $\tilde{X}_j = X_j + X_j^\dagger$ by

$$\tilde{X}'_j = \sum_{(n,n')\in M}\langle n|(X_j + X'_j)|n'\rangle|n\rangle\langle n'| \tag{21}$$

so the iteration step is thus modified to $H_c \to H_c + \varepsilon \sum_j \tilde{X}'_j$. In our numerical experiments, we also imposed the constraint that H_c is real in the basis $\{|n\rangle\}$, which can be easily taken into account in the iterations by adding the step $H_c \to (H_c + H_c^*)/2$.

4. Numerical results

In this section, we present the results of the design of the XOR, AND and HALF-ADDER intramolecular gates. In all the examples, the input bits are encoded into the values of the coupling constants. We will start with the AND gate and then proceed to the XOR gate. Finally, we will design a HALF-ADDER gate, which simultaneously outputs the XOR and AND of the input bits. The HALF-ADDER logic gate is a basic building block of the digital circuit that adds two binary numbers, so it can be viewed as a benchmark to intramolecular computing. Note that the electronic circuit realization of a HALF-ADDER gate requires at least six transistors so it can be considered as a relatively complex gate.

4.1. Intramolecular AND gate

Here, we design the Hamiltonian AND gate in a six-level molecular system as depicted in Fig. 1. The input bits are encoded into the amplitude of the coupling constants α_{12} and α_{13}. The particular encoding that we have chosen is shown in Table 1, with the parameters α and q being specified later on. The quantum system is initially prepared in state $|1\rangle$. The AND gate outputs a single bit which is obtained by measuring the system in the basis $\{|1\rangle, \ldots, |6\rangle\}$ at time T. Here, we assume that the output bit is represented by the occupation of the level $|5\rangle$ at time T. If we find that the system is in state $|5\rangle$ then the output is 1, otherwise it is 0. More formally, the POVM describing this gate reads

$$\Pi_{00} = \Pi_{01} = \Pi_{10} = I - |5\rangle\langle 5|,$$
$$\Pi_{11} = |5\rangle\langle 5|. \tag{22}$$

We have performed the optimization for many different readout times T, choosing for the parameters $\alpha = 2$, $q = 3$, and $\beta = 0.5$. The optimization was repeated many times for each T with different initial values of H_c. Typically, several hundreds of iterations (19) are required to reach a (local) maximum of F. For each T, we picked the largest obtained fidelity. We have found that F almost monotonically grows with T until it reaches a plateau. Gate fidelities F as high as 99% can be obtained.

A typical example for the readout time $T = 3\pi = 9.4$ is provided by the intramolecular Hamiltonian

$$H_{c,\mathrm{AND}} = \begin{pmatrix} -1.8216 & 0.0544 & 0.3387 & 0.4986 \\ 0.0544 & -0.1686 & -0.5702 & -0.6595 \\ 0.3387 & -0.5702 & 1.8583 & -0.1297 \\ 0.4986 & -0.6595 & -0.1297 & -0.0444 \end{pmatrix},$$

where we only display the non-zero elements of H_c, i.e. the projection onto the subspace spanned by $|2\rangle$, $|3\rangle$, $|4\rangle$, $|5\rangle$. Note that the matrix elements of the optimal H_c are of the order of $|\alpha|$ or $|\beta|$. In Fig. 2, we plot the time evolution of the probability of obtaining correct outcome (6) when performing the measurement at time t. The gate fidelity at $T = 3\pi = 9.4$ exceeds 99%, so the AND gate is practically perfect. This illustrates that reliable logic gates can be obtained within this framework.

Table 1
Encoding of the input bits into the coupling constants of the intramolecular Hamiltonian

Bit value	α_{12}	α_{13}
0	α	α
1	α/q	α/q

4.2. Intramolecular XOR gate

One can similarly devise an XOR gate for this six-level molecule using the amplitude encoding as given in Table 1. An example of the numerically found optimal intramolecular Hamiltonian is

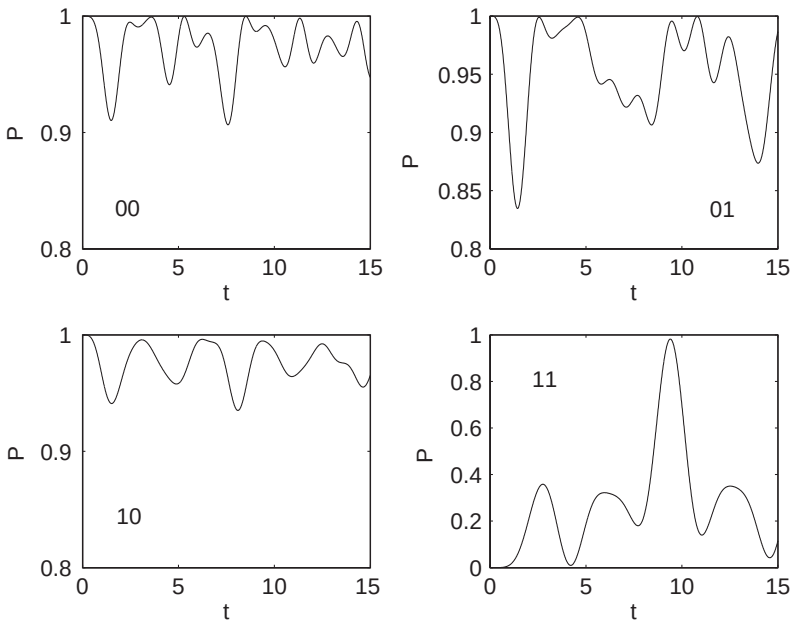

Fig. 2. Time dependence of the probability of correct outcome of the intramolecular AND gate. At $T = 3\pi = 9.4$ the gate is practically perfect, as the fidelity is larger than 99%. The figures are labeled by the values of the two input bits. The parameters are $\alpha = 2$, $\beta = 0.5$, and $q = 3$.

given by

$$H_{c,\mathrm{XOR}} = \begin{pmatrix} 1.4607 & -3.2687 & 3.7692 & 0.3011 \\ -3.2687 & 1.2413 & 3.9233 & 0.2816 \\ 3.7692 & 3.9233 & -0.7491 & 1.9971 \\ 0.3011 & 0.2816 & 1.9971 & 0.6331 \end{pmatrix}$$

The parameters of the gate are the same as before, and $T = 2\pi = 6.3$. The time evolution of the probabilities of correct outcome is shown in Fig. 3. Notice the sharp peaks at $T = 2\pi = 6.3$, where the gate achieves its optimal performance. This XOR gate also attains a very high fidelity $F = 97\%$.

4.3. Intramolecular HALF-ADDER gate

The AND and XOR gates form the basic building blocks of the digital half-adder. However, instead of combining the two Hamiltonian gates as constructed above, a more integrated solution is to incorporate the whole half-adder into a single molecular system. The design of the half-adder proceeds basically along the same lines as before except that the output consists of two bits. An important step is then to explore certain symmetry in the half-adder by choosing a convenient representation of the outcomes. The half-adder outputs two bits, namely the XOR bit and the AND bit. However, only three different outcomes are actually possible as it never happens that XOR = AND = 1. Thus, the outcomes of the half-adder can be determined by performing a three-component POVM on the system.

In our example we assume the measurement in the basis $\{|1\rangle, \ldots, |6\rangle\}$, and we focus on the populations of the levels $|4\rangle$, $|5\rangle$, and the rest of the system at time T. It is convenient to associate the most probable outcome (XOR = 1, AND = 0) with the case where neither $|4\rangle$ nor $|5\rangle$ are populated. Thus, the three possible outputs of the half-adder are given by: system is in state $|4\rangle$, system is in state $|5\rangle$, and system is in some other state. The details are given in Table 2.

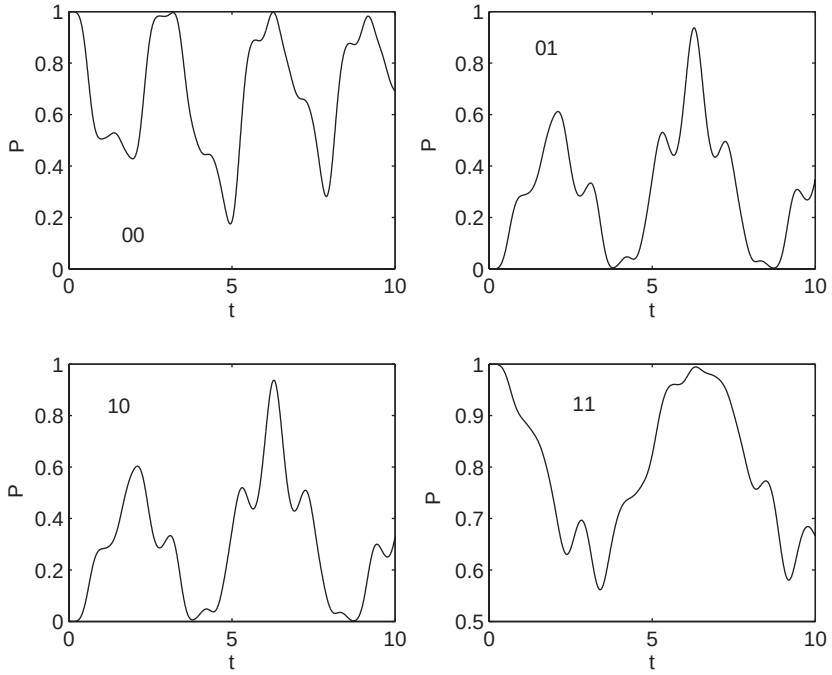

Fig. 3. Time dependence of the probability of correct outcome of the intramolecular XOR gate. At $T = 2\pi = 6.3$ the gate fidelity is almost 97%. The figures are labeled by the values of the two input bits. The parameters are $\alpha = 2$, $\beta = 0.5$, and $q = 3$.

Table 2
Definition of the outcomes of the intramolecular HALF-ADDER gate

The observed state	XOR	AND
$\|4\rangle$	0	0
$\|1\rangle$, $\|2\rangle$, $\|3\rangle$, $\|6\rangle$	1	0
$\|5\rangle$	0	1

Mathematically, the POVM associated with this gate reads

$$\Pi_{00} = |4\rangle\langle 4|,$$
$$\Pi_{01} = \Pi_{10} = I - |4\rangle\langle 4| - |5\rangle\langle 5|,$$
$$\Pi_{11} = |5\rangle\langle 5|. \quad (23)$$

With this particular encoding, we have been able to design a HALF-ADDER gate which achieves a fidelity of 91.5% by choosing for the readout time $T = 4\pi = 12.6$. The optimal intramolecular Hamiltonian reads

$$H_c = \begin{pmatrix} -1.8606 & 0.3592 & -0.7026 & 0.9935 \\ 0.3592 & -2.3734 & 2.7535 & -0.1064 \\ -0.7026 & 2.7535 & 0.4484 & -0.0508 \\ 0.9935 & -0.1064 & -0.0508 & -0.7542 \end{pmatrix}$$

The parameters of the gate are similar as in the previous cases. The time evolution of the probability of correct outcome of the gate is plotted in Fig. 4 for the four possible values of the input bits.

Although the fidelity of this HALF-ADDER gate is reasonably high, this construction is not entirely satisfactory. One particular disadvantage is the peculiar representation of the outcomes. Another drawback is that the errors are asymmetrically distributed. While the gate is almost perfect for input bits 01 and 10, an error of about 20% occurs for the input 11. Moreover, the probability of correct outcome P exhibits rather narrow peaks so

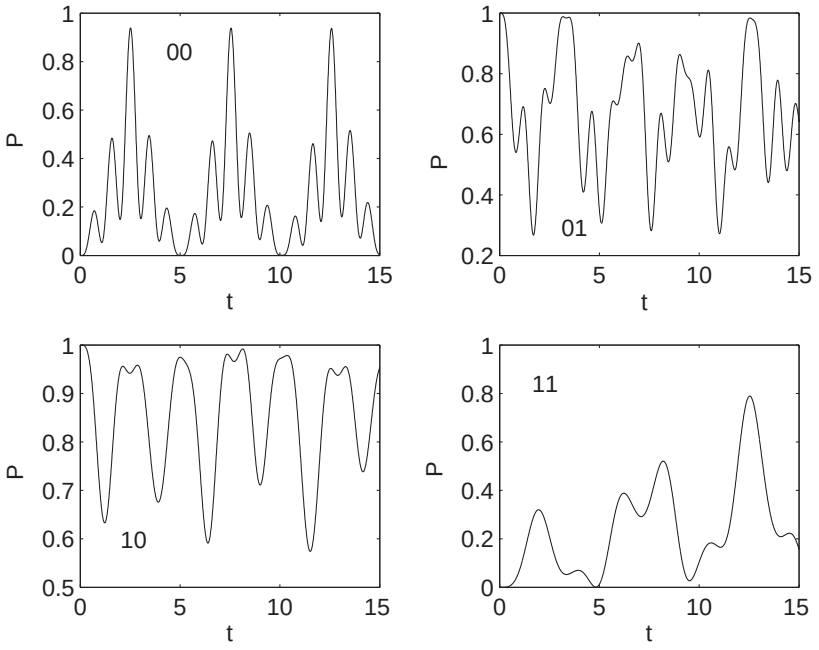

Fig. 4. Time dependence of the probability of correct outcome of the intramolecular HALF-ADDER gate. At $T = 4\pi = 12.6$ the gate achieves average fidelity 91.5%. The figures are labeled by the values of the two input bits. The parameters of the system are $\alpha = 2$, $\beta = 0.5$ and $q = 3$.

that the reliable readout of the result of the computation would require a quite precise timing.

A possible way of overcoming—at least partially—these obstacles is to monitor the average population of the molecular levels over the time period T. This is discussed in Ref. [12]. An alternative approach is to consider a more refined model where the molecular system interacts with some ancillas (auxiliary systems). The outcome of the computation is then determined by measuring the state of these ancillas at time T. This approach to the construction of Hamiltonian logic gates will be the subject of the next section.

5. Intramolecular logic gates with ancillary readout

Here we shall consider a design that involves the interaction of the main system with one or more ancillas. The output bits are determined by measurements applied on the ancillas at some time T. The simplest example with single-qubit ancilla is given in Fig. 5. Loosely speaking, the

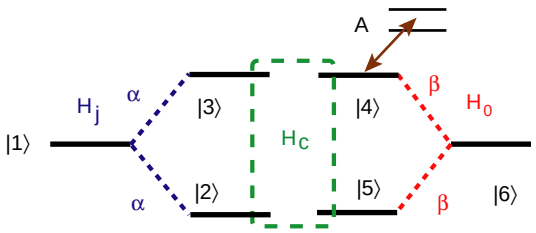

Fig. 5. Schematic model of the six-level main molecular system coupled to the ancilla qubit A used for the readout.

ancilla monitors the population of the molecular level $|4\rangle$. Suppose, for instance, that a fluorescence center is attached to the molecule. The presence of the tunneling electron in (say) state $|4\rangle$ may influence the state of the fluorescence center. In particular, we may expect that the electron could cause a transition between the dark state $|d\rangle$ and a bright state $|b\rangle$ of the center. These two states $|d\rangle$ and $|b\rangle$ span a basis of a single-qubit ancillary system A. The output of the computation is read out by measuring the state of the ancillary system in the computational basis $|0\rangle, |1\rangle \equiv |d\rangle, |b\rangle$.

More generally, we may envision a situation where some local probe is used to monitor the occupation of the level $|4\rangle$ of the molecular system. The qubit is conceptually the simplest model of such a probe, although other (and possibly more realistic) models, such us a harmonic oscillator system, may also be considered. The purpose of the probe is essentially to carry out a continuous quantum non-demolition measurement of the population of level $|4\rangle$ via appropriate interaction. Here, we model this coupling in such a way that the ancillary qubit may change its state if the main system is in state $|4\rangle$,

$$H_{\mathrm{int},A} = g_A |4\rangle_M\langle 4| \otimes (|0\rangle_A\langle 1| + |1\rangle_A\langle 0|), \quad (24)$$

where g_A is the coupling strength, and the index M stands for the main molecular system.

5.1. AND gate

The AND gate involves the main six-level system depicted in Fig. 1 with a single qubit ancilla A attached to the state $|4\rangle$, see Fig. 5. The total Hilbert space is 12-dimensional and the whole system is initially prepared in a product state $|1\rangle_M|0\rangle_A$. The evolution is governed by the Hamiltonian

$$H_{j,\mathrm{tot}} = (H_j + H_c + H_0) \otimes I_A + H_{\mathrm{int},A}, \quad (25)$$

where H_j and H_0 are given by formulas (2) and (3), respectively. The Hamiltonian H_c that we shall optimize only acts on the main molecular system, and I_A in Eq. (25) denotes the identity on the Hilbert space of the ancilla qubit. The input bits are encoded into the values of the coupling constants α_{12} and α_{13} in the same manner as in the preceeding section.

We have optimized H_c by maximizing the average gate fidelity (7) where $j \in \{00, 01, 10, 11\}$ and the relevant POVM elements are given by

$$\Pi_{00} = \Pi_{01} = \Pi_{10} = I_M \otimes |0\rangle_A\langle 0|,$$
$$\Pi_{11} = I_M \otimes |1\rangle_A\langle 1|. \quad (26)$$

Here I_M denotes the identity operator on the Hilbert space of the main molecular six-level system.

A typical result of the numerical optimization is shown in Fig. 6. The designed AND gate achieves a fidelity of about 95%. The optimal Hamiltonian H_c explicitly reads

$$H_c = \begin{pmatrix} 0.9084 & 0.3454 & 0.9110 & 0.6394 \\ 0.3454 & -0.5976 & -0.9833 & -0.4852 \\ 0.9110 & -0.9833 & -0.3055 & -0.9283 \\ 0.6394 & -0.4852 & -0.9283 & -3.2269 \end{pmatrix}. \quad (27)$$

We note that the ancilla serves as a sort of integrator, which is sensitive to the average population of the level $|4\rangle$ in the time interval $[0, T]$ rather than at a specific time. In fact, for the particular Hamiltonian (27) the average population of level $|4\rangle$ is about 25% on the time interval $[0, T]$ when both input bits are equal to 1 and only about 5% in the remaining three cases when at least one input bit is equal to 0.

5.2. HALF-ADDER gate

The HALF-ADDER gate can be designed similarly as the AND gate in the case of ancillary readout. However, we have not been able to find a reliable half adder with a six-level system and a real Hamiltonian H_c. Better results have been obtained for an extended seven-level main system, see Fig. 7. In what follows we present the optimized half-adder for the level scheme depicted in Fig. 7. As the half adder has two output bits, we need to use two ancillary qubits A and B that are coupled to levels $|4\rangle$ and $|5\rangle$ of the main molecular system, respectively.

The total Hamiltonian of the system is given by

$$H_{j,\mathrm{tot}} = (H_j + H_c + H_0) \otimes I_A \otimes I_B + H_{\mathrm{int},A} \otimes I_B + H_{\mathrm{int},B} \otimes I_A, \quad (28)$$

where H_j is given by Eq. (2), the interaction of the main system with ancillas A and B is described by

$$H_{\mathrm{int},A} = g_A |4\rangle\langle 4| \otimes (|0\rangle_A\langle 1| + |1\rangle_A\langle 0|),$$
$$H_{\mathrm{int},B} = g_B |5\rangle\langle 5| \otimes (|0\rangle_B\langle 1| + |1\rangle_B\langle 0|), \quad (29)$$

and we have

$$H_0 = \beta(|4\rangle\langle 7| + |5\rangle\langle 7| + |6\rangle\langle 7|) + \mathrm{h.c.} \quad (30)$$

Here again it is helpful to exploit the symmetry of the HALF-ADDER gate when assigning the values of the coupling constants to the values of the input

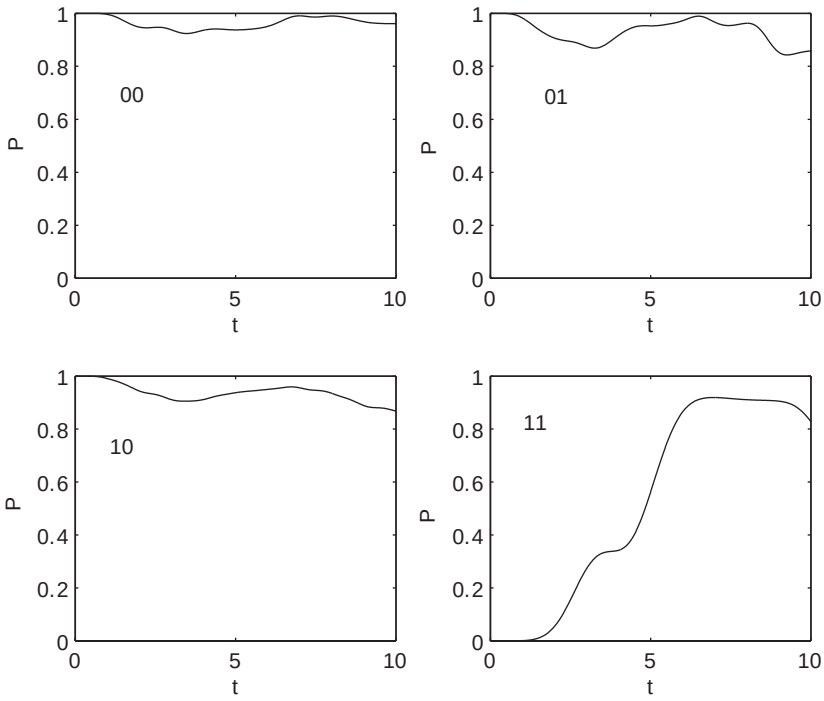

Fig. 6. The time dependence of the probability of correct output P of the intramolecular AND gate with ancillary readout. The bit encoding is described in the text, $\alpha = 2$, $q = 3$, $\beta = 1$, $g_A = 1$ and $T = 2\pi = 6.3$. The output bit is read by measuring the ancilla in the computational basis $|0\rangle$, $|1\rangle$. If at least one of the input bits is 0, then the ancilla almost remains in state $|0\rangle$, while, if both input bits are equal to 1, then the population of the ancilla state $|1\rangle$ builds up in time and reaches a maximum higher than 90%.

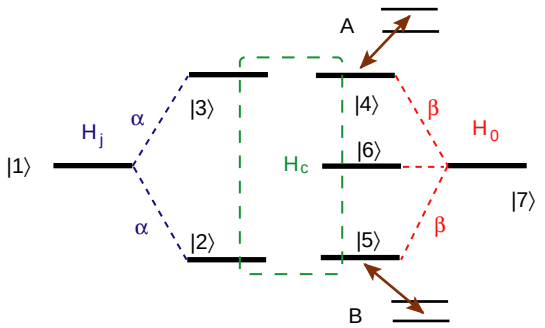

Fig. 7. Schematic model of the seven-level main molecular system coupled to two ancilla qubits A and B which are used for the readout.

bits. Recall that the first input bit is encoded in coupling constant between levels $|1\rangle$ and $|2\rangle$, while the second bit is encoded as the value of coupling constant between $|1\rangle$ and $|3\rangle$. Our particular encoding is specified in Table 3. We

Table 3
Truth table for the digital half-adder and the encoding of the input bits into the values of the coupling constants

Bit 1	α_{12}	Bit 2	α_{13}	XOR	AND
0	α	0	α/q	0	0
0	α	1	α	1	0
1	α/q	0	α/q	1	0
1	α/q	1	α	0	1

can see from Table 3 that in 50% of the cases (when the two input bits have different parity), the output should be XOR = 1 and AND = 0. The XOR bit is determined by measuring the state of ancilla qubit A, while the AND bit is found by measuring on the ancilla qubit B in the computational basis. It is convenient to assume that the ancilla qubits are initially prepared in the state that corresponds to the most probable outcome. We assume that initially A and B are prepared in state $|0\rangle_A|0\rangle_B$,

which implies the logical encoding of the output bits that is specified in Table 4.

We have numerically determined the optimal H_c that couples the five internal levels of the main molecular system shown in Fig. 7. The optimization has been carried on for the readout time $T = 4\pi = 12.6$ and results in

$$H_c = \begin{pmatrix} 2.5540 & 2.4640 & 0.0478 & 1.0959 & 0.2433 \\ 2.4640 & 2.2345 & 0.4547 & -1.5868 & 0.0966 \\ 0.0478 & 0.4547 & -1.1264 & 0.0821 & -0.1190 \\ 1.0959 & -1.5868 & 0.0821 & -0.6702 & -0.0640 \\ 0.2433 & 0.0966 & -0.1190 & -0.0640 & 0.2795 \end{pmatrix}$$

Table 4
Logical encoding of the output bits

XOR (A)	Level	AND (B)	Level
0	$\|1\rangle_A$	0	$\|0\rangle_B$
1	$\|0\rangle_A$	1	$\|1\rangle_B$

With this Hamiltonian the HALF-ADDER intramolecular gate operates with a mean fidelity $F = 86\%$. The time evolution of the probability of correct outcomes for the four possible combinations of the input bits is plotted in Fig. 8. The calculation also reveals that a significant average population of the level $|4\rangle$ or $|5\rangle$ in time interval $[0, 4\pi]$ occurs only if the correct operation of the half-adder gate requires flipping of the initial state of the corresponding ancilla qubit.

6. Conclusions and outlook

These results demonstrate how the rich structure of the quantum Hilbert space makes it possible to compute with a single molecule. By coupling the effective quantum levels that describe the molecule in the tight-binding approximation, it is possible to design reliable XOR and AND gates using only six quantum levels. This is even more interesting for the HALF-ADDER gate whose integrated design

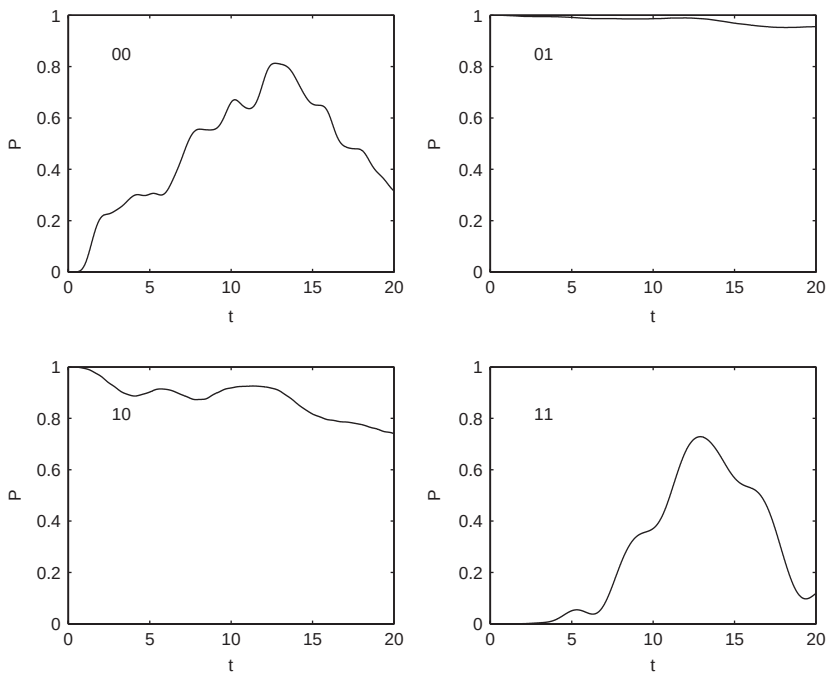

Fig. 8. The time dependence of the probability of correct output P of the intramolecular HALF-ADDER gate with ancillary readout. The bit encoding is described in Table 3, $\alpha = 2$, $q = 3$, $\beta = 0.5$, $g_A = g_B = 1$ and $T = 4\pi$. The two output bits are read by measuring the ancillas A and B in the computational basis $|0\rangle_{A,B}$, $|1\rangle_{A,B}$ and the results are interpreted according to Table 4.

requires much less levels than a simple combination of the AND and XOR gates. This opens new avenues for the design of more complex logic functions with a minimal number of quantum levels. This also puts forward the need to experimentally design real molecular structures that are characterized by the desired Hamiltonians, and to develop measurement schemes to access internal molecular levels.

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References

[1] F. Moresco, L. Gross, M. Alemani, K.H. Rieder, H. Tang, A. Gourdon, C. Joachim, Phys. Rev. Lett. 91 (2003) 036601.
[2] G.V. Nazin, X.H. Qiu, W. Ho, Science 302 (2003) 77.
[3] C. Joachim, J.K. Gimzewski, A. Aviram, Nature (London) 408 (2000) 541.
[4] C. Joachim, Nanotechnology 13 (2002) R1.
[5] Ch. Loppacher, B. Barmmerlin, M. Guggisberg, O. Pfeiffer, E. Meyer, R. Luthi, R. Schlittler, J.K. Gimzewski, H. Tang, C. Joachim, Phys. Rev. Lett. 90 (2003) 066107.
[6] J.C. Ellenbogen, J.C. Love, Proc. IEEE 88 (2000) 386.
[7] F.L. Carter, Physica D 10 (1984) 175.
[8] S. Ami, M. Hliwa, C. Joachim, Chem. Phys. Lett. 367 (2003) 662.
[9] F. Moresco, G. Meyer, K.H. Rieder, H. Tang, A. Gourdon, C. Joachim, Phys. Rev. Lett. 86 (2001) 674.
[10] A. Acín, Phys. Rev. Lett. 87 (2001) 177901.
[11] G.M. D'Ariano, P. Lo Presti, M.G.A. Paris, J. Opt. B: Quantum Semiclass. Opt. 4 (2002) 273.
[12] C. Joachim, I. Duchemin, J. Fiurášek, N.J. Cerf, Hamiltonian logic gates: computing inside a molecule, TNT 2003 "Trends in Nanotechnology", Salamanca, Spain, September 2003; Int. J. Nanoscience, submitted, 2004.