The driving power of the quantum superposition principle for molecule-machines

C Joachim

The Nanosciences Group, CEMES/CNRS, 29 Rue J Marvig, BP 94347, 31055 Toulouse Cedex, France

Abstract

To work, a unimolecular machine will ultimately depend on its preparation in a non-stationary superposition of its quantum states. We provide a description of the possible unimolecular devices or machineries for mechanics, information transmission, molecular electronics and molecular transduction. Experimenting on each category of machines must help to identify the physics behind the quantum superposition principle which is the driving force of most of those machines. This will help in optimizing their design and efficiency in such areas as the motive power for unimolecular mechanical machines, the capacity for molecular transmission channels, the computing power, speed and dissipated energy for molecular electronics and the sensitivity and response time for a unimolecular transducer.

1. Introduction

Nobody ignores the fact that the physics phenomena behind the superposition principle of quantum mechanics can drive a machine. Those quantum machines may present a very large efficiency as compared with their classical counterparts. Emulated using solid state mesoscopic devices, quantum logic gates are a good example of what a quantum machinery can do [1, 2]. On the other hand, there is no physics limitation for miniaturizing a machine down to the scale of a single molecule or conversely to monumentalize a molecule until it becomes a machine [3]. The limitations arise from the technical difficulties to communicate with a single well identified molecule. Therefore, nanoscale machines whose parts or full size measure less than a nanometre are good candidates to explore the physics behind the quantum superposition principle.

In this review, we propose a unified presentation of the different kinds of unimolecular devices and machines. Such molecules are mechanical machineries, transmission channels for classical and quantum information, calculators based on molecular electronics and transducers. They are the ultra miniaturized versions of our daily life macroscopic machines

or the miniaturized versions of micro-machines fabricated using standard micro- and nano-lithography techniques. They are all working at the single molecule level, meaning that information (orders, data) and energy are exchanged with a single (and always the same) molecule. We will not consider molecular machines in solution where there is no known way to access the function performed by only one molecule in the solution [4]. In those cases, it is not the same molecule which is maintained 'on line' during the experiment. It is a large population of identical molecules which is characterized by spectroscopy tools [5].

The comparison between different types of molecular machines may help in optimizing the chemical composition of a given molecular machine. Here, the applied goal is to embody a large computing power in a molecule, to optimize the motive power of a single molecular motor, and to increase the channel capacity of a molecular wire or the transduction efficiency of a unimolecular transducer. Optimizing the computing power, the channel capacity, and the motive power or the transduction efficiency of a nanoscale molecular machine may help to identify the driving force behind the superposition principle of stationary and non-stationary quantum states.

2. Driving a unimolecular machine by the quantum superposition principle

The running power of a quantum molecular machine is provided by the preparation of this molecule in a non-stationary quantum superposition of states, increasing its internal energy in reference to its ground state energy. After this preparation, the molecule responds internally by a redistribution of energy, spin or charge. This non-stationary preparation is characterized by an intramolecular density of energy no longer proportional to the electronic probability density of the molecule [6]. It is this non-proportionality which drives the initial internal response of a molecule to the de-equilibrium created by the initial non-stationary quantum preparation. Then, the decoherence and the relaxation processes occur: the decoherence without releasing energy out of the molecule and the relaxation for a progressive return of the molecule to its ground state.

Therefore, a unimolecular machine can perform during its internal response phase, during the decohence or during the relaxation phase of the response process. It can also perform by repeating the preparation–decoherence–relaxation cycle after each relaxation step as in the case of a molecular wire used to transmit classical information between two metallic electrodes or two dielectric waveguides (see below).

But what is the driving force behind a non-stationary quantum state superposition? We are dealing with a mathematical concept for driving a machine [2]. How do we attribute a motive power, a computing power, and a transduction efficiency to a linear superposition of vectors in a Hilbert space? In contrast to the heat engine or to the electronic solid state computer, we have not yet identified the physical quantity which is 'activated' when a molecule is prepared in a non-stationary quantum state. We certainly know that a non-stationary quantum state of a molecule has a finite lifetime. Various intramolecular magnetic, electronics or mechanics phenomena can occur during this time interval. Is the superposition principle, inherited from a Fourier-like series description of a physical phenomenon, able to describe all the possible responses of a single molecule after an increase of its internal energy?

One way to work on those questions is to design, drive and observe diverse unimolecular machines at work. There is not a lot of examples of unimolecular nanoscale machines at work at present. But as their number increases, the question of the efficiency of a given design and the choice of a given nano-communication device will arise, re-enforcing the need for a clear identification of the physics behind the superposition principle.

3. Mechanical unimolecular machines

Formally, a single molecule can be prepared in a non-stationary quantum superposition of its ro-vibronic states to perform a mechanical function like a deterministic and directional motion of the molecule on a surface, a unidirectional rotation of a molecular wheel or a controlled activation of the molecular clip bonded at the end of a molecular arm [7]. But in general, the detail of the mechanical vibration and rotation quantum states of a large molecule render very difficult the application of the superposition principle to define a coherent quantum superposition of states. In most cases, the initial prepared mechanical quantum wave packet decoheres well before the relaxation, leaving the mechanics of the molecule in a random motion with no resemblance to the targeted classical motion. In some cases, the decoherence process can be controlled by kicking up the mechanical wave packet by a well designed excitation [8]. But the technical difficulties of accessing a single well identified molecule with a wide band communication access render this technique still very delicate to apply. As a consequence, the motive power of the superposition principle is unknown for unimolecular mechanical machineries.

To perform molecular mechanics with a single molecule, it is generally preferred to adsorb the molecule on a surface, therefore placing the molecule in interaction with a thermal reservoir [7]. In this case, the mechanics of the molecule becomes semi-classical on its electronic ground state multi-dimensional potential energy surface. Of course, the interaction of the molecule with the surface and its intramolecular mechanics is still described by quantum mechanics. Up to now, a popular way of performing such a mechanics is to increase the ro-vibronic ground state potential energy of the molecule by bringing the apex end atom of an STM tip into interaction with a part of the molecule [9–11]. This corresponds to an incoherent superposition of those ro-vibronic quantum states and the mechanics of the molecule is semi-classical.

A lateral manipulation of a molecule along the surface or an intramolecular conformation change can be performed this way. For certain molecules, it is expected that a part of the potential energy gain during the tip apex interaction will trigger a specific intramolecular conformation change of a given chemical group like a molecular wheel rotation or a gear effect [11, 12]. All those conformation changes remain in the ground state of the molecule. This already indicates the difficult task of a molecular designer since the ground state potential energy surface is in general very complex. One has to determine the best reaction pathway to pass over a specific potential energy barrier to trigger a given internal motion. On its ground state multi-dimensional potential energy surface, this may open the way to determine the efficiency of a unimolecular motor depending on the detailed pathway followed to pass from one station of its rotor to another one as a function of its load. Of course, the load itself may also transform the landscape of this surface, which renders the optimization of a molecular motor an open question.

More recently, electronic excited states have been used experimentally on simple molecules to help in passing over the potential barrier on a reaction pathway of the ground state potential energy surface. This is the case for the biphenyl conformation change on Si(100) reaching the first excited state by STM spectroscopy to trigger a surface conformation change [13]. This solution is also at the basis of the proposed design of a molecular motor driven by a total reduction of the first electronic excited state of the molecule [14]. The interest in such a preparation is that the internal energy increase is not due to a large deformation of the molecule by the STM tip apex. The energy delivery to the targeted mechanical degrees of freedom is expected to be more precise in this case. Superposing ro-vibronic quantum states from the excited and ground electronic states of the molecule can be viewed as an approach to

drive the mechanics of the molecule by a quantum superposition of states. But on a surface, this requires a very good quantum insulation of the molecule from the surface for the non-stationary superposition to trigger the intramolecular response before the relaxation of the excited states used in the process.

4. Intramolecular communication channels

Quantum superposition of states can be used to conceive encryption codes and quantum communication procedures [15]. Some channels are immaterial and statistical in nature, using entangled states of particles to introduce a correlation between the emitter and the receiver. Others channels are truly material in nature, like macromolecular carbon nanotubes for the transport of ballistic electrons or molecular wires to guide in space the electronic super-exchange interaction.

An example is given by a molecular wire connected to an electrical circuit, jumping over an insulating nano-gap between two metallic nano-electrodes. Electronically interacting to the source and the drain of the circuit, the nano-electrodes are preparing billons of non-stationary quantum electronic states of this molecule per second [16]. Each preparation triggers an electronic super-exchange quantum process through the molecule. Decoherence and then relaxation occur at the nano-electrodes and a measurable tunnel current arises by averaging in time all those electron transfer events. A properly interconnected metal–molecule–metal tunnel junction is performing such a 'non-stationary preparation–relaxation' cycle natively with no more than biasing the junction with a voltage or a current source [16]. For a transfer of classical information defined by the instantaneous presence of one electron more on one electrode than on the other, there is nothing more to do than to optimize the contact conductance and the chemical structure of the molecular wire for the super-exchange decay constant to be as small as possible. For a transfer of quantum information through the molecular wire, one is also interested by the detailed quantum state superposition of the electrons to be transferred. Therefore, playing the role of the source, the nano-electrode must be able to prepare such quantum state superposition. This state will have to be preserved all along or restored after the long distance transfer process through the molecular wire. The detailed design of the nano-electrodes able to perform such a task is not known.

Whatever the type of information to be transferred, it remains that the long range transfer process of information through a molecular wire has only been considered from its super-exchange inverse decay length point of view [16]. Considered as a quantum channel for transferring classical or quantum information, the characteristics of a molecular wire like its channel capacity, its quantum noise level and its bandwidth remain to be evaluated.

5. Calculating molecules

There are multiple possibilities to build up a calculator with molecule(s) [17]. Aside from using molecular mechanics (see section 3) and assembling molecule per molecule a molecular abacus, a molecular cascade or playing with molecular gears in an attempt to assemble a Pascaline, it is more attractive to play with electrons to encode the information and to compute. Molecular electronics can be hybrid (molecular or macromolecular) or mono-molecular, playing with intramolecular tunnel circuits or the quantum superposition principle directly [17]. In all cases, the data in, the data out, or both, are electronic in nature. According to the previous discussion on molecular transmission of information, this means that the basics of the function will be performed using electron transfer phenomena through the molecule.

In the most simple hybrid molecular electronics case, each molecule in the circuit is a device (transistor, rectifier). In each device, the tunnel current passing through the molecule from the source to the drain results from billions of electronic non-stationary quantum states time averaged in the electrodes as in the case of information transfer from one electrode to the other [16]. The difference is that a third lateral electrode is controlling this transfer process. The resulting grid effect can affect the electronic coupling between the molecule and the electrodes, the source to drain electrodes electronic coupling through the molecule, the position of the molecule energy level relative to the electrode Fermi level, the homo–lumo gap of the molecule, or a combination of all of these [18]. Finally, a switch or some power gain results with a device made of a single molecule interacting with three electrodes. At least two of those electrodes, the source and the drain, play the role of a quantum-classical converter since in the bulk of the nano-electrodes, a few tens of nanometres away from the molecule, the tunnelling current becomes detectable by a macroscopic ammeter. A full calculator may be built by interconnecting those molecular devices in a vast circuit using mesoscopic metallic wires for the interconnects between the molecular devices.

In terms of architecture, one may find that it is not very efficient to structure a machine with so many quantum-classical conversions, one per device. A more elegant solution is to take benefit of the intramolecular behaviour to perform the full computation inside the same molecule and then to introduce the quantum-classical converters on the input and output on this necessarily large molecule before and after the full computation stage. This is called mono-molecular electronics, in which the metallic interconnection wires between each molecular device of the hybrid molecular electronic solution disappear and the full interconnection circuit is embedded in the molecule [17]. This mono-molecular architecture opens four distinct solutions:

(1) to force the molecule to have the shape of an electronic circuit with well identified molecular wires and a three-terminal device chemical group embedded in the same molecule [19–21],
(2) to keep the circuit shape but play with electronic waves by introducing a chemical group with a loop shape to create electronic interferences [22],
(3) to cancel the device or loop structure of the molecule and divide the molecule in qubits interacting through space or through a specific molecular wire group [15],
(4) to suppress also the qubits in the molecule and consider the full molecule as a gigantic quantum Hamiltonian processor [23, 24].

Each of these solutions is now actively explored and the reader may refer to technical papers about them. Aside from the difficult technological and chemistry problems to implement each of these solutions, the question is: for a given complexity, which one will show up with the best calculation efficiency in terms, for example, of speed and power dissipation. This again will depend on how the molecular structure is designed to handle its preparation in a non-stationary quantum state to compute, and for some solutions, even using entangled states.

For example, solution (1) seems very attractive since part of the knowledge about electronic circuit rules may be applicable, as is assumed sometimes [20]. This is not true because the electron transfer process occurring between the electrodes are not following the standard Kirchhoff electrical circuit laws [17]. New laws have been demonstrated which take into account, for example, that an electron transfer process through a molecule is not a resonant process but a quantum phenomenon resulting from the super-exchange mechanisms [16]. Taking into account the specificities of this phenomenon is the first intervention of the non-stationary character of the electronic state of the molecular wire to establish a rule for building a machine.

At the molecular scale, solution (3) had been proposed using, for example, nuclear spin resonance [15]. But as with (1), this solution preserves a bit of the macroscopic circuit spirit: to divide a complex system into small parts and to link those parts together by an interconnection system. This may not be very well adapted for a quantum system. Furthermore, it requires the presence of the interconnections of the molecule to define the phase of the electrons. It is still very delicate to play with time-dependent interferences during the electron transfer process since they average out at the electrodes.

Solution (4), also called a quantum Hamiltonian approach [23], uses the peculiar topology of the quantum state space to drive the quantum trajectory in certain directions by changing the Hamiltonian. The molecule is not divided in small device parts [23]. Therefore, the data input are parameterized on the Hamiltonian and not on the initial quantum state vector as in quantum computers [15]. This appears to be the best way to exploit intramolecular quantum dynamics. But this requires a full knowledge of the quantum state space and of the controllability of a quantum trajectory on this state space. This is not yet available [23]. Furthermore, and like with solution (3), it appears very delicate to run a full complex computation using a large molecule by feeding up the molecule only with the initial non-stationary quantum state preparation. With many quantum states involved in the process, not all have the ideal energy level position nor are prepared with a good initial phase. Decoherence interplays very early in the quantum evolution. At this point, we really need to know more about the physics of quantum evolution of a non-stationary state to control this phenomenon.

Molecular electronics is converging towards the integration of the arithmetic and logic unit of a computer in a large molecule in a tentative approach to bond more atoms together to achieve a complex computation [25]. It was predicted that such computers built up from atomic scale technology will be achieved with a very large computing power, that they will be very fast and will dissipate much less energy than the micro- and future nano-electronic solid state computers. This computing power depends on the efficiency of the initial non-stationary quantum electronic state to drive the computation. It was recognized that for the mono-molecular options (1) and (2), the importance is more on the efficiency of the quantum-classical conversion occurring at the interconnection than on the detail of the superposition of the quantum states prepared natively by the electrodes. In contrast, for options (3) and (4), it is essential to optimize this preparation. Each non-stationary state preparation is supposed to support a computation step. In the absence of tools to appreciate the trajectory of a quantum state describing the quantum time evolution of quantum system with more than four quantum states [26], it is very difficult to predict the computing power of such quantum systems.

6. Unimolecular transducers

Finally, and again in a single molecule, the preparation of a given set of degrees of freedom in a non-stationary quantum state can serve to transfer the energy provided to the molecule during this preparation to other degrees of freedom of the same molecule or even to external degrees of freedom like the electromagnetic field. A large variety of transduction effects may be performed by a single molecule. A first type involves the electronic super-exchange phenomenon of electrons through a molecule between two electrodes. This process can activate the conformation change of a given chemical group in the molecule, the rotation of the full molecule on the surface [27], the light emission of a part of the molecule, the generation of a magnetic field or the control of a chemical reaction. Another type of transduction involves light adsorption, which may be able to drive the motion of the molecule on a surface or to generate a charge separation inside the molecule. Deformation of the molecule by the STM or the AFM tip apex may also be used to convert a mechanical motion in a

chemical reaction or in the modulation of the surface electronic waves at the surface of a metal [28].

Unimolecular machineries for transduction are not very well developed because they generally require more than two atomic scale interconnects to set up a pump–probe-like experiment. But such unimolecular devices are now starting to be designed on computers. These simulations are raising questions on the efficiency of an intramolecular transduction effect, like its sensitivity or its response time. One 'simple' example is the design of a single molecule ammeter, that is a molecule able to change its conformation as a function of the tunnel current intensity passing through it [29]. This conformation change is supposed to be detected by a third electrode. A sensitivity curve can be easily calculated in a semi-classical approximation relating the current intensity measured via the third electrode to the driving input current. On the one hand, this sensitivity depends on the spring constant associated with the conformation change. On the other hand, the sensitivity depends on the conversion between the 'quality' of the non-stationary state prepared by the driving electrodes and the release of this energy on the soft nuclear degrees of freedom of this molecule. What is the best quantum superposition to be prepared for the transferred electrons to trigger the conformation change? We do not yet have an answer to this question.

7. Conclusion

Whatever the technical difficulties to exchange data, orders, information, or synchronization signal and to provide energy to a single and always the same large organic molecule, we have shown here that the ultimate driving force behind any unimolecular machine is an initial preparation of its quantum states in non-stationary quantum superposition. The response of the molecule-machine to this excitation provides the basis of the work that it will perform. One can design the molecule and its nano-communication channels to perform before the decoherence of its time-dependent quantum state, during the energy relaxation of this initial state. One can also benefit from the native 'excitation–decoherence–relaxation' sequence generally observed when a molecule interacts at least with one surface and permanently feeds in this sequence. However, the origin of the driving force triggered by the superposition principle is not known. This explains why, in many cases, the design rules applied are totally classical in nature. This may be not very well adapted to what a single molecule-machine can do, even adsorbed on a surface.

References

[1] Nakamura Y, Pashkin Y A and Tsai J S 1999 *Nature* **398** 786
[2] Vion D, Aassime A, Cottet A, Joyez P, Pothier H, Urbina C, Esteve D and Devoret M H 2002 *Science* **296** 886
[3] Gimzeswki J K and Joachim C 1999 *Science* **283** 1683
[4] Balzani V, Credi A, Raymo F M and Stoddart J F 2000 *Angew Chem. Int. Edn* **39** 3348
[5] Koumura N, Zijlstra R W J, van Delden R A, Harada N and Feringa B L 1999 *Nature* **401** 152
[6] Joachim C 1986 *J. Phys. A: Math. Gen.* **19** 2549
[7] Joachim C and Gimzewski J K 2001 *Struct. Bond.* **99** 1
[8] Villeneuve D M, Aseyev S A, Dietrich P, Spanner M, Ivanov M Y and Corkum P B 2000 *Phys. Rev. Lett.* **85** 542
[9] Jung T A, Schlittler R R, Gimzeswki J K, Tang H and Joachim C 1996 *Science* **271** 181
[10] Keeling D L, Humphry M J, Fawcett R H J, Beton P H, Hobbs C and Kantorovich L 2005 *Phys. Rev. Lett.* **94** 146104
[11] Shirai Y, Osgood A J, Zhao Y, Kelly K F and Tour J M 2005 *Nano Lett.* **5** 2330
[12] Gross L, Moresco F, Wang C, Rapenne G, Jimenez G and Joachim C 2005 *Surf. Sci. Lett.* **584** L153
[13] Lastapis M, Martin M, Riedel D, Hellner L, Comtet G and Dujardin G 2005 *Science* **308** 1000
[14] Rapenne G, Launay J P and Joachim C 2006 *J. Phys.: Condens. Matter* **18** S1797

[15] Nielsen M A and Chuang I L 2001 *Quantum Computation and Quantum Information* (Cambridge: Cambridge University Press)

[16] Joachim C and Ratner M 2005 *Proc. Natl Acad. Sci. USA* **102** 8801

[17] Joachim C, Gimzewski J K and Aviram A 2000 *Nature* **408** 541

[18] Joachim C, Gimzewski J K and Tang H 1998 *Phys. Rev.* B **58** 16407

[19] Carter F L 1984 *Physica* D **10** 175

[20] Ellenbogen J C and Love J C 2000 *Proc. IEEE* **88** 386

[21] Ami S, Hliwa M and Joachim C 2003 *Chem. Phys. Lett.* **367** 662

[22] Baer R and Neuhauser D 2002 *Chem. Phys.* **281** 353

[23] Duchemin I and Joachim C 2005 *Chem. Phys. Lett.* **406** 167

[24] Remacle F and Levine R D 2001 *Chem. Phys.* **114** 10239

[25] Joachim C 2002 *Nanotechnology* **13** R1

[26] Mosseri R and Dandoloff R 2001 *J. Phys. A: Math. Gen.* **34** 10243

[27] Stipe B C, Rezaei M A and Ho W 1998 *Science* **279** 1907

[28] Gross L, Moresco F, Savio L, Gourdon A, Joachim C and Rieder K H 2004 *Phys. Rev. Lett.* **93** 056103

[29] Hliwa M, Ami S and Joachim C 2006 *Chem. Phys. Lett.* submitted