

Quantum dynamics study of the hydrogen molecule confined in single-walled carbon nanotubes

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Abstract—In the present work a full-dimensional study of the dynamics of a hydrogen molecule confined in a narrow Single-walled Carbon Nanotube (SWCNT) is performed by using the Multi-configurational Time-dependent Hartree approach. New insights on the coupling between the different degrees of freedom of the molecule during the diffusion along the nanotube are found and discussed.

I. INTRODUCTION

Storage of low-density gaseous species has become a field of intensive research in the last few years. Its interest arises with two basic objectives in mind: store large amounts of potential fuels in order to make their transport from the production centers feasible, and capture known pollutants from the atmosphere to prevent, for instance, greenhouse effect [1-5]. Concerning the first application, the paradigmatic case of hydrogen is the one in which we focus our study.

Hydrogen has a very low density that makes its storage in sufficient amounts not viable with the common storage devices like high-pressure tanks [3]. This is the reason why novel alternatives are being studied to store high amounts of hydrogen in a non-expensive, reversible way. Nanostructured materials, such as Carbon Nanotubes (CNT) or some Metal-organic Frameworks (MOFs) show the potential to be used for this purpose.

Hydrogen confined in nanostructured materials has been a matter of intensive research both theoretically and experimentally in the last few years [6-10]. The studies carried out in this kind of systems have shown not only the effectivity of some of these materials as storage devices, but also some distortions of the confined molecules at the molecular level when the cavities in which they are trapped are of the order of the nanometer. These changes of the electronic structure and the dynamics of confined species are of great importance since they not only allow a better understanding of the affinity of the confined molecules by the adsorbant, but because they have allowed the discovery of new potential applications for nanostructured materials, such as *quantum sievings*, which allow the separation of isotopomers of a given molecule, like H_2 and D_2 , due to the different Zero-point energy (ZPE) of molecules with different mass [11]. Also, some investigations point to the possibility of controlling chemical reactions at the molecular level using nanostructured materials [12].

There are mainly two theoretical approaches to study these systems. The first one is the study of adsorption through Molecular Dynamics simulations. This allows the study of bulk diffusion effects with hundreds of molecules in a non-expensive way, but relies completely on classical mechanics

and therefore cannot be used to study quantum phenomena, such as quantum confinement. The second approach, which is the one used in the present work, treats the problem quantum mechanically. This so-called Quantum Dynamics approach is much more expensive and has been rarely used to treat more than a few molecules, but on the other hand is the only tool which allows the study of intrinsically quantum effects.

The present work is structured in two main sections: first the computational tools, namely Multiconfigurational Time-dependent Hartree approach, as well as the model used to study our system, will be explained. Then the results of the study will be outlined and the main conclusions summarized.

II. COMPUTATIONAL TOOLS AND MODELLING OF THE SYSTEM

A. The Multiconfigurational Time-depend Hartree method

The MCTDH method allows an efficient propagation of multidimensional wave packets [13]. This is possible due to the use of a two-layer representation for the wave functions: it is represented in a relatively small basis set of time-dependent, low-dimensional basis functions, known as Single-Particle Functions (SPFs, ϕ), which in turn are expanded in a time-independent basis of primitive functions:

$$\Psi(Q_1, \dots, Q_p, t) = \sum_{j_1=1}^{n_1} \dots \sum_{j_p=1}^{n_p} A_{(j_1, \dots, j_p)}(t) \prod_{k=1}^p \phi_{j_k}^{(k)}(Q_k, t)$$

This *Ansatz* in combination with the Dirac-Frenkel variational principle, yields a system of coupled equations of motion for the system which must be integrated to solve the dynamics of the problem. The two-layer approach allows an important decreasing of the size of the matrices to work with during the integration of the equations of motion, since the time-dependent basis set is able to adapt to the total wave function, yielding the best possible basis set at each time step.

B. Modeling of the system:

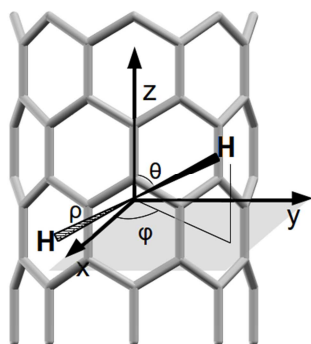
In our model, hydrogen is treated with a full-dimensional Hamiltonian. The degrees of freedom of the system are depicted in Fig. 1. This model allows to see the effects of the coupling between the different degrees of freedom. On the other hand, the carbon nanotube is considered in the rigid cage approach, and therefore all atoms are fixed in their equilibrium geometry positions. Therefore this model will allow us to observe effects of the confinement in the structure of the

hydrogen molecule, but will not treat the energy exchange between the nanostructure and the confined molecule.

Due to the periodicity of the carbon nanotube, the computation and interpretation of the eigenstates of the hydrogen molecule in full dimension is not a trivial task. Instead, we will focus on another interesting and more straightforward property of this system such as the diffusion of the hydrogen molecule along the nanostructure. In order to study this particular feature of the system, a meaningful initial state must be propagated. In order to obtain this state, we add a harmonic trapping potential in the z coordinate. This allows us to calculate several eigenstates of the system with mainly no dependence on z and which mimic a thermal ensemble. These states can be propagated afterwards by “turning off” the trapping potential.

III. RESULTS

The propagation of the wave packets in six dimensions for a time of 200 fs showed only a small distortion of the function in all coordinates except z . This small coupling is explained by the low corrugation of the potential along the z coordinate in the studied nanotube. Hence, the system is almost separable,



which opens a way to study the diffusion phenomena using a simplified model in the future, using the present full

Figure 5: Scheme of the degrees of freedom used to study the hydrogen molecule in the hollow cavity of a SWCNT.

dimensional study as a benchmark.

The study yielded satisfactory results for the diffusion coefficients of the hydrogen molecule at several temperatures. This property of the system was calculated following two different approaches. The first one was based on the time the wave packet needed to pass from a unit cell to the following. The second approach used the thermal flux correlation function formalism in order to obtain a reliable approximation to the rate of the process, which can be afterwards related to the diffusion coefficient.

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