

Quantum dynamics of H atom transmission across carbon nanotubes

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Abstract Exact quantum dynamics calculations have been performed for the transmission of an H atom across a carbon nanotube. The time dependent wavepacket method used is the one coded in the modified version of our RWAVEPR program. The interaction potential used is based on a simple, pairwise additive Lennard–Jones 6–12 atom–atom interaction. S matrix elements (and, consequently, transmission probabilities) are calculated over a wide range of energies for the first radially and angularly excited states of the H atom.

1 Introduction

It is well known that, apart from systems comprising three or four atoms at maximum, the exact quantum mechanical treatment of a dynamical system is prohibitive at present. This is particularly the case for systems of interest in biology, such as the passage of ions along semipermeable membranes, or in engineering, where semipermeable membranes are substituted by structures which can be modelled in a simplistic way, such as carbon nanotubes [1]. Additionally, carbon nanotubes are interesting in themselves because of their potential technological uses, for example to store hydrogen for use in fuel cells.

The best way of attacking this problem is, at present, through the use of classical mechanics (for example through a molecular dynamics scheme). The potential energy for such systems, arising from the electronic motion, is typically formulated in terms of tentative force fields [2]. As far as the actual nuclear dynamics is concerned, quantum mechanics enters only (at maximum) as a perturbation, for example when one wishes to include specific interference or tunnelling contributions to the dynamics.

Given the situation as it is, it would be interesting to confront standard dynamics results using classical mechanics with quantum mechanical ones. Not only would the latter ones serve as a benchmark for various approximate treatments of quantum effects (such as the tunnelling mentioned above) but one can conceive of effects such as quasibound states arising from a temporary trapping of molecules in potential wells, which are difficult to account for classically.

The problem of hydrogen molecules confined in carbon nanotubes has been treated quantum mechanically by Lu et al. [3,4]. These authors have tackled the problem of computing bound states of an H₂ molecule inside a C nanotube, treating rigorously all degrees of freedom of the molecule. Such studies are intimately connected with the use of C nanotubes as ‘quantum sieves’ to separate molecules similar in size [5–9].

In this paper, we present a method to tackle molecules in carbon nanotubes in the continuous (as opposed to discrete) energy spectrum. The passage of an H atom across a carbon nanotube is studied from a purely quantum mechanical view, utilising a time dependent wavepacket propagation algorithm. The algorithm is an adaptation of the RWAVEPR code written by us to study three-atom chemical reactions [10,11] to the atom-in-

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nanotube problem. The coordinates of the atom are the only degrees of freedom treated quantum mechanically, while the nanotube itself is assumed rigid, without internal vibrations. This paper is a continuation of our previous work studying the quantum dynamics of an H⁺ ion passing along a carbon nanotube [12].

2 Theory

The formulation of the problem is in terms of a wavepacket being propagated in the interior of a rigid cylinder and subject to an external potential. Because of the inherent quasi-cylindrical symmetry of the problem, the wavefunction is expressed in cylindrical polar coordinates (r, θ, z) where z is the longitudinal distance (along the nanotube), r is the distance from the axis of the nanotube and θ is the azimuthal angle ranging from 0 to 2π . In these coordinates, the Hamiltonian for the system is:

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) + V(r, \theta, z) \quad (1)$$

which can be written in an alternative way, avoiding the first derivative term:

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial z^2} + r^{-1/2} \frac{\partial^2}{\partial r^2} r^{1/2} + \frac{1}{4r^2} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) + V(r, \theta, z) \quad (2)$$

and, finally, using the substitution $\Psi = r^{1/2}\psi$ for the wavefunction, we get the Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial r^2} + \frac{1}{4r^2} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) + V(r, \theta, z) \quad (3)$$

(Notice that a negative, inverse-square ‘centripetal’ potential has been added as a result of the transformation).

The potential is a function of the three coordinates of the atom. In this work, it has been calculated simply as a sum of Lennard–Jones (6–12) contributions arising from atom–atom interactions between the H atom and each of the C atoms of the nanotube within a certain threshold distance from the atom. The parameters used for the potential, as well as the grid parameters, are seen in Table 1. We are fully aware of the fact that such a treatment of the interactions neglects many important effects, not least of which is the possibility of a bond formation between the H atom and the nanotube due to short range chemical interactions. The purpose of the

Table 1 Grid parameters used in the calculation (distances are in bohr)

z spacing	Number of points (z)	r spacing	Number of points (r)	Number of angular points
0.1	216	0.1	72	16

paper, at this stage, is a semi-quantitative assessment of the quantum and classical effects of the nanotube potential on the H atom migration. Through such an assessment, one can more readily gain insight into problems of a similar nature, such as the migration of atoms or ions through the cylindrical-like potentials of environments such as cellular membranes.

The mean position and energy of the wavepacket, as well as its angular momentum K around the central axis of the nanotube, are initially read from an input file, and subsequently the wavepacket is set up on a grid in the three cylindrical polar coordinates. The grid parameters have been suitably chosen to represent well the maximum energies and angular momenta of the wavepacket. The z -part of the wavepacket is normally a suitable Gaussian, whereas the radial-angular part is a product of a suitably scaled Bessel function of the r coordinate and an imaginary exponential dependent on the angle θ .

$$\phi(r, \theta, z) \propto \exp\left(-\frac{(z - z_0)^2}{2\sigma^2}\right) \times J_K(kr) \times \exp(iK\theta) \quad (4)$$

In this way, the transverse energy (radial and angular) is equal to

$$E_r = \frac{k^2 \hbar^2}{2m} \quad (5)$$

Here k is proportional to a zero of the J_K Bessel function, suitably chosen to give a transverse energy as close as possible to the one desired. After that, the wavepacket propagates in time, and the expectation value of the flux operator across two surfaces with constant z is monitored. These two surfaces correspond to the two ends of the nanotube. Suitable artificial potentials have been included (an imaginary one near the longitudinal ends of the nanotube and a real, high one near the radial end) to avoid unphysical behaviour of the wavepacket.

The flux operator has the form:

$$\hat{F} = \frac{i}{\hbar} [\hat{H}, \theta(z - z_0)] \quad (6)$$

where $\theta(z)$ is a Heaviside step function corresponding to the surface $z = z_0$. The expectation value of the flux operator corresponds to the temporal derivative of the fraction of the wavepacket that has already exited from the nanotube. Thus, its integral over time gives the total probability of exit from the particular part of the nanotube and the sum of the two probabilities (for the two sides) should give one. This has been checked to ensure that no scaling errors occurred in the calculation.

2.1 The S matrix formalism

The quantum dynamics of the passage of an atom through a nanotube (or, indeed, any cylindrical potential) can be most conveniently described by the S matrix formalism widely used in molecular, atomic and nuclear dynamics. The S matrix contains all information experimentally obtainable for the process under study and thus represents the ultimate scope of all quantum scattering calculations.

In our context, the energy eigenfunctions describing the passage of an atom through a nanotube have definite asymptotic forms at the two extremes of the nanotube (henceforth termed the incoming extreme and the outgoing extreme). It is assumed that, outside the nanotube, the cylindrical symmetry of the potential is retained in the form of an impenetrable cylindrical wall around the atom but without the fine structure of the nanotube. This serves to facilitate the calculation by imposing well defined asymptotic conditions on the wavefunction.

At the incoming extreme of the nanotube, the energy eigenfunction has the form:

$$\psi_{n,E}(r, \theta, z) = v_n^{-1/2} \phi_n(r, \theta) e^{ik_n z} - \sum_{n'} v_{n'}^{-1/2} S_{n,n'}^R(E) \phi_{n'}(r, \theta) e^{-ik_{n'} z} \quad (7)$$

where ϕ_n is the n -th internal eigenstate of the particle, assumed to be the initial one, k, v are, respectively, the wavevector and the velocity and S^R is the reflection S matrix.

On the other hand, at the outgoing extreme of the nanotube, the energy eigenfunction has the form:

$$\psi_{n,E}(r, \theta, z) = - \sum_{n'} v_{n'}^{-1/2} S_{n,n'}^T(E) \phi_{n'}(r, \theta) e^{ik_{n'} z} \quad (8)$$

where now S^T is the transmission S matrix element. The square modulus of each S matrix element (generally complex) gives the probability that the particle exits in the particular state n' and from the particular extreme of the nanotube.

In order to evaluate the relevant S matrix elements, at each point in the propagation the overlap integral of our wavepacket with a suitably constructed (fixed) product wavepacket is evaluated. There is one product wavepacket for each exit state, which has the form:

$$\chi_{n'}'(r, \theta, z) = \phi_{n'}(r, \theta) \times \chi(z) \quad (9)$$

where ϕ is the energy eigenfunction (discrete) and χ an outgoing Gaussian wavepacket. At the start of the calculation, both overlap integrals of the initial wavepacket with each energy dependent incoming wavefunction and the product wavepackets with each outgoing energy eigenfunctions are calculated:

$$c_{v,in}(E) = \langle \chi_{v,in} | \phi_{v,in}(E) \rangle \quad (10)$$

$$c_{v',out}(E) = \langle \chi_{v',out} | \phi_{v',out}(E) \rangle \quad (11)$$

Thus, for each possible product state, a time dependent overlap function is constructed (which, in principle, is limited in time because of the dynamics of the problem). From this overlap function the S matrix element can be constructed using a half-Fourier transform:

$$S_{v,v'}(E) = \frac{\int_0^\infty \langle \chi_{v',out} | e^{i(E-\hat{H})t} | \chi_{v,in} \rangle dt}{c_{v,in}(E) c_{v',out}(E)} \quad (12)$$

3 Computational details

3.1 Nanotube system and initial preparation

The nanotube where the propagation takes place is essentially formulated as a cylindrical well (with a high constant potential on the walls to prevent escape of the H atom) where, for a certain length, carbon atoms are placed in prespecified positions. The particular characteristics of the nanotube are in Table 2.

The carbon atoms are arranged in annular layers consisting of 20 atoms each. The layers are arranged longitudinally according to an ABABAB... pattern, where layer B is identical to layer A rotated by 18°. The nanotube has been constructed so that the minimum of the Lennard–Jones atom–atom potential used in this calculation is approximately on the axis of the cylinder. This is expected to permit an assessment of the dynamical effects of the nanotube on the H atom, where the

Table 2 Nanotube dimensions (in bohr)

Radius	Length	Interlayer distance
7.2	8.0	2.0

potential is neither too repulsive to prevent all longitudinal motion nor too low to prevent all inelastic excitations of the H atom.

The initial wavepacket is prepared in the energetically lowest state (ground state) corresponding to $K = 0$ and a radial quantum number $\nu = 0$. This way, the amplitude is maximised around the centre of the cylinder and there is no initial angular momentum component (helicity) along the nanotube axis. This state corresponds to an approximate zero point energy of $3.5E - 05$ hartree. The longitudinal energy of the wavepacket covers an approximate range between 0.01 and 0.03 hartree.

3.2 Wavepacket propagation

As is common with time dependent algorithms, the wavepacket is represented on a discrete grid for all three cylindrical polar coordinates. For the two coordinates z and r , the grid points are equidistant and constitute a basis set corresponding to a discrete variable representation complementary to the ‘sine’ finite basis representation. Such a representation is legitimate since the amplitude of the wavefunction is assumed to vanish at sufficiently large distances from the axis (on the wall of the cylinder) and at sufficiently large longitudinal distances (where the wavepacket has been absorbed long before it has had time to reach). Such a representation is very convenient from a computational point of view since, as will be shown later, it facilitates considerably the calculation of the translational and radial kinetic energy terms.

At each point of the propagation, the Hamiltonian of the system needs to operate on the wavepacket. The potential energy part amounts to a simple multiplication of the wavepacket at each grid point (corresponding to a DVR function) with the value of the potential at this point. The angular kinetic energy terms are evaluated at each r and z coordinate values using a basis set transformation of the DVR angular functions to the ‘particle on a ring’ eigenfunctions where the kinetic energy operator is diagonal:

$$\begin{aligned} \langle \theta' | \hat{T}_\theta | \theta \rangle &= \langle \theta' | K \rangle \frac{K^2 \hbar^2}{2mr^2} \langle K | \theta \rangle \\ &= e^{iK(\theta' - \theta)} \frac{K^2 \hbar^2}{2mr^2} \end{aligned} \quad (13)$$

The translational (along the z coordinate) and the radial (along the r coordinate) kinetic energy is evaluated using a two dimensional Fourier transform. By multiplying the wavepacket by $r^{1/2}$ (an operation analogous to the multiplication by r in three dimensions) we

reduce the kinetic energy term to:

$$\hat{T}_{rz} = -\frac{\hbar^2}{2m} \left(\frac{d^2}{dz^2} + \frac{d^2}{dr^2} \right) \quad (14)$$

i.e., a sum of second derivatives whose effect can be calculated using a two-dimensional Fast Fourier Transform algorithm.

Moreover, at each point of the propagation, the overall flux of the wavepacket across the centre of the product wavepacket is calculated by calculating the expectation value of the flux operator mentioned in the previous section. Apart from giving us an approximate time-dependent picture of the transmission dynamics (which is, in a sense, complementary to the energy dependent S matrix elements), the time dependence of the flux serves as an additional control measure of the calculation, for example, as regards the absorption efficiency of the optical potentials placed.

4 Results and Discussion

In Fig. 1 is shown the flux of the propagated wavepacket across the centre of the product wavepacket as a function of time. Because of the convention used for the flux operator, its value is negative. As a result of the normalisation of the wavepacket, and the fact that the flux represents the outgoing square amplitude of the wavepacket per unit time, its integral with respect to time is equal to one. It can be seen that the flux function reflects approximately the initial form of the wavepacket, i.e., it is Gaussian. It is interesting that the shape of the flux function is distorted from a perfectly symmetric Gaussian, exhibiting a long tail at later times. An explanation for this observation is the retarding effect of the atoms of the nanotube, which is expected

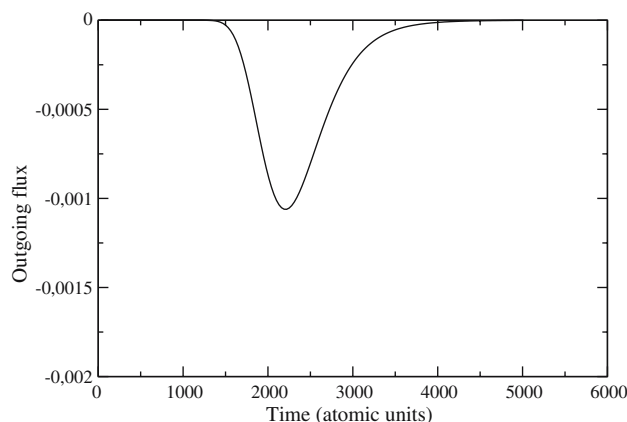


Fig. 1 Outgoing flux of the wavepacket as a function of time

to be larger on the low energy components of the wavepacket (which are expected to arrive later at the product wavepacket where analysis takes place). Nevertheless, the maximum transmission amplitude across the product wavepacket occurs at around 2000 atomic time units and before 5,000 atomic time units it has practically decayed to zero and the results are final.

In Fig. 2 are shown the probabilities (as a function of longitudinal energy) that the wavepacket exits from the nanotube in its initial state (which, in our case, corresponds to zero quanta of radial excitation and a zero component of longitudinal angular momentum). It can be seen that, at all energies, the probability is very close to one. This is an indication that the perturbation caused by the interaction potential with the walls of the nanotube is relatively minor and does not cause a significant change in the state of the *H* atom.

In Fig. 3 are shown the probabilities for radial excitation to the first, second and third radially excited states

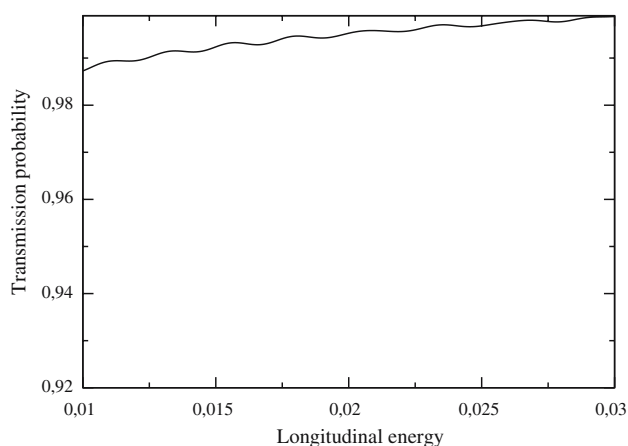


Fig. 2 Exit probability for the state $v' = 0, K = 0$, i.e., the initial state

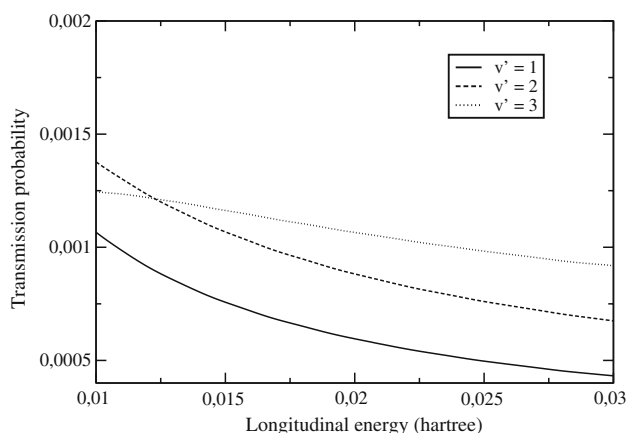


Fig. 3 As in Fig. 2, but for the states $v' = 1$ (straight line), $v' = 2$ (dashed) and $v' = 3$ (dotted)

respectively. They are all of the order of 10^{-3} because of the small interaction perturbation mentioned earlier. However, some trends can be seen in the curves. In particular, all of them are decreasing with increasing longitudinal energy. A simple classical explanation can be given for this trend. Namely, the more longitudinal energy the wavepacket has, the faster it traverses the length of the nanotube. As a result, the surrounding net of carbon atoms has less time to exert its radial perturbation on the travelling atom and hence there is less radial excitation. It can also be seen that, at least at high translational energies, there is more excitation to the higher radial levels. The reason for this effect certainly lies on the nature of the interaction potential, and in particular on its radial dependence. The nanotube has been so constructed that its centre coincides roughly with the Lennard–Jones minimum of the C–H interaction. Given the fact that the H atom experiences the radial interaction from all directions, this amounts to a potential which varies reasonably rapidly with the radius (albeit of small overall magnitude). Such a variation of the potential can explain the preference for higher radial excitations.

In Fig. 4 the corresponding probabilities for angular excitation are shown. It can be seen that, for all practical purposes, these probabilities are zero (they are all of the order of 10^{-20}). As a result, it can be concluded that the only effect of the nanotube on the H atom is radial rather than angular excitation. The reason for this specificity lies in the quasi-cylindrical symmetry of the potential. In particular, even though the potential can vary reasonably rapidly with the radial position of the atom (which is the effect that causes radial excitation), the *angular* dependence of the potential inside the nanotube can never be very high. Because of the fact that, at each point along the nanotube, the potential has a

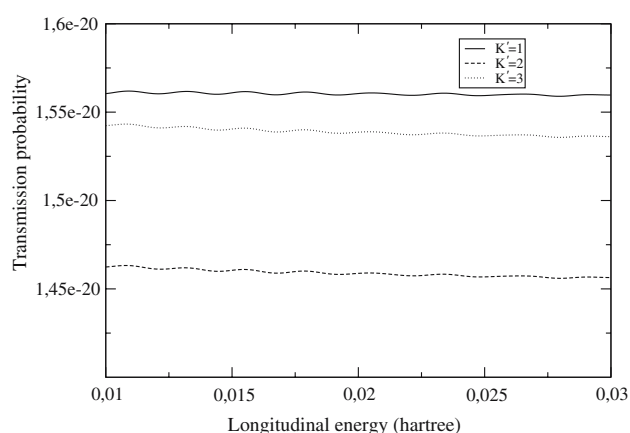


Fig. 4 As in Fig. 2, but for the states $K' = 1$ (straight line), $K' = 2$ (dashed) and $K' = 3$ (dotted)

C_{20} symmetry (by construction, since each ring of the nanotube comprises 20 carbon atoms), it is expected, on symmetry grounds alone, that, from $K = 0$, excitations can only take place to $K = 20$. More generally, if the nanotube exhibits a C_n symmetry, then angular excitations can only take place between K and $K \pm n$ (and also between the same values of K because of the isotropic part of the potential). However, as K increases in magnitude, so does the energy level corresponding to the ground radial state for the particular value of K (one can interpret this as the centrifugal potential energy). Hence, if symmetry dictates a change of value in K too high, a high perturbation would be needed to induce transitions to even the lowest radial state. We see, then, that, in the quasi-cylindrical environment of the nanotube, radial excitations are much preferred to angular ones.

Of course, the situation would be different for non-zero initial values of K . In our case, for an initial value of $K = 10$, the symmetry of the nanotube (as well as the isotropic part) would permit transitions to $K' = 10$ (itself) thus enhancing the exit probability for $K' = \pm 10$ (both helicities). Further calculations are under way to verify effects of this kind.

5 Conclusions

In this work exact quantum dynamics calculations have been carried out for an H atom moving along a suitably constructed carbon nanotube. It must be noted that the nanotube was constructed so that the minimum of the Lennard–Jones atom–atom potentials used was placed in the centre of the cylinder. The scope was to assess, both qualitatively and quantitatively, the effects of the discrete nature of the nanotube potential on the cylindrical energy levels of the H atom. In particular, the concepts of radial and angular excitations were invoked (which correspond to bound degrees of freedom in a cylindrical environment) to assess such effects.

It was found that, over a wide range of energies, the H atom retained its initial state $v = 0, K = 0$ on transmission across the nanotube. Moreover, all excitation

observed was of a *radial* as opposed to *angular* nature. This effect was rationalised by taking into account the quasi-cylindrical symmetry of the nanotube potential. Whereas the radial variation of the potential made it possible to excite radial energy levels of the atom, the discrete symmetry of the nanotube (dictated by the angular disposition of the C atoms) effectively forbade angular transitions and restricted the exit states of the atom to $K' = 0$. As mentioned in the text, however, this need not be the case for higher initial values of K' where angular excitation to nearby levels can be enhanced by the potential.

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