A Computer-Based Approach to Teaching Quantum Dynamics

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Introductory quantum chemistry courses typically include a discussion of the solution of the time independent Schrödinger equation for models such as the particle in a box, potential step, and harmonic oscillator in order to demonstrate fundamental quantum mechanical concepts. A treatment of quantum dynamics is conspicuously absent. The purpose of this paper is to use numerical integration of the time dependent Schrödinger equation to demonstrate the benefits of teaching dynamics in quantum chemistry courses.

Specifically, quantum dynamics helps students see the correspondence between classical and quantum mechanics. Since quantum chemistry students have learned that time is a natural variable in classical mechanics, they are likely to be uneasy with a strictly time-independent description of quantum mechanics. They may wonder why trajectories, which were so important in their Newtonian physics course are not encountered in quantum chemistry. Since time-dependent quantum mechanics is intuitively appealing and is a natural avenue to the study of the classical–quantum correspondence, I expect it to have pedagogical use in helping students of quantum chemistry make the transition from classical to quantum mechanics. We will see that inspection of the time evolution of the wave function in a potential energy curve provides a clear, visual connection (see Figs. 2 and 3) between classical and quantum trajectories, while reinforcing fundamental quantum concepts. Another reason for including the time-dependent description in quantum chemistry courses is that quantum dynamics is currently an area of vigorous research. Topics include the pioneering work of Heller on semiclassical Gaussian wave packet techniques (1–3), the use of the fast Fourier transform to solve the time-dependent Schrödinger equation (4–6), the study of simple gas phase inelastic (7, 8) and reactive (9, 10) collisions, the interpretation of molecular spectra (11–14) and femtosecond spectroscopy experiments (15, 16), the dynamics of gas–surface interactions (17–20), migration of an excess electron in liquids (21–23), and the modeling of laser-induced molecular dissociation (24–28). See the review article by Kosloff (29) for a more exhaustive survey of the methods and applications of quantum molecular dynamics.

I adopt a numerical approach because the analysis of quantum trajectories is inherently graphics oriented and because it allows us to address problems that do not admit an analytical solution. Therefore, the standard time-independent formulation should precede quantum dynamics in an undergraduate course, or perhaps the dynamical picture should be reserved for a first year graduate course. This is an example of how the computer is affecting not only the methods of teaching chemistry but the subjects we are able to address as well (30).

The organization of this paper is as follows. In the next section I discuss the split operator fast Fourier transform method for solving the time-dependent Schrödinger equation (4). Following the numerical methods section, I present the quantum dynamics of two simple systems, the harmonic oscillator and the symmetric double well. I then calculate the time-independent energy level spectra of these models by Fourier transforming the wave function autocorrelation. I conclude with a discussion of how quantum dynamics calculations might be implemented in the classroom and laboratory.

Split Operator Fast Fourier Transform Grid Solution of the Time-Dependent Schrödinger Equation

Our goal is to solve the time-dependent Schrödinger equation so that we may inspect the wave function and quantum expectation values as functions of time. Several
numerical schemes are available, such as Gaussian wave packet techniques (1–3), the Chebychev expansion method (31), and the Lanczos recurrence scheme (32). I adopt the split operator fast Fourier transform (FFT) grid technique (4). A discussion of the advantages and disadvantages of these numerical methods may be found in ref 29.

The time-dependent Schrödinger equation, written in atomic units ($h/2\pi = 1$), is

$$\frac{d\psi(t)}{dt} = -i[H(\hat{p}, \hat{x})\psi(t)]$$

(1)

where $|\psi(t))$ is the time-dependent state vector of the system, and the Hamiltonian is a function of the momentum and position operators.

$$H(\hat{p}, \hat{x}) = \hat{p}^2/2m + V(\hat{x})$$

(2)

For a time-independent Hamiltonian I may write eq 1 in the form of a propagator,

$$|\Psi(t + \Delta t)\rangle = \exp[-i(\hat{p}^2/2m + V(\hat{x}))\Delta t] |\Psi(t)\rangle$$

(3)

Note that eq 3 is also valid for time-dependent Hamiltonians provided that the time step, $\Delta t$, is small enough such that the Hamiltonian is nearly constant over the interval $\Delta t$. The first step in the split operator FFT method is to split the exponent of eq 3 into the product of exponentials. Since this exponent is the sum of two noncommuting operators, it may not be split exactly into the product of exponentials. However, the splitting may be performed approximately via the symmetric form of the Trotter product formula (4),

$$\exp[-i(\hat{p}^2/2m + V(\hat{x}))\Delta t] \approx \exp[-i\hat{p}^2\Delta t/4m] \times \exp[-iV(\hat{x})\Delta t] \exp[-i\hat{p}^2\Delta t/4m]$$

(4)

We call eq 4 the short-time propagator because it is accurate to order $O(\Delta t^3)$, and thus the value of $\Delta t$ must be small. In the applications below $\Delta t = 0.1$ fs. Since the propagator is split, one may calculate the operation of the potential energy part of the propagator in the position basis, where it is diagonal, whereas the action of the kinetic energy part of the propagator will be handled in the momentum basis, where it is diagonal. The fast Fourier transform will be used to flip back and forth between the two representations.

To see how the Fourier transform comes into play, let us define the eigenstates of the position operator as

$$\hat{x}|x\rangle = x|x\rangle$$

(5a)

The completeness relation $I_x = \int |x\rangle \langle x| dx$. Likewise the eigenstates of momentum are defined as

$$\hat{p}|p\rangle = p|p\rangle$$

(5b)

with completeness relation $I_p = \int |p\rangle \langle p| dp$. If we use the short-time propagator eq 4 and the completeness relations for momentum, $\hat{p}$, and position, $\hat{x}$, in the right-hand side of eq 3, we obtain

$$(\langle p|\Psi(t + \Delta t)\rangle = (2\pi)^{-1} \int dx dp \exp[-i\hat{p}^2\Delta t/4m] \exp(-ipx)$$

$$\times \exp[-iV(x)\Delta t] \exp[ip\hat{x}\Delta t] \exp[-i\hat{p}^2\Delta t/4m] |\Psi(t)\rangle (p)$$

(6)

for the time evolution of the momentum space wave function over a single time step. In eq 6, I used the fact that the overlap of the position and momentum eigenstates is $\langle px \rangle = (2\pi)^{-1/2} \exp(-ipx)$. We recognize the integrals in eq 6 to be the forward and reverse Fourier transforms, which may be efficiently calculated using packaged routines (33, 34).

To summarize this section so far, the split operator FFT recipe for solving the time-dependent Schrödinger equation consists of three steps. First, multiply the momentum space wave function at time $t$ by the kinetic energy short-time propagator, $\exp[-i\hat{p}^2\Delta t/4m]$. Second, Fourier transform the result of step 1 to position space, and multiply with the potential energy short-time propagator, $\exp[-iV(x)\Delta t]$. Third, Fourier transform the result of the second step to momentum space, and multiply again with the kinetic-energy short-time propagator. These three steps advance the system ahead in time by $\Delta t$. $M$ applications of this recipe evolve the system over time $M\Delta t$.

In addition to the discretization of time, the position and momentum spaces are also discretized. The spacings of the $x$- and $p$-space grids are

$$\Delta x = \pi/p_{\max}$$

(7a)

and

$$\Delta p = 2\pi/(N\Delta x)$$

(7b)

where $N$ is the number of grid points, and $p_{\max}$ is the highest positive value on the momentum grid (4, 29). In practice, the wave function, along with the kinetic- and potential-energy short-time propagators, are stored in complex vectors of length $N$. These grids must have fine enough resolution to represent the oscillations of the wave function in both $x$ and $p$ space accurately. I use $N = 128$ and $\Delta x = 0.04\text{Å}$ in the calculations below. Unreasonable grid parameters, such as too small a value of $N$ or too large a value of $\Delta x$, cause the wave function to become appreciable at the ends of its array during time evolution. This "wave function reflection" causes spurious results (35), and may be detected by viewing the wave function or by checking the wave function normalization, which typically fluctuates by more than 1% when "reflection" occurs. The wave function normalization is constant to better than 0.01% during the present calculations.

Finally, the FFT grid method must be primed by specifying the time $= 0$ wave function. The form of the initial wave function is not critical and depends on the particular application (29). Since we want to be able to select the position and spatial extent of the initial wave function easily, we adopt the intuitively appealing and widely used Gaussian form,

$$\Psi(x,0) = \exp[-\sigma(x-x_0)^2 + ip_0(x-x_0)]$$

(8)

where $x_0$ and $p_0$ are the centers of the packet in position and momentum space, respectively, and $\sigma$ governs the width of the wave packet.

Wave Function Trajectories

In this section I use the split-operator FFT scheme to solve the one-dimensional, time-dependent Schrödinger equation for the harmonic oscillator and the symmetric double well. The two potential curves for these models are displayed in Figure 1. The mass of the particle is 1 g/mol. The initial wave function for both calculations is centered at $x_0 =$
The Schrödinger equation is a fundamental equation of quantum mechanics. It describes how the quantum state of a physical system changes with time. The equation is named after Erwin Schrödinger, who first proposed it in 1926. It is a wave equation, and its solutions are wave functions, which describe the probability distribution of finding a particle at a given position. The Schrödinger equation operates in a complex vector space and can be solved for various initial conditions.
Figure 4. The survival probability, defined as the square of the autocorrelation function of eq 9, for the (a) harmonic oscillator trajectory and (b) the symmetric double well trajectory. Note the scales of the two plots are identical.

Dynamic Calculation of Energy Levels

Wave function trajectories may be used to calculate the time-independent energy-level spectrum of the Hamiltonian. The split-operator FFT method was originally used for this purpose by Feit, Fleck, and Steiger (4), who showed that the Fourier transform of the wave function autocorrelation is the energy level spectrum. The wave function autocorrelation,

$$C(t) = \int \Psi(x,0)^* \Psi(x,t) dx$$

is the overlap of the wave function at time \( t \) with the initial wave function. Since the correlation is a complex quantity, we will plot its square, the survival probability \( S(t) = |C(t)|^2 \), for convenience. Note that, whereas the Fourier transform of the autocorrelation gives a spectrum with peaks centered at the energy eigenvalues, the Fourier transform of the survival probability produces a "spectrum" with peaks centered at the differences between the energy eigenvalues. Thus, the significance of the autocorrelation (or survival probability) is that it provides the connection between the time scale of motion and the time-independent energy-level structure.

The survival probabilities for the two trajectories of the previous section are plotted in Figure 4. The major points to notice are: The survival probability for the harmonic oscillator exhibits a single frequency (Fig. 4a), whereas the double-well trajectory displays a number of frequencies (Fig. 4b). And, the dominant time scale of motion of the double well, which has period approximately 135 fs, is much longer than that of the harmonic oscillator, which has period of approximately 22 fs.

The eigenvalue spectra for the two models are plotted in Figure 5. These were obtained by Fourier transforming the first 5000 fs segments of the respective wave function autocorrelations. The autocorrelation was sampled at 1-fs intervals. Only part of the spectrum is obtained with this method, and the peaks appearing in this partial spectrum reflect the

![Figure 5. Eigenvalue spectra of the (a) harmonic oscillator and (b) symmetric double well, determined from the Fourier transform of the first 5 ps of their respective autocorrelation function. A quantum number, \( n \), has been assigned to, and listed beside, each peak. Note the energy scales of the two plots are different. After Fourier transforming the complex autocorrelation, the complex spectrum was squared to obtain a real quantity, and then the fourth root of this real spectrum is plotted. Each spectrum is scaled so that the tallest peak has unity height. Thus, the peak heights are proportional to the magnitude of the expansion coefficients in eq 10, \( |c_n| \).](image)

expansion of the initial wave function in terms of the stationary states of the Hamiltonian (4). If the initial Gaussian wave function is expressed as a linear combination of the stationary states,

$$\Psi(x,0) = \sum c_n (x/n)$$

where the \( (x/n) \) are the stationary states with energy \( E_n \), and the \( c_n \) are coefficients, then the resulting spectrum will have peaks at energy \( E_n \) if \( c_n \neq 0 \). Stationary states that are not represented in the initial packet are absent from the resulting eigenvalue spectrum. The heights of the peaks in the spectra of Figure 5 are proportional to the magnitude of the weights, \( |c_n| \).

The single time scale of motion observed in the harmonic oscillator trajectory is manifested in the constant energy level spacing of 1500 cm\(^{-1} \) in the spectrum of Figure 5a. Note that the \( n = 5 \) state does not contribute to the initial wave function; rather, the initial Gaussian is composed of states \( n = 2, 1, 3, 0, 4, 6, 7 \).

In contrast, the multiple frequencies of the double-well trajectory result in a spectrum (Fig. 5b) having peaks with unequal spacing. Examination of the relative peak heights in Figure 5b shows that the two dominant contributors to the initial wave function are the two lowest energy states, which differ in energy by about 250 cm\(^{-1} \). In addition, these two states have nearly equal weights, that is, they have equal peak height in the energy spectrum (Fig. 5b). This result accounts for the dominant time scale of motion having period 135 fs (see Fig. 4b). The higher frequency motion ob-
served on top of the dominant 135 fs motion in the double-well trajectory (see Fig. 4b) gives rise to the peaks labeled 3 and 4 in Figure 5b. The frequency associated with the ground state energy level splitting of a symmetric double well is called the tunneling frequency (36), and our dynamics exercise has demonstrated the basis for this. We observe that the wave function composed of equal amplitudes of the two lowest eigenstates tunnels back and forth with frequency \((E_2 - E_1)/\hbar\). Additionally, we observe that if the initial packet contains additional stationary states, the time evolution is not simply characterized by the tunneling frequency.

**Summary and Discussion**

I have suggested some of the insights students might obtain from a treatment of quantum dynamics through numerical studies of two models. First, the concept of a trajectory is demonstrated to appear as naturally in quantum mechanics as it does in classical mechanics. Second, basic quantum principles are conveyed: The quantum trajectory consists of an evolving wave function that has an inherent uncertainty in position and momentum, and the wave function may explore classically forbidden regions of the potential. Third, the relationship between the time scale of quantum motion and the discrete energy-level structure is depicted through calculation of the eigenvalue spectrum from dynamic information. Finally, a dynamic calculation of the energy-level spectrum demonstrates the equivalency between time-dependent and time-independent quantum mechanics.

How would one implement quantum dynamics in the classroom or laboratory? I envision a numerical package coupled to a graphics device that would allow the student to follow the quantum dynamics of a wave packet launched in an arbitrary potential curve. The user would be able to choose a potential curve, select the initial wave packet, assign values to the mass, wave function grid parameters, time step, and duration of the calculation, as well as select the data to be written out. In a laboratory setting, each student could be assigned a different potential surface (an “unknown”) whose quantum dynamics, energy levels, etc., are to be determined. Alternatively, students could devise their own potential curves. Once they understand the time evolution of a particular system, students might be asked to apply an external field to their particle. Note that the iterative procedure of setting parameters and analyzing output gives students the feeling for doing a research-level calculation. Such a suite of programs would be the quantum analogue of existing classical trajectory educational software (30).

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**Literature Cited**

33. International Mathematical and Statistical Libraries User’s Manual, ed. 9.3; IMSL: Houston, 1984, Chapter F.