Numerical Quantum Dynamics and Visualising Quantum Chemistry with MATLAB

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In this modelling exercise, you will use WavePacket [1], which is a MATLAB package for numerical simulation of quantum-mechanical wavepacket dynamics. It can be used to solve one or more (i.e. coupled channels) time-independent or time-dependent linear Schrödinger equations. Optionally accounting for the interaction with external electric fields (semiclassical dipole approximation), WavePacket can simulate modern experiments using ultrashort laser pulses. Thus it can be used as a flexible tool for many simulation tasks in photoinduced physics and chemistry.

1   Harmonic Oscillator

Once you download the package, go to Demos. There are some nice easy examples to try first to get a feeling for what the package can do.

Go to HarmOscillator Gaussian_1D and run the scrip called qm_run. A complicated plot will appear on the screen. Do not resize it or try to pause it! There will be a recording of it which you can have a look once it is done with the computation. In subdirectories 1-3 correspond to 3 different initial conditions for the wavepacket in the Harmonic Oscillator. The plot shows you both the position and the momentum distribution of the wavepacket, as well as energies and the autocorrelation function.

1.1   Squeezed States - subdirectories 1 and 2

In general, the center of a Gaussian wavepacket oscillates according to the classical equations of motion. This is a manifestation of Ehrenfest's theorem stating that the expectation values of a quantum mechanical wavefunction obey the laws of classical mechanics. However, both the width and the phase of the wavefunction vary in a complicated manner with time. Due to the interchange of minima and maxima of the width in position and momentum space representation, these states are referred to as squeezed states. The dynamics of width and phases give rise to two classes of quantum phenomena: (1) The finite width of the wavepacket implies that the edge of a wavepacket penetrates to a certain amount into the classically forbidden region (tunneling). (2) The (complex) phase of the wavepacket governs the interference of wavepackets and various kinds of spectroscopic properties.

1.2   Coherent States - subdirectory 3

If the initial width of a quantum mechanical wavepacket exactly equals the width of the (stationary) ground state wavefunction of the harmonic oscillator, again, the wavepacket oscillates with its center following the classical equations of motion. In addition, this time the width of the WavePacket remains constant. This is because the curvature of the potential exactly compensates the tendency for wavepacket spreading (dispersion) observed, e.g., for a free particle dynamics. This type of quantum mechanics is the closest correspondence with classical mechanics. In the literature, this phenomenon is known as coherent state.

2   How does it work?

After becoming familiar with the simple example, you may wonder how it all works. Just like in classical molecular dynamics, quantum dynamics first of all requires a definition of the equation of motion. As we know, in quantum mechanics this is the Schrödinger equation. In WavePacket, the Hamiltonian of the system has the following components:

- kinetic energy operator

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[1] WavePacket is developed by B. Schmidt and U. Lorenz as an open-source project. The examples and parts of the text are credited to the people involved in this project.

- potential energy; in the case of multiple states, the coupling should be introduced as off-diagonal terms (i.e. diabatic representation)

- (optional) negative imaginary potential to smoothly absorb wavefunctions near the boundaries

- (optional) an external electric field based on the semi-classical treatment within the electric dipole approximation where the electric field couples to the system through its dipole operator

- (optional) dipole moment - permanent and transition

WavePacket employs an expansions of wave function and the Hamiltonian into a truncated orthonormal basis and/or discretise the wavefunction (represent in on a grid). The wavefunction is represented in a suitable basis set such as Legendre or Hermite polynomials, or plane waves. Just like in classical MD, there are algorithms to "integrate" the equation of motion, e.g. split-operator or Chebychev method.

3   Quantum Dynamics on Coupled Potential Energy Surfaces

Although the Born-Oppenheimer (adiabatic) approximation provides the most intuitive picture of molecular quantum dynamics in terms of densities/wavepackets moving along uncoupled potential energy surfaces, many chemical reactions, most notably in photochemistry and photobiology are governed by non-adiabatic processes, i.e., they involve nuclear dynamics on at least two different electronic states. This breakdown of the adiabatic approximation occurs most drastically where the gaps between electronic eigenstates become sufficiently small or vanish altogether. Prominent examples are avoided-crossings of potential energy curves in one dimension and conical intersections in two or more dimensions.

The simplest example consists of a single crossing of two potential energy curves which are designed such that an incoming wavepacket passes the crossing once without returning to the crossing zone. Hence, interference effects are limited to the oscillations during the passage. Full quantum dynamics can often be well approximated by the semiclassical Landau-Zener formula:

$$P_{crossing} = \exp\left(-2\pi \frac{V_{12}^d}{\hbar(d\Delta E/dt)}\right) = \exp\left(-2\pi \frac{V_{12}^d}{\hbar(d\Delta E/dx)v}\right), \qquad (1)$$

where V_{12} is the diabatic coupling between the two states, ΔE is the separation between the adiabatic states, and $v = dx/dt$ is the velocity.

To see an example of this behaviour, Go to Demos/CrossingTully/Single. This time have a look into the qm_init files in the subdirectories. As other packages for computational chemistry, WavePacket is instructed what to do by the commands you provide in a script file. qm_init is the default name for such a file. Can you recognise some of the important features such as the propagator and the wavefunction representation? From the top level directory, run execute qm_run. There will be four separate simulations with different initial conditions. Is that what you expect to see?

Let's move on to a bit more complicated example. The photoinduced isomerization of the retinal molecule in rhodopsin is considered as the primary step in vision. It serves as a real-life example for the importance of avoided crossings and conical intersections in photochemical and photobiological processes. Go to MolElec-tronic/retinal/1D and execute qm_run. In this model, there are two electronic states vibronically coupled by a collective reaction coordinate describing the isomerization proces. The corresponding potential energy curves exhibit two avoided crossings giving rise to nonadiabatic processes. What is the significance of the dynamics you **see**? Try also the 2D model, where the new coordinate is an effective mode representing the ethylene C=C stretching coordinate, and instead of avoided-crossings, you see conical intersections.

Going Further: Let's now include explicitly the laser field. Go to MolElectronic/OH/BareState. Running qm_run will provide you with an example of a state selective electronic excitation, in this case a OH radical. The pulse parameters are optimized with respect to amplitude and frequency such that a 1-photon transition $v'' = 0 \rightarrow v' = 1$ is enhanced.