Physical Chemistry II: Quantum Chemistry
Lecture 10: Quantum Dynamics Demo

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Time-dependent Schrodinger Equation

- Time-evolution of a quantum state is fully described by the Schrodinger equation:

$$i\hbar \frac{\partial}{\partial t}\left|\Psi(t)\right\rangle = \hat{H}\left|\Psi(t)\right\rangle$$

- Solving the energy eigenstates $\hat{H}\left|\phi_n\right\rangle = E_n\left|\phi_n\right\rangle$ gives the ideal "basis" to describe time-evolution:

$$\left|\Psi(t)\right\rangle = \sum_n c_n(0) e^{-\frac{iE_n t}{\hbar}} \left|\phi_n\right\rangle$$

This is necessary for analytical solutions.

Time-evolution of Wave Functions

- Time-evolution in the energy eigenbasis:

$$\left|\Psi(t)\right\rangle = \sum_n c_n(0) e^{-\frac{iE_n t}{\hbar}} \left|\phi_n\right\rangle$$

  Easy to solve when the energy eigenstates are known ← not an easy task

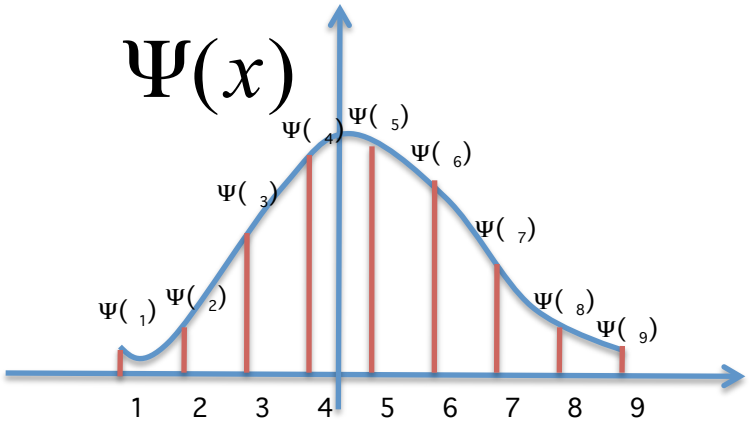
- Wave functions are "COMPLEX"
- Each eigenstate oscillates in a different frequency
- Interferences between different oscillating waves constitutes the full quantum dynamics

Time-dependent Schrodinger Equation

- Actually, any orthonormal basis sets are equally valid for solving the Schrodinger equation
- Numerically solve the Schrodinger equation:
  1. Find a numerically convenient & efficient basis
  2. Construct the Hamiltonian matrix and the initial wavefunction ket (column vector) in the basis
  3. Find eigenvalues & eigenvectors of the Hamiltonian to solve the time-independent problem
  4. *Propagate* the wavefunction step by step in time using an efficient & robust algorithm

Poorman's Discrete Variable Representation

- The simplest basis choice is to use discrete grid points in space
- Wavefunction then represents by a vector of "point values"



$$\left|\Psi\right\rangle = \begin{pmatrix} \Psi(x_1) \\ \Psi(x_2) \\ \Psi(x_3) \\ \Psi(x_4) \\ \vdots \end{pmatrix}$$

Poorman's Discrete Variable Representation

- Hamiltonian: $\hat{H} = \hat{T} + \hat{V}$
- The potential operator is diagonal in position and easy to construct in the discrete basis

$$\hat{V} = \begin{pmatrix} V(x_1) & 0 & 0 & 0 & \cdots \\ 0 & V(x_2) & 0 & 0 & \cdots \\ 0 & 0 & V(x_3) & 0 & \cdots \\ 0 & 0 & 0 & V(x_4) & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

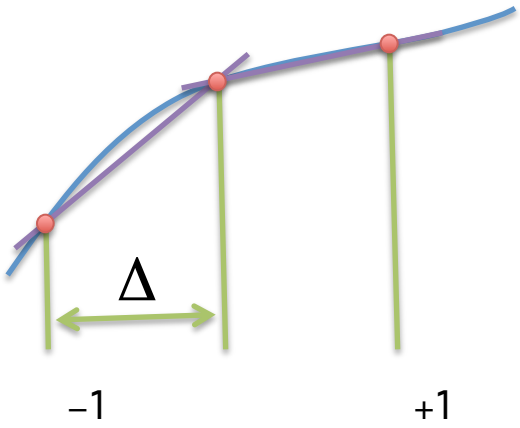
Poorman's Discrete Variable Representation

- The kinetic energy operator:

$$\hat{T} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\left.\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x)\right|_{x=x_n} \approx \frac{-\hbar^2}{2m}\frac{1}{\Delta}\left(\frac{\Psi_{n+1}-\Psi_n}{\Delta}-\frac{\Psi_n-\Psi_{n-1}}{\Delta}\right)$$

$$= \frac{\hbar^2}{2m\Delta^2}\left(2\Psi_n-\Psi_{n-1}-\Psi_{n+1}\right)$$



$$\hat{T} = \begin{pmatrix} 2k & -k & 0 & 0 & \cdots \\ -k & 2k & -k & 0 & \cdots \\ 0 & -k & 2k & -k & \ddots \\ 0 & 0 & -k & 2k & \ddots \\ \vdots & \vdots & \ddots & \ddots & \ddots \end{pmatrix} \qquad k = \frac{\hbar^2}{2m\Delta^2}$$

Time Propagation

- Schrodinger equation:

$$i\hbar\frac{\partial}{\partial t}\left|\Psi(t)\right\rangle = \hat{H}\left|\Psi(t)\right\rangle$$

- ***Iteration*** with a small time step δt:

$$\left|\Psi(t+\delta t)\right\rangle \approx \left|\Psi(t)\right\rangle - \frac{i\delta t}{\hbar}\hat{H}\left|\Psi(t)\right\rangle$$

- Normally, an algorithm that includes higher-order contributions (e.g. δt^2) is used to ensure efficiency and accuracy. For example, the Crank-Nicolson method provided significant improvement in accuracy.

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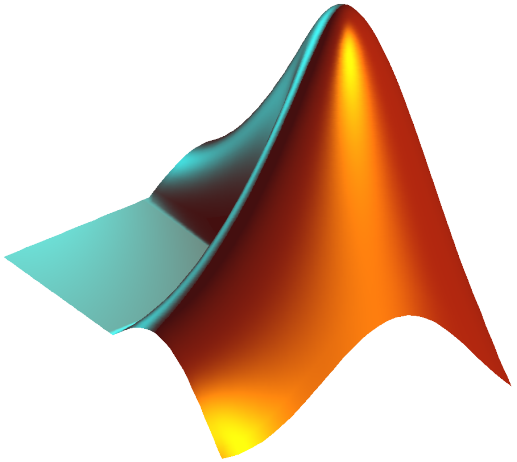
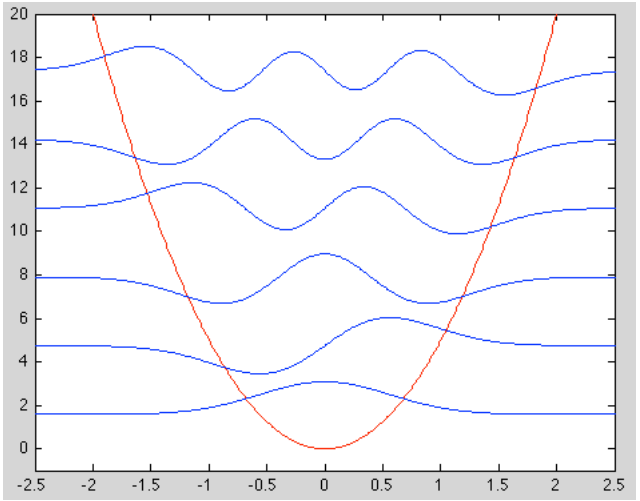
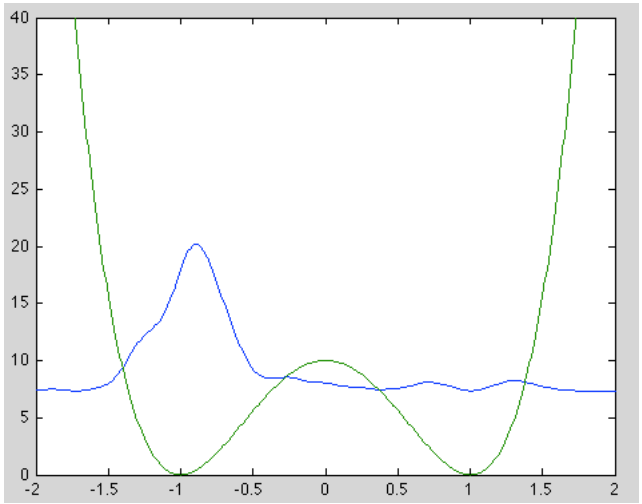
Matlab: http://www.mathworks.com/



Matlab Examples





Discrete Variable Representation

- dvr_eigen.m
- Poorman's DVR: 801 points from x=-4 to x=4
- Kinetic Op:
  T(n,n)=2*k
  T(n,n+1)=T(n+1,n)=-k
- Potential Op:
  V(x) on the diagonal
- DVR eigenstates yields wavefunctions directly
  - Harmonic
  - Quartic double well
  - Biased quartic double well
  - Any bound potential!!

```
T=zeros(Nx);
for idxi = 1:(Nx-1)
   T(idxi,idxi)=2*k;
   T(idxi,idxi+1)=-1*k;
   T(idxi+1,idxi)=-1*k;
end
T(Nx,Nx)=2*k;

V=diag(potential(xvec));

% Hamiltonian
H=T+V;

% eigen values and vectors
[U, E] = eig(H);
```

Dynamics via DVR

- Poorman's DVR + Crank-Nicolson
- Additional tricks: focus on low energy eigenstates
- Gaussian wavepacket dynamics
  - Harmonic potential
  - Quartic double well potential
  - Biased quartic potential

```
% eigen values and vectors
[U, E] = eig(H);

% num of eigenstates to use
Nred=50

 % truncated Hamiltonian (diag form)
Hred=E(1:Nred,1:Nred);

% eigenvectors, used for basis change
Ured=U(:,1:Nred);

% transform Psi_0 to the eigenspace
Psi_0red=Ured' * Psi_0;
```

Gaussian Wavepacket Dynamics via DVR

- Gaussian wavepacket: superposition of eigenstates, normally non-stationary
- Ground state? (dvr_propagate1.m)
- Low energy Gaussian wavepacket in a harmonic potential (dvr_propagate2.m)
  - Oscillations in position and width (p)
  - Center of the wavepacket behaves classically
- Displaced ground-state Gaussian (dvr_propagate3.m)
  - Minimum uncertainty wavepacket
  - Width & shape invariant: coherent state

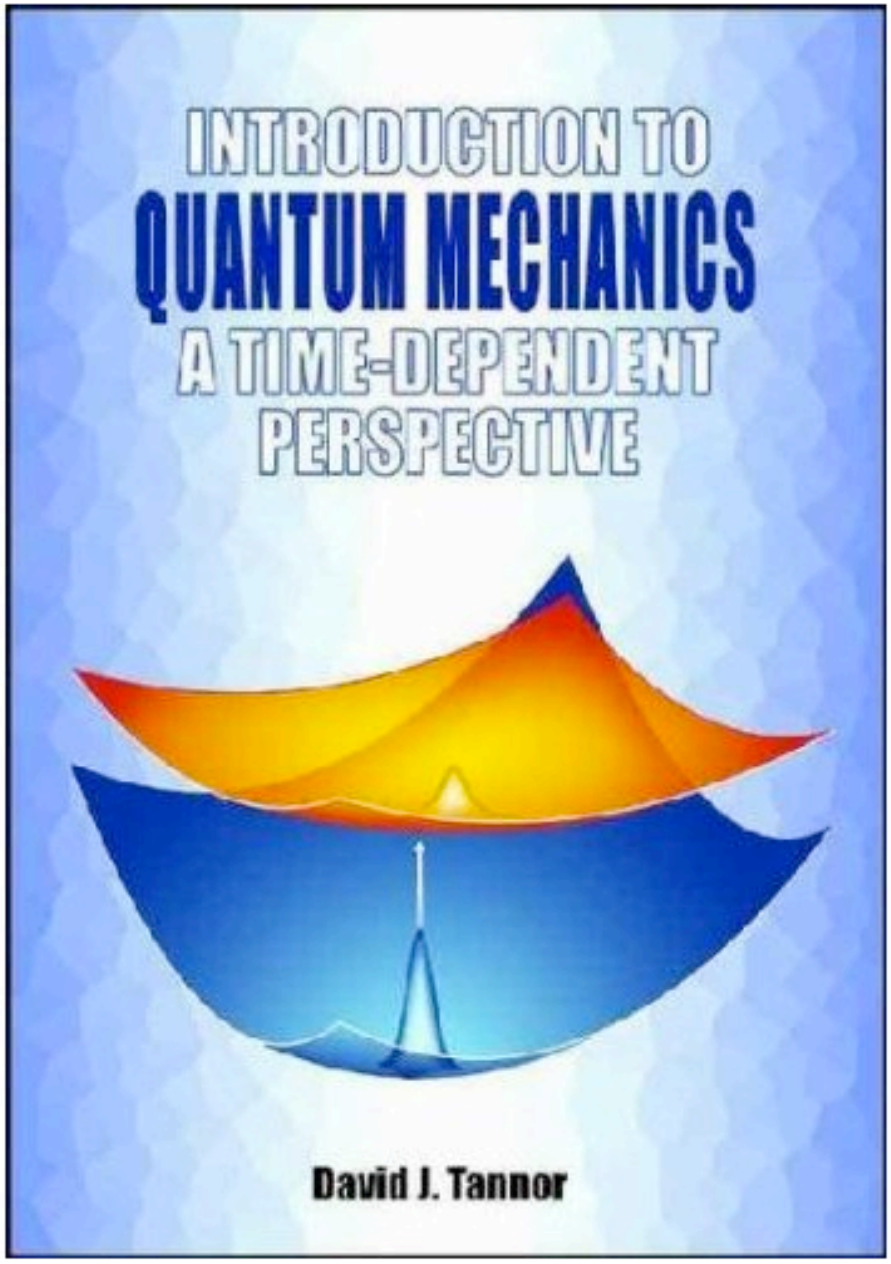
Gaussian Wavepacket Dynamics via DVR

- High energy Gaussian wavepacket in a harmonic potential (dvr_propagate4.m)
  - Superposition of many more eigenstates because of energetic accessibility
  - More complex dynamics due to interferences of modes with a broad distribution of frequencies
  - Recurrences occur due to symmetry
- Quartic double well (dvr_propagate[5,6].m)
  - Low energy: tunneling
  - High energy: scattering

Limitations of DVR+CN

- Infeasible for treating high dimensional systems: $N=(Nx)^d$
- Unfit for extensive systems & highly excited states
- Difficult & computationally expensive for accurate long time dynamics
- Inefficient for systems exhibiting separation of temporal or spatial scales
- Inefficient for calculating rates, yields,… etc.

Introduction to Quantum Mechanics **ISBN: 9781891389238**



Internet Resources

- Matlab scripts shown today already on CEIBA
- Java Applet demo of 1D QM systems: http://www.falstad.com/qm1d
- Java Applet demo of 2D QM systems: http://www.falstad.com/qm2dbox
- PhET Simulations of Quantum Phenomena: http://phet.colorado.edu/simulations/index.php?cat=Quantum_Phenomena

Remarks

- Intuitions from classical mechanics still explains many quantum phenomena, however, adjustments are required for superpositions & interferences (coherence), tunneling, measurement… etc.
- Energy eigenstates form the basis for describing time evolution of quantum states
- Solutions to the time-independent Schrodinger equation are fundamental to understand quantum phenomena in physics & chemistry

Scheme for Time Propagation

- tls_prog_exactdiag.m: exact propagator through diagonalizing H
- tls_prog_euler.m: Euler method
- tls_prog_cranknicolson.m: Crank-Nicolson scheme

- TLS dynamics as an example

- Implementations
- Stability, accuracy, & efficiency
  - Size of each time step
  - Accuracy at longer times
  - Efficiency of the algorithm
- By the way, TLS dynamics: fix energy gap, vary J