Quantum Molecular Dynamics **Autumn 2001-2002**

Project 2

I. EIGENSTATES AS FOURIER TRANSFORMS OF WAVE PACKETS

- Program name: har_eigfuncFT.m
- What program does: Calculates the eigenstates of the harmonic oscillator by Fourier transforming a (numerical) Gaussian wavepacket from time to energy. The Fourier transform may be viewed as constructing a superposition of wavepackets at different times with a phase factor determined by the energy of the Fourier transform. The method is based on the simple formula: $\psi_n \propto \int_{-\infty}^{\infty} \Psi(t) e^{iEt/\hbar} dt = \int_{-\infty}^{\infty} e^{-iHt/\hbar} \Psi e^{iEt/\hbar} dt$
- References in text: a) Ch. 3.3, Gaussian wavepackets b) Ch. 6.3, spectral method for calculating eigenstates c) Ex. 6.EOC.5 where the harmonic oscillator eigenstates are calculated analytically from the Fourier transform of the Gaussian wavepacket.
- Assignments:
  1. Compare the calculated harmonic oscillator eigenstates with the analytical eigenstates. Use MATLAB also for the latter.
  2. What is the dependence on the energy at which the Fourier transform is performed? What happens if an energy other than an eigenvalue energy is used?
  3. What is the dependence on the displacement of the initial wavepacket? What happens if the energy of the initial wavepacket is very different from the energy of the eigenstate that one wishes to extract?
  4. What is the dependence of the wavefunction produced on the total propagation time? What if the propagation time is:
     (a) less than one period of motion?
     (b) exactly one period?
     (c) 1-1/2 periods?
     (d) 10 periods?
     (e) 10.5 periods?

II. 'IMAGINARY TIME' OR 'RELAXATION' METHOD

- Program name: har_eigfuncRlx.m
- What program does: Calculates the eigenstates for an harmonic potential by starting with an arbitrary initial state and propagating in imaginary time $t \rightarrow i\tau$.

  The method is based on the following formula for obtaining the lowest eigenfunction ψ_0 from some arbitrary initial state Ψ: $e^{-(H-E_0)\tau}\Psi = \sum_m e^{-(E_m-E_0)\tau} a_m \psi_m \rightarrow_{\tau\rightarrow\infty} a_0\psi_0$. In order to obtain higher eigenfunctions we first find the lowest eigenfunction by relaxation. Then we extract this component out of the initial Wave Packet $\Psi \rightarrow \Psi - a_0\psi_0$. We can now relax Ψ using E_1 to obtain ψ_1. In an inductive manner given the $n-1$ lowest eigenfunctions we can extract all these components out of Ψ, and then relax using E_n to obtain ψ_n.

  In the program we simultaneously obtain all eigenfunctions, ψ_n, by assuming for each that all lower eigenfunctions are already known. Using the analytic eigenfunctions a set of initial wavepackets are constructed such that all ψ_m with $m < n$ are extracted out. These are now simultaneously propagated to obtain each of the n eigenfunctions.
- References in text: None. This project is included with Ch. 6, so that the spectral method can be compared with alternative methods for constructing eigenstates.

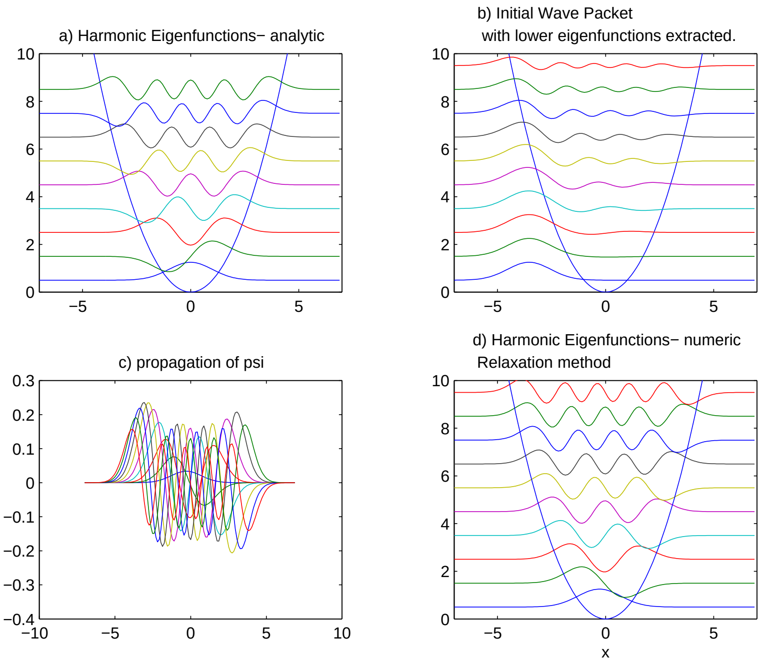

FIG. 1: Harmonic Eigenfunctions -Relaxation method. a) analytic eigenfunctions b) Initial Wave Packet c) Propagation d)numeric eigenfunctions

III. ‘ADIABATIC SWITCHING’

- Program name: adia_2well.m (utility functions: hpsi.m, poten.m, eigf.m, switch2.m)
- What the program does: Calculates the eigenstates of a double well potential by starting with any of the harmonic oscillator eigenstates and adiabatically switching the potential to the final desired double well potential. In practice, although the time evolving state is close to an eigenstate at all instants in time, it is treated as a wavepacket propagating in a slowly varying potential. The potential is given by $H(t) = H(0) + S(t)\Delta H$, where $\Delta H = H(T) - H(0)$, and $S(t)$ is a switching function that is zero at $t = 0$ and 14 at $t = T$.
- References in text:
  1. Ch. 9.4, quantum adiabatic theorem
  2. This project is included with Ch. 6, so that the spectral method can be compared with alternative methods for constructing eigenstates.
- Assignments:
  1. Compare the eigenvalues and eigenfunction of the double well obtained by adiabatic switching with those obtained by any of the other methods in this directory (i.e. spectral method, relaxation method, shooting method, DVR method and FGH method).
  2. What is the dependence of the quality of the result on the switching time? On the switching function?

IV. ‘FOURIER GRID HAMILTONIAN’ (FGH) METHOD

- Program name: FGH.m
- What program does: Calculates eigenvalues and eigenfunctions by the method of Marston et al. as improved by Willner et al. The Hamiltonian operator $H = T + V$ is constructed in a pseudospectral basis of Hardy functions. In practice this means that an evenly spaced grid of points is chosen in coordinate space. The diagonal matrix

$V(x)$ is simply the value of the potential at that grid point. The kinetic matrix T is found by using the analytic matrix elements for $\frac{\partial^2}{\partial x^2}$:

$$\left(\frac{\partial^2}{\partial x^2}\right)_{nm} = \begin{cases} -\frac{K^2}{3} & (n = m) \\ -\frac{2K^2}{\pi^2}\frac{(-1)^{n-m}}{(n-m)^2} & (n \neq m). \end{cases} \tag{1}$$

where $K = \pi/\Delta x$, and $T = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. The matrix $H = T + V$ is then diagonalized numerically; the eigenvalues are the (approximate) energies of the system and the eigenvectors are the coefficients of the Hardy functions in the (approximate) eigenfunctions of the system, which for this purpose can be viewed as delta functions, each at its own respective grid point.

- References in text: Ch. 11.3 FGH method for construction of the Hamiltonian in a pseudospectral representation.
- Assignments: Use this program to generate eigenfunctions and eigenvalues for the double well potential and compare the quality of your results with those obtained using the Adiabatic Switching method above.