Path-Integral Quantum Mechanics

Kuntal Ghosh, The University of Chicago

Introduction

Quantum mechanics is crucial to the understanding of the way nature works. Traditionally, quantum mechanics is formulated in terms of the wave function, proposed by Schrodinger. It is this wave function which carries all the information about the system under consideration, and is deduced from the Schrodinger's equation. Alternatively, quantum mechanics can also be formulated in terms of the wave vector, using the Dirac notation. In fact, there are nine different formulations of quantum mechanics. One of the most fundamental as well as strikingly beautiful formulations of quantum mechanics is Feynman's path integral. This worksheet explores a few fundamental concepts of path integrals, with special emphasis on the harmonic oscillator model.

Path integral calculations are often carried out in the framework of molecular dynamics (MD) simulations, popularly called Path Integral Molecular Dynamics (PIMD). PIMD simulations are critically important to capture nuclear quantum effects (NQEs) in atomistic simulations, simply because most MD methods treat the nuclei classically, even if the electronic motion is treated quantum mechanically. PIMD, due to its very construction, effectively does away with this issue. This worksheet also gives a brief introduction to PIMD with a simple numerical illustration using the harmonic oscillator model.

Theoretical Background

While traditional wave mechanics emphasises on the probability of finding a particle in a particular state, the path integral formalism (as the name suggests) talks about the path traversed by the particle. Say a particle traverses from a position x to a position x'. Instead of following a unique path between the two points, the particle follows an infinite number of paths simultaneously and the total amplitude of the particle to be observed at x' at time t is the sum of amplitudes of all such paths. Now, the amplitude for the detection of the particle at x' written in terms of the quantum mechanical propagator is

$$U(x, x', t) = \left\langle x' \middle| e^{-\frac{iHt}{\hbar}} \middle| x \right\rangle$$

More generally, for an arbitrary state vector,

$$\left| \Psi(t) \right\rangle = e^{-\frac{iHt}{\hbar}} \left| \Psi(0) \right\rangle$$

In the language of path integrals, this propagator is also referred to as the kernel. Now, to transition to a more statistical mechanical framework, a very interesting substitution can be made. Substituting t = -iβh,

$$U(x, x', -i\beta\hbar) = \rho(x, x', \beta) = \left\langle x' \middle| e^{-\beta H} \middle| x \right\rangle$$

where ρ is simply the canonical density matrix, or the so-called imaginary time propagator. Such transformations or rotations between the quantum propagator and the canonical density matrix over imaginary time are called Wick rotations.

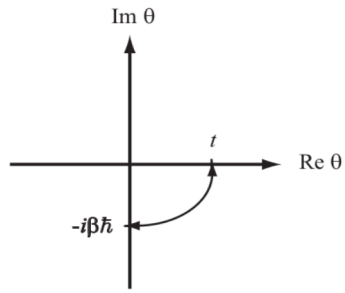


Fig 1: Wick rotation in the complex time plane (figure from Ref 1)

Following a series of steps involving Trotter factorisation of an infinite number of interim points between x and x' ($\{x_1, x_2 ... x_P\}$), the density matrix can be derived as,

$$\rho(x,x',\beta) = \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{\frac{P}{2}}\int dx_2...dx_P \exp\left\{-\frac{1}{\hbar}\sum_{k=1}^{P}\left(\frac{mP}{2\beta\hbar}\left(x_{k+1}-x_k\right)^2+\frac{\beta\hbar}{2P}\left(U\left(x_{k+1}\right)+U\left(x_k\right)\right)\right)\right\}$$

where $x_1 = x$ and $x_{P+1} = x'$. Thus, a path integral representation for the propagator can be obtained by substituting $\beta = it/\hbar$,

$$U(x,x',t) = \lim_{P\to\infty}\left(\frac{mP}{2\pi i t\hbar}\right)^{\frac{P}{2}}\int dx_2...dx_P \exp\left\{\frac{i}{\hbar}\sum_{k=1}^{P}\left(\frac{mP}{2t}\left(x_{k+1}-x_k\right)^2-\frac{t}{2P}\left(U\left(x_{k+1}\right)+U\left(x_k\right)\right)\right)\right\}$$

Finally, the canonical partition function Q(L,T) can be obtained,

$$Q(L,T) = Tr\left[e^{-\beta H}\right] = \int_0^L dx\,\langle x'|e^{-\beta H}|x\rangle = \int_0^L dx\,\rho(x,x',\beta)$$

$$= \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{\frac{P}{2}}\int_{D(L)} dx_1...dx_P \exp\left\{-\frac{1}{\hbar}\sum_{k=1}^{P}\left(\frac{mP}{2\beta\hbar}\left(x_{k+1}-x_k\right)^2+\frac{\beta\hbar}{P}U\left(x_k\right)\right)\right\}\Bigg|_{x_{P+1}=x_P} \cdot (\mathbf{1})$$

Furthermore, path integrals can also be written as *functional integrals*, where the action (S) is the corresponding functional.

$$\rho(x,x',\beta) = \int_{x(0)=x}^{x(\beta\hbar)=x'} Dx(\tau)\exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\cdot\left(\frac{1}{2}m\dot{x}^2(\tau)+U(x(\tau))\right)\right] = \int_x^{x'} Dx e^{-\frac{S[x]}{\hbar}}$$

The Harmonic Oscillator

Deriving the density matrix

We take the example of a one-dimensional harmonic oscillator to illustrate the path integral formalism. Using the functional integral approach, we can write the full density matrix as

$$\rho(x,x',\beta) = \int_{x(0)=x}^{x(\beta\hbar)=x'} Dx(\tau)\exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\cdot\left(\frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2x^2\right)\right]$$

Performing a change of variables about the classical path given by $x_{cl}(\tau)$, we have $x(\tau) = x_{cl}(\tau) + y(\tau)$. Thus, the action integral becomes

$$S = \int_0^{\beta\hbar} d\tau\cdot\left(\frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2x^2\right) = \int_0^{\beta\hbar} d\tau\cdot\left(\frac{1}{2}m\dot{x}_{cl}^2 + \frac{1}{2}m\omega^2x_{cl}^2\right) + \int_0^{\beta\hbar} d\tau\cdot\left(\frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\omega^2y^2\right) + \int_0^{\beta\hbar} d\tau\cdot\left(m\dot{x}_{cl}\dot{y} + m\omega^2x_{cl}y\right)$$

Using the boundary conditions and further solving, we simply get,

$$\int_0^{\beta\hbar} d\tau\cdot\left(\frac{1}{2}m\dot{x}_{cl}^2(\tau) + \frac{1}{2}m\omega^2x_{cl}^2(\tau)\right) = \frac{m\omega}{2\sinh(\beta\hbar\omega)}\left[\left(x^2 + x'^2\right)\cosh(\beta\hbar\omega) - 2xx'\right]$$

Thus, the density matrix becomes

$$\rho(x,x',\beta) = I[y]\exp\left[-\frac{m\omega}{2\hbar\sinh(\beta\hbar\omega)}\left[\left(x^2 + x'^2\right)\cosh(\beta\hbar\omega) - 2xx'\right]\right]$$

where I[y] is,

$$I[y] = \int_{y(0)=0}^{y(\beta\hbar)=0} Dy(\tau)\exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\cdot\left(\frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\omega^2y^2\right)\right]$$

Following a series of steps which includes the expansion of $y(\tau)$ in terms of a Fourier series, the solution of I[y] can be derived as,

$$I[y] = \left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{\frac{1}{2}}$$

Thus, the full density matrix can be given by

$$\rho(x,x',\beta) = \left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{\frac{1}{2}}\exp\left[-\frac{m\omega}{2\hbar\sinh(\beta\hbar\omega)}\left[\left(x^2 + x'^2\right)\cosh(\beta\hbar\omega) - 2xx'\right]\right]$$

Deriving the energy eigenvalues and eigenstates

We know that the quantum mechanical propagator or the kernel is related to the density matrix by a Wick rotation. Moreover, a key property of kernels is that they can be expanded in terms of their energy eigenfunctions. Thus, on carrying out a Wick rotation and an expansion, we get,

$$\left[\frac{m\omega}{2\pi i\hbar \sin\omega T}\right]^{\frac{1}{2}} \exp\left[\frac{im\omega}{2\hbar\sin(\omega T)}\left[\left(x^2+x'^2\right)\cos(\omega T)-2xx'\right]\right] = \sum_{n=0}^{\infty} e^{-\left(\frac{i}{\hbar}\right)E_n T}\phi_n(x')\phi_n^*(x)$$

Using standard trigonometric identities, the left hand side of the above equation becomes,

$$\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} e^{-\frac{i\omega T}{2}}\left(1-e^{-2i\omega T}\right)^{-\frac{1}{2}} \exp\left\{-\frac{m\omega}{2\hbar}\left[\frac{\left(x'^2+x^2\right)\left(1+e^{-2i\omega T}\right)}{\left(1-e^{-2i\omega T}\right)} - \frac{4xx'e^{-i\omega T}}{1-e^{-2i\omega T}}\right]\right\}$$

Expanding the exponential series and comparing with Eq,

$$e^{-\left(\frac{i}{\hbar}\right)E_n T} = e^{-\frac{i\omega T}{2}} e^{-in\omega T}$$

and we get the energy levels as,

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right)$$

Further expansion is required for getting the eigenfunctions,

$$\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} e^{-\frac{i\omega T}{2}}\left(1+\frac{1}{2}e^{-2i\omega T}+\ldots\right)e^{-\left(\frac{m\omega}{2\hbar}\right)(x'^2+x^2)}\left[1+\frac{2m\omega}{\hbar}xx'e^{-i\omega T}+\frac{1}{2}\left(\frac{2m\omega}{\hbar}\right)^2 x^2x'^2e^{-2i\omega T}-\frac{m\omega}{\hbar}(x^2+x'^2)e^{-2i\omega T}+\ldots\right]$$

Comparing term by term to our initial expansion,

$$\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} e^{-\frac{i\omega T}{2}} e^{-\left(\frac{m\omega}{2\hbar}\right)(x'^2+x^2)} = e^{-\left(\frac{i}{\hbar}\right)E_0 T}\phi_0(x')\phi_0^*(x)$$

Thus, $E_0 = \frac{\hbar\omega}{2}$ (obtained earlier) and,

$$\phi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega x^2}{2\hbar}}$$

This is the ground state wavefunction for the harmonic oscillator, which can also be readily derived from the Schrodinger equation. There is an phase factor outside the expression, but since it does not impact the physical implications as such, it has been safely ignored. Similarly, the next two terms can also be derived,

$$\phi_1(x) = \left(\frac{2m\omega}{\hbar}\right)^{\frac{1}{2}} x\,\phi_0(x)$$

$$\phi_2(x) = \frac{1}{\sqrt{2}}\left(\frac{2m\omega}{\hbar}x^2-1\right)\phi_0(x)$$

In this way, all the energy eigenvalues and eigenstates of the quantum harmonic oscillator can be obtained using the path integral formalism.

Numerical implementation (model system: TiO)

Maple's quantum chemistry toolbox has been used to plot the PES of the Ti-O bond. Within a specified range, at each point the electronic energy is calculated using Hartree Fock and Density Functional Theory (cc-PVDZ basis in both cases). With more powerful machines, more sophisticated electronic structure methods with larger basis sets can be used. The curves are then fitted using the NonLinearFit option of the Statistics package. The fitting function used is,

$$f(x) = \frac{1}{2} \cdot k(x - c)^2 + d$$

Instead of using our system directly, we will take a roundabout approach and treat it using path integrals on the harmonic oscillator, where the force constant of the harmonic oscillator is taken as the fitted 'k' value and the mass is taken as the reduced mass of our model chemical system. The first three wave functions of the HO model, derived from the PIQM formalism have been plotted, as well as the density matrix, as a function of β. The obtained PES plots also show how good an approximation the harmonic oscillator model is near the equilibrium bond length.

> *Loading the packages*

```
Digits := 15:
with(QuantumChemistry):
with(Statistics):
```

> *Initialising parameters*

```
n := 200:
rmin := 1.4:
rmax := 1.7:
dr := (rmax-rmin)/(n-1):
xx := rmin:
e_v := []:
r_v := []:
```

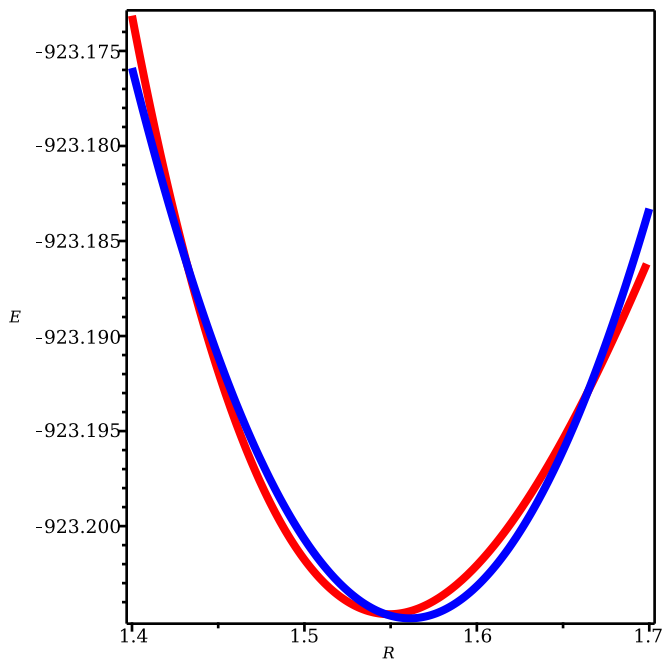
> *Computing energies using HF for different bond lengths*

```
for i from 1 while i < n do
  mol := [["Ti", 0, 0, 0],["O", 0, 0, xx]]:
  energy := Energy(mol, method = HartreeFock, basis = "cc-pVDZ"):
  e_v := [op(e_v),energy]:
  r_v := [op(r_v),xx]:
  xx := xx + dr:
end do:
```

> *Plotting and fitting the PES using a HO type function*

```
p_actual := plot(r_v,e_v,axes = boxed, labels = ['R', 'E'], color = red, thickness = 3):
NonlinearFit(0.5*k*(var-c)^2+d,r_v,e_v,var);
p_fitted := plot (1.11625206*(var - 1.56105199)^2 - 923.20485176,var=1.4..1.7,axes = boxed, labels = ['R', 'E'],
color = blue, thickness = 3):
plots:-display({p_actual,p_fitted});
```

$$1.11625146\,(var - 1.56105199)^2 - 923.20485175$$



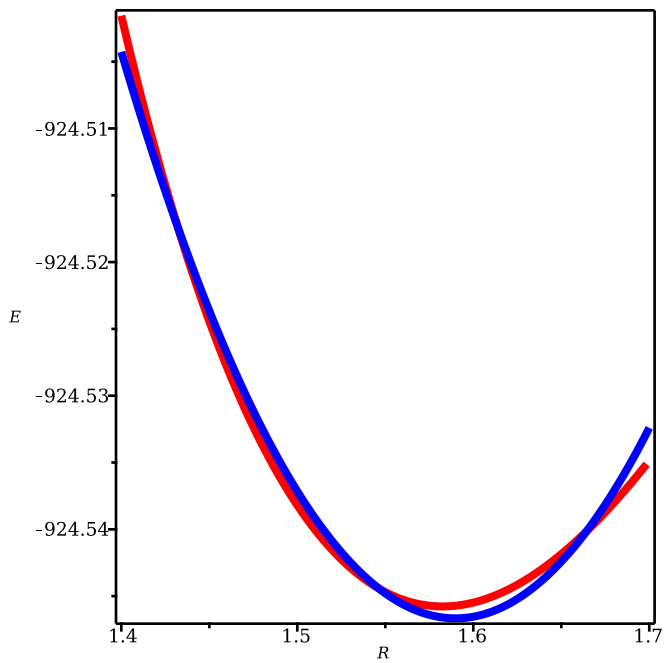
> *Computing energies using DFT for different bond lengths*

```
xx := rmin:
e_v := []:
r_v := []:
for i from 1 while i < n do
  mol := [["Ti", 0, 0, 0],["O", 0, 0, xx]]:
  energy := Energy(mol, method = DensityFunctional, basis = "cc-pVDZ"):
  e_v := [op(e_v),energy]:
  r_v := [op(r_v),xx]:
  xx := xx + dr:
end do:
```

> *Plotting and fitting the PES using a HO type function*

```
p_actual := plot(r_v,e_v,axes = boxed, labels = ['R', 'E'], color = red, thickness = 3):
NonlinearFit(0.5*k*(var-c)^2+d,r_v,e_v,var);
p_fitted := plot (1.17555127*(var - 1.58989466)^2 - 924.54665957,var=1.4..1.7,axes = boxed, labels = ['R', 'E'],
color = blue, thickness = 3):
plots:-display({p_actual,p_fitted});
```

$$1.17555124\,(var - 1.58989467)^2 - 924.54665957$$

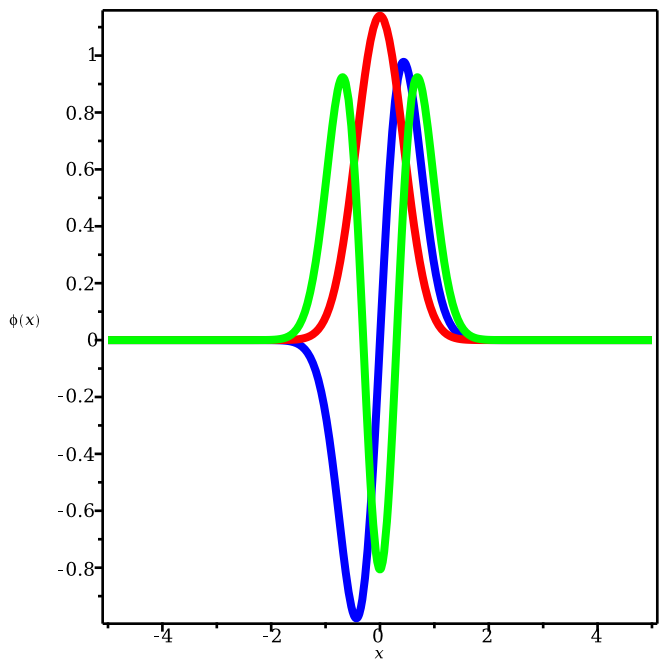



```
> mTi := 47.876:
  mO := 15.999:
  m := (mTi*mO)/(mTi + mO):
  khf := 2.2325:
  kdft := 2.3511:
  omegahf := sqrt(khf/m):
  omegadft := sqrt(kdft/m):
```

All are atomic units (and ħ = 1, hence ignored)

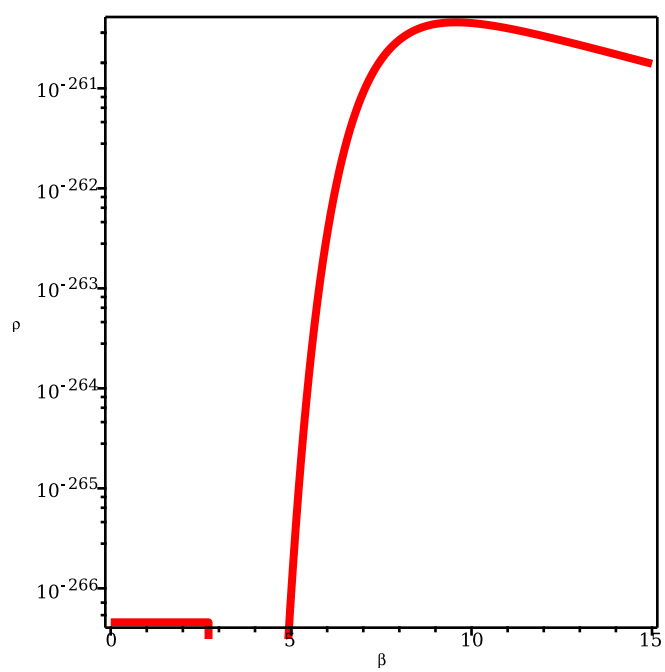
Plotting the HO wave functions using the DFT-fitted k values

```
> phi0dft := (m*omegadft/Pi)^(1/4)*exp(-(m*omegadft/2)*x^2):
  phi1dft := sqrt(2*m*omegadft)*x*phi0dft:
  phi2dft := (2*m*omegadft*x^2 - 1)*phi0dft/sqrt(2):
  p0dft := plot(phi0dft(x), x = -5.0 .. 5.0, axes = boxed, labels = ['x', 'phi(x)'], color = red, thickness = 3):
  p1dft := plot(phi1dft(x), x = -5.0 .. 5.0, axes = boxed, labels = ['x', 'phi(x)'], color = blue, thickness = 3):
  p2dft := plot(phi2dft(x), x = -5.0 .. 5.0, axes = boxed, labels = ['x', 'phi(x)'], color = green, thickness = 3):
  plots:-display({p0dft,p1dft,p2dft});
```



Plotting the density matrix as a function of β with specified end points (keeping things real, as plotting the kernel directly would involve complex numbers):

```
> x1 := 0.0:
  x2 := 15.0:
  denmatdft := sqrt((m*omegadft)/(2*Pi*sinh(beta*omegadft)))*exp(-(m*omegadft)/(2*sinh(beta*omegadft))*(
  (x1^2 + x2^2)*cosh(beta*omegadft) - 2*x1*x2)):
> with(plots):
  logplot(denmatdft(beta), beta = 0.0..15.0, axes = boxed, labels = ['beta', 'rho'], color = red, thickness = 3);
```



Path Integral Molecular Dynamics

To understand PIMD, the prefactor of Eq (1) can be written as a set of Gaussian integrals over the momenta $p_1, p_2 ... p_P$ and the partition function can be expressed as

$$Q(L,T) = \int dp_1 ... dp_P \int_{D(L)} dx_1 ... dx_P \exp\left\{ -\beta \sum_{k=1}^{P} \left(\frac{p_i^2}{2m'} + \frac{m\omega_P^2}{2} \left(x_{k+1} - x_k \right)^2 + \frac{1}{P} U(x_k) \right) \right\} \Bigg|_{x_{P+1} = x_P} \quad (2)$$

where $m' = \frac{mP}{(2\pi\hbar)^2}$ and $\omega_P = \frac{\sqrt{P}}{\beta\hbar}$. Eq (2) remarkably resembles a classical cyclic polymer chain of P points moving in a classical potential U(x)/P. P can now be interpreted as the number of beads or replicas of the classical particle needed to obtain quantum effects - it is simply a measure of the *quantumness* of the system. In other words, a purely quantum mechanical expression has been mapped onto a classical expression, hence the term *quantum-classical isomorphism.* From this, a Hamiltonian can be constructed and the corresponding equations of motion can be derived and simulated. However, such a framework has quite a few drawbacks, including the immense computational effort required for converging the simulations. Efficient thermostatting and the use of Generalised Langevin Equations (GLE) are some advanced ways of tackling this convergence issue.

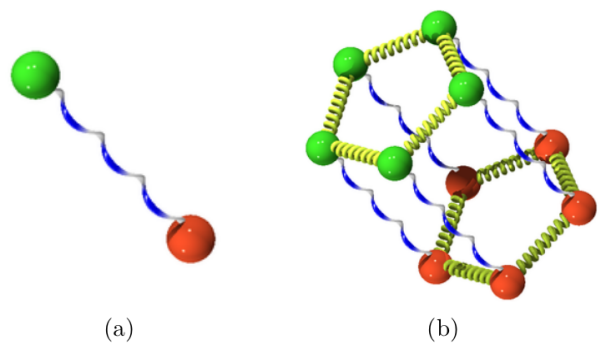


Fig 2: Quantum-classical isomorphism - (a) Interatomic potential (blue and white curly bonds) between two atoms (in green and orange) (b) The 'ring polymer' molecule with P = 5 (or 5 beads/replicas of (a)) connected by harmonic springs
(figures taken from Ref 5)

PIMD using the Harmonic Oscillator model

As an illustration of PIMD, we will consider a particular moving under a harmonic oscillator potential. The potential term in Eq (2) is given by

$$U(x) = \frac{1}{2} k x^2$$

Thus, the partition function can be written as,

$$Q(L,T) = \int dp_1 ... dp_P \int_{D(L)} dx_1 ... dx_P \exp\left\{ -\beta \sum_{k=1}^{P} \left(\frac{p_i^2}{2m'} + \frac{m\omega_P^2}{2} \left(x_{k+1} - x_k \right)^2 + \frac{k x_k^2}{2P} \right) \right\} \Bigg|_{x_{P+1} = x_P}$$

and the classical Hamiltonian can be written as,

$$H_{cl}(x,p) = \sum_{k=1}^{P} \left(\frac{p_k^2}{2m'} + \frac{m\omega_P^2}{2} \left(x_{k+1} - x_k \right)^2 + \frac{k x_k^2}{2P} \right)$$

subject to the constraint that $x_{P+1} = x_P$. Now, using Hamilton's equations of motion, the equations of motion can be derived as

$$\dot{x}_k = \frac{p_k}{m'}$$

and

$$\dot{p}_k = -m\omega_P^2\left(2x_k - x_{k+1} - x_{k-1}\right) - \frac{1}{P}\frac{\partial U}{\partial x_k} = -m\omega_P^2\left(2x_k - x_{k+1} - x_{k-1}\right) - \frac{1}{P}kx_k = f_k$$

where f_k is the force acting on the kth bead. These equations can be conveniently written in the form of a Velocity Verlet loop, and the beads (and hence the original quantum particle) can be propagated accordingly. The next section demonstrates this using a small code.

Simple illustration of PIMD

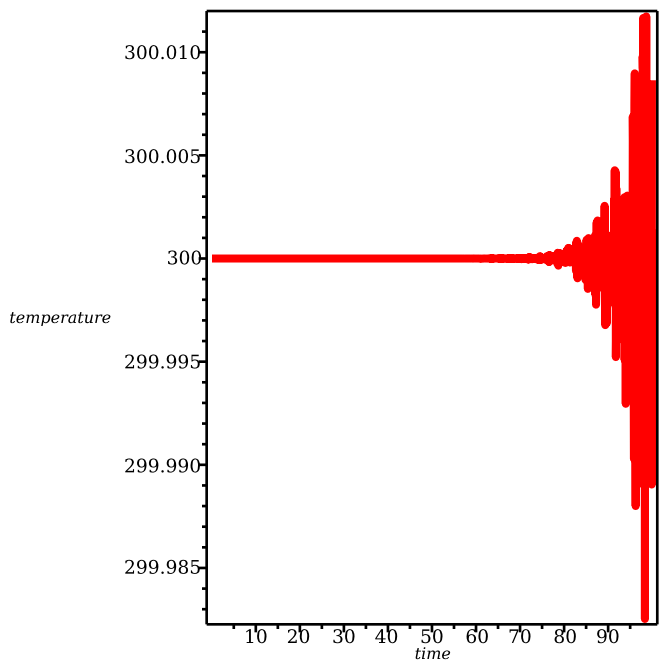
This is a very simple illustration of PIMD using a toy system. As explained in the previous section, this code uses a particle under a harmonic oscillator potential, and its dynamics can be described using the dynamics of a collection of beads. In this example, 10 beads are used for describing one particle, over 2000 time steps. The parameters for PIMD have been chosen arbitrarily (it does not represent any real system, just highlights the method).

```
> Initialising/declaring the PIMD parameters. For simplicity, all masses and force constants have been taken as 1
  pp := 10: (number of beads)
  nstep := 2000: (number of time steps)
  dt := 0.05: (time step)
  kk := 1: (force constant in the harmonic potential)
  m :=1:
  omegap :=1:

  Defining a random number generator and initialising the coordinates, momenta and forces
> randno := rand(0.0..1.0):
> x := array(1..pp,1..nstep):
  p := array(1..pp,1..nstep):
  F := array(1..pp,1..nstep):
  for k from 1 to pp do
    for i from 1 to (nstep-1) do
      x[k,i] := 0.0:
      p[k,i] := m*randno():
      F[k,i] := 0.0:
    end do:
  end do:

> for k from 1 to pp do
    kp := k+1:
    km := k-1:
    if k = pp then kp:=1:
    end if:
    if k = 1 then km:=pp:
    end if:

    Velocity Verlet loop for all the beads
    for i from 1 to (nstep-1) do
      F[k,i] := -m*omegap^2*(2*x[k,i]-x[km,i]-x[kp,i])-(kk*x[k,i])/pp:
      x[k,i+1] := x[k,i] + dt*p[k,i]/m + (0.5*F[k,i]*dt^2)/m:
      F[k,i+1] := -m*omegap^2*(2*x[k,i+1]-x[km,i+1]-x[kp,i+1])-(kk*x[k,i+1])/pp:
      p[k,i+1] := p[k,i] + 0.5*dt*F[k,i] + 0.5*dt*F[k,i+1]:

      Berendsen thermostat (standard velocity rescaling used here)
      tactual := (0.5*p[k,i]^2)/m:
      lambda := sqrt(1.0 + (dt/0.05)*((300.0/tactual)-1.0)):
```

```
      p[k,i] := p[k,i]*lambda:

    end do:
  end do:

> tempv := []:
  timev := []:
```

Plotting the evolution of temperature (NVT simulation)

```
> t := 0.0:
  temp := 0.0:
  for i from 1 to (nstep-1) do
    for k from 1 to pp do
      kp := (k+1):
      if k = (pp+1) then kp:=1:
      end if:
      temp := temp + 0.5*p[k,i]^2:
    end do:
    t := t + dt;
    tempv := [op(tempv),temp/pp]:
    timev := [op(timev),t]:
    temp := 0.0;
  end do:

> plot(timev,tempv,axes = boxed, labels = ['time', 'temperature'], color = red, thickness = 3);
```



From the plot, it can be clearly seen that in this NVT simulation, the temperature remains perfectly constant up to a certain point, beyond which there is a sharp increase in the fluctuations. This is so because PIMD simulations are very difficult to converge without efficient thermostatting. A simple velocity rescaling scheme was used here (written in the form of a more general Berendsen thermostat), but for larger number of steps, more efficient methods are required. Furthermore, ideally one should propagate the beads such that the motion of the centroid is also accounted for. A Box-Muller sampling algorithm can also be used for initialising the velocities of the beads from the Boltzmann distribution. As a final remark, it can be stated that though this simple code can generate a constant temperature run up to a certain limit, to get an accurate canonical distribution and constant temperature throughout the entire simulation, advanced methods must be resorted to.

Discussions

This worksheet broadly consists of two parts - PIQM and PIMD. In the first part, the basics of the path integral formalism was introduced, including the density matrix and the action integral. In particular, the eigenvalues and eigenstates of the harmonic oscillator were derived. Electronic structure calculations were carried out on a model system and were used for fitting parameters of a harmonic oscillator type function. These fitted parameters were finally used for plotting the HO wavefunctions and the path integral kernel.
The second part of this worksheet is much more specific in the sense that it deals with a widely used numerical method of implementing path integrals - PIMD. Following a brief introduction to how PIMD is carried out, the concept of quantum-classical isomorphism and finally an illustrative example of a PIMD simulation on a toy system are presented. The short PIMD simulation proves that for better convergence, advanced techniques must be used.

References

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