Computational Quantum Mechanics

• Will now be looking into non-relativistic quantum mechanics from a computational perspective
• Solving Schroedinger equation for several system:
  – Hydrogen atom
  – Helium atom
  – Harmonic oscillator

• Will look at a few different computational techniques:
  – Variational methods
  – MC methods
Hydrogen Atom

- 2-body quantum system
- Exactly solvable
- Great test case for numerical methods

Phys. Rev. Lett. 110, 213001
Helium Atom

- 3-body quantum system
- Not exactly solvable (even classically!)
- Approximation methods abound
- Ripe for computation!
Variational Methods

• Recall from your quantum mechanical class:
  – Given Hamiltonian $H$, the quantum system is described by a vector $|\psi\rangle$ in an infinite-dimensional Hilbert space.
  – The energy $E$ of the wavefunction is the expectation value of the Hamiltonian:
    \[ E[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \]

  – Variational theorem states that the extrema of $E$ are eigenstates of $H$:
    • if $\delta E = E[\psi + \delta \psi] - E[\psi] = 0$
    • then: $H\psi = E\psi$

The Hilbert space is infinite-dimensional, though, so too expensive to search the entire space.
Variational Methods

• Instead look for stationary states in a finite subspace
• Suppose subspace is N dimensional
• Orthonormal basis vectors \( \chi \) satisfy:

\[
< \chi_p | \chi_q > = \delta_{pq}
\]

• Then H is approximated by NxN matrix:

\[
H_{pq} = < \chi_p | H | \chi_q >
\]

• Now want stationary states:

\[
\psi = \sum_{p=1}^{N} C_p | \chi_p >
\]
Variational Methods

• This is a matrix eigenvalue problem!

\[ HC = EC \]

\[ \sum_{q=1}^{N} H_{pq} C_q = EC_p \]

• H is always Hermitian

• Often a real symmetric matrix (hydrogen and helium are)
  – Exactly N real eigenvalues
  – N eigenvalues span the subspace (linearly independent) and can be made orthonormal, but not necessary
  – Look for linearly independent set:

\[ \sum_{q=1}^{N} H_{pq} C_q = E \sum_{q=1}^{N} S_{pq} C_p \]

Overlap matrix S:

\[ S_{pq} = \langle \chi_p | \chi_q \rangle \]
Variational Methods

• Overlap matrix S:
  – Hermitian
  – Eigenvalues of S are real and positive definite (>0)

• Now reduced this problem to a linear algebra problem for linear equations in a finite dimensional space
Hydrogen Atom

• Hamiltonian is:

\[
H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}
\]

• Work in coordinates such that proton is at origin:

\[
\vec{r} = \vec{r}_e - \vec{r}_p
\]

• Also use reduced mass of the system:

\[
m = \frac{m_e m_p}{m_e + m_p}
\]
Hydrogen Atom

• Now look at ground state (spherically symmetric)
• 1d problem:

\[
H = -\frac{\hbar^2}{2m} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] - \frac{e^2}{4\pi\varepsilon_0 r}
\]

• Exact ground state energy and wavefunction:

\[
E_0 = -\frac{e^2}{2a_0} \quad \psi_0(r) \sim e^{-r/a_0}
\]

with Bohr radius:

\[
a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}
\]

• Convert to units with \( \hbar = m = e^2/(4\pi\varepsilon_0) = 1 \)

\[
H = -\frac{1}{2} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] - \frac{1}{r} \quad E_0 = -1/2 \quad \psi_0(r) \sim e^{-r}
\]
Hydrogen Atom

• Trial functions can be:

\[ \psi_{T,\alpha}(r) = e^{-\alpha r} \]

• Hamiltonian on this is:

\[ H \psi_{T,\alpha}(r) = E(r) \psi_{T,\alpha}(r) \]

• We have defined \( E(r) \) as the “local energy” of the trial wavefunction

• If \( \alpha = a_0 \), this is just proportional to the exact wavefunction
Hydrogen Atom

• Now apply trial wavefunctions as a linear combination of atomic orbitals (LCAO)

• Define:
  – Slater orbitals: \[ \chi(\vec{r}) = Y_{lm}(\theta, \phi)e^{-\alpha r} \]
  – Gaussian orbitals: \[ \chi(\vec{r}) = Y_{lm}(\theta, \phi)e^{-\alpha r^2} \]

• On hydrogen atom, Slater orbitals are exact, so let’s try with Gaussian orbitals. Define basis set for l=0 s-wave states:
\[
\psi(r) = \sum_{i=0}^{N-1} d_i g_s(\alpha_i, \vec{r}) \quad g_s(\alpha, \vec{r}) = \left( \frac{2\alpha}{\pi} \right)^{3/4} e^{-\alpha r^2}
\]
Hydrogen Atom

- Products of Gaussians are Gaussians so we can directly compute matrix elements:

\[
S_{ij} = \int d^3r \, e^{-\alpha_i r^2} e^{-\alpha_j r^2} = \left( \frac{\pi}{\alpha_i + \alpha_j} \right)^{3/2}
\]

\[
T_{ij} = -\frac{\hbar^2}{2m} \int d^3r \, e^{-\alpha_i r^2} \nabla^2 e^{-\alpha_j r^2} = \frac{3\hbar^2}{m} \frac{\alpha_i \alpha_j \pi^{3/2}}{(\alpha_i + \alpha_j)^{5/2}},
\]

\[
V_{ij} = -e^2 \int d^3r \, e^{-\alpha_i r^2} \frac{1}{r} e^{-\alpha_j r^2} = -\frac{2\pi e^2}{\alpha_i + \alpha_j}.
\]
Hydrogen Atom

• Now reduce this to a simple N-dimensional minimization problem

• Need only use something like BFGS to perform the minimization

• Jupyter notebook in Lecture36!
Helium Atom

• You will compute the Helium Atom for your homework assignment

• Using our same units with the nucleus at the origin, the Hamiltonian is:

\[ H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}, \]

\[ r_{12} = |\vec{r}_{12}| = |\vec{r}_1 - \vec{r}_2| \]
Helium Atom

• If there were no repulsive term, it would be a Hamiltonian consisting of two hydrogen-like atoms with nuclear charge $Z$:

$$E_0 = -\frac{Z^2}{2}, \quad \psi_0 \sim e^{-Zr}.$$ 

Then the combined wavefunction if the two electrons didn’t interact would be:

$$\psi(r_1, r_2) \sim e^{-2r_1} e^{-2r_2}$$

• So let’s start with a trial wavefunction like:

$$\psi_{T, \alpha} = e^{-\alpha r_1} e^{-\alpha r_2}$$
Helium Atom

• With electron-electron interactions neglected, average energy would be:

\[
\left\langle -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} \right\rangle = 2 \times \frac{\alpha^2}{2} - 2 \times 2 \times \alpha ,
\]

• This has a minimum at alpha=2, which gives \( \langle E \rangle = -4 \).

• The experimental value is \( E_0 = -2.904 \).

• It can actually be solved exactly even if you do include electron-electron interactions:

\[
\left\langle -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right\rangle = \alpha^2 - \frac{27}{8} \alpha ,
\]

• Minima are at alpha = \( 27/16 \), so \( \langle E \rangle = -2.8477 \).

• You will solve this for your HW problem!
Computational Quantum Mechanics

- Already solved some simple cases (Hydrogen and Helium atom) using LCAO
- Now will turn to MC-based methods
- Will look at QHO as a prototype system:

\[ H \psi(x) = \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right] \psi(x) = E \psi(x) \]

\[ \lim_{x \to \pm \infty} \psi(x) = 0 \]

- With solutions:

\[ E_n = \left( n + \frac{1}{2} \right) \hbar \omega \quad n = 0, 1, 2, 3, \ldots \]

\[ \psi_n(x) = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n \left( x \sqrt{\frac{m \omega}{\hbar}} \right) e^{-m \omega x^2 / (2 \hbar)} \]

Hermite polynomials:

\[ H_0(y) = 1, \quad H_1(y) = 2y, \quad H_2(y) = 4y^2 - 2, \]
Variational Monte Carlo

- Instead of trial wave functions, we will now try a MC based technique
- Consider N particles
- Want to find a (very large) multi-dimensional integral:

\[
\langle E \rangle = \frac{\int dR \, \psi^* H \psi}{\int dR \, \psi^* \psi} \quad R = \{\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N\}
\]

- Fantastic for MC techniques!
  - Just need to make this positive-definite for the Metropolis algorithm to work
Variational Monte Carlo

- Define the weight function:

\[ \rho(R) = \frac{|\Psi_{T,\alpha}(R)|^2}{\int dR |\Psi_{T,\alpha}|^2} \]

- Energy can be written as:

\[ \langle E \rangle = \frac{\int dR |\Psi_{T,\alpha}|^2 \frac{H\Psi_{T,\alpha}}{\Psi_{T,\alpha}}}{\int dR |\Psi_{T,\alpha}|^2} = \int dR \rho(R) E_L(R) \]

- With local energy:

\[ E_L(R) = \frac{H\Psi_{T,\alpha}(R)}{\Psi_{T,\alpha}(R)} \]
Variational Monte Carlo

• Goal is to generate M sets of positions that spans the relevant space reasonably well, according to the weight function

\[ R_i = \{ R_1, R_2, \ldots, R_M \} \]

(remember each R is itself a set of N positions)

• Then we have an approximation by summing over MC steps:

\[ \langle E \rangle = \frac{1}{M} \sum_{i=1}^{M} E_L(R_i) . \]
Variational Monte Carlo

• Consider Gaussian trial wavefunctions:

\[ \Psi_{T,\alpha}(x) = e^{-\alpha x^2} \]

• Consider units so that

\[ \hbar = m = \omega^2 = 1 \]

• Then the Hamiltonian is:

\[ H = -\frac{d^2}{dx^2} + \frac{1}{2}x^2 \]

• With local energies:

\[ E_L(x) = \alpha + x^2 \left( \frac{1}{2} - 2\alpha^2 \right) \]

Note: Exact solution for ground state is alpha=1/2
Variational Monte Carlo

- We will consider the Metropolis algorithm with $M$ random walkers with density:

$$\rho(x) \sim e^{-2\alpha x^2}$$

Note: In the code, $M$ is denoted as $N$

- Evaluates the Metropolis weight function:

$$w = \frac{\rho(x_{\text{trial}})}{\rho(x)}$$

- If $w \geq 1$, step is accepted
- If $w < 1$, step if larger than a uniform deviate between 0-1
Example for QHO

• Software is provided in C++ for the case of the QHO

• You will adapt this to Hydrogen (undergrads) and Helium (grads) for your homework
Cusp conditions

• The wrinkle in your homework is that you must remove singularities in the Metropolis algorithm!

• One way to avoid this is to use trial functions that avoid the discontinuity
  – For example, for Helium-like atoms:

\[
\psi(\vec{r}_1, \vec{r}_2) = e^{-Zr_1} e^{-Zr_2} e^{\beta r_{12}/(1+\alpha r_{12})}
\]

For some parameters Z and beta

• Can show that the local energy is:

\[
E_L(\vec{r}_1, \vec{r}_2) = -Z^2 + \frac{Z - 2}{r_1} + \frac{Z - 2}{r_2} + \frac{1}{r_{12}} \left[ 1 - \frac{2\beta}{(1 + \alpha r_{12})^2} \right] + \frac{2\alpha\beta}{(1 + \alpha r_{12})^3} - \frac{\beta^2}{(1 + \alpha r_{12})^4} + \frac{Z \beta \hat{r}_{12} \cdot (\hat{r}_1 - \hat{r}_2)}{(1 + \alpha r_{12})^2}
\]
Cusp conditions

• If $Z=2$ (i.e. Helium itself) and beta = 1/2, the singularities cancel

$$E_L(\vec{r}_1, \vec{r}_2) = -4 + \frac{\alpha}{(1 + \alpha r_{12})} + \frac{\alpha}{(1 + \alpha r_{12})^2} + \frac{\alpha}{(1 + \alpha r_{12})^3}$$

$$- \frac{1}{4 (1 + \alpha r_{12})^4} + \frac{\hat{r}_{12} \cdot (\hat{r}_1 - \hat{r}_2)}{(1 + \alpha r_{12})^2}$$

• If not, the code spends a lot of time computing the Metropolis step near the singularities, and affects the precision of the calculation
• Have been saying that the Schroedinger equation is just diffusion with imaginary time
• Will now make that explicit!

• First, consider ordinary diffusion
  – In your homework problems, you created diffusion with random walkers
  – Now expand this: density of walkers at time $t$ is computed from initial density by evolution of a Green’s function:

\[
\rho(y, t) = \int dx \ G(x, y; t) \rho(x, 0) , \quad G(x, y; t) = \frac{1}{\sqrt{4\pi \gamma t}} e^{-\frac{(x-y)^2}{4\gamma t}}
\]
Diffusion

- Green’s function: Impulse response of a dynamical system
- Formally:

\[ G(x, y; 0) = \delta(x - y) , \quad \text{and} \quad \int dx \ G(x, y; t) = 1 \]

- Gives probability that a walker at \( x \) (or \( y \)) at time \( t=0 \) will evolve to \( y \) (or \( x \)) in time \( t \)

- So, can compute a random walk by:
  - Choose step size \( \Delta t \) in time
  - Walker: \( x(t) \rightarrow x(t + \Delta t) = x(t) + \eta \sqrt{\Delta t} \)

Gaussian deviate with variance \( \sigma^2 = 2\gamma \)

You calculated gamma in your HW problems!
Diffusion

• Diffusion is really just Brownian motion, so look at Einstein’s relation:

\[ \gamma = \frac{k_B T}{\beta} \]

• where beta is the drag coefficient
  – For Brownian motion of spheres of radius R and fluid viscosity \( \nu \), \( \beta = 6\pi R\nu \)

• In the continuum limit, density satisfies:

\[ \frac{\partial \rho}{\partial t} = \gamma \frac{\partial^2 \rho}{\partial x^2} \]

• Now recall Schroedinger’s equation:

\[ \frac{\partial \psi(x, t)}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} = \gamma_{\text{im}} \frac{\partial^2 \psi(x, t)}{\partial x^2} \]

<--- Imaginary diffusion constant!
We can alternatively describe this as diffusion with imaginary time if we set $\tau = -it$

So this becomes:

$$\frac{\partial \psi(x, \tau)}{\partial \tau} = \frac{\hbar}{2m} \frac{\partial^2 \psi(x, \tau)}{\partial x^2}$$

Precisely diffusion in imaginary time!
Can now evolve to a ground state by taking the long-time limit of the initial state, evolved according to the diffusion equation in imaginary time.

So set the initial function to be:

\[ \Psi(x, 0) = \sum_{n=0}^{\infty} c_n \psi_n(x) \]

Evolve via Schroedinger eqn:

\[ \Psi(x, t) = \sum_{n=0}^{\infty} c_n e^{-iE_n t/\hbar} \psi_n(x) \]

Then analytically continue to imaginary time:

\[ \Psi(x, \tau) = \sum_{n=0}^{\infty} c_n e^{-E_n \tau/\hbar} \psi_n(x) \]

Ground state is the long-time limit:

\[ \lim_{\tau \to \infty} e^{E_0 \tau/\hbar} \Psi(x, \tau) = \lim_{\tau \to \infty} \sum_{n} c_n e^{-(E_n-E_0) \tau/\hbar} \psi_n(x) = c_0 \psi_0(x) \]
Now add a potential:

\[
\frac{\partial \psi(x, \tau)}{\partial \tau} = \frac{1}{2} \frac{\partial^2 \psi(x, \tau)}{\partial x^2} - V(x) \psi(x, \tau),
\]

Trying to evolve via a Green’s function doesn’t work because the probability is not conserved!

For a particle at rest:

\[
\frac{\partial \psi(x, \tau)}{\partial \tau} = -V(x) \psi(x, \tau), \quad \psi(x, \tau) = e^{-V(x)\tau} \psi(x, 0),
\]

Would have:

\[
\lim_{\tau \to \infty} \psi(x, \tau) = \begin{cases} 
0 & \text{where } V(x) > 0 \\
\psi(x, 0) & \text{where } V(x) = 0 \\
\infty & \text{where } V(x) < 0
\end{cases}
\]

No bueno.
Diffusion Quantum MC

• Try to adjust this numerically:

\[ \frac{\partial \psi(x, \tau)}{\partial \tau} = \frac{1}{2} \frac{\partial^2 \psi(x, \tau)}{\partial x^2} - (V(x) - E_T)\psi(x, \tau) . \]

• In the long-time limit, independent of tau so

\[ -\frac{1}{2} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E_T\psi(x) \]

• Tends to an eigenfunction of the QM problem with ET as the eigenvalue!

• Therefore, can evolve the function in imaginary time and the solution tends toward the actual solution!
Diffusion Quantum MC

• Initialize:
  – Choose step size $\Delta t$, target number of walkers $N_T$, and $E_T$

• Time step:
  – Diffusion: K.E. shifts walkers to a new position chosen at random from Gaussian distribution with variance $\Delta t$
  – Branching: P.E. (modified by $E_T$) grows or decays number of walkers
    • Compute: $q = e^{-\Delta \tau [V(x) - E_T]}$
    • Compute integer part of $q$: int($q$)
    • Then $q - \text{int}(q)$ is distributed in $[0,1)$.
    • If int($q$) == 0, destroy the walker
    • Else produce int($q$) - 1 copies

  – Adjust $E_T \rightarrow E_T + \alpha \log \left( \frac{N_T}{N} \right)$
    • This is to make sure the number of walkers doesn’t grow too large or too small
• Try for a 3-d oscillator
• Ground state energy and wavefunction:

\[ E_0 = \frac{3}{2}, \quad \psi_0 = \frac{e^{-r^2/2}}{(2\pi)^{3/2}} \]

• Start with some random initial state, evolve it toward the ground state after a long (imaginary) time
• Now we look into the path integral formulation of QM from a numerical standpoint:

https://en.wikipedia.org/wiki/Path_integral_formulation
• Another application of imaginary time is the path integral formulation for QM
• Consider N particles with positions \( \mathcal{R} = \{ r_i \} \) and mass \( m \) in d dimensions
• Hamiltonian is:

\[
H = -\hbar^2 \sum_i \frac{1}{2m_i} \frac{\partial^2}{\partial r_i^2} + V(\mathcal{R})
\]

• The time evolution of the wavefunction is

\[
\psi(\mathcal{R}, t) = \langle \mathcal{R} | e^{-itH/\hbar} | \psi \rangle
\]

• Two problems:
  – Exponential is complex so not positive-definite to be used as a probability density
  – Infinite dimensional
Path Integral Formulation

• Instead, define a partition function (like in stat mech) in imaginary time (like in diffusion QMC):

\[
Z(\beta) = \int d^{Nd} R \langle R | e^{-\tau H / \hbar} | R \rangle = \text{Tr} e^{-\beta H}, \quad \beta = \frac{\tau}{\hbar}
\]

– Then this defines the quantum statistical mechanics for the system at temperature \( k_B T = 1/\beta = \hbar/\tau \)
Path Integral Formulation

• Then discretize and approximate in M steps with $\Delta \tau = \tau / M$
  – Break up the partition function into these M-1 intermediate steps along these coordinate eigenstates:

$$1 = \int d^{Nd}R_i \left| R_i \right\rangle \left\langle R_i \right|, \quad i = 1, \ldots, M - 1$$

– Partition function then becomes

$$Z(\beta) = \int d^{Nd}R \left\langle R \right| e^{-\tau H / \hbar} \left| R \right\rangle$$

$$= \int dR_0 \int dR_1 \ldots \int dR_{M-1} \left\langle R_0 \right| e^{-\Delta \tau H / \hbar} \left| R_{M-1} \right\rangle \ldots$$

$$\times \left\langle R_2 \right| e^{-\Delta \tau H / \hbar} \left| R_1 \right\rangle \left\langle R_1 \right| e^{-\Delta \tau H / \hbar} \left| R_0 \right\rangle$$
Path Integral Formulation

• Baker-Campbell-Hausdorff theorem states:

\[ e^A e^B = e^C \]

iff

\[ C = A + B + \frac{1}{2} [A, B] + \cdots \]

• In our case, we set:

\[ C = -\Delta \tau H/\hbar , \quad B = -\Delta \tau V/\hbar , \quad A = -\Delta \tau K/\hbar , \]

where the kinetic energy operator \( K \) is:

\[ K = -\hbar^2 \sum_i \frac{1}{2m_i} \frac{\partial^2}{\partial r_i^2} , \]

• Commutators of \( A \) and \( B \) are of order \( (\Delta \tau)^2 \), thus negligible!
Path Integral Formulation

• The time step evolution in the first-order approximation is therefore:

\[
\langle \mathcal{R}_1 | e^{-\Delta \tau H/\hbar} | \mathcal{R}_0 \rangle \approx \langle \mathcal{R}_1 | e^{-\Delta \tau K/\hbar} e^{-\Delta \tau V/\hbar} | \mathcal{R}_0 \rangle = \langle \mathcal{R}_1 | e^{-\Delta \tau K/\hbar} | \mathcal{R}_0 \rangle e^{-\Delta \tau V(\mathcal{R}_0)/\hbar}.
\]

• We can use complete sets of momentum eigenstates to compute these matrix elements:

\[
\langle \mathcal{R}_1 | e^{-\Delta \tau K/\hbar} | \mathcal{R}_0 \rangle = \int d\mathcal{P}_0 \int d\mathcal{P}_1 \langle \mathcal{R}_1 | \mathcal{P}_1 \rangle \langle \mathcal{P}_1 | e^{-\Delta \tau K/\hbar} | \mathcal{P}_0 \rangle \langle \mathcal{P}_0 | \mathcal{R}_0 \rangle
\]

\[
= \left( \frac{m}{2\pi \hbar \Delta \tau} \right)^{Nd/2} \exp \left[ -\frac{m \Delta \tau}{2\hbar} \sum_i \left( \frac{\mathbf{r}_{i1} - \mathbf{r}_{i0}}{\Delta \tau} \right)^2 \right].
\]

Product of \(N^d\) free particle diffusion Green’s functions!

\[
G(x, y; t) = \frac{1}{\sqrt{4\pi \gamma t}} e^{-\left(x-y\right)^2/(4\gamma t)}
\]
Path Integral Formulation

• Apply the Green’s function to the partition function to get a QM-operator-free expression:

\[
Z(\beta) \simeq \left( \frac{m}{2\pi \hbar \Delta \tau} \right)^{MN \Delta d/2} \int d\mathcal{R}_0 \int d\mathcal{R}_1 \ldots \int d\mathcal{R}_{M-1} \times \exp \left\{ -\frac{\Delta \tau}{\hbar} \sum_{j=0}^{M-1} \left[ \frac{m}{2} \left( \frac{\mathcal{R}_{j+1} - \mathcal{R}_j}{\Delta \tau} \right)^2 + V(\mathcal{R}_j) \right] \right\}
\]

Classical action!
Recall Sakurai’s treatment of the Path-Integral Formulation:

\[
\langle x_M, t_M | x_1, t_1 \rangle = \lim_{M \to \infty} \left( \frac{m}{2\pi\hbar\Delta t} \right)^{(M-1)/2} \int dx_{M-1} \ldots \int dx_2 \prod_{j=2}^{M} \exp \left[ \frac{iS(j, j-1)}{\hbar} \right]
\]

\[
= \int_{x_1}^{x_M} \mathcal{D}[x(t)] \exp \left[ \frac{i}{\hbar} \int_{t_1}^{t_M} dt \ L_{\text{classical}}(x, \dot{x}) \right]
\]

So we just integrate (in imaginary time) over the entire spatial range by summing over all possible periodic paths with period \( \tau \)!
Path Integral Formulation

• This is the potential energy function for a system of MNd classical particles at the positions R

\[ \sum_{j=0}^{M-1} \left[ \frac{m}{2} \left( \frac{\mathcal{R}_{j+1} - \mathcal{R}_j}{\Delta \tau} \right)^2 + V(\mathcal{R}_j) \right] \]

• Neighboring SPACES are coupled by V(R)
• Neighboring TIMES are coupled by classical harmonic oscillator forces
• Temperature is fixed, so we can numerically choose it such that “thermal” fluctuations are smaller than differences in energy levels, and it will converge to the desired state!
• Since \( k_B T = \hbar / \tau \)
  longer taus correspond to smaller T (i.e. smaller fluctuations)
Path Integral Formulation

• Code will also make use of the Virial theorem:

\[ 2 \langle K(x) \rangle = \left\langle x \frac{dV}{dx} \right\rangle \]