

PY411 / 506
Computational Physics 2

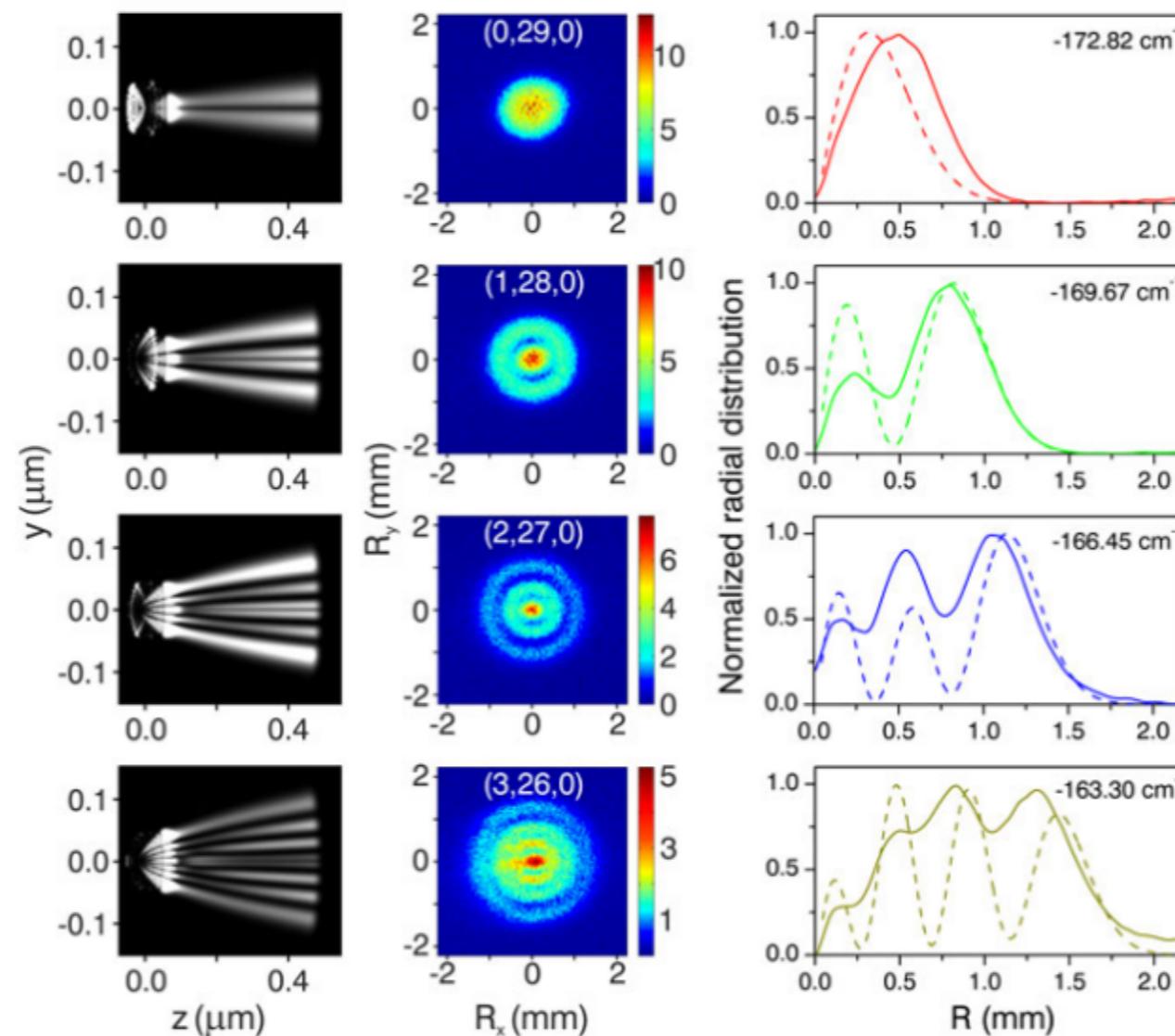
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Computational Quantum Mechanics

- 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

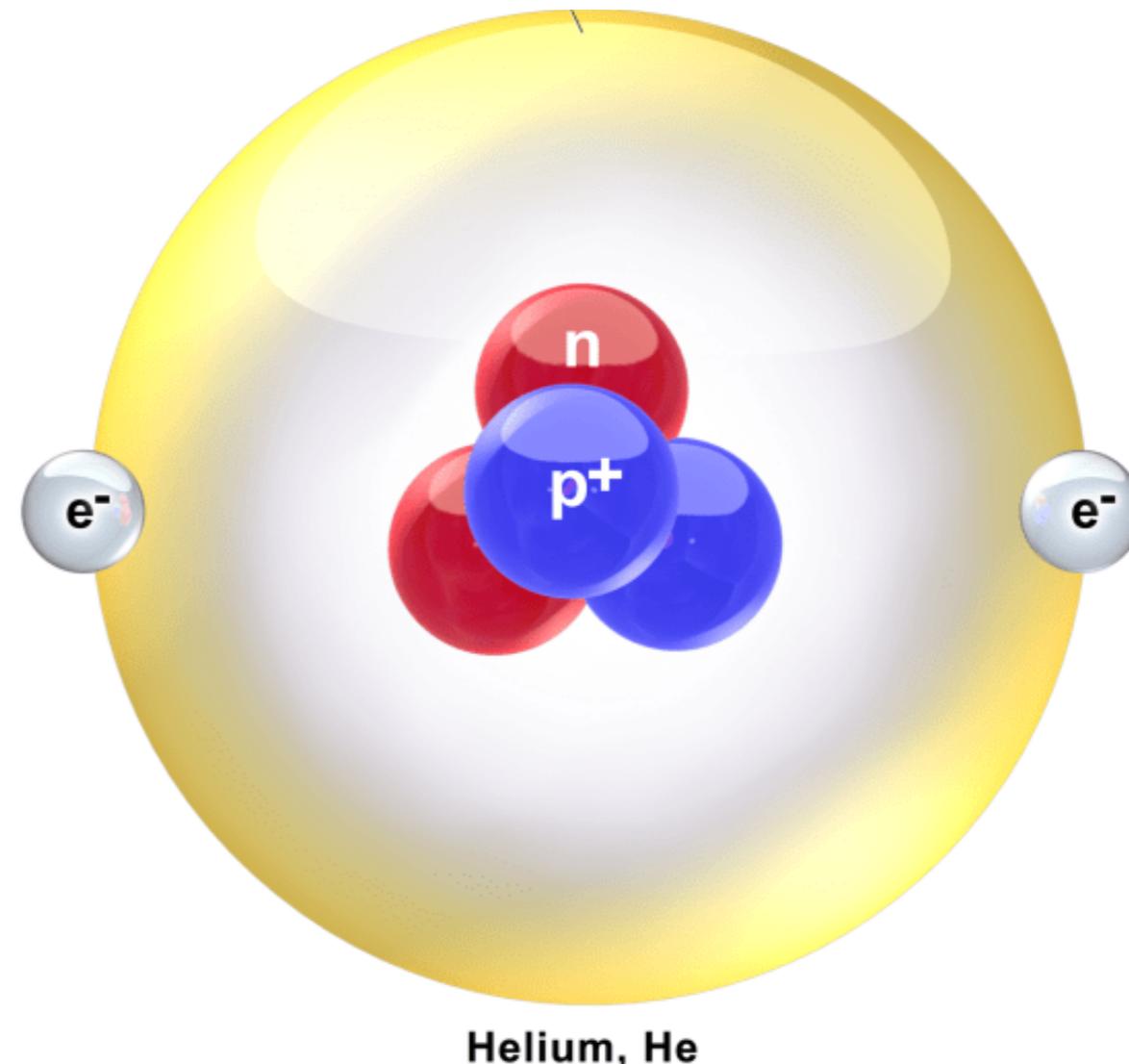
Hydrogen Atom

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



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:
$$\langle \chi_p | \chi_q \rangle = \delta_{pq}$$
- Then H is approximated by NxN matrix:

$$H_{pq} = \langle \chi_p | H | \chi_q \rangle$$

- Now want stationary states:

$$\psi = \sum_{p=1}^N C_p |\chi_p \rangle$$

Variational Methods

- This is a matrix eigenvalue problem!

$$HC = EC$$

$$\sum_{q=1}^N H_{pq} C_q = E C_p$$

- 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:

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

- 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:

$$H = -\frac{\hbar^2}{2m} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] - \frac{e^2}{4\pi\epsilon_0 r}$$

- 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:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

- Convert to units with $\hbar = m = e^2/(4\pi\epsilon_0) = 1$

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

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:

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

Attractive
to nucleus Repulsive
to each other



$$r_{12} = |\vec{r}_{12}| = |\vec{r}_1 - \vec{r}_2|$$

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:

$$\psi(\vec{r}_1, \vec{r}_2) \sim e^{-2r_1} e^{-2r_2}$$

- 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:

$$H\psi(x) = \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2 \right] \psi(x) = E\psi(x) \quad \lim_{x \rightarrow \pm\infty} \psi(x) = 0$$

- With solutions:

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

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

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:

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

- 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

$$R_i = \{R_1, R_2, \dots, R_M\}$$

(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

Singularities

- Can show that the local energy is:

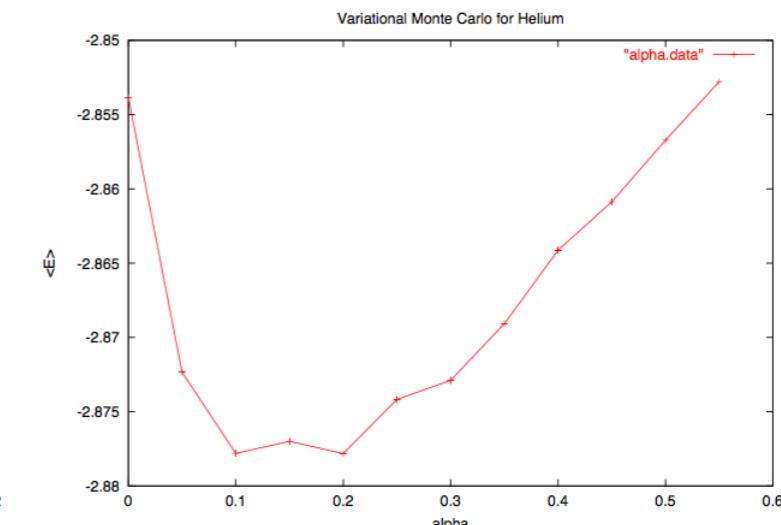
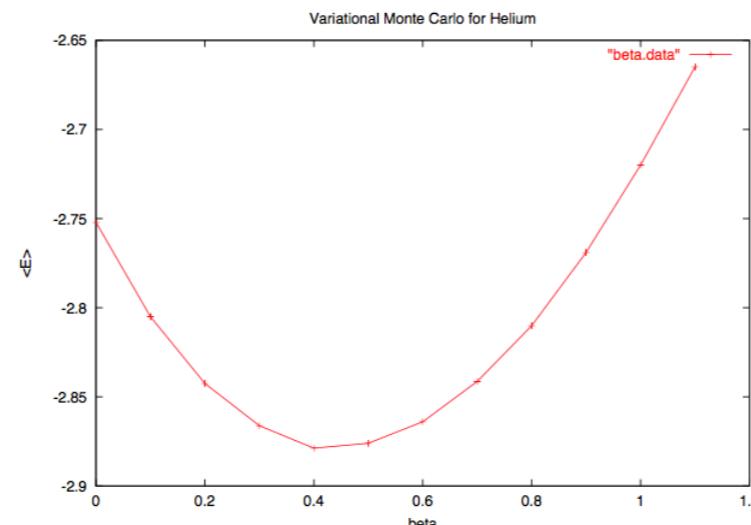
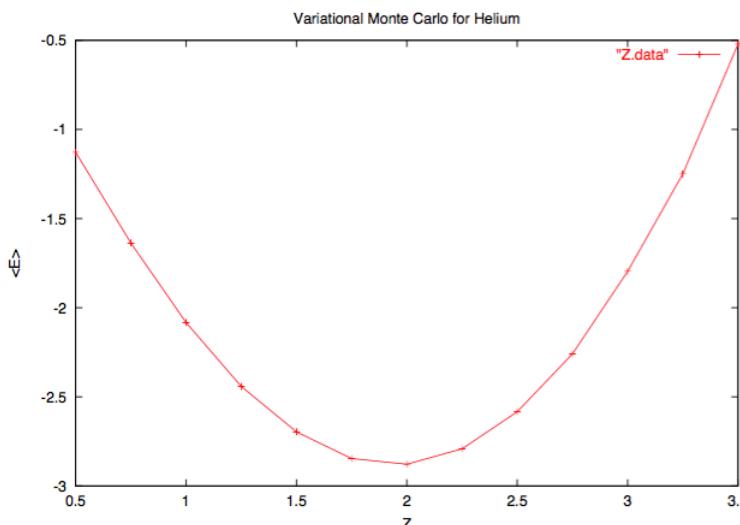
$$E_L(\vec{r}_1, \vec{r}_2) = -Z^2 + \frac{Z-2}{\boxed{r_1}} + \frac{Z-2}{\boxed{r_2}} + \frac{1}{\boxed{r_{12}}} \left[1 - \frac{2\beta}{(1+\alpha r_{12})^2} \right] \\ + \frac{2\alpha\beta}{(1+\alpha r_{12})^3} - \frac{\beta^2}{(1+\alpha r_{12})^4} + \frac{Z\beta \hat{r}_{12} \cdot (\hat{r}_1 - \hat{r}_2)}{(1+\alpha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

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



Computational Quantum Mechanics

- 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:

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

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 Δt 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!

Diffusion->QM

- 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!

Diffusion Quantum MC

- 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:

$$\lim_{\tau \rightarrow \infty} e^{E_0 \tau / \hbar} \Psi(x, \tau) = \lim_{\tau \rightarrow \infty} \sum_n c_n e^{-(E_n - E_0) \tau / \hbar} \psi_n(x) = c_0 \psi_0(x)$$

Diffusion Quantum MC

- 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:

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

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 Δt , 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 Δt
 - 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: $\text{int}(q)$
 - Then $q - \text{int}(q)$ is distributed in $[0,1)$.
 - If $\text{int}(q) == 0$, destroy the walker
 - Else produce $\text{int}(q) - 1$ copies
 - Adjust $E_T \rightarrow E_T + \alpha \log(N_T/N)$
 - This is to make sure the number of walkers doesn't grow too large or too small

Diffusion Quantum MC

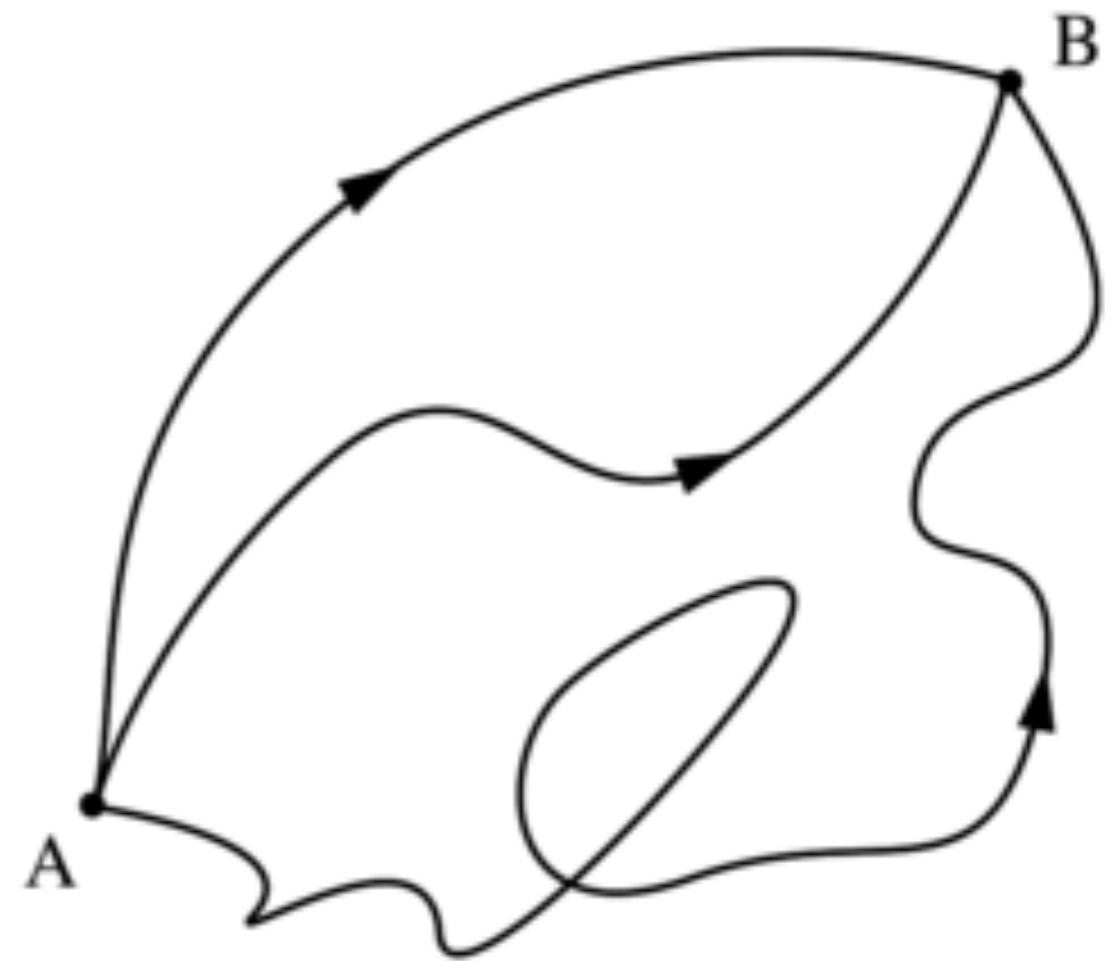
- Try for a 3-d oscillator
- Ground state energy and wavefunction:

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

- Start with some random initial state, evolve it toward the ground state after a long (imaginary) time

Path Integral MC

- Now we look into the path integral formulation of QM from a numerical standpoint:



[https://en.wikipedia.org/wiki/
Path_integral_formulation](https://en.wikipedia.org/wiki/Path_integral_formulation)

Path Integral Formulation

- Another application of imaginary time is the path integral formulation for QM
- Consider N particles with positions $\mathcal{R} = \{\mathbf{r}_i\}$ and mass m in d dimensions
- Hamiltonian is:

$$H = -\hbar^2 \sum_i \frac{1}{2m_i} \frac{\partial^2}{\partial \mathbf{r}_i^2} + V(\mathcal{R})$$

- The time evolution of the wavetunction 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):

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

- 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:

$$1 = \int d^{Nd} \mathcal{R}_i \ |\mathcal{R}_i\rangle\langle\mathcal{R}_i| , \quad i = 1, \dots, M-1$$

– Partition function then becomes

$$\begin{aligned} Z(\beta) &= \int d^{Nd} \mathcal{R} \left\langle \mathcal{R} \left| e^{-\tau H/\hbar} \right| \mathcal{R} \right\rangle \\ &= \int d\mathcal{R}_0 \int d\mathcal{R}_1 \dots \int d\mathcal{R}_{M-1} \left\langle \mathcal{R}_0 \left| e^{-\Delta\tau H/\hbar} \right| \mathcal{R}_{M-1} \right\rangle \dots \\ &\quad \times \left\langle \mathcal{R}_2 \left| e^{-\Delta\tau H/\hbar} \right| \mathcal{R}_1 \right\rangle \left\langle \mathcal{R}_1 \left| e^{-\Delta\tau H/\hbar} \right| \mathcal{R}_0 \right\rangle \end{aligned}$$

Path Integral Formulation

- Baker-Campbell-Hausdorff theorem states:

$$e^{\mathcal{A}} e^{\mathcal{B}} = e^{\mathcal{C}}$$

iff

$$\mathcal{C} = \mathcal{A} + \mathcal{B} + \frac{1}{2}[\mathcal{A}, \mathcal{B}] + \dots$$

- In our case, we set:

$$\mathcal{C} = -\Delta\tau H/\hbar, \quad \mathcal{B} = -\Delta\tau V/\hbar, \quad \mathcal{A} = -\Delta\tau K/\hbar,$$

where the kinetic energy operator K is:

$$K = -\hbar^2 \sum_i \frac{1}{2m_i} \frac{\partial^2}{\partial \mathbf{r}_i^2},$$

- 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:

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

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

$$\begin{aligned}\langle \mathcal{R}_1 | e^{-\Delta\tau K/\hbar} | \mathcal{R}_0 \rangle &= \int d\mathcal{P}_0 \int d\mathcal{P}_1 \langle \mathcal{R}_1 | \mathcal{P}_1 \rangle \langle \mathcal{P}_1 | e^{-\Delta\tau K/\hbar} | \mathcal{P}_0 \rangle \langle \mathcal{P}_0 | \mathcal{R}_0 \rangle \\ &= \left(\frac{m}{2\pi\hbar\Delta\tau} \right)^{Nd/2} \exp \left[-\frac{m\Delta\tau}{2\hbar} \sum_i \left(\frac{\mathbf{r}_{i1} - \mathbf{r}_{i0}}{\Delta\tau} \right)^2 \right],\end{aligned}$$

Product of N^d free particle diffusion Green's functions!

$$G(x, y; t) = \frac{1}{\sqrt{4\pi\gamma t}} e^{-(x-y)^2/(4\gamma t)}$$

Path Integral Formulation

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

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

Classical action!

Path Integral Formulation

- Recall Sakurai's treatment of the Path-Integral Formulation:

$$\begin{aligned}\langle x_M, t_M | x_1, t_1 \rangle &= \lim_{M \rightarrow \infty} \left(\frac{m}{2\pi\hbar\Delta t} \right)^{(M-1)/2} \int dx_{M-1} \dots \int dx_2 \Pi_{j=2}^M \exp \left[\frac{iS(j, j-1)}{\hbar} \right] \\ &= \int_{x_1}^{x_M} \mathcal{D}[x(t)] \exp \left[\frac{i}{\hbar} \int_{t_1}^{t_M} dt L_{\text{classical}}(x, \dot{x}) \right],\end{aligned}$$

- 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 \mathbf{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 $V(\mathbf{R})$
- 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:

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