Computational Nanoscience

NSE C242 & Phys C203

Spring, 2008

Lecture 21:

Diffusion Monte Carlo:

Going beyond guessing at the wave function

Guest lecturer:

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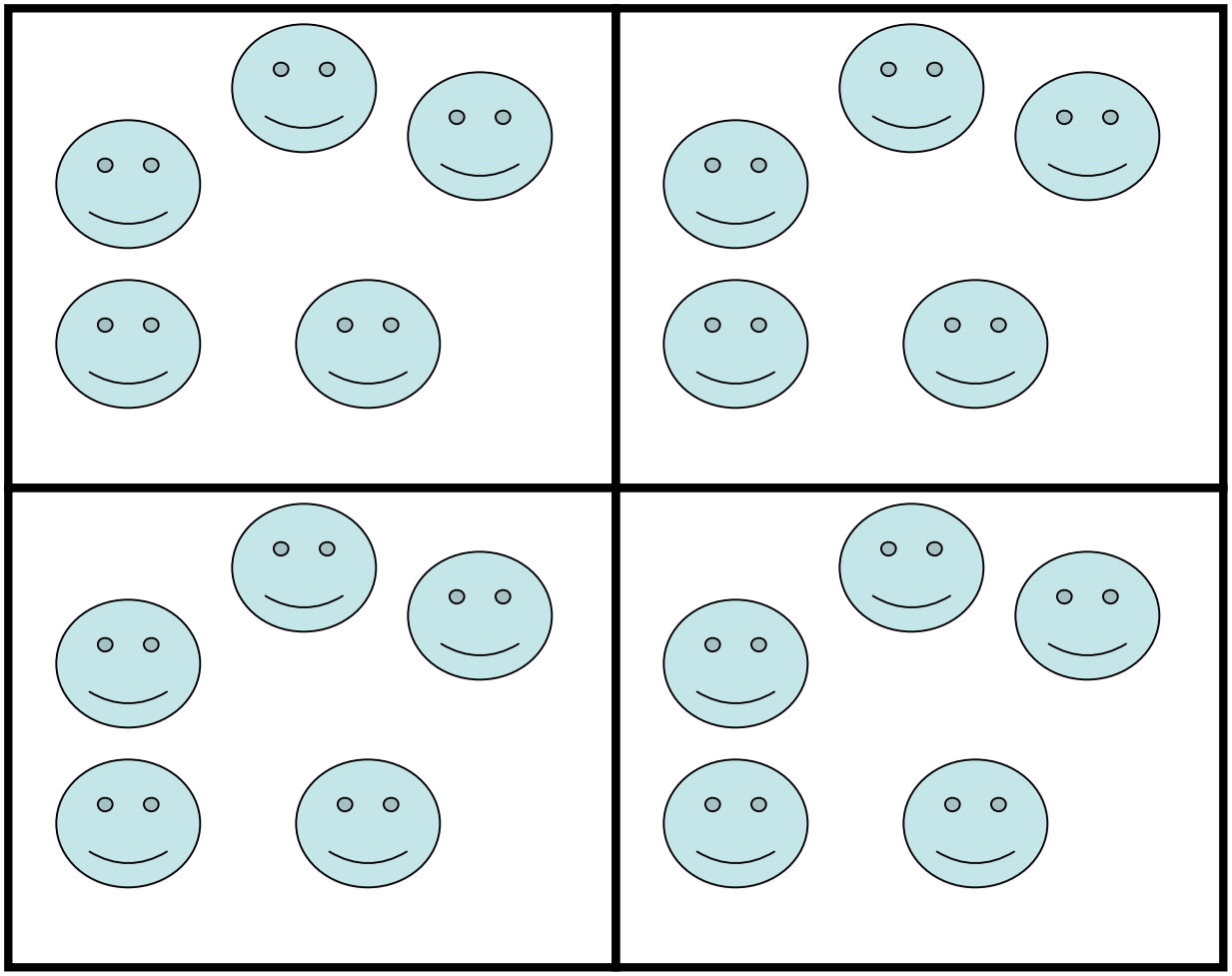
PBC's revisited



We make a repeating cell of interacting particles.

If the cell is too small, the particles can interact with themselves

This is just like classical molecular dynamics

Correlated wave functions in periodic boundary conditions

This is a finite size effect, which is physical!

Bloch's theorem and k-points, etc are very useful approximations, but not what physically happens in a real solid.

There is a soup of interacting particles.

Last time in this class

We went over a way of putting correlation into a wave function and optimizing it using Monte Carlo.

This correlation is responsible for about half the binding energy of molecules and solids.

But this method (variational Monte Carlo) is limited by the choice of variational wave function.

Going beyond a variational guess

Guys, stochastic processes!

Remember that we're limited by the form of our guess wave function.

For a few dimensions, we can just use a grid. But this scales poorly with the number of dimensions.

To sample with 100 points in each direction:
1D: 100 points
2D: 10,000 points
3D: 1,000,000 points
4D: 100,000,000 points

And so on. Since we're often dealing with 100's or 1000's of dimensions, this is obviously not a good strategy.

Monte Carlo sampling

So what do we do when the dimensionality is too big for grids? Monte Carlo

What we want to do is to find a way to guide our Monte Carlo walkers to where the wave function is large.

The density of walkers will determine the magnitude of the wave function.

Brief digression: simulating diffusion

The diffusion equation: $$\frac{\partial p(x)}{\partial t} = D\frac{\partial^2 p(x)}{\partial x^2}$$

This is an equation for the time evolution of a probability function.

What does it do?

When is the equation stationary?

If you start a bunch of diffusing particles "lumped up", they'll tend to spread out

Can simulate this directly with a bunch of walkers or just use the equation

DMC strategy

General strategy: stochastically simulate a differential equation that converges to the eigenstate

Equation: $$-\frac{d\Psi(R,t)}{dt} = (H - E)\Psi(R,t)$$

Must propagate an entire function forward in time <=> distribution of walkers

How our master equation leads us to eigenfunctions

We want to get a function that satisfies: $H\Psi = E\Psi$

I claim that this differential equation does it: $-\frac{d\Psi(R,t)}{dt} = (H - E)\Psi(R,t)$

After some manipulations:

$$-\frac{1}{\Psi}\frac{d\Psi(R,t)}{dt} = E_L(R) - E$$

$$E_L(R,t) = \frac{H\Psi(R,t)}{\Psi(R,t)}$$

So if E_L is a constant for a function, then the wave function will increase/decrease evenly everywhere

Remember that a total normalization doesn't matter for a wave function. We can set E so that it stays constant for convenience.

The master equation II

So how does our equation go towards the eigenfunction?

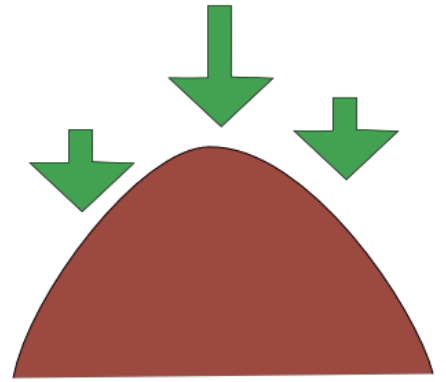
$$-\frac{1}{\Psi}\frac{d\Psi(R,t)}{dt} = E_L(R) - E$$

Note that $E_L(R,t) = \frac{H\Psi(R,t)}{\Psi(R,t)} = -\frac{1}{2}\frac{\nabla^2\Psi(R,t)}{\Psi(R,t)} + V(R)$

The time derivative is dependent only on the curvature.

If the curvature is too big, it will be decreased, too little, increased

How much curvature is determined by the potential energy.



t=0

t=infinity

Story so far..

This is a differential equation for a function that pushes that function towards an eigenfunction.

We didn't specify which eigenfunction it is.

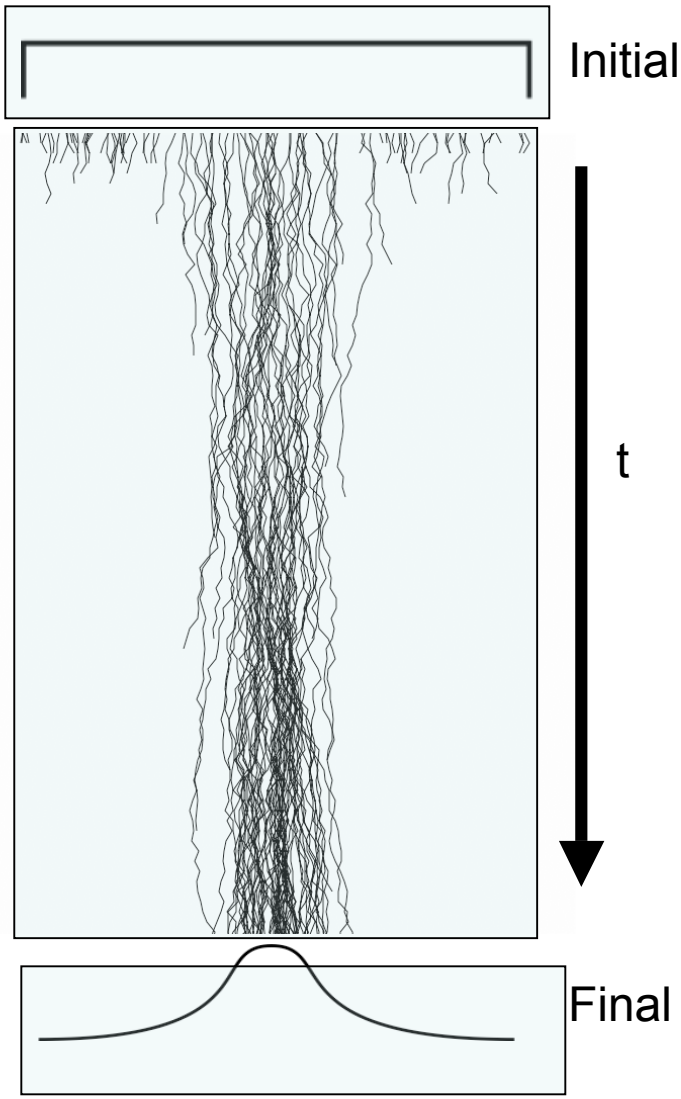
One can prove (by spectral expansion) that it's the ground (lowest energy) state.

Now we're going to map this equation onto a population of random walks, just like the diffusion equation <-> random walkers relationship.

Mapping the function onto a population of walkers

$$-\frac{d\Psi(R,t)}{dt} = \underbrace{-\frac{1}{2}\nabla^2\Psi(R,t)}_{\text{Diffusion}} + \underbrace{(V(R)-E)\Psi(R,t)}_{\text{Birth/death}}$$

- Generate walkers with a guess distribution
- Each time step:
  - Take a random step (diffuse)
  - A walker can either die, give birth, or just keep diffusing
- Keep following rules, and we find the ground state!
- Works in an arbitrary number of dimensions



What is the ground state?

So we have a method that automatically finds the exact ground state for a given Hamiltonian in polynomial time!

This is the holy grail of quantum mechanics, this is wonderful!

But wait. The Hamiltonian doesn't contain the Pauli exclusion principle.

$$\hat{H} = -\frac{1}{2}\nabla^2 - \sum \frac{Z_n}{r_{e-n}} + \sum \frac{1}{r_{e-e}}$$

It could apply to bosons, which can be in the same place.

Extra freedom => lower energy.

Story so far..

We found rules for moving walkers that simulated our differential equation

This is very much like the diffusion equation; there are just birth and death processes

But our rules will go to the absolute ground state of the Hamiltonian, which is not the one we want.

The fixed-node approximation

One way to do this is to take a trial function that satisfies the Pauli exclusion principle as a starting guess, and design our rules so that we don't break it.

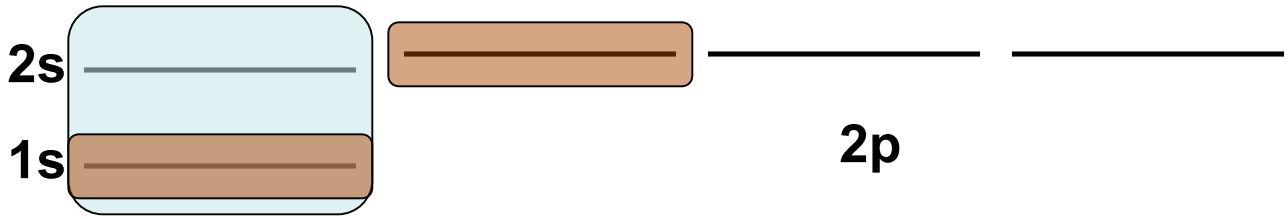
Turns out one can do this by just not allowing the walkers to cross a zero--we always have either "positive" or "negative" walkers

This also allows us to treat excited states (approximately)

Where does the fixed-node approximation fail?

Most of the time, the approximation is good. Some intelligent and young-looking person did some great work benchmarking FN-DMC (look in JCP)

Let's look at a classic case where it fails: Be atom.



Hartree-Fock ground state

Almost the same energy

HF trial nodes: ~85% of the correlation energy
Including the 2p orbitals: ~99% -- almost exact!

Things that I didn't cover

Can use a trial function to increase the efficiency tremendously by sampling only the changes from the guess.

There is always time discretization error. You always should extrapolate to zero time step, just like molecular dynamics.

Algorithm summary

1) Perform Hartree-Fock or DFT to get initial wave function
2) Add Jastrow factor, optimize wave function
3) Using optimized wave function as a guide, perform diffusion Monte Carlo for the most accurate results

In practical use, DMC is very automatic; you just choose the time step and it goes to the fixed-node solution--very few tweaking needed.

Good thing, because it's pretty expensive. Small time steps and error bars make for substantial cost.

Correlation energy

Methane (CH_4)

	Correlation energy (Hartrees)	Time taken
CCSD	0.193	18 seconds
DMC	0.240(1)	13 minutes

Ethane (C_2H_6)

CCSD	0.404	82 minutes
DMC	0.438(2)	37 minutes

Always more of the correlation energy. Huge difference in scaling and prefactor!

What do we get?

Very accurate total energies

Large prefactor in the computational cost, but good scaling

Many observables such as densities, electron correlation holes and more!

Good scaling on multiple processors (10,000 processors with 99% efficiency!)

Each state requires an additional calculation, so gaps are easy, but whole band structures are hard.

Fixed-node approximation is usually good, but sometimes fails for simple guesses.

Error bars make geometry optimization difficult.

Where is this method used?

The question is often not whether a calculation can be done; it's how much you want to do it.

Places where it's very useful:

1) **Matter under extreme conditions (high pressure)**
2) **Superfluidity (^{4}He)**
3) **Weak binding (Van der Waals, physabsorption)**
4) **Any cohesive/binding energy**

Rule of thumb: When electron correlation is important or you want to compare very different systems, DMC will be useful.

Trial functions in the tool

- **General form of wave function**

$$\Psi_T(R) = Det[\varphi_i(r_j)]\exp(U)$$

  - **Slater determinant (Hartree-Fock)**

$$U = 0$$

  - **Two-body Jastrow**

$$U = \sum_{iI}\sum_{k} c_k^{ei} a_k(r_{iI}) + \sum_{ij}\sum_{k} c_k^{ee} b_k(r_{ij})$$

  - **Three-body Jastrow**

$$U = two-body + \sum_{ijI}\sum_{klm} c_{klm}^{eei}[a_k(r_{iI})a_l(r_{jI}) + a_k(r_{jI})a_l(r_{iI})]b_k(r_{ij})$$

- **Live demo!**

Final questions?

There will be a QMC homework given out on Thursday. We'll cover some more of the specifics of the tool in the assignment.