Computational Nanoscience
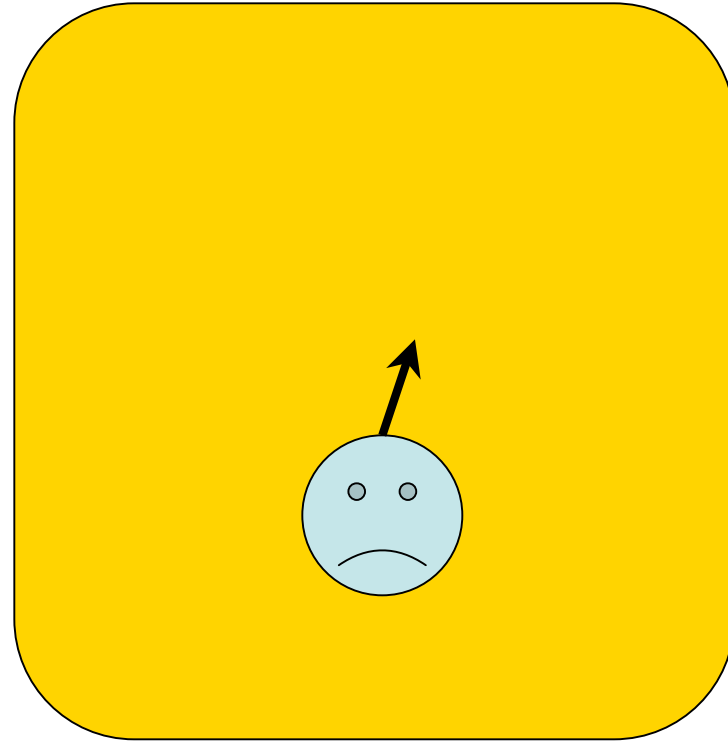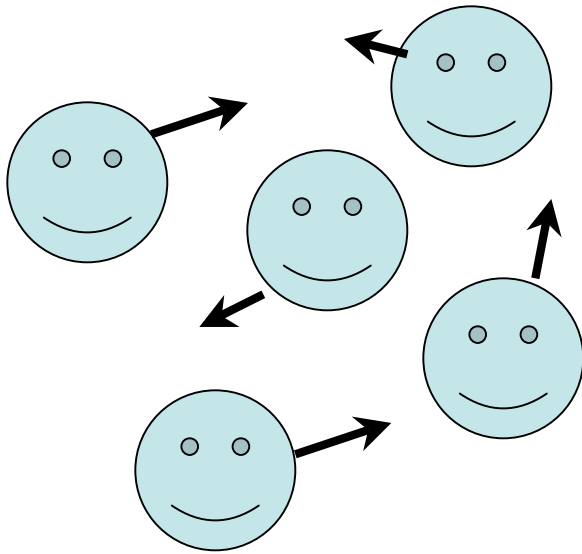**NSE C242 & Phys C203**
Spring, 2008

Lecture 20:

Going beyond the mean-field approximation: letting electrons interact

Guest lecturer:

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The mean-field approximation

We replace a bunch of interacting particles with a set of solitary particles in an effective field

Amazingly it works most of the time in quantum mechanics: reverse lottery

The mean-field approximation II

Reasons to go beyond mean-field
   Case in point: FeO, important in Earth's core

If we treat it with DFT (any mainstream functional):

1) **The lowest energy structure in DFT doesn't exist in reality**

2) **Even if we fix the structure to the experimental one, DFT predicts a metal when FeO is an insulator**

3) **Between the two phases that do exist, there is no predicted phase transition (one is always more stable)**

Variational method

Want to do something a bit more systematically improvable.

Suppose we want to find the ground state wave function for a given Hamiltonian. We can use the variational method:

Guess a trial wave function dependent on some parameters

$$\Psi(R,P) \qquad R = (r_1, r_2, ..., r_N)$$

Minimize the expectation value of the total energy

$$E(P) = \frac{\int \Psi^*(R,P)\hat{H}\Psi(R,P)dR}{\int |\Psi(R,P)|^2 \, dR}$$

Ground state has the lowest energy of all the states, so as our parameter set becomes complete, we approach it.

This is like Hartree-Fock and the post-HF methods, but today we're going to change the parameter set somewhat.

What parameterization is efficient?

Hartree-Fock: Single determinant of one-particle orbitals

Coupled cluster/Configuration interaction: Many determinants of one-particle orbitals

This converges very slowly. The Hamiltonian tells us why..

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

Solved by Hartree-Fock   **Contains an electron-electron distance!**

The determinant expansions don't contain an electron-electron distance, so they get at the interaction in a roundabout way.

What kind of representation would be more efficient?

We'd like a term that contains an electron-electron distance.
But then the we can't separate the 3N-dimensional integral.
We'll use Monte Carlo to evaluate that integral.

But just to show you what one can do..

10x faster

Methane (CH_4)

	Correlation energy (Hartrees)	Number of variational parameters
CCSD	0.193	~40,000
VMC	0.200	10

5x slower

Ethane (C_2H_6)

CCSD	0.404	~1,000,000
VMC	0.375(1)	10

Ok, how did we do that?

The VMC wave function that I used looks like this

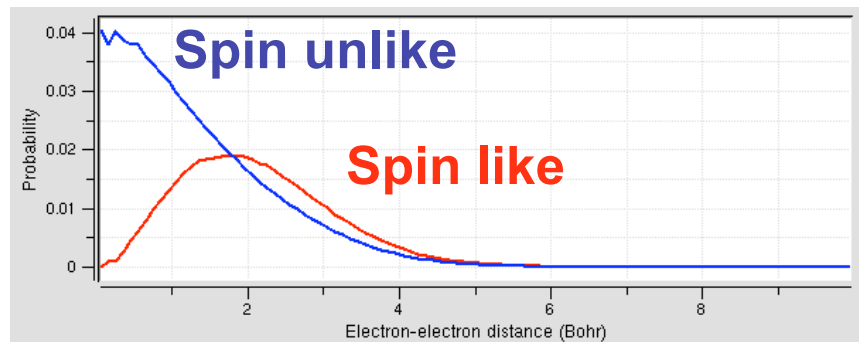$$\boxed{Det(\phi_i(r_j))}\boxed{\exp(\sum u(r_{e-n}, r_{e-e}))}$$

Hartree-Fock   **Correlation**

The u function (Jastrow factor) depends on the electron-electron distances explicitly, which is the next term in the Hamiltonian.
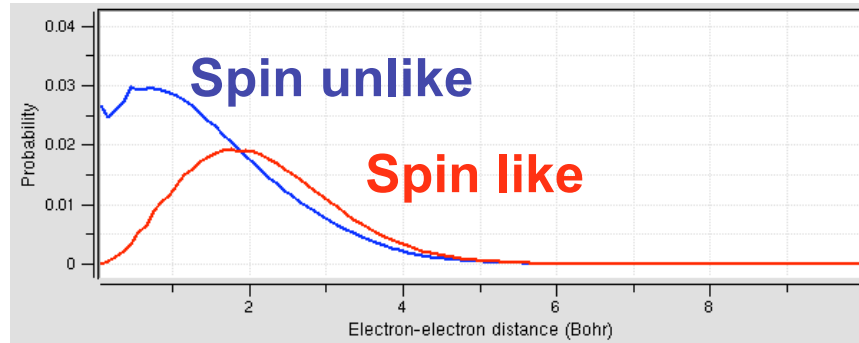
Let's look at what that does to the electrons..

The leading physical effect of correlation

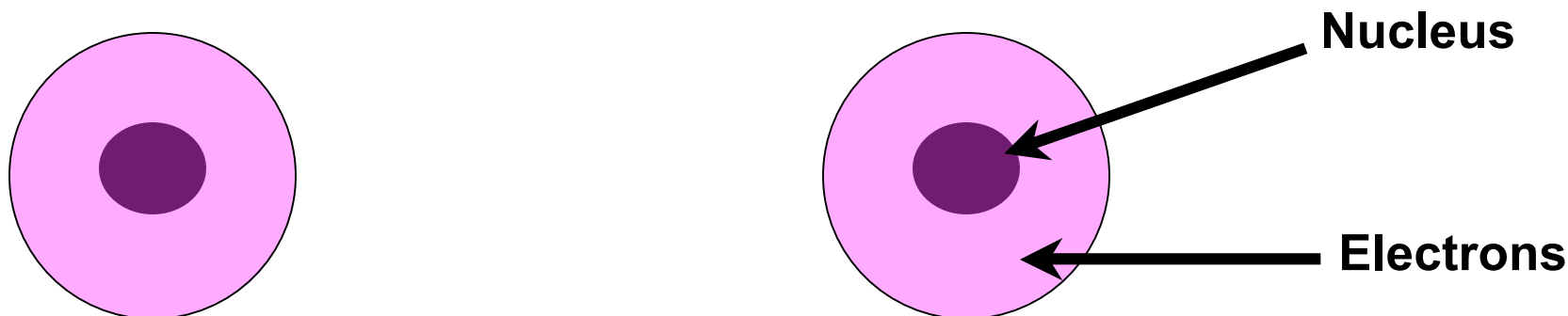**We look at the radial distribution function between electrons: CH_4**

Hartree-Fock:
Only Pauli exclusion
Like spins repulsed
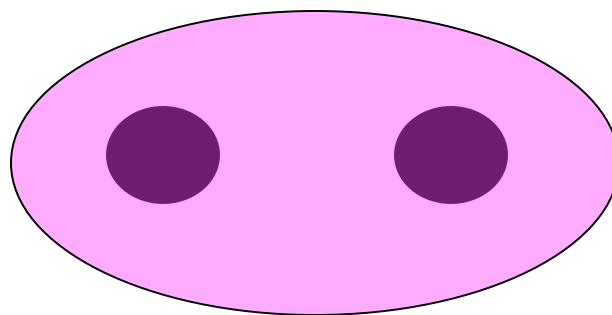**Unlike spins ignore each other**

VMC (Slater-Jastrow):
Like spins similar to HF
Unlike spins repulse each other

The effect of correlation on bonding

About half of the binding energy of molecules is from the electron repulsion.

Nucleus

Electrons

When the atoms are apart, their electrons must stay near the nucleus and near each other.

When atoms are covalently bound, the electrons have more room to avoid each other while still remaining near a nucleus.

The story so far

By introducing an electron-electron term in our variational wave function, we can get close to the ground state without using many parameters.

The major effect of this term is to push electrons of unlike spins away from each other--repulsion due to the Coulomb interaction.

This is a compact many-body wave function that scales well with system size.

We still haven't talked much about how to calculate anything efficiently--that's where the Monte Carlo comes in.

Monte Carlo: reminder

Remember the awesome lecture Elif gave on Monte Carlo? We wanted to evaluate

$$< A >= \int dr^N dp^N \frac{\exp[-E(r^N, p^N)/kT]}{\int dr^N dp^N \exp[-E(r^N, p^N)/kT]} A(r^N, p^N)$$

Sample this   **Average this**

We do this huge integral by sampling the probability distribution function and averaging A.

Quantum Monte Carlo

We want to evaluate this integral

$$E(P) = \frac{\int \Psi^*(R,P)\hat{H}\Psi(R,P)dR}{\int |\Psi(R,P)|^2\, dR}$$

This is a probability distribution function

$$\frac{|\Psi(R,P)|^2}{\int |\Psi(R,P)|^2\, dR}$$

We can sample it using the Metropolis algorithm! Just need to rearrange the integral:

$$E(P) = \int \underbrace{\frac{|\Psi(R,P)|^2}{\int |\Psi(R,P)|^2}}_{\textbf{Sample this}}\underbrace{\frac{\hat{H}\Psi(R,P)}{\Psi(R,P)}}_{\textbf{Average this}}dR$$

The story so far

Interpreted the square of the wave function as a probability distribution function

One can sample this pdf, just like classical Monte Carlo

This lets us put in explicit electron-electron terms in the wave function…which lets us quickly get close to the ground state.

Next up, optimizing the parameters. Monte Carlo is noisy, derivatives are difficult to take. There are many ways; I'll show you one.

The local energy

Our averaging quantity is called the local energy.

$$\frac{H\Psi(R)}{\Psi(R)}$$

If the wave function is an eigenfunction of the Hamiltonian,
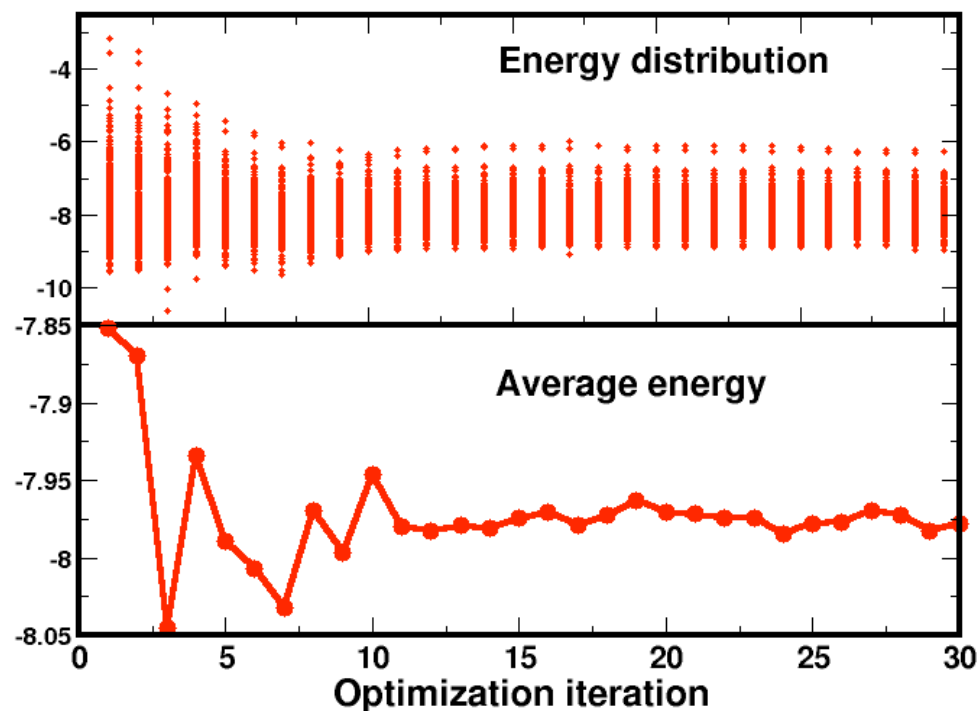
$$\hat{H}\Psi(R) = E\Psi(R)$$

So the local energy for the exact wave function is

$$\frac{\hat{H}\Psi(R)}{\Psi(R)} = \frac{E\Psi(R)}{\Psi(R)} = E$$

A constant independent of R!
We can optimize wave functions using this property.

Optimizing the variance

CH$_4$: 500 MC samples

Samples are kept fixed and the variance is optimized

Average energy decreases as the variance decreases

Fixed set of samples: cancellation of much statistical error

Why can't we just optimize the energy in this way? On a fixed sample size, the average energy is unbounded from below, so the optimizer finds weird parameter sets to find a minimum, which don't translate to accurate wave functions.

Final variational quantum Monte Carlo algorithm

1) Choose a parameter set

2) Generate Monte Carlo configurations

3) Optimize the variance on a fixed set of MC configurations

4) With the new parameters, use MC to evaluate properties of the wave function like energy, radial distribution functions, etc.

+Can use explicitly correlated wave functions (more than just the Slater-Jastrow that I showed)
+Good scaling ~N^3

-Biased by the choice of wave function
-Stochastic optimization
-Error bars!

How VMC fits in the big picture

People rarely do VMC by itself, because with a little more effort, we can do much better.

Next time, I'll tell you about a much more powerful method called diffusion Monte Carlo that is able to treat all electron correlations.

I'll give you some hints on this, just to think about before the next class.

Diffusion Monte Carlo preview

I mentioned that the variational guess biases the results--you only get what you put in the wave function.

DMC does better by getting rid of the variational function--the wave function is given by the distribution of Monte Carlo samples.

We find some simple rules for moving Monte Carlo samples that will sample the ground state--without finding the functional representation.

For bosons, we can solve the quantum problem exactly within stochastic errors, and for fermions, there is one major approximation.
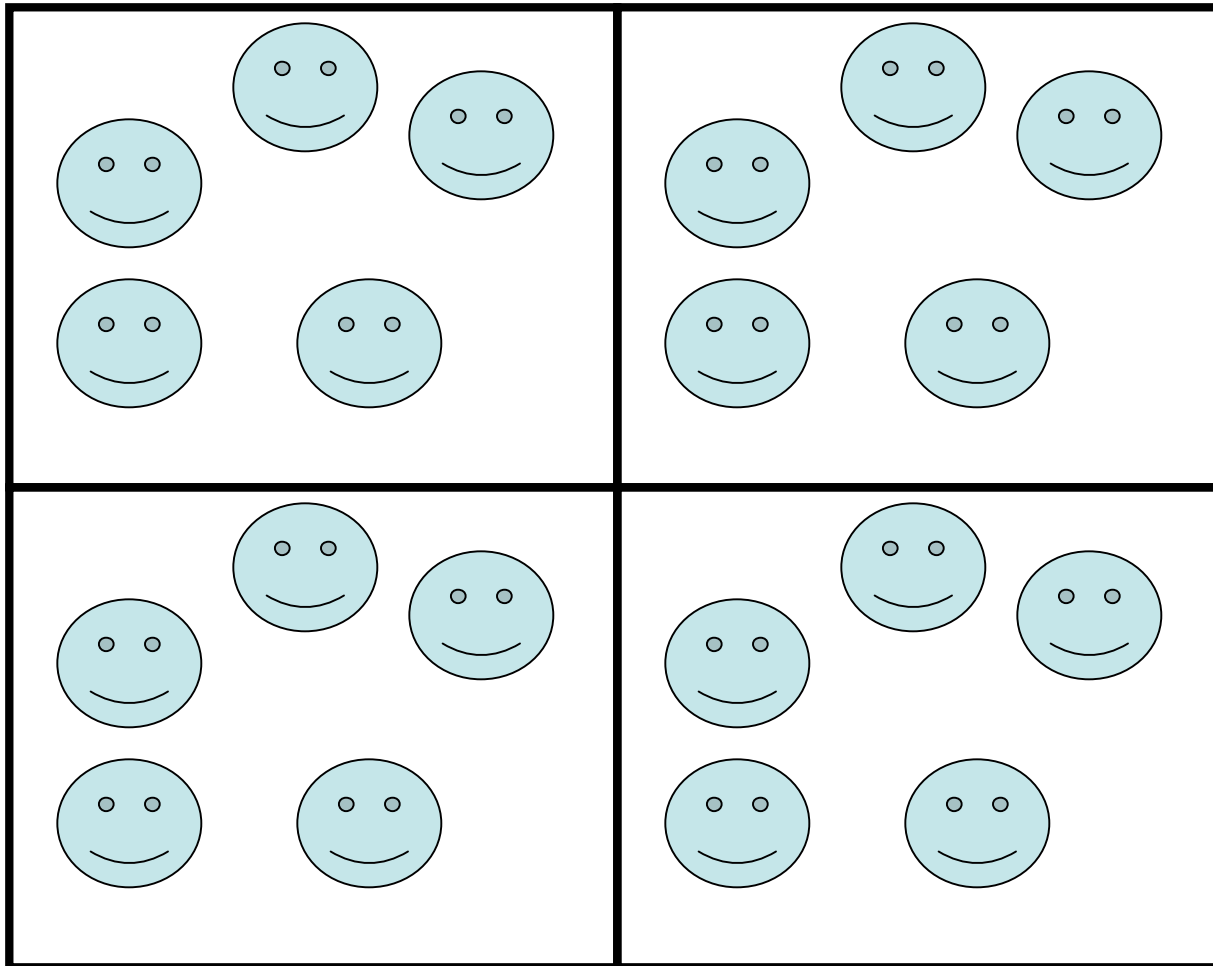
Correlated wave functions in periodic boundary conditions

Remember that Bloch's theorem let us separate an infinite solid into a real space part and a reciprocal space part

But the derivation was only for a single electron moving in a periodic field--the mean field in DFT.

With correlated wave functions, we don't have a mean field any more..what happens, then?

We make a repeating cell of interacting particles.

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

Notice also that the distribution is repeated

The PBC's are just to get rid of surfaces, like in classical MD calculations

Question and answer period

Let's wait in uncomfortable silence until someone asks a question.