

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

**Lecture 14:**  
**Hartree-Fock Calculations**  
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# *Ab Initio* Calculations

We are now in a position to perform *ab initio* calculations.

*Ab initio* simply means “from the beginning” - which implies that the calculation requires as input only physical constants, masses, and charge state.

There are methods that incorporate approximations (beyond choice of basis) to solve the quantum mechanical Schrödinger equation.

These are called “semi-empirical” approaches, and we will discuss them a little later (two examples include the Tight Binding approximation and MNDO, among many others.)

# A Little Bit of Schrödinger

Now that we've done everything we can to **avoid** using quantum mechanics, let's take a look at what we've been avoiding.

What is the central difference between a quantum mechanical simulation and one using classical potentials?

The starting point for any discussion on quantum mechanics is, of course, the Schrödinger equation:

$$\hat{H}\Psi = i\hbar \frac{d\Psi}{dt}$$

Hamiltonian Operator

$$\hat{H} = \hat{T} + \hat{V} = KE + PE$$

$\Psi(\mathbf{r}, t)$   
wavefunction

Written out explicitly, the Schrödinger equation looks like this:

$$\left\{ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \right\} \Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t}$$

# Some Things

$$\Psi_{nlm} = R_n(r)Y_{lm}(\theta, \varphi)$$

A couple of things to note:

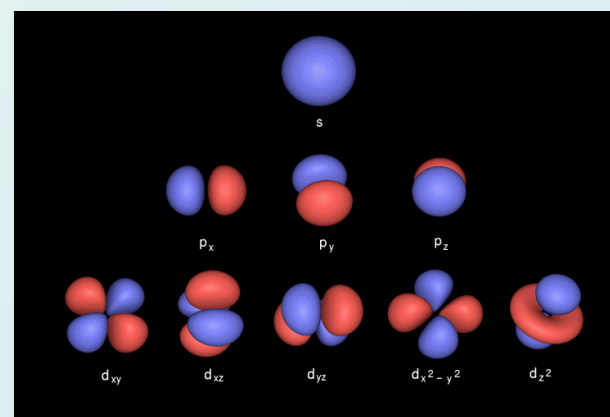
The solution for  $R(r)$  and  $Y(\theta, \varphi)$  can be derived analytically for a 1-electron - 1-nucleus system like the hydrogen atom.

The Energy is a function of the principle quantum number ( $n$ ) only.

This means that orbitals with the same value of  $n$  but different values of  $l$  and  $m$  are “degenerate.”

Here are some pictures of atomic orbitals:

Note that each orbital is orthogonal to each other.



[www.chemcomp.com/journal/molorbs.htm](http://www.chemcomp.com/journal/molorbs.htm)

# Multi-electron Atoms and Molecules

Are not solvable exactly\*, as we have discussed. What happens as we go from the hydrogen case to a multiple particle, interacting system?

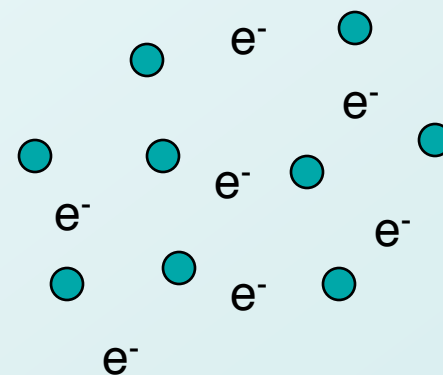
Given a collection of nuclei and electrons in some arrangement, what does the Hamiltonian look like?

Let  $R_1, \dots, R_N$  = positions of the  $N$  nuclei

$eZ_1, \dots, eZ_N$  = charge of the  $N$  nuclei

$M_1, \dots, M_N$  = masses of the nuclei

$r_1, \dots, r_n$  = positions of the  $n$  electrons



Now, our wavefunction is more complicated

$$\Psi(r) \Rightarrow \Psi(R_1, \dots, R_N, r_1, \dots, r_n)$$

\* at least, not in any finite amount of time or resource.

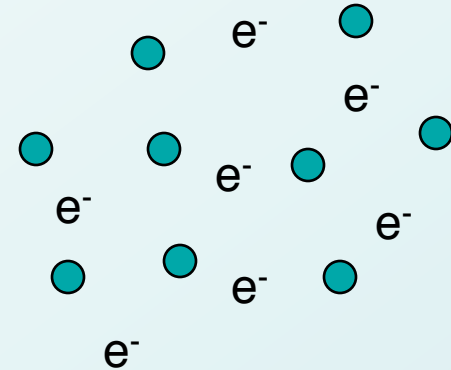
# Multi-electron Atoms and Molecules

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$M_1, \dots, M_N$  = masses of the nuclei

$r_1, \dots, r_n$  = positions of the  $n$  electrons



The Hamiltonian looks like:

$$\hat{H} = \sum_{j=1}^N \left( -\frac{\hbar^2}{2M_j} \right) \nabla_{R_j}^2 + \frac{1}{2} \sum_{j=1}^N \sum_{i=1}^N \frac{Z_i Z_j e^2}{|R_i - R_j|} + \sum_{j=1}^n \left( -\frac{\hbar^2}{2m} \right) \nabla_{r_j}^2 + \frac{1}{2} \sum_{j=1}^n \sum_{i=1}^n \frac{e^2}{|r_i - r_j|} - \sum_{j=1}^N \sum_{i=1}^n \frac{Z_j e^2}{|r_i - R_j|}$$

And our eigenvalue problem looks like:

$$\hat{H}\Psi(R_1, \dots, R_N, r_1, \dots, r_n) = \varepsilon \Psi(R_1, \dots, R_N, r_1, \dots, r_n)$$

In general, we really cannot solve this. We need to make some approximations first.

# Hartree

Remember that Hartree-Fock begins with the Hartree product for a guess at a complex wavefunction, based on a product of single-particle “orbitals”:

$$\Psi(1,2,\dots,N) = \varphi_1(1)\varphi_2(2),\dots,\varphi_N(N)$$

If the Hamiltonian is the usual kinetic and potential terms,

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + \sum_i V_{ion}(\mathbf{r}_i) + \frac{e^2}{2} \sum_{ij(j \neq i)} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Then by applying the variational argument, one can obtain the single-particle Hartree equations:

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + V_{ion}(\mathbf{r}_i) + e^2 \sum_{j \neq i} \left\langle \varphi_j \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \varphi_j \right\rangle \right] \varphi_i(\mathbf{r}_i) = \varepsilon_i \varphi_i(\mathbf{r}_i)$$

# Hartree

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + V_{ion}(\mathbf{r}_i) + e^2 \sum_{j \neq i} \left\langle \varphi_j \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \varphi_j \right\rangle \right] \varphi_i(\mathbf{r}_i) = \varepsilon_i \varphi_i(\mathbf{r}_i)$$

The single-particle picture (or “mean-field” picture) comes from the fact that the Hartree product is a product of single-particle states.

Each orbital can be determined by solving these single-particle Schrödinger equations, **if all the other orbitals are known**.

However, this is not the case, and instead what we do is simply to guess at some set of initial orbitals.

Then, the Hamiltonian can be “constructed” from these orbitals, and the single-particle equations can be solved for a “new” set of orbitals.

This process is repeated until the new and old orbitals don’t change (by much).

This process is known as Self Consistency, or the Self Consistent Field approach.



# Hartree-Fock

The Hartree-Fock method is one of the foundations (if not *the* foundation) of molecular orbital theory.

We've already discussed that it is based upon a **choice of wavefunction**, namely a Slater determinant, which is the simplest way to write an appropriate antisymmetrized wavefunction.

The Hartree-Fock equations, then, are a result of **minimizing the energy** with respect to that particular choice of the wavefunction, for a given Hamiltonian.

Note that the Hartree-Fock method begins with an exact Hamiltonian, one which includes many-body interactions.

However, upon introducing the Slater determinant as an approximation to the wavefunction, the picture becomes single-particle in nature.

# Hartree-Fock

By going from a Hartree product to a Slater determinant, the sign of the wavefunction is changed when the coordinates of two electrons are interchanged, as is necessary.

$$\Psi(1,2,\dots,N) = \varphi_1(1)\varphi_2(2)\dots\varphi_N(N) \longrightarrow \Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \dots & \varphi_N(1) \\ \varphi_1(2) & \varphi_2(2) & \dots & \varphi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(N) & \varphi_2(N) & \dots & \varphi_N(N) \end{vmatrix}$$

One can derive another set of single-particle equations to solve for the Hartree-Fock wavefunction and energies.

Comparing with the Hartree equations, we find one additional term:

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + V_{ion}(\mathbf{r}_i) + e^2 \sum_{j \neq i} \left\langle \varphi_j \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \varphi_j \right\rangle \right] \varphi_i(\mathbf{r}_i) - e^2 \sum_{j \neq i} \left\langle \varphi_j \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \varphi_i \right\rangle \varphi_j(\mathbf{r}_i) = \varepsilon_i \varphi_i(\mathbf{r}_i)$$

# Hartree-Fock

$$e^2 \sum_{j \neq i} \langle \varphi_j | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \varphi_j \rangle - e^2 \sum_{j \neq i} \langle \varphi_j | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \varphi_i \rangle = V_i^H(\mathbf{r}_i) + V_i^X(\mathbf{r}_i)$$

Let's examine this exchange term a bit more closely.

One can rewrite the two electronic potential terms, referred to as the Hartree term and the exchange term, as sums over densities.

$$\rho_i(\mathbf{r}) = |\varphi_i(\mathbf{r})|^2 \quad \rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r})$$

$$V_i^H = e^2 \sum_{j \neq i} \int \frac{\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = e^2 \int \frac{\rho(\mathbf{r}') - \rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$V_i^X = -e^2 \int \frac{\rho_i^X(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad \rho_i^X(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i} \frac{\varphi_i(\mathbf{r}') \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}')}{\varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r}')}$$

# Basis Sets

Basis sets are usually composed of atomic functions. Why?

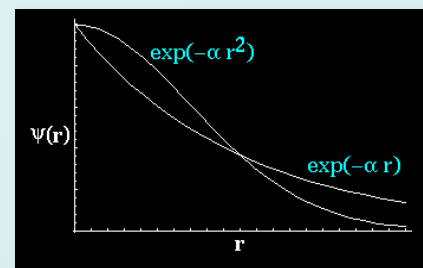
“Slater type” orbitals are exponential in form and are solutions to the radial part of the simple Hydrogen atomic orbital picture.

However, Slater orbitals are never used because it takes too long to evaluate exponentials, and the multi-center integrals are very difficult to solve.

Instead, what is almost exclusively done is to use Gaussian functions, of the form  $\exp(-ar^2)$ . If  $a$  is large, the function does not spread out very far, while if  $a$  is small it gives a large spread.

Since the product of two Gaussians can be represented by a third Gaussian, the two-electron integrals become much simpler to evaluate.

One disadvantage, though, is that a Gaussian doesn't look quite like what we want.



# A Bit About the Outputs

So what do we expect to get out of an *ab initio* simulation?

First and foremost, we can compute, for a given combination of basis set and method, the total energy of the system.

If the basis set could be saturated, the energy for a given method is said to be that of the “complete basis set limit.”

Since one can never reach this limit, a careful basis set study must be carried out for at least some parts of the system.

The complete basis set limit can be approximated by taking successive basis sets (each larger than the previous), computing the energy, and fitting the curve to an exponential function.

In the case of the Hartree-Fock approach the total energy is the exact solution to the Hamiltonian given an approximation to the wavefunction of using the simplest way to make it antisymmetric (Slater determinant).

# The Total Energy

What can we gain by knowing the total energy of a system?

For starters, we can compare one structure with another that has the same stoichiometry and number of atoms.

The total energy tells us which structure is more energetically favorable, sort of.

For example: silicon clusters. Even for very small numbers of atoms, the actual ground state structure is not yet known experimentally.

Here's a randomly selected article from only a few years ago on  $\text{Si}_6$

PHYSICAL REVIEW A, VOLUME 64, 023202

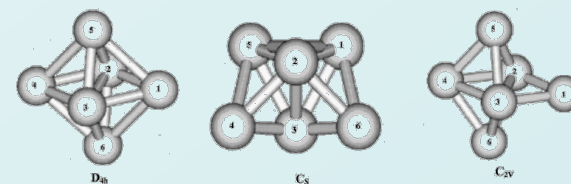
## The real structure of the $\text{Si}_6$ cluster

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(Received 10 September 1999; revised manuscript received 4 January 2001; published 12 July 2001)

Contrary to well-established recent theoretical results based on second-order Moller-Plesset perturbation theory, it is illustrated here that the distorted octahedron of  $D_{4h}$  symmetry cannot be the ground state of the “magic”  $\text{Si}_6$  cluster, but a transition state, connecting two almost isoenergetic structures of lower symmetry, which can coexist. This conclusion, the consequences of which could be far reaching for other magic clusters, is based on higher-order perturbation theory, accurate coupled-cluster CCSD(T) calculations and density-functional theory at the hybrid B3LYP level. The discrepancy is due to the poor convergence of the perturbation expansion, related to the flatness of the energy hypersurface near the minimum. As a result, the structural and electronic properties of  $\text{Si}_6$  are still not well understood, although several suggestions are put forward here.



Which one of these is the most stable?

# *Eigenvalues*

As we discussed in the previous lecture, a solution to the Schrödinger equations provides a wavefunction, which in practice is written as a product of molecular orbitals.

Each molecular orbital represents the spatial probability distribution of an electron, or actually of two electrons - 1 spin up and 1 spin down.

Remember that solutions exist for the Schrödinger equation only for certain values of energy.

Thus, each orbital (or eigenfunction) has an associated eigenvalue that corresponds to the electronic energy of that level.

# ***Ionization Energies and Koopmans Theorem***

The energy of a given electron orbital is often equated with the energy required to remove an electron to form an ion.

This is also known as Koopmans Theorem.

A couple of important points, however, must be taken into account.

First, the orbital in the ionized state is assumed to be the same as in the un-ionized state - in other words, it's "frozen."

This means that the energy in the ionized state will tend to be higher than it should be, giving too large an ionization potential.

The second point is that if electron correlation effects are not taken into account, there will be a bias in favor of the un-ionized state - why?

Note that in practice, these two errors actually cancel fairly well, and Koopmans theorem isn't all that bad an approximation.



# *Electron Affinity and Koopmans Theorem*

A calculation with  $K$  basis functions provides  $K$  molecular orbitals.

Many of these may not be occupied by electrons. If not, they are called “virtual” or “unoccupied” orbitals.

In Hartree-Fock, the energy of any virtual orbital is positive.

Thus, using Koopmans theorem for the electron affinity, we would always find adding an electron to be unstable (in Hartree-Fock).

This can be understood from the fact that electron correlation would be expected to add to the error due to the “frozen” orbital approximation, rather than to counteract it as for ionization potentials.

# Delta-SCF

One could attempt to take into account the relaxation of the orbitals when an electron is either removed or added.

The “delta-SCF” approach is a method to compute the ionization potential and electronic affinity by taking a difference of total energies.

This requires 2 calculations instead of 1.

For example, the ionization energy would be  $E(N-1)-E(N)$  and the electron affinity is  $E(N)-E(N+1)$ , where  $N$  is the number of electrons in the system.

One can go a bit further to compute difference between the ionization energy and the electron affinity, as  $E_{QP} = E(N+1)+E(N-1)-2E(N)$ .

This known as the quasiparticle gap...but we're getting a little bit ahead of ourselves.

# *Binding Energies*

Binding energies are computed by taking the difference between the energy of a system and the sum of energies of parts of the system (i.e., the atoms).

As with any other property, this will depend on the basis set and the method.

The Hartree-Fock method tends to underbind nearly all systems.

This is because there is no electron correlation, resulting in a substantially weaker bond than is actually the case.

Let's do a few examples now...

## *A few examples to get us into the right mood*

- 1) Hydrogen atom: total energy? Basis set effects?
- 2) Oxygen atom: eigenvalues? spin state?
- 3) Hydrogen molecule: binding energy?
- 4) Water molecule: binding energy? HOMO-LUMO gap? Ionization potential?
- 5) Methane: more similar questions...you get the idea.
- 6) Which are linear and which are straight/planar: CO<sub>2</sub>, NH<sub>3</sub>, BH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>