Computational Nanoscience
NSE C242 & Phys C203
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Lecture 16:

More and Less than Hartree-Fock:

Our Last Bit of Quantum Chemistry,

and Pseudopotentials Too

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UHF vs. RHF

A system is open shell if it contains one or more unpaired electrons.

There are effectively two ways to handle open shell systems:

1) Spin restricted (or RHF, for Restricted Hartree-Fock)

   This approach uses combinations of singly and doubly occupied molecular orbitals. Doubly occupied orbitals use the same spatial functions for electrons of both spins (say, α and β).
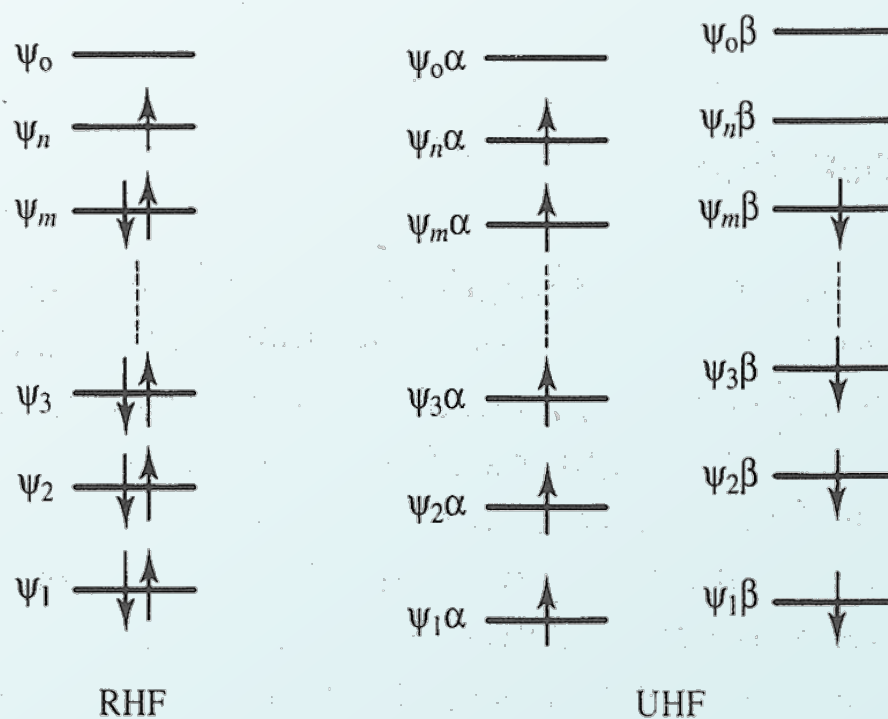
2) Spin unrestricted (or UHF, for Unrestricted Hartree-Fock)

   Here, two distinct sets of orbitals are used: one for electrons of α spin and one for electrons of β spin. As a result, effectively two densities are used, one for each spin.

UHF vs. RHF

The UHF approach is more general than RHF.

Here's a conceptual picture I copied from a book* without permission:

UHF vs. RHF

Unrestricted wavefunctions are the appropriate way to deal with dissociation.

Consider a simple example - the H_2 molecule. It has a ground state wavefunction that is a spin singlet and a bond length of ~ 0.75 Å.

The restricted wavefunction is appropriate for this ground state. In fact the UHF and RHF wavefunctions are identical for the ground state (2 electrons paired in a single orbital).

However, if we increase the bond length towards the dissociation limit, this description is inappropriate, since we know that H_2 dissociates into 2 H atoms.

This dissociation behavior cannot be achieved with a restricted wavefunction, which requires two electrons to occupy the same spatial orbital, leading to H^+ and H^-.

UHF vs. RHF

Here's a plot of the H_2 molecule dissociation curve for RHF and UHF.
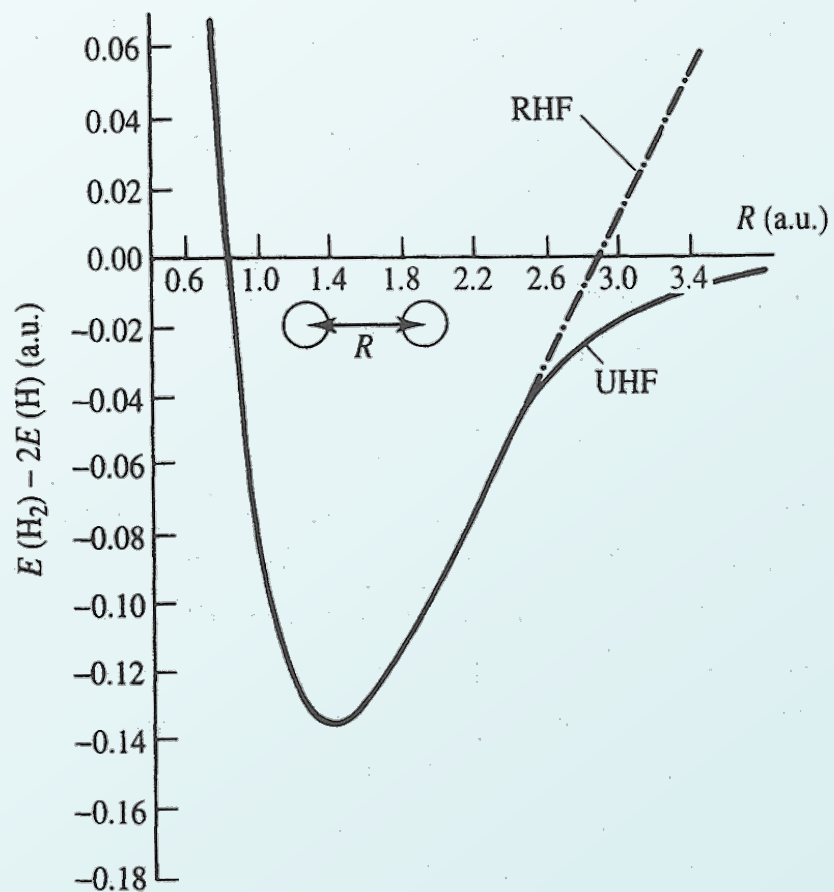
Post Hartree-Fock

The most significant drawback of Hartree-Fock theory is that it does not include correlation between electrons.

In fact, as we have discussed, the correlation energy is defined as the difference in energy between the Hartree-Fock energy and the exact energy.

Neglecting correlation energy can lead to anomalous results, especially, e.g., in the dissociation limit.

For example, in an H2 molecule, the uncorrelated calculation predicts that electrons spend equal time on both nuclei, even when they are infinitely separated.

Hartree-Fock geometries and relative energies for equilibrium structures do tend to be not too bad.

Still, electron correlation is too important in too many processes to leave out of the picture.

Post Hartree-Fock

Usually electron correlation is discussed in the context of *ab initio* calculations, rather than, say, classical or semi-empirical ones. Why is this?

In quantum chemistry, there are many approaches to "recovering" the missing correlation energy.

Typically, they fall into two classes:
- Wavefunction expansion
- Perturbation theory

The most common wavefunction expansion approaches are Configuration Interaction "CI" and Coupled Cluster "CC" or "CCSD".

The most common perturbation approach is Moller-Plesset "MP2" or "MP4".

Configuration Interaction

CI has many variants but is always based on the idea of expanding the wavefunction as a sum of Slater determinants.

In principle, it is an exact theory - i.e., if one could expand the wavefunction completely, we'd have an exact wavefunction and therefore the exact solution to the Schrödinger equation.

This is, of course, not possible in practice. Instead, the summation is truncated.

Straight CI involves optimizing coefficients in front of Slater Determinants constructed from the Hartree-Fock orbitals.

One common variant is MCSCF (or CASSCF), which optimizes both the coefficients of the determinants as well as the orbitals themselves.

Big problem with CI: it scales badly (N^{5-6}) and it is not size consistent.

One of the most popular approaches in this category is Coupled Cluster, which is size consistent (but still scales very poorly).

MP Theories

Perturbation theories such as MP2 or MP4 tackle the electron correlation problem in a different way.

Namely, they expand the true Hamiltonian as a sum of a "zeroth-order" Hamiltonian (for which we can solve the wavefunction) plus a perturbation.

The MP theories are nice because they are size independent, unlike CI.

However, MP methods are very slow and scale not too well (N^4 scaling).

And much worse, it is no longer a variational method - i.e., it can give energies that are lower than the true energy.

Still, MP2 especially but also MP4 are very widely used.

Other methods exist, such as the "Gaussian-N" approaches (G1, G2, and G3 theory). I will not go into these, mainly because they are kind of silly.

Semi-Empirical Methods

Now, let's suppose that instead improving upon the accuracy of Hartree-Fock, we wish to make it worse.

Well, then we've arrived at so-called semi-emprical methods.

These are, in some cases, not too bad, although one should exercise caution in their application.

The motivation is fairly simple: pure *ab initio* methods are slow, for the most part.

In some cases, semi-empirical methods are better than the best *ab initio* methods since they incorporate parameters derived from experiment.

There are many, many, many semi-empirical methods.

Most of them were developed (at least originally) by two groups: Pople and Dewar.

Semi-Empirical Methods

Most computational effort in *ab initio* calculations is spent in calculating integrals.

What many semi-empirical methods do is to either approximate or neglect completely many of these integrals.

We will not go into any technical details here.

One line of approaches has the "NDO" (Neglect of Differential Overlap) series, starting with CNDO, then INDO, then NDDO, then MINDO, then MNDO.

All of these differ mainly in how they choose to throw away integrals, and somewhat in how experimental data is parametrized.

Another, more recent line of semi-empirical methods is the "something-M-something" approaches, where the "M" stands for "Model".

There was the AM1, then the PM3, then the SAM1, and so on.

Empirical Tight Binding

The Tight Binding (TB) model was initially developed for solids (band structures) but currently is widely used for both solids and molecules.

TB is based on a description of electronic states starting from the limit of isolated atomic orbitals.

It is a simple model that gives good quantitative results for bands derived from strongly localized atomic orbitals, which decay to essentially zero on a radius much smaller than the next neighbor half-distance in the solid.

For the conduction bands (or "extended states"), the results of tight-binding are usually in rather poor agreement with experiment.

Tight binding can be systematically improved by including additional levels/bands, so that the accuracy of the calculated bands increases, at the expense of the simplicity and transparency of the model.

Tight Binding

The approximation of the TB method is to assume that phase space is spanned by atomic-like orbitals and that this is sufficient to describe the wave function solution of the Schrodinger equation (at least in restricted energy range).

TB is also referred to as LCAO - linear combination of atomic orbitals.

Such an atomic-like basis provides a natural, physically motivated description of electronic states in matter.

In practice there are many versions of TB, depending on the degree of "ab-initio". Some methods use true atomic-like orbitals and others are semi-empirical using fitted parameters.
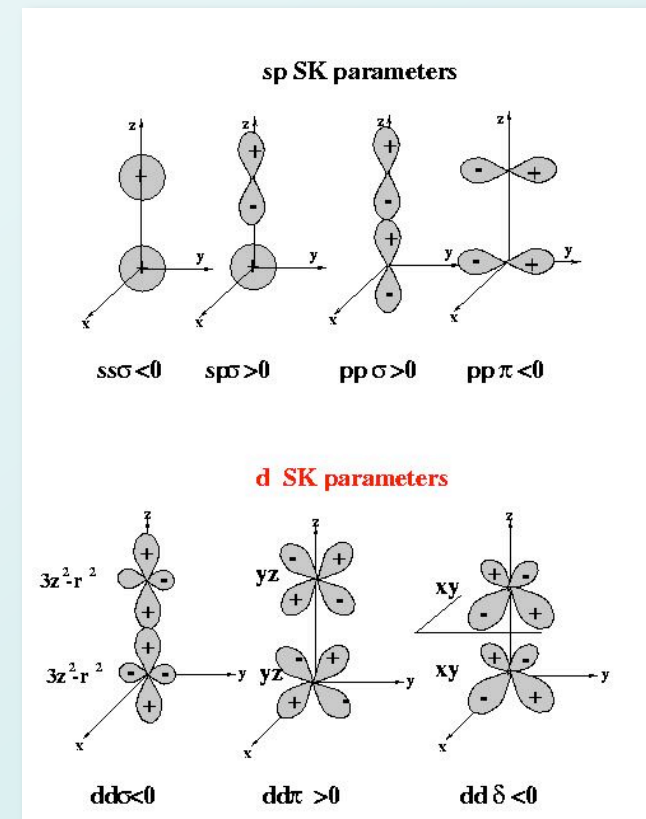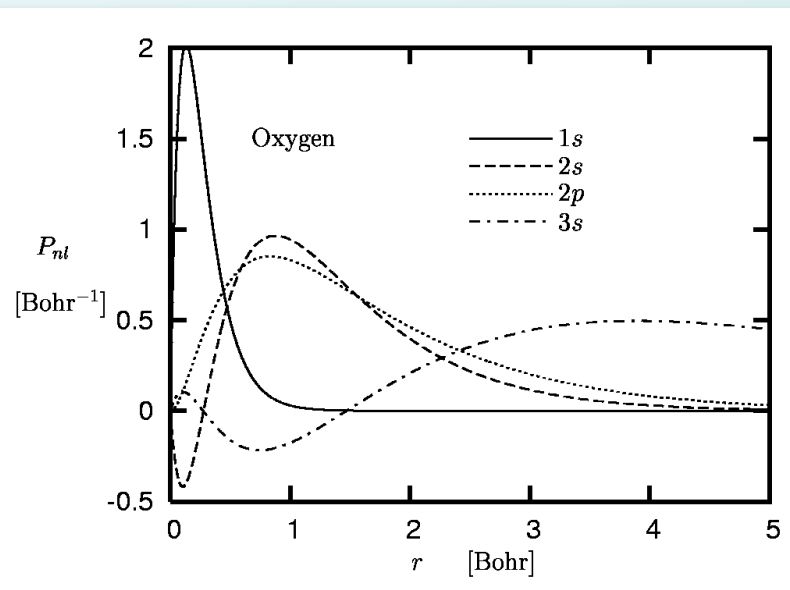
Pseudopotentials

In chemistry the use of pseudopotentials has become a standard procedure to reduce the computational effort in quantum chemical calculations.

The idea is to divide the electrons in an atom into a part that is rather irrelevant and a part that is constitutive for a specific property.

In many cases the core electrons are of minor importance for properties calculated in chemistry (e.g. bond lengths).

Here's a good illustration of why the core electrons play such little role in valence chemistry.

Pseudopotentials

The core is then represented by an effective potential; The other electrons are given a modified basis set of so-called *pseudo-orbitals*.
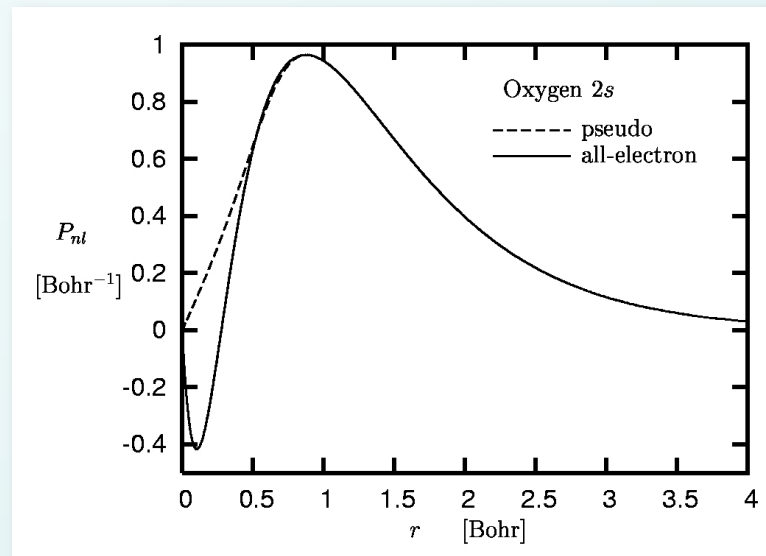
There are only few situations in which the core states are directly affected by neighboring atoms, so that the PP concept breaks down.

This is typically the case if charge centers are present and the core states are not sufficiently attracted by their own nucleus. The deformation of the *1s*-orbital of lithium in LiF is an example.

Pseudopotentials

The pseudopotentials and pseudo-orbitals are derived such that a calculation of a specific property using pseudopotentials and pseudo-orbitals yields the same value as in a calculation with a basis set for all electrons.

Pseudopotentials and the associated pseudo-orbitals have been derived for a large amount of elements.

Moreover, for specific elements pseudopotentials exist representing different numbers of core electrons.
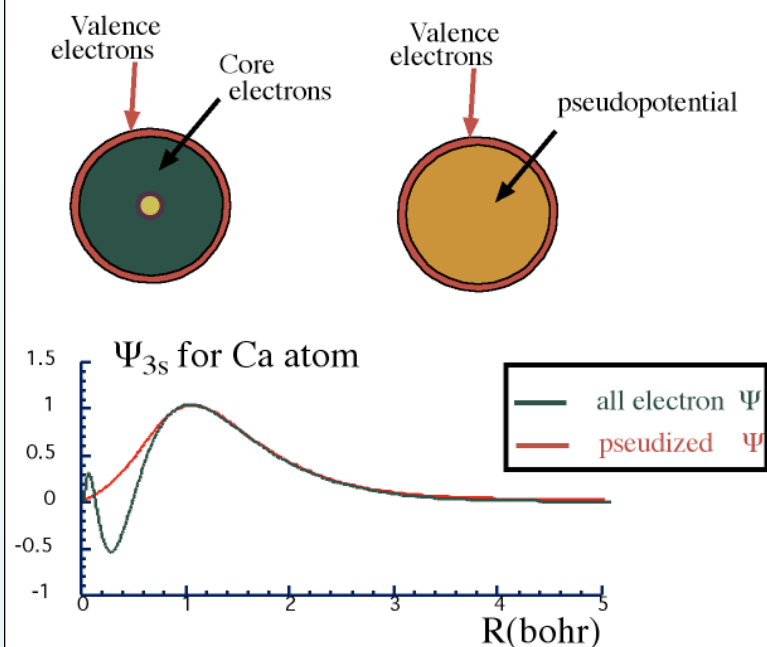
For example, for gallium there are pseudopotentials representing the ten innermost electrons only, but also others representing 18 or 28 electrons, respectively.

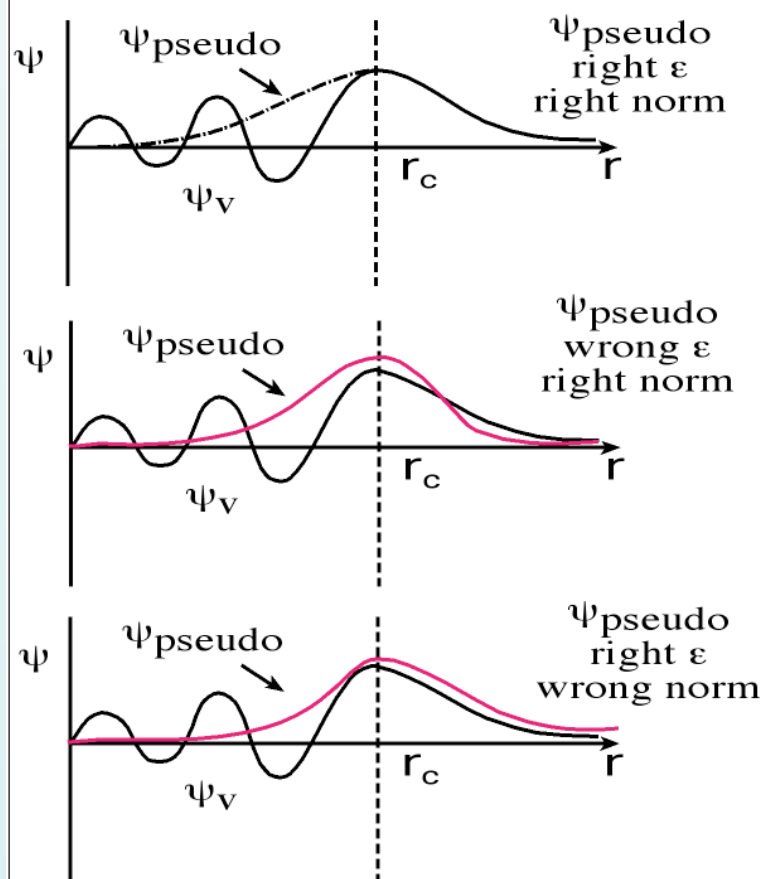Let's take a look at some images I found on Google.

Pseudopotentials

lorax.chem.upenn.edu/ Research/Talk/Pseudo/

Note: We're Working This Graph