

The orbital approximation: basis sets and shortcomings of Hartree-Fock theory

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Background:

The wavefunction for a quantum system contains enough information to determine all of the properties for that system (the energy, dipole moment, etc.). The wavefunction, Ψ , can be determined by solving the Schrödinger equation

$$\hat{H}\Psi = E\Psi, \quad (1)$$

where \hat{H} is the Hamiltonian operator (the energy operator) and E is the energy of the system. Unfortunately, the wavefunction for a many-electron atom or molecule is an extremely complicated mathematical object. It is so complicated that an analytic form cannot be determined for even a simple two-electron atom like He! In order to determine the wavefunction for atoms and molecules with more than one electron, we tend to make approximations that lead to mathematical equations that are much simpler to solve. One of the most important approximations in quantum chemistry is known as **the orbital approximation**, which states that each electron in a many-electron system occupies its own one-electron function, which is called an **orbital**. For hydrogenic atoms, these orbitals are the solutions to the Schrödinger equation (the 1s, 2s, 2p orbitals, etc.). For a many-electron molecule, these orbitals might look like linear combinations of hydrogenic wavefunctions. For example, consider the σ_g bonding orbital (ϕ_{σ_g}) in the H_2 molecule, constructed as a linear combination of 1s atomic orbitals from atom 1 ($\chi_{1s,1}$) and atom 2 ($\chi_{1s,2}$):

$$\phi_{\sigma_g} = N(\chi_{1s,1} + \chi_{1s,2}), \quad (2)$$

where N is a normalization constant. A molecular orbital constructed in this way is known as a linear combination of atomic orbitals-molecular orbital (LCAO-MO). In an electronic structure computation, we refer to the atomic orbital functions from which molecular orbitals are constructed as **basis functions**.

In **Hartree-Fock theory**, the total electronic wavefunction is approximated as an antisymmetrized product of these molecular orbitals (such a wavefunction is called a Slater determinant). The Hartree-Fock method is one of the most important methods in modern electronic structure theory. It does not provide a quantitative description of chemical bonding, but it often provides a *qualitative* description and serves as a useful starting point for more sophisticated methods.

So, how do we determine these molecular orbitals? Recall the **variational principle**:

The energy of an approximate wavefunction is always an upper bound to the true energy.

So, if we express the molecular orbitals as linear combinations of atomic basis functions, we can vary the coefficients in this expansion until we find the lowest-energy solution, and we are guaranteed that this energy is an upper bound to the true energy for the system. This is the essence of the Hartree-Fock method. A consequence of this procedure is that, as we include more atomic basis functions in a computation, the wavefunction becomes more flexible, and the resulting total energy is lower.

Quantum chemists use special names for the basis sets used in electronic structure calculations based on their size. A **minimal** basis set is one that contains the minimum number of functions to describe the valence space for the atoms in the molecule. For example, the minimal basis set for a second-row atom includes the 1s, 2s, and 2p orbitals. A “double-zeta” basis set includes twice as many functions as are necessary to describe the valence space. A “triple-zeta” set includes three times as many, and so forth. In general, as the size of the basis set increases, the quality of the solution increases. Be careful, though, the cost of the computation increases as well!

Prelab question:

How can you combine 1s atomic orbitals to represent a σ_u antibonding molecular orbital in H_2 ?

Procedure

1. The complete basis set limit

Using the WebMO interface, compute the energy of the hydrogen atom at the Hartree-Fock level of theory using a minimal basis set (STO-3G) using the following procedure.

At the WebMO job manager, click the new job tab. Select the periodic table tool and click on the symbol for hydrogen. Place a single hydrogen on the screen. Click the next button (the right arrow at the bottom of the screen). On the job options screen, make sure that the method is Hartree-Fock and that the charge is 0. Since H only has one electron, we can't use a restricted reference. Switch the reference to Unrestricted and make sure the multiplicity is a doublet. Click the next arrow to submit your job. When your job finishes, click the magnifying glass icon to view the results screen. Scroll to the bottom to see the Hartree-Fock energy.

a) Record the energy to 5 decimal places and include the appropriate units. Convert the energy to kcal mol^{-1} .

b) Next, click on the “raw output” link to view the output file. Scroll down until you find the “Primary Basis.” Record the number of basis functions (not the number of cartesian basis functions).

c) Repeat parts a) and b) for each basis set given here:

6-31G
cc-pVDZ
cc-pVTZ

What value does the energy approach? Which basis set is most accurate? Why?

d) Evaluate the complete basis set (CBS) energy according to the following 2-point extrapolation formula:

$$E_x = E_{\text{CBS}} + \beta e^{-\alpha x}, \quad (3)$$

Here, $\alpha = 1.63$, β and E_{CBS} are unknown, E_x is the energy computed in a given basis, and x represents the zeta-level of that basis. For example, $x = 2$ for cc-pVDZ and $x = 3$ for cc-pVTZ. Evaluate the SCF energy in the cc-pVDZ and cc-pVTZ basis sets and determine β and E_{CBS} . Show your work, and give E_{CBS} in E_h to 5 decimal places.

e) Set up your H atom job again. This time, after you set the reference and multiplicity, click the Preview tab. Click Generate to generate a preview of the input file, and change the line

```
energy('scf')
```

to read

```
cbs('scf',scf_basis='cc-pV[DT]Z',scf_scheme=scf_xtpl_helgaker_2)
```

This line will now have Psi4 perform a 2-point extrapolation using the cc-pVXZ (X = D, T) basis sets. Click the next arrow and confirm that you want to submit the modified input file. Once the job finishes, open the raw output file, and search for the CBS computation (“CBS Results”). Record the CBS limit SCF energy. How does it compare to your result in part d)?

2. Limitations in Hartree-Fock theory

The Hartree-Fock method is a very powerful and very important method in quantum chemistry, but it has a number of shortcomings. Here, you will explore two of these limitations.

a) Hartree-Fock theory cannot properly describe the breaking of chemical bonds, even in simple molecules like H₂! Compute a potential energy curve (PEC) for H₂ at the Hartree-Fock / 6-31G and singles and doubles coupled cluster (CCSD) / 6-31G levels of theory (for this system, CCSD will provide the exact result).

Plot (using some graphical software, like Excel) the energy as a function of bond length using the following bond lengths (Å):

0.5, 0.7, 0.9, 1.1, 1.5, 2.0, 2.5, 3.0

Using your results, estimate the dissociation energy at the CCSD / 6-31G level of theory (in kcal mol⁻¹). By how much does Hartree-Fock overestimate the dissociation energy, relative to CCSD?

b) Compute the non-bonded interaction energy for the FH dimer at the SCF / aug-cc-pVDZ level of theory in the linear configuration



using this procedure:

- 1) perform a geometry optimization the F-H molecule. In the Job Options tab, set the Calculation Type to “Geometry Optimization.” Record the energy of the F-H molecule.
- 2) Set up another geometry optimization job. Generate a Psi4 input file at Preview tab and set the molecule geometry to

```
H 0.0 0.0 0.0
F 0.0 0.0 1.0
H 0.0 0.0 2.0
F 0.0 0.0 3.0
```

This geometry corresponds to an FH dimer with an intermolecular distance of 1 Å. Perform a geometry optimization. Record the energy.

- 3) Compute the interaction energy as

$$E_{\text{int}} = E_{\text{dimer}} - 2E_{\text{monomer}}. \quad (4)$$

What is the interaction energy? How does it compare the interaction energy computed at the coupled-cluster through perturbative triple excitations [CCSD(T)] / aug-cc-pVDZ level of theory (-3.846 kcal mol⁻¹)?

c) Compute the interaction energy for the Argon dimer in the aug-cc-pVDZ basis. This time, do not optimize the Argon dimer geometry. Instead, assume an interatom separation of 3.999 Å. How does your result compare to the CCSD(T) / aug-cc-pVDZ value of -0.262 kcal mol⁻¹. What does the sign of your result say about the interaction (is it favorable / unfavorable)?

d) Below you will find the interaction energy (kcal mol⁻¹) of the argon dimer computed at the CCSD(T) / aug-cc-pVDZ level of theory. Compute and record the interaction energy for the Argon dimer at the Hartree-Fock / aug-cc-pVDZ level of theory at these Ar-Ar distances (Å), and plot your results alongside the following CCSD(T) results.

Ar-Ar distance (Å)	CCSD(T) IE(kcal mol ⁻¹)
3.4	0.136
3.6	-0.146
3.8	-0.244
4.0	-0.262
4.2	-0.245
4.4	-0.214

Does Hartree-Fock predict a minimum in the IE? Why or why not? What types of intermolecular interactions would you expect to dominate in the FH dimer and the Ar dimer? Based on your results here and in part 3 c), what can you say about the ability of the Hartree-Fock method to describe these types of interactions?

e) The idea of an MO diagram falls naturally out of the orbital approximation and Hartree-Fock theory. Draw the MO diagram for the Ar dimer when considering only the valence electrons. What is the bond order? Does your simple MO diagram agree or disagree with your Hartree-Fock results?