

Quantum Calculations in CHEM 870

Important details to avoid bad calculations

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Outline

1 Calculation Parameters

- Fundamental Considerations - Open shell systems
- Exchange Energy and the Fermi Hole
- Basis Sets

2 Post-Hartree Fock methods

Simulating Unpaired Electrons in Open-shell Systems

From Cramer Section 6.3.3:

When simulating a closed-shell singlet, a spin-up (α) and spin-down (β) electrons will occupy the same spatial orbital (wavefunction).

When simulating an open-shell system, choices must be made:

- Unrestricted Hartree-Fock (UHF)
- Restricted open-shell Hartree-Fock (ROHF)
- Restricted Hartree-Fock (RHF)

The methyl radical, ROHF wavefunction

$$\Psi = |C1s^2\sigma_{CH_a}^2\sigma_{CH_b}^2\sigma_{CH_c}^2C2p_z^1|$$

All electrons are paired, except for the one in the $2p_z$ orbital on the carbon. Otherwise, the same spatial orbitals are used for the α and β electrons.

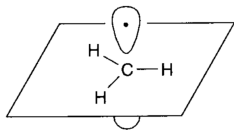
Comparing ROHF and UHF

The methyl radical, ROHF wavefunction

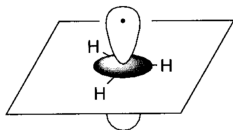
$$\Psi = |C1s^2\sigma_{CH_a}^2\sigma_{CH_b}^2\sigma_{CH_c}^2C2p_z^1|$$

The methyl radical, UHF wavefunction

$$\Psi = |C1s^\alpha C1s'^\beta \sigma_{CH_a}^\alpha \sigma_{CH_a}'^\beta \sigma_{CH_b}^\alpha \sigma_{CH_b}'^\beta \sigma_{CH_c}^\alpha \sigma_{CH_c}'^\beta C2p_z^1|$$



ROHF



UHF

See Cramer section 6.3.3!

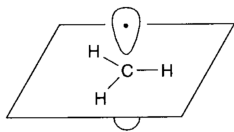
Comparing ROHF and UHF - Benefits

ROHF

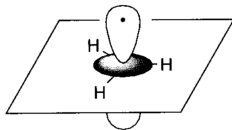
In restricted HF, the α and β electrons share spatial orbitals. In the restricted - open shell HF, the same spatial orbitals are used for paired electrons and additional half filled orbitals are included for the unpaired electrons. The benefit is the resulting wavefunctions are eigenfunctions of the \hat{S}^2 operator, giving reliable values of the total spin magnetic moment.

UHF

UHF separately computes spatial wavefunctions for the α and β electrons, giving reliable information about spin polarization.



ROHF



UHF

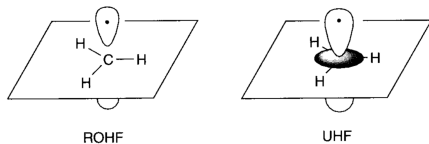
Comparing ROHF and UHF - Drawbacks

ROHF

ROHF does not calculate spin polarization correctly. In the methyl radical, there is NO spin density ($\rho_\alpha - \rho_\beta$) in the molecular plane.

UHF

The total spin magnetic moment, S , is often incorrect, due to 'spin contamination' from excited state with higher spin magnetic moments.



There should be spin density in the plane due to the 'Fermi hole' around the unpaired α electron in the p_z orbital. This exchange correlation effect allows more ρ_α above and below the plane and more ρ_β in the plane.

Exchange Energy and the Fermi Hole

The interaction of the charge and spin of electrons causes their density to be different than if they were charge-less and spin-less. The effect is thought of in terms of exchange and correlation *holes*.

Hole Definitions

- Coulomb Hole: The dynamical correlation (Coulomb repulsion) gives rise to an area around the electron where other electrons are less likely to be found. But they are more likely to be found farther away.
- Fermi Hole: A static reduction in the probability of finding an electron with the same spin near a "fixed electron", due to the exchange energy, a quantum correction to the classical Coulomb repulsion.

Fermi Hole Effects

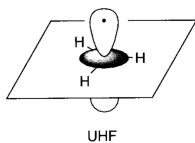
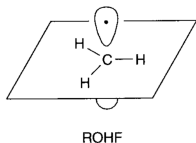
For the methyl radical: "The Fermi hole that surrounds the unpaired electron allows other electrons of the same spin to localize above and below the molecular plane slightly more than electrons of opposite spins." This same spin density is pulled from the molecular plane.

Exchange Energy and the Fermi Hole

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Fermi Hole Effects - Cramer section 6.3.3

For the methyl radical: "The Fermi hole that surrounds the unpaired electron allows other electrons of the same spin to localize above and below the molecular plane slightly more than electrons of opposite spins." This same spin density is pulled from the molecular plane.



Bigger Basis Sets = Wait Exponentially Longer

For polyatomic molecules, there are basis functions centered on each nuclei. The electron-electron interaction integrals (Coulomb and exchange) contain basis functions centered on more than two nuclei. Multicentered integrals are difficult to evaluate, especially with Slater orbitals.

Slater Orbitals

$$S_{nlm_l}(r, \theta, \phi) = N_{nl} r^{n-1} e^{-\zeta r} Y_l^{m_l}(\theta, \phi) \quad (1)$$

N_{nl} is the normalization constant, ζ can be fit, but is often pre-optimized.

Gaussian Functions Ease Integral Evaluation

$$\begin{aligned} g_s(r, \alpha) &= N_{s\alpha} e^{-\alpha r^2} & g_x(r, x, \alpha) &= N_{p\alpha} x e^{-\alpha r^2} \\ g_y(r, y, \alpha) &= N_{p\alpha} y e^{-\alpha r^2} & g_z(r, z, \alpha) &= N_{p\alpha} z e^{-\alpha r^2} \end{aligned}$$

For d orbitals, you can have x^2 , y^2 , z^2 , xy , xz , or yz multiplied by $e^{-\alpha r^2}$.

The Cost/Benefit Analysis of Gaussian functions

Benefit: Gaussian functions centered at two different nuclei can be combined into a single Gaussian centered at one position (like reducing the actual basis set size).

Cost: Gaussian functions do not look like Slater orbitals, and thus do not model radial electron probability!

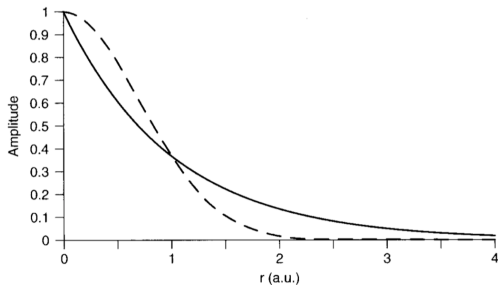


Figure 6.1 Behavior of e^x where $x = r$ (solid line, STO) and $x = r^2$ (dashed line, GTO)

Solution: Fit Slater with many Gaussian functions

Contracted Gaussian functions - S_{1s} example

$$S_{1s}(r) = \sum_{i=1}^3 c_{1si} g_s(r, \alpha_{1si})$$
$$= 0.44g_s(r, 0.10982) + 0.54g_s(r, 0.40577) + 0.15g_s(r, 2.2277)$$

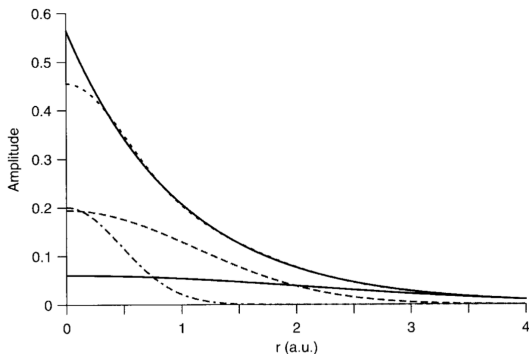


Figure 6.2 The radial behavior of various basis functions in atom-centered coordinates.

Solution: STO-NG

Contracted Gaussian functions, Definition = Sum of Primitives

Slater Type Orbital (STO) fit with N Gaussians.

A contraction of 3 Gaussians for each basis function gives STO-3G:

$$S_{1s}(r) = \sum_{i=1}^3 c_{1si} g_s(r, \alpha_{1si})$$

Each g_s is called a primitive Gaussian.

Minimal basis sets include enough STO-NG orbitals to accommodate all the electrons, but are usually not sufficient. Addition of $g_p(r, \alpha)$ orbitals improves simulations of atoms or molecules with H - Be.

The Gaussians are fit to Slater-type orbitals with $\zeta = 1$ and then scaled. The linear coefficients from the fit are unchanged.

Solution: STO-NG

The Gaussians are fit to Slater-type orbitals with $\zeta = 1$ and then scaled. The linear coefficients from the fit are unchanged.

Figure: from McQuarrie Chapter 12

TABLE 12.2

Orbital Exponents, ζ , for the Slater Orbitals of the Atoms of the First Two Rows of the Periodic Table

Atom	ζ_{1s}	$\zeta_{2s} = \zeta_{2p}$
H	1.24	
He	1.69	
Li	2.69	0.80
Be	3.68	1.15
B	4.68	1.50
C	5.67	1.72
N	6.67	1.95
O	7.66	2.25
F	8.56	2.55
Ne	9.64	2.88

A Better Solution: Multiple ζ and Split-Valence

"One inadequacy of a minimal basis set is due to the fact that the orbital exponents are fixed, and so an orbital is unable to contract or expand in different molecular environments. The fixed orbital exponents simply make the orbitals too rigid." - McQuarrie 12.3

Use Linear Combinations of Slater Type Orbitals

Example, 2s

$$\phi_{2s}(r) = S_{2s}(r, \zeta_1) + dS_{2s}(r, \zeta_2)$$

Each S_{2s} is made of contracted Gaussians and d will be optimized in the Hartree-Fock procedure.

Why even bother with Slater? Use Pople 3-21G

The dash represents the split valence. Split-Valence basis sets describe the inner-shell electrons by a single orbital and the valence shell electrons by a sum of orbitals.

Pople contracted Gaussian functions N-MPG

Why even bother with Slater? Use Pople 3-21G

Example of Hydrogen:

For the valence electrons (21), use a linear combination of two orbitals (both 1s), $\{\prime\}$ with M=2 primitive Gaussians and $\{\prime\prime\}$ with only P=1 .

$$\phi'_{1s}(r) = \sum_{i=1}^2 d'_{1si} g_s(r, \alpha'_{1si}) \text{ and } \phi''_{1s}(r) = g_s(r, \alpha''_{1s})$$

Example of Lithium:

The non-valence electrons are represented by a sum of N=3 primitive Gaussians. $\phi'_{1s}(r) = \sum_{i=1}^3 d'_{1si} g_s(r, \alpha'_{1si})$

The valence electrons are split (21) and require orbitals for 2s and 2p. These will look similar to the hydrogen valence format above.

Pople 6-31G basis sets are very popular, as is adding more orbitals to account for polarization.

The benefits of More Orbitals!

In Tutorial 2, you tested three basis sets: SVP, TZVP, and cc-pVTZ and whether they improved the ground state energy of the helium atom (and hence the ionization energy).

Using more than the minimal basis set gives better bond lengths and bond angles, as we will see in Tutorial 4.

We also need to cover Configuration Interaction to get the correct dissociation energy for molecules.

Configuration Interaction (CI) is needed

Consider using only the ground state wavefunction to describe H_2 .

The single Slater determinant wavefunction for H_2

$$\psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_b\alpha(1) & \sigma_b\beta(1) \\ \sigma_b\alpha(2) & \sigma_b\beta(2) \end{vmatrix} \quad (2)$$

$$= \sigma_b(1)\sigma_b(2) \left\{ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \right\} \quad (3)$$

$$\psi_{MO} = \frac{1}{2(1+S)} [1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)] \quad (4)$$

Where we drop the spin part and recall the bonding orbital is a linear combination of atomic $1s$ orbitals.

The energy $E_{MO} = \langle \psi_{MO} | \hat{H} | \psi_{MO} \rangle$ depends on ζ and R , the H-H bond distance.

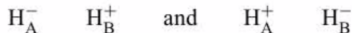
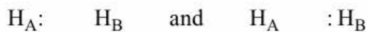
CI is needed to fix bond dissociation - example H_2

Consider the using only the ground state wavefunction to describe H_2 .

The single Slater determinant overestimates the ionic terms.

$$\begin{aligned}\psi_{MO} &= \frac{[1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)]}{2(1 + S)} \\ &= \frac{[1s_A(1)1s_B(2) + 1s_A(2)1s_B(1) + 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)]}{2(1 + S)} \\ &= \psi_{VB} + \psi_{ionic}\end{aligned}$$

Figure: Ionic components of single determinant from McQuarrie



CI is needed: H_2 dissociation $E(R = \infty)$ and ζ are wrong

Figure: Ionic components of single determinant from McQuarrie

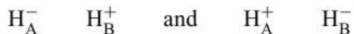
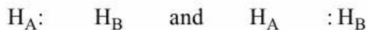
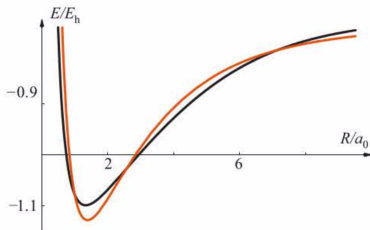


Figure: The energy should go to $-1 E_h$. ζ should go to 1.



CI uses multiple Slater Determinants!

From all configurations, we keep ψ_1 and ψ_2

$$\sigma_b = \frac{1s_A + 1s_B}{\sqrt{2(1+S)}} \quad \sigma_a = \frac{1s_A - 1s_B}{\sqrt{2(1-S)}}$$

$$\psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_b\alpha(1) & \sigma_b\beta(1) \\ \sigma_b\alpha(2) & \sigma_b\beta(2) \end{vmatrix}$$

$$\psi_1 = \sigma_b(1)\sigma_b(2)$$

$$\psi_2 = \sigma_a(1)\sigma_a(2)$$

$$\psi_3, \psi_4, \psi_5 = \sigma_b(1)\sigma_a(2) - \sigma_a(1)\sigma_b(2)$$

$$\psi_6 = \sigma_b(1)\sigma_a(2) + \sigma_a(1)\sigma_b(2)$$

$$\psi_{\text{CI}} = c_1\psi_1 + c_2\psi_2$$

CI can be exact using an infinite basis set

Optimize c_1 and c_2 during the Hartree-Fock SCF

$$\psi_{\text{CI}} = c_1\psi_1 + c_2\psi_2$$

ψ_2 is an excited-state configuration. A linear combination with the ground state is called configuration interaction.

The larger the basis set, the greater the number of virtual orbitals, which can contribute to the configuration interaction.

Configuration interaction converges very slowly (as basis functions are added) and is expensive.

The coupled-cluster (CC) method is more accurate than CI and is built on a similar principle, adding excited state wavefunctions (configurations). We'll use CC because it's included in many quantum codes (ORCA).