Modeling Bound States in H_2 using Hartree-Fock

Sam Cochran

December 2022

Hartree-Fock

We assume the N-body wave function can be approximated by a single Slater determinant. The goal is to find a Slater determinant that minimizes the energy of the system.

- Fock operator: $f = h + \sum_i^{N/2} 2J_i - K_i$
- Hartree-Fock equation: $f|\chi_i\rangle = \epsilon_i|\chi_i\rangle$
- Basis $\{\phi_i\}$
- Fock matrix $\mathbf{F}$: representation of Fock operator in our basis
- Roothaan equations: $\mathbf{FC} = \mathbf{SC}\epsilon$

Choosing Basis Functions

Minimal basis set–single basis element per nucleus

- ▶ $1s$ Slater-type: $\phi_{1s}^{SF}(\zeta, \mathbf{r} - \mathbf{R_A}) = (\zeta^3/\pi)^{1/2} e^{-\zeta|\mathbf{r}-\mathbf{R_A}|}$
- ▶ $1s$ Gaussian-type: $\phi_{1s}^{GF}(\alpha, \mathbf{r} - \mathbf{R_A}) = (2\alpha/\pi)^{3/4} e^{-\alpha|\mathbf{r}-\mathbf{R_A}|^2}$

Slater functions more correctly describe molecular orbitals, but are difficult to integrate.
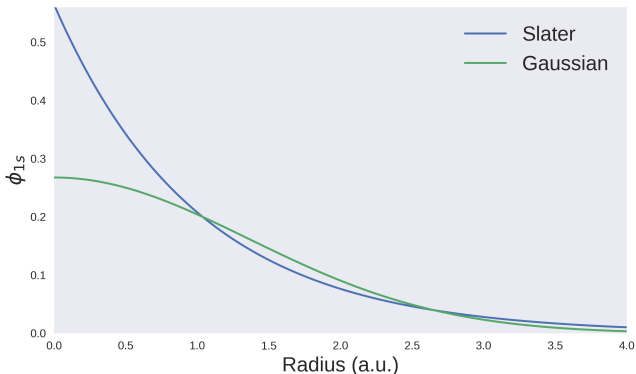
Product of Gaussians

We can write a product of Gaussian functions as a single Gaussian function on a new center:

$$\phi_{1s}^{GF}(\alpha, \mathbf{r} - \mathbf{R_A})\phi_{1s}^{GF}(\beta, \mathbf{r} - \mathbf{R_B}) = K_{AB}\phi_{1s}^{GF}(p, \mathbf{r} - \mathbf{R_P})$$

$$K_{AB} = exp(-\alpha\beta/(\alpha + \beta)|\mathbf{R_A} - \mathbf{R_B}|^2)$$

$$\mathbf{R_P} = (\alpha\mathbf{R_A} + \beta\mathbf{R_B})/(\alpha + \beta)$$

$$p = \alpha + \beta$$

This greatly simplifies the integrals we will need to carry out.

Contracted Gaussian Functions

Slater-type functions better encode the physics of our problem, but we would like to use Gaussians to simplify our integrals. A solution is to use contracted Gaussian Functions (CGF).

$$\phi_{1s}^{CGF}(\boldsymbol{\alpha}, \mathbf{r} - \mathbf{R_A}) = \sum_{i=1}^{N} c_i \phi_{1s}^{GF}(\alpha_i, \mathbf{r} - \mathbf{R_A})$$

This way we can better approximate Slater-type functions while still only integrating Gaussians.

STO-NG Basis

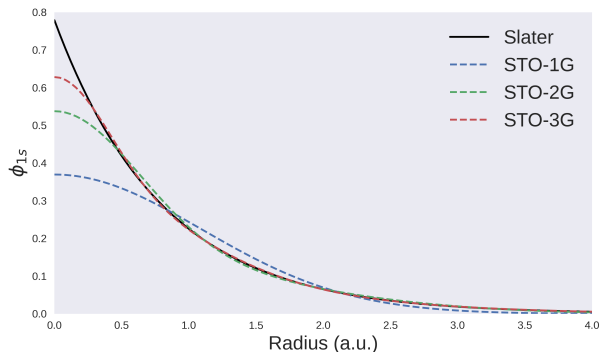Fit a Slater-type orbital to a CGF with N Gaussian summands.

▶ STO-1G:
$\phi_{1s}^{CGF}(\alpha_1, \mathbf{r} - \mathbf{R_A}) = \phi_{1s}^{GF}(\alpha_1, \mathbf{r} - \mathbf{R_A})$

▶ STO-2G:
$\phi_{1s}^{CGF}(\boldsymbol{\alpha}, \mathbf{r} - \mathbf{R_A}) = \sum_{i=1}^{2} c_i \phi_{1s}^{GF}(\alpha_i, \mathbf{r} - \mathbf{R_A})$

▶ STO-3G:
$\phi_{1s}^{CGF}(\boldsymbol{\alpha}, \mathbf{r} - \mathbf{R_A}) = \sum_{i=1}^{3} c_i \phi_{1s}^{GF}(\alpha_i, \mathbf{r} - \mathbf{R_A})$

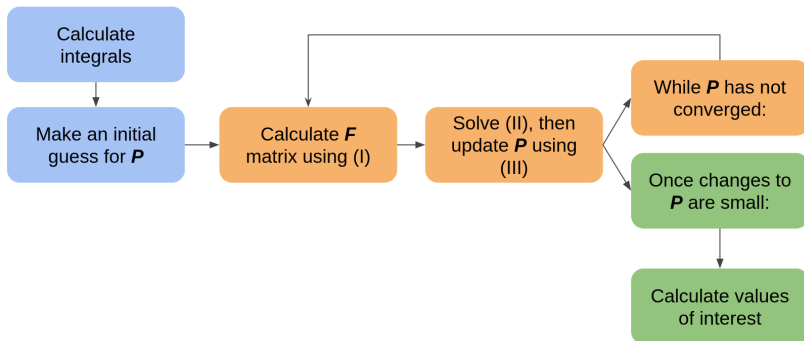# Integration

4 types of integrals we need to solve:

- ▶ 2-center overlap integral: $(A|B)$
- ▶ Kinetic energy integral: $(A|\frac{1}{2}\nabla^2|B)$
- ▶ Nuclear attraction integral: $(A|Z_C/r_{1C}|B)$
- ▶ Two-electron integral: $(AB|CD)$

$$(A|\xi|B) = \int d\mathbf{r_1}\phi_{1s}^{GF}(\alpha_1, \mathbf{r} - \mathbf{R_A})[\xi]\phi_{1s}^{GF}(\alpha_2, \mathbf{r} - \mathbf{R_B})$$

$$(AB|CD) = \int d\mathbf{r_1}d\mathbf{r_2}\phi_{1s}^{GF}(\alpha_1, \mathbf{r} - \mathbf{R_A})\phi_{1s}^{GF}(\alpha_2, \mathbf{r} - \mathbf{R_B})r_{12}^{-1}$$

$$\phi_{1s}^{GF}(\alpha_3, \mathbf{r} - \mathbf{R_C})\phi_{1s}^{GF}(\alpha_4, \mathbf{r} - \mathbf{R_D})$$

Iteration Procedure

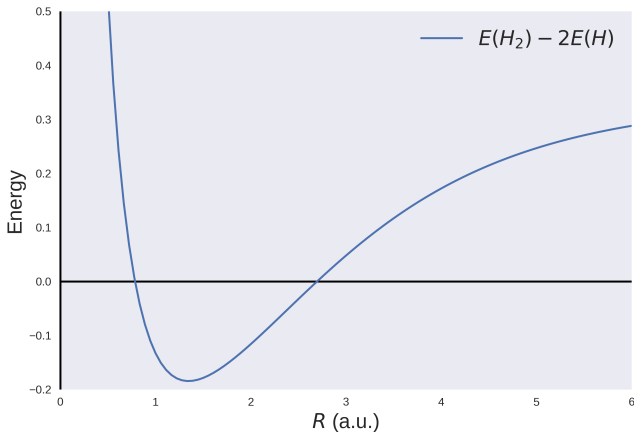(I) $F_{ij} = H_{ij}^{core} + \sum_{kl} P_{kl}[(ij|lk) - \frac{1}{2}(ik|jl)]$
(II) $\mathbf{FC} = \mathbf{SC}\epsilon$
(III) $P_{ij} = 2\sum_{a}^{N/2} C_{ia}C_{ja}^{*}$

Energy Calculation

We can compute the total energy as $E(H_2) = E_0 + E_{repulsion}$, where $E_0 = \frac{1}{2} \sum_i \sum_j P_{ji}(H_{ij}^{core} + F_{ij})$ and $E_{repulsion} = \frac{1}{R}$.

Calculated equilibrium distance $R_{eq} = 1.346$ atomic units.

Generalizations

▶ Though we focused exclusively on H_2 here, we can apply Hartree-Fock to different elements and larger molecules.

▶ We can add more elements to our basis to improve accuracy (though the number of integrals to be evaluated increases rapidly with the size of the basis).

▶ Neglect of electron correlation reduces accuracy. Post-Hartree-Fock methods find ways to include electron correlation in the model to improve accuracy.

References

Szabo, Attila, and Neil S. Ostlund. Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, Dover Publications, 1996. ProQuest Ebook Central.

Thank you!