Basis functions and SCF procedure

The spatial Hartree-Fock equation:

$$f(\vec{r}_1)\psi_i(\vec{r}_1) = \epsilon_i \ \psi_i(\vec{r}_1)$$

can be solved numerically for atoms. The results of such calculations have been tabulated (see, for example, NIST web site). However, for molecules there is no practical procedure known for solving the equation directly (recall f depends on the orbitals) and the orbitals ψ_i are instead expanded in some known basis functions ϕ_μ:

$$\psi_i = \sum_{\mu}^{K} C_{\mu i} \ \phi_\mu \qquad i = 1, 2, \ldots, K.$$

If the number of basis functions is K, we can generate K different orbitals. If the set $\{\phi_\mu\}$ is complete the results would be the same as a direct numerical solution to the Hartree-Fock equation. But, for practical reasons the set $\{\phi_\mu\}$ is always finite and therefore not complete and some error is introduced by expanding ψ_i. This is called the *basis set error.*

The problem now is reduced to determining the expansion coefficients $C_{\mu i}$. Inserting the expansion into the Hartree-Fock equation gives

$$f(1) \sum_{\gamma} C_{\gamma i}\phi_\gamma(1) = \epsilon_i \sum_{\gamma} C_{\gamma i}\phi_\gamma(1).$$

Left multiplying with $\phi_\mu^*(1)$ and integrating gives:

$$\sum_{\gamma} C_{\gamma i} \underbrace{\int d\vec{r}_1 \phi_\mu^*(1) f(1) \phi_\gamma(1)}_{\substack{\equiv F_{\mu\gamma} \\ \text{the Fock matrix}}} = \epsilon_i \sum_{\gamma} C_{\gamma i} \underbrace{\int d\vec{r}_1 \phi_\mu^*(1)\phi_\gamma(1)}_{\substack{\equiv S_{\mu\gamma} \\ \text{the overlap matrix}}}$$

$$\sum_{\gamma} F_{\mu\gamma} C_{\gamma i} = \epsilon_i \sum_{\gamma} S_{\mu\gamma} C_{\gamma i}$$

$$\tilde{F}\tilde{C} = \tilde{S}\tilde{C}\tilde{\epsilon}.$$

Note that the basis functions are usually not orthogonal so one needs to include an overlap matrix, S. This is a matrix representation of the Hartree-Fock equation and is called the *Roothaan equation.* The matrices $\tilde{F}, \tilde{S}$ and $\tilde{C}$ are $K \times K$ matrices and $\bar{\epsilon}$ is a vector of length K. The problem is therefore reduced to solving algebraic equations using matrix techniques. Only if $K \to \infty$ are the Roothan equations equivalent to the Hartree-Fock equation.

The Roothaan equation is non-linear since $\tilde{F}$ depends on $\tilde{C}$

$$\tilde{F}_{(\tilde{C})}\tilde{C} = \tilde{S}\tilde{C}\bar{\epsilon}.$$

It can be solved in an iterative fashion. Given an estimate for C, say $\tilde{C}_n$ in iteration n, F can be evaluated from the current estimate, $\tilde{F}_{(\tilde{C}_n)}$, and then the equation

$$\tilde{F}_{(\tilde{C}_n)}\tilde{C}_{n+1} = \tilde{S}\tilde{C}_{n+1}\bar{\epsilon}$$

can be solved to obtain a new estimate for the $\tilde{C}$ matrix, $\tilde{C}_{n+1}$. If $\tilde{C}_{n+1} = \tilde{C}_n$ to within reasonable tolerance, then self consistency has been achieved and $\tilde{C}_n$ is the solution. Most workers refer to such a solution as self-consistent-field (SCF) solution for any finite basis set $\{\phi_i\}$ and reserve the term Hartree-Fock to the infinite basis solution. The equation is solved at each step by diagonalizing the overlap matrix $\tilde{S}$, i.e., by finding a unitary transformation $\tilde{X}$ such that

$$X^\dagger S X = 1.$$

The transformed basis function are

$$\phi'_\mu = \sum_\gamma X_{\gamma\mu}\phi_\gamma \qquad \mu = 1, 2, \ldots, K$$

and form an orthonormal set, i.e.,

$$\int d\vec{r}\phi'^*_\mu \phi'_\gamma = \delta_{\mu\gamma}.$$

Then the equation becomes an ordinary eigenvalue equation:

$$F'C' = C'\epsilon \qquad \text{where } F' \equiv X^\dagger F X \qquad \text{and } C' \equiv X^{-1}C.$$

The main computational effort in doing a large SCF calculation lies in the evaluation of the two-electron integrals. If there are K basis functions then there will be on the order of $K^4/8$ unique two-electron integrals. This can be on the order of millions even for small basis sets and moderately large molecules. The accuracy and efficiency of the calculation depends very much on the choice of basis functions, just as any variational calculation depends strongly on the choice of trial functions.

Commonly used basis functions

Two types of basis functions are frequently used:

(1) Slater type functions, which for a 1S orbital centered at $\vec{R}_A$ has the form

$$\phi_{1S}^{SF}(\zeta, \vec{r} - \vec{R}_A) = \sqrt{\zeta/\pi}\ e^{-\zeta|\vec{r}-\vec{R}_A|}$$

with ζ a free parameter and

(2) Gaussian type function

$$\phi_{1S}^{GF}(\alpha, \vec{r} - \vec{R}_A) = \left(\frac{2\alpha}{\pi}\right)^{3/2}\ e^{-\alpha|\vec{r}-\vec{R}_A|^2}$$

with α a free parameter.

The Slater type functions have a shape which matches better the shape of typical orbital functions.In fact, the wave function for the hydrogen atom is a Slater type function with $\zeta = 1$. More generally, it can be shown that molecular orbitals decay as $\psi_i \sim e^{-ar}$ just like Slater type functions and at the position of nuclei $|\vec{r} - \vec{R}_A| \to 0$ there is a cusp because the potential $-e/|r - R_A|$ goes to $-\infty$.

Gaussian type functions have zero slope at $|\vec{r} - \vec{R}_A| = 0$ (i.e., no cusp) and decay much more rapidly than Slater functions. Since Slater type functions more correctly describe qualitative features of molecular orbitals than Gaussian functions, fewer Slater type functions are needed to get comparable results. However, the time it takes to evaluate the integrals over Slater function is much longer than for Gaussian functions. The two electron integrals can involve four different centers $\vec{R}_A, \vec{R}_B, \vec{R}_C$ and $\vec{R}_D$ which makes the evaluation of integrals over Slater functions very time consuming. The product of two Gaussians, on the other hand, is again a Gaussian

$$\phi_{1S}^{GF}(\alpha, \vec{r} - \vec{R}_A)\ \phi_{1S}^{GF}(\beta, \vec{r} - \vec{R}_B) = K_{AB}\ \phi_{1S}^{GF}(p, \vec{r} - \vec{R}_p)$$

where the new Gaussian is centered at

$$\vec{R}_p = \frac{\alpha \vec{R}_A + \beta \vec{R}_B}{\alpha + \beta}.$$

A common practice is to choose basis functions ϕ_μ that are constructed from a few Gaussians

$$\phi_\mu^{CGF}(\gamma, \vec{r} - \vec{R}_A) = \sum_{p=1}^{L} dp\mu\ \phi_p^{GF}(\alpha_{p\mu}, \vec{r} - \vec{R}_A)$$

in such a way as to mimic (in a least squares sense) a Slater function. Those are called *contracted Gaussian functions* and a standard notation for such basis functions is $STO - NG$, meaning Slater Type Orbital constructed from N Gaussians. A typical value for N is 3, i.e. three gaussians are used in each orbital.

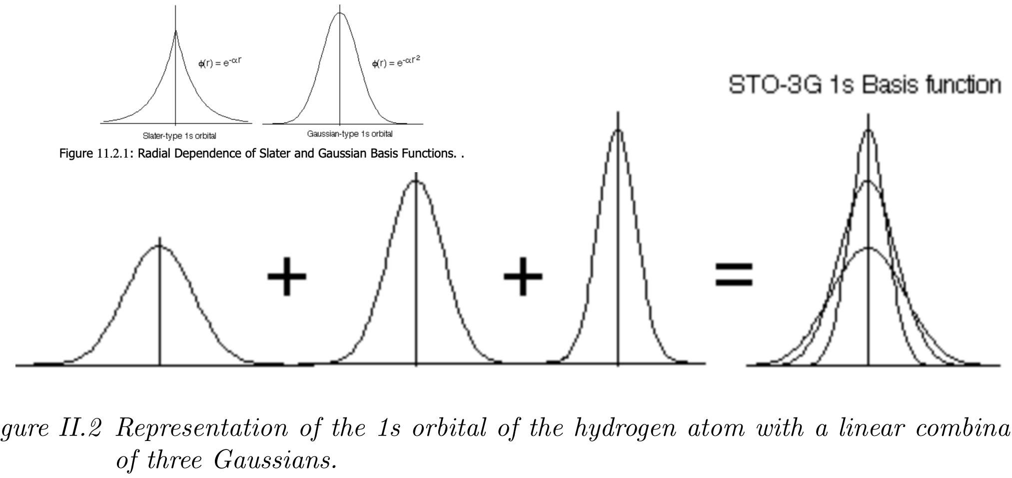

Figure II.2 Representation of the 1s orbital of the hydrogen atom with a linear combination of three Gaussians.

In a more flexible basis set called **6-31G**, the core electrons are represented by a single Slater type orbital which is described by six Gaussians (contracted) while valence electrons are represented by two Slater type orbitals, one described by three Gaussians (contracted) and the other described by a single Gaussian. When an atom is placed in an external field, the electron cloud is distorted (polarized). To describe this, it is necessary to include also excited atomic orbitals, i.e. orbitals which are not occupied in the ground state. In the **6-31G**** basis set, excited atomic orbitals are included for all atoms (for example d-orbital functions for O atoms), while in the **6-31G*** basis set, the excited atomic orbitals are included for all elements but H atoms. It turns out that H atoms are hard to polarize so it is often a good approximation to only include polarization of the heavier atoms.

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