Slater Determinants

Wavefunctions must be antisymmetric with respect to simultaneous exchange of space and spin coordinates. We can obtain antisymmetrized wavefunctions using Slater Determinants, where the rows represent spin orbitals and the columns represent electrons.

A spin orbital is the product of a spatial and a spin part, such as $1s(1)\alpha(1)$

For He, the Slater determinant is:

$$
\psi_{He} = \frac{1}{\sqrt{2}} \left[ \begin{array}{cc}
1s(1)\alpha(1) & 1s(2)\alpha(2) \\
1s(1)\beta(1) & 1s(2)\beta(2)
\end{array} \right]
$$

In general, for a system of N electrons with spin orbitals $U_i$ the Slater determinant is:

$$
\psi = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc}
U_1(1) & U_1(2) & \cdots & U_1(N) \\
U_2(1) & U_2(2) & \cdots & U_2(N) \\
\vdots & \vdots & \ddots & \vdots \\
U_N(1) & U_N(2) & \cdots & U_N(N)
\end{array} \right|
$$

Slater Type Orbitals

A convenient alternate form of a hydrogen-like orbital is a Slater Type Orbital (STO).

The functional form of an STO is:  

$$
\psi_{STO} = R(n,Z,s)Y_{l,m}
$$

where $R(n,Z,s) = r^{(n-1)} \exp\left[-(Z-s)r/n\right]$

and $Y_{l,m}$ are the spherical harmonics that were derived for the hydrogen-like wavefunctions.
Variation Theorem

If the Hamiltonian $\hat{H}$ is time-independent and the trial function $\phi$ is well behaved, then

$$\langle E \rangle = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_1,$$

where $E_1$ is the lowest energy eigenvalue of the system described by $\hat{H}$.

The goal is to find the $\phi$ that gives the lowest $\langle E \rangle$. The lower the value of $\langle E \rangle$, the closer $\phi$ approaches the real wavefunction $\psi_1$.

Procedure for linear variation method:

1. Define the basis from which to construct molecular orbitals in $\phi$.
2. Calculate terms $H_{ij}$ and $S_{ij}$ and build up the secular determinant which equals zero.
3. Expand the secular determinant and solve for the energy roots.
4. Substitute energy roots into the secular equations to solve for the coefficients of the basis functions for each MO (one MO per energy root).

Linear variation functions:

$$\phi = \sum_{i=1}^{n} c_i \psi_i$$

$$S_{ij} = \langle \psi_i | \psi_j \rangle = \int \psi_i^* \psi_j d\tau$$

$$H_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle = \int \psi_i^* \hat{H} \psi_j d\tau$$

$$\langle E \rangle = \frac{\sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j \langle \psi_i | \hat{H} | \psi_j \rangle}{\sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j \langle \psi_i | \psi_j \rangle}$$

Minimize $\langle E \rangle$ with respect to $c$’s:

$$\frac{\partial \langle E \rangle}{\partial c_i} = 0 \quad i = 1, 2, \ldots, n$$

$$\sum_{j=1}^{n} \left[ (H_{ij} - \langle E \rangle S_{ij}) c_j \right] = 0 \quad i = 1, 2, \ldots, n$$

$n$ simultaneous, linear homogeneous equations.

Parenthetical terms make up the secular determinant, equal to zero.

$n$ roots $\langle E \rangle_i \quad i = 1, 2, \ldots, n$

Each root corresponds to a molecular orbital $\phi^{(i)} = c_1^{(i)} \psi_1 + c_2^{(i)} \psi_2 + \ldots + c_n^{(i)} \psi_n$.  

\[ 2 \]
For 2 variation functions (n=2), the secular determinant is:

\[
\begin{vmatrix}
H_{11} - \langle E \rangle S_{11} & H_{12} - \langle E \rangle S_{12} \\
H_{21} - \langle E \rangle S_{21} & H_{22} - \langle E \rangle S_{22}
\end{vmatrix} = 0
\]

To obtain the ground state variational solution, solve for the lowest energy solution, \( \langle E \rangle_1 \), from the secular determinant and plug \( \langle E \rangle_1 \) back into the simultaneous, linear homogeneous equations to determine the coefficients, \( c_1^{(1)} \) and \( c_2^{(1)} \), using the normalization of the trial function

\[
\int \phi^{(1)*} \phi^{(1)} d\tau = 1.
\]

To obtain the excited state variational solution, do the same for the second energy, \( \langle E \rangle_2 \), to solve for the coefficients, \( c_1^{(2)} \) and \( c_2^{(2)} \).

In general, the determinant of a 2 x 2 matrix is:

\[
\begin{vmatrix}
M_{11} & M_{12} \\
M_{21} & M_{22}
\end{vmatrix} = M_{11}M_{22} - M_{12}M_{21}
\]

If a degeneracy is encountered where \( \langle E \rangle_i = \langle E \rangle_j \), then the n simultaneous, linear homogeneous equations and the normalization constraint will not specify a unique solution for either energy. To determine the corresponding MOs, select a convenient form of the MO corresponding to \( \langle E \rangle_i \) and another convenient form of a different MO for \( \langle E \rangle_j \). Then use the Schmidt orthogonalization procedure to make the two MO’s orthogonal. Normalize the new MO.
Hückel Molecular Orbital Method

Focus only on $\pi$ electrons.

Assumes that $\pi$ electrons independent of $\sigma$ electrons and that $\pi$ electrons are independent of each other. We applied the method only to hydrocarbons.

Construct $\pi$ molecular orbitals by taking linear combinations of $2p_x$ atomic orbitals on N carbon atoms. If a carbon atom has no $\pi$ electrons, it is not included in the MO.

$$\phi = \sum_{i=1}^{N} c_i \chi_i$$

Uses secular determinant to calculate energies associated with $\pi$ molecular orbitals. The method differs from the variational method in that the integrals $H_{ij}$ and $S_{ij}$ of the secular determinant are never evaluated. These are replaced by experimental values $\alpha$ for $H_{ii}$ and $\beta$ for $H_{ij}$ where $i$ and $j$ are nearest neighbors. $H_{ij} = 0$ if $i$ and $j$ are not nearest neighbors. The $S_{ij}$ of the secular determinant are set equal to the Kronecker delta $S_{ij} = \delta_{ij}$. The method is semiempirical.

$\alpha$ is called the coulomb integral. It describes the attraction of a $\pi$ electron to its nucleus. $\beta$ is called the bond integral. It describes attraction of a $\pi$ electron to two neighboring nuclei.

We defined a variable $x$ as: $x \equiv (\alpha - E) / \beta$

The Hückel determinant for a molecule contains $x$’s along the diagonal, 1’s for off-diagonal elements connecting nearest neighboring atoms, and 0’s for all other elements.

The Hückel determinant for the allyl radical $H_2C^1 - C^2H - C^3H_2$ is

$$\begin{vmatrix} x & 0 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 = x^3 - 2x : \quad x = 0, \pm \sqrt{2}$$

Arrange energies in order of lowest to highest. Substitute each energy into simultaneous equations associated with secular determinant. Solve for coefficients for each MO.

In cases of degeneracy, use Schmidt orthogonalization procedure to produce orthogonal MOs.

Calculate the charge density on atom $i$ with: $q_i = \sum_{k}^{all\ MOs} n_k c_{ik}^2$

Calculate the $\pi$-bond order between atoms $i$ and $j$ with: $p_{ij} = \sum_{k}^{all\ MOs} n_k c_{ik} c_{jk}$

where $n_k$ is the occupation number of orbital $k$ (0, 1, or 2).
SCF LCAO-MO Theory

Based on variational method. We restricted our discussion to closed shell species, meaning that each MO is doubly occupied.

Molecular Hamiltonian:
\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{2n} \nabla_i^2 - \sum_{\mu=1}^{N} \sum_{i=1}^{2n} Z_\mu / r_{\mu i} + \sum_{i=1}^{2n-1} \sum_{j=i+1}^{2n} 1/r_{ij}
\]

Nuclear Repulsion:
\[
V_{nm} = \sum_{\mu=1}^{N-1} \sum_{\nu=\mu+1}^{N} Z_\mu Z_\nu / r_{\mu \nu}
\]

Wavefunction is the antisymmetrized product of one electron MOs:
\[
\psi = \left| \phi_1(1)\phi_2(2)\cdots\phi_n(2n-1)\phi_n(2n) \right|, \text{ where the straight brackets indicate a Slater determinant.}
\]

Each MO is a linear combination of atomic orbitals (AO):
\[
\phi = \sum_{i=1}^{q} c_i \chi_i
\]

The choice of which AOs to include in the MOs is determined by the basis set. Minimal basis: only include those AOs that are occupied in the isolated atoms. Double zeta basis: represent the radial part of each AO as a sum of two radial functions, one having a large \( \zeta \) (contracted) and another having a small \( \zeta \) (diffuse). Polarization functions: d-type AO to allow polarization of electron density by molecular environment.

The Fock operator is used to calculate the SCF one electron energy:
\[
\hat{F}(1) = -\frac{1}{2} \nabla_1^2 - \sum_{\mu=1}^{N} Z_\mu / r_{\mu 1} + \sum_{j=1}^{n} \left( 2\hat{J}_j - \hat{K}_j \right)
\]

where \( N \) is the number of nuclei, \( n \) is the number of MOs and \( \hat{J}_j \) and \( \hat{K}_j \) are defined as:
\[
\hat{J}_j = \int \phi_1^*(2)(1/r_{12})\phi_2(2)d\tau(2)
\]
\[
\hat{K}_j \phi_1(1) = \int \phi_1^*(2)(1/r_{12})\phi_2(2)d\tau(2)\phi_1(1)
\]

These operators are used to produce:
\[
\langle \phi | \hat{J}_j | \phi \rangle = J_{ij}
\]
\[
\langle \phi | \hat{K}_j | \phi \rangle = K_{ij}
\]
\[
\langle \phi | \hat{F} | \phi \rangle = \varepsilon_i \text{ interpreted as the one electron energy for orbital } i.
\]
\[
\varepsilon_i = H_{ii} + \sum_{j=1}^{N} \left( 2J_{ij} - K_{ij} \right)
\]
The sum over one electron energies is not the total energy because it over counts the interelectron repulsion and exchange terms. The total electronic energy is given by:

\[
E_{\text{elec}} = \sum_{i=1}^{n} \left[ 2\epsilon_i - \sum_{j=1}^{n} \left( 2J_{ij} - K_{ij} \right) \right] \quad \text{or} \quad E_{\text{elec}} = \sum_{i=1}^{n} \left[ 2H_{ii} + \sum_{j=1}^{n} \left( 2J_{ij} - K_{ij} \right) \right] \quad \text{or} \quad E_{\text{elec}} = \sum_{i=1}^{n} \left[ \epsilon_i + H_{ii} \right]
\]

The total SCF energy is given by

\[
E_{\text{tot}} = E_{\text{elec}} + V_{nn}
\]

Koopmans’ theorem states that if we neglect orbital reorganization after ionization, the ionization energy, \( I_k^o \), for removing an electron from orbital \( k \) of the neutral ground state molecule or atom is

\[
I_k^o = -\epsilon_k
\]

The electron affinity under the same assumptions is given by

\[
E_{A_k}^o = \epsilon_k
\]

The SCF method does not calculate electron correlation energy because the independent electron wavefunction cannot account for this behavior.

Configuration Interaction (CI) is a method that uses multiple electronic configurations to account for electron correlation. The method does this by defining a wavefunction which is itself a linear combination of single determinental wavefunctions each corresponding to a particular electronic configuration.

\[
\psi_{\text{ci}} = C_1\psi_1 + C_2\psi_2 + \cdots
\]

For electronic configurations to mix in a CI calculation, they must have:

1) like symmetry (gerade or ungerade)
2) same angular momentum (spin and orbital)

In the limit of full CI and a complete basis, the method can calculate all of the correlation energy and obtain an exact solution to the Schrödinger equation.
Perturbation Theory

Unperturbed system described by:
\[ \hat{H}^{(0)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \]

Perturbed system described by:
\[ \hat{H} \phi_n = W_n \phi_n \]
\[ \hat{H} = \hat{H}^{(0)} + \lambda \hat{H}' : \lambda = 1 \]
\[ W_n = E_n^{(0)} + \lambda W_n^{(1)} + \lambda^2 W_n^{(2)} + \cdots : \lambda = 1 \]
\[ \phi_n = \psi_n^{(0)} + \lambda \phi_n^{(1)} + \lambda^2 \phi_n^{(2)} + \cdots : \lambda = 1 \]

where \( W_n^{(1)} \) is the first order correction to the energy, \( W_n^{(2)} \) is the second order energy correction, and so on. \( \phi_n^{(1)} \) is the first order correction to the wavefunction, \( \phi_n^{(2)} \) is the second order correction, and so on.

The first order energy correction is given by:
\[ W_n^{(1)} = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} \, d\tau \]

The first order correction to the wavefunction is:
\[ \phi_n^{(1)} = \sum_{j \neq n} \frac{\langle \psi_j^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_j^{(0)}} \psi_j^{(0)} \]

Procedure:
1. Separate the system into an unperturbed part, for which the wavefunctions and energies are known (or are easy to calculate), and a perturbation.
2. Determine the unperturbed wavefunction and energies.
3. Calculate the first order energy and wavefunction corrections, and use these to determine the first order approximation to the energy and wavefunction.
4. Continue to calculate higher order corrections to improve the solution.

We applied perturbation theory to the He atom. In this case, the unperturbed system was the sum of two independent hydrogen-like atom systems, and the perturbation was the electron-electron repulsion term.