Foundations of Molecular Orbital Theory

Quantum mechanics and the wave function

The rules governing microscopic and macroscopic systems are different. Max Plank (1900): blackbody radiation emitted by microscopic particles was limited to certain discrete values – 'quantized'. Such quantization was essential for reconciling large differences between predictions from classical models and experiment. Quantization is not only a characteristic of light, but also of the fundamental particles from which matter is constructed. Bound electrons in atoms, in particular, are clearly limited to discrete energies (levels) as indicated by their ultraviolet and visible line spectra. This phenomenon has no classical correspondence – in a classical system, obeying Newtonian mechanics, energy can vary continuously – a different mechanics was required.

Wave mechanics – standing waves are also a quantized phenomenon. De Broglie – matter can indeed be shown to have wavelike properties. However, it also has particle-like properties – to properly account for this duality, quantum mechanics was developed.

The fundamental postulate of quantum mechanics – wave function exists for any chemical system, appropriate operators (functions), which act upon Ψ return the observable properties of the system:

$$\vartheta\Psi = e\Psi$$

ϑ - an operator, e – a scalar value for some property of the system. When the equation holds,
Ψ - an eigenfunction, e – an eigenvalue.
$|\Psi|^2$: the probability that a chemical system will be found within some region of multidimensional space is equal to the integral of $|\Psi|^2$ over that region of space.

The postulates place certain constraints on an acceptable wave function: 1) for a bound particle, the normalized integral of $|\Psi|^2$ over all space must be unity (the probability of finding it somewhere is one); 2) Ψ must be continuous and single-valued.

The Hamiltonian operator

The operator that returns the system energy, E, as an eigenvalue is called Hamiltonian operator: $H\Psi = E\Psi$ **- Shrödinger equation**

The Hamiltonian operator takes into account five contributions to the total energy: the kinetic energy of the electrons and nuclei, the attraction of the electrons to the nuclei, and the interelectronic and internuclear repulsions:

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_k \frac{\hbar^2}{2m_e}\nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}}$$

$\hbar$ - Plank's constant divided by 2π; ∇^2 - the Laplasian operator: $\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$

The Hamiltonian operator is composed from the kinetic and potential energy parts. The potential energy parts are the same as in classical mechanics. The kinetic energy for a QM particle is not $|\mathbf{p}|^2/2m$ but $T = -\frac{\hbar^2}{2m}\nabla^2$

The Shrödinger equation has many acceptable eigenfunctions Ψ for a given molecule, each characterized by a different associated eigenvalue E. There is a complete set of Ψ_i with eigenvalues E_i. These eigenfunctions are orthonormal:

$\int \Psi_i \Psi_j dr = \delta_{ij}$ - 1 if $i = j$ and 0 otherwise.

$$\int \Psi_j H \Psi_i = \int \Psi_j E_i \Psi_i \qquad \int \Psi_j H \Psi_i dr = E_i \delta_{ij} \qquad \int \Psi_i H \Psi_i = E_i$$

With a wave function in hand, one can simply construct and calculate the integral to get the molecular energy.

The variational principle

Let's assume we can pick and arbitrary function, Φ, which is indeed an eigenfunction for the specific case of the Shrödinger equation. Since we defined the set of orthonormal wave functions Ψ_i to be complete, the function Φ must be some linear combination of the Ψ_i,

$$\Phi = \sum_i c_i \Psi_i$$

$$\int \Phi^2 dr = 1 = \int \sum_i c_i \Psi_i \sum_j c_j \Psi_j dr = \sum_{ij} c_i c_j \int \Psi_i \Psi_j dr = \sum_{ij} c_i c_j \delta_{ij} = \sum_i c_i^2$$

$$\int \Phi H \Phi dr = 1 = \int \left(\sum_i c_i \Psi_i \right) H \left(\sum_j c_j \Psi_j \right) dr = \sum_{ij} c_i c_j \int \Psi_i H \Psi_j dr = \sum_{ij} c_i c_j E_j \delta_{ij} = \sum_i c_i^2 E_i$$

The energy associated with the generic function Φ is determinable from all the coefficients c_i and their associated energies E_i. In the set of all E_i there must be a lowest energy value – we call that energy, corresponding to the ground state, E_0. Now, we can combine the results of the two equations:

$$\int \Phi H \Phi dr - E_0 \int \Phi^2 dr = \sum_i c_i^2 \left(E_i - E_0 \right)$$

Assuming the coefficients to be real numbers, $c_i^2 \geq 0$, $E_i - E_0 \geq 0$

$$\int \Phi H \Phi dr - E_0 \int \Phi^2 dr \geq 0 \qquad \frac{\int \Phi H \Phi dr}{\int \Phi^2 dr} \geq E_0$$

When Φ is normalized, $\int \Phi H \Phi dr \geq E_0$ - the variational principle.

If we are looking for the best wave function to define the ground state of a system, we can judge the quality of wave functions by their associated energies: *the lower the better*. We can use the calculus tools to minimize the integral with respect to the coefficients.

The Born-Oppenheimer Approximation

Under typical conditions, the nuclei of molecular systems are moving much more slowly than the electrons (proton and neutrons are ~1800 times more massive than electrons) – electronic relaxation with respect to nuclear motion is instantaneous. It is convenient to decouple these two motions and compute electronic energies for fixed nuclear positions. The nuclear kinetic motion term is taken to be independent of the electrons, correlation in the attractive electron-nuclear potential energy term is eliminated, and the repulsive nuclear-nuclear potential energy term becomes a simply evaluated constant for a given geometry. The electronic Schrödinger equation: $(H_{el} + V_N)\Psi_{\text{el}}(\mathbf{q}_i;\mathbf{q}_k) = E_{\text{el}}\Psi_{\text{el}}(\mathbf{q}_i;\mathbf{q}_k)$

Wave functions are invariant to the appearance of constant term in the Hamiltonian – in practice, one can almost always solve this equation without the inclusion of V_N and then add V_N to the obtained eigenvalue to obtain E_{el}.

The Born-Oppenheimer approximation is entirely justified in most cases. It has very profound consequences – without it we would lack the concept of a potential energy surface: The PES is the surface defined by E_{el} over all possible nuclear coordinates. We would further lack the concepts of equilibrium and transition state geometries, since these are defined as critical points on the PES; instead we would be reduced to discussing high-probability regions of the nuclear wave functions.

Construction of trial wave functions

Due to the Born-Oppenheimer approximation, electron-nuclear correlation has been removed, but the correlation between individual electrons is still present and is hard to deal with. The simplest possible approach – to ignore it. Let's consider systems with only a single electron. The electronic wave function is then reduced to depending only on the fixed nuclear coordinates and the three Cartesian coordinates of the single electron. The eigenfunctions of the electronic Schrödinger equation are called molecular orbitals (MOs). The pure electronic energy eigenvalue associated with each molecular orbital is the energy of the electron in that orbital. One might determine this energy experimentally by measuring the ionization potential of the electron when it occupies this orbital. To measure E_{el}, which includes the nuclear repulsion energy, one would need to determine the atomization energy – the energy required to ionize the electron and to remove all of the nuclei to infinite separation – can be derived from heats of formation.

The LCAO basis set approach

We may imagine constructing wave functions in any fashion and we may judge the quality of our wave functions by evaluation of the energy eigenvalues associated with each. The one with the lowest energy will be the most accurate and presumably the best one to use for computing other properties by the application of other operators. How can an arbitrary function be represented by a combination of more convenient functions? The convenient functions are called a '**basis set**'.

In our QM system, we have temporarily restricted ourselves to systems of one electron. If our system has only one nucleus, the Schrödinger equation can be solved exactly – the eigenfunctions are hydrogenic orbitals: 1s, 2s, 2p, 3s, 3p, 3d, …

These orbitals, as functions, may be useful in the construction of more complicated molecular orbitals. We will construct a guess wave function ϕ as a linear combination of atomic wave functions φ:

$$\phi = \sum_{i=1}^{N} a_i \varphi_i$$

This construction is known as the linear combination of atomic orbitals (MO-LCAO) approach. LCAO are normally centered on the atoms of the molecule. The summation in the equation has an upper limit N – we cannot work with an infinite basis set in any convenient way. However, the more atomic orbitals we allow into our basis set, the closer our basis will come to covering the true molecular orbital space. There may be very many 'true' one-electron MOs that are very high in energy. Accurately describing these MOs may require some unusual basis functions, e.g. very diffuse functions to describe weakly bound electrons – in Rydberg states. In general, we have to distinguish between chemically meaningful AOs and basis functions as a mathematical tool.

The Secular Equation

$$E = \frac{\int \left(\sum_i a_i \varphi_i \right) H \left(\sum_j a_j \varphi_j \right) dr}{\int \left(\sum_i a_i \varphi_i \right) \left(\sum_j a_j \varphi_j \right) dr} = \frac{\sum_{ij} a_i a_j \int \varphi_i H \varphi_j dr}{\sum_{ij} a_i a_j \int \varphi_i \varphi_j dr} = \frac{\sum_{ij} a_i a_j H_{ij}}{\sum_{ij} a_i a_j S_{ij}}$$

$H_{ij} = \int \varphi_i H \varphi_j dr$ - a resonance integral, $S_{ij} = \int \varphi_i \varphi_j dr$ - an overlap integral characterizes the extent to which any two basis functions overlap in a phase-matched fashion in space.

H_{ii} – corresponds to the energy of a single electron occupying basis function i – essentially equivalent to the ionization potential of AO.

According to the variational principle, as we get closer and closer to the 'true' one-electron ground-state wave functions, we will obtain lower and lower energies from our guess. Thus, once we have selected a basis set, we would like to choose the coefficients a_i so as to minimize the energy for all possible combinations of our basis functions. A necessary condition for a function to be at its minimum is that its derivatices with respect to all of its free variables are zero: for all k $\dfrac{\partial E}{\partial a_k} = 0$

After partial differentiation, we obtain the following equations:

For all k $\displaystyle\sum_{i=1}^{N} a_i \left(H_{ki} - ES_{ki} \right) = 0$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0$$

Secular Equation

In general, there will be N roots E which satisfy the secular equation – N energies E_j, each of them give rise to a different set of coefficients, a_{ij}, which can be found by solving the set of line equations using E_j, and these coefficients will define an optimal wave function φ_j within the gi set:

$$\varphi_j = \sum_i^N a_{ij} \varphi_i$$

In a one-electron system, the lowest energy molecular orbital defines the ground state of the system and the higher energy orbitals are excited states. These are different MOs and they have different basis function coefficients. The variational principle holds for the excited states the calculated energy of a guess wave function for an excited state will be bounded from below by the true excited state energy.

To find the optimal one-electron wave function for a molecular system:

1. Select a set of N basis functions.
2. For that set of basis functions, determine all N^2 values of both H_{ij} and S_{ij}.
3. Form the secular determinant, and determine the N roots E_j of the secular equation.
4. For each of the N values of E_j, solve the set of linear equations in order to determine the basis set coefficients a_{ij} for that MO.

Hückel Theory

Fundamental Principles

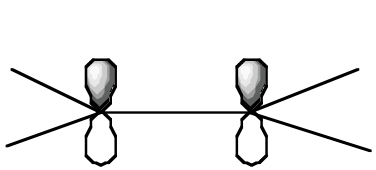
Hückel theory – was developed in the 1930s to explain some of the unique properties of unsaturated and aromatic hydrocarbons:

(a) The basis set is formed entirely from parallel carbon 2p orbitals, one per atom (π systen

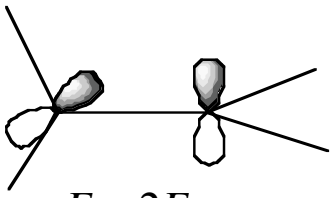
(b) The overlap matrix is defined by $S_{ij} = \delta_{ij}$

(c) Matrix elements H_{ii} are set equal to the negative of the ionization potential of the methy radical – the orbital energy of the singly occupied 2p orbital in the prototypical system defining sp^2 carbon hybridization (written as α).

(d) Matrix elements H_{ij} between neighbors are also derived from experimental information: 90° rotation in ethylene.



$E = E_\pi$

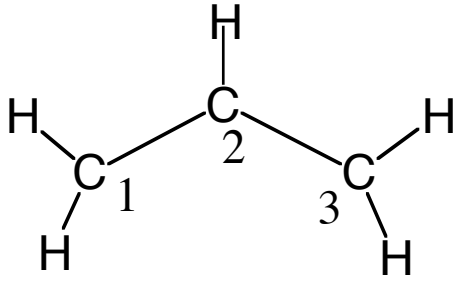


$E = 2E_p$

$E_p = \alpha \qquad E_\pi = 2\alpha + 2\beta \qquad \Delta E = 2E_p - E_\pi \qquad \Delta E/2 = \beta$

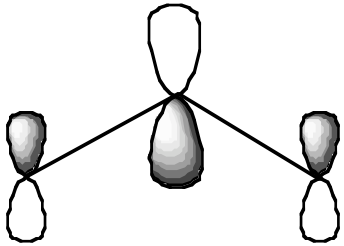
(e) Matrix elements H_{ij} between carbon 2p orbitals more distant than nearest neighbors are set equal to zero.

Application to the allyl system



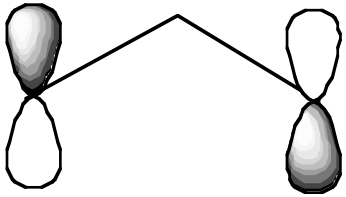
p_C

$\phi_1 =$



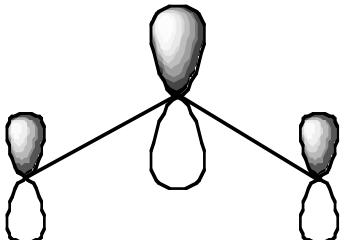
$\alpha - \sqrt{2}\beta$

$\phi_2 =$

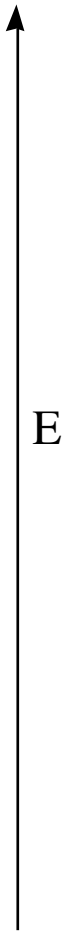


α

$\phi_3 =$



$\alpha + \sqrt{2}\beta$



E

Secular equation: $\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$

$(\alpha - E)^3 + (\beta^2 \times 0) - [0 \times (\alpha - E) \times 0] - \beta^2(\alpha - E) - (\alpha - E)\beta^2 = 0$

$E = \alpha + \sqrt{2}\beta \;, \qquad \alpha, \qquad \alpha - \sqrt{2}\beta$

The lowest (ground) state solution is $\alpha + \sqrt{2}\beta \qquad (\alpha,\ \beta < 0)$

$$a_1\left[\alpha - \left(\alpha + \sqrt{2}\beta\right)\cdot 1\right] + a_2\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\cdot 0\right] + a_3\left[0 - \left(\alpha + \sqrt{2}\beta\right)\cdot 0\right] = 0$$

$$a_1\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\cdot 0\right] + a_2\left[\alpha - \left(\alpha + \sqrt{2}\beta\right)\cdot 1\right] + a_3\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\cdot 0\right] = 0$$

$$a_1\left[0 - \left(\alpha + \sqrt{2}\beta\right)\cdot 0\right] + a_2\left[\beta - \left(\alpha + \sqrt{2}\beta\right)\cdot 0\right] + a_3\left[\alpha - \left(\alpha + \sqrt{2}\beta\right)\cdot 1\right] = 0$$

$a_2 = \sqrt{2}a_1 \qquad a_3 = a_1$

From normalization: $a_{11} = \frac{1}{2}\,, \quad a_{21} = \frac{\sqrt{2}}{2}, \quad a_{31} = \frac{1}{2} \qquad\qquad \phi_1 = \frac{1}{2}p_1 + \frac{\sqrt{2}}{2}p_2 + \frac{1}{2}p_3$

By choosing the higher energy roots, we may solve two other sets of linear equations and determine the coefficients required to construct ϕ_2 (from $E = \alpha$) and ϕ_3 (from $E = \alpha - \sqrt{2}\beta$):

$$a_{12} = \frac{\sqrt{2}}{2}, \qquad a_{22} = 0, \quad a_{32} = -\frac{\sqrt{2}}{2}$$

$$a_{13} = \frac{1}{2}, \qquad a_{23} = -\frac{\sqrt{2}}{2}, \qquad a_{32} = \frac{1}{2}$$

Many-electron Wave Functions

Hartree-product wave functions

When the only terms in the Hamiltonian are the one-electron kinetic energy and nuclear-electron attraction terms, the operator is 'separable' and may be expressed as

$$H = \sum_{i=1}^{N} h_i \qquad h_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{r_{ik}}$$

N – the total number of electrons, M – the total number of nuclei

Eigenfunctions of the one-electron Hamiltonian must satisfy the corresponding one-electron Schrödinger equation: $h_i \psi_i = \varepsilon_i \psi_i$

Because the Hamiltonian is separable in this case, its many-electron eigenfunctions can be constructed as products of one-electron eigenfunctions: $\Psi_{HP} = \psi_1 \psi_2 \cdots \psi_N$

$$H\Psi_{HP} = H\psi_1\psi_2\cdots\psi_N = \sum_{i=1}^{N} h_i\psi_1\psi_2\cdots\psi_N = (h_1\psi_1)\psi_2\cdots\psi_N + \psi_1(h_2\psi_2)\cdots\psi_N + \ldots + \psi_1\psi_2\cdots(h_N\psi_N)$$

$$= (\varepsilon_1\psi_1)\psi_2\cdots\psi_N + \psi_1(\varepsilon_2\psi_2)\cdots\psi_N + \ldots + \psi_1\psi_2\cdots(\varepsilon_N\psi_N) = \sum_{i=1}^{N} \varepsilon_i\psi_1\psi_2\cdots\psi_N = \left(\sum_{i=1}^{N} \varepsilon_i\right)\Psi_{HP}$$

The Hartree Hamiltonian

The 'separable' Hamiltonian defined above does not include interelectronic repulsion, computation of which is complicated because it depends not on one electron but on all possible simultaneous pairwise interactions. How useful is the Hartree-product wave function in computing energies from the correct Hamiltonian? We wish to find orbitals ψ that minimize $\langle \Psi_{HP} | H | \Psi_{HP} \rangle$. One can show that each orbital ψ_i is an eigenfunction of its own operator h_i defined by

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{r_{ik}} + V_i\{j\}$$

$V_i\{j\} = \sum_{j \neq i} \int \frac{\rho_j}{r_{ij}} dr$ - an interaction potential with all of the other electrons occupying orbitals $\{j\}$, ρ_j – the charge probability density associated with electron j. Electrons are treated as wave functions and have their charge spread out, so integration over all space is necessary. Recall that $\rho_j = |\psi_j|^2$. Our goal is find the one-electron wave functions, but the one-electron Hamiltonians in turn depend on them. What can be done to solve this problem?

Hartree (1928) – **'self-consistent field' (SCF) method**.

In the first step of the SCF process, one guesses the wave function ψ for all of the occupied MOs and uses these to construct the necessary one-electron operators h. Solution of each one-electron Schrödinger (differential) equation provides a new set of ψ, presumably different from the initial guess. Then, the one-electron Hamiltonians are formed anew using these presumably more accurate ψ to determine each necessary ρ, and the process is repeated to obtain a still better set of ψ. At some point, the difference between a newly determined set and the immediately preceding set is below some threshold criterion, and the final set of ψ is referred to as the 'converged' SCF orbitals.

The sum of the individual operators h defines a separable Hamiltonian operator for which Ψ_{HP} is an eigenfunction. This separable Hamiltonian corresponds to a 'non-interacting' system of electrons in the sense that each individual electron sees simply a constant potential with which it interacts. The potential does derive in an average way from the other electrons but their interaction is not accounted for instantaneously. Double count of electron repulsion: both h_i and h_j include the repulsion between electron i and electron j. To take care of this problem, the energy is computed

$$E = \sum_i \varepsilon_i - \frac{1}{2}\sum_{i \neq j} \int\int \frac{|\psi_i|^2 |\psi_j|^2}{r_{ij}} dr_i dr_j \qquad \int\int \frac{|\psi_i|^2 |\psi_j|^2}{r_{ij}} dr_i dr_j = J_{ij} \quad \text{-} \quad \text{Coulomb integral}$$

Now we have some (approximate) way to calculate MOs and their energies. The next question is: How electrons should be placed on these orbitals?

Electron Spin and Antisymmetry

All electrons are characterized by a spin quantum number. The electron spin function is an eigenfunction of the operator S_z and has only two eigenvalues, $\pm\hbar/2$ (usually denoted as α and β). Spin quantum number – a consequence of relativistic quantum mechanics (Einstein theory) to the electron. Another consequence – the Pauli exclusion principle – no two electrons can be characterized by the same set of quantum numbers. Therefore, in a given MO (which defines all electronic quantum numbers except spin) there are only two possible choices for the remaining quantum number, α or β - maximum two electrons may be placed in any MO. We may try to write a ground state Hartree-product wave function for a system with two electrons of the same spin α as $^3\Psi_{HP} = \psi_a(1)\alpha(1)\psi_b(2)\alpha(2)$

However, this wave function has a fundamental flaw – relativistic quantum field theory requires that electronic wave function must change sign whenever the coordinates of two electrons are interchanged – 'antisymmetric' property. Let's introduce the permutation operator P_{ij} – the operator that interchanges the coordinates of electrons i and j. The Pauli principle for a system of N electrons: $P_{ij}\Psi\left[q_1(1),\ldots,q_i(i),\ldots,q_j(j),\ldots q_N(N)\right] =$

$$\Psi\left[q_1(1),\ldots,q_j(i),\ldots,q_i(j),\ldots q_N(N)\right] = -\Psi\left[q_1(1),\ldots,q_i(i),\ldots,q_j(j),\ldots q_N(N)\right]$$

If we apply P_{12} to the Hartree-product wave function:

$$P_{12}\left[\psi_a(1)\alpha(1)\psi_b(2)\alpha(2)\right] = \psi_b(1)\alpha(1)\psi_a(2)\alpha(2) \neq -\psi_a(1)\alpha(1)\psi_b(2)\alpha(2)$$

A slight modification to the Hartree-product wave function can performed to make it to satisfy to the Pauli principle.

$$^3\Psi_{SD} = \frac{1}{\sqrt{2}}\left[\psi_a(1)\alpha(1)\psi_b(2)\alpha(2) - \psi_a(2)\alpha(2)\psi_b(1)\alpha(1)\right]$$

Slater determinants

$$^3\Psi_{SD} = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_a(1)\alpha(1) & \psi_b(1)\alpha(1)\\ \psi_a(2)\alpha(2) & \psi_b(2)\alpha(2)\end{vmatrix}$$

The permutation operator P applied to a determinant has the effect of interchanging two of the rows. A general property of a determinant – it changes sign when any two rows (columns) are interchanged – can be utilized for constructing antisymmetric wave functions.

For a general case:

$$\Psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix}$$

N – the total number of electrons, χ - a spin-orbital, a product of a spatial orbital and an electron spin eigenfunction. More compactly

$$\Psi_{SD} = \left| \chi_1 \chi_2 \chi_3 \cdots \chi_N \right\rangle$$

If two spin-orbitals differ only by the spin eigenfunction (together they represent a doubly filled orbital) this is typically represented by writing the spatial wave function with a superscript 2 to indicate double occupation. Thus, if χ_1 and χ_2 represented α and β spins in spatial orbital ψ_1, one writes

$$\Psi_{SD} = \left| \psi_1^2 \chi_3 \cdots \chi_N \right\rangle$$

Interesting properties of Slater determinants: every electron appears in every spin orbital of the expansion – a manifestation of the fact that quantum particles are indistinguishable. A second feature – so-called quantum mechanical exchange.

Consider the energy of interelectronic repulsion for ${}^3\Psi_{SD}$:

$$\int {}^3\Psi_{SD}\frac{1}{r_{12}}{}^3\Psi_{SD}dr_1d\omega_1dr_2d\omega_2 =$$

$$\frac{1}{2}\left[\int|\psi_a(1)|^2\frac{1}{r_{12}}|\psi_b(2)|^2dr_1dr_2 - 2\int\psi_a(1)\psi_b(1)\frac{1}{r_{12}}\psi_b(2)\psi_a(2)dr_1dr_2 + \int|\psi_a(2)|^2\frac{1}{r_{12}}|\psi_b(1)|^2dr_1dr_2\right]$$

$$= \frac{1}{2}\left(J_{ab} - 2\int\psi_a(1)\psi_b(1)\frac{1}{r_{12}}\psi_b(2)\psi_a(2)dr_1dr_2 + J_{ab}\right) = J_{ab} - K_{ab}$$

For this wave function the classical Coulomb repulsion between the electron clouds in orbitals *a* and *b* is reduced by K_{ab} (**exchange integral**) – a consequence of the Pauli principle – reflects the reduced probability of finding two electrons of the same spin close to one another – a so-called 'Fermi hole' surrounding each electron. This property is a correlation effect unique to electrons of the same spin. If we consider the Slater determinant wave function formed from different spins:

$${}^1\Psi_{SD} = \frac{1}{\sqrt{2}}\left[\psi_a(1)\alpha(1)\psi_b(2)\beta(2) - \psi_a(2)\alpha(2)\psi_b(1)\beta(1)\right]$$

$$\int {}^1\Psi_{SD}\frac{1}{r_{12}}{}^1\Psi_{SD}dr_1d\omega_1dr_2d\omega_2 = \frac{1}{2}\left(J_{ab} - 2\cdot 0 + J_{ab}\right) = J_{ab}$$

The disappearance of the exchange correlation follows from the orthogonality of the α and β spin functions.

The Hartree-Fock Self-consistent Field Method

Fock first proposed the extension of Hartree's SCF procedure to Slater-determinant wave functions. Similar to Hartree product orbitals, the HF MOs can be individually determined as eigenfunctions of a set of one-electron operators, but the interaction of each electron with the static field of all other electrons includes exchange effects on the Coulomb repulsion. Later, Roothaan (1951) described matrix algebraic equations to carry out HF calculations using a basis set representation for the MOs. We represent MOs in their typical form for closed-shell systems (all electrons spin-paired, two per occupied orbital) with wave unctions represented as a single Slater determinant.

The one-electron Fock operator is defined for each electron *i*: $$f_i = \frac{1}{2}\nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{r_{ik}} + V_i^{HF}\{j\}$$

The final term, the HF potential, is $2J_i - K_i$, and the J_i and K_i operators are Coulomb and exchange operators defined so as to compute the J_{ij} and K_{ij} integrals. To determine the MOs using the Roothaan approach, we follow the procedure analogous to that described for Hückel theory. First, given a set of *N* basis functions, we solve the secular equations:

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \cdots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \cdots & F_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \cdots & F_{NN} - ES_{NN} \end{vmatrix} = 0$$

and find its various roots E_j. The values for the matrix elements *F* and *S* are computed explicitly

S – overlap matrix elements: $$S_{ij} = \int \varphi_i \varphi_j dr$$

For a general matrix element $F_{\mu\nu}$ we compute

$$F_{\mu\nu} = \langle\mu|-\frac{1}{2}\nabla^2|\nu\rangle - \sum_{k}^{nuclei} Z_k\langle\mu|\frac{1}{r_{ik}}|\nu\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma}\left[(\mu\nu\,|\,\lambda\sigma) - \frac{1}{2}(\mu\lambda\,|\,\nu\sigma)\right]$$

$\langle\mu|g|\nu\rangle$ - one-electron integral, where g is some operator: $\langle\mu|g|\nu\rangle = \int \phi_\mu g \phi_\nu dr$

For example, if $g = 1/r_{ik}$, $\langle\mu|g|\nu\rangle = \int \phi_\mu \frac{1}{r_{ik}} \phi_\nu dr$

$(\mu\nu|\lambda\sigma)$ – two-electron (four-index) integral: $(\mu\nu\,|\,\lambda\sigma) = \int\int \phi_\mu(1)\phi_\nu(1)\frac{1}{r_{12}}\phi_\lambda(2)\phi_\sigma(2)dr(1)dr(2$

ϕ_μ and ϕ_ν represent wave function of one electron and ϕ_λ and ϕ_σ the other. $(\mu\nu|\lambda\sigma)$ – Coulomb integral and $(\mu\lambda|\nu\sigma)$ – exchange integral.

The exchange integrals are preceded by a factor of 1/2 because they are limited to electrons of the same spin while Coulomb interactions are present for any combination of spins.

The final term in the equation for matrix element $F_{\mu\nu}$ is weighted by elements of the 'density matrix' **P**. This matrix describes the degree to which individual basis functions contribute to the many-electron wave function – how energetically important the Coulomb and exchange integrals should be. If a basis function does not contribute in a significant way to any occupied MO, the integrals involving that basis function should not be important:

$$P_{\lambda\sigma} = 2\sum_{i}^{occupied} a_{\lambda i} a_{\sigma i}$$

$a_{\xi i}$ – the coefficients specifying the normalized contributions of basis function ξ to MO i. The factor of 2 – due to the fact that we are considering only singlet wave functions in which all orbitals are doubly occupied.

We need to know the orbital coefficients to form the density matrix that is used in the Fock matrix elements, but the purpose of solving the secular equation is to determine those orbital coefficients. Just as in the Hartree method, the HF method follows a SCF procedure: first we guess the orbital coefficients and then we iterate to convergence. The full process is described schematically by the flow chart (see the next page).

The chief chemical limitation of the Hartree-Fock theory – the one-electron nature of the Fock operators – other than exchange, all electron correlation is ignored. Electron correlation may be important for various molecular properties. From a practical standpoint, HF theory had some very challenging technical problems to early computational chemists. One problem – choice of a basis set. The LCAO approach using hydrogenic orbitals is attractive but this basis set requires numerical solution of the four-index integrals (in Fock matrix elements) – a very tedious process. The number of four-index integrals is huge: each index runs over the total number of basis functions – N^4 total integrals to be evaluated – this quartic scaling behavior with respect to basis-set size is the bottleneck in HF theory.

Two philosophies how to make further progress. The first one: the HF equations are very powerful but still chemically flawed. Thus, other approximations may be introduced to simplify their solution and possibly at the same time improve their accuracy (by some parameterization to reproduce key experimental quantities) – the motivation of so-called 'semiempirical' MO theories. The second philosophy – HF theory is considered as a stepping stone on the way to exact solution of the Schrödinger equation, starting from it one can develop more sophisticated methods (wave functions) to eventually approach the exact solution – '*ab initio*' MO theory.

Flaw Chart of the HF SCF procedure