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CEM 402: Advanced Physical Chemistry-III (Physical Spl.) Marks: 50 Credits: 4

Classes: 45L

Unit-1: Quantum mechanics of many electron systems-I: PG

Identical particle and Pauli's Antisymmetry principle, Slater determinant for system with more than two electrons, Eigen functions of many electron spin operator: Pure spin states, Energy expectation value of pure spin states; Orbitals in many electron atoms: The Hartree-Fock Theory, Koopman's theorem, The Hatree-Fock-Roothaan method for closed cell systems, Roothaan equation, Brillouin's theorem.

Unit-4: Computational Chemistry-I PG

Exteded Huckel theory, CNDO formalism, INDO formalism, Basic NDDO formalism: MNDO, AM1, PM3.

Ab Initio HF theory: Basis set: Gaussian functions, single Zeta, multiple Zita and split valence functions, polarization and diffuse functions.

Electron correlation in MO theory: Configuration interaction: single determinant reference, multi reference.

Unit-5: Computational Chemistry-II PG

Density Functional Theory (DFT): Philosophy, early approximations, Hohenberg-Kohn existence theorem, Hohenberg-Kohn variational theorem, Kohn-Sham SCF methodology, Exchange correlation functionals: Local density approximation, density gradient and kinetic energy corrections.

Advantages and dis-advantages of DFT compare to MO theory, General performance of DFT.

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Unit-III: Macromolecules: PG

Classification of polymers, kinetics of polymerization, Molecular weight of polymers, molecular weight determination by viscosity, osmometry, light scattering, diffusion and ultracentrifugation methods. Thermodynamics of polymer solutions. Polymer conformation.

Unit –V: Advanced electrochemistry PG

Debye Huckel theory, its modifications and extensions, mean ionic activity co-efficients, ion association, and precise determination of dissociation constants of weak electrolytes by method of emf and conductance measurements, ion-solvent interaction and solvation number. Non stationary processes in electrolytic solutions, Onsager conductance equation, effect of high electric field and frequency on ion conductance.

Overvoltage, polarography, amperometric titration, basic principles of cyclic voltammetry and coulometry, polyelectrolyte. Mechanism of multi-step electrochemical reactions, hydrogen overvoltage, thermodynamics of ideally polarized electrodes, structures of metal and semiconductor-electrolyte junctions, fuel cell, photoelectrochemical cells.

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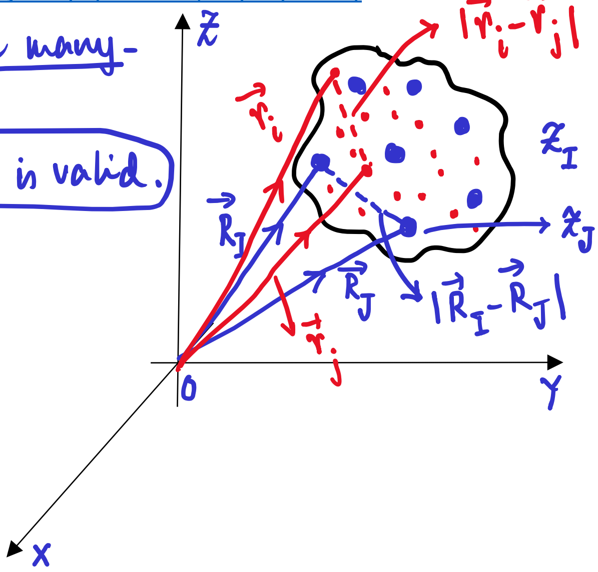
Quantum mechanical description of the many-electron systems.



$\boxed{\text{Born-Oppenheimer (BO) approximation is valid.}}$

N = no. of electrons in the molecule

N_n = no. of nuclei in the molecule

Coordinates of electrons: $\vec r_i, \vec r_j, \dots$

Coordinates of nuclei: $\vec R_I, \vec R_J, \dots$

all the nuclei in the molecule are fixed.

Hamiltonian Operator (in atomic units, under BO approximation) for the system

$$\hat H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{J=1}^{N_n}\frac{Z_J}{|\vec r_i - \vec R_J|} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{1}{|\vec r_i - \vec r_j|} \qquad \boxed{\hat H\psi = E\psi}$$

$$= \sum_{i=1}^{N}\left[\left(-\frac{1}{2}\nabla_i^2\right) - \sum_{J=1}^{N_n}\frac{Z_J}{|\vec r_i - \vec R_J|}\right] + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|\vec r_i - \vec r_j|}$$

$$= \sum_{i=1}^{N} h(r_i) + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|\vec r_i - \vec r_j|} \leftarrow \text{two-body term}$$

$\uparrow$ One-body term

* * *

How to represent a multi-electron wavefunction?

orbital ⇒ one-electron function

$$\underbrace{\phi_i}_{\text{spatial function}}(\underbrace{\vec r_j}_{\text{spatial coordinate}})\,\overbrace{\alpha}^{\text{spin function}}(\underbrace{\sigma}_{\text{spin coordinate}})$$

$\phi_i(\vec r_j)\,\beta(\sigma)$

$$\text{Spin orbital, } \chi_i(x_j) = \begin{cases} \phi_i(r_j)\,\alpha(\sigma) & \uparrow \\ \phi_i(r_j)\,\beta(\sigma) & \downarrow \end{cases}$$

x_j : combined space-spin coordinate

$x_j \equiv \{\vec r_j, \sigma\}$

Spin orbitals are orthonormal (orthogonal, as well as normalized)

$$\int_{\text{all space}} \chi_i(x_j)\,\chi_j(x_j)\,dx_j = \delta_{ij}$$

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$$\sum_{i=1}^{N} h(\vec{r}_i) = h(\vec{r}_1) + h(\vec{r}_2) + \cdots + h(\vec{r}_N)$$

If the energies (or the energy operators) are additively separable, then the corresponding wavefunction is product separable.

$\chi_i(x_1)\cdot\chi_j(x_2)\cdots\chi_k(x_N) = \psi^{HP}$: Hartree-product

$$\sum_{i=1}^{N} h(\vec{r}_i)\,\psi^{HP} = [h(r_1)+h(r_2)+\cdots+h(r_N)]\,\chi_i(x_1)\chi_j(x_2)\cdots\chi_k(x_N)$$

$$= [h(r_1)\chi_i(x_1)]\chi_j(x_2)\cdots\chi_k(x_N) + \chi_i(x_1)[h(r_2)\chi_j(x_2)]\cdots\chi_k(x_N)$$

$$\cdots + \chi_i(x_1)\chi_j(x_2)\cdots[h(r_N)\chi_k(x_N)]$$

$$= \epsilon_1\chi_i(x_1)\chi_j(x_2)\cdots\chi_k(x_N) + \epsilon_2\chi_i(x_1)\chi_j(x_2)\cdots\chi_k(x_N) + \cdots + \epsilon_N\chi_i(x_1)\chi_j(x_2)\cdots\chi_k(x_N)$$

$$= [\epsilon_1+\epsilon_2+\cdots+\epsilon_N]\,\psi^{HP}$$

or, $\sum_{i=1}^{N} h(r_i)\,\psi^{HP} = E_{HP}\,\psi^{HP} \rightarrow$ not a proper representation of a multi-electron wavefunction.

ψ^{HP} violates the antisym. principle.

$$\left.\begin{aligned}\psi^{HP}_{12}(x_1,x_2) &= \chi_i(x_1)\chi_j(x_2)\\ \psi^{HP}_{21}(x_2,x_1) &= \chi_i(x_2)\chi_j(x_1)\end{aligned}\right\}$$ none of these obey the antisym. principle

$$\psi(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\psi^{HP}_{12} - \psi^{HP}_{21}\right] = \frac{1}{\sqrt{2}}\left[\chi_i(x_1)\chi_j(x_2) - \chi_i(x_2)\chi_j(x_1)\right]$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix}\chi_i(x_1) & \chi_j(x_1)\\ \chi_i(x_2) & \chi_j(x_2)\end{vmatrix} \rightarrow$$ obeys the antisym principle

Slater determinant.

$$\psi(x_1,x_2,x_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix}\chi_i(x_1) & \chi_j(x_1) & \chi_k(x_1)\\ \chi_i(x_2) & \chi_j(x_2) & \chi_k(x_2)\\ \chi_i(x_3) & \chi_j(x_3) & \chi_k(x_3)\end{vmatrix}$$

$$\psi_{SD} = \frac{1}{\sqrt{2}}|\chi_i(x_1)\chi_j(x_2)\rangle = |\chi_i(x_1)\chi_j(x_2)\rangle = \boxed{|\chi_i\chi_j\rangle}$$

$$\psi_{SD} = |\chi_i\chi_j\chi_k\rangle$$

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Let us start with the BO Hamiltonian operator for a N electron system,

$$H = -\sum_{i=1}^{N} \frac{\nabla_{r_i}^2}{2} + \sum_{i=1}^{N}\sum_{J=1}^{N_n} -\frac{Z_j}{|r_i - R_J|} + \sum_{i=1}^{N}\sum_{j>i}^{N_n} \frac{1}{|r_i - r_j|} = \sum_{i=1}^{N} h(r_i) + \sum_{i=1}^{N}\sum_{j>i}^{N_n} \frac{1}{|r_i - r_j|}$$

Although it is obviously a bad approximation to neglect the inter-electronic repulsion term, let us assume for the moment that we have a non-interacting (NI) system.

$$H^{NI} = \sum_{i=1}^{N} h(r_i)$$

In a multi-electron system, for each electron we define a spin orbital, $\chi_i(x_j)$, to be an eigenstate of the single-particle Hamiltonian operator, $h(r_j)$.

$$\chi_i(x_j) = \begin{cases} \Phi_i(r_j)\alpha(\sigma) \\ \Phi_i(r_j)\beta(\sigma) \end{cases}$$

Therefore,

$$h(r_j)\chi_i(x_j) = \epsilon_i \chi_i(x_j), \text{ with } \delta_{ij} = \int \chi_i(x_j)\chi_j(x_j)\, dx_j$$

Since all the $h(x)$ in H^{NI} act on the single orbital dependent on x_i only, the eigenfunction of H is the product of all the single-particle spin orbitals and the corresponding eigenvalue is just the sum of their eigenvalues.

$$\Psi^{HP} = \chi_i(x_1)\chi_j(x_2)\cdots\chi_k(x_N)$$

Therefore, with Ψ^{HP}, the corresponding energy becomes,

$$E^{HP} = \epsilon_i + \epsilon_j + \cdots + \epsilon_k$$

The wave function Ψ^{HP} is called the Hartree product and is an example for an uncorrelated wave function, because the probability of finding electron 1 in a volume element dx_1 and electron 2 in dx_2 is simply the product of the individual probabilities:

$$|\chi_i(x_1)|^2 dx_1 |\chi_j(x_2)|^2 dx_2 \cdots |\chi_k(x_N)|^2 dx_N$$

In other words, we have factorized our wave function. However, Ψ^{HP} violates the anti-symmetry principle, because it is obviously symmetric when we interchange any two electronic coordinates.

Consider (for simplicity) a two-electron system, like the hydrogen molecule, where we have two possible Ψ^{HP}:

$$\Psi_{12}^{HP}(x_1, x_2) = \chi_i(x_1)\chi_j(x_2)$$
$$\Psi_{21}^{HP}(x_1, x_2) = \chi_i(x_2)\chi_j(x_1)$$

These two products can be combined into a new wave function, which obeys the anti-symmetry principle:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}[\Psi_{12}^{HP} - \Psi_{21}^{HP}] = \frac{1}{\sqrt{2}}[\chi_i(x_1)\chi_j(x_2) - \chi_i(x_2)\chi_j(x_1)]$$

Thus, the anti-symmetric wave function $\Psi(x_1, x_2)$may also be represented in the form of a determinant:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) \\ \chi_i(x_2) & \chi_j(x_2) \end{vmatrix} = \Psi^{\mathrm{SD}}(x_1, x_2)$$

This determinant is called the **Slater determinant**.

$$\psi_{SD}(x_1, x_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) \\ \chi_i(x_2) & \chi_j(x_2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left[\chi_i(x_1)\chi_j(x_2) - \chi_i(x_2)\chi_j(x_1)\right]$$

Interchanging x_1 and x_2

$$\psi_{SD}(x_2, x_1) = \frac{1}{\sqrt{2}}\left[\chi_i(x_2)\chi_j(x_1) - \chi_i(x_1)\chi_j(x_2)\right] = -\psi_{SD}(x_1, x_2)$$

$\therefore$ Any SD preserves the antisym. property of an electronic wavefunction.

For any N-electron system

$$\psi_{SD}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & & & \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix}$$

or, $\psi_{SD}(x_1, x_2, \ldots, x_N) = |\chi_i \chi_j \ldots \chi_k\rangle$

$$|\ldots \chi_m \ldots \chi_n \ldots\rangle \xrightarrow[\text{m and n}]{\text{interchange}} -|\ldots \chi_n \ldots \chi_m \ldots\rangle$$

Interchanging two orbital labels is equivalent to interchanging two cols. of the SD.

Say we have two SDs: $|K\rangle = |\chi_i \chi_j\rangle$ and $|L\rangle = |\chi_k \chi_l\rangle$.

What is the overlap between $|K\rangle$ and $|L\rangle$?

$$|K\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) \\ \chi_i(x_2) & \chi_j(x_2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right]$$

$$|L\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_k(x_1) & \chi_l(x_1) \\ \chi_k(x_2) & \chi_l(x_2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left[\chi_k(x_1)\chi_l(x_2) - \chi_l(x_1)\chi_k(x_2)\right]$$

$$\therefore \langle K|L\rangle = \int \frac{1}{\sqrt{2}}\left[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right]^{*} \frac{1}{\sqrt{2}}\left[\chi_k(x_1)\chi_l(x_2) - \chi_l(x_1)\chi_k(x_2)\right] dx_1 dx_2$$

$$= \frac{1}{2}\Big[\int \chi_i^*(x_1)\chi_j^*(x_2)\underset{\textcircled{1}}{\chi_k(x_1)}\chi_l(x_2)\,dx_1 dx_2 - \int \chi_i^*(x_1)\chi_j^*(x_2)\chi_l(x_1)\underset{\textcircled{2}}{\chi_k(x_2)}\,dx_1 dx_2$$

$$- \int \chi_j^*(x_1)\chi_i^*(x_2)\underset{\textcircled{3}}{\chi_k(x_1)}\chi_l(x_2)\,dx_1 dx_2 + \int \chi_j^*(x_1)\chi_i^*(x_2)\chi_l(x_1)\underset{\textcircled{4}}{\chi_k(x_2)}\,dx_1 dx_2$$

$$\textcircled{1} = \int \chi_i^*\overset{\checkmark}{(x_1)}\,\chi_j^*\overset{\checkmark\checkmark}{(x_2)}\,\chi_k\overset{\checkmark}{(x_1)}\,\chi_l\overset{\checkmark\checkmark}{(x_2)}\,d\overset{\checkmark}{x_1}\,d\overset{\checkmark\checkmark}{x_2} = \int \chi_i^*(x_1)\chi_k(x_1)dx_1 \int \chi_j^*(x_2)\chi_l(x_2)dx_2$$

$$= \delta_{ik}\delta_{jl}$$

② $= \delta_{il}\delta_{jk}$

③ $= \delta_{jk}\delta_{il}$

④ $= \delta_{jl}\delta_{ik}$

$$\therefore \langle K|L\rangle = \frac{1}{2}\left[\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} - \delta_{jk}\delta_{il} + \delta_{jl}\delta_{ik}\right]$$

or, $\langle K|L\rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$

Probability calculated using HP: $\psi_{HP}(x_1, x_2, \ldots, x_N) = \chi_i(x_1)\chi_j(x_2)\cdots\chi_k(x_N)$

prob. density, $\psi^*_{HP}\psi_{HP} = |\psi_{HP}|^2$

prob., $|\psi_{HP}|^2 dx_1 dx_2 \cdots dx_N = |\chi_i(x_1)|^2 dx_1 \boxed{|\chi_j(x_2)|^2 dx_2} \cdots |\chi_k(x_N)|^2 dx_N$

prob. of finding electron-2 within dx_2 located at x_2

$\therefore$ Any HP is an example of an independent electron wavefunction.

Thus, the anti-symmetric wave function

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\Psi_{12}^{HP} - \Psi_{21}^{HP}\right] = \frac{1}{\sqrt{2}}\left[\chi_i(x_1)\chi_j(x_2) - \chi_i(x_2)\chi_j(x_1)\right]$$

may also be represented in the form of a determinant:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) \\ \chi_i(x_2) & \chi_j(x_2) \end{vmatrix} = \Psi^{\mathrm{SD}}(x_1, x_2)$$

This determinant is called the Slater determinant. The Slater determinant can be generalized for a N electron system as,

$$\Psi^{\mathrm{SD}}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix}$$

The factor $1/\sqrt{N!}$ is a normalization factor. This SD has N electrons occupying N spin orbitals $(\chi_i, \chi_j, \ldots, \chi_k)$ without specifying which electron is in which orbital. Thus, in the Slater determinant,

$$\Psi^{\mathrm{SD}}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix}$$

note that,

- the rows of an N-electron SD are labeled by electrons: first row (x_1), second row (x_2), …,
- the columns are labeled by spin orbitals: first column (χ_i), second column (χ_j), …
- interchanging the coordinates of two electrons corresponds to interchanging two rows of the SD, which changes the sign of the determinant, and
- thus, the SDs meet the requirement of the antisymmetry principle,
- having two electrons occupying the same spin orbital corresponds to having two columns of the determinant equal, which makes the determinant zero.
- Therefore, no more than one electron can occupy a spin orbital (Pauli exclusion principle).

A short-hand notation for a normalized SD, which includes the normalization constant, and only shows the diagonal elements of the determinant,

$$\Psi(x_1, x_2, \ldots, x_N) = \left|\chi_i(x_1)\chi_j(x_2)\cdots\chi_k(x_N)\right\rangle$$

If we always choose the electron labels to be in the order, $x_1, x_2, \ldots, x_N$, then,

$$\Psi(x_1, x_2, \ldots, x_N) = \left|\chi_i\chi_j\cdots\chi_k\right\rangle$$

Because the interchange of any two columns changes the sign of a SD, the ordering of spin orbitals in

$$\Psi(x_1, x_2, \ldots, x_N) = \left|\chi_i\chi_j\cdots\chi_k\right\rangle$$

is important.

∴ The antisymmetry property of SDs is

$$|\cdots\chi_m\cdots\chi_n\cdots\rangle = -|\cdots\chi_n\cdots\chi_m\cdots\rangle$$

Let us try to work out the algebra associated with the SDs. Consider the SDs $|K\rangle = \left|\chi_i\chi_j\right\rangle$ and $|L\rangle = |\chi_k\chi_l\rangle$. Let us evaluate $\langle K|L\rangle$.

$$\langle K|L\rangle = \int \frac{1}{\sqrt{2}}[\chi_i^*(x_1)\chi_j^*(x_2) - \chi_j^*(x_1)\chi_i^*(x_2)]\frac{1}{\sqrt{2}}[\chi_k(x_1)\chi_l(x_2) - \chi_l(x_1)\chi_k(x_2)]dx_1dx_2$$

$$= \frac{1}{2}\int \left[\chi_i^*(x_1)\chi_j^*(x_2)\chi_k(x_1)\chi_l(x_2) - \chi_i^*(x_1)\chi_j^*(x_2)\chi_l(x_1)\chi_k(x_2) - \chi_j^*(x_1)\chi_i^*(x_2)\chi_k(x_1)\chi_l(x_2) + \chi_j^*(x_1)\chi_i^*(x_2)\chi_l(x_1)\chi_k(x_2)\right] dx_1dx_2$$

$$= \frac{1}{2}\left(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} - \delta_{jk}\delta_{il} + \delta_{jl}\delta_{ik}\right) = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}.$$

We have seen that a Hartree product is truly an independent-electron wavefunction since the simultaneous probability of finding electron-1 in dx_1 at x_1, electron-2 in dx_2 at x_2, etc. is

$$|\Psi(x_1, x_2, \ldots, x_N)|^2 = |\chi_i(x_1)|^2dx_1\left|\chi_j(x_2)\right|^2dx_2\cdots|\chi_k(x_N)|^2dx_N$$

The process of antisymmetrizing a Hartree product to form a SD introduces exchange effects, so-called because they arise from the requirement that $|\Psi|^2$ be invariant to the exchange of space and spin coordinates of any two electrons. A SD incorporates exchange correlation, which means that the motion of two electrons with parallel spins is correlated. Since the motion of electrons with opposite spins remains uncorrelated, it is customary to refer to a single determinantal wavefunction as an uncorrelated wavefunction.

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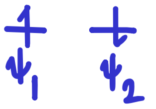
A two-electron Slater determinant

$$\psi(x_1,x_2) = |\chi_1(x_1)\chi_2(x_2)\rangle = \frac{1}{\sqrt{2}}\left[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\right]$$

① Electrons are of opposite spins and occupy different spatial orbitals

$$\chi_1(x_1) = \psi_1(r_1)\alpha(\omega_1)$$

$$\chi_2(x_2) = \psi_2(r_2)\beta(\omega_2)$$



$x_1 \rightarrow r_1, \omega_1$

$x_2 \rightarrow r_2, \omega_2$

$$|\psi|^2 dx_1 dx_2 = \psi^*(x_1,x_2)\psi(x_1,x_2)\,dx_1 dx_2$$

$$= \frac{1}{2}\left[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\right]^*\left[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\right]dx_1 dx_2$$

$$= \frac{1}{2}\left|\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\right|^2 dx_1 dx_2$$

$$= \frac{1}{2}\left|\psi_1(r_1)\alpha(\omega_1)\psi_2(r_2)\beta(\omega_2) - \psi_2(r_1)\beta(\omega_1)\psi_1(r_2)\alpha(\omega_2)\right|^2 dr_1 d\omega_1 dr_2 d\omega_2$$

$$P(r_1,r_2)\,dr_1 dr_2 = \frac{1}{2}\left[|\psi_1(r_1)|^2|\psi_2(r_2)|^2 + |\psi_1(r_2)|^2|\psi_2(r_1)|^2\right]dr_1 dr_2$$

Expansion for the prob. is dependent on space only.

$$\alpha(\omega_1)\beta(\omega_2)\,d\omega_1 d\omega_2 \Downarrow \alpha^*(\omega_1)\alpha(\omega_1)\,d\omega_1\ \beta^*(\omega_2)\beta(\omega_2)\,d\omega_2$$

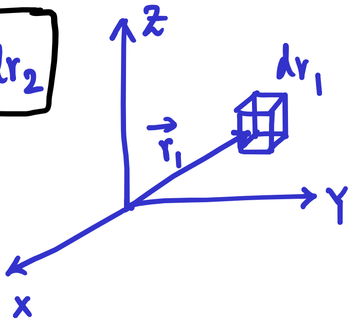
$$\alpha(\omega_2)\beta(\omega_1)\,d\omega_1 d\omega_2 \Downarrow \alpha^*(\omega_2)\alpha(\omega_2)\,d\omega_2\ \beta^*(\omega_1)\beta(\omega_1)\,d\omega_1$$

$$\therefore P(r_1,r_2)\,dr_1 dr_2 = \frac{1}{2}\left[|\psi_1(r_1)|^2|\psi_2(r_2)|^2 + |\psi_1(r_2)|^2|\psi_2(r_1)|^2\right]dr_1 dr_2$$

$$|\psi_1(r_1)|^2|\psi_2(r_2)|^2 dr_1 dr_2 \equiv \boxed{|\psi_1(r_1)|^2 dr_1}\boxed{|\psi_2(r_2)|^2 dr_2}$$

prob. of locating electron 1 in ψ_1 within dr_1 at r_1

prob. of locating electron 2 in ψ_2 within dr_2 at r_2



$$|\psi_2(r_1)|^2|\psi_1(r_2)|^2 dr_1 dr_2 \equiv |\psi_2(r_1)|^2 dr_1\ |\psi_1(r_2)|^2 dr_2$$

$\therefore P(r_1,r_2)\,dr_1 dr_2$ is an $\boxed{\text{average}}$ of the two terms.

$\boxed{\text{No correlation between the electrons.}}$

② Electrons occupy different spatial orbitals, but have the same spin.

$$\left.\begin{aligned}\chi_1(x_1) &= \psi_1(r_1)\beta(\omega_1)\\ \chi_2(x_2) &= \psi_2(r_2)\beta(\omega_2)\end{aligned}\right\} \quad \psi(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\right]$$

$$|\psi|^2 dx_1 dx_2 = \frac{1}{2}\left[|\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2) - \psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)|^2\right] dx_1 dx_2$$

$$P(r_1,r_2)\,dr_1 dr_2 = \int |\psi|^2 dr_1 d\omega_1 dr_2 d\omega_2 \qquad \underset{\psi_1}{\uparrow} \quad \underset{\psi_2}{\uparrow} \qquad\qquad \underset{\psi_1}{\downarrow} \quad \underset{\psi_2}{\downarrow}$$

$$\begin{aligned}P(r_1,r_2)\,dr_1 dr_2 = &\left[\frac{1}{2}|\psi_1(r_1)|^2|\psi_2(r_2)|^2 + \frac{1}{2}|\psi_1(r_2)|^2|\psi_2(r_1)|^2\right] dr_1 dr_2\\ &\left.\begin{aligned}&- \frac{1}{2}\int \psi_1^*(r_1)\psi_2(r_1)\,dr_1 \int \psi_2^*(r_2)\psi_1(r_2)\,dr_2\\ &- \frac{1}{2}\int \psi_2^*(r_1)\psi_1(r_1)\,dr_1 \int \psi_1^*(r_2)\psi_2(r_2)\,dr_2\end{aligned}\right\}\end{aligned}$$

When the spins of the two electrons are same, these two cross terms appear.

∴ The overall prob. is not an average of the individual probabilities.

⇒ the electrons are correlated.

For a three-electron system: $\psi(x_1,x_2,x_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix}\chi_a(x_1) & \chi_b(x_2) & \chi_c(x_1)\\ \chi_a(x_2) & \chi_b(x_2) & \chi_c(x_2)\\ \chi_a(x_3) & \chi_b(x_3) & \chi_c(x_3)\end{vmatrix}$

Consider a two-electron SD in which the spin orbitals χ_1 and χ_2 are occupied.

$$\Psi(x_1,x_2) = |\chi_1(x_1)\chi_2(x_2)\rangle$$

If the two electrons have opposite spins and occupy different spatial orbitals,

$$\chi_1(x_1) = \psi_1(r_1)\alpha(\omega_1)$$
$$\chi_2(x_2) = \psi_2(r_2)\beta(\omega_2)$$

then, the corresponding SD is

$$\Psi(x_1,x_2) = \frac{1}{\sqrt{2}}[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)]$$

and by expanding the determinant one obtains

$$|\Psi|^2 dx_1 dx_2 = \Psi^*(x_1,x_2)\Psi(x_1,x_2)dx_1 dx_2$$
$$= \frac{1}{2}[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)]^*[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)]dx_1 dx_2$$
$$\therefore |\Psi|^2 dx_1 dx_2 = \frac{1}{2}|\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)|^2 dx_1 dx_2$$

Now, since,

$$\chi_1(x_1) = \psi_1(r_1)\alpha(\omega_1)$$
$$\chi_2(x_2) = \psi_2(r_2)\beta(\omega_2)$$

we have

$$|\Psi|^2 dx_1 dx_2 = \frac{1}{2}|\psi_1(r_1)\alpha(\omega_1)\psi_2(r_2)\beta(\omega_2) - \psi_1(r_2)\alpha(\omega_2)\psi_2(r_1)\beta(\omega_1)|^2 dx_1 dx_2$$

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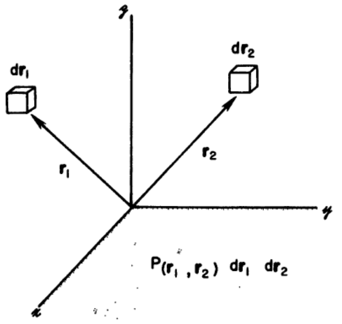
which represents the simultaneous probability of electron-1 being in dx_1 and electron-2 being in dx_2. Say, $P(r_1, r_2)dr_1dr_2$ be the simultaneous probability of finding electron-1 in dr_1 at r_1 and electron-2 in dr_2 at r_2.



This probability is obtained by integrating/averaging $|\Psi|^2 dx_1dx_2$ over the spins of the two electrons.

$$P(r_1, r_2)dr_1dr_2 = \int |\Psi|^2 dx_1dx_2 = \int |\Psi|^2 dr_1 d\omega_1 dr_2 d\omega_2$$

Therefore, we have,

$$P(r_1, r_2)dr_1dr_2$$
$$= \frac{1}{2}[|\psi_1(r_1)|^2|\psi_2(r_2)|^2 + |\psi_1(r_2)|^2|\psi_2(r_1)|^2]dr_1dr_2$$

Thus, we have,

$$P(r_1, r_2)dr_1dr_2 = \frac{1}{2}[|\psi_1(r_1)|^2|\psi_2(r_2)|^2 + |\psi_1(r_2)|^2|\psi_2(r_1)|^2]dr_1dr_2$$

The first term,

$$|\psi_1(r_1)|^2|\psi_2(r_2)|^2$$

is the product of the probability of finding electron-1 in dr_1 at r_1 and the probability of finding electron-2 in dr_2 at r_2 if electron-1 occupies ψ_1 and electron-2 occupies ψ_2. The second term has electron-1 occupying ψ_2 and electron-2 occupying ψ_1. Since the electrons are indistinguishable, the correct probability is the average of the two terms.

∴ The motion of the two electrons is uncorrelated. This is particularly obvious if $\psi_1 = \psi_2$, in which case,

$$P(r_1, r_2) = |\psi_1(r_1)|^2|\psi_2(r_2)|^2$$

Also, note that $P(r_1, r_1) \neq 0$, so that there is a finite probability of finding the two electrons with opposite spins at the same point in space. If the two electrons have the same spin (say β) and if they occupy different spatial orbitals as before,

$$\chi_1(x_1) = \psi_1(r_1)\beta(\omega_1)$$
$$\chi_2(x_2) = \psi_2(r_2)\beta(\omega_2)$$

then the corresponding SD is

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)]$$

Thus, from

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)]$$

by expanding the determinant one obtains

$$|\Psi|^2 dx_1dx_2 = \Psi^*(x_1, x_2)\Psi(x_1, x_2)dx_1dx_2$$
$$= \frac{1}{2}[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)]^*[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)]dx_1dx_2$$
$$\therefore |\Psi|^2 dx_1dx_2 = \frac{1}{2}|\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)|^2 dx_1dx_2$$

so that using

$$\chi_1(x_1) = \psi_1(r_1)\beta(\omega_1)$$
$$\chi_2(x_2) = \psi_2(r_2)\beta(\omega_2)$$

we have

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$$|\Psi|^2 dx_1 dx_2 = \frac{1}{2}|\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2) - \psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)|^2 dx_1 dx_2$$

which represents the simultaneous probability of electron-1 being in dx_1 and electron-2 being in dx_2. Say, $P(r_1, r_2)dr_1dr_2$ be the simultaneous probability of finding electron-1 in dr_1 at r_1 and electron-2 in dr_2 at r_2. This probability is obtained by integrating/averaging $|\Psi|^2 dx_1 dx_2$ over the spins of the two electrons.

$$P(r_1, r_2)dr_1dr_2 = \int |\Psi|^2 dx_1 dx_2 = \int |\Psi|^2 dr_1 d\omega_1 dr_2 d\omega_2$$

Let us evaluate

$$P(r_1, r_2)dr_1dr_2 = \int |\Psi|^2 dx_1 dx_2 = \int |\Psi|^2 dr_1 d\omega_1 dr_2 d\omega_2$$

using

$$|\Psi|^2 dx_1 dx_2 = \frac{1}{2}|\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2) - \psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)|^2 dx_1 dx_2.$$

$$\therefore P(r_1, r_2)dr_1dr_2 = \frac{1}{2}\int |\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2) - \psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)|^2 dr_1 dr_2 d\omega_1 d\omega_2$$

$$= \frac{1}{2}\int [\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2) - \psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)]^*$$
$$[\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2) - \psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)] dr_1 dr_2 d\omega_1 d\omega_2$$

$$\text{or, } P(r_1, r_2)dr_1dr_2 = \frac{1}{2}\int \psi_1^*(r_1)\beta^*(\omega_1)\psi_2^*(r_2)\beta^*(\omega_2)\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2)\, dr_1 dr_2 d\omega_1 d\omega_2$$
$$-\frac{1}{2}\int \psi_1^*(r_1)\beta^*(\omega_1)\psi_2^*(r_2)\beta^*(\omega_2)\psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)\, dr_1 dr_2 d\omega_1 d\omega_2$$
$$-\frac{1}{2}\int \psi_1^*(r_2)\beta^*(\omega_2)\psi_2^*(r_1)\beta^*(\omega_1)\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2)\, dr_1 dr_2 d\omega_1 d\omega_2$$
$$+\frac{1}{2}\int \psi_1^*(r_2)\beta^*(\omega_2)\psi_2^*(r_1)\beta^*(\omega_1)\psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)\, dr_1 dr_2 d\omega_1 d\omega_2$$

$$\therefore P(r_1, r_2)dr_1dr_2 = \frac{1}{2}\int \psi_1^*(r_1)\beta^*(\omega_1)\psi_2^*(r_2)\beta^*(\omega_2)\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2)\, dr_1 dr_2 d\omega_1 d\omega_2$$
$$-\frac{1}{2}\int \psi_1^*(r_1)\beta^*(\omega_1)\psi_2^*(r_2)\beta^*(\omega_2)\psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)\, dr_1 dr_2 d\omega_1 d\omega_2$$
$$-\frac{1}{2}\int \psi_1^*(r_2)\beta^*(\omega_2)\psi_2^*(r_1)\beta^*(\omega_1)\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2)\, dr_1 dr_2 d\omega_1 d\omega_2$$
$$+\frac{1}{2}\int \psi_1^*(r_2)\beta^*(\omega_2)\psi_2^*(r_1)\beta^*(\omega_1)\psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)\, dr_1 dr_2 d\omega_1 d\omega_2$$

Now,

$$\frac{1}{2}\int \psi_1^*(r_1)\beta^*(\omega_1)\psi_2^*(r_2)\beta^*(\omega_2)\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2)\, dr_1 dr_2 d\omega_1 d\omega_2$$
$$= \frac{1}{2}|\psi_1(r_1)|^2|\psi_2(r_2)|^2 dr_1 dr_2 \int \beta^*(\omega_1)\beta(\omega_1)d\omega_1 \int \beta^*(\omega_2)\beta(\omega_2)d\omega_2$$
$$= \frac{1}{2}|\psi_1(r_1)|^2|\psi_2(r_2)|^2 dr_1 dr_2$$

Similarly,

$$\frac{1}{2}\int \psi_1^*(r_2)\beta^*(\omega_2)\psi_2^*(r_1)\beta^*(\omega_1)\psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)\, dr_1 dr_2 d\omega_1 d\omega_2$$
$$= \frac{1}{2}|\psi_1(r_2)|^2|\psi_2(r_1)|^2 dr_1 dr_2 \int \beta^*(\omega_1)\beta(\omega_1)d\omega_1 \int \beta^*(\omega_2)\beta(\omega_2)d\omega_2$$
$$= \frac{1}{2}|\psi_1(r_2)|^2|\psi_2(r_1)|^2 dr_1 dr_2$$

$$\therefore P(r_1, r_2)dr_1dr_2 = \frac{1}{2}|\psi_1(r_1)|^2|\psi_2(r_2)|^2 dr_1 dr_2 + \frac{1}{2}|\psi_1(r_2)|^2|\psi_2(r_1)|^2 dr_1 dr_2$$
$$-\frac{1}{2}\int \psi_1^*(r_1)\beta^*(\omega_1)\psi_2^*(r_2)\beta^*(\omega_2)\psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)\, dr_1 dr_2 d\omega_1 d\omega_2$$

$$-\frac{1}{2}\int \psi_1^*(r_2)\beta^*(\omega_2)\psi_2^*(r_1)\beta^*(\omega_1)\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2)\, dr_1 dr_2 d\omega_1 d\omega_2$$

Now,

$$\frac{1}{2}\int \psi_1^*(r_1)\beta^*(\omega_1)\psi_2^*(r_2)\beta^*(\omega_2)\psi_1(r_2)\beta(\omega_2)\psi_2(r_1)\beta(\omega_1)\, dr_1 dr_2 d\omega_1 d\omega_2$$

$$= \frac{1}{2}\psi_1^*(r_1)\psi_2(r_1)\psi_2^*(r_2)\psi_1(r_2) dr_1 dr_2 \int \beta^*(\omega_1)\beta(\omega_1)\, d\omega_1 \int \beta^*(\omega_2)\beta(\omega_2) d\omega_2$$

$$= \frac{1}{2}\psi_1^*(r_1)\psi_2(r_1)\psi_2^*(r_2)\psi_1(r_2) dr_1 dr_2$$

Similarly,

$$\frac{1}{2}\int \psi_1^*(r_2)\beta^*(\omega_2)\psi_2^*(r_1)\beta^*(\omega_1)\psi_1(r_1)\beta(\omega_1)\psi_2(r_2)\beta(\omega_2)\, dr_1 dr_2 d\omega_1 d\omega_2$$

$$= \frac{1}{2}\psi_2^*(r_1)\psi_1(r_1)\psi_1^*(r_2)\psi_2(r_2) dr_1 dr_2 \int \beta^*(\omega_1)\beta(\omega_1)\, d\omega_1 \int \beta^*(\omega_2)\beta(\omega_2) d\omega_2$$

$$= \frac{1}{2}\psi_2^*(r_1)\psi_1(r_1)\psi_1^*(r_2)\psi_2(r_2) dr_1 dr_2$$

$$\therefore P(r_1, r_2) dr_1 dr_2 = \frac{1}{2}|\psi_1(r_1)|^2|\psi_2(r_2)|^2 dr_1 dr_2 + \frac{1}{2}|\psi_1(r_2)|^2|\psi_2(r_1)|^2 dr_1 dr_2$$

$$-\frac{1}{2}\psi_1^*(r_1)\psi_2(r_1)\psi_2^*(r_2)\psi_1(r_2) dr_1 dr_2 - \frac{1}{2}\psi_2^*(r_1)\psi_1(r_1)\psi_1^*(r_2)\psi_2(r_2) dr_1 dr_2$$

Thus,

$$P(r_1, r_2) dr_1 dr_2 = \frac{1}{2}|\psi_1(r_1)|^2|\psi_2(r_2)|^2 dr_1 dr_2 + \frac{1}{2}|\psi_1(r_2)|^2|\psi_2(r_1)|^2 dr_1 dr_2$$

$$-\frac{1}{2}\psi_1^*(r_1)\psi_2(r_1)\psi_2^*(r_2)\psi_1(r_2) dr_1 dr_2 - \frac{1}{2}\psi_2^*(r_1)\psi_1(r_1)\psi_1^*(r_2)\psi_2(r_2) dr_1 dr_2$$

so that,

$$P(r_1, r_2) = \frac{1}{2}[|\psi_1(r_1)|^2|\psi_2(r_2)|^2 + |\psi_1(r_2)|^2|\psi_2(r_1)|^2 - \{\psi_1^*(r_1)\psi_2(r_1)\psi_2^*(r_2)\psi_1(r_2)$$
$$- \psi_2^*(r_1)\psi_1(r_1)\psi_1^*(r_2)\psi_2(r_2)\}]$$

Thus, we now have an extra term, within $\{\cdots\}$, that makes the probabilities correlated. This is the exchange correlation between the electrons of parallel spin. Note that in this case $P(r_1, r_1) = 0$. Thus, the probability of finding two electrons with parallel spins at the same point in space is zero.

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Hartree-Fock (HF) approximation

$|\psi_0\rangle = |\chi_1 \chi_2 \ldots \chi_N\rangle$ H = full electronic Hamiltonian

$E_0 = \langle \psi_0 | H | \psi_0 \rangle$

$\chi(x_i) \rightarrow \phi(r_i)\alpha(\omega)$

$\quad\;\;\; \rightarrow \phi(r_i)\beta(\omega)$

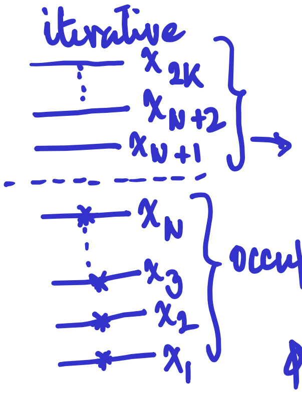
$x_i = \{r_i, \omega\}$

$$\boxed{f(i)\,\chi(x_i) = \varepsilon\, \chi(x_i)}$$

$f(i)$ = Fock operator ε = orbital energy

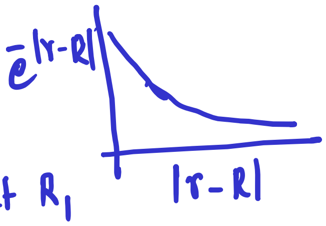
$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + v^{HF}(i) \leftarrow$$

average potential on electron i due to all other N-1 electrons and M no. of nuclei



if we have K no. of spatial orbitals, we have 2K no. of spin orbitals.

$\boxed{H_2 \text{ molecule}}$ LCAO-MO



ϕ_1 : AO centred on an atom at R_1

$\phi_1(r) \equiv \phi_1(r - R_1)$ Slater type function

$\phi_2(r - R_2)$ $\phi(r-R) = (\alpha^3/\pi)^{1/2} e^{-\alpha|r-R|}$ Slater type orbital (STO)

$\phi(r-R) = (2\alpha/\pi)^{3/4} e^{-\alpha|r-R|^2}$: $\sim e^{-\alpha x^2}$ Gaussian type orbital (GTO)

$S_{12} = \int \phi_1^*(r)\phi_2(r)\,dr$: overlap integral

Overlap will depend on $R_{12} = |R_1 - R_2|$

$S_{12} = 1$, when $R_{12} = 0$; $S_{12} = 0$, when $R_{12} = \infty$

$$\psi_1 = \frac{1}{\sqrt{2(1+S_{12})}}(\phi_1 + \phi_2) \; ; \; \psi_2 = \frac{1}{\sqrt{2(1-S_{12})}}(\phi_1 - \phi_2)$$

How are ψ_1 and ψ_2 relatd to each other?

$$\langle \psi_1 | \psi_2 \rangle = \frac{1}{\sqrt{4(1-S_{12}^2)}} \int (\phi_1^* + \phi_2^*)(\phi_1 - \phi_2)\,dv = \frac{1}{2\sqrt{1-S_{12}^2}}\left[1 - 1 - S_{12} + S_{12}\right] = 0$$

$\langle \psi_1 | \psi_1 \rangle = 1$, $\langle \psi_2 | \psi_2 \rangle = 1$ Orthonormal set.

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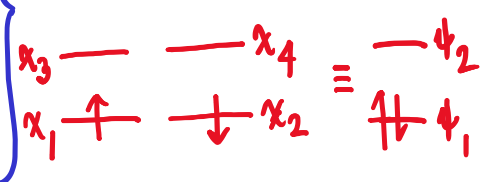
$$\left.\begin{aligned}\chi_1(x) &= \psi_1(r)\alpha(\omega)\\ \chi_2(x) &= \psi_1(r)\beta(\omega)\\ \chi_3(x) &= \psi_2(r)\alpha(\omega)\\ \chi_4(x) &= \psi_2(r)\beta(\omega)\end{aligned}\right\} \quad |\psi_0\rangle = |\chi_1\chi_2\rangle$$



$$|\psi_0\rangle = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle$$

for K no. of spatial orbitals, we have 2K no. of spin functions

N no. of electrons have to be distributed among 2K no. of spin orbitals

$$C^{2K}_{N} = \frac{(2K)!}{N!\,(2K-N)!}$$

The Hartree-Fock (HF) Approximation

Main challenge of Quantum Chemistry: to solve the time-independent Schrödinger equation for molecular systems. Trivial case: H_2^+ ion. The simplest antisymmetric wavefunction that can be used to describe the ground state of an N-electron system is a single SD,

$$|\Psi_0\rangle = |\chi_1\chi_2 \dots \chi_N\rangle$$

Variation principle: the best wavefunction of this functional form is the one which gives the lowest possible energy

$$E_0 = \langle\Psi_0|H|\Psi_0\rangle$$

where H is the full electronic Hamiltonian. The variational flexibility in the wavefunction $|\Psi_0\rangle = |\chi_1\chi_2 \dots \chi_N\rangle$ is in the choice of the spin orbitals. By minimizing E_0 with respect to the choice of spin orbitals, one can derive an equation, called the Hartree-Fock equation, which determines the optimal spin orbitals. We will show that the HF equation is an eigenvalue equation of the form

$$f(i)\chi(x_i) = \varepsilon\chi(x_i)$$

where $f(i)$ is an effective one-electron operator, called the Fock operator. The Fock operator has the form,

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + v^{HF}(i)$$

$v^{HF}(i)$ is the average potential experienced by the ith electron due to the presence of the other electrons. The essence of the HF approximation is to replace the complicated many-electron problem by a one-electron in which the actual electron-electron repulsion term,

$$\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|r_i - r_j|}$$

is treated in an average manner through the sum over the average HF potential

$$\sum_{i=1}^{N} v^{HF}(i)$$

The HF potential, $v^{HF}(i)$, or equivalently the field seen by the ith electron, depends on the spin orbitals of the other electrons, that is, the Fock operator depends on its own eigenfunctions. The procedure for solving the HF equation

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$$f(i)\chi(x_i) = \varepsilon\chi(x_i)$$

is called the self-consistent-field (SCF) method. The basic idea of the SCF method is simple:

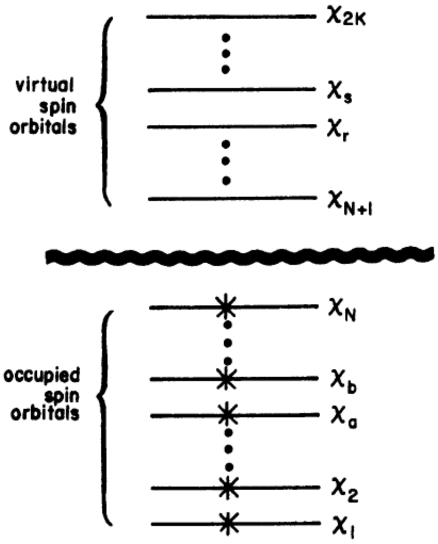
- By making an initial guess at the spin orbitals, one can evaluate the average field (that is, v^{HF}) seen by each electron.
- Then one can solve the eigenvalue equation $f(i)\chi(x_i) = \varepsilon\chi(x_i)$ for a new set of spin orbitals.
- Using these new spin orbitals, one can obtain new fields.
- This process is repeated until self-consistency is reached, that is, the fields no longer change the spin orbitals used to construct the Fock operator are the same as its eigenfunctions.

The solution of the HF eigenvalue problem $f(i)\chi(x_i) = \varepsilon\chi(x_i)$ yields a set of $\{\chi_k\}$ of orthonormal HF spin orbitals with orbital energies $\{\varepsilon_k\}$. The N spin orbitals with the lowest energies are called the occupied or hole spin orbitals.

The SD formed from these orbitals is the HF ground state wavefunction and is the best variational approximation to the ground state of the system, of the single determinant form. The occupied/hole spin orbitals will be henceforth labeled by the indices $a,\ b,\ c,\ \ldots$ and denoted by $\chi_a,\ \chi_b,\ \chi_c,\ \ldots$ The remaining members of the set $\{\chi_k\}$ are called virtual/unoccupied/particle spin orbitals. We will henceforth label the virtual orbitals by the indices $r,\ s,\ t,\ \ldots$ and denote the spin orbitals by $\chi_r,\ \chi_s,\ \chi_t,\ \ldots$ In principle, there are an infinite number of solutions to the HF equation $f(i)\chi(x_i) = \varepsilon\chi(x_i)$ and an infinite number of virtual spin orbitals. In practice, the HF equation $f(i)\chi(x_i) = \varepsilon\chi(x_i)$ is solved by introducing a finite set of spatial basis functions

$$\{\phi_\mu(r),\ \mu = 1,\ 2,\ 3,\ \ldots,\ K\}.$$

The spatial parts of the spin orbitals with the α spin function can then be expanded in terms of the known set of functions $\{\phi_\mu\}$. The spatial parts of the spin orbitals with the β spin function can then be expanded in the same way. Then both these expansions are substituted in $f(i)\chi(x_i) = \varepsilon\chi(x_i)$ to obtain matrix eigenvalue equations for the expansion coefficients. A basis set of K spatial functions $\{\phi_\mu\}$ leads to a set of $2K$ spin orbitals (K with α spin and K with β spin). This leads to a set of N occupied spin orbitals $\{\chi_a\}$ and a complementary set of $2K - N$ unoccupied/virtual spin orbitals $\{\chi_r\}$. A single SD formed from the set $\{\chi_a\}$ is the variational HF ground state, for which we will use the symbol Ψ_0 or $|\Psi_0\rangle$.



The $2K$ HF spin orbitals have been ordered according to their energy, and we have neglected possible degeneracies. The larger and more complete the set of basis functions $\{\phi_\mu\}$, the greater is the degree of flexibility in the expansion for the spin orbitals and the lower will be the expectation value

$$E_0 = \langle\Psi_0|H|\Psi_0\rangle$$

Larger and larger $\{\phi_\mu\}$ will keep lowering E_0 until a limit called the Hartree-Fock limit is reached. Any finite value of K will lead to an energy somewhat above the HF limit.

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The Minimal Basis H_2 Model

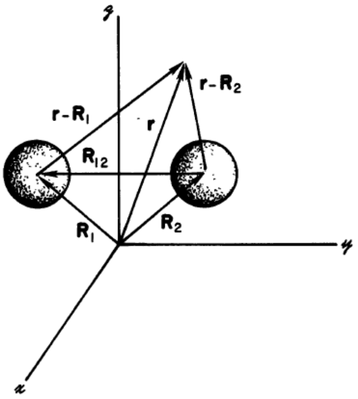
This is a model system visualized in light of the familiar LCAO-MO description. Each H atom has a $1s$ AO and as the two atoms approach, Mos are formed as a linear combination of AOs (LCAO). The first AO, ϕ_1, is centered on atom 1 at R_1. The value of ϕ_1 at a point r is $\phi_1(r)$, or, since its value depends on the distance from its origin, we sometimes write $\phi_1 \equiv \phi_1(r - R_1)$. The second AO is centered on atom 2 at R_2, that is $\phi_2 \equiv \phi_2(r - R_2)$. The exact $1s$ orbital of a H atom centered at R has the form

$$\phi(r - R) = (\xi^3/\pi)^{1/2} e^{-\xi|r-R|}$$

where ξ, the orbital exponent, has a value 1.0. This is a case of a Slater type orbital (STO). However, we will be concerned mostly with the Gaussian type orbitals (GTOs) since the GTOs lead to simpler integral evaluations than STOs. The $1s$ GTO has the form

$$\phi(r - R) = (2\alpha/\pi)^{3/4} e^{-\alpha|r-R|^2}$$

where α is the Gaussian orbital exponent.



For the present, we need not be concerned with the particular form of the $1s$ AOs. The two AOs ϕ_1 and ϕ_2 can be assumed to be normalized, but they are not orthogonal. They will overlap, such that the overlap integral is

$$S_{12} = \int \phi_1^*(r)\phi_2(r)\, dr$$

The overlap will depend on the distance $R_{12} = |R_1 - R_2|$, such that,

$$S_{12} = 1 \text{ when } R_{12} = 0 \text{ and } S_{12} = 0 \text{ when } R_{12} = \infty$$

From the two localized AOs, ϕ_1 and ϕ_2, one can form, by linear combination, two delocalized MOs. The symmetric combination leads to a bonding MO of *gerade* symmetry (that is, it is symmetric with respect to inversion about the point centered between the nuclei)

$$\psi_1 = \frac{1}{\sqrt{2(1 + S_{12})}}(\phi_1 + \phi_2)$$

The antisymmetric combination leads to a antibonding MO of *ungerade* symmetry (that is, it is antisymmetric with respect to inversion about the point centered between the nuclei)

$$\psi_2 = \frac{1}{\sqrt{2(1 - S_{12})}}(\phi_1 - \phi_2)$$

How are ψ_1 and ψ_2 related to each other? We note that,

$$\begin{aligned}\langle\psi_1|\psi_1\rangle &= \frac{1}{2(1 + S_{12})}\int (\phi_1^* + \phi_2^*)(\phi_1 + \phi_2)\, d\tau \\ &= \frac{1}{2(1 + S_{12})}[\langle\phi_1|\phi_1\rangle + \langle\phi_2|\phi_2\rangle + \langle\phi_1|\phi_2\rangle + \langle\phi_2|\phi_1\rangle] \\ &= \frac{1}{2(1 + S_{12})}[1 + 1 + 2S_{12}] = 1\end{aligned}$$

In the same manner, $\langle\psi_2|\psi_2\rangle = 1$. However,

$$\langle\psi_1|\psi_2\rangle = \frac{1}{\sqrt{2(1 + S_{12})}}\frac{1}{\sqrt{2(1 - S_{12})}}\int (\phi_1^* + \phi_2^*)(\phi_1 - \phi_2)\, d\tau$$

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$$\therefore \langle\psi_1|\psi_2\rangle = \frac{1}{\sqrt{4(1-S_{12}^2)}}[1-1-S_{12}+S_{12}] = 0$$

Thus, ψ_1 and ψ_2 form an orthonormal set. The above procedure is the simplest example of the general technique of expanding a set of spatial MOs in a set of known spatial basis functions

$$\psi_i(r) = \sum_{\mu=1}^{K} c_{\mu i}\,\phi_\mu(r)$$

To obtain the exact MOs for $\mathrm{H_2}$ one would need an infinite number of terms in such an expansion. Using only two basis functions for $\mathrm{H_2}$ is an example of a minimal basis set and the obvious choice for the two functions ϕ_1 and ϕ_2 is the $1s$ AOs of the toms. The correct linear combinations for this simple choice are determined by symmetry, and one need not solve the HF equations. The MOs ψ_1 and ψ_2 in

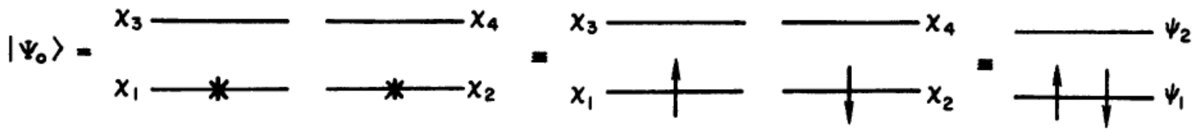
$$\psi_1 = \frac{1}{\sqrt{2(1+S_{12})}}(\phi_1+\phi_2) \text{ and } \psi_2 = \frac{1}{\sqrt{2(1-S_{12})}}(\phi_1-\phi_2)$$

are the HF spatial orbitals in the space spanned by ϕ_1 and ϕ_2. Given the two spatial orbitals ψ_1 and ψ_2, we can form four spin orbitals

$$\chi_1(x) = \psi_1(r)\alpha(\omega)$$
$$\chi_2(x) = \psi_1(r)\beta(\omega)$$
$$\chi_3(x) = \psi_2(r)\alpha(\omega)$$
$$\chi_4(x) = \psi_2(r)\beta(\omega)$$

The orbital energies associated with these spin orbitals can be obtained only by explicitly considering the HF operator. However, as might be expected, χ_1 and χ_2 are degenerate and have the lower energy corresponding to the bonding situation. Similarly, χ_3 and χ_4 are also degenerate having a higher energy corresponding to an antibonding situation. The HF ground state in this model is the single determinant,

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle$$



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Excited determinants

for an N-electron system, HF ground state function,

$$|\Psi_0\rangle = |\chi_1\chi_2\ldots\chi_a\chi_b\ldots\chi_N\rangle$$

total no. of spin orbitals = 2K $(2K > N)$

No. of possible single determinants that can be formed from 2K spin orbitals and N electrons

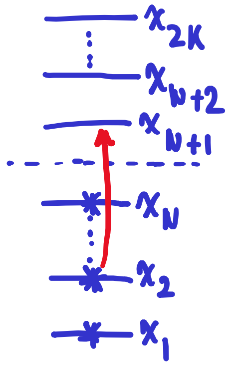
$|\Psi_0\rangle$ is just one of the C_N^{2K} determinants

$$C_N^{2K} = \frac{(2K)!}{N!\,(2K-N)!}$$

$$\left.\begin{array}{l}\text{Occupied set of orbitals} \longrightarrow N \text{ orbitals}\\ \text{virtual \quad " \quad " \quad "} \longrightarrow (2K-N) \text{ orbitals}\end{array}\right\} 2K$$

$a \rightarrow r$ $\quad |\Psi_a^r\rangle$

$a \rightarrow r$, $b \rightarrow s$ $\quad |\Psi_{ab}^{rs}\rangle$



$|\Psi_2^{N+1}\rangle$

$$|\Psi_0\rangle = |\chi_1\chi_2\ldots\chi_N\rangle$$

$$|\Psi_2^{N+1}\rangle = |\chi_1\chi_{N+1}\ldots\chi_N\rangle$$

$\boxed{H_2 \text{ molecule}}$: minimal basis

$\psi_1(r)$, $\psi_2(r)$; $K=2$

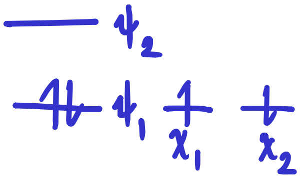
$2K=4$, $N=2$

$\chi_1(x) = \psi_1(r)\alpha(\omega)$

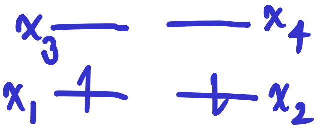
$\chi_2(x) = \psi_1(r)\beta(\omega)$

$\chi_3(x) = \psi_2(r)\alpha(\omega)$

$\chi_4(x) = \psi_2(r)\beta(\omega)$



$$C_N^{2K} = \frac{4!}{2!\,2!} = 6$$



$|\Psi_0\rangle = |\chi_1\chi_2\rangle$

$|\Psi_1^3\rangle, |\Psi_2^4\rangle, |\Psi_1^4\rangle, |\Psi_2^3\rangle, |\Psi_{12}^{34}\rangle$

C_6H_6 in minimal basis

$N = 42$

$$K = \begin{cases}\text{One } 1s \text{ AO for each H atom}\\ \text{One } 1s\text{, one } 2s\text{, three } 2p \text{ AOs} = 5 \text{ AOs for each atom}\end{cases}$$

6 AOs for 6 H atoms + 30 AOs for 6 C atoms, $K = 36$

No. of spin orbitals, $2K = 72$

$$C_N^{2K} = \frac{72!}{42!\,30!} = 1.643\times10^{20}$$

$|\Psi_0\rangle$ is just one among 1.643×10^{20} possible determinants.

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for any singly excited determinant an electron can jump from any $\boxed{\chi_a} \rightarrow N$ spin orbital to any $\boxed{\chi_r} \rightarrow 2K-N$

∴ there are $N(2K-N) = 30 \times 42 = 1260$ possible singly excited determinants

$$\left.\begin{matrix}\chi_a\\ \chi_b\end{matrix}\right\} \rightarrow \left.\begin{matrix}\chi_r\\ \chi_s\end{matrix}\right\} \qquad \boxed{\frac{N(N-1)}{2}} \rightarrow \boxed{\frac{(2K-N)(2K-N-1)}{2}}$$

∴ No. of doubly excited determinants $= \frac{N(N-1)(2K-N)(2K-N-1)}{4}$

$= 374535$

No. of triply excited determinants $= 186435200$

$|\psi_0\rangle$ normalized, $E_0 = \langle\psi_0|H|\psi_0\rangle$

$$|\Phi\rangle = c_0|\psi_0\rangle + \sum_{a,r} c_a^r|\psi_a^r\rangle + \sum_{\substack{a,b\\ r,s}} c_{ab}^{rs}|\psi_{ab}^{rs}\rangle + \cdots$$

$E = \langle\Phi|H|\Phi\rangle$, E : theoretically exact energy.

$E - E_0 = E_{correlation}$

$$\Phi = c_0|\psi_0\rangle + \sum_{a,r} c_a^r|\psi_a^r\rangle + \overset{c_{ab}^{rs}}{\wedge}|\psi_{ab}^{rs}\rangle$$

$|\psi_0\rangle$, $\boxed{|\psi_a^r\rangle}$, $|\psi_{ab}^{rs}\rangle$

4 fns.

full configuration interaction function

FCI

$E = \langle\Phi|H|\Phi\rangle$: FCI energy

$$\boxed{\Phi_0 = c_0|\psi_0\rangle + c_{12}^{34}|\psi_{12}^{34}\rangle}$$

$$H = \begin{pmatrix} \langle\psi_0|H|\psi_0\rangle & \langle\psi_0|H|\psi_{12}^{34}\rangle \\ \langle\psi_{12}^{34}|H|\psi_0\rangle & \langle\psi_{12}^{34}|H|\psi_{12}^{34}\rangle \end{pmatrix}$$

approximated values

Excited Determinants

The HF procedure produces a set $\{\chi_i\}$ of $2K$ spin orbitals. The HF ground state,

$$|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$$

is the best (in a variational sense) approximation to the ground state. $|\Psi_0\rangle$ has a single determinantal form. However, $|\Psi_0\rangle$ is only one of the many determinants that could be formed from $2K > N$ spin orbitals. How many possible single determinants can be formed from $2K$ spin orbitals and N electrons?

$$C_N^{2K} = \frac{(2K)!}{N!\,(2K-N)!}$$

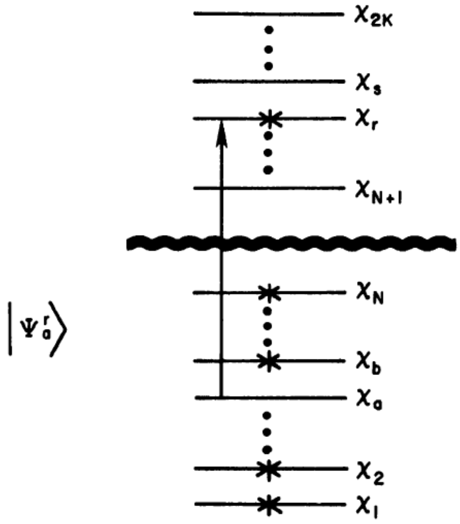
$|\Psi_0\rangle$ is just one of them. A convenient way of describing the determinants other than $|\Psi_0\rangle$ is to consider the HF ground state $|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$ to be a reference state. We classify the other possible determinants by how they differ from the reference state $|\Psi_0\rangle$. For example, we may state which occupied/hole spin orbitals of the set $\{\chi_a\}$ in $|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$ have been replaced by which virtual/unoccupied/particle spin orbitals of the set $\{\chi_r\}$. These other determinants are representations of the approximate excited states of the system. These other determinants when linearly combined with the HF ground state determinant $|\Psi_0\rangle$ can be seen to be a more accurate description of the ground state or any excited state of the system. A singly excited determinant is one in which an electron, which occupied χ_a in the HF ground state $|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$, has been promoted to a virtual χ_r,

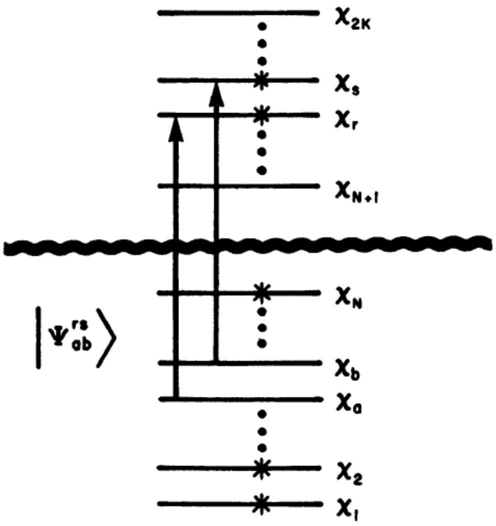
$$|\Psi_a^r\rangle = |\chi_1\chi_2 \cdots \chi_r\chi_b \cdots \chi_N\rangle$$

A doubly excited determinant is one in which the electrons have been excited from χ_a and χ_b in the HF ground state $|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$, to the virtual orbitals χ_r and χ_s

$$|\Psi_{ab}^{rs}\rangle = |\chi_1\chi_2 \cdots \chi_r\chi_s \cdots \chi_N\rangle$$

All the C_N^{2K} determinants can thus be classified as either the HF ground state or singly, doubly, triply, quadruply, …, N-tuply excited states. The importance of these determinants as approximate representations of the true states of the system diminishes in the above order. While the excited determinants are not accurate representations of the excited states of the system, they are important as N-electron basis functions for an expansion of the exact N-electron states of the system. All the C_N^{2K} determinants can thus be classified as either the HF ground state or singly, doubly, triply, quadruply, …, N-tuply excited states. The importance of these determinants as approximate representations of the true states of the system diminishes in the above order. While the excited determinants are not accurate representations of the excited states of the system, they are important as N-electron basis functions for an expansion of the exact N-electron states of the system.





Form of the Exact Wave Function and Configuration Interaction

We consider the use of these excited determinants as N-electron basis functions. Suppose we have a complete set of functions $\{\chi_i(x)\}$. Any function $\Phi(x_1)$ of a single variable can then be exactly expanded as,

$$\Phi(x_1) = \sum_i a_i\,\chi_i(x_1)$$

where a_i is an expansion coefficient. How can we expand a function of two variables $\Phi(x_1, x_2)$ in an analogous way? If we think of x_2 as being held fixed, then we can expand $\Phi(x_1, x_2)$ as

$$\Phi(x_1, x_2) = \sum_i a_i\,(x_2)\chi_i(x_1)$$

In the expansion

$$\Phi(x_1, x_2) = \sum_i a_i\,(x_2)\chi_i(x_1)$$

the expansion coefficients are now functions of x_2. Since $a_i(x_2)$ is a function of a single variable, it can be expanded in the complete set $\{\chi_i\}$ as

$$a_i(x_2) = \sum_j b_{ij}\,\chi_j(x_2)$$

Thus, we have,

$$\Phi(x_1, x_2) = \sum_{ij} b_{ij}\,\chi_i(x_1)\chi_j(x_2)$$

If, however, we require Φ to be antisymmetric,

$$\Phi(x_1, x_2) = -\Phi(x_2, x_1)$$

then, $b_{ij} = -b_{ji}$ and $b_{ii} = 0$, or

$$\Phi(x_1, x_2) = \sum_i \sum_{j>i} b_{ij}\left[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right] = \frac{1}{\sqrt{2}} \sum_{i<j} b_{ij}\left|\chi_i\chi_j\right\rangle$$

Thus, an arbitrary antisymmetric function of the two variables can be exactly expanded in terms of all unique determinants formed from a complete set of one-variable functions $\{\chi_i(x)\}$. This argument is readily extended to more than two variables, so that the exact wavefunction for the ground and excited states of our N-electron problem can be written as a linear combination of all possible N-electron SDs formed from a complete set of spin orbitals $\{\chi_i\}$. Since all possible determinants can be described by reference to the HF determinant, we can write the exact wavefunction for any state of the system as,

$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_{ra} c_a^r\,|\Psi_a^r\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}\,|\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c\\ r<s<t}} c_{abc}^{rst}\,\left|\Psi_{abc}^{rst}\right\rangle + \cdots$$

Thus, the infinite set of N-electron determinants

$$\{|\Psi_i\rangle\} = \left\{|\Psi_0\rangle, |\Psi_a^r\rangle, |\Psi_{ab}^{rs}\rangle, \left|\Psi_{abc}^{rst}\right\rangle, \dots\right\}$$

is a complete set for the expansion of any N-electron wavefunction. The exact energies of the ground and excited states of the system are the eigenvalues of the Hamiltonian matrix, that is, the matrix with elements $\left\langle\Psi_i\middle|H\middle|\Psi_j\right\rangle$ formed from the complete set $\{|\Psi_i\rangle\}$. Since every $|\Psi_i\rangle$ can be defined by specifying a configuration of spin orbitals from which it is formed, this procedure is called configuration interaction (CI). The lowest eigenvalue of the Hamiltonian matrix, denoted by $\mathcal{E}_0$, calculated variationally as $\mathcal{E}_0 = \langle\Phi|H|\Phi\rangle$, is the exact non-relativistic ground state energy of the system within the BO approximation. The difference between the exact non-relativistic ground state energy $\mathcal{E}_0$ and the energy in the HF limit E_0 is called the correlation energy, $E_{\text{correlation}}$:

$$E_{\text{correlation}} = \mathcal{E}_0 - E_0 \text{ where } \mathcal{E}_0 = \langle\Phi|H|\Phi\rangle \text{ and } E_0 = \langle\Psi_0|H|\Psi_0\rangle$$

since the motion of electrons with opposite spins is not correlated within the HF approximation. Unfortunately, the above procedure for the complete solution to many-electron problem cannot be implemented in practice, because one cannot handle infinite basis sets. If we work with a finite set of spin orbitals $\{\chi_i | i = 1,\ 2,\ 3,\ \dots,\ 2K\}$, then the C_N^{2K} determinants formed from these spin orbitals do not form a complete N-electron basis. However, diagonalizing the finite Hamiltonian matrix formed from these C_N^{2K} determinants lead to solutions that are exact within the one-electron subspace spanned by the $2K$ spin orbitals, or, equivalently, within the N-electron subspace spanned by the C_N^{2K} determinants. This procedure is called the full CI (FCI). Even for relatively small systems and minimal basis sets, the number of determinants that must be included in a FCI calculation is extremely large. To illustrate how large a FCI calculation can be even with the minimal basis, let us consider the case of benzene in the minimal basis.

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A minimal basis set for benzene consists of 72 spin orbitals ($2K = 72$). [one $1s$ AO for each H atom, one $1s$, one $2s$ and three $2p$ for each C atom (five AOs per C atom); this makes a total of 36 spatial AOs in the whole molecule; thus, there are 72 spin AOs.] There are a total of 42 electrons ($N = 42$). The size of the FCI matrix:

$$C_N^{2K} = \frac{72!}{42!\,30!} = 1.643 \times 10^{20}$$

For singly excited determinants an electron can jump from any of the χ_a spin orbitals (there are N of them) to any of the χ_r spin orbitals (there are $2K - N$ of them).

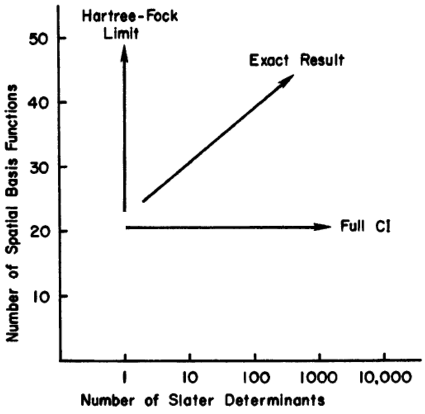
∴ There are $N(2K - N) = 30 \times 42 = 1260$ singly excited determinants. For doubly excited determinants there are $\frac{N(N-1)}{2}$ pairs $\chi_a\chi_b$ spin orbitals and $\frac{(2K-N)(2K-N-1)}{2}$ pairs of $\chi_r\chi_s$ spin orbitals.

∴ There are $\frac{N(N-1)(2K-N)(2K-N-1)}{4} = 374535$ possible doubly excited determinants. Similarly, there are 186435200 possible triply excited determinants, and so on. Let us illustrate these ideas with the minimal basis $\mathrm{H_2}$ model. There are ($2K = 4$) spin orbitals

$$\chi_1(x) = \psi_1(r)\alpha(\omega)$$
$$\chi_2(x) = \psi_1(r)\beta(\omega)$$
$$\chi_3(x) = \psi_2(r)\alpha(\omega)$$
$$\chi_4(x) = \psi_2(r)\beta(\omega)$$

Since $N = 2$, we can form $C_N^{2K} = 4!/(2!\,2!) = 6$ unique determinants. The HF ground state determinant is $|\Psi_0\rangle = |\chi_1\chi_2\rangle = |\psi_1\bar{\psi}_1\rangle = |1\,\bar{1}\rangle$. The singly excited determinants are

$$|\Psi_1^2\rangle = |2\,\bar{1}\rangle$$
$$|\Psi_1^{\bar{2}}\rangle = |\bar{2}\,\bar{1}\rangle$$
$$|\Psi_{\bar{1}}^2\rangle = |1\,2\rangle$$
$$|\Psi_{\bar{1}}^{\bar{2}}\rangle = |1\,\bar{2}\rangle$$



There is only one doubly excited determinant,

$$|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |2\,\bar{2}\rangle = |\chi_3\chi_4\rangle = |\Psi_{12}^{34}\rangle$$

Within the space spanned by the minimal basis set, the exact wavefunction will be a linear combination of these six determinants. The HF ground state $|\Psi_0\rangle$ has two electrons in a g symmetric orbital and is of g symmetry (⊕⊗⊕=⊕). The doubly excited determinant $|\Psi_{12}^{34}\rangle$ has two electrons in an u orbital and hence is also of g symmetry (⊖⊗⊖=⊕). However, the singly excited determinants have one electron in a g symmetric orbital and one in a u symmetric orbital, so that the overall symmetry is u (⊕⊗⊖=⊖). The exact ground state wavefunction of the minimal basis $\mathrm{H_2}$, $|\Phi_0\rangle$, like the HF approximation to it, $|\Psi_0\rangle$, is of g symmetry. Therefore, only the determinants of g symmetry can appear in the expansion for $|\Phi_0\rangle$, so that, we have

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + c_{12}^{34}|\Psi_{12}^{34}\rangle$$

The exact value of the coefficients c_0 and c_{12}^{34} in the exact wavefunction $|\Phi_0\rangle$ and the value of the exact energy $\langle\Phi_0|H|\Phi_0\rangle$ can be determined by diagonalizing the FCI matrix. The FCI matrix is a 2×2

Hamiltonian matrix in the basis spanned by $\{|\Psi_0\rangle\}$ and $\left|\Psi_{12}^{34}\right\rangle$. The FCI Hamiltonian matrix for this system will be,

$$\boldsymbol{H} = \begin{pmatrix} \langle\Psi_0|H|\Psi_0\rangle & \left\langle\Psi_0\middle|H\middle|\Psi_{12}^{34}\right\rangle \\ \left\langle\Psi_{12}^{34}\middle|H\middle|\Psi_0\right\rangle & \left\langle\Psi_{12}^{34}\middle|H\middle|\Psi_{12}^{34}\right\rangle \end{pmatrix}$$

To proceed any further with this problem, we need to be able to evaluate the matrix elements.

Evaluation of the matrix elements of the minimal basis H_2 system

Last class: Hamiltonian matrix for the minimal basis H_2 system

$$\underline{\underline{H}} = \begin{pmatrix} \boxed{\langle \psi_0 | H | \psi_0 \rangle} & \langle \psi_0 | H | \psi_{12}^{34} \rangle \\ \langle \psi_{12}^{34} | H | \psi_0 \rangle & \langle \psi_{12}^{34} | H | \psi_{12}^{34} \rangle \end{pmatrix}$$

Note that, $E_0 = \langle \psi_0 | H | \psi_0 \rangle$, the Hartree-Fock energy of the system

For any operator $\hat{O}$, the two N-electron determinants $|K\rangle$ and $|L\rangle$, our problem is to evaluate $\langle K | \hat{O} | L \rangle$.

For $\underline{\underline{H}}$, we need to evaluate

$$\boxed{\langle \psi_0 | H | \psi_0 \rangle},\ \langle \psi_0 | H | \psi_{12}^{34} \rangle,\ \langle \psi_{12}^{34} | H | \psi_0 \rangle,\ \langle \psi_{12}^{34} | H | \psi_{12}^{34} \rangle$$

Hamiltonian operator, in atomic units

$$\hat{H} = \left(-\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \sum_A \frac{Z_A}{r_{2A}}\right) + \frac{1}{r_{12}} = \left[h(1) + h(2)\right] + r_{12}^{-1} = \hat{O}_1 + \hat{O}_2$$

$$r_{12} = |\vec{r}_1 - \vec{r}_2| = |\vec{r}_2 - \vec{r}_1| = r_{21}$$

$$\therefore \langle \psi_0 | H | \psi_0 \rangle = \langle \psi_0 | O_1 + O_2 | \psi_0 \rangle = \langle \psi_0 | O_1 | \psi_0 \rangle + \langle \psi_0 | O_2 | \psi_0 \rangle$$

$$= \langle \psi_0 | h(1) | \psi_0 \rangle + \langle \psi_0 | h(2) | \psi_0 \rangle + \langle \psi_0 | r_{12}^{-1} | \psi_0 \rangle$$

$$\langle \psi_0 | h(1) | \psi_0 \rangle = \int dx_1 dx_2 \left[\frac{1}{\sqrt{2}}\left\{\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\right\}\right]^* h(r_1) \left[\frac{1}{\sqrt{2}}\left\{\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\right\}\right]$$

$$= \underbrace{\frac{1}{2}\int dx_1 dx_2\, \chi_1^*(x_1)\chi_2^*(x_2) h(r_1) \chi_1(x_1)\chi_2(x_2)}_{①} + \underbrace{\frac{1}{2}\int dx_1 dx_2\, \chi_2^*(x_1)\chi_1^*(x_2) h(r_1) \chi_2(x_1)\chi_1(x_2)}_{②}$$

$$\underbrace{- \frac{1}{2}\int dx_1 dx_2\, \chi_1^*(x_1)\chi_2^*(x_2) h(r_1) \chi_2(x_1)\chi_1(x_2)}_{③} \underbrace{- \frac{1}{2}\int dx_1 dx_2\, \chi_2^*(x_1)\chi_1^*(x_2) h(r_1) \chi_1(x_1)\chi_2(x_2)}_{④}$$

$$① = \frac{1}{2}\int dx_1 dx_2\, \chi_1^*(x_1)\chi_2^*(x_2) h(r_1) \chi_1(x_1)\chi_2(x_2) = \frac{1}{2}\int dx_1\, \chi_1^*(x_1) h(r_1) \chi_1(x_1) \int dx_2\, \chi_2^*(x_2)\chi_2(x_2)$$

$$= \frac{1}{2}\int dx_1\, \chi_1^*(x_1) h(r_1) \chi_1(x_1)$$

$$② = \frac{1}{2}\int dx_1 dx_2\, \chi_2^*(x_1)\chi_1^*(x_2) h(r_1) \chi_2(x_1)\chi_1(x_2) = \frac{1}{2}\int dx_1\, \chi_2^*(x_1) h(r_1) \chi_2(x_1) \int dx_2\, \chi_1^*(x_2)\chi_1(x_2)$$

$$= \frac{1}{2}\int dx_1\, \chi_2^*(x_1) h(r_1) \chi_2(x_1)$$

$$③ = \frac{1}{2}\int dx_1 dx_2\, \chi_1^*(x_1)\chi_2^*(x_2) h(r_1) \chi_2(x_1)\chi_1(x_2) = \frac{1}{2}\int dx_1\, \chi_1^*(x_1) h(r_1) \chi_2(x_1) \int dx_2\, \chi_2^*(x_2)\chi_1(x_2)$$

$$= 0$$

④ $= \frac{1}{2}\int dx_1 dx_2\, \chi_2^*(x_1)\, \chi_1^*(x_2)\, h(r_1)\, \chi_1(x_1)\, \chi_2(x_2) = \frac{1}{2}\int dx_1\, \chi_2^*(x_1)\, h(r_1)\, \chi_1(x_1) \int dx_2\, \chi_1^*(x_2)\, \chi_2(x_2)$

$= 0$

$\therefore \langle \Psi_0 | h(1) | \Psi_0 \rangle = \frac{1}{2}\int dx_1\, \chi_1^*(x_1)\, h(r_1)\, \chi_1(x_1) + \frac{1}{2}\int dx_1\, \chi_2^*(x_1)\, h(r_1)\, \chi_2(x_1)$

Similarly, $\langle \Psi_0 | h(2) | \Psi_0 \rangle = \frac{1}{2}\int dx_1\, \chi_1^*(x_1)\, h(r_1)\, \chi_1(x_1) + \frac{1}{2}\int dx_1\, \chi_2^*(x_1)\, h(r_1)\, \chi_2(x_1)$

$\langle \Psi_0 | h(1) | \Psi_0 \rangle + \langle \Psi_0 | h(2) | \Psi_0 \rangle = \int dx_1\, \chi_1^*(x_1)\, h(r_1) \chi_1(x_1) + \int dx_1\, \chi_2^*(x_1)\, h(r_1)\, \chi_2(x_1)$

or, $\langle \Psi_0 | h(1) + h(2) | \Psi_0 \rangle = \int dx_1\, \chi_1^*(x_1) h(r_1) \chi_1(x_1) + \int dx_1\, \chi_2^*(x_1)\, h(r_1)\, \chi_2(x_1)$

or, $\boxed{\langle \Psi_0 | O_1 | \Psi_0 \rangle = \int dx_1 \chi_1^*(x_1)\, h(r_1) \chi_1(x_1) + \int dx_1\, \chi_2^*(x_1) h(r_1) \chi_2(x_1)}$

or, $\langle \Psi_0 | O_1 | \Psi_0 \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle$

$\langle \Psi_0 | O_2 | \Psi_0 \rangle$, where $O_2 = r_{12}^{-1}$

$$\langle \Psi_0 | O_2 | \Psi_0 \rangle = \int dx_1 dx_2 \left[\frac{1}{\sqrt{2}}\{\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\}\right]^* r_{12}^{-1} \left[\frac{1}{\sqrt{2}}\{\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\}\right]$$

$$= \frac{1}{2}\int dx_1 dx_2 \Big[\underset{①}{\chi_1^*(x_1)\chi_2^*(x_2) r_{12}^{-1} \chi_1(x_1)\, \chi_2(x_2)} + \underset{②}{\chi_2^*(x_1)\chi_1^*(x_2) r_{12}^{-1} \chi_2(x_1)\, \chi_1(x_2)}$$
$$- \underset{③}{\chi_1^*(x_1)\chi_2^*(x_2) r_{12}^{-1} \chi_2(x_1)\chi_1(x_2)} - \underset{④}{\chi_2^*(x_1)\chi_1^*(x_2) r_{12}^{-1} \chi_1(x_1)\, \chi_2(x_2)}\Big]$$

Since $r_{12} = r_{21}$

$\therefore$ interchange of dummy variables in integration in ② ⇒ equal to ①

" " " " " " " ④ ⇒ " " ③

$$\therefore \langle \Psi_0 | O_2 | \Psi_0 \rangle = \int dx_1 dx_2\, \chi_1^*(x_1)\, \chi_2^*(x_2)\, r_{12}^{-1} \chi_1(x_1)\, \chi_2(x_2) - \int dx_1\, dx_2\, \chi_1^*(x_1)\, \chi_2^*(x_2) r_{12}^{-1} \chi_2(x_1)\, \chi_1(x_2)$$

or, $\boxed{\langle \Psi_0 | O_2 | \Psi_0 \rangle = \langle 12 | 12 \rangle - \langle 12 | 21 \rangle}$

$\therefore$ The HF ground state energy,

$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \langle \Psi_0 | O_1 | \Psi_0 \rangle + \langle \Psi_0 | O_2 | \Psi_0 \rangle$

or, $\boxed{E_0 = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle - \langle 12 | 21 \rangle}$

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The FCI Hamiltonian matrix for the minimal basis $\mathrm{H_2}$ system will be,

$$\boldsymbol{H} = \begin{pmatrix} \langle\Psi_0|H|\Psi_0\rangle & \langle\Psi_0|H|\Psi_{12}^{34}\rangle \\ \langle\Psi_{12}^{34}|H|\Psi_0\rangle & \langle\Psi_{12}^{34}|H|\Psi_{12}^{34}\rangle \end{pmatrix}$$

To proceed any further with this problem, we need to be able to evaluate the matrix elements.

Operator and Matrix Elements

Given an operator $\mathcal{O}$ and two N-electron determinants $|K\rangle$ and $|L\rangle$, our problem is to evaluate $\langle K|\mathcal{O}|L\rangle$.

Minimal Basis $\mathrm{H_2}$ Matrix Elements

Let us evaluate the matrix elements that appear in $\boldsymbol{H}$, that is, $\langle\Psi_0|H|\Psi_0\rangle$, $\langle\Psi_{12}^{34}|H|\Psi_{12}^{34}\rangle$, $\langle\Psi_0|H|\Psi_{12}^{34}\rangle$ and $\langle\Psi_{12}^{34}|H|\Psi_0\rangle$. The Hamiltonian,

$$H = \left(-\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \sum_A \frac{Z_A}{r_{2A}}\right) + \frac{1}{r_{12}} = h(1) + h(2) + \frac{1}{r_{12}}$$

where $h(i)$, $i = 1,\ 2$ is the core Hamiltonian for electron i, describing its KE and PE in the field of the nuclei (the core). We define the one-body portion of H as $\mathcal{O}_1 = h(1) + h(2)$. Similarly, the two-body portion of H is defined as $\mathcal{O}_2 = r_{12}^{-1}$. Therefore,

$$H = h(1) + h(2) + \frac{1}{r_{12}} = \mathcal{O}_1 + \mathcal{O}_2$$

so that, any matrix element, $\langle K|H|L\rangle = \langle K|\mathcal{O}_1 + \mathcal{O}_2|L\rangle = \langle K|\mathcal{O}_1|L\rangle + \langle K|\mathcal{O}_2|L\rangle$, for any $|K\rangle$ and $|L\rangle$.

$$\therefore \langle\Psi_0|H|\Psi_0\rangle = \langle\Psi_0|\mathcal{O}_1 + \mathcal{O}_2|\Psi_0\rangle = \langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle + \langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle$$

so that,

$$\langle\Psi_0|H|\Psi_0\rangle = \langle\Psi_0|h(1)|\Psi_0\rangle + \langle\Psi_0|h(2)|\Psi_0\rangle + \left\langle\Psi_0\left|\frac{1}{r_{12}}\right|\Psi_0\right\rangle$$

For the other three integrals in the Hamiltonian matrix,

$$\begin{pmatrix} \langle\Psi_0|H|\Psi_0\rangle & \langle\Psi_0|H|\Psi_{12}^{34}\rangle \\ \langle\Psi_{12}^{34}|H|\Psi_0\rangle & \langle\Psi_{12}^{34}|H|\Psi_{12}^{34}\rangle \end{pmatrix}$$

similar expressions can be written. For the other three integrals in the Hamiltonian matrix, $\langle\Psi_{12}^{34}|H|\Psi_{12}^{34}\rangle$, $\langle\Psi_0|H|\Psi_{12}^{34}\rangle$ and $\langle\Psi_{12}^{34}|H|\Psi_0\rangle$ similar expressions can be written. Let us first consider the matrix element $\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle$, which from $h(1) + h(2) = \mathcal{O}_1$ may be expressed as

$$\langle\Psi_0|h(1)|\Psi_0\rangle = \int dx_1 dx_2 \left[\frac{1}{\sqrt{2}}\{\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\}\right]^* \times h(r_1)\left[\frac{1}{\sqrt{2}}\{\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\}\right]$$

$$= \frac{1}{2}\int dx_1 dx_2\, [\chi_1^*(x_1)\chi_2^*(x_2)h(r_1)\chi_1(x_1)\chi_2(x_2) + \chi_2^*(x_1)\chi_1^*(x_2)h(r_1)\chi_2(x_1)\chi_1(x_2) - \chi_1^*(x_1)\chi_2^*(x_2)h(r_1)\chi_2(x_1)\chi_1(x_2) - \chi_2^*(x_1)\chi_1^*(x_2)h(r_1)\chi_1(x_1)\chi_2(x_2)]$$

Thus, we have

$$\langle\Psi_0|h(1)|\Psi_0\rangle = \frac{1}{2}\int dx_1 dx_2\, \chi_1^*(x_1)\chi_2^*(x_2)h(r_1)\chi_1(x_1)\chi_2(x_2) + \frac{1}{2}\int dx_1 dx_2\, \chi_2^*(x_1)\chi_1^*(x_2)h(r_1)\chi_2(x_1)\chi_1(x_2) - \frac{1}{2}\int dx_1 dx_2\, \chi_1^*(x_1)\chi_2^*(x_2)h(r_1)\chi_2(x_1)\chi_1(x_2) - \frac{1}{2}\int dx_1 dx_2\, \chi_2^*(x_1)\chi_1^*(x_2)h(r_1)\chi_1(x_1)\chi_2(x_2)$$

Now,

$$\frac{1}{2}\int dx_1 dx_2\, \chi_1^*(x_1)\chi_2^*(x_2)h(r_1)\chi_1(x_1)\chi_2(x_2) = \frac{1}{2}\int dx_1\, \chi_1^*(x_1)h(r_1)\chi_1(x_1)\int dx_2\, \chi_2^*(x_2)\chi_2(x_2)$$

$$= \frac{1}{2}\int dx_1\, \chi_1^*(x_1)h(r_1)\chi_1(x_1)$$

Similarly,

$$\frac{1}{2}\int dx_1 dx_2\, \chi_2^*(x_1)\chi_1^*(x_2)h(r_1)\chi_2(x_1)\chi_1(x_2) = \frac{1}{2}\int dx_1\, \chi_2^*(x_1)h(r_1)\chi_2(x_1)\int dx_2\, \chi_1^*(x_2)\chi_1(x_2)$$

$$= \frac{1}{2}\int dx_1\, \chi_2^*(x_1)h(r_1)\chi_2(x_1)$$

Again,

$$\frac{1}{2}\int dx_1dx_2\,\chi_1^*(x_1)\chi_2^*(x_2)h(r_1)\chi_2(x_1)\chi_1(x_2)=\frac{1}{2}\int dx_1\,\chi_1^*(x_1)h(r_1)\chi_2(x_1)\int dx_2\,\chi_2^*(x_2)\chi_1(x_2)=0$$

In the same manner

$$\frac{1}{2}\int dx_1dx_2\,\chi_2^*(x_1)\chi_1^*(x_2)h(r_1)\chi_1(x_1)\chi_2(x_2)=0$$

$$\therefore\ \langle\Psi_0|h(1)|\Psi_0\rangle=\frac{1}{2}\int dx_1\,\chi_1^*(x_1)h(r_1)\chi_1(x_1)+\frac{1}{2}\int dx_1\,\chi_2^*(x_1)h(r_1)\chi_2(x_1)$$

In an identical manner,

$$\langle\Psi_0|h(2)|\Psi_0\rangle=\frac{1}{2}\int dx_1\,\chi_2^*(x_1)h(r_1)\chi_2(x_1)+\frac{1}{2}\int dx_1\,\chi_1^*(x_1)h(r_1)\chi_1(x_1),$$

so that,

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle=\langle\Psi_0|h(1)|\Psi_0\rangle+\langle\Psi_0|h(2)|\Psi_0\rangle$$

$$or,\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle=\int dx_1\,\chi_1^*(x_1)h(r_1)\chi_1(x_1)+\int dx_1\,\chi_2^*(x_1)h(r_1)\chi_2(x_1)$$

The integrals in the above expression are one-electron integrals, that is, the integration is over the coordinates of a single electron. The dummy variables of integration are, by convention, chosen to be the coordinates of electron-1. Introducing the following notation for the one-electron integrals involving spin orbitals,

$$\langle i|h|j\rangle=\langle\chi_i|h|\chi_j\rangle=\int dx_1\,\chi_i^*(x_1)h(r_1)\chi_j(x_1)$$

Therefore, using the notation,

$$\langle i|h|j\rangle=\langle\chi_i|h|\chi_j\rangle=\int dx_1\,\chi_i^*(x_1)h(r_1)\chi_j(x_1)$$

the integral,

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle=\langle\Psi_0|h(1)|\Psi_0\rangle+\langle\Psi_0|h(2)|\Psi_0\rangle$$

becomes,

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle=\langle 1|h|1\rangle+\langle 2|h|2\rangle$$

Let us now evaluate the integral $\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle$.

$$\begin{aligned}\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle&=\int dx_1dx_2\left[\frac{1}{\sqrt{2}}\{\chi_1(x_1)\chi_2(x_2)-\chi_2(x_1)\chi_1(x_2)\}\right]^*\\&\quad\times r_{12}^{-1}\left[\frac{1}{\sqrt{2}}\{\chi_1(x_1)\chi_2(x_2)-\chi_2(x_1)\chi_1(x_2)\}\right]\\&=\frac{1}{2}\int dx_1dx_2\,[\chi_1^*(x_1)\chi_2^*(x_2)r_{12}^{-1}\chi_1(x_1)\chi_2(x_2)+\chi_2^*(x_1)\chi_1^*(x_2)r_{12}^{-1}\chi_2(x_1)\chi_1(x_2)\\&\quad-\chi_1^*(x_1)\chi_2^*(x_2)r_{12}^{-1}\chi_2(x_1)\chi_1(x_2)-\chi_2^*(x_1)\chi_1^*(x_2)r_{12}^{-1}\chi_1(x_1)\chi_2(x_2)]\end{aligned}$$

Since, $r_{12}=r_{21}$, we can interchange the dummy variables of integration in the second term of the above expression and show that it is equal to the first term. Similarly, the third and fourth terms are equal.

$$\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle=\int dx_1dx_2\,\chi_1^*(x_1)\chi_2^*(x_2)r_{12}^{-1}\chi_1(x_1)\chi_2(x_2)-\int dx_1dx_2\,\chi_1^*(x_1)\chi_2^*(x_2)r_{12}^{-1}\chi_2(x_1)\chi_1(x_2)$$

The integrals in the above expression are two-electron integrals, that is, the integration is over the 8 space and spin coordinates of two electrons (why 8?). Therefore, using the notation,

$$\langle ij|kl\rangle=\langle\chi_i\chi_j|\chi_k\chi_l\rangle=\int dx_1dx_2\,\chi_i^*(x_1)\chi_j^*(x_2)r_{12}^{-1}\chi_k(x_1)\chi_l(x_2),$$

for

$$\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle=\int dx_1dx_2\,\chi_1^*(x_1)\chi_2^*(x_2)r_{12}^{-1}\chi_1(x_1)\chi_2(x_2)-\int dx_1dx_2\,\chi_1^*(x_1)\chi_2^*(x_2)r_{12}^{-1}\chi_2(x_1)\chi_1(x_2)$$

we have,

$$\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle=\langle 12|12\rangle-\langle 12|21\rangle$$

$\therefore$ The HF ground state E_0 energy is,

$$E_0=\langle\Psi_0|H|\Psi_0\rangle=\langle\Psi_0|\mathcal{O}_1+\mathcal{O}_2|\Psi_0\rangle=\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle+\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle$$

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For a two electron system,

$$\hat{O}_1 = h(1) + h(2) = \sum_{i=1}^{2} h(i) \quad \text{and} \quad \hat{O}_2 = r_{12}^{-1} \equiv v(1,2)$$

$$\boxed{|\psi_0\rangle = |\chi_1\chi_2\rangle = \frac{1}{\sqrt{2}}\left[\chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2)\right]}$$

Also, HF energy

$$E_0 = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle$$

Generalization for a N-electron system

$$\langle\psi_0|H|\psi_0\rangle = \langle\psi_0|\hat{O}_1 + \hat{O}_2|\psi_0\rangle$$

One-electron operator,

$$\hat{O}_1 = \sum_{i=1}^{N} h(i)$$

$$|K\rangle = |\ldots\chi_m\chi_n\ldots\rangle$$

$|K\rangle$ contains N no. of spin orbitals

$$\langle\psi_0|H|\psi_{12}^{34}\rangle$$

Two-electron operator,

$$\hat{O}_2 = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} r_{ij}^{-1} \equiv \sum_{i=1}^{N}\sum_{j>i}^{N} v(i,j)$$

$$|L\rangle = |\ldots\chi_p\chi_q\ldots\rangle$$

Case-I: $|K\rangle = |L\rangle = |\ldots\chi_m\chi_n\ldots\rangle$

When $|K\rangle$ and $|L\rangle$ have an identical set of spin orbitals

$$\langle K|O_1|K\rangle = \sum_{m=1}^{N}\langle m|h|m\rangle \qquad \langle K|O_2|K\rangle = \frac{1}{2}\sum_{m=1}^{N}\sum_{n=1}^{N}\left[\langle mn|mn\rangle - \langle mn|nm\rangle\right]$$

Case-II: The two determinants $|K\rangle$ and $|L\rangle$ differ by one spin orbital

χ_m in $|K\rangle$ is replaced by χ_p in $|L\rangle$

$$|K\rangle = |\ldots\chi_m\chi_n\ldots\rangle; \quad |L\rangle = |\ldots\chi_p\chi_n\ldots\rangle$$

$$\langle K|O_1|L\rangle = \langle m|h|p\rangle \qquad \langle K|O_2|L\rangle = \sum_{n=1}^{N}\left[\langle mn|pn\rangle - \langle mn|np\rangle\right]$$

Case-III: The two determinants $|K\rangle$ and $|L\rangle$ differ by two spin orbitals

$$|K\rangle = |\ldots\chi_m\chi_n\ldots\rangle, \quad |L\rangle = |\ldots\chi_p\chi_q\ldots\rangle$$

$$\langle K|O_1|L\rangle = 0 \qquad \langle K|O_2|L\rangle = \langle mn|pq\rangle - \langle mn|qp\rangle$$

How to apply these rules for any situation? max. coincidence

$$|\psi_1\rangle = |\chi_a\chi_b\chi_c\chi_d\rangle = |abcd\rangle \qquad |\psi_2\rangle = |crds\rangle = -|crsd\rangle = |sr\underline{cd}\rangle$$

$$|\psi_2\rangle = |\chi_c\chi_r\chi_d\chi_s\rangle = |crds\rangle \qquad |\psi_1\rangle = |ab\underline{cd}\rangle$$

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$|K\rangle = |\Psi_1\rangle$; $m \equiv a, n \equiv b$

$|L\rangle = |\Psi_2\rangle$, $p \equiv s, q \equiv r$

Since, $|\Psi_1\rangle$ and $|\Psi_2\rangle$ differ by two spin orbitals,

$$\langle \Psi_1 | O_1 | \Psi_2 \rangle = 0$$

But, $\langle \Psi_1 | O_2 | \Psi_2 \rangle = \langle ab | sr \rangle - \langle ab | rs \rangle$

Second Quantization Approach

Creation Operator, $a_i^\dagger$: creates an electron in the spin orbital χ_i

$$a_i^\dagger |\chi_k \cdots \chi_l\rangle = |\chi_i \chi_k \cdots \chi_l\rangle$$

$$a_i^\dagger a_j^\dagger |\chi_k \cdots \chi_l\rangle = a_i^\dagger |\chi_j \chi_k \cdots \chi_l\rangle = |\chi_i \chi_j \chi_k \cdots \chi_l\rangle \text{ ——— } ①$$

$$a_j^\dagger a_i^\dagger |\chi_k \cdots \chi_l\rangle = a_j^\dagger |\chi_i \chi_k \cdots \chi_l\rangle = |\chi_j \chi_i \chi_k \cdots \chi_l\rangle = -|\chi_i \chi_j \chi_k \cdots \chi_l\rangle \text{ ——— } ②$$

$$(a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger) |\chi_k \cdots \chi_l\rangle = 0 \Rightarrow a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$$

$\therefore$ Anti-commutator rule: $\{a_i^\dagger, a_j^\dagger\} = 0$

$$a_1^\dagger a_1^\dagger |\chi_2 \chi_3\rangle = a_1^\dagger |\chi_1 \chi_2 \chi_3\rangle = |\chi_1 \chi_1 \chi_2 \chi_3\rangle = 0$$

$$a_i^\dagger |\chi_k \cdots \chi_l\rangle = 0, \text{ if } i \in \{k, \ldots, l\}$$

General Rules for Matrix Elements

It is fairly easy to evaluate matrix elements between two-electron SDs. The N-electron case is more complicated. We present a set of rules (which will derive) to evaluate these matrix elements. There are two types of operators in Quantum Chemistry. The first type of operator is a sum of the one-electron operators,

$$\mathcal{O}_1 = \sum_{i=1}^{N} h(i)$$

where $h(i)$ is any operator involving the ith electron only. These operators represent dynamic variables that depend only on the position or momentum of the electron in question, independent of the position or momentum of other electrons. Examples are: operators for the kinetic energy and operators for the attraction of an electron to a nucleus, etc. The second type of operator is a sum of the two-electron operators,

$$\mathcal{O}_2 = \sum_{i=1}^{N} \sum_{j>i}^{N} v(i,j) \equiv \sum_{i<j} v(i,j)$$

where $v(i,j)$ is an operator that depends on the position (or momentum) of both the ith and jth electron. The Coulomb interaction between two electrons $v(i,j) = r_{ij}^{-1}$ is such an operator. The summation in the above expression is over all unique pairs of electrons. The rules for evaluating the matrix element $\langle K|\mathcal{O}|L\rangle$ between the determinants $|K\rangle$ and $|L\rangle$ depend on

- whether the operator $\mathcal{O}$ is a sum of the one-electron operators $(\mathcal{O}_1)$ or a sum of the two-electron operators $(\mathcal{O}_2)$, and
- the degree to which the two determinants $|K\rangle$ and $|L\rangle$ differ.

We can distinguish three cases:

Case-I: When the two determinants $|K\rangle$ and $|L\rangle$ are identical. Therefore, the matrix element is a diagonal matrix element, $\langle K|\mathcal{O}|K\rangle$. We choose the determinant to be,

$$|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle$$

Case-II: When the two determinants $|K\rangle$ and $|L\rangle$ differ by one spin orbital, χ_m in $|K\rangle$ being replaced by χ_p in $|L\rangle$.

$$|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle, |L\rangle = |\cdots \chi_p \chi_n \cdots\rangle$$

Case-III: When the two determinants $|K\rangle$ and $|L\rangle$ differ by two spin orbitals, χ_m and χ_n in $|K\rangle$ being replaced by χ_p and χ_q in $|L\rangle$.

$$|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle, |L\rangle = |\cdots \chi_p \chi_q \cdots\rangle$$

When the two determinants differ by three or more spin orbitals, the matrix element is always zero.

Rules for the matrix elements for

$$\mathcal{O}_1 = \sum_{i=1}^{N} h(i)$$

Case-I: $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle$

$$\langle K|\mathcal{O}_1|K\rangle = \sum_{m=1}^{N} \langle m|h|m\rangle$$

Case-II: $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle, |L\rangle = |\cdots \chi_p \chi_n \cdots\rangle$

$$\langle K|\mathcal{O}_1|L\rangle = \langle m|h|p\rangle$$

Case-III: $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle, |L\rangle = |\cdots \chi_p \chi_q \cdots\rangle$

$$\langle K|\mathcal{O}_1|L\rangle = 0$$

Rules for the matrix elements for

$$\mathcal{O}_2 = \sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij}^{-1}$$

Case-I: $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle$

$$\langle K|\mathcal{O}_2|K\rangle = \frac{1}{2} \sum_{m=1}^{N} \sum_{n=1}^{N} [\langle mn|mn\rangle - \langle mn|nm\rangle]$$

Case-II: $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle, |L\rangle = |\cdots \chi_p \chi_n \cdots\rangle$

$$\langle K|\mathcal{O}_2|L\rangle = \sum_{n=1}^{N} [\langle mn|pn\rangle - \langle mn|np\rangle]$$

Case-III: $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle, |L\rangle = |\cdots \chi_p \chi_q \cdots\rangle$

$$\langle K|\mathcal{O}_2|L\rangle = \langle mn|pq\rangle - \langle mn|qp\rangle$$

To use the rules, the two determinants must first be in maximum coincidence. Consider, for example, a matrix element between $|\Psi_1\rangle$ and $|\Psi_2\rangle$, where,

$$|\Psi_1\rangle = |abcd\rangle$$

$$|\Psi_2\rangle = |crds\rangle$$

At first glance, it might appear that the two determinants differ in all 4 columns. But, by interchanging columns of $|\Psi_2\rangle$ and keeping track of the sign, we have,

$$|\Psi_2\rangle = |crds\rangle = -|crsd\rangle = |srcd\rangle$$

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Now, $|\Psi_1\rangle = |abcd\rangle$ and $|\Psi_2\rangle = |srcd\rangle$ are in maximum coincidence. They differ in two columns, and we can use the rules obtained in Case-3. We realize that,

$$|K\rangle \equiv |\Psi_1\rangle; |L\rangle \equiv |\Psi_2\rangle; m \equiv a; n \equiv b; p \equiv s; q \equiv r$$

From the rules, it immediately follows that,

$$\langle\Psi_1|\mathcal{O}_1|\Psi_2\rangle = 0; \langle\Psi_1|\mathcal{O}_2|\Psi_2\rangle = \langle ab|sr\rangle - \langle ab|rs\rangle$$

Using the rules, we can immediately write down the expression for the energy of a single determinant $|K\rangle$, that is,

$$\langle K|H|K\rangle = \langle K|\mathcal{O}_1 + \mathcal{O}_2|K\rangle = \sum_{m=1}^{N}\langle m|h|m\rangle + \frac{1}{2}\sum_{m=1}^{N}\sum_{n=1}^{N}[\langle mn|mn\rangle - \langle mn|nm\rangle]$$

Matrix elements with the HF ground state for one-electron operators

$$\mathcal{O}_1 = \sum_{i=1}^{N} h(i)$$

$$\text{Case} - \text{I: } \langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle = \sum_{a=1}^{N}\langle a|h|a\rangle$$

$$\text{Case} - \text{II: } \langle\Psi_0|\mathcal{O}_1|\Psi_a^r\rangle = \langle a|h|r\rangle$$

$$\text{Case} - \text{III: } \langle\Psi_0|\mathcal{O}_1|\Psi_{ab}^{rs}\rangle = 0$$

Matrix elements with the HF ground state for two-electron operators

$$\mathcal{O}_2 = \sum_{i=1}^{N}\sum_{j>i}^{N} r_{ij}^{-1}$$

$$\text{Case} - \text{I: } \langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}[\langle ab|ab\rangle - \langle ab|ba\rangle]$$

$$\text{Case} - \text{II: } \langle\Psi_0|\mathcal{O}_2|\Psi_a^r\rangle = \sum_{b=1}^{N}[\langle ab|rb\rangle - \langle ab|br\rangle]$$

$$\text{Case} - \text{III: } \langle\Psi_0|\mathcal{O}_2|\Psi_{ab}^{rs}\rangle = \langle ab|rs\rangle - \langle ab|sr\rangle$$

∴ The HF ground state energy is

$$E_0 = \sum_{a=1}^{N}\langle a|h|a\rangle + \frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}[\langle ab|ab\rangle - \langle ab|ba\rangle]$$

If $|K\rangle = |\chi_1\chi_2\chi_3\rangle$, let us evaluate the integral $\langle K|H|K\rangle$, by using the rules for matrix elements.
Now,

$$\langle K|H|K\rangle = \sum_{m=1}^{N}\langle m|h|m\rangle + \frac{1}{2}\sum_{m=1}^{N}\sum_{n=1}^{N}[\langle mn|mn\rangle - \langle mn|nm\rangle]$$
$$= \sum_{m=1}^{N}\langle m|h|m\rangle + \sum_{m=1}^{N}\sum_{n>m}^{N}[\langle mn|mn\rangle - \langle mn|nm\rangle]$$

$$\therefore \langle K|H|K\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 3|h|3\rangle + \langle 12|12\rangle - \langle 12|21\rangle + \langle 13|13\rangle - \langle 13|31\rangle$$
$$+\langle 23|23\rangle - \langle 23|32\rangle$$

Rules for the matrix elements for

$$\mathcal{O}_1 = \sum_{i=1}^{N} h(i)$$

Case-I: $|K\rangle = |\cdots\chi_m\chi_n\cdots\rangle$

$$\langle K|\mathcal{O}_1|K\rangle = \sum_{m=1}^{N}\langle m|h|m\rangle$$

Case-II: $|K\rangle = |\cdots\chi_m\chi_n\cdots\rangle, |L\rangle = |\cdots\chi_p\chi_n\cdots\rangle$

$$\langle K|\mathcal{O}_1|L\rangle = \langle m|h|p\rangle$$

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Case-III: $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle, |L\rangle = |\cdots \chi_p \chi_q \cdots\rangle$

$$\langle K|\mathcal{O}_1|L\rangle = 0$$

Rules for the matrix elements for

$$\mathcal{O}_2 = \sum_{i=1}^{N}\sum_{j>i}^{N} r_{ij}^{-1}$$

Case-I: $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle$

$$\langle K|\mathcal{O}_2|K\rangle = \frac{1}{2}\sum_{m=1}^{N}\sum_{n=1}^{N}[\langle mn|mn\rangle - \langle mn|nm\rangle]$$

Case-II: $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle, |L\rangle = |\cdots \chi_p \chi_n \cdots\rangle$

$$\langle K|\mathcal{O}_2|L\rangle = \sum_{n=1}^{N}[\langle mn|pn\rangle - \langle mn|np\rangle]$$

Case-III: $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle, |L\rangle = |\cdots \chi_p \chi_q \cdots\rangle$

$$\langle K|\mathcal{O}_2|L\rangle = \langle mn|pq\rangle - \langle mn|qp\rangle$$

SECOND QUANTIZATION

Antisymmetry principle: an axiom of QM quite apart from the Schrödinger equation. This principle is satisfied by the use of Slater determinants and linear combinations of such determinants for the wavefunctions. Can we satisfy the antisymmetry principle without invoking the Slater determinants? Second quantization: a theoretical idea in which the antisymmetry property of the wavefunction gets transferred onto the algebraic properties of certain operators. Second quantization introduces no new physics. It is an elegant way of treating many-electron systems. This approach shifts much of the emphasis from the N-electron wavefunction to the one- and two-electron integrals, $\langle i|h|j\rangle$ and $\langle ij|kl\rangle$. Second quantization approach begins with the definitions of creation and annihilation operators.

CREATION AND ANNIHILATION OPERATORS

For a spin orbital χ_i we associate a creation operator, $a_i^\dagger$. We define $a_i^\dagger$ by its action on an arbitrary SD, $|\chi_k \dots \chi_l\rangle$ as

$$a_i^\dagger|\chi_k \dots \chi_l\rangle = |\chi_i \chi_k \dots \chi_l\rangle$$

$\therefore$ $a_i^\dagger$ creates an electron in the spin orbital χ_i. The order in which two creation operators are applied to a determinant is crucial. Consider,

$$a_i^\dagger a_j^\dagger|\chi_k \dots \chi_l\rangle = a_i^\dagger|\chi_j \chi_k \dots \chi_l\rangle = |\chi_i \chi_j \chi_k \dots \chi_l\rangle$$

On the other hand,

$$a_j^\dagger a_i^\dagger|\chi_k \dots \chi_l\rangle = a_j^\dagger|\chi_i \chi_k \dots \chi_l\rangle = |\chi_j \chi_i \chi_k \dots \chi_l\rangle = -|\chi_i \chi_j \chi_k \dots \chi_l\rangle$$

where we have used the antisymmetry property of the SDs.

$$\therefore\ (a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger)|\chi_k \dots \chi_l\rangle = 0$$

$\because$ $|\chi_k \dots \chi_l\rangle$ is an arbitrary determinant,

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$$

so that,

$$\{a_i^\dagger, a_j^\dagger\} = 0$$

where we have used the notation for the anticommutator of two operators $a_i^\dagger$ and $a_j^\dagger$. Since

$$a_i^\dagger a_j^\dagger = -a_j^\dagger a_i^\dagger$$

we can interchange the order of two creation operators provided we change the sign. If $i = j$, we have,

$$a_i^\dagger a_i^\dagger = -a_i^\dagger a_i^\dagger = 0$$

which states that we cannot create two electrons in the same spin orbital χ_i (Pauli exclusion principle).

$$\therefore\ a_1^\dagger a_1^\dagger|\chi_2 \chi_3\rangle = a_1^\dagger|\chi_1 \chi_2 \chi_3\rangle = |\chi_1 \chi_1 \chi_2 \chi_3\rangle = 0$$

In general,

$$a_i^\dagger|\chi_k \dots \chi_l\rangle = 0, \text{ if } i \in \{k, \dots, l\},$$

that is, we cannot create an electron in a spin orbital χ_i is there is one already there.

Destruction/Annihilation operator, a_i

destroys an electron in χ_i : $a_i|\chi_i\chi_k\cdots\chi_l\rangle = |\chi_k\cdots\chi_l\rangle$

$a_i|\chi_k\chi_l\chi_i\rangle = -a_i|\chi_k\chi_i\chi_l\rangle = a_i|\chi_i\chi_k\chi_l\rangle = |\chi_k\chi_l\rangle$

$a_i = (a_i^\dagger)^\dagger$: Why is a_i defined as $(a_i^\dagger)^\dagger$?

$|K\rangle = |\chi_i\chi_j\rangle$
$= \frac{1}{\sqrt{2}}[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)]$

$|K\rangle = |\chi_i\chi_j\rangle \Rightarrow \boxed{|K\rangle = a_i^\dagger|\chi_j\rangle}$

Taking the adjoint : $\langle K| = \langle\chi_j|(a_i^\dagger)^\dagger = \langle\chi_j|a_i$ ——— ①

Since, for any operator $\hat{O}$, if $\hat{O}|a\rangle = |b\rangle$, then $\langle a|\hat{O}^\dagger = \langle b|$

Right multiplication of ① by $|K\rangle$

$$\langle K|K\rangle = \langle\chi_j|a_i|K\rangle$$

Now, $\langle K|K\rangle = 1$. Hence, to satisfy this $\langle\chi_j|a_i|K\rangle = 1$

RHS $= \langle\chi_j|a_i|\chi_i\chi_j\rangle = 1$ or, $\langle\chi_j|\chi_j\rangle = 1$

Satisfied only when a_i destroys χ_i from $|K\rangle = |\chi_i\chi_j\rangle$.

$$\langle\chi_j|a_i|\chi_i\chi_j\rangle = \langle\chi_j\chi_i|\chi_i\chi_j\rangle = \langle K|K\rangle = 1$$

Anti-commutation relation for the creation operators

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = \{a_i^\dagger, a_j^\dagger\} = 0$$

Say we have two operators
$\hat{A}, \hat{B}$
$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$

$$\boxed{a_j a_i + a_i a_j = \{a_j, a_i\} = 0}$$

$$a_i a_j = -a_j a_i$$

If $i=j$, $a_i a_i = -a_i a_i = 0$

$\Rightarrow$ we cannot destroy an electron twice

$a_i|\chi_k\cdots\chi_l\rangle = 0$, if $i \notin \{k,\ldots,l\}$

How do we interchange creation and destruction operators?

$$(a_i a_i^\dagger + a_i^\dagger a_i)|\chi_k\ldots\chi_l\rangle = a_i a_i^\dagger|\chi_k\ldots\chi_l\rangle + a_i^\dagger a_i|\chi_k\ldots\chi_l\rangle$$
$$= a_i|\chi_i\chi_k\ldots\chi_l\rangle + 0 = |\chi_k\ldots\chi_l\rangle$$

When χ_i is not occupied in $|\chi_k\ldots\chi_l\rangle$

$$\therefore \boxed{(a_i a_i^\dagger + a_i^\dagger a_i)|\chi_k\ldots\chi_l\rangle = |\chi_k\ldots\chi_l\rangle}$$

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If χ_i is occupied in $|\chi_k \ldots \chi_l\rangle$

$$(a_i a_i^\dagger + a_i^\dagger a_i)|\chi_k\ldots\chi_i\ldots\chi_l\rangle = a_i a_i^\dagger|\chi_k\ldots\chi_i\ldots\chi_l\rangle + a_i^\dagger a_i|\chi_k\ldots\chi_i\ldots\chi_l\rangle$$

$$= 0 + a_i^\dagger a_i|\chi_k\ldots\chi_i\ldots\chi_l\rangle = -a_i^\dagger a_i|\chi_i\ldots\chi_k\ldots\chi_l\rangle = -a_i^\dagger|\ldots\chi_k\ldots\chi_l\rangle$$

$$= -|\chi_i\ldots\chi_k\ldots\chi_l\rangle = |\chi_k\ldots\chi_i\ldots\chi_l\rangle$$

$$\therefore \boxed{(a_i a_i^\dagger + a_i^\dagger a_i)|\chi_k\ldots\chi_i\ldots\chi_l\rangle = |\chi_k\ldots\chi_i\ldots\chi_l\rangle}$$

$$\therefore \quad a_i a_i^\dagger + a_i^\dagger a_i = \{a_i, a_i^\dagger\} = 1$$

$(a_j^\dagger a_i + a_i a_j^\dagger)|\chi_k\ldots\chi_l\rangle$, when $i \neq j$

or, $(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_k\ldots\chi_l\rangle = a_j^\dagger a_i|\chi_k\ldots\chi_l\rangle + a_i a_j^\dagger|\chi_k\ldots\chi_l\rangle$

the entire RHS is non-zero only when χ_i appears and χ_j does not appear in $|\chi_k\ldots\chi_l\rangle$.

When $i \in \{k,\ldots,l\}$ and $j \notin \{k,\ldots,l\}$

$$(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_k\ldots\chi_i\ldots\chi_l\rangle = -(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_i\ldots\chi_k\ldots\chi_l\rangle$$

$$= -a_i a_j^\dagger|\chi_i\ldots\chi_k\ldots\chi_l\rangle - a_j^\dagger \overset{\curvearrowright}{a_i|\chi_i}\ldots\chi_k\ldots\chi_l\rangle$$

$$= -a_i|\chi_j\chi_i\ldots\chi_k\ldots\chi_l\rangle - a_j^\dagger|\ldots\chi_k\ldots\chi_l\rangle$$

$$= \overset{\curvearrowright}{a_i|\chi_i}\chi_j\ldots\chi_k\ldots\chi_l\rangle - |\chi_j\ldots\chi_k\ldots\chi_l\rangle$$

$$= |\chi_j\ldots\chi_k\ldots\chi_l\rangle - |\chi_j\ldots\chi_k\ldots\chi_l\rangle$$

$$= 0$$

$$\therefore \boxed{a_i a_j^\dagger + a_j^\dagger a_i = \{a_i, a_j^\dagger\} = 0}$$

$$a_i a_j^\dagger + a_j^\dagger a_i = \{a_i, a_j^\dagger\} = \delta_{ij}$$

Let us now introduce the annihilation operator, a_i, which is the adjoint of the creation operator, $a_i^\dagger$, that is, $(a_i^\dagger)^\dagger = a_i$. In analogy with $a_i^\dagger|\chi_k \ldots \chi_l\rangle = |\chi_i\chi_k \ldots \chi_l\rangle$, a_i is defined as $a_i|\chi_i\chi_k \ldots \chi_l\rangle = |\chi_k \ldots \chi_l\rangle$. So, a_i annihilates/destroys an electron in χ_i. The annihilation operator can only act on a determinant if the spin orbital, which will disappear, is immediately to the left. If a spin orbital is not in the proper position, it must be placed there by interchanging the columns of the determinant. For example,

$$a_i|\chi_k\chi_l\chi_i\rangle = -a_i|\chi_k\chi_i\chi_l\rangle = a_i|\chi_i\chi_k\chi_l\rangle = |\chi_k\chi_l\rangle$$

Why is the annihilation operator defined as the adjoint of the creation operator? Consider the determinant

$$|K\rangle = |\chi_i\chi_j\rangle$$

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Clearly,

$$|K\rangle = a_i^\dagger|\chi_j\rangle$$

The adjoint of $|K\rangle = a_i^\dagger|\chi_j\rangle$ is,

$$\langle K| = \langle\chi_j|\left(a_i^\dagger\right)^\dagger = \langle\chi_j|a_i$$

since, for an operator $\mathcal{O}$, if $\mathcal{O}|a\rangle = |b\rangle$, then, $\langle a|\mathcal{O}^\dagger = \langle b|$. Multiplying $\langle K| = \langle\chi_j|\left(a_i^\dagger\right)^\dagger = \langle\chi_j|a_i$ on the right by $|K\rangle$, we have,

$$\langle K|K\rangle = \langle\chi_j|a_i|K\rangle$$

Since, $\langle K|K\rangle = 1 = \langle\chi_j|\chi_j\rangle$, our theory is consistent when

$$a_i|K\rangle \equiv a_i|\chi_i\chi_j\rangle = |\chi_j\rangle$$

in agreement with the definition $a_i|\chi_i\chi_k \dots \chi_l\rangle = |\chi_k \dots \chi_l\rangle$ of the annihilation operator. $\langle K| = \langle\chi_j|\left(a_i^\dagger\right)^\dagger = \langle\chi_j|a_i$ shows that a_i acts like a creation operator if it operates on a determinant to the left. Similarly, $a_i^\dagger$ acts like an annihilation operator if it operates to the left. For example, the adjoint of $a_i|K\rangle \equiv a_i|\chi_i\chi_j\rangle = |\chi_j\rangle$ is $\langle K|a_i^\dagger = \langle\chi_j|$. To obtain the anti-commutation relation satisfied by annihilation operators we take the adjoint of

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 = \{a_i^\dagger, a_j^\dagger\}.$$

We recall that,

$$(\mathcal{AB})^\dagger = \mathcal{B}^\dagger\mathcal{A}^\dagger$$

so that,

$$a_j a_i + a_i a_j = 0 = \{a_j, a_i\}.$$

Since,

$$a_i a_j = -a_j a_i$$

we can interchange the order of two annihilation operators provided we change the sign. If $i = j$, we have

$$a_i a_i = -a_i a_i = 0$$

which states that we cannot destroy an electron twice. A consequence of this is that we cannot remove an electron from a spin orbital χ_i, if it is not already there,

$$a_i|\chi_k \dots \chi_l\rangle = 0,\ \text{if}\ i \notin \{k, \dots, l\}$$

How do we interchange creation and annihilation operators? Consider the operator $a_i a_i^\dagger + a_i^\dagger a_i$ acting on an arbitrary determinant acting on an arbitrary determinant, $|\chi_k \dots \chi_l\rangle$. If χ_i is not occupied in $|\chi_k \dots \chi_l\rangle$, then

$$\left(a_i a_i^\dagger + a_i^\dagger a_i\right)|\chi_k \dots \chi_l\rangle = a_i a_i^\dagger|\chi_k \dots \chi_l\rangle + a_i^\dagger a_i|\chi_k \dots \chi_l\rangle = a_i a_i^\dagger|\chi_k \dots \chi_l\rangle = a_i|\chi_i\chi_k \dots \chi_l\rangle$$

$$\therefore \left(a_i a_i^\dagger + a_i^\dagger a_i\right)|\chi_k \dots \chi_l\rangle = |\chi_k \dots \chi_l\rangle$$

However, if χ_i is occupied in $|\chi_k \dots \chi_l\rangle$, then

$$\left(a_i a_i^\dagger + a_i^\dagger a_i\right)|\chi_k \dots \chi_i \dots \chi_l\rangle = a_i a_i^\dagger|\chi_k \dots \chi_i \dots \chi_l\rangle + a_i^\dagger a_i|\chi_k \dots \chi_i \dots \chi_l\rangle = a_i^\dagger a_i|\chi_k \dots \chi_i \dots \chi_l\rangle$$
$$= -a_i^\dagger a_i|\chi_i \dots \chi_k \dots \chi_l\rangle = -a_i^\dagger|\dots \chi_k \dots \chi_l\rangle = -|\chi_i \dots \chi_k \dots \chi_l\rangle$$
$$\therefore \left(a_i a_i^\dagger + a_i^\dagger a_i\right)|\chi_k \dots \chi_i \dots \chi_l\rangle = |\chi_k \dots \chi_i \dots \chi_l\rangle$$

Therefore, in both the cases,

$$\left(a_i a_i^\dagger + a_i^\dagger a_i\right)|\chi_k \dots \chi_l\rangle = |\chi_k \dots \chi_l\rangle\ (\text{when}\ \chi_i\ \text{is not occupied})\ \text{and}$$
$$\left(a_i a_i^\dagger + a_i^\dagger a_i\right)|\chi_k \dots \chi_i \dots \chi_l\rangle = |\chi_k \dots \chi_i \dots \chi_l\rangle\ (\text{when}\ \chi_i\ \text{is occupied}),$$

we recover the same determinant.

$$\therefore a_i a_i^\dagger + a_i^\dagger a_i = 1 = \{a_i, a_i^\dagger\}$$

Finally, we consider $\left(a_j^\dagger a_i + a_i a_j^\dagger\right)|\chi_k \dots \chi_l\rangle$, when $i \neq j$. $\left(a_i a_j^\dagger + a_j^\dagger a_i\right)|\chi_k \dots \chi_l\rangle = a_j^\dagger a_i|\chi_k \dots \chi_l\rangle + a_i a_j^\dagger|\chi_k \dots \chi_l\rangle$ is non-zero only if χ_i appears and χ_j does not in $|\chi_k \dots \chi_l\rangle$. Otherwise, we obtain zero

- either because $a_j^\dagger$ tries to create an electron that is already there,
- or a_i tries to destroy an electron that is not there.

However, even when $i \in \{k, \dots, l\}$ and $j \notin \{k, \dots, l\}$, we obtain zero for the antisymmetry.

$$\left(a_i a_j^\dagger + a_j^\dagger a_i\right)|\chi_k \dots \chi_i \dots \chi_l\rangle = -\left(a_i a_j^\dagger + a_j^\dagger a_i\right)|\chi_i \dots \chi_k \dots \chi_l\rangle$$

$$\text{or, } (a_i a_j^\dagger + a_j^\dagger a_i)|\chi_k \dots \chi_i \dots \chi_l\rangle = -a_i a_j^\dagger|\chi_i \dots \chi_k \dots \chi_l\rangle - a_j^\dagger a_i|\chi_i \dots \chi_k \dots \chi_l\rangle$$

$$\text{or, } (a_i a_j^\dagger + a_j^\dagger a_i)|\chi_k \dots \chi_i \dots \chi_l\rangle = -a_i|\chi_j \chi_i \dots \chi_k \dots \chi_l\rangle - a_j^\dagger|\dots \chi_k \dots \chi_l\rangle$$

Therefore, from,

$$(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_k \dots \chi_i \dots \chi_l\rangle = -a_i|\chi_j \chi_i \dots \chi_k \dots \chi_l\rangle - a_j^\dagger|\dots \chi_k \dots \chi_l\rangle$$

we have,

$$(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_k \dots \chi_i \dots \chi_l\rangle = a_i|\chi_i \chi_j \dots \chi_k \dots \chi_l\rangle - |\chi_j \dots \chi_k \dots \chi_l\rangle$$

$$\text{or, } (a_i a_j^\dagger + a_j^\dagger a_i)|\chi_k \dots \chi_i \dots \chi_l\rangle = |\chi_j \dots \chi_k \dots \chi_l\rangle - |\chi_j \dots \chi_k \dots \chi_l\rangle = 0$$

Thus, we have,

$$a_i a_j^\dagger + a_j^\dagger a_i = 0 = \{a_i, a_j^\dagger\}$$

Let us now combine $a_i a_i^\dagger + a_i^\dagger a_i = 1 = \{a_i, a_i^\dagger\}$ and $a_i a_j^\dagger + a_j^\dagger a_i = 0 = \{a_i, a_j^\dagger\}$ to yield

$$a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} = \{a_i, a_j^\dagger\}$$

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Summary of anti-commutator relationships

(a) between two creation operators: $a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = \{a_i^\dagger, a_j^\dagger\} = 0$

(b) between two destruction operators: $a_j a_i + a_i a_j = \{a_j, a_i\} = 0$

(c) between a creation and a destruction operator: $a_i a_j^\dagger + a_j^\dagger a_i = \{a_i, a_j^\dagger\} = \delta_{ij}$

Definition: a vacuum state (or a zero-particle) : $|\,\rangle$

a state containing no electron

any vacuum state is normalized ; $\langle\,|\,\rangle = 1$

vacuum state has the property : $a_i|\,\rangle = 0 = \langle\,|a_i^\dagger$

(a vac. state contains no electrons, so we cannot remove an electron from it)

$|\chi_i\rangle = a_i^\dagger|\,\rangle$

$a_i^\dagger a_k^\dagger \cdots a_l^\dagger|\,\rangle = a_i^\dagger a_k^\dagger \cdots |\chi_l\rangle = a_i^\dagger a_k^\dagger|\ldots\chi_l\rangle = a_i^\dagger|\chi_k \cdots \chi_l\rangle = |\chi_i \chi_k \cdots \chi_l\rangle$

Second quantized representation of a Slater determinant.

Say, we have two determinants : $|K\rangle = |\chi_i \chi_j\rangle = a_i^\dagger a_j^\dagger|\,\rangle$

$|L\rangle = |\chi_k \chi_l\rangle = a_k^\dagger a_l^\dagger|\,\rangle$

What is the value of the overlap $\langle K|L\rangle$?

$\therefore \langle K| = \langle\,|(a_i^\dagger a_j^\dagger)^\dagger = \langle\,|a_j a_i$

$\langle K|L\rangle = \langle\,|a_j \underline{a_i a_k^\dagger} a_l^\dagger|\,\rangle$

Strategy/Rule: move the destruction operators to the right of the creation operators, until they operate on $|\,\rangle$, using the anti-commutator relationship.

$a_i a_k^\dagger + a_k^\dagger a_i = \delta_{ik}$

or, $a_i a_k^\dagger = \delta_{ik} - a_k^\dagger a_i$

$$\therefore \langle K|L\rangle = \langle\,|a_j(\delta_{ik} - a_k^\dagger a_i)a_l^\dagger|\,\rangle = \delta_{ik}\langle\,|a_j a_l^\dagger|\,\rangle - \langle\,|a_j a_k^\dagger \underline{a_i a_l^\dagger}|\,\rangle$$

$$= \delta_{ik}\langle\,|(\delta_{jl} - a_l^\dagger a_j)|\,\rangle - \langle\,|a_j a_k^\dagger(\delta_{il} - a_l^\dagger a_i)|\,\rangle$$

$$= \delta_{ik}\delta_{jl}\cancelto{1}{\langle\,|\,\rangle} - \delta_{ik}\cancelto{0}{\langle\,|a_l^\dagger a_j|\,\rangle} - \delta_{il}\langle\,|a_j a_k^\dagger|\,\rangle + \cancelto{0}{\langle\,|a_j a_k^\dagger a_l^\dagger a_i|\,\rangle}$$

$$= \delta_{ik}\delta_{jl} - \delta_{il}\langle\,|(\delta_{jk} - a_k^\dagger a_j)|\,\rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}\cancelto{1}{\langle\,|\,\rangle} + \delta_{il}\cancelto{0}{\langle\,|a_k^\dagger a_j|\,\rangle}$$

$$\therefore \boxed{\langle K|L\rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}}$$

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Second quantized operators and their matrix elements

$$\hat{O}_1 = \sum_{i=1}^{N} h(i) = \sum_{ij} \langle i|h|j\rangle a_i^\dagger a_j$$ (definition of $\hat{O}_1$ in the second quantized representation)

$$\hat{O}_2 = \sum_{i=1}^{N}\sum_{j>i}^{N} r_{ij}^{-1} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} r_{ij}^{-1} = \frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle a_i^\dagger a_j^\dagger a_l a_k$$

(Definition of $\hat{O}_2$ in the second quantized representation)

Say, we have a N-electron system:

$$|\Psi_0\rangle = |\chi_1 \chi_2 \ldots \chi_a \chi_b \ldots \chi_N\rangle$$

$$\langle\Psi_0|\hat{O}_1|\Psi_0\rangle = \sum_{ij}\langle i|h|j\rangle\langle\Psi_0|a_i^\dagger a_j|\Psi_0\rangle$$

∵ Both $a_i^\dagger$ and a_j are trying to destroy an electron each ($a_i^\dagger$ to the left, a_j to the right), both i and j must belong to $\{a, b, \ldots\}$ (set of occ. orbitals in Ψ_0)

$$\therefore \langle\Psi_0|\hat{O}_1|\Psi_0\rangle = \sum_{ab}\langle a|h|b\rangle \boxed{\langle\Psi_0|a_a^\dagger a_b|\Psi_0\rangle}$$

Now, $a_a^\dagger a_b + a_b a_a^\dagger = \delta_{ab}$ or, $a_a^\dagger a_b = \delta_{ab} - a_b a_a^\dagger$

$$\therefore \langle\Psi_0|a_a^\dagger a_b|\Psi_0\rangle = \langle\Psi_0|(\delta_{ab} - a_b a_a^\dagger)|\Psi_0\rangle = \delta_{ab}\langle\Psi_0|\Psi_0\rangle - \cancelto{0}{\langle\Psi_0|a_b a_a^\dagger|\Psi_0\rangle}$$

Since $a_a^\dagger$ attempts to create an electron in χ_a which is already occupied in $|\Psi_0\rangle$.

or, $\langle\Psi_0|a_a^\dagger a_b|\Psi_0\rangle = \delta_{ab}$

$$\therefore \langle\Psi_0|\hat{O}_1|\Psi_0\rangle = \sum_{ab}\langle a|h|b\rangle\delta_{ab}$$

or, $\langle\Psi_0|\hat{O}_1|\Psi_0\rangle = \sum_{a}\langle a|h|a\rangle$

We have derived three crucial anticommutation relationships of the creation-annihilation operators:

(a) Between two creation operators:

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 = \{a_i^\dagger, a_j^\dagger\}$$

(b) Between two annihilation operators:

$$a_j a_i + a_i a_j = 0 = \{a_j, a_i\}$$

(c) Between a creation and an annihilation operator:

$$a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} = \{a_i, a_j^\dagger\}$$

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These three anticommutators contain all the properties of Slater determinants. To define a SD in the formalism of second quantization, we define a vacuum state,$|\square\rangle$. The vacuum state represents the state of a system that contains no electrons. The vacuum state,$|\square\rangle$ is normalized.

$$\langle\square|\square\rangle = 1$$

It has the property:

$$a_i|\square\rangle = 0 = \langle\square|a_i^\dagger$$

that is, as the vacuum state contains no electrons, we cannot remove an electron from it. We can construct any state of the system by applying a series of creation operators on $|\square\rangle$. For example, $|\chi_i\rangle = a_i^\dagger|\square\rangle$. In general,

$$a_i^\dagger a_k^\dagger \cdots a_l^\dagger|\square\rangle = |\chi_i\chi_k \cdots \chi_l\rangle$$

The relation,

$$a_i^\dagger a_k^\dagger \cdots a_l^\dagger|\square\rangle = |\chi_i\chi_k \cdots \chi_l\rangle$$

is the second-quantized representation of a Slater determinant (SD). Any result that can be obtained using the properties of determinants can also be proved using only the algebraic properties of creation and annihilation operators. Say we have the determinants,

$$|K\rangle = |\chi_i\chi_j\rangle = a_i^\dagger a_j^\dagger|\square\rangle$$
$$|L\rangle = |\chi_k\chi_l\rangle = a_k^\dagger a_l^\dagger|\square\rangle$$

Ordinarily, we can evaluate the overlap between $|K\rangle$ and $|L\rangle$ by

- expanding out the determinants,
- integrating over the space and spin coordinates of the two electrons, and
- using the orthonormality relation of spin orbitals.

Let us evaluate the overlap by using the formalism of second quantization. Since the adjoint of $|K\rangle = |\chi_i\chi_j\rangle = a_i^\dagger a_j^\dagger|\square\rangle$ is

$$\langle K| = \langle\square|\left(a_i^\dagger a_j^\dagger\right)^\dagger = \langle\square|a_j a_i$$

we have

$$\langle K|L\rangle = \langle\square|a_j a_i a_k^\dagger a_l^\dagger|\square\rangle$$

The general strategy for evaluating such matrix elements is to move, using the anticommutation relations, the annihilation operators to the right until they operate directly on the vacuum state. We begin with a_i, and note that $a_i a_k^\dagger + a_k^\dagger a_i = \delta_{ik} = \{a_i, a_k^\dagger\}$, so that $a_i a_k^\dagger = \delta_{ik} - a_k^\dagger a_i$. Therefore, we have

$$\langle K|L\rangle = \langle\square|a_j a_i a_k^\dagger a_l^\dagger|\square\rangle = \langle\square|a_j\left(\delta_{ik} - a_k^\dagger a_i\right)a_l^\dagger|\square\rangle$$
$$\therefore \langle K|L\rangle = \delta_{ik}\langle\square|a_j a_l^\dagger|\square\rangle - \langle\square|a_j a_k^\dagger a_i a_l^\dagger|\square\rangle$$

To continue,

- we move a_j to the right in the first term, and
- keep moving a_i to the right in the second term.

$$\therefore \langle K|L\rangle = \delta_{ik}\langle\square|\left(\delta_{jl} - a_l^\dagger a_j\right)|\square\rangle - \langle\square|a_j a_k^\dagger\left(\delta_{il} - a_l^\dagger a_i\right)|\square\rangle$$
$$\text{or}, \langle K|L\rangle = \delta_{ik}\delta_{jl}\langle\square|\square\rangle - \delta_{ik}\langle\square|a_l^\dagger a_j|\square\rangle - \delta_{il}\langle\square|a_j a_k^\dagger|\square\rangle + \langle\square|a_j a_k^\dagger a_l^\dagger a_i|\square\rangle$$

The second and fourth terms now have an annihilation operator acting on the vacuum and hence are zero.

$$\therefore \langle K|L\rangle = \delta_{ik}\delta_{jl}\langle\square|\square\rangle - \delta_{il}\langle\square|a_j a_k^\dagger|\square\rangle$$

Finally, we move a_j to the right using the suitable anticommutator to get,

$$\langle K|L\rangle = \delta_{ik}\delta_{jl}\langle\square|\square\rangle - \delta_{il}\langle\square|\left(\delta_{jk} - a_k^\dagger a_j\right)|\square\rangle$$
$$\text{or}, \langle K|L\rangle = \delta_{ik}\delta_{jl}\langle\square|\square\rangle - \delta_{il}\delta_{jk}\langle\square|\square\rangle + \delta_{il}\langle\square|a_k^\dagger a_j|\square\rangle$$

The term $\langle\square|a_k^\dagger a_j|\square\rangle = 0$, since the annihilation operator acts on the vacuum. Since, $\langle\square|\square\rangle = 1$, we have,

$$\langle K|L\rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$$

Second Quantized Operators and Their Matrix Elements

- We can represent determinants by using creation and annihilation operators; these operators obey a set of anticommutation relations and vacuum state.

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- We have found a representation of a many-electron wavefunction that satisfies the requirement of the antisymmetry principle, but which can be manipulated without any knowledge of the properties of determinants.

To be able to develop the entire theory of many-electron systems without using determinants, we must express the many-particle operators, $\mathcal{O}_1$ and $\mathcal{O}_2$, in terms of creation and annihilation operators.

In the first quantization, the one-electron operators are written as

$$\mathcal{O}_1 = \sum_{i=1}^{N} h(i)$$

where the summation runs over all the N electrons in the system. Since each term in $\mathcal{O}_1$ involves a single electron, this operator gives a vanishing matrix element whenever the SDs differ in more than one pair of spin orbitals. The second quantization analogue of $\mathcal{O}_1$ therefore has the structure,

$$\mathcal{O}_1 = \sum_{ij} \langle i|h|j\rangle\, a_i^\dagger a_j$$

since the excitation operators $a_i^\dagger a_j$ shift a single electron in a wavefunction. The summation is over all pairs of spin orbitals to secure the highest possible flexibility.

In the first quantization, the two-electron operators are written as

$$\mathcal{O}_2 = \sum_{i=1}^{N}\sum_{j>i}^{N} r_{ij}^{-1} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} r_{ij}^{-1}$$

where the summations run over all the N electrons in the system. The operator $\mathcal{O}_2$ gives non-vanishing matrix elements between SDs

- if the determinants contain at least two electrons, and
- if they differ in the occupations of at most two pair of electrons.

The second quantized representation of a two-electron operator therefore has the form

$$\mathcal{O}_2 = \frac{1}{2}\sum_{ijkl} \langle ij|kl\rangle\, a_i^\dagger a_j^\dagger a_l a_k$$

The annihilation operators appear to the right of the creation operators in order to ensure that $\mathcal{O}_2$ gives zero when it works on a wavefunction with less than two electrons. To demonstrate that the second quantization is equivalent to our previous development based on the SDs, we calculate the energy of the HF ground state $|\Psi_0\rangle = |\chi_1 \cdots \chi_a \chi_b \cdots \chi_N\rangle$ using the second quantization. For the sum of one-electron operators, we have,

$$\langle \Psi_0|\mathcal{O}_1|\Psi_0\rangle = \sum_{ij} \langle i|h|j\rangle \langle \Psi_0|a_i^\dagger a_j|\Psi_0\rangle$$

Since both a_j and $a_i^\dagger$ are trying to destroy an electron (a_j to the right, and $a_i^\dagger$ to the left), the indices i and j must belong to the set $\{a,\ b,\ \ldots\}$ (the set of occupied orbitals). Therefore, we have,

$$\langle \Psi_0|\mathcal{O}_1|\Psi_0\rangle = \sum_{ab} \langle a|h|b\rangle \langle \Psi_0|a_a^\dagger a_b|\Psi_0\rangle$$

Now, using the relation, $a_a^\dagger a_b = \delta_{ab} - a_b a_a^\dagger$, to move $a_a^\dagger$ to the right, we have,

$$\langle \Psi_0|a_a^\dagger a_b|\Psi_0\rangle = \langle \Psi_0|\delta_{ab} - a_b a_a^\dagger|\Psi_0\rangle = \delta_{ab}\langle \Psi_0|\Psi_0\rangle - \langle \Psi_0|a_b a_a^\dagger|\Psi_0\rangle$$

The term $\langle \Psi_0|a_b a_a^\dagger|\Psi_0\rangle$ is zero since $a_a^\dagger$ attempts to create an electron in χ_a, which is already occupied in $|\Psi_0\rangle$. Since, $\langle \Psi_0|\Psi_0\rangle = 1$, we finally have,

$$\langle \Psi_0|\mathcal{O}_1|\Psi_0\rangle = \sum_{ab} \langle a|h|b\rangle \langle \Psi_0|a_a^\dagger a_b|\Psi_0\rangle = \sum_{ab} \langle a|h|b\rangle\, \delta_{ab} = \sum_{a} \langle a|h|a\rangle$$

This is in agreement with our previous result.

From the last class:

$$\langle\Psi_0|\hat{O}_1|\Psi_0\rangle = \sum_{ab}\langle a|h|b\rangle\langle\Psi_0|a_a^\dagger a_b|\Psi_0\rangle = \sum_{ab}\langle a|h|b\rangle\delta_{ab} = \sum_a\langle a|h|a\rangle$$

For the sum of two-electron operators ($\hat{O}_2$)

$$\langle\Psi_0|\hat{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle\langle\Psi_0|a_i^\dagger a_j^\dagger a_l a_k|\Psi_0\rangle$$

$a_i^\dagger, a_j^\dagger$ are trying to destroy two electrons while acting on $|\Psi_0\rangle$ from the left.

a_l, a_k 〃 〃 〃 〃 〃 〃 〃 〃 〃 〃 〃 〃 right.

$\therefore i,j,k,l$ must belong to the set of occupied orbitals $\{a,b,c,d,\ldots\}$ in $|\Psi_0\rangle$.

$$\therefore \langle\Psi_0|\hat{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{abcd}\langle ab|cd\rangle\boxed{\langle\Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle}$$

Strategy: to move $a_a^\dagger, a_b^\dagger$ to the right until they operate on $|\Psi_0\rangle$ to give 0.

$$\therefore \langle\Psi_0|a_a^\dagger \underline{a_b^\dagger a_d} a_c|\Psi_0\rangle = \langle\Psi_0|a_a^\dagger(\delta_{bd} - a_d a_b^\dagger)a_c|\Psi_0\rangle$$

$$= \delta_{bd}\langle\Psi_0|\underline{a_a^\dagger a_c}|\Psi_0\rangle - \langle\Psi_0|a_a^\dagger a_d \underline{a_b^\dagger a_c}|\Psi_0\rangle$$

$$= \delta_{bd}\langle\Psi_0|(\delta_{ac} - a_c a_a^\dagger)|\Psi_0\rangle - \langle\Psi_0|a_a^\dagger a_d(\delta_{bc} - a_c a_b^\dagger)|\Psi_0\rangle$$

$$= \delta_{bd}\delta_{ac}\cancelto{1}{\langle\Psi_0|\Psi_0\rangle} - \delta_{bd}\cancelto{0}{\langle\Psi_0|a_c a_a^\dagger|\Psi_0\rangle} - \delta_{bc}\langle\Psi_0|a_a^\dagger a_d|\Psi_0\rangle$$
$$+ \cancelto{0}{\langle\Psi_0|a_a^\dagger a_d a_c a_b^\dagger|\Psi_0\rangle}$$

$$= \delta_{bd}\delta_{ac} - \delta_{bc}\langle\Psi_0|a_a^\dagger a_d|\Psi_0\rangle = \delta_{bd}\delta_{ac} - \delta_{bc}\langle\Psi_0|(\delta_{ad} - a_d a_a^\dagger)|\Psi_0\rangle$$

$$= \delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad}\langle\Psi_0|\Psi_0\rangle + \delta_{bc}\langle\Psi_0|a_d a_a^\dagger|\Psi_0\rangle$$

$$= \delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad}$$

$$\therefore \langle\Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad}$$

$$\text{or, } \langle\Psi_0|\hat{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{abcd}\langle ab|cd\rangle\left[\delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad}\right]$$

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or, $\langle \Psi_0|\hat{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{abcd}\langle ab|cd\rangle\delta_{bd}\delta_{ac} - \frac{1}{2}\sum_{abcd}\langle ab|cd\rangle\delta_{bc}\delta_{ad}$

$\big\downarrow$ Set $d=b, c=a$ $\qquad\qquad$ $\big\downarrow$ Set $c=b, d=a$

$$= \frac{1}{2}\sum_{ab}\langle ab|ab\rangle - \frac{1}{2}\sum_{ab}\langle ab|ba\rangle$$

or, $\langle \Psi_0|\hat{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{ab}\left[\langle ab|ab\rangle - \langle ab|ba\rangle\right]$

HF energy, $E_0 = \langle \Psi_0|H|\Psi_0\rangle = \langle \Psi_0|\hat{O}_1+\hat{O}_2|\Psi_0\rangle = \langle \Psi_0|\hat{O}_1|\Psi_0\rangle + \langle \Psi_0|\hat{O}_2|\Psi_0\rangle$

$\therefore E_0 = \sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_{ab}\left[\langle ab|ab\rangle - \langle ab|ba\rangle\right]$

For the sum of two-electron operators, we have,

$$\langle \Psi_0|\mathcal{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle\langle \Psi_0|a_i^\dagger a_j^\dagger a_l a_k|\Psi_0\rangle$$

Since both a_l and a_k, and $a_i^\dagger$ and $a_j^\dagger$ are trying to destroy two electrons (a_l and a_k to the right, and$a_i^\dagger$ and $a_j^\dagger$ to the left), the indices i, j, k, l must belong to the set $\{a, b, \ \ldots\}$ (the set of occupied orbitals).

Thus, we have,

$$\langle \Psi_0|\mathcal{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{abcd}\langle ab|cd\rangle\langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle$$

Thus, our strategy, as before, is to move $a_a^\dagger$ and $a_b^\dagger$ to the right in $\langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle$ until they operate on $|\Psi_0\rangle$.

$$\therefore \langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \langle \Psi_0|a_a^\dagger(\delta_{bd} - a_d a_b^\dagger)a_c|\Psi_0\rangle$$

$$\text{or, } \langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \delta_{bd}\langle \Psi_0|a_a^\dagger a_c|\Psi_0\rangle - \langle \Psi_0|a_a^\dagger a_d a_b^\dagger a_c|\Psi_0\rangle$$

$$\text{or, } \langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \delta_{bd}\langle \Psi_0|\delta_{ac} - a_c a_a^\dagger|\Psi_0\rangle - \langle \Psi_0|a_a^\dagger a_d(\delta_{bc} - a_c a_b^\dagger)|\Psi_0\rangle$$

$$\text{or, } \langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \delta_{bd}\delta_{ac}\langle \Psi_0|\Psi_0\rangle - \delta_{bd}\langle \Psi_0|a_c a_a^\dagger|\Psi_0\rangle - \langle \Psi_0|a_a^\dagger a_d(\delta_{bc} - a_c a_b^\dagger)|\Psi_0\rangle$$

The term, $\langle \Psi_0|a_c a_a^\dagger|\Psi_0\rangle = 0$, since $a_a^\dagger$ acts on an already occupied χ_a in $|\Psi_0\rangle$. Also, since, $\langle \Psi_0|\Psi_0\rangle = 1$, we have,

$$\langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \delta_{bd}\delta_{ac} - \langle \Psi_0|a_a^\dagger a_d(\delta_{bc} - a_c a_b^\dagger)|\Psi_0\rangle$$

$$\text{or, } \langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \delta_{bd}\delta_{ac} - \delta_{bc}\langle \Psi_0|a_a^\dagger a_d|\Psi_0\rangle + \langle \Psi_0|a_a^\dagger a_d a_c a_b^\dagger|\Psi_0\rangle$$

The term, $\langle \Psi_0|a_a^\dagger a_d a_c a_b^\dagger|\Psi_0\rangle = 0$, since $a_b^\dagger$ acts on an already occupied χ_b in $|\Psi_0\rangle$.

$$\therefore \langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \delta_{bd}\delta_{ac} - \delta_{bc}\langle \Psi_0|a_a^\dagger a_d|\Psi_0\rangle = \delta_{bd}\delta_{ac} - \delta_{bc}\langle \Psi_0|\delta_{ad} - a_d a_a^\dagger|\Psi_0\rangle$$

$$\text{or, } \langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad}\langle \Psi_0|\Psi_0\rangle + \delta_{bc}\langle \Psi_0|a_d a_a^\dagger|\Psi_0\rangle$$

The term, $\langle \Psi_0|a_d a_a^\dagger|\Psi_0\rangle = 0$, since $a_a^\dagger$ acts on an already occupied χ_a in $|\Psi_0\rangle$. Also, since, $\langle \Psi_0|\Psi_0\rangle = 1$, we have,

$$\langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad}$$

Thus,

$$\langle \Psi_0|\mathcal{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{abcd}\langle ab|cd\rangle\langle \Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle = \frac{1}{2}\sum_{abcd}\langle ab|cd\rangle\left[\delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad}\right]$$

that is, we have two terms. Hence, from,

$$\langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle = \frac{1}{2} \sum_{abcd} \langle ab|cd\rangle \left[\delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad}\right]$$

we write,

$$\langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle = \frac{1}{2} \sum_{abcd} \langle ab|cd\rangle\, \delta_{bd}\delta_{ac} - \frac{1}{2} \sum_{abcd} \langle ab|cd\rangle\, \delta_{bc}\delta_{ad}$$

We set $c = a$ and $d = b$ in the first term to get $\langle ab|ab\rangle$. We set $c = b$ and $d = a$ in the second term to get $\langle ab|ba\rangle$.

$$\therefore \langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle = \frac{1}{2}\sum_{ab} \langle ab|ab\rangle - \frac{1}{2}\sum_{ab} \langle ab|ba\rangle = \frac{1}{2}\sum_{ab} \left[\langle ab|ab\rangle - \langle ab|ba\rangle\right]$$

This too is in agreement with our previous result.

$$\therefore E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_{a} \langle a|h|a\rangle + \frac{1}{2}\sum_{ab} \left[\langle ab|ab\rangle - \langle ab|ba\rangle\right]$$