Hamiltonian of a system of N electrons, K nuclei, with Z_n charges:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{n=1}^{K} \frac{P_n^2}{2M_n} + \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{i,j=1;i\neq j}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \frac{1}{4\pi\varepsilon_0}\sum_{n=1}^{K}\sum_{i=1}^{N} \frac{Z_n e^2}{|\vec{r}_i - \vec{R}_n|} + \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{i,j=1;i\neq j}^{N} \frac{Z_n Z_{n'} e^2}{|\vec{R}_n - \vec{R}_{n'}|} \quad (4.1)$$

Index i for electrons, n for nuclei, m = electron mass, M_n = nuclei masses.

First 2 terms represent kinetic energies of electrons and nuclei.

3rd term = Coulomb repulsion between electrons.

4th term = Coulomb attraction between electrons and nuclei.

Last term = Coulomb repulsion between nuclei.

Born-Oppenheimer approximation separate the degrees of freedom connected with the motion of the nuclei from those of the electrons, justified with the fact that the nuclei are much heavier that they move much slower than electron. Hamiltonian (4.1) reduced to Born-Oppenheimer Hamiltonian:

$$H_{BO} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{i,j=1;i\neq j}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \frac{1}{4\pi\varepsilon_0}\sum_{n=1}^{K}\sum_{i=1}^{N} \frac{Z_n e^2}{|\vec{r}_i - \vec{R}_n|} \quad (4.2)$$

is a Hamiltonian for the electrons in the field generated by a static configuration of nuclei, and a separate Schrödinger equation for the nuclei in which electronic energy enters as a potential.

Further approximation reduce the 2nd term of (4.2) to an uncoupled Hamiltonian, in which the interaction of one electron with the remaining ones is incorporated in an averaged way into a potential felt by the electron. The independent-particle (IP) Hamiltonian:

$$H_{IP} = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + V(\vec{r}_i)\right] \quad (4.3)$$

Within Born-Oppenheimer approximation, by restricting the electronic wave function to a simple form, we find an approximate independent-particle Hamiltonian (4.3). The coordinates of the wave function are $\vec{x}_1$ and $\vec{x}_2$, $\vec{x}_i = (\vec{r}_i, s_i)$. As electrons are fermions, we use the following anti-symmetric trial wave function for ground state:

$$\Psi(\vec{x}_1, \vec{x}_2) = \Psi(\vec{r}_1, s_1; \vec{r}_2, s_2) = \phi(\vec{r}_1)\phi(\vec{r}_2)\frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)] \quad (4.4)$$

where $\alpha(s) =$ spin up, $\beta(s) =$ spin down, ϕ is an orbital which share the same basis.

Born-Oppenheimer Hamiltonian for the helium atom reads:

$$H_{BO} = -\frac{1}{2}{\nabla_1}^2 + \frac{1}{2}{\nabla_2}^2 + \frac{1}{|\vec{r}_1 - \vec{r}_2|} - \frac{2}{r_1} - \frac{2}{r_2} \tag{4.5}$$

Acting on (4.4),

$$\left[-\frac{1}{2}{\nabla_1}^2 + \frac{1}{2}{\nabla_2}^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right] \phi(\vec{r}_1)\phi(\vec{r}_2) = E\phi(\vec{r}_1)\phi(\vec{r}_2) \tag{4.6}$$

multiply both side by $\phi^*(\vec{r}_1)$ and integrate over $\vec{r}_2$:

$$\left[-\frac{1}{2}{\nabla_1}^2 - \frac{2}{r_1} + \int d^3r_2 |\phi(\vec{r}_2)|^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right] \phi(\vec{r}_1) = E'\phi(\vec{r}_1) \tag{4.7}$$

All the integrals which yield constant multiple of $\phi(\vec{r}_1)$ are absorbed into E'. Hereby, we have used $\phi^*(\vec{r}_i)\phi(\vec{r}_j) = \delta_{ij}$. Equation (4.7) is self-consistent.

Now, beyond restricting the wave function to be **uncorrelated**; by **writing it as a linear combination of 4 fixed, real basis functions.**

$$\phi(\vec{r}) = \sum_{p=1}^{4} C_p \chi_p(\vec{r}) \tag{4.12}$$

leads directly from (4.7) that:

$$\left[-\frac{1}{2}{\nabla_1}^2 - \frac{2}{r_1} + \sum_{r,s=1}^{N} C_r C_s \int d^3r_2 \chi_r(\vec{r}_2)\chi_s(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right] \sum_{q=1}^{4} C_q \chi_q(\vec{r}_1) = E' \sum_{q=1}^{4} C_q \chi_q(\vec{r}_1) \tag{4.13}$$

C_p are real as $\chi_p(\vec{r})$ are real.

Multiply $\chi_p(\vec{r}_1)$ from the left and integrate over $\vec{r}_1$:

$$\sum_{pq} \left(h_{pq} + \sum_{rs} C_r C_s Q_{prqs}\right) C_q = E' \sum_{pq} S_{pq} C_q \tag{4.14}$$

with $$h_{pq} = \left\langle \chi_p \middle| -\frac{1}{2}\nabla^2 - \frac{2}{r} \middle| \chi_q \right\rangle \tag{4.15a}$$

$$Q_{prqs} = \int d^3r_1 d^3r_2 \chi_p(\vec{r}_1)\chi_r(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \chi_q(\vec{r}_1)\chi_s(\vec{r}_2) \tag{4.15b}$$

$S_{pq} = \langle \chi_p | \chi_q \rangle$, overlap matrix (4.15c)

At this stage, we shall take **Gaussian s-basis function**:

$$\chi_p(\vec{r}) = e^{-\alpha_p r^2} \tag{4.16}$$

while $$Q_{prqs} = \frac{2\pi^{5/2}}{(\alpha_p + \alpha_q)(\alpha_r + \alpha_s)\sqrt{\alpha_p + \alpha_q + \alpha_r + \alpha_s}} \tag{4.17}$$

$\alpha_1 = 0.298073$, $\alpha_2 = 1.242567$, $\alpha_3 = 5.782948$, $\alpha_4 = 38.474970$

Program flow

- The 4×4 matrices h_{pq} , S_{pq} and $4 \times 4 \times 4 \times 4$ array Q_{prqs} are calculated.

- Initial values for C_p are chosen.

- Use **C**-values to construct matrix F:

$$F_{pq} = h_{pq} + \sum_{rs} Q_{prqs} C_r C_s \tag{4.18}$$

always check that $\sum_{p,q=1}^{4} C_p S_{pq} C_q = 1$, as the normalisation. (4.19)

- Solve for generalised eigenvalue problem

$$\boldsymbol{FC} = E' \boldsymbol{SC} \tag{4.20}$$

For ground state, the vector **C** is the one corresponding to the lowest eigenvalue.

- Solution **C** from (4.20) is used to build matrix **F** again and so on.

- Ground state energy can be found by evaluating the expectation value of the Hamiltonian for the ground state:

$$E_G = 2 \sum_{pq} C_p C_q h_{pq} + \sum_{pqrs} Q_{prqs} C_p C_q C_r C_s \tag{4.21}$$

Particle-exchange operator, $\boldsymbol{P}_{ij}$

$$\boldsymbol{P}_{ij}\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_i, \dots \vec{x}_j, \dots, \vec{x}_N) = \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_j, \dots \vec{x}_i, \dots, \vec{x}_N) \tag{4.22}$$

For the case of an independent-particle Hamiltonian, which is a sum of one-electron Hamiltonian as in (4.3), we can write the solution of the Schrödinger equation as a product of one-electron states:

$$\Psi(\vec{x}_1, \dots, \vec{x}_N) = \psi_1(\vec{x}_1) \dots \psi_N(\vec{x}_N) \tag{4.24}$$

The one-electron states ψ_k are eigenstates of one-particle Hamiltonian.

Of course, the same state as (4.24) but with the spin-orbitals permuted, is a solution too, as are linear combinations of several such states,

$$\Psi_{AS}(\vec{x}_1, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \sum_{\boldsymbol{P}} \epsilon_P \boldsymbol{P} \psi_1(\vec{x}_1) \dots \psi_N(\vec{x}_N) \tag{4.26}$$

$\boldsymbol{P}$ is a permutation operator which permutes the coordinates of the spin-orbitals only, and not their labels, or acting on labels only (acting on one at a time).

We can write (4.26) in the form of a **Slater determinant**:

$$\Psi_{AS}(\vec{x}_1, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \cdots & \psi_N(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \cdots & \psi_N(\vec{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \cdots & \psi_N(\vec{x}_N) \end{vmatrix} \tag{4.27}$$

Fock extended the Hartree equation by **taking anti-symmetry into account**.

$\mathcal{F}\psi_k = \epsilon_k \psi_k$ with (4.30)

$$\mathcal{F}\psi_k = \left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\vec{r} - \vec{R}_n|} \right] \psi_k(\vec{x}) + \sum_{l=1}^{N} \int dx' |\psi_l(\vec{x}')|^2 \frac{1}{|\vec{r} - \vec{r}'|} \psi_k(\vec{x}) - \sum_{l=1}^{N} \int dx' \psi_l{}^*(\vec{x}') \frac{1}{|\vec{r} - \vec{r}'|} \psi_k(\vec{x}') \psi_l(\vec{x}) \tag{4.31}$$

The operator $\mathcal{F}$ is called the **Fock operator**. The forth term is the same as the third, with two spin-orbital labels k and l interchanged and a minus sign in front resulting from the anti-symmetry of the wave function – it is called the exchange term.

It is clear that (4.31) is a nonlinear equation, which must be solved by a self-consistency iterative procedure analogously to the previous section. Sometimes the name "**self-consistent field theory**" (SCF) is used for this type of approach.

Expanding the spin-orbitals ψ_k as **linear combinations of a finite number of basis states** χ_p:

$$\psi_k(\vec{x}) = \sum_{p=1}^{M} C_{pk}\,\chi_p(\vec{x}) \tag{4.55}$$

Then (4.30) assumes a matrix form

$$\boldsymbol{FC_k} = \boldsymbol{\epsilon_k S C_k} \tag{4.56}$$

where $\boldsymbol{S}$ is the overlap matrix for the basis used.

The **general form of the Fock operator** is

$$\mathcal{F} = h + J - K \tag{4.59}$$

with

$$\begin{aligned} J(\vec{x})\psi(\vec{x}) &= \sum_l \int dx' {\psi_l}^*(\vec{x}')\psi_l(\vec{x}')\frac{1}{r_{12}}\psi(\vec{x}) \\ K(\vec{x})\psi(\vec{x}) &= \sum_l \int dx' {\psi_l}^*(\vec{x}')\psi(\vec{x}')\frac{1}{r_{12}}\psi_l(\vec{x}) \end{aligned} \tag{4.60}$$

The sum over l is over all occupied Fock levels. The Coulomb and exchange operators, written in terms of the orbital parts only, read

$$\begin{aligned} \tilde{J}(\vec{r})\psi(\vec{r}) &= 2\sum_l \int d^3r' {\phi_l}^*(\vec{r}')\phi_l(\vec{r}')\frac{1}{|\vec{r}' - \vec{r}|}\phi(\vec{r}) \\ \tilde{K}(\vec{r})\psi(\vec{r}) &= \sum_l \int d^3r' {\phi_l}^*(\vec{r}')\phi(\vec{r}')\frac{1}{|\vec{r}' - \vec{r}|}\phi_l(\vec{r}) \end{aligned} \tag{4.61}$$

In contrast with (4.60), the sums over l run over half the number of electrons because the spin degrees of freedom have been summed over. The Fock operator now becomes

$$\tilde{\mathcal{F}}(\vec{r}) = h(\vec{r}) + 2\tilde{J}(\vec{r}) - \tilde{K}(\vec{r}) \tag{4.62}$$

The corresponding expression for the **energy** is found analogously and is given by

$$E_g = 2\sum_k \langle\phi_k|h|\phi_k\rangle + \sum_k (2\langle\phi_k|J|\phi_k\rangle - \langle\phi_k|K|\phi_k\rangle) \tag{4.63}$$

For a given basis $\chi_p(\vec{r})$, we obtain the following matrix equation, which is known as the **Roothaan equation**:

$$\boldsymbol{FC}_k = \epsilon \boldsymbol{S C}_k \tag{4.64}$$

$\boldsymbol{S}$ is the overlap matrix for the orbital basis $\chi_p(\vec{r})$ and the matrix $\boldsymbol{F}$ is given by

$$F_{pq} = h_{pq} + \sum_k \sum_{rs} {C_{rk}}^* C_{sk}(2\langle pr|g|qs\rangle - \langle pr|g|sq\rangle) \tag{4.65}$$

where $$h_{pq} = \langle p|h|q\rangle = \int d^3r \chi_p{}^*(\vec{r})\left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\vec{R}_n - \vec{r}|}\right]\chi_q(\vec{r}) \tag{4.66}$$

and $$\langle pr|g|qs\rangle = \int d^3r_1 d^3r_2 \chi_p{}^*(\vec{r}_1)\chi_r{}^*(\vec{r}_2)\frac{1}{|\vec{r}_1 - \vec{r}_2|}\chi_q(\vec{r}_1)\chi_s(\vec{r}_2) \tag{4.67}$$

k labels the orbitals ϕ_k and *p, q,* and *s* label the basis functions.

The **density matrix** for restricted Hartree-Fock is defined as

$$P_{pq} = 2\sum_{k} C_{pk}{C_{qk}}^{*} \tag{4.68}$$

Using (4.68), the Fock matrix can be written as

$$F_{pq} = h_{pq} + \frac{1}{2}\sum_{rs} P_{sr}(2\langle pr|g|qs\rangle - \langle pr|g|sq\rangle) \tag{4.70}$$

and the energy is given by

$$E = \sum_{pq} P_{pq}h_{pq} + \frac{1}{2}\sum_{pqrs} P_{pq}P_{sr}\left(\langle pr|g|qs\rangle - \frac{1}{2}\langle pr|g|sq\rangle\right) \tag{4.71}$$

Gaussian function:

$$\chi_{\alpha}(\vec{r}) = P_M(x,y,z)e^{-\alpha\left(\vec{r}-\vec{R}_A\right)^2} \tag{4.78}$$

which is centred around a nucleus located at $\vec{R}_A$. The polynomials P_M contain the angular-dependent part of the orbitals, which is given by the spherical harmonics $Y_m^l(\theta,\phi)$. For $l = 0$, these functions are spherically symmetric, 1s-orbital is given as

$${\chi_{\alpha}}^{(s)}(\vec{r}) = e^{-\alpha\left(\vec{r}-\vec{R}_A\right)^2} \tag{4.81}$$

For $l = 1$, there are three p-orbitals,

$${\chi_{\alpha}}^{(p_x)}(\vec{r}) = xe^{-\alpha\left(\vec{r}-\vec{R}_A\right)^2} \tag{4.82}$$

The two-electron integral

$$\begin{aligned}
&\langle 1s,\alpha,A;1s,\beta,B|g|1s,\gamma,C;1s,\delta,D\rangle \\
&\quad= \int d^3r_1 d^3r_2 e^{-\alpha|\vec{r}_1-\vec{R}_A|^2} e^{-\beta|\vec{r}_2-\vec{R}_B|^2} \frac{1}{r_{12}} e^{-\gamma|\vec{r}_1-\vec{R}_C|^2} e^{-\delta|\vec{r}_2-\vec{R}_D|^2} \\
&\quad= \frac{2\pi^{(5/2)}}{(\alpha+\gamma)(\beta+\delta)\sqrt{\alpha+\beta+\gamma+\delta}} \\
&\quad\times exp\left[-\frac{\alpha\gamma}{\alpha+\gamma\gamma}\left|\vec{R}_A-\vec{R}_C\right|^2 - \frac{\beta\delta}{\beta+\delta}\left|\vec{R}_B-\vec{R}_D\right|^2\right] \\
&\quad\times F_0\left[\frac{(\alpha+\gamma)(\beta+\delta)}{(\alpha+\beta+\gamma+\delta)}\left|\vec{R}_P-\vec{R}_Q\right|^2\right]
\end{aligned} \tag{4.123}$$

$$\vec{R}_P = \frac{\vec{R}_A-\vec{R}_C}{2} \qquad \vec{R}_Q = \frac{\vec{R}_B-\vec{R}_D}{2} \qquad F_0(x) = erf(x) = \frac{2}{\sqrt{\pi}}\int_0^x dx' e^{-x'^2}$$