Introduction to Quantum Chemistry

part III

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Approximations

Variational principle

If we don't know the solutions of Schrödinger equation

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

we can take a trial function ϕ which depends on the same set of parameters like the ψ_n function and calculate an average value of Hamiltonian

$$\varepsilon[\phi] = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$$

The variational principle says that

$$\varepsilon[\phi] \geq E_0 \wedge \varepsilon = E_0 \Leftrightarrow \phi = \psi_0$$

Variational principle - proof

1. If we will take $\phi = \psi_0$ then $\varepsilon[\phi] = E_0$.

2. Let's take linear combination of eigenfunctions of Hamiltonian $\hat{H}$ as our unknown function ϕ.

$$|\phi\rangle = \sum_{k=0}^{\infty} c_k |\psi_k\rangle, \qquad \langle\psi_k|\psi_l\rangle = \delta_{kl}$$

Let's assume that the function $|\phi\rangle$ is normalized $\langle\phi|\phi\rangle = 1 \Leftrightarrow \sum_{k=0}^{\infty} |c_k|^2 = 1$
Then

$$\varepsilon = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_k^* c_l \langle\psi_k|\hat{H}|\psi_l\rangle = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} c_k^* c_l E_l \delta_{kl} = \sum_{k=0}^{\infty} |c_k|^2 E_k$$

$$\varepsilon - E_0 = \sum_{k=0}^{\infty} |c_k|^2 E_k - E_0 \underbrace{\sum_{k=0}^{\infty} |c_k|^2}_{1} = \sum_{k=0}^{\infty} |c_k|^2 (E_k - E_0) \geq 0$$

Variational principle - practically

In practice we introduce to the trial function a set of variational parameters $\{c_1, c_2, \ldots, c_p\}$ and if the function $|\psi_k\rangle$ depended on m variables $\psi_n(q_1, q_2, \ldots, q_m)$, the function $|\phi\rangle$ now depends on $m + p$ variables $\phi(q_1, q_2, \ldots, q_m, c_1, c_2, \ldots, c_p)$.

But when we integrate ($\langle\phi|\hat{H}|\phi\rangle$) we integrate over $\{q_1, q_2, \ldots, q_m\}$ and ε depends on p parameters.

Our purpose is to find a minimum of the function $|\phi\rangle$

$$\frac{\partial\varepsilon(c_1, c_2, \ldots, c_p)}{\partial c_i} = 0 \qquad i \in \langle 1, p\rangle \cap \mathbb{N}$$

The above expression is a set of equations, most frequently - nonlinear. Moreover, it is only a necessary condition but insufficient.

Variational principle - example

By means of variational method let's evaluate the energy of the lowest energy state of hydrogen atom. As a trial function let's take the

$$\phi(\boldsymbol{r}, c) = N(c)e^{-cr}$$

1. At the beginning we have to find normalization factor N.

$$1 = \langle\phi|\phi\rangle = |N(c)|^2 \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 e^{-2cr} \sin\theta d\theta dr d\phi =$$

$$4\pi|N(c)|^2 \int_0^\infty r^2 e^{-2cr} dr = \frac{\pi}{c^3}|N(c)|^2 \quad \Rightarrow N(c) = \sqrt{\frac{c^3}{\pi}}$$

Variational principle - example

2. Next we have to act by means of the Hamiltonian on the trial function.

$$\langle\phi|\hat{H}|\phi\rangle = -\frac{\hbar^2}{2\mu}\langle\phi|\Delta|\phi\rangle - \frac{Ze^2}{4\pi\epsilon_0}\langle\phi|\frac{1}{r}|\phi\rangle$$

First the $\langle\phi|\Delta|\phi\rangle$

$$\langle\phi|\Delta|\phi\rangle =$$

$$\frac{c^3}{\pi}\int e^{-cr}\Delta e^{-cr} d^3r = \frac{c^3}{\pi}4\pi\int_0^\infty r^2 e^{-cr}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}e^{-cr}dr =$$

$$4c^3\int_0^\infty (c^2r^2 - 2cr)e^{-2cr}dr =$$

$$4c^3\left(c^2\frac{2!}{2c^3} - 2c\frac{1!}{(2c)^2}\right) = -4c^3\frac{1}{4c} = -c^2$$

Variational principle - example, continuation ...

Next, the $\langle\phi|\frac{1}{r}|\phi\rangle$

$$\langle\phi|\frac{1}{r}|\phi\rangle =$$

$$\frac{c^3}{\pi}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} r^2 dr \frac{1}{r} e^{-2cr} =$$

$$4c^3 \int_0^{\infty} r e^{-2cr} dr = 4c^3 \frac{1}{(2c)^2} = c$$

Thus,

$$\varepsilon(c) = \frac{\hbar^2}{2\mu}c^2 - \frac{Ze^2}{4\pi\epsilon_0}c$$

Variational principle - example, continuation ...

We are looking for the minimum of the $\varepsilon(c)$ function

$$0 = \frac{d}{dc}\varepsilon(c) = \frac{\hbar^2}{\mu}c - \frac{Ze^2}{4\pi\epsilon_0} \qquad \Rightarrow c = \frac{Ze^2\mu}{4\pi\epsilon_0\hbar^2} = \frac{Z}{a_0}$$

In atomic units ($\mu = e = \hbar = a_0 = 1$) we get $\varepsilon(c) = -\frac{1}{2}$

Notice, that we obtained the exact function of the lowest energy state of hydrogen-like atom.

$$\phi(\boldsymbol{r}, c) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$$

It is a rule: When in the family of trial functions will be an exact function then the variational method will find the function.

Variational principle - second example

By means of variational principle let's evaluate the lowest energy state of hydrogen atom using following trial function

$$\phi(\boldsymbol{r}, c) = e^{-cr^2}$$

Again, we have to calculate the normalization factor and calculate average value of Hamiltonian

$$\langle\phi|\hat{H}|\phi\rangle = -\frac{\hbar^2}{2\mu}\langle\phi|\Delta|\phi\rangle - \frac{Ze^2}{4\pi\epsilon_0}\langle\phi|\frac{1}{r}|\phi\rangle$$

In atomic units the energy equals $-\frac{4}{3\pi} \simeq -0.424$. In previous case it was $-\frac{1}{2}$

Ritz method

In Ritz method we assume that the trial function is a linear combination of p known functions, unnecesarily normalized.

$$\phi = \sum_{k=1}^{p} c_k \chi_k$$

According to the variational principle

$$\varepsilon = \frac{\sum_{k=1}^{p} \sum_{l=1}^{p} c_k^* c_l \langle \chi_k | \hat{H} \chi_l \rangle}{\sum_{k=1}^{p} \sum_{l=1}^{p} c_k^* c_l \langle \chi_k | \chi_l \rangle} = \frac{F}{G}$$

Denoting

$$\begin{aligned} \langle \chi_k | \hat{H} \chi_l \rangle &= H_{kl} \\ \langle \chi_k | \chi_l \rangle &= S_{kl} \qquad \leftarrow \text{overlap integral} \end{aligned}$$

Ritz method - continuation ...

And using the variational requirements

$$\frac{\partial \varepsilon}{\partial c_i^*} = 0 \qquad \text{additionaly} \qquad \frac{\partial c_i^*}{\partial c_k^*} = \delta_{ik}$$

we get

$$\frac{G \sum_{l=1}^{p} c_l H_{il} - F \sum_{l=1}^{p} c_l S_{il}}{G^2} =$$

$$= \frac{\sum_{l=1}^{p} c_l H_{il} - \varepsilon \sum_{l=1}^{p} c_l S_{il}}{G} = \frac{\sum_{l=1}^{p} c_l \left(H_{il} - \varepsilon S_{il} \right)}{G} = 0$$

and thus

$$\sum_{l=1}^{p} c_l \left(H_{il} - \varepsilon S_{il} \right) = 0 \qquad i \in \langle 1, p \rangle \cap \mathbb{N}$$

Ritz method - continuation ...

In matrix form

$$(\boldsymbol{H} - \varepsilon \boldsymbol{S})\boldsymbol{c} = \boldsymbol{0}$$

For nontrivial solutions

$$|\boldsymbol{H} - \varepsilon \boldsymbol{S}| = 0$$

i.e.

$$\begin{vmatrix} H_{11} - \varepsilon S_{11} & H_{12} - \varepsilon S_{12} & \dots & H_{1p} - \varepsilon S_{1p} \\ H_{21} - \varepsilon S_{21} & H_{22} - \varepsilon S_{22} & \dots & H_{2p} - \varepsilon S_{2p} \\ \vdots & \vdots & \ddots & \vdots \\ H_{p1} - \varepsilon S_{p1} & H_{p2} - \varepsilon S_{p2} & \dots & H_{pp} - \varepsilon S_{pp} \end{vmatrix} = 0$$

Ritz method - continuation ...

The solution leads to polynomial of p_{th} degree with unknown ε.

Because the $\hat{H}$ are hermitian all the $\varepsilon_i, i \in \{1, p\} \cap \mathbb{N}$ are real. One can order them increasingly

$$\varepsilon_1 \leq \varepsilon_2 \leq \varepsilon_3 \leq \cdots \leq \varepsilon_p$$

Then, the ε_i is the i-th approximation of i-th state, E_i.

Basically

$$\varepsilon_i \geq E_i$$

which is the MacDonald-Undheim-Hylleraas-Löwdin theorem.

Many-electrons systems

One-electron approximation

To every electron we assign one-electron function, so called *spinorbital*. Spinrobital depends only on the coordinates of one electron.

$$\phi(\boldsymbol{q}_i) = \phi(\boldsymbol{r}_i, \sigma_i)$$

Typically spinorbitals are products of spatial function (called orbitals) and appropriate spin punction.

$$\begin{cases} \phi_k(\boldsymbol{r}_i)\alpha(\sigma_i) \\ \phi_k(\boldsymbol{r}_i)\beta(\sigma_i) \end{cases}$$

$$\begin{cases} \alpha(\sigma_i) = \delta_{\sigma_i, \frac{1}{2}} \\ \beta(\sigma_i) = \delta_{\sigma_i, -\frac{1}{2}} \end{cases}$$

Slater determinant

Antisymmetrical wave function for many-electron system.

$$\Psi(\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{q}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\boldsymbol{q}_1) & \phi_1(\boldsymbol{q}_2) & \ldots & \phi_1(\boldsymbol{q}_N) \\ \phi_2(\boldsymbol{q}_1) & \phi_2(\boldsymbol{q}_2) & \ldots & \phi_2(\boldsymbol{q}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\boldsymbol{q}_1) & \phi_N(\boldsymbol{q}_2) & \ldots & \phi_N(\boldsymbol{q}_N) \end{vmatrix}$$

Advantages of this type of many-electron wavefunction

- **Antisymmetry** - changing of coordinates of two electrons (changing of two columns) changes sign of the determinant,
- **Pauli's correlation** - if two electrons will occupy the same spinorbital then two rows will be the same and the determinant will equal 0. At best one electron can occupy one spiorbital, i.e. Slater detrminant take into account the correlation of electrons with the same spin.

Helium atom

$$\Psi(\boldsymbol{q}_1, \boldsymbol{q}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\boldsymbol{q}_1) & \phi_1(\boldsymbol{q}_2) \\ \phi_2(\boldsymbol{q}_1) & \phi_2(\boldsymbol{q}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left[\phi_1(\boldsymbol{q}_1)\phi_2(\boldsymbol{q}_2) - \phi_1(\boldsymbol{q}_2)\phi_2(\boldsymbol{q}_1)\right]$$

In the first approximation we can take 1s orbital of hydrogen-like atoms to represent the spatial part of the spinorbitals.

$$\begin{cases} \phi_1(\boldsymbol{r}_i, \sigma_i) = 1s(\boldsymbol{r}_i)\alpha(\sigma_i) \\ \phi_2(\boldsymbol{r}_i, \sigma_i) = 1s(\boldsymbol{r}_i)\beta(\sigma_i) \end{cases}$$

$$\Psi(\boldsymbol{q}_1, \boldsymbol{q}_2) = \frac{1}{\sqrt{2}} 1s(\boldsymbol{r}_1) 1s(\boldsymbol{r}_2) \left[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)\right]$$

So, the function is now a product of a function of only spatial coordinates and a function of only spin coordinates

Helium atom - continuation ...

$$\Psi(\boldsymbol{q}_1, \boldsymbol{q}_2) = \Phi(\boldsymbol{r}_1, (\boldsymbol{r}_2))\Omega(\sigma_1, \sigma_2)$$

$$\begin{aligned} \Phi(\boldsymbol{r}_1, (\boldsymbol{r}_2)) &= 1s(\boldsymbol{r}_1)1s(\boldsymbol{r}_2) \\ \Omega(\sigma_1, \sigma_2) &= \frac{1}{\sqrt{2}}\left[\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1)\right] \end{aligned}$$

One can act by means of $\hat{S}^2$ and $\hat{S}_z$ on the spin functions and thus obtain that $S = 0$ and $M_s = 0$.

Multiplicity

In general one define the *multiplicity*

$$d_s = 2S + 1$$

S	d_s	state
0	1	singlet
1/2	2	doublet
1	3	triplet
3/2	4	quartet
...	...	...

Excited helium atom

Let's excite one electron 1s $\rightarrow$ 2s. In this case two electrons can have different spins because they occupy different space orbital (different space). Thus we can build 4 Slater determinants

$$\begin{aligned}\Psi_1(\boldsymbol{q}_1, \boldsymbol{q}_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(\boldsymbol{r}_1)\alpha(\sigma_1) & 1s(\boldsymbol{r}_2)\alpha(\sigma_2) \\ 2s(\boldsymbol{r}_1)\alpha(\sigma_1) & 2s(\boldsymbol{r}_2)\alpha(\sigma_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \left[1s(\boldsymbol{r}_1)2s(\boldsymbol{r}_2) - 2s(\boldsymbol{r}_1)1s(\boldsymbol{r}_2)\right] \alpha(\sigma_1)\alpha(\sigma_2)\end{aligned}$$

$$\begin{aligned}\Psi_2(\boldsymbol{q}_1, \boldsymbol{q}_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(\boldsymbol{r}_1)\alpha(\sigma_1) & 1s(\boldsymbol{r}_2)\alpha(\sigma_2) \\ 2s(\boldsymbol{r}_1)\beta(\sigma_1) & 2s(\boldsymbol{r}_2)\beta(\sigma_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} \left[1s(\boldsymbol{r}_1)2s(\boldsymbol{r}_2)\alpha(\sigma_1)\beta(\sigma_2) - 2s(\boldsymbol{r}_1)1s(\boldsymbol{r}_2)\alpha(\sigma_2)\beta(\sigma_1)\right]\end{aligned}$$

Excited helium atom

$$\Psi_3(\boldsymbol{q}_1, \boldsymbol{q}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(\boldsymbol{r}_1)\beta(\sigma_1) & 1s(\boldsymbol{r}_2)\beta(\sigma_2) \\ 2s(\boldsymbol{r}_1)\alpha(\sigma_1) & 2s(\boldsymbol{r}_2)\alpha(\sigma_2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} [1s(\boldsymbol{r}_1)2s(\boldsymbol{r}_2)\beta(\sigma_1)\alpha(\sigma_2) - 2s(\boldsymbol{r}_1)1s(\boldsymbol{r}_2)\alpha(\sigma_1)\beta(\sigma_2)]$$

$$\Psi_4(\boldsymbol{q}_1, \boldsymbol{q}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(\boldsymbol{r}_1)\beta(\sigma_1) & 1s(\boldsymbol{r}_2)\beta(\sigma_2) \\ 2s(\boldsymbol{r}_1)\beta(\sigma_1) & 2s(\boldsymbol{r}_2)\beta(\sigma_2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} [1s(\boldsymbol{r}_1)2s(\boldsymbol{r}_2) - 2s(\boldsymbol{r}_1)1s(\boldsymbol{r}_2)]\,\beta(\sigma_1)\beta(\sigma_2)$$

Functions Ψ_1 and Ψ_4 have S = 1 and M_s = 1 and M_s = -1 respectively (triplet states). Functions Ψ_2 and Ψ_3 are not eigenfunctions of $\hat{S}^2$ operator and they are characterised by the same occupancies, thus their energy is the same and those two functions are degenerated.

Excited helium atom

We can build linear combinations of those two functions

$$\begin{aligned}\Phi_2(\boldsymbol{q}_1,\boldsymbol{q}_2) &= \frac{1}{\sqrt{2}}\left[\Psi_2(\boldsymbol{q}_1,\boldsymbol{q}_2)+\Psi_3(\boldsymbol{q}_1,\boldsymbol{q}_2)\right] \\ &= \frac{1}{\sqrt{2}}\left[1s(\boldsymbol{r}_1)2s(\boldsymbol{r}_2)-2s(\boldsymbol{r}_1)1s(\boldsymbol{r}_2)\right]\left[\alpha(\sigma_1)\beta(\sigma_2)+\beta(\sigma_1)\alpha(\sigma_2)\right]\end{aligned}$$

$$\begin{aligned}\Phi_3(\boldsymbol{q}_1,\boldsymbol{q}_2) &= \frac{1}{\sqrt{2}}\left[\Psi_2(\boldsymbol{q}_1,\boldsymbol{q}_2)-\Psi_3(\boldsymbol{q}_1,\boldsymbol{q}_2)\right] \\ &= \frac{1}{\sqrt{2}}\left[1s(\boldsymbol{r}_1)2s(\boldsymbol{r}_2)+2s(\boldsymbol{r}_1)1s(\boldsymbol{r}_2)\right]\left[\alpha(\sigma_1)\beta(\sigma_2)-\beta(\sigma_1)\alpha(\sigma_2)\right]\end{aligned}$$

Now, function Φ_2 have $S=1$ and $M_s=0$ while the function Φ_3 have $S=0$ and $M_s=0$.

Excited helium atom

We can now order the triplet-state functions marking the spin functions as $^{2S+1}\Omega_{M_s}$

$$\begin{cases} \Psi_{T1}(\boldsymbol{q}_1, \boldsymbol{q}_2) = \Phi_{\text{asym}}\, {}^3\Omega_1(\sigma_1, \sigma_2) \\ \Psi_{T2}(\boldsymbol{q}_1, \boldsymbol{q}_2) = \Phi_{\text{asym}}\, {}^3\Omega_0(\sigma_1, \sigma_2) \\ \Psi_{T3}(\boldsymbol{q}_1, \boldsymbol{q}_2) = \Phi_{\text{asym}}\, {}^3\Omega_{-1}(\sigma_1, \sigma_2) \end{cases}$$

where

$$\Phi_{\text{asym}} = \frac{1}{\sqrt{2}}\left[1s(\boldsymbol{r}_1)2s(\boldsymbol{r}_2) + 2s(\boldsymbol{r}_1)1s(\boldsymbol{r}_2)\right]$$

is asymettrical spatial function. The spin functions

$$\begin{cases} {}^3\Omega_1(\sigma_1, \sigma_2) = \alpha(\sigma_1)\alpha(\sigma_2) \\ {}^3\Omega_0(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}}\left[\alpha(\sigma_1)\beta(\sigma_2) + \beta(\sigma_1)\alpha(\sigma_2)\right] \\ {}^3\Omega_{-1}(\sigma_1, \sigma_2) = \beta(\sigma_1)\beta(\sigma_2) \end{cases}$$

Excited helium atom

The spin functions are symmetrical, and the spatial functions are asymmetrical which finaly assure the antisimmetry of the whole function.

the Ψ_{T1} and Ψ_{T3} are one-determinantal wave functions, while the Ψ_{T2} is two-determinantal.

In the case of helium atom it was possible to separate spatial part and spin part of the wave function. In the case of tri-electron and larger systems it is not even possible.

Adiabatic approximation

$$\Psi(\boldsymbol{r}, \boldsymbol{R}) = \Psi_{el}(\boldsymbol{r}, \boldsymbol{R}) \Psi_{\text{nucl}}(\boldsymbol{R})$$

The electronic wavefunction is a solution of appropriate equation with electronic hamiltonian.

$$\hat{H}_{el} \Psi_{el}(\boldsymbol{r}, \boldsymbol{R}) = E_{el} \Psi_{el}(\boldsymbol{r}, \boldsymbol{R})$$

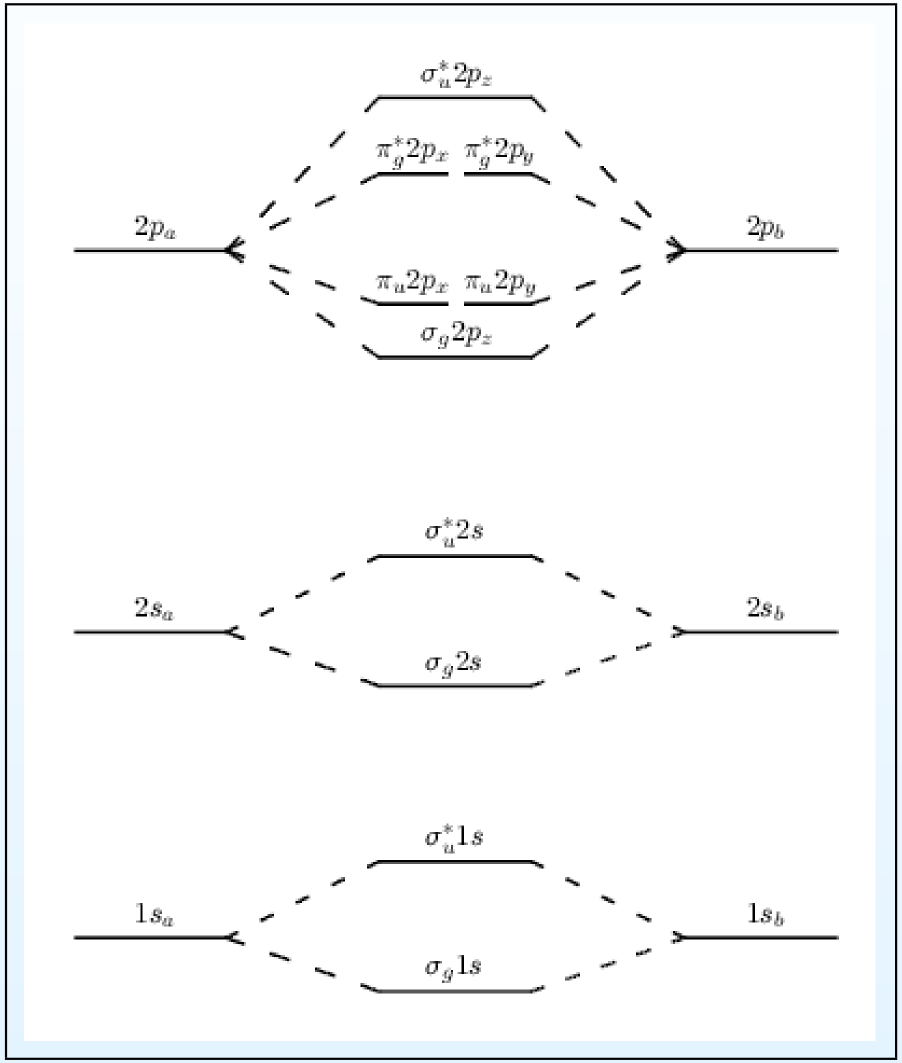
$$\hat{H}_e = \sum_{i=1}^{N} \hat{h}_i + \sum_{i=1}^{N} \sum_{j>i}^{N} \hat{g}_{ij} + \hat{V}_{nn}$$

$$\hat{h}_i = \frac{1}{2} \nabla_i^2 - \sum_a \frac{Z_a}{|\boldsymbol{R}_a - \boldsymbol{r}_i|}$$

$$\hat{g}_{ij} = \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

$$\hat{V}_{nn} = \sum_a \sum_{b>a} \frac{Z_a Z_b}{|\boldsymbol{R}_a - \boldsymbol{R}_b|}$$

LCAO-MO



1. The most frequent energetical order of molecular orbitals of homo-nuclear molecule.

Hartree-Fock Method

Douglas Rayner Hartree (27 March 1897 - 12 February 1958).

Vladimir Aleksandrovich Fock (December 22, 1898-December 27, 1974).

Hartree-Fock Method

Electrons occupy orbitals - chemical interpretation. But we have one-electron approximation and in reality the solutions will never be accurate from chemical point of view.

Enyway, the question is - what spinorbitals we should use in this approximation?

The answer - use the spinorbitals obtained from Hartree-Fock calculations.

The Hartree-Fock method is a variational method in which the trial function is in the form of Slater determinant. We look for such determinant which will give us the lowest eigenvalue of Hamiltonian.

HF equations

We use the variational procedure.

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$\hat{H} = \sum_{i=1}^{N} \hat{h}(x_i) + \sum_{i>j}^{N} \frac{1}{r_{ij}}$$

where the $\hat{h}(x_i)$ is one-electron hamiltonian which contain kinetic energy and interactin with external field (for instance with nucleus charge)

$$\hat{h} = -\frac{1}{2}\Delta_i + \hat{U}(x_i)$$

where $x_i = (\boldsymbol{r}_i, \sigma_i)$.

HF equations - continuation ...

When we will use the hamiltonian in the energy expression in variational procedure we will get

$$E = \sum_{i=1}^{N} I_i + \frac{1}{2} \sum_{i,j=1}^{N} (J_{ij} - K_{ij})$$

where we have

$$\begin{aligned} I_i &= \langle \phi_i | \hat{h} | \phi_i \rangle && \leftarrow \text{one-electron integral} \\ J_{ij} &= \langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_i(1)\phi_j(2) \rangle && \leftarrow \text{coulomb integral} \\ K_{ij} &= \langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_i(2)\phi_j(1) \rangle && \leftarrow \text{exchange integral} \end{aligned}$$

HF equations

Using the Lagrange multipliers method and performing variations over orbitals we can get HF equations.

$$L[\phi'_1, \phi'_2, \ldots, \phi'_N; \boldsymbol{\varepsilon}] = E[\phi'_1, \phi'_2, \ldots, \phi'_N] - \sum_i^N \sum_j^N \varepsilon_{ij} (\langle \phi'_i | \phi'_j \rangle - \delta_{ij})$$

$$\delta^{(1)} (E - \sum_i^N \sum_j^N \varepsilon_{ij} \langle \phi'_i | \phi'_j \rangle) = 0$$

and finally

$$\hat{f} \phi_i = \varepsilon_i \phi_i$$

where

$$\hat{f} = \hat{h} + \hat{J} - \hat{K}$$

where $\hat{J} = \sum_{i=1}^N \hat{J}_i$ and $\hat{K} = \sum_{i=1}^N \hat{K}_i$

HF equations

the definition of operators $\hat{J}_j$ and $\hat{K}_j$ is as follows

$$\hat{J}_j|\phi_j(2)\rangle = \langle\phi_i(1)|\hat{g}_{12}|\phi_i(1)\rangle\,|\phi_j(2)\rangle$$
$$\hat{K}_j|\phi_j(2)\rangle = \langle\phi_i(1)|\hat{g}_{12}|\phi_j(1)\rangle\,|\phi_i(2)\rangle$$

Those of the eigenfunctions of $\hat{f}$ operator which construct the Slater determinant are called occupied orbitals, wile the rest (unoccupied) are called virtual orbitals.

the orbital energy is

$$\varepsilon_i = \langle\phi_i|\hat{f}|\phi_i\rangle = \langle\phi_i|\hat{h} + \sum_{b=1}^{N}(\hat{J}_b - \hat{K}_b)|\phi_i\rangle$$
$$= \langle\phi_i|\hat{h}|\phi_i\rangle + \sum_{b=1}^{N}\Big(\langle\phi_i|\hat{J}_b|\phi_i\rangle - \langle\phi_i|\hat{K}_b|\phi_i\rangle\Big) = I_i + \sum_{b=1}^{N}(J_{ib} - K_{ib})$$

HF equations

frequently we use another notation

$$\langle \phi_i|\hat{h}|\phi_j\rangle = \langle i|\hat{h}|j\rangle$$
$$J_{ij} = \langle ij|ij\rangle$$
$$K_{ij} = \langle ij|ji\rangle$$
$$J_{ij} - K_{ij} = \langle ij||ji\rangle$$
$$\varepsilon_i = \langle i|\hat{h}|i\rangle + \sum_{b=1}^{N}\langle ib||ib\rangle$$

The sum of energies of occupied orbitals is not equal to of the total energy of the system, because we included twice the electron-electron interactions.

$$\sum_{a=1}^{N}\varepsilon_a = \sum_{a=1}^{N} I_a + \sum_{a,b}^{N}(J_{ab} - K_{ab})$$
$$E_{HF} = \sum_{a=1}^{N}\varepsilon_a - \frac{1}{2}\sum_{a,b}^{N}(J_{ab} - K_{ab})$$

Hartree-Fock-Roothan approximation

Analytical approximation to the HF method.

The Hartree-Fock method is widely used for simple and symmetrical one- or two-atomic systems by mapping the orbitals on a set of grid points. These are referred to as *numerical Hartree-Fock* method.

But, essentially all calculations use LCAO MO approximations, where every molecular orbital is expressed as a linear combination of atomic orbitals, although they are generally not solutions to the atomic HF method.

$$\phi_i = \sum_{\nu} c_{\nu i} \chi_{\nu}$$

where greek letters denote basis functions (atomic orbitals) χ_ν and latin symbols denote molecular orbitals ϕ_i.

Using the LCAO expansion instead differential-integral equations we have to solve algebraic system of equations.

$$\boldsymbol{FC} = \boldsymbol{SCE}$$

HFR method

$F_{\mu\nu}$ matrix elements

$$\langle\chi_\mu|\hat{F}|\chi_\nu\rangle = \langle\chi_\mu|\hat{h}|\chi_\nu\rangle + \sum_j^{occ.MO} \langle\chi_\mu|(2\hat{J}_j - \hat{K}_j)|\chi_\nu\rangle$$

$$= h_{\mu\nu} + \sum_\lambda^{AO}\sum_\sigma^{AO}\left(\sum_j^{occ.MO} c^*_{\lambda j} c_{\sigma j}\right)\left(\langle\chi_\mu\chi_\nu|\hat{g}|\chi_\lambda\chi_\sigma\rangle - \frac{1}{2}\langle\chi_\mu\chi_\sigma|\hat{g}|\chi_\lambda\chi_\nu\rangle\right)$$

$$= h_{\mu\nu} + \sum_\lambda^{AO}\sum_\sigma^{AO} G_{\mu\nu\lambda\sigma} D_{\lambda\sigma}$$

Now, the Fock matrix can be expressed in more general form

$$\boldsymbol{F} = \boldsymbol{h} + \boldsymbol{G}\cdot\boldsymbol{D}$$

where D is density matrix, $\boldsymbol{G}$ is four-dimensional tensor of two-electron integrals, and $\boldsymbol{h}$ denotes matrix of integrals of one-electron operator.

HFR method

The expression for energy is now

$$E = \sum_{i}^{N} \langle \phi_i | \hat{h}_i | \phi_i \rangle + \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} \left(\langle \phi_i \phi_j | \hat{g} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g} | \phi_j \phi_i \rangle \right) + V_{nn}$$

$$= \sum_{\mu}^{M} \sum_{\nu}^{M} D_{\mu\nu} h_{\mu\nu}$$

$$+ \frac{1}{2} \sum_{\mu}^{M} \sum_{\nu}^{M} \sum_{\lambda}^{M} \sum_{\sigma}^{M} D_{\mu\nu} D_{\lambda\sigma} \left(\langle \chi_\mu \chi_\lambda | \hat{g} | \chi_\nu \chi_\sigma \rangle - \langle \chi_\mu \chi_\lambda | \hat{g} | \chi_\sigma \chi_\nu \rangle \right)$$

$$+ V_{nn}$$

Secular equation

In mathematics it is also called the characteristic equation.

After LCAO approximation we don't need to look for undefined function but instead coeeficients of expansion for linear combination of basis functions.

$$(\boldsymbol{H} - \varepsilon \boldsymbol{S})\boldsymbol{c} = 0$$

If we would have orthonormal basis functions the above equation would be automatically our eigen probme $(\boldsymbol{H} - \varepsilon \mathbf{1})\boldsymbol{c} = 0$ but they are not orthonormal.

This we have to orthogonalize the old functions. The best is the Löwdin method. Instead of old basis ϕ we will get new - orthogonal ϕ'

$$\boldsymbol{\phi}' = \boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{\phi}$$

because in this type of orthogonalisation

$\sum^{N}$

Löwdin orthogonalisation

This kind of orthogonalisation is also called symmetrical orthogonalisation.

we need new - orthogonal basis of functions instead of old - nonorthogonal functions.

$$\boldsymbol{\phi} = [\phi_1, \phi_2, \phi_3, \ldots, \phi_N]^T \rightarrow \boldsymbol{\phi}' = [\phi_1', \phi_2', \phi_3', \ldots, \phi_N']^T$$

We will use a special matrix $\boldsymbol{S}^{-\frac{1}{2}}$ to do this.

1. Diagonalization of $\boldsymbol{S}$ matrix - $\boldsymbol{U}^\dagger \boldsymbol{S} \boldsymbol{U}$
2. The eigenvalues of diagonalized $\boldsymbol{S}$ matrix are always greater then zero, thus we can define $\boldsymbol{S}^{\frac{1}{2}} = \boldsymbol{U} \boldsymbol{S}_{\text{diag}}^{\frac{1}{2}} \boldsymbol{U}^\dagger$ and $\boldsymbol{S}^{-\frac{1}{2}} = \left(\boldsymbol{S}^{\frac{1}{2}}\right)^{-1} = \boldsymbol{U} \boldsymbol{S}_{\text{diag}}^{-\frac{1}{2}} \boldsymbol{U}^\dagger$
3. The symbols of these matrices are compatible with their properties
   $\boldsymbol{S}^{\frac{1}{2}} \boldsymbol{S}^{\frac{1}{2}} = \boldsymbol{U} \boldsymbol{S}_{\text{diag}}^{\frac{1}{2}} \boldsymbol{U}^\dagger \boldsymbol{S}_{\text{diag}}^{\frac{1}{2}} \boldsymbol{U}^\dagger = \boldsymbol{U} \boldsymbol{S}_{\text{diag}}^{\frac{1}{2}} \boldsymbol{S}_{\text{diag}}^{\frac{1}{2}} \boldsymbol{U}^\dagger = \boldsymbol{U} \boldsymbol{S}_{\text{diag}} \boldsymbol{U}^\dagger = \boldsymbol{S}$
   similarly $\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}^{-\frac{1}{2}} = \boldsymbol{S}^{-1}$

Secular equation

We have to multiply our secular equation by $\boldsymbol{S}^{-\frac{1}{2}}$ from left side and obtain a sequence of transformations

$$(\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{H} - \varepsilon\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{S})\boldsymbol{c} = 0$$

$$(\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{H}\mathbf{1} - \varepsilon\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{S})\boldsymbol{c} = 0$$

$$(\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{H}\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{S}^{\frac{1}{2}} - \varepsilon\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{S})\boldsymbol{c} = 0$$

$$(\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{H}\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{S}^{\frac{1}{2}} - \varepsilon\boldsymbol{S}^{\frac{1}{2}})\boldsymbol{c} = 0$$

$$(\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{H}\boldsymbol{S}^{-\frac{1}{2}} - \varepsilon\mathbf{1})\boldsymbol{S}^{\frac{1}{2}}\boldsymbol{c} = 0$$

$$(\tilde{\boldsymbol{H}} - \varepsilon\mathbf{1})\tilde{\boldsymbol{c}} = 0$$

where $\tilde{\boldsymbol{H}} = \boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{H}\boldsymbol{S}^{-\frac{1}{2}}$ and $\tilde{\boldsymbol{c}} = \boldsymbol{S}^{\frac{1}{2}}\boldsymbol{c}$

Thus, we obtained characteristic equation $(\tilde{\boldsymbol{H}} - \varepsilon\mathbf{1})\tilde{\boldsymbol{c}} = 0$. To obtain $\tilde{\boldsymbol{H}}$ first we must diagonalize $\boldsymbol{S}$ to obtain $\boldsymbol{S}^{-\frac{1}{2}}$ and $\boldsymbol{S}^{\frac{1}{2}}$.

SCF convergence

- **extrapolation** - faster convergence is achieved by extrapolation of previous Fock matrices which can be better then the this calculated from curent density matrix. Typically three last Fock matrices are used.
- **Direct inversion in Iterative Space - DIIS** - method worked out by Pulay is one of the most effective. The idea: As the iterative procedure runs, a sequence of Fock matrices and density matrices $(\boldsymbol{F}_0, \boldsymbol{F}_1, \boldsymbol{F}_2, \ldots, \boldsymbol{D}_0, \boldsymbol{D}_1, \boldsymbol{D}_2, \ldots)$ is produced. At each iterration it is also assumed that an estimate of the error is available, i.e. how far from the current Fock/density matrix is from the converged solution. DIIS method forms a linear combination of the error indicators which in a least squares sense is a minimum (as close to zero as possible).

$$
\begin{aligned}
errF(\boldsymbol{c}) &= tr(\boldsymbol{E}_{n+1} \cdot \boldsymbol{E}_{n+1}) \\
\boldsymbol{E}_{n+1} &= \sum_{k=0}^{n} c_k \boldsymbol{E}_k \\
\sum_{k=0}^{n} c_k &= 1
\end{aligned}
\tag{1}
$$

CF convergence - continuation ...

- Minimisation of the $errF$ subject by means of Lagrange multipliers which develop the c_k coefficients which are used in building of new Fock matrix in n-th iteration, which, in turn, is used to build new density matrix in iteration $(n+1)$.
- **Dumping** - also very effective method. It is used when during the SCF energy oscillates. The damping method tries to replace the current density matrix with a weighted average $\boldsymbol{D}_{k+1} = \alpha \boldsymbol{D}_k + (1-\alpha)\boldsymbol{D}_{k+1}$. The weighted factor α can be chosen as a constant or changed during the SCF procedure.
- **Level Shifting** - The iterative SCF procedure normally involve mixing of occupied and virtual MOs which frequently leads to shifting of energy or to oscillations. It the **Level Shifting** method we introduce a constant value K which is simply added to the energy of virtual orbitals and decrease in this way the total energy value and force the convergence of SCF.

Configuration Interaction

We know that the wave function Ψ of N electrons can not be a single Slater determinant. On the other hand, we know that Slater determinants $N \times N$ form a basis of N-particle Hilbert space. Thus, we can form the Ψ as a linear combination of these Slater determinants.

$$\Psi = \sum_i \Phi_i$$

where the Φ_i are determinant wave functions.

The question is - how to create the $\{\Phi_i\}$?

The answer - start with the Φ_0 (i.e. Hartree-Fock solution) and build excitated determinants replacing some of the spinorbitals from Φ_0 by virtual spinorbitals also obtained from the HF calculations.

Configuration Interaction

$$\Phi_a^r = e_a^r \Phi_0$$

where the a index runs over occupied spinorbitals and r index over virtual orbitals. The Φ_a^r determinant instead of ϕ_a contain ϕ_r spinorbital. The e_a^r is called *excitation operator* from spinorbital a to spinorbital r.

We can also form doubly-excited configurations

$$\Phi_{ab}^{rs} = e_a^r e_b^s \Phi_0$$

and even more-excited configurations.

Finally we can write

$$\Psi = c_0 \Phi_0 + c_1 \Phi_1 + c_2 \Phi_2 + \ldots$$

It is the exact solution but only when it is unfinished.

Full Configuration Interaction

If we had N electrons and K spinorbitals, then the number of determinants equals D

$$D = \binom{K}{N}$$

and approximated wavefunction to exact solution is as follows:

$$\Psi = \sum_{j}^{D} c_j \Phi_j$$

The number of determinants in FCI method grows up very quickly $D \sim K^N$. For water molecule ($N = 10$) with one-electron bais set containing $K = 100$ spinorbitals we get $100^{10} = 10^{20}$ determinants. It is absolutely out of range now.

CID, CISD, ...

1 - only singly-excited determinants. Number of Φ_1 determinants = $N(K-N)$.
But due to the Brillouin theorem - singly-excited configurations and the ground-state determinant do not mix together (suitable hamilton matrix element $\langle \Phi_0 | \hat{H} | \Phi_1 \rangle = 0$).

2 - only doubly excited configurations - CID. Number of Φ_2 determinants = $\begin{pmatrix} N \\ 2 \end{pmatrix} \begin{pmatrix} K-N \\ 2 \end{pmatrix}$. It can reproduce approximately 90% of electron correlation.

3 - doubly and singly-excited configurations - CISD.

$$\mathbb{H} = \begin{pmatrix} H_{00} & 0 & H_{02} \\ 0 & H_{11} & H_{12} \\ H_{20} & H_{21} & H_{22} \end{pmatrix}$$

4 - singly, doubly and triply-excited configurations - CISDT.

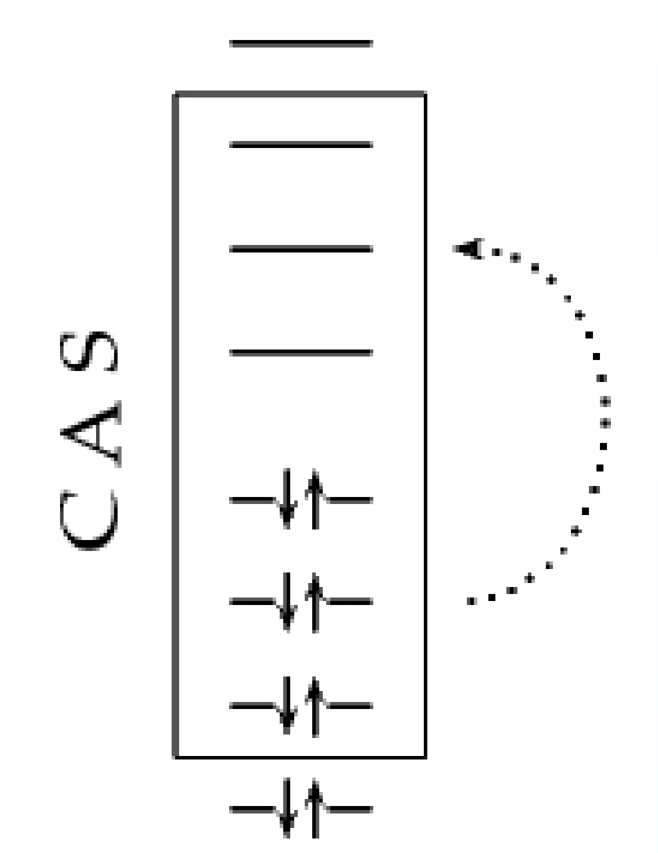
CAS SCF method

$$\Psi = a_{00}\psi_{00} + \sum_{t=1}^{n}\sum_{u=n+1}^{\omega-n} a_{tu}\psi_{tu}$$

n doubly occupied orbitals $\phi_1, \ldots, \phi_n$

$\phi_{n+1}, \ldots, \phi_\omega$ unoccupied orbitals

excitation t from n to $(\omega - n)$ orbs.



we optimize a_{tu} coefficients

AND ψ_{tu} wavefunction, i.e.

$$(\partial E/\partial \phi_t) = (\partial E/\partial \phi_u) = 0$$

$$(\partial E/\partial a_{00}) = (\partial E/\partial a_{tu}) = 0$$