

Advanced Physical Chemistry (fizkemhk17em)

Electronic Structure

Péter G. Szalay
ELTE Eötvös Loránd University
Institute of Chemistry
szalay@chem.elte.hu



Methods

The Independent Particle Approximation (IPA)

Hartree-method: Approximation of the wave function in a product form

$$\underbrace{\Psi(r_1, r_2, \dots, r_n)}_{\text{wave function}} = \underbrace{\phi_1(r_1) \cdot \phi_2(r_2) \dots \cdot \phi_n(r_n)}_{\text{product of spin orbitals}}$$

spinorbital:

$$\begin{aligned} \varphi_i(i) = \varphi_i(x_i, y_i, z_i, \sigma_i) &= u(x_i, y_i, z_i) \alpha(\sigma_i) \\ \text{or} &= \underbrace{u(x_i, y_i, z_i)}_{\text{spatial orbital}} \beta(\sigma_i) \end{aligned}$$

The Independent Particle Approximation (IPA)

Hartree-method: Approximation of the wave function in a product form

$$\underbrace{\Psi(r_1, r_2, \dots, r_n)}_{\text{wave function}} = \underbrace{\phi_1(r_1) \cdot \phi_2(r_2) \dots \cdot \phi_n(r_n)}_{\text{product of spin orbitals}}$$

In this case the Schrödinger equation reduces to one-electron equations:

$$\begin{aligned} \hat{H}\Psi = E\Psi \quad \Rightarrow \quad & \hat{h}_1(1)\varphi_1(1) = \varepsilon_1\varphi_1(1) \\ & \hat{h}_2(2)\varphi_2(2) = \varepsilon_2\varphi_2(2) \\ & \dots \\ & \hat{h}_n(n)\varphi_n(n) = \varepsilon_n\varphi_n(n) \end{aligned}$$

One n-electron equation \Rightarrow system of n one-electron equations

$$\hat{h}_i \rightarrow \hat{h}_i^{eff} = -\frac{1}{2}\Delta_i - \frac{Z_A}{r_{iA}} + V_i^{eff}$$

where V_i^{eff} is the interaction of electron i with all other electrons.

Slater-determinant

According to the *Pauli principle*, the wave function of the electrons is anti-symmetric with respect to the interchange of two electrons:

$$\hat{P}_{12}\Psi(1, 2, \dots, n) = -\Psi(1, 2, \dots, n)$$

To fulfill anti-symmetry, instead of product wave function we have to use determinant (*Slater determinant*):

$$\Psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_n(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_n(2) \\ \vdots & \vdots & \vdots & \vdots \\ \varphi_1(n) & \varphi_2(n) & \cdots & \varphi_n(n) \end{vmatrix}$$

$$= \frac{1}{\sqrt{n!}} (\varphi_1(1) \cdot \varphi_2(2) \cdot \dots \cdot \varphi_n(n) - \varphi_1(2) \cdot \varphi_2(1) \cdot \dots \cdot \varphi_n(n) + \dots)$$

Expectation value of the energy with determinant wave function

Split up the Hamiltonian into zero-, one- and two-electron parts:

$$\hat{H} = \underbrace{-\sum_i \frac{1}{2} \Delta_i}_{\hat{H}_1 =: \sum_i \hat{h}(i)} - \underbrace{\sum_i \sum_A \frac{Z_A}{r_{iA}}}_{\hat{H}_2} + \underbrace{\sum_{i>j} \frac{1}{r_{ij}}}_{\hat{H}_2} + \underbrace{\sum_{A<B} \frac{Z_A Z_B}{r_{AB}}}_{\hat{H}_0}$$

The expression for the energy (Ψ stands for a determinant):

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \left\langle \Psi \left| \sum_i \hat{h}_i \right| \Psi \right\rangle + \left\langle \Psi \left| \sum_{i>j} \frac{1}{r_{ij}} \right| \Psi \right\rangle + H_0$$

Expectation value of the energy with determinant wave function

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \left\langle \Psi \left| \sum_i \hat{h}_i \right| \Psi \right\rangle + \left\langle \Psi \left| \sum_{i < j} \frac{1}{r_{ij}} \right| \Psi \right\rangle + H_0$$

One can derive that

$$E = \sum_i H_{ii} + \sum_{i > j} (J_{ij} - K_{ij}) + H_0$$

- $H_{ii} = \int \phi_i | \hat{h} | \phi_i dv_1$
– one-electron contribution of electron i including the kinetic energy and the attraction to the nuclei;
- $J_{ij} = \int \int \phi_i(1) \phi_j(2) \frac{1}{r_{12}} \phi_i(1) \phi_j(2) dv_1 dv_2$
– Coulomb integral representing the electron-electron interaction;
- $K_{ij} = \int \int \phi_i(1) \phi_j(2) \frac{1}{r_{12}} \phi_j(1) \phi_i(2) dv_1 dv_2$
– exchange integral, consequence of the anti-symmetry.

The Hartree-Fock method

Wave function: determinant:

$$\Psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_n(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_n(2) \\ \vdots & \vdots & \vdots & \vdots \\ \varphi_1(n) & \varphi_2(n) & \cdots & \varphi_n(n) \end{vmatrix}$$

We look for the „*the best*” determinant!

- Since the determinant consist of orbitals, we have to obtain those orbitals which result in „*the best*” determinant.

What is „*the best*” ?

- According to the variation principle, the best determinant gives the lowest energy.

The Hartree-Fock method

Expression of the energy:

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_i H_{ii} + \frac{1}{2} \sum_{i>j} (J_{ij} - K_{ij}),$$

which is the *functional* of the orbitals ($\{\phi_i, i = 1, \dots, n\}$). Therefore we have to look for the minimum of this functional.

Required condition: orbitals are orthonormal:

$$\langle \phi_i | \phi_j \rangle = S_{ij} = \delta_{ij} \quad \forall i, j \quad \rightarrow \quad \langle \Psi | \Psi \rangle = 1$$

Therefore the functional to be varied is (ε 's are Lagrange-multipliers):

$$G = E - \sum_i \sum_j \varepsilon_{ij} (S_{ij} - \delta_{ij})$$

$$\delta G = \sum_i \delta H_{ii} + \frac{1}{2} \sum_{ij} (\delta J_{ij} - \delta K_{ij}) - \sum_{ij} \varepsilon_{ij} \delta S_{ij} = 0$$

The Hartree-Fock method

G functional has extremum for those orbitals which fulfill:

$$\left[\hat{h} + \sum_j \left(\hat{J}_j - \hat{K}_j \right) \right] |\phi_i\rangle = \sum_j \varepsilon_{ij} |\phi_j\rangle \quad i = 1, \dots, n$$

By defining the operator:

$$\hat{f} := \hat{h} + \sum_j \left(\hat{J}_j - \hat{K}_j \right) = \hat{h} + \hat{U}^{HF}$$

we arrive at the following equation:

$$\hat{f}\phi_i = \varepsilon_i \phi_i \quad i = 1, \dots, n$$

This is the so called *Hartree-Fock equation*.

The orbitals satisfying the *Hartree-Fock-equation* are called *canonical orbitals*.

The Hartree-Fock-Roothaan method

Above we have derived the HF equations which, as solution to them, result in orbitals (one-electron wave functions):

$$\hat{f}\phi_i = \varepsilon_i \phi_i \quad i = 1, \dots, n$$

Further approximation: look for the orbitals as the linear combination of atomic basis function (*LCAO-MO* approximation):

$$\phi_i = \sum_a C_{ai} \chi_a$$

with χ_a standing for the atomic orbitals. Inserting this into the HF equations:

$$\hat{f} \sum_a C_{ai} \chi_a = \varepsilon_i \sum_a C_{ai} \chi_a$$

The Hartree-Fock-Roothaan method

$$\hat{f} \sum_a C_{ai} \chi_a = \varepsilon_i \sum_a C_{ai} \chi_a \quad / \langle \chi_b |$$

$$\sum_a C_{ai} \underbrace{\langle \chi_b | \hat{f} | \chi_a \rangle}_{F_{ba}} = \varepsilon_i \sum_a C_{ai} \underbrace{\langle \chi_b | \chi_a \rangle}_{S_{ba}}$$

$$\underline{\underline{F}} \underline{\underline{C}}_i = \varepsilon_i \underline{\underline{S}} \underline{\underline{C}}_i$$

or by gathering all vectors $\underline{\underline{C}}_i$ into a matrix:

$$\underline{\underline{F}} \underline{\underline{C}} = \underline{\underline{\varepsilon}} \underline{\underline{S}} \underline{\underline{C}}$$

This is a matrix eigenvalue equation (Hartree-Fock-Roothaan equation).

Interpretation of the results of the Hartree-Fock method

The orbitals (ϕ_i) are obtained from the Hartree-Fock equations:

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

In praxis, the orbitals are linear combination of atomic orbitals:

$$\phi_i = \sum_a C_{ai} \chi_a$$

The wave function of the system should be built from the orbitals:

$$\Psi = \frac{1}{\sqrt{n!}} \det(\phi_1, \dots, \phi_n)$$

Interpretation of the results of the Hartree-Fock method

The density matrix

According to the quantum mechanics, instead of the wave function, it is the probability density, which bears physical meaning

$$\Psi^*(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_n) \Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_n) dv_1 dv_2 \dots dv_n$$

The probability of finding an electron at point \underline{r} (*electron density*):

$$\rho(\underline{r}) = n \int \int \dots \int \Psi^*(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_n) \Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_n) dv_2 dv_3 \dots dv_n$$

In front of the integral the multiplier n is used to add up the contribution of all undistinguishable electrons.

Interpretation of the Hartree-Fock results

In case of determinant wave function, the electron density can be given as the sum of the density of the individual electrons (c.f. Independent Particle Approximation):

$$\begin{aligned}
 \rho(\underline{r}) &= \sum_i^n \phi_i(\underline{r})\phi_i(\underline{r}) \\
 &= \sum_i^n \sum_a C_{ai}\chi_a(\underline{r}) \sum_b C_{bi}\chi_b(\underline{r}) \\
 &= \sum_a \sum_b \underbrace{\sum_i^n C_{ai}C_{bi}}_{P_{ab}} \chi_a(\underline{r})\chi_b(\underline{r})
 \end{aligned}$$

In the second row of the above equation, the orbitals have been expanded on the atomic orbitals, in the last, the *density matrix* $\underline{\underline{P}}$ has been introduced.

Interpretation of the Hartree-Fock results

Population analysis according to Mulliken

From the above formula it is clear that by integrating the electron density over the whole space, we obtain the number of electrons:

$$\begin{aligned}n &= \int \rho(\underline{r}) dv = \sum_a \sum_b P_{ab} \int \chi_a(\underline{r}) \chi_b(\underline{r}) dv \\ &= \sum_a \sum_b P_{ab} S_{ab}\end{aligned}$$

According to the last equation, the electron density can be distributed according to contribution by the individual basis functions:

- $P_{aa}S_{aa} = P_{aa}$ gives the charge associated with the basis function χ_a
- $P_{ab}S_{ab}$ gives the charge associated with the overlap $\chi_a\chi_b$

Interpretation of the Hartree-Fock results

From this contributions one can obtain:

- $\sum_{a \in A} P_{aa} S_{aa} = \sum_{a \in A} P_{aa}$, which is the charge on atom A
- $\sum_{a \in A} \sum_{b \in B} P_{ab} S_{ab}$, which gives the charge associated with the overlap of atoms A and B (NOT bond-order!!)

Finally, the total (Mulliken) charge on atom A can be obtained if we add all contributions associated with atom A :

$$\sum_{a \in A} \sum_b P_{ab} S_{ab} = \sum_{a \in A} (\underline{P} \underline{S})_{aa}$$

Interpretation of the Hartree-Fock results

Orbital energy, total energy

The eigenvalue of the *Fock-operator* appearing in the Hartree-Fock equation (ε_i) is the orbital energy:

$$\varepsilon_i = \langle \phi_i | \hat{f} | \phi_i \rangle = \left\langle \phi_i \left| \hat{h} + \sum_j (\hat{J}_j - \hat{K}_j) \right| \phi_i \right\rangle = H_{ii} + \sum_j (J_{ij} - K_{ij})$$

The sum of the orbital energies of all occupied orbitals *is not equal* to the total energy:

$$E \neq \sum_i \varepsilon_i = \sum_i H_{ii} + \sum_i \sum_j (J_{ij} - K_{ij})$$

$$E = \sum_i H_{ii} + \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij}) = \sum_i \varepsilon_i - \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij})$$

Thus one has to subtract the electron-electron interaction since it appears twice in the sum of the orbital energies.

Interpretation of Hartree-Fock results

Ionization energy, Koopmans' theorem

Consider a closed shell system (M), and remove an electron from it (M^+). We assume that the orbitals do not change in this process:

$$E_M = 2H_{11} + 2H_{22} + 4J_{12} - 2K_{12} + J_{11} + J_{22}$$

$$E_{M^+} = 2H_{11} + H_{22} + 2J_{12} - K_{12} + J_{11}$$

$$\Delta E = E_{M^+} - E_M = -H_{22} - 2J_{12} + K_{12} - J_{22} = -\varepsilon_2$$

Interpretation of Hartree-Fock results

The ionization energy is therefore equals the negative of the energy of the orbitals from where the electron has been removed (*Koopmans' theorem*):

$$IP = -\varepsilon_i$$

This approximation works since the errors of the two approximations cancel each other:

- we use determinantal wave function (the so called electron correlation is not considered);
- orbitals of the ions are not optimized (no orbital relaxation).

Interpretation of Hartree-Fock results

The ionization energy is therefore equals the negative of the energy of the orbitals from where the electron has been removed (*Koopmans' theorem*):

$$IP = -\varepsilon_i$$

This approximation works since the errors of the two approximations cancel each other:

- we use determinantal wave function (the so called electron correlation is not considered);
- orbitals of the ions are not optimized (no orbital relaxation).

Similarly, one could calculate electron affinity:

$$EA = E_{M^-} - E_M = \varepsilon_a$$

this is, however, a much worse approximation.