The Independent Particle Model

The full many-body problem can only be solved for very few particles (two or three). Strategy: Start with **reasonable** approximation and improve it systematically:

- All electrons move in the **average** field from all the other.
- Best possible choice ($\rightarrow$ lowest energy) with the (unrestricted) Hartree-Fock potential $u_{HF}(\mathbf{r})$
- But different spatial wave function for different spin-components $\rightarrow$ complications
- Common starting point *Restricted Hartree-Fock* with additional approximation that the potential is spherically symmetric: $u_{HF}(r)$
- For a closed shell system *Restricted Hartree-Fock* =*Unrestricted Hartree-Fock*
- Correlation Energy $\equiv$ True Energy - Hartree-Fock
- Or Correlation Energy = True Energy - my starting point ...

The Independent Particle Model

$$H = \sum_i^N \left(-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r_i} \right) + \sum_{i<j}^N \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{ij}}$$

$$H = H_0 + V = \sum_i^N h_0(i) + V$$

$$h_0(i) = -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r_i} + u(i), \quad h_0\phi_n = \epsilon_n\phi_n, \quad \text{orbitals!}$$

$$V = \sum_{i<j}^N \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{ij}} - \sum_i^N u(i)$$

Well chosen $u \rightarrow$ small corrections from V

The Independent Particle Model

With

$$\Psi = \phi_1(1)\phi_2(2)\phi_3(3)\ldots \rightarrow H_0\Psi = \left(\sum_i^N h_0(i)\right)\Psi = \left(\sum_i^N \epsilon_i\right)\Psi$$

$$\rightarrow E_0 = \left(\sum_i^N \epsilon_i\right)$$

Pauli principle $\rightarrow$ Slater determinant

$$\Psi = \sqrt{\frac{1}{N!}}\left\{\phi_1\phi_2\phi_3\ldots\right\},\ \langle\phi_i \mid \phi_j\rangle = \delta_{ij}$$

E.g. two particles

$$\Psi = \sqrt{\frac{1}{2}}\left\{\phi_1\phi_2\right\} = \sqrt{\frac{1}{2}}\Big(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)\Big)$$

Matrix Elements between Slater determinants

Slater determinant $\Psi = |\{abc\ldots\}\rangle$ (position gives particle number).

- one-particle operator f_i

$$\langle \Psi \mid \sum_i f_i \mid \Psi \rangle = \sum_i \langle \phi_i \mid f_i \mid \phi_i \rangle$$

Example

$$\langle \frac{ab - ba}{\sqrt{2}} \mid f_1 + f_2 \mid \frac{ab - ba}{\sqrt{2}} \rangle = \langle a \mid f \mid a \rangle + \langle b \mid f \mid b \rangle$$

$\Psi_1 = \{abce\ldots\}$, $\Psi_2 = \{abde\ldots\}$, differ on one orbital

$$\langle \Psi_1 \mid \sum_i f_i \mid \Psi_2 \rangle = \langle c \mid f \mid d \rangle$$

zero if they differ on two or more orbitals

Matrix Elements between Slater determinants

Slater determinant $\Psi = \{abc\ldots\}$ (position gives particle number).

- two-particle operator $\sum_{i<j} g_{ij}$

Example

$$\langle \frac{ab-ba}{\sqrt{2}} \mid g_{12} \mid \frac{ab-ba}{\sqrt{2}} \rangle =$$

$$\frac{1}{2}\Big(\langle ab \mid g_{12} \mid ab\rangle + \langle ba \mid g_{12} \mid ba\rangle - \langle ab \mid g_{12} \mid ba\rangle - \langle ba \mid g_{12} \mid ab\rangle\Big) =$$

$$\Big(\langle ab \mid g_{12} \mid ab\rangle - \langle ba \mid g_{12} \mid ab\rangle\Big)$$

$\Psi_1 = \{abcdg\ldots\}$, $\Psi_2 = \{abefg\ldots\}$, differ on two orbitals

$$\langle \Psi_1 \mid \sum_{i<j} g_{ij} \mid \Psi_2 \rangle = \langle cd \mid g \mid ef \rangle - \langle dc \mid g \mid ef \rangle$$

zero if they differ on three or more orbitals

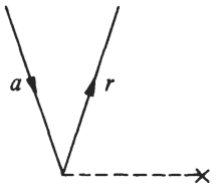
Slightly new notation

Initial state α, relative to α, α_a^r is singly excited:

$$\alpha = |\ \{abc\ldots\}\rangle,\ \alpha_a^r = |\ \{rbc\ldots\}\rangle$$

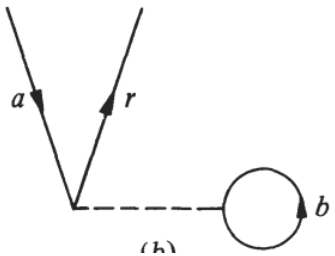
and thus

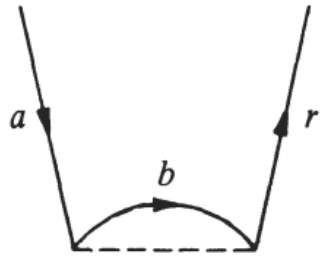
$$\langle \alpha_a^r \mid \sum_i f_i \mid \alpha \rangle = \langle r \mid f \mid a \rangle =$$



$$\langle \alpha_a^r \mid \sum_{i<j} g_{ij} \mid \alpha \rangle =$$

$$\sum_b \langle rb \mid g \mid ab \rangle - \langle br \mid g \mid ab \rangle =$$





Find the lowest expectation value of H (full H!) with a *single* Slater determinant α

$$\langle E \rangle = \langle \alpha \mid H \mid \alpha \rangle$$

Since the eigenfunctions to h_0 form a complete set we can use this set to improve any function. Let's vary orbital a

$$\begin{aligned} \mid a\rangle &\rightarrow \mid a\rangle + \eta \mid r\rangle \rightarrow \\ \mid \alpha\rangle &\rightarrow \mid \alpha\rangle + \eta \mid \alpha_a^r\rangle \end{aligned}$$

$$\langle E \rangle \rightarrow \langle E \rangle + \eta \left(\langle \alpha_a^r \mid H \mid \alpha \rangle + \langle \alpha \mid H \mid \alpha_a^r \rangle \right)$$

H Hermitian $\rightarrow$

$$\langle \alpha_a^r \mid H \mid \alpha \rangle = \langle \alpha \mid H \mid \alpha_a^r \rangle^*$$

can be chosen to be real, and the equal

At the minimum!

$$\langle \alpha_a^r \mid H \mid \alpha \rangle = 0$$

- With a Slater determinant constructed from Hartree-Fock orbitals H has no matrix elements between it and any determinant with a *single* substitution.

$$\langle \alpha_a^r \mid H \mid \alpha \rangle = \langle \alpha_a^r \mid \sum_i^N \left(-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r_i} \right) + \sum_{i<j}^N \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{ij}} \mid \alpha \rangle =$$

$$\langle r \mid -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r} \mid a \rangle + \frac{e^2}{4\pi\epsilon_0}\sum_b^{occ} \langle rb \mid \frac{1}{r_{12}} \mid ab \rangle - \langle br \mid \frac{1}{r_{12}} \mid ab \rangle$$

$$= 0$$

Hartree-Fock

$$h_{hf} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r} + u_{HF}$$

$$\langle i \mid u_{HF} \mid j \rangle = \frac{e^2}{4\pi\epsilon_0}\sum_{b}^{occ}\langle ib \mid \frac{1}{r_{12}} \mid jb\rangle - \langle bi \mid \frac{1}{r_{12}} \mid jb\rangle$$

- The Hartree-Fock potential is *non-local*
- One-particle eigenvalue equation

$$h_{hf} \mid a\rangle = \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r} + u_{HF}\right) \mid a\rangle = \epsilon_a \mid a\rangle$$

ϵ_a is the *orbital energy*. The basis where h_{hf} is diagonal is our HF-basis since then $\langle r \mid h_{hf} \mid a\rangle = \langle \alpha_a^r \mid H \mid \alpha\rangle = 0$

Koopman's theorem

Slater determinant $\alpha = |\{abc\ldots\}\rangle$, expectation value of H:

$$\langle E\rangle = \langle\alpha \mid H \mid \alpha\rangle = \sum_{a}^{occ}\langle a \mid -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r} \mid a\rangle +$$
$$\frac{1}{2}\frac{e^2}{4\pi\epsilon_0}\sum_{ab}^{occ}\langle ab \mid \frac{1}{r_{12}} \mid ab\rangle - \langle ba \mid \frac{1}{r_{12}} \mid ab\rangle$$

Remove one electron (e.g. c)?

- same expression, but sum runs over one electron less:

$$\langle E_{atom}\rangle - \langle E_{ion}\rangle = \langle c \mid -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r} \mid c\rangle +$$
$$\frac{e^2}{4\pi\epsilon_0}\sum_{b}^{occ}\langle cb \mid \frac{1}{r_{12}} \mid cb\rangle - \langle bc \mid \frac{1}{r_{12}} \mid cb\rangle = \epsilon_c$$

Koopman's theorem

- The orbital energy is equal to the negative of the *binding energy*
- IF we assume that all the other electrons remain unaffected when one electron is removed from the system
- This is a rather good approximation for outer electrons

Example

- Ar 3p: exp. ionization energy 15.8 eV Hartree-Fock: 16.1 eV.
- Ar 3s: exp. ionization energy 29.2 eV Hartree-Fock: 34.8 eV.

Why does it work less well for 3s?

Restricted Hartree-Fock

- With $u_{HF}(r)$ i.e. spherically symmetric

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r} + u_{HF}(r)\right)\psi_a = \epsilon_a\psi_a$$

and

$$\psi = R(r)Y_{\ell m_\ell}(\theta,\phi)\,\chi_{m_s} = \frac{P(r)}{r}Y_{\ell m_\ell}(\theta,\phi)\,\chi_{m_s}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) = \frac{1}{r}\frac{\partial^2}{\partial r^2}P(r)$$

- radial equation

$$\left(\frac{\hbar^2}{2m}\left(-\frac{\partial^2}{\partial r^2} + \frac{\ell(\ell+1))}{r^2}\right) - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r} + u_{HF}(r)\right)P(r) = \epsilon P(r)$$

Restricted Hartree-Fock

- The radial solution and the energy depends on ℓ, but not on m_ℓ or m_s
- we number the solutions with $n = \ell + \nu + 1$ where ν is the number of wave function nodes
- Hydrogenlike - no ℓ-dependence of the energy (but still on the wave function). Here ℓ-dependent energies
- Pauli principle: each ℓ-*shell* can house $2(2\ell + 1)$ electrons - and is then called a *filled* or *closed* shell (otherwise an *open* shell).
- Configurations: $1s^2 2s^2 2p^6$ for neon for example.

$$\left(\frac{\hbar^2}{2m} \left(-\frac{\partial^2}{\partial r^2} + \frac{\ell(\ell+1))}{r^2} \right) - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r} + u_{HF}(r) \right) P_{n\ell}(r) = \epsilon_{n\ell} P_{n\ell}(r)$$

How to obtain Hartree-Fock orbitals?

- self-consistent procedure
- start with a good guess for all the orbitals in your atom
- construct the Hartree-Fock potential
- solve the eigenvalue equation and get new orbitals
- construct the Hartree-Fock potential with the new orbitals
- repeat until convergence

The Hartree-Fock Energy

$$\langle \alpha \mid H \mid \alpha \rangle = \langle \alpha \mid \sum_{i}^{N} h_{HF}(i) + \sum_{i<j}^{N} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} - \sum_{i}^{N} u_{HF}(i) \mid \alpha \rangle$$

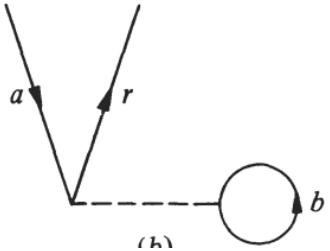
$$= \sum_{a}^{occ} \epsilon_a + \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \sum_{ab}^{occ} \langle ab \mid \frac{1}{r_{12}} \mid ab \rangle - \langle ba \mid \frac{1}{r_{12}} \mid ab \rangle \right)$$

$$- \left(\frac{e^2}{4\pi\epsilon_0} \sum_{ab}^{occ} \langle ab \mid \frac{1}{r_{12}} \mid ab \rangle - \langle ba \mid \frac{1}{r_{12}} \mid ab \rangle \right)$$

- When we add all the orbital energies we double count

How to setup the Hartree-Fock potential?

Direct term

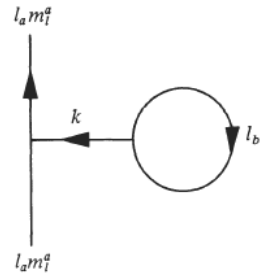


$$= \sum_{m_b} \langle rb \mid \frac{1}{r_{12}} \mid ab \rangle =$$

$$\int\int P_r(r_1) P_b(r_2) \frac{1}{r_>} P_a(r_1) P_b(r_2) dr_1 dr_2$$
$$\times \langle \ell_r \mid\mid \mathbf{C}^0 \mid\mid \ell_a \rangle \langle \ell_b \mid\mid \mathbf{C}^0 \mid\mid \ell_b \rangle$$

Only $k = 0$,
$\ell_a = \ell_r$

$\times$

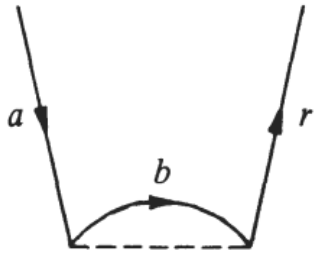


$$= \int\int P_r(r_1) P_b(r_2) \frac{1}{r_>} P_a(r_1) P_b(r_2) dr_1 dr_2 \times \sqrt{2\ell_a + 1}\sqrt{2\ell_b + 1}\frac{\sqrt{2\ell_b + 1}}{\sqrt{2\ell_a + 1}}$$

and then there will be a factor of two from the spin-diagram (c.f. Lecture 4) $\rightarrow 2(2\ell_b + 1)$ i.e. number of electrons in the shell.

How to setup the Hartree-Fock potential?

Exchange term

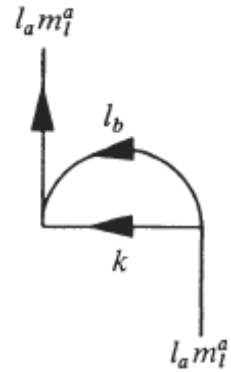


$$= -\sum_{m_b} \langle br \mid \frac{1}{r_{12}} \mid ab \rangle = -\sum_k \int\int P_b(r_1)\, P_r(r_2)\, \frac{r_<^k}{r_>^{k+1}}\, P_a(r_1)\, P_b(r_2)\, dr_1\, dr_2$$

$$\times (-1)^k \langle \ell_a \,||\, \mathbf{C}^k \,||\, \ell_b \rangle \langle \ell_b \,||\, \mathbf{C}^k \,||\, \ell_b \rangle$$

$\ell_a = \ell_r$

$\times$



where the last diagram gives (note that $k + \ell_a + \ell_b =$ even)

$$\frac{1}{2\ell_a + 1}(-1)^{k+\ell_a+\ell_b+2\ell_b} = \frac{1}{2\ell_a + 1}$$

Hartree-Fock includes full exchange

- Non-local. Why is that a problem?
- Density functional theory based on a **local** approximation of the exchange potential, derived from a free-electron gas model:

$$V_{ex}(\mathbf{r}) \sim \rho^{1/3}(\mathbf{r})$$

- ρ is the charge density
- original idea from Dirac, used by Slater.
- Formalized in a practical approach: *Self-Consistent Equations Including Exchange and Correlation Effects* by W. Kohn and L. J. Sham ($> 50\,000$ citations), Nobel prize 1998 (to Kohn).

RPAE

- RPAE is Time-Dependent Hartree-Fock