Hartree Fock Theory for the many-body problem

① $$H^{\text{Full}} = \sum_{i=1}^{N} \left(\frac{-\hbar^2 \nabla_i^2}{2m} + \underset{\uparrow \text{ e.g. ionic pot.}}{V_{\text{ext.}}(r_i)} - \mu N \right) + \frac{1}{2} \sum_{i \neq j} \underset{\uparrow \text{ Coulomb int.}}{V(|r_i - r_j|)}$$

$$= \sum_{i=1}^{N} h_i^0 + \frac{1}{2} \sum_{i \neq j} U_{ij}$$

$$= H_0 + H_1$$

$$\mathcal{O}(N) \sim 10^{23}$$

Strategy ①

approximate single particle solutions of H^{Full}

- Hartree Fock
- DFT

Strategy ②

many-body solution of approximate H^{Full} (model Hamiltonians)

- Dynamical Mean-Field Theory

I Hartree Fock

In principle Hamiltonian ① leads to many body wavefunctions for $N \simeq 10^{23}$ particles → hopeless...

But we can ask a different question:

"What is the best single-particle potential mimiching the effect of Coulomb interaction?"

with such potential we would have to solve only Sp Schrödinger Eq.

$$② \quad \tilde{H} = \sum_{i=1}^{N} \left(\frac{-\hbar^2 \nabla_i^2}{2m} \underbrace{- \mu N}_{\text{this is only an energy offset}} + \tilde{V}(r_i) \right)$$

⇒ einfach Diagonalisierbar denn N · Ungekoppelte Einteilchen-Probleme

Let's assume we have solved this single particle problem with wave-functions $|\varphi_\alpha\rangle$

$\uparrow$ Quantum number : $\underline{p}$: for translational invariant Prob.

$\underline{k}$: for translationally invariant Lattice problems (Bloch waves)

$\underline{l}$: for atomic problems (spherical symmetry)

Including spin σ if not explicitely written!

$\downarrow$

How to get the many-body WF ? $\Rightarrow$ Slater determinants

{ product wave-functions with proper antisymetric properties upon particle exchange!

* show that a product wave fkt will solve ② + antisym. $\longrightarrow$

We then remember that (very generally) for any Hamiltonian the functional

$$E[\Psi] := \frac{\langle\Psi|H^{Full}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad ③$$

is minimal for the ground state $|\Psi_0\rangle$

we can use this for our Slaterdeterminant Ansatz to find a defining equation for the $|\varphi_\alpha\rangle$

Ingredients:

④ $|\Psi\rangle = \frac{1}{\sqrt{N!}} \sum_{\text{perm } P} (-1)^{\overset{\text{order of Perm.}}{\nu_P}} |\varphi_{P(1)}\rangle^{(1)} \cdots |\varphi_{P(N)}\rangle^{(N)}$ and $E[\Psi] = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$

for a minimization of $E[\Psi]$ we insert $|\Psi\rangle$ and $H = H_0 + H_1$
(assuming that $|\varphi_\alpha\rangle$ form an orthonormal basis)

⑤ $\langle\Psi|H_0|\Psi\rangle = \sum_{i=1}^{N} \frac{1}{N} \sum_{P\tilde{P}} (-1)^{\nu_P + \nu_{\tilde{P}}} \, {}^{(N)}\langle\varphi_{\tilde{P}(N)}| \cdots {}^{(1)}\langle\varphi_{\tilde{P}(1)}| h_i^0 |\varphi_{P(1)}\rangle^{(1)} \cdots |\varphi_{P(N)}\rangle^{(N)}$

For each summand in ⑤ we have the matrix element ${}^{(i)}\langle\varphi_{\tilde{P}(i)}| h_i^0 |\varphi_{P(i)}\rangle^{(i)}$
while the rest of the product yields the Kronecker $\delta_{P(j)\tilde{P}(j)}$ for all $j \neq i$
However, when it holds for ALL $j \neq i$ it eventually also holds for $P(i)$ and $\tilde{P}(i)$

$\Rightarrow P \overset{!}{=} \tilde{P} \Rightarrow \nu_P = \nu_{\tilde{P}}$

$$\Rightarrow \langle\Psi|H_0|\Psi\rangle = \sum_{i=1}^{N} \frac{1}{N!} \sum_{P} {}^{(i)}\langle\varphi_{P(i)}|h_i^0|\varphi_{P(i)}\rangle^{(i)}$$

such sum over Permutations will lead to duplicates

$$= \sum_{i=1}^{N} \frac{(N-1)!}{N!} \sum_{\alpha=1}^{N} {}^{(i)}\langle\varphi_\alpha|h_i^0|\varphi_\alpha\rangle^{(i)}$$

matrix element does not depend on the particle index! (since r_i is only an integration variable)

$$= \sum_{\alpha=1}^{N} \langle\varphi_\alpha|h^0|\varphi_\alpha\rangle \qquad ⑥$$

Now the two-particle operator $H_1 = \frac{1}{2}\sum_{i\neq j} v_{ij}$

$$\langle\Psi|H_1|\Psi\rangle = \frac{1}{2}\sum_{i\neq j}\frac{1}{N!}\sum_{P\tilde{P}}(-1)^{\nu_P+\nu_{\tilde{P}}}\;{}^{(N)}\langle\varphi_{\tilde{P}(N)}|\cdots{}^{(1)}\langle\varphi_{\tilde{P}(1)}|v_{ij}|\varphi_{P(1)}\rangle^{(1)}\cdots|\varphi_{P(N)}\rangle^{(N)}$$

exploit again orthonormality of the $|\varphi_\alpha\rangle$, but remember that v_{ij} now mixes single particle wave functions (anyway most summands get killed)

$$= \frac{1}{2}\sum_{i\neq j}\frac{1}{N!}\sum_{P\tilde{P}}(-1)^{\nu_P+\nu_{\tilde{P}}}\prod_{\substack{l=1\\ l\neq i\\ l\neq j}}^{N}\delta_{P(l),\tilde{P}(l)}\;{}^{i}\langle\varphi_{\tilde{P}(i)}|\,{}^{j}\langle\varphi_{\tilde{P}(j)}|v_{ij}|\varphi_{P(j)}\rangle^{j}|\varphi_{P(i)}\rangle^{i}$$

we remain with two terms : $P(i) = \tilde{P}(i)$ and $P(j) = \tilde{P}(j)$ $\quad n_P = n_{\tilde{P}}$

$P(i) = \tilde{P}(j)$ and $P(j) = \tilde{P}(i)$ $\quad (n_P + n_{\tilde{P}}$ odd$)$

$$\langle \Psi | H_1 | \Psi \rangle = \frac{1}{2} \sum_{i \neq j} \frac{1}{N!} \sum_{P} \Big({}^{i}\langle \varphi_{P(i)} | {}^{j}\langle \varphi_{P(j)} | u_{ij} | \varphi_{P(j)} \rangle^{j} | \varphi_{P(i)} \rangle^{i} - {}^{i}\langle \varphi_{P(j)} | {}^{j}\langle \varphi_{P(i)} | u_{ij} | \varphi_{P(j)} \rangle^{j} | \varphi_{P(i)} \rangle^{i} \Big)$$

it's an exchange of particles

$$= \frac{1}{2} \sum_{i \neq j} \frac{(N-2)!}{N!} \sum_{\alpha \neq \gamma} \Big({}^{i}\langle \varphi_{\alpha} | {}^{j}\langle \varphi_{\gamma} | u_{ij} | \varphi_{\gamma} \rangle^{j} | \varphi_{\alpha} \rangle^{i} - {}^{i}\langle \varphi_{\gamma} | {}^{j}\langle \varphi_{\alpha} | u_{ij} | \varphi_{\gamma} \rangle^{j} | \varphi_{\alpha} \rangle^{i} \Big)$$

and again the matrix-element will not depend on indices $\underbrace{i \text{ or } j}_{\text{only integration variables}}$, only the character of the wave-function matters:

$$= \frac{1}{2} \sum_{\alpha \neq \gamma} \Big({}^{i}\langle \varphi_{\alpha} | {}^{j}\langle \varphi_{\gamma} | u_{ij} | \varphi_{\gamma} \rangle^{j} | \varphi_{\alpha} \rangle^{i} - {}^{i}\langle \varphi_{\gamma} | {}^{j}\langle \varphi_{\alpha} | u_{ij} | \varphi_{\gamma} \rangle^{j} | \varphi_{\alpha} \rangle^{i} \Big) \qquad ⑦$$

we will be interested in the case where v_{ij} is the Coulomb potential $v_{ij} = \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$ and we frequently define our single-particle wave functions via (angular) momentum and spin $|\varphi_\alpha\rangle = |\varphi_{\alpha\sigma}\rangle$ with this seperated, explicit spin index ⑦ reads

$$\langle\Psi|H_1|\Psi\rangle = \frac{1}{2}\sum_{\alpha\gamma,\sigma\sigma'}\left({}^{i}\langle\varphi_{\alpha\sigma}|\,{}^{j}\langle\varphi_{\gamma\sigma'}|\,v_{ij}\,|\varphi_{\gamma\sigma'}\rangle^{j}\,|\varphi_{\alpha\sigma}\rangle^{i} - \underbrace{{}^{i}\langle\varphi_{\gamma\sigma'}|\,{}^{j}\langle\varphi_{\alpha\sigma}|\,v_{ij}\,|\varphi_{\gamma\sigma'}\rangle^{j}\,|\varphi_{\alpha\sigma}\rangle^{i}}_{\substack{\text{since the Coulomb potential does}\\ \text{not act in spin-space this here}\\ \text{generates a } \delta_{\sigma\sigma'}}} \right)$$

We can now write down $E[\Psi] = E[\varphi_{\alpha\sigma}] =$ as

$$= \sum_{\alpha,\sigma}\int d^3_r\, \varphi^*_{\alpha\sigma}(\vec{r})\, h(\vec{r})\, \varphi_{\alpha\sigma}(\vec{r}) \qquad ⑧$$

$$+ \frac{1}{2}\sum_{\alpha\gamma,\sigma}\int d^3_r\, d^3_{r'}\, \frac{e^2}{|r-r'|}\left(\sum_{\sigma'}|\varphi_{\alpha\sigma}(\vec{r})|^2\,|\varphi_{\gamma\sigma'}(\vec{r})|^2 - \varphi^*_{\alpha\sigma}(\vec{r})\,\varphi^*_{\gamma\sigma}(\vec{r}')\,\varphi_{\alpha\sigma}(\vec{r}')\,\varphi_{\gamma\sigma}(\vec{r})\right)$$

How to minimize this? Variational principle with takeing care of normalization of the wave-functions by means of the Lagrange multiplicator ε_α

$$\delta\left(E[\varphi^*_{\alpha\sigma}] + \varepsilon_\alpha \left(\int d^3r \, |\varphi_\alpha(\vec{r})|^2 - 1 \right) \right) = 0$$

Functional derivative $\frac{\delta}{\delta \varphi^*_{\alpha\sigma}(\vec{R})}$ kills all $\vec{r}$ integrations with $\delta(\vec{r}-\vec{R})$ and one arrives at

$$⑨ \quad \varepsilon_\alpha \varphi_{\alpha\sigma}(\vec{r}) = h(\vec{r})\varphi_\alpha(\vec{r}) + \overbrace{\sum_{\gamma,\sigma'} \int d^3r' \frac{e^2}{|\vec{r}-\vec{r}'|} |\varphi_{\gamma\sigma'}(\vec{r}')|^2 \varphi_{\alpha\sigma}(r)}^{\text{Hartree}} - \overbrace{\sum_{\gamma} \int d^3r' \varphi^*_{\gamma\sigma}(\vec{r}') \frac{e^2}{|\vec{r}-\vec{r}'|} \varphi_{\alpha\sigma}(\vec{r}')\varphi_{\gamma\sigma}(\vec{r})}^{\text{Foch}}$$

Remarks:
- Hartree term has a straight forward classical interpretation as potential coming from the density of the other electrons at r
- Foch is much more complicated and originates in the Pauli principle: it has an opposite sign than Hartree which accounts for the reduced overlap of electron WF due to Pauli principle

(A product Ansatz for $|\Psi\rangle$ would lead to Hartree only!)

We see that the Hartree term in ⑨ is of the form

$U^{el}(r)\,\varphi(r)$, i.e. like an external potential while the Fock term is considerably more difficult and of the form

$$\int V(r,r')\,\varphi(r')\,dr'$$ Integration operator!

In anyway we can try to write the terms as operators of a Hamiltonian in 2nd Quantization. It will be helpfull for this to introduce the Wannier functions (for a lattice)* with which the field operators $\psi(r)$ and $\hat{\psi}(r)$ can be expressed as

$$\hat{\psi}^{\dagger}(r) = \sum_m w_m^*(r)\, c_m^{\dagger} \quad \text{and} \quad \hat{\psi}(r) = \sum_m w_m(r)\, c_m$$

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* if our original Hamiltonian is an atomic proble- we could use at. WF

and so we get for the Hartree term

$$\int dr\ \hat{\Psi}^{\dagger}(r)\ U(r)\ \hat{\Psi}(r) = \sum_{m,n} \int dr\ \phi_m^{*}(r)\ U(r)\ \phi_n(r)\ c_m^{\dagger} c_n = \sum_{m,n} U_{mn}^{H} c_m^{\dagger} c_n$$

while for the Fock term we get

$$\int dr\, dr'\ \hat{\Psi}^{\dagger}(r)\ V(r,r')\ \hat{\Psi}(r') = \sum_{m,n} \int dr\, dr'\ \phi_m^{*}(r)\ V(r,r')\ \phi_n^{x}(r')\ c_m^{\dagger} c_n$$

$$= \sum_{m,n} U_{mn}^{F}\ c_m^{\dagger} c_n$$

So all in all $\quad \sum_{m,n} \left(U_{mn}^{H} + U_{mn}^{F} \right) c_m^{\dagger} c_n$

↳ Realize that Hartree-Fock boiled down the two-particle operator to a single particle operator!

From Hartree Fock to Density Functional Theory (same same but different)

The Hohenberg-Kohn theorem: (nobel prize 1998 in chemistry (!))

> The ground state energy is a functional of the electron density $E[\rho(r)]$ which is minimized with the ground state density $\rho_0(r)$

$$E[\rho(r)] = \min \left\{ \langle \Psi | \hat{H}^{full} | \Psi \rangle \;\middle|\; \langle \Psi | \sum_{i=1}^{N} \delta(r - r_i) | \Psi \rangle = \rho(r) \right\}$$

$|\Psi\rangle$ has to yield density

$\Psi(r_1, \ldots, r_N)$ is a general many-body WF

ground state energy $E_0 = \min_\rho E[\rho]$

(notice the difference to HF $\rightsquigarrow E[\Psi]$)

? How does this functional look like?

Different from HF we cannot make an Ansatz for Ψ because we have to vary with respect to ρ !

↳ Hartree - Fock : wave-function based

↳ DFT: density based

Actually, we can formulate $E[\rho]$ at least partially :

External potentials such as the ionic one or the mean-field potential of the other electrons (i.e. a Hartree potential) are straight forward:

$$E_{ion}[\rho] = \int d^3r \, V_{ion}(r) \, \rho(r)$$

$$E_{Hartree}[\rho] = \int d^3r \, V_{hartree}(r) \, \rho(r) \qquad V_{hartree}(r) = \frac{1}{2} \int dr' \frac{\rho(r')}{|r - r'|}$$

But there are tricky ones: How to express kinetic energy in terms of the density $\rho(r)$?

$$E_{kin}[\rho]$$

Where is the energy coming from exchange (like Fock) and the remaining correlation effects (from H_1 in H^{Full}) ?

$$E_{xc}[\rho]$$

$$E[\rho] = E_{ion}[\rho] + E_{hartree}[\rho] + E_{kin}[\rho] + E_{xc}[\rho]$$

$$\delta_{\rho(r)} \left\{ E[\rho] - \mu \left(\int d^3r \, \rho(r) - N \right) \right\} = 0$$

To treat $E_u[\rho]$ introduce Kohn-Sham auxiliary set of single particle wave functions that yield a density:

$$\rho(r) = \sum_{\alpha=1}^{N} |\varphi_\alpha^{KS}(r)|^2$$

no physical meaning

so that we can minimize w.r.t. φ_α^{KS} instead of $\rho(r)$
(this starts to smell like Hartree Fock again... but not quite*)

$$\delta_{\varphi_\alpha^{KS}(r)} \left\{ E[\rho] - \varepsilon_\alpha \left(\int d^3r \, |\varphi_\alpha^{KS}(r)|^2 - 1 \right) \right\} = 0$$

leads to the defining equations for $\varphi_\alpha^{KS}(r)$

$$\boxed{\left[\frac{-\hbar^2 \nabla^2}{2m} + V_{ion}(r) + V_{hartree}(r) + \frac{\delta E_{xc}[\rho]^*}{\delta \rho(r)} \right] \varphi_\alpha^{KS}(r) = \varepsilon_\alpha \varphi_\alpha^{KS}(r)}$$

So far we have not done much but rewritten everything inspired by the Hohenberg-Kohn theorem!

We can, however, make approximations to $E_{xc}[\rho]$ which up to this point is just a black box in which all the many-body physics is hidden!

Local Density Approximation

In principle $E_{xc}[\rho]$ is non-local but in LDA:

$$\underset{\text{Functional of } \rho}{E_{xc}[\rho]} = \int d^3r \, \underset{\text{Function of } \rho}{E_{xc}^{LDA}(\rho(r))}$$

$E_{xc}^{LDA}(\rho(r))$ calculated numerically or from perturbation theory of the Jellium model: $V_{ion} = \text{const.} \Rightarrow \rho(r) = \rho_0$

aka uniform/homogeneous electron gas

$\Rightarrow$ With the correct E_{xc}^{LDA} we could calculate the gs energy of any material with constant electron density exactly!

(the more variation in $\rho(r)$ the less accurate is LDA by definition)

Honourable mentions:

$$L\overset{\substack{\text{spin}\\ \downarrow}}{S}DA: \quad E_{xc}[\rho] = E_{xc}[\rho_\uparrow, \rho_\downarrow] \cong \int d\vec{r}\, E_{xc}^{LSDA}(\rho_\uparrow(r), \rho_\downarrow(r))$$

generalized gradient

$$GGA: \quad E_{xc}[\rho_\downarrow, \rho_\uparrow] \simeq \int d\vec{r}\, E_{xc}^{loc}(\rho_\uparrow(r), \rho_\downarrow(r), \nabla\rho_\uparrow, \nabla\rho_\downarrow)$$

hybrid functionals: mix Hartree-Fock with Kohn-Sham equations.