Introduction to Density functional theory.

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- A function f maps one number x to one number y.

$$y = f(x) \quad \text{example:} \quad y = f(x) = x^2$$

- A functional A maps one function f to one number y.

$$y = A[f(x)] \quad \text{example:} \quad y = A[f(x)] = \int dx f(x)^2$$

- Functional derivative:
  Let's modify the function f by a tiny increase δf localized at x_0 : $\delta f = \epsilon \delta(x - x_0)$.
- Let's now evaluate the variation of $A[f(x)] = \int dx f(x)^2$:

$$
\begin{aligned}
A[f(x) + \delta f] - A[f(x)] &= \int dx [f(x) + \epsilon \delta(x - x_0)]^2 - f(x)^2 \\
&= \int dx \, 2 f(x) \epsilon \delta(x - x_0) = 2\epsilon f(x_0)
\end{aligned}
$$

- More generally, if $A[f(x)] = \int dx g(f(x))$ where g is a function, one have:

$$
A[f(x) + \delta f] - A[f(x)] = \epsilon g'(f(x_0))
$$

The functional derivative is the variation of A divided by ϵ.

$$
\frac{\delta A}{\delta f(x_0)} = \frac{A[f(x) + \delta f] - A[f(x)]}{\epsilon} = g'(f(x_0))
$$

- Functional derivatives of complex functionals can be computed just by a simple derivation, using at the end the simple rule

$$\frac{\delta f(x)}{\delta f(x')} = \delta(x - x')$$

- Example 1: $A[f(x)] = \int dx g(f(x))$

$$
\begin{aligned}
\frac{\delta A}{\delta f(x_0)} &= \int dx \frac{\delta g(f(x))}{\delta f(x_0)} \\
&= \int dx \frac{dg(f(x))}{df(x)} \frac{\delta f(x)}{\delta f(x_0)} \\
&= \int dx g'(f(x))\delta(x - x_0) \\
&= g'(f(x_0))
\end{aligned}
$$

We recover the previous result

- Example 2: the classical energy of a distribution of charge

$$E_{\text{Hartree}}[n(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$
\begin{aligned}
\frac{\delta E}{\delta n(\mathbf{r}_0)} &= \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\delta(n(\mathbf{r})n(\mathbf{r}'))}{\delta n(\mathbf{r}_0)} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \\
&= \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \left[\frac{\delta n(\mathbf{r})}{\delta n(\mathbf{r}_0)} n(\mathbf{r}') + n(\mathbf{r}) \frac{\delta n(\mathbf{r}')}{\delta n(\mathbf{r}_0)} \right] \frac{1}{|\mathbf{r} - \mathbf{r}'|} \\
&= \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \left[\delta(\mathbf{r} - \mathbf{r}_0) n(\mathbf{r}') + n(\mathbf{r}) \delta(\mathbf{r}' - \mathbf{r}_0) \right] \frac{1}{|\mathbf{r} - \mathbf{r}'|} \\
&= \frac{1}{2} \left[\int d\mathbf{r}' n(\mathbf{r}') \frac{1}{|\mathbf{r}_0 - \mathbf{r}'|} + \int d\mathbf{r} n(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}_0|} \right] \\
&= \int d\mathbf{r} n(\mathbf{r}) \frac{1}{|\mathbf{r}_0 - \mathbf{r}|}
\end{aligned}
$$

- In the Born Oppenheimer approximation, the electronic Hamiltonian is:

$$H(\mathbf{r}_1, \mathbf{r}_2.....\mathbf{r}_N) = \sum_{i=1}^{N}[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + v_{\text{ext}}(\mathbf{r}_i)] + \frac{1}{2}\sum_{i \neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$H = T + V_{\text{ne}} + V_{\text{ee}}$$

v_{ext} is the external potential (due to nuclei).

- The eigenvectors are normalized wavefunctions

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N)$$

which depends on $3N$ spatial and N spin coordinates. It is a quantity that contains a huge amount of information.

- The electronic density can be written as the expectation value of the density operator $\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$.

$$
\begin{aligned}
n(\mathbf{r}) &= \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle \\
&= \iiint ... \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 ... d\mathbf{r}_N \left| \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) \right|^2 \left[\sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \right] \\
&= \sum_{i=1}^{N} \iiint ... \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 ... d\mathbf{r}_N \left| \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) \right|^2 \delta(\mathbf{r} - \mathbf{r}_i) \\
&= \sum_{i=1}^{N} \int ... \iint ... \int d\mathbf{r}_1 ... d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} ... d\mathbf{r}_N \left| \Psi(\mathbf{r}_1, ..., \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1} ..., \mathbf{r}_N) \right|^2 \\
&= N \iiint d\mathbf{r}_2 d\mathbf{r}_3 ... d\mathbf{r}_N \left| \Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) \right|^2
\end{aligned}
$$

because of the antisymmetry of the wavefunction.

- The integral of the density is the number of electron

$$
N = \int n(\mathbf{r}) d\mathbf{r}
$$

The variational theorem shows that the ground state (GS) energy E_{GS} of the system can be obtained by minimization of the energy as a function of Ψ.

$$E_{\mathrm{GS}} = \min_{\Psi}\langle\Psi|H|\Psi\rangle = \min_{\Psi}[\langle\Psi|T|\Psi\rangle + \langle\Psi|\sum_{i=1}^{N}v_{\mathrm{ext}}(\mathbf{r}_i)|\Psi\rangle + \langle\Psi|V_{\mathrm{ee}}|\Psi\rangle]$$

$$\text{and } \langle\Psi|\sum_{i=1}^{N}v_{\mathrm{ext}}(\mathbf{r}_i)|\Psi\rangle = \int..\int d\mathbf{r}_1...d\mathbf{r}_N \left|\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_N)\right|^2 \left[\sum_{i=1}^{N}v_{\mathrm{ext}}(\mathbf{r}_i)\right]$$

$$= \sum_{i=1}^{N}\int..\int d\mathbf{r}_1...d\mathbf{r}_N \left|\Psi(\mathbf{r}_1,.....,\mathbf{r}_i,...,\mathbf{r}_N)\right|^2 v_{\mathrm{ext}}(\mathbf{r}_i)$$

$$= \sum_{i=1}^{N}\int..\int d\mathbf{r}_1...d\mathbf{r}_N \left|\Psi(\mathbf{r}_i,.....,\mathbf{r}_1,...,\mathbf{r}_N)\right|^2 v_{\mathrm{ext}}(\mathbf{r}_i)$$

$$= \sum_{i=1}^{N}\int..\int d\mathbf{r}_1...d\mathbf{r}_N \left|\Psi(\mathbf{r}_1,.....,\mathbf{r}_i,...,\mathbf{r}_N)\right|^2 v_{\mathrm{ext}}(\mathbf{r}_1)$$

$$= N\int..\int d\mathbf{r}_1...d\mathbf{r}_N \left|\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_N)\right|^2 v_{\mathrm{ext}}(\mathbf{r}_1)$$

$$= \int d\mathbf{r}v_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})$$

using as before the antisymmetry of the wavefunction.

- Thus

$$E_{\mathrm{GS}} \quad = \quad \min_{\Psi}\langle\Psi|H|\Psi\rangle = \min_{\Psi}[\langle\Psi|T|\Psi\rangle + \int d\mathbf{r}\,v_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) + \langle\Psi|V_{\mathrm{ee}}|\Psi\rangle]$$

- Without electronic interactions, the Hamiltonian would be a sum of one particle hamiltonian.

$$H(\mathbf{r}_1, \mathbf{r}_2 ..... \mathbf{r}_N) = \sum_{i=1}^{N} [-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + v_{\text{ext}}(\mathbf{r}_i)]$$

- In this case, the many body wavefunction can be written as a product of one particle wavefunctions $\phi_i(\mathbf{r}_i)$:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_N) = \prod_i \phi_i(\mathbf{r}_i)$$

- The density can be written as the sum of probability density of each electron.

$$n(\mathbf{r}) = \iiint ... \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 ... d\mathbf{r}_N \left| \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) \right|^2 \left[\sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \right]$$

$$n(\mathbf{r}) = \iiint ... \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 ... d\mathbf{r}_N \left| \prod_j \phi_j(\mathbf{r}_j) \right|^2 \left[\sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \right]$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} \int d\mathbf{r}_i \left| \phi_i(\mathbf{r}_i) \right|^2 \delta(\mathbf{r} - \mathbf{r}_i) \times \prod_{j \neq i} 1 = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

- The total energy is :

$$
\begin{aligned}
E_{\text{GS}}^{\text{no interaction}} &= \langle \Psi | H | \Psi \rangle \\
&= \langle \prod_j \phi_j(\mathbf{r}_j) | H | \prod_j \phi_j(\mathbf{r}_j) \rangle \\
&= \langle \prod_j \phi_j(\mathbf{r}_j) \left| \sum_{i=1}^{N} [-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + v_{\text{ext}}(\mathbf{r}_i)] \right| \prod_j \phi_j(\mathbf{r}_j) \rangle \\
&= -\frac{1}{2} \sum_i \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r} + \sum_i \int d\mathbf{r} \, v_{\text{ext}}(\mathbf{r}) |\phi_i(\mathbf{r})|^2 \\
&= -\frac{1}{2} \sum_i \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r} + \int d\mathbf{r} \, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r})
\end{aligned}
$$

- In this case, the many body Schrödinger equation can be decomposed into N one electron equations :

$$
[-\frac{1}{2}\nabla^2 + v_{\text{ext}}]\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})
$$

- Hartree (1927) proposed to keep the electronic interaction but to write the many body wavefunction as the product of one particles wavefunction.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N) = \prod_i \phi_i(\mathbf{r}_i)$$

- The total energy $\langle \Psi | H | \Psi \rangle$ can be written as

$$
E_{\text{GS}}^{\text{Hartree}} = \underbrace{- \sum_i \int \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) d\mathbf{r} + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r})}_{\text{Kinetic}}
$$

$$
+ \underbrace{\frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{\sum_{i \neq j} |\phi_i(\mathbf{r})|^2 |\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}}_{\text{electron electron interaction}}
$$

- If one uses the variational principle to compute the ground state energy, one finds that the one particle wavefunctions are solution of the Hartree equation:

$$
\big[- \frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \sum_{j \neq i} |\phi_j(\mathbf{r}')|^2 \big] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})
$$

- As electrons are fermions, the Hartree many body wavefunction should be antisymmetrized to obtain:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \cdots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \cdots & \phi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

- If one uses this wavefunction to compute the ground state energy, one finds:

$$E_{\text{GS}}^{\text{Hartree Fock}} = -\frac{1}{2} \sum_i \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r} + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{Hartree}}[n(\mathbf{r})]$$

$$-\frac{1}{2} \sum_{i \neq j, \sigma} \iint d\mathbf{r} d\mathbf{r}' \left(\frac{\phi_i^{*\sigma}(\mathbf{r}) \phi_j^{\sigma}(\mathbf{r}) \phi_i^{\sigma}(\mathbf{r}') \phi_j^{*\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right)$$

- The last term is the Fock energy which comes from the antisymmetry of the wavefunctions. It explains in particular the first Hund's rule.

cf also the lecture of Eric Bousquet on Magnetism.

- The configuration of interaction (CI) method consists of using all possible determinants starting from the occupied and empty eigenfunctions of the Hartree Fock equation.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_N) = \sum_{i_1, i_2, ... i_N = 1}^{M} C_{i_1, i_2, ... i_N} \begin{vmatrix} \phi_{i_1}(\mathbf{r}_1) & \phi_{i_1}(\mathbf{r}_2) & \cdots & \phi_{i_1}(\mathbf{r}_N) \\ \phi_{i_2}(\mathbf{r}_1) & \phi_{i_2}(\mathbf{r}_2) & \cdots & \phi_{i_2}(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{i_N}(\mathbf{r}_1) & \phi_{i_N}(\mathbf{r}_2) & \cdots & \phi_{i_N}(\mathbf{r}_N) \end{vmatrix}$$

- The coefficients $C_{i_1, i_2, ... i_N}$ can be computed only for small systems. Indeed, the number of coefficients is equal to $\frac{M!}{N!(M-N)!}$, where M is the dimension of the Hilbert space.

- Intractable for solid state physics and large molecules.

DFT: density functional theory ?

- What is it ?
- The total energy is a functional of the density ?
- A trial density or the density of the GS ?

- For a system with a potential $v_{\text{ext}}(\mathbf{r})$, One can in theory solve the Hamiltonian:

$$H(\mathbf{r}_1, \mathbf{r}_2.....\mathbf{r}_N) = \sum_{i=1}^{N}[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + v_{\text{ext}}(\mathbf{r}_i)] + \frac{1}{2}\sum_{i \neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- and find the ground state wavefunction $\Psi_{\text{GS}}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$:

$$H(\mathbf{r}_1, \mathbf{r}_2.....\mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N)$$

- From the wavefunction, the ground state density $n_{\text{GS}}(\mathbf{r})$ can be computed. It is unique

$$n(\mathbf{r}) = \langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle$$

$$v_{\text{ext}}(\mathbf{r}) \quad \xrightarrow{\text{Schrödinger}} \quad \Psi_{\text{GS}}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \quad \longrightarrow \quad n_{\text{GS}}(\mathbf{r})$$

- Thus the ground state density is a functional of the external potential.

$$n_{\text{GS}}(\mathbf{r}) = \hat{n}(\mathbf{r})[v_{\text{ext}}(\mathbf{r})]$$

- The first Hohenberg Kohn Theorem establishes the inverse relation:
  For any system of interacting particles in an external potential $v_{\text{ext}}(\mathbf{r})$, the potential $v_{\text{ext}}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density $n(\mathbf{r})$.

$$n(\mathbf{r}) \xrightarrow{\text{HK}} v_{\text{ext}}(\mathbf{r})$$

- Thus the external potential is a functional of the ground state density.

$$v_{\text{ext}}(\mathbf{r}) = \widehat{v}_{\text{ext}}(\mathbf{r})[n(\mathbf{r})]$$

- As the wavefunction Ψ_{GS} is a functional of $v_{\text{ext}}(\mathbf{r})$, it is also a functional of the density.

$$\Psi_{\text{GS}}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) = \widehat{\Psi}[n(\mathbf{r})]$$

$$n(\mathbf{r}) \xrightarrow{\text{HK}} v_{\text{ext}}(\mathbf{r}) \xrightarrow{\text{Schrödinger}} \Psi_{\text{GS}}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$$

- A universal functional for the energy $\widehat{E}[n(\mathbf{r})]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external (<u>fixed</u>) potential $v_{\text{ext}}(\mathbf{r})$.

- From the many body wavefunction, one saw previously that:

$$E_{v_{\text{ext}}(\mathbf{r})}[\Psi] = \langle \Psi|H|\Psi \rangle = \langle \Psi|T|\Psi \rangle + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r})[\Psi] + \langle \Psi|V_{\text{ee}}|\Psi \rangle$$

- The second Hohenberg theorem says that:

$$E_{v_{\text{ext}}(\mathbf{r})}[n(\mathbf{r})] = \langle \Psi[n(\mathbf{r})]|T|\Psi[n(\mathbf{r})] \rangle + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + \langle \Psi[n(\mathbf{r})]|V_{\text{ee}}|\Psi[n(\mathbf{r})] \rangle$$

where $\Psi[n(\mathbf{r})]$ has to be understood as $\Psi[v_{\text{ext}}[n(\mathbf{r})]]$.

- Thus, one has the following **universal functional** that does not depend on v_{ext}:

$$F_{\text{HK}}[n(\mathbf{r})] = \langle \Psi[n(\mathbf{r})]|T|\Psi[n(\mathbf{r})] \rangle + \langle \Psi[n(\mathbf{r})]|V_{\text{ee}}|\Psi[n(\mathbf{r})] \rangle = T[n(\mathbf{r})] + E_{\text{ee}}[n(\mathbf{r})]$$

- For any particular <u>fixed</u> $v_{\text{ext}}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of the functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_{\text{GS}}(\mathbf{r})$.

- From the variational principle, one saw previously that:

$$E_{\text{GS } v_{\text{ext}}(\mathbf{r})} = \min_{\Psi}\langle\Psi|H|\Psi\rangle = \min_{\Psi}\left[\langle\Psi|T|\Psi\rangle + \int d\mathbf{r}v_{\text{ext}}(\mathbf{r})n(\mathbf{r})[\Psi] + \langle\Psi|V_{\text{ee}}|\Psi\rangle\right]$$

- As Ψ is a functional of the density $n(\mathbf{r})$, one has the second part of the Hohenberg-Kohn theorem

$$
\begin{aligned}
E_{\text{GS } v_{\text{ext}}(\mathbf{r})} &= \min_{n(\mathbf{r})} E_{v_{\text{ext}}(\mathbf{r})}[n(\mathbf{r})] \\
&= \min_{n(\mathbf{r})}\left[\langle\Psi[n(\mathbf{r})]|T|\Psi[n(\mathbf{r})]\rangle + \int d\mathbf{r}v_{\text{ext}}n(\mathbf{r}) + \langle\Psi[n(\mathbf{r})]|V_{\text{ee}}|\Psi[n(\mathbf{r})]\rangle\right]
\end{aligned}
$$

This is the variational theorem for DFT.

- Kohn et Sham introduced a fictituous non interacting system with the same density as the interacting system.

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

- The universal functional Hohenberg and Kohn can be decomposed as

$$F_{\text{HK}}[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_{\text{Hartree}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})]$$

- $T_s[n(\mathbf{r})]$ is the non interacting kinetic energy functional for the fictituous system

$$T_S[n(\mathbf{r})] = -\sum_i \int \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) d\mathbf{r}$$

- $E_{\text{Hartree}}[n(\mathbf{r})]$ is the Hartree energy (or electrostatic energy).

$$E_{\text{Hartree}}[n(\mathbf{r})] = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- $E_{\mathrm{xc}}[n(\mathbf{r})]$ is defined by

$$E_{\mathrm{xc}}[n(\mathbf{r})] = F_{\mathrm{HK}}[n(\mathbf{r})] - T_s[n(\mathbf{r})] - E_{\mathrm{Hartree}}[n(\mathbf{r})]$$

and is called the exchange and correlation energy and is unknown.

- Using the expression of $F_{\mathrm{HK}}[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{\mathrm{ee}}[n(\mathbf{r})]$, one can rewrite $E_{\mathrm{xc}}[n(\mathbf{r})]$ as:

$$E_{\mathrm{xc}}[n(\mathbf{r})] = T[n(\mathbf{r})] - T_s[n(\mathbf{r})] + E_{\mathrm{ee}}[n(\mathbf{r})] - E_{\mathrm{Hartree}}[n(\mathbf{r})]$$

- $E_{\mathrm{xc}}[n(\mathbf{r})]$ thus contains both a part coming from electron interactions and a part coming from the difference between the exact kinetic energy and the kinetic energy of the fictituous non interacting system.

- The total energy expression as a function of $\phi(\mathbf{r})$ is

$$E_{v_{\text{ext}}}[n(\mathbf{r})] = -\sum_i \int \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) d\mathbf{r} + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{Hartree}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})]$$

  and can be minimized.

- One obtains the one electron Kohn-Sham Equations

$$\left[-\frac{\nabla^2}{2} + V_{\text{KS}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

- The effective Kohn Sham potential $V_{\text{KS}}(\mathbf{r})$ is defined as the functional derivative of the last three terms of the energy:

$$V_{\text{KS}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}(\mathbf{r})$$

- The exchange and correlation potential $v_{\text{xc}}(\mathbf{r})$ is

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

- The Kohn Sham equation are:

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{KS}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

- The effective Kohn Sham potential $V_{\mathrm{KS}}(\mathbf{r})$ depends on the density $n(\mathbf{r})$.

$$V_{\mathrm{KS}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{Hartree}}[n(\mathbf{r})](\mathbf{r}) + v_{\mathrm{xc}}[n(\mathbf{r})](\mathbf{r})$$

- The density $n(\mathbf{r})$ can be compute from wavefunctions on the $\phi_i(\mathbf{r})$.

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

- The Kohn Sham equations for the wavefunctions can thus be solved self-consistently.

- The Kohn Sham equation are:

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{KS}}[n(\mathbf{r})](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

- The effective Kohn Sham potential $V_{\mathrm{KS}}(\mathbf{r})$ depends on the density $n(\mathbf{r})$.

$$V_{\mathrm{KS}}[n(\mathbf{r})](\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{Hartree}}[n(\mathbf{r})](\mathbf{r}) + v_{\mathrm{xc}}[n(\mathbf{r})](\mathbf{r})$$

- The density $n(\mathbf{r})$ can be compute from wavefunctions on the $\phi_i(\mathbf{r})$.

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

- The Kohn Sham equations for the wavefunctions can thus be solved self-consistently.

Solve Kohn Sham Equations
$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{KS}}[n(\mathbf{r})](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Use Kohn Sham functions to built density
$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

Compute Kohn Sham potential from density
$$V_{\mathrm{KS}}[n(\mathbf{r})](\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{Hartree}}[n(\mathbf{r})](\mathbf{r}) + v_{\mathrm{xc}}[n(\mathbf{r})](\mathbf{r})$$

The DFT Loop

Solve Kohn Sham Equations
$$\left[-\frac{\nabla^2}{2} + V_{\text{KS}}[n(\mathbf{r})](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$
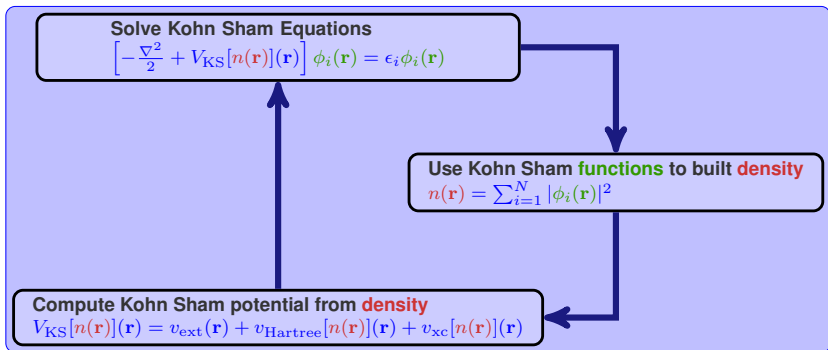
Use Kohn Sham functions to built density
$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

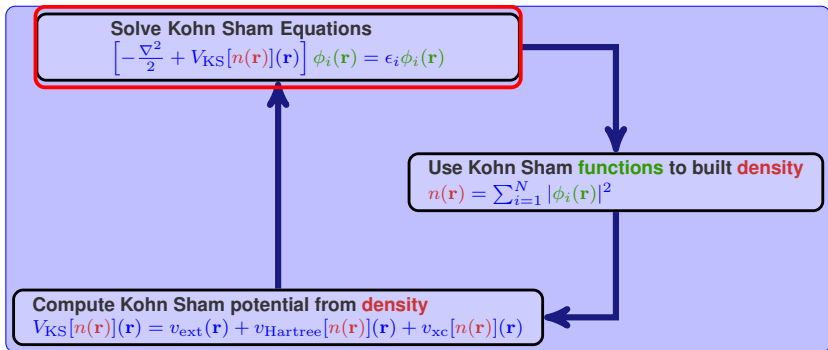**Compute Kohn Sham potential from density**
$$V_{\text{KS}}[n(\mathbf{r})](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n(\mathbf{r})](\mathbf{r}) + v_{\text{xc}}[n(\mathbf{r})](\mathbf{r})$$

- The Kohn Sham Equations are solved by diagonalisation of the Hamiltonian
- One very convenient and simple way to express the equations is to express the wavefunctions in a plane wave basis and use Fourier transformation:
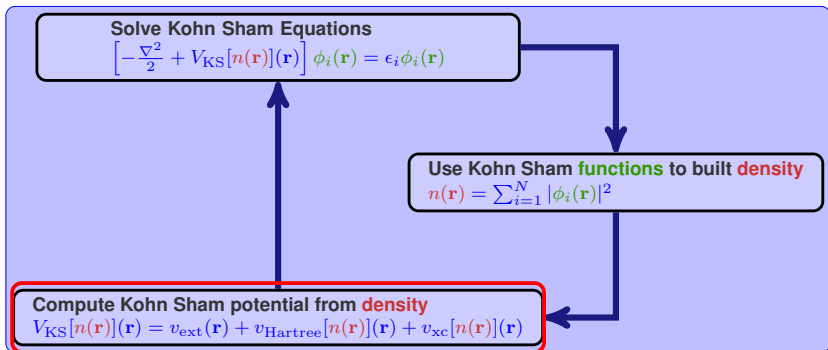- $\phi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}}^i e^{i\mathbf{G}\mathbf{r}}$
- cf next lecture of F. Jollet.

Solve Kohn Sham Equations
$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{KS}}[n(\mathbf{r})](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

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Compute Kohn Sham potential from density
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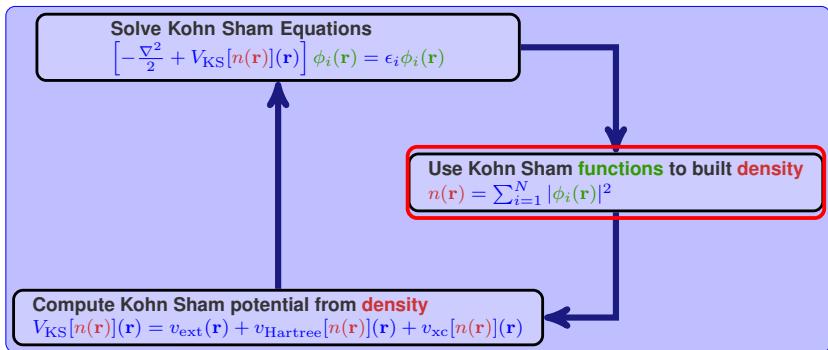
- The density is the sum of occupied wavefunctions

Solve Kohn Sham Equations
$$\left[-\frac{\nabla^2}{2} + V_{\text{KS}}[n(\mathbf{r})](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Use Kohn Sham functions to built density
$$n(\mathbf{r}) = \sum_{i=1}^{N}|\phi_i(\mathbf{r})|^2$$

Compute Kohn Sham potential from density
$$V_{\text{KS}}[n(\mathbf{r})](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n(\mathbf{r})](\mathbf{r}) + v_{\text{xc}}[n(\mathbf{r})](\mathbf{r})$$

- The density used to compute the KS potential can be mixed.
- The simplest solution: $n_{\text{new}} = \alpha n_{\text{new}} + (1-\alpha)n_{\text{old}}$
- When $|n_{\text{new}} - n_{\text{old}}| < \text{tolerance}$, the cycle is stopped.

- We use the expression of the total energy from Hohenberg and Kohn

$$E[n(\mathbf{r})] = F_{\mathrm{HK}}[n(\mathbf{r})] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r})$$

- Then we use the expansion of F_{HK} which defines E_{xc}

$$F_{\mathrm{HK}}[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_{\mathrm{Hartree}}[n(\mathbf{r})] + E_{\mathrm{xc}}[n(\mathbf{r})]$$

- Thus

$$E[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_{\mathrm{Hartree}}[n(\mathbf{r})] + E_{\mathrm{xc}}[n(\mathbf{r})] + \int d\mathbf{r} v_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r})$$

- Then we use the definition of T_s:

$$T_s[n(\mathbf{r})] = -\sum_i \int \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) d\mathbf{r}$$

- The total energy writes:

$$E_{v_{\text{ext}}}[n(\mathbf{r})] = -\sum_i \int \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) d\mathbf{r} + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) + E_{\text{Hartree}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})]$$

- It can also be written as a sum over Kohn-Sham eigenvalues ϵ_i minus double counting terms:

$$E_{v_{\text{ext}}}[n(\mathbf{r})] = \sum_{i=1}^N \epsilon_i - E_{\text{Hartree}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})] - \int d\mathbf{r} v_{\text{xc}}(\mathbf{r}) n(\mathbf{r})$$

- It can be demonstrated using the fact that:

$$\sum_{i=1}^N \epsilon_i = \sum_i \langle \phi_i | -\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) | \phi_i \rangle$$

$$\sum_{i=1}^N \epsilon_i = -\sum_i \int \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) d\mathbf{r} + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r})$$

$$+ 2E_{\text{Hartree}}[n(\mathbf{r})] + \int d\mathbf{r} v_{\text{xc}}(\mathbf{r}) n(\mathbf{r})$$

- These two expressions are implemented in `ABINIT`.

- Forces, stresses can be obtained by differentiation of the total energy
- Phonons can be obtained as the second derivative of the total energy

cf lecture by G. Geneste about relaxation effects and lecture by X. Gonze and B. Dorado about phonons with DFPT.

- In the local Density Approximation, one writes the exchange and correlation energy as

$$E_{\text{xc}}^{\text{LDA}}[n(\mathbf{r})] = \int n(\mathbf{r})\varepsilon_{\text{xc}}^{\text{HEG}}(\bar{n} = n(\mathbf{r}))d\mathbf{r}$$

where $\varepsilon_{\text{xc}}^{HEG}(\bar{n})$ is the exchange and correlation energy per electron in the homogeneous electron gas (HEG) of density $\bar{n}$

- As each point $\mathbf{r}$ in the integral, the expression uses the exchange correlation energy of an HEG of density $\bar{n} = n(\mathbf{r})$.
- The exchange part of the functional can be calculated analytically.
- The correlation part can be obtained numerically using quantum Monte Carlo calculations.

- A natural progression beyond LDA could be to include gradient of the density in the functional.

$$E_{xc}^{GGA}[n(\mathbf{r})] = \int f(n(\mathbf{r}), \nabla n(\mathbf{r})) d\mathbf{r}$$

- A large number of variants exists based on the gradient and also on various physical sum rules. (Perdew Wang 1991, Perdew Burke and Ernzerhof 1996...).
- The LDA and GGA functionals gives a surprisingly good description of cohesive and structural properties of solids made from elements of the first lines of the periodic table.

DFT is exact for ground state properties. But which functional should we used ?

- Spin density functional theory: (e.g LSDA). Allows to describe more easily spin polarized systems.
- Hybrid functionals: Add a portion of Hartree Fock exchange energy to the GGA functional $\rightarrow$ Partially correct the self interaction error of LDA and GGA.
- LDA+U, GGA+U: Add explicitly interactions between strongly correlated electrons (transition metal/lanthanides/actinides).
- Van der Walls functionals (Semi empirical or *ab initio*).
- More that 250 functionals are available in `ABINIT` thanks to libxc.

DFT only describes ground state properties. Excitations can be described by other methods

- For weakly correlated systems, excitations can be described by e.g GW, or TDDFT.
- For strongly correlated systems, DFT+DMFT allows for the description of excitations and structural properties.