Introduction to density functional methods

References


✓ MIT's 3.320 course notes (Prof. N. Marzari)
Recalling the variational principle

- Recall that we reformulated the Schrödinger equation in terms of the variational principle:

\[ E[\Phi] = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E_0 \]

- Entering any arbitrary wavefunction \( \Phi \) in this functional will give us an expectation of the energy. The closer the function \( \Phi \) is to the true ground state wave function, the closer that energy will be to the ground state energy.

- This approach can be improved in a systematic way by using trial wavefunctions \( \Phi \) of higher and higher complexity.
Hartree-Fock approximation

- Hartree-Fock approach is based on the variational approach. In the original Hartree approach, the many-body wave function was written as a product of single particle orbitals.

\[ \psi(\vec{r}_1, \ldots, \vec{r}_n) = \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) \cdots \phi_n(\vec{r}_n) \]

- These wave functions do not satisfy the fundamental symmetry of interacting fermions -- they are not antisymmetric. This is why Hartree and Fock introduced the *Slater determinant*.

\[ \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_\alpha(\vec{r}_1) & \phi_\beta(\vec{r}_1) & \cdots & \phi_\nu(\vec{r}_1) \\ \phi_\alpha(\vec{r}_2) & \phi_\beta(\vec{r}_2) & \cdots & \phi_\nu(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_\alpha(\vec{r}_n) & \phi_\beta(\vec{r}_n) & \cdots & \phi_\nu(\vec{r}_n) \end{vmatrix} \]

- Now we need to determine the shape of these \( n \)-single particle orbitals \( \phi_i \) such that they minimize the expectation value of the variational principle.
Hartree-Fock equations

\[
\left[ -\frac{1}{2} \nabla_i^2 + \sum_I V(\vec{R}_I - \vec{r}_i) \right] \varphi_\lambda(\vec{r}_i) + \\
\sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_j \right] \varphi_\lambda(\vec{r}_i) - \\
\sum_\mu \left[ \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) d\vec{r}_j \right] \varphi_\mu(\vec{r}_i) = \varepsilon \varphi_\lambda(\vec{r}_i)
\]

- These are the Hartree-Fock equations. Each single particle’s orbital \( \phi_\lambda \) satisfies the Hartree-Fock equation (a Schrödinger like equation).
- There is a kinetic energy term – \( -\frac{1}{2} \nabla_i^2 \).
- There is the interaction with the external potential (nuclei attraction) \( \sum_I V(\vec{R}_I - \vec{r}_i) \).
Hartree-Fock equations

\[
\left[ -\frac{1}{2} \nabla_i^2 + \sum_i V(\vec{R}_i - \vec{r}_i) \right] \phi_\lambda(\vec{r}_i) + \\
\sum_\mu \int \phi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \phi_\mu(\vec{r}_j) d\vec{r}_j \right] \phi_\lambda(\vec{r}_i) - \\
\sum_\mu \left[ \int \phi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \phi_\lambda(\vec{r}_j) d\vec{r}_j \right] \phi_\mu(\vec{r}_i) = \varepsilon \phi_\lambda(\vec{r}_i)
\]

- We then have the **mean field terms** – the electron \( \lambda \) interacts with every electron \( \mu \) via an electrostatic interaction.

- The charge density for the orbital \( \mu \) is given as \( \phi_\mu^*(\vec{r}_j) \phi_\mu(\vec{r}_j) \) and the field the electron \( \lambda \) feels is the electrostatic average density.

- In this sum, electron \( \lambda \) is also included (**self-interaction**).
Hartree-Fock equations

\[
\begin{align*}
-\frac{1}{2} \nabla_i^2 + \sum_i V(\vec{R}_i - \vec{r}_i) \varphi_\lambda(\vec{r}_i) + \\
\sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_j \bigg] \varphi_\lambda(\vec{r}_i) - \\
\sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) d\vec{r}_j \bigg] \varphi_\mu(\vec{r}_i) = \varepsilon \varphi_\lambda(\vec{r}_i)
\end{align*}
\]

- At this point an electron \( \lambda \) feels the electrostatic interaction with itself (which obviously does not make sense).

- Fortunately, the exchange term cancels this self-interaction.

- The exchange term is a direct result of writing the wave function as an anti-symmetric expression.
Hartree-Fock equations

\[
\left(-\frac{1}{2} \nabla_i^2 + \sum_{I} V(\vec{R}_I - \vec{r}_i)\right) \varphi_\lambda(\vec{r}_i) + \\
\sum_{\mu} \int \varphi^*_\mu(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_j \right] \varphi_\lambda(\vec{r}_i) - \\
\sum_{\mu} \left[ \int \varphi^*_\mu(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) d\vec{r}_j \right] \varphi_\mu(\vec{r}_i) = \varepsilon \varphi_\lambda(\vec{r}_i)
\]

- This is a Schrödinger-like equation for one electron.

- Recall that an advantage with respect to the Hartree equation is that the Hartree operator does not change depending on the index \( \lambda \) (the sum is over all electrons).

- We have to find the \( n \)-lowest eigenstates of this single differential equation.
Hartree-Fock equations

\[
\left[-\frac{1}{2} \nabla_i^2 + \sum_l V(\vec{R}_l - \vec{r}_i)\right] \varphi_\lambda(\vec{r}_i) + \\
\sum_\mu \left[ \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_j \right] \varphi_\lambda(\vec{r}_i) - \\
\sum_\mu \left[ \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) d\vec{r}_j \right] \varphi_\mu(\vec{r}_i) = \varepsilon \varphi_\lambda(\vec{r}_i)
\]

- For a system with \(n\)-electrons we have \(n\) identical differential equations and we need to find the \(n\)-lowest energy states and \(\phi_i\) will be the single particle orbitals.

- We already have discussed how to improve the Hartree-Fock approximation: Use more Slater determinants with different coefficients, use perturbation theory, etc.

- Unfortunately post-Hartree–Fock techniques developed by chemists are too computationally expensive.
Density Functional theory (DFT) vs Hartree-Fock

- DFT is a theory that starts from a very different set of hypothesis. The net result however will be a set of single particle equations that are similar to Hartree-Fock equations.

- DFT is less expensive than Hartree-Fock and more accurate especially for solids. The Hartree-Fock solution for metals (interacting electron gas) makes them semi-conducting or insulating like, so Hartree-Fock works poorly for solids.

- DFT comes from the solid state community while Hartree-Fock that tends to work very well for atoms and molecules comes from the quantum chemistry community.
DFT was developed from Walter Kohn and co-workers. It was in the 1980’s that the community calculated for the first time e.g. the phase diagram of Si as a function of pressure or volume and properties of solids from first principles.

W. Kohn and J. Pople received the Nobel in chemistry in 1998 – John Pople was instrumental in the development of Hartree-Fock and post H-F approaches in quantum chemistry.
Localized orbitals in the electronic structure of the BaTiO$_3$ crystal, calculated using DFT.
The first idea towards DFT: Thomas-Fermi

- DFT started with the Thomas-Fermi approach (late 20’s and early 30’s).

- The basic idea is that the wave function of many-body interacting problem is too difficult to work with. It will be nice if we treat it with a single scalar object such as the charge density. Effectively, we move from the complexity of

\[ \psi(\mathbf{r}_1, \ldots, \mathbf{r}_n, \mathbf{R}_1, \ldots, \mathbf{R}_N) \]

to a scalar charge density field \( \rho(x,y,z) \).

- Thomas and Fermi posed the problem as follows: Can we try to solve not for the many body wave function in the Schrödinger equation but rather solve some other equation where the only unknown is the charge density.

- The charge density will be treated as a fundamental variable in the solution of the interacting many electron problem.
The Charge Density

- Thomas and Fermi came up with a heuristic function that gives the energy of a set of electrons in a potential as a functional of their charge density.

- The charge density (electrons per unit volume) is defined as follows (which electron coordinate you leave out from the integration below is not important):

\[
\rho(x) \equiv N_{el} \int \psi^*(x, x_2, \ldots, x_{N_{el}}) \psi(x, x_2, \ldots, x_{N_{el}}) \, dx_2 \, dx_3 \ldots \, dx_{N_{el}}
\]

- Note the normalization factor is needed so that:

\[
\int \rho(x) \, dx = N_{el}
\]
Interaction between the e’s and external potential

- The energy of the electrons in the potential of the nuclei can be written as:

\[
\mathcal{E}_{\text{ext}} = \sum_{i=1}^{N_{\text{el}}} \left( \int \psi^*(x_1, x_2, \ldots, x_{N_{\text{el}}}) U_{\text{ext}}(x_i) \psi(x_1, x_2, \ldots, x_{N_{\text{el}}}) \, dx_1 \ldots dx_{N_{\text{el}}} \right)
\]

where:

\[
U_{\text{ext}}(x_i) = \sum_{\beta} \frac{-Z_{\beta}}{\|x_i - r_{\beta}\|}
\]

- For \(i=1\), the term above is as follows:

\[
\int U_{\text{ext}}(x_1) \left[ \int \psi^*(x_1, x_2, \ldots, x_{N_{\text{el}}}) \psi(x_1, x_2, \ldots, x_{N_{\text{el}}}) \, dx_2, \ldots, dx_{N_{\text{el}}} \right] \, dx_1
\]

- Identifying the second integral as \(\rho(x)/N_{\text{el}}\), and summing the \(N_{\text{el}}\) identical terms:

\[
\mathcal{E}_{\text{ext}}[\rho] = \int \rho(x) U_{\text{ext}}(x) \, dx
\]

- We can thus easily write down the interaction of the electrons with an external potential through the charge density.
The electron-electron interaction energy is:

\[ \mathcal{E}^{ee} = \left\langle \psi \right| \frac{1}{2} \sum_{\substack{i,j \neq i,j}} \frac{1}{||x_i - x_j||} \left| \psi \right\rangle \]

We concentrate only on the electrostatic electron-electron interactions (Hartree term) as a functional of the charge density. Let us consider two infinitesimal electronic charges:

\[ d\mathcal{E}^H = \frac{dC_x dC_{x'}}{||x - x'||} = \frac{\rho(x)\rho(x')}{||x - x'||} dxdx' \]

We can compute the total Coulomb energy with double integration (the factor \(1/2\) comes from double counting):

\[ \mathcal{E}^H(\rho) = \frac{1}{2} \int \frac{\rho(x)\rho(x')}{||x - x'||} dxdx' \]
It is convenient to define the Hartree potential as:

\[ U^H(x) \equiv \frac{\delta E^H}{\delta \rho} = \int \frac{\rho(x')}{\|x - x'\|} \, dx', \]

Finally the electrostatic electron-electron interactions as a functional of the charge density can be written in any of these two forms:

\[ E^H = \frac{1}{2} \int \rho(x) U^H(x) \, dx = \frac{1}{2} \int \frac{\rho(x)\rho(x')}{\|x - x'\|} \, dx \, dx' \]

Note that all other interactions between electrons are not considered in this term (exchange & correlation).
The local density approximation (LDA)

- Obtaining the quantum kinetic energy (2\textsuperscript{nd} derivative of the wave function) from the charge density is not easy.

- Let us think for a moment of the extreme case of a plane wave, \( e^{i \mathbf{k} \cdot \mathbf{r}} \).

- Recall that the charge density given by a plane wave is a constant.

- However, the quantum kinetic energy of a plane wave depends on the wavelength of that plane wave \( \frac{1}{2} k^2 \).

- Thus there is not a good way to extract information on the 2\textsuperscript{nd} derivative from the charge density.

- Thomas and Fermi tried to find a functional that will give us a good estimate of the quantum KE in terms of the charge density. The solution to this problem is what we will call a local density approximation (LDA).
The local density approximation (LDA)

- We have a non-homogeneous charge density everywhere and we try to find the quantum kinetic energy.

- Thomas and Fermi divided this non-homogeneous charge in small infinitesimal volumes and inside each volume the charge density was approximated as constant.

- They assumed that the contribution coming from each infinitesimal volume to the overall quantum KE will be given by that volume times the kinetic energy density of the homogeneous electron gas at that density.

- The overall quantum KE is thus the integral across space of the quantum KE of the homogeneous electron gas integrated across space.

- The quantum KE per particle of a uniform electron gas of density \( \rho(r) \) is \( \rho^{2/3} \). This energy per particle is weighted with the probability \( \rho(r) \) that there is in fact an electron at this position \( r \) in space. This gives us \( \sim \rho^{5/3} \).

\[
T(\vec{r}) = A \rho^3(\vec{r})
\]
Exchange term in the Thomas-Fermi approach

- This kinetic energy at every point thus corresponds to the kinetic energy density of the homogenous electron gas.

\[ T(\vec{r}) = A\rho^3(\vec{r}) \]

- We can approximate the needed exchange term by using the exchange energy coming from the Hartree-Fock equation for a homogeneous electron gas. This give a \( \rho^{1/3} \) term.

- For the non-homogeneous system we will approximate its overall exchange energy by taking the integral of that energy density \( \rho^{1/3} \) times the local volume of the charge density – thus we will have \( \rho^{4/3} \).

- Dirac proposed to add the LDA exchange energy:

\[ -C \int \rho(\vec{r})^4 d\vec{r} \]
The Thomas-Fermi approach

We can now write the energy for the Thomas-Fermi approach as:

\[
E_{\text{Th-Fe}}[\rho] = A\int \rho \frac{5}{3} (\vec{r}) d\vec{r} + \int \rho(\vec{r}) v_{\text{ext}}(\vec{r}) d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2
\]

\[ -C\int \rho(\vec{r})^4 d\vec{r} \]

The LDA approximation is exact in the limit of a homogeneous system, and it will be good for a non-homogeneous system that has very slowly changing charge density.

The more non-homogeneous our system becomes, the less accurate this approximation is. For example, atoms and molecules are very inhomogeneous systems (you go from a charge density very close to zero to values that are very high near the nuclei)
The Thomas-Fermi approach

\[ E_{Th-Fe}[\rho] = A \int \rho^\frac{5}{3} (\vec{r}) d\vec{r} + \int \rho(\vec{r}) v_{ext}(\vec{r}) d\vec{r} + \frac{1}{2} \iiint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 - C \int \rho(\vec{r})^4 d\vec{r} \]

- This is postulated by Thomas and Fermi for a system with a charge distribution \( \rho \).

- Without finding the wave function by solving the Schrödinger equation, they postulated that the energy can be written as interaction of the electron with the external potential

\[ \cdot \int \rho(\vec{r}) v_{ext}(\vec{r}) d\vec{r} \cdot \]

and electrostatic electron-electron interaction:

\[ \frac{1}{2} \iiint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \]

- The quantum kinetic energy was computed using the LDA approximation \( \int \rho^3(\vec{r}) d\vec{r} \)

- Similarly for the exchange energy. The Thomas-Fermi approach is not a good approximation since it is difficult to calculate the curvature of the wave function just from the density that this wave function produces.
The Thomas-Fermi solution

- Thus for any potential $v_{\text{ext}}(\vec{r})$ we can find the final $\rho$ that minimizes $E_{\text{Th–Fe}}[\rho]$ with the constraint that the total number of electrons is preserved.

$$E_{\text{Th–Fe}}[\rho] = A \int \rho^{\frac{5}{3}}(\vec{r}) d\vec{r} + \int \rho(\vec{r}) v_{\text{ext}}(\vec{r}) d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2$$

$$- C \int \rho(\vec{r})^3 d\vec{r}$$

- This is a heuristic approach – it’s not like the Hartree-Fock eqs that were derived from the variational principle and the solution could be improved indefinitely (at a cost).

- In addition, the TF approach does not explicitly introduce the concept of anti-symmetry that fermions need to have – that many body wave function needs to be antisymmetric upon exchange.

- As we see above, the exchange energy is included in the functional using LDA.
The Thomas-Fermi approach

- Having an energy functional of only $\rho(r)$ (scalar function) is inexpensive from computation point of view.

- **This problem scales linearly** – if you double the size of the system, the computational complexity doubles.

- Because of the approximation in the KE this solution has a fundamental defect – it does a very poor job in describing non-homogeneous systems (atoms and molecules).

- It does very well in describing metals – e.g. Li or Al are systems for which the valence electrons produce a charge density that is very homogeneous. The Thomas-Fermi approach has been used successfully to compute properties of metals, study their melting, defect formation, etc.

- Clear example of what is going wrong is when you study an inhomogenous system like the Argon atom.
Thomas-Fermi not appropriate for atoms

- Let us think of $\rho$ of Argon as a function of the radial distance from the center of the nucleus.

- If we try to solve the Argon atom with a Thomas-Fermi approach, all the fine structure of the core cells in the atom does not show in the calculations.

- Thomas-Fermi only gives a reasonable approximation as the charge density is decaying.

- The Thomas-Fermi approach was thus not developed beyond the 30’s except for the applications to some metals (homogeneous gas density).

- However, Thomas-Fermi introduced an important idea that is the starting point of DFT: **the focus should be not on the wave function but on the charge density.**

The distribution (here using Hartree-Fock) of electronic charge in an argon atom as a function of the distance from the nucleus (from D. McQuarrie)
Density Functional Theory (DFT)

- The basic difference of Thomas-Fermi and DFT is that DFT is based on a concise mathematical theory.

- We will start with theorems and then derive the equations that the charge density needs to satisfy. In principle, DFT is an exact theory equivalent to the Schrödinger equation for the wave function.

- Let us start with the Schrödinger equation. For any given external potential and knowing how many electrons this potential will feel, the quantum problem is formally well defined, i.e. ‘in principle’ its solution exists and is unique. Once we know the many body wave function solution, we know everything about our quantum system.

- Thus given an external potential, we obtain by the Schrödinger equation the wave function which determines all the properties of our system and in particular determines the ground state charge density.
Once we have defined the potential, in principle we have uniquely defined what is the ground state charge density of our system.

In that sense we say that the ground state charge density and all properties of our system are in some complex way a functional of our external potential and the number of electrons. This functional is implicitly through the Schrödinger equation.

Hohenberg and Kohn figure out (1964) that the opposite is also true! The ground state density is as a fundamental quantity as the external potential. In particular not only the external potential determines uniquely the ground state charge density of the system but also the reverse is true.

Given a ground state charge density `in principle’ one can prove that there is a unique external potential for which that ground state charge density is the ground state solution for that external potential.
Going from the external potential though the Schrödinger equation to the charge density is easy. Based on Hohenberg and Kohn if someone gives us a charge density and he tells us that this charge density is the ground state charge density of a number of $N$-electrons in an external potential, in principle the information of what is that external potential is completely contained into the charge density.

Going from the ground state charge density to the external potential is not trivial at all. This is what is contained in the first Hohenberg-Kohn theorem.

You can at first easily show that if there were 2 different external potentials that that give you the same ground state charge density, then you arrive at a contradiction – so there is a single external potential.

Note that this unique relation between the charge density and the external potential is not applicable to excited states: you cannot recover the external potential from the charge density of an excited electronic state.
The Hohenberg-Kohn theorems

1. **The 1st Hohenberg and Kohn theorem:** The charge density as the basic variable -- the external potential determines uniquely the charge density, and the charge density determines uniquely the external potential.

2. **The 2nd Hohenberg and Kohn theorem:** It writes down the equivalent equation to the Schrödinger equation for the ground state charge density.
For a given ground state $\rho$ there is a unique $V_{\text{ext}}$

- Suppose that there were two different external potentials $V_{\text{ext}}^{(1)}(r)$ and $V_{\text{ext}}^{(2)}(r)$ with the same ground state density $n(r)$.

- The two external potentials lead to two different Hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$ which have different ground state wavefunctions, $\Psi^{(1)}$ and $\Psi^{(2)}$, which are hypothesized to have the same density $n(r)$. Then:

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle$$

from which we derive the following (we use here that the difference between the 2 Hamiltonians is the difference in the external potentials):

$$E^{(1)} < E^{(2)} + \int d^3r \{ V_{\text{ext}}^{(1)}(r) - V_{\text{ext}}^{(2)}(r) \} n(r)$$

- Changing the labels 1 and 2 gives the following:

$$E^{(2)} < E^{(1)} + \int d^3r \{ V_{\text{ext}}^{(2)}(r) - V_{\text{ext}}^{(1)}(r) \} n(r)$$

Contradition, unless

$$V_{\text{ext}}^{(1)}(r) = V_{\text{ext}}^{(2)}(r)$$
Density Functional Theory

- Our attention is not any more the many body wave function but the charge density which is a fundamental quantity. We will need to derive the equivalent of the Schrödinger equation for the charge density.

- Hohenberg and Sham postulated instead of thinking in terms of the wave function we should now think in terms of the charge density as being the fundamental descriptor of our quantum system and write a density equation that will give us the ground state and all the properties of the system.
The Hohenberg-Kohn theorems

The steps for deriving an equation for the charge density are the following:

1. For any charge density, there is a uniquely defined external potential from which this charge density is the ground state.

2. Because there is a unique $V_{ext}$, there is a many body Schrödinger equation with that external potential and there is a ground state wave function which is going to be the ground state wave function of that many body Schrödinger equation with that external potential.

Given a $\rho$, in principle the $\psi$ (the ground state wave function of the Schrödinger equation in the external potential that is uniquely defined by $\rho$) is also a well defined object – We do not know what $\psi$ is but it is a well defined object.

3. With that well defined $\psi$, we can now determine the expectation of the quantum kinetic energy (sum over all electrons) and of the electron-electron interaction.
(4) We this, we can introduce the universal density functional of the energy (in principle a well defined functional) as:

\[ F[\rho(\vec{r})] = \left\langle \Psi \left\vert \hat{T} + \hat{V}_{e-e} \right\vert \Psi \right\rangle \]

Notice that we have introduced terms in this functional that are well defined in principle but we have no explicit expressions for any of them.

We can write down now for our given external potential \( v_{ext}(\vec{r}) \) and for any charge density \( \rho'(\vec{r}) \):

\[ E_v[\rho'(\vec{r})] = F[\rho'(\vec{r})] + \int v_{ext}(\vec{r}) \rho'(\vec{r}) d\vec{r} \geq E_0 \]
The first term on the right hand side is the universal density functional of $\rho'$ (we know it in principle), and the 2nd term is the integral of the external potential times $\rho'$. The functional $E_v$ is well defined for any $\rho'$ and any $v_{ext}$.

Hohenberg and Sham proved that there is a variational principle:

For every $\rho'$, $E_v[\rho'(\vec{r})] \geq E_0$ (the ground state charge energy that we will obtain from the Schrödinger equation with external potential $v_{ext}$).

We thus have a well defined density functional – with a given external potential (here of the $Z/r$ form) we try out not wave functions that are difficult to work with but charge densities. **The charge density that gives you the lowest expectation will give you the ground state energy.**
2nd Hohenberg-Kohn theorem

\[ E_v[\rho'(\vec{r})] = F[\rho'(\vec{r})] + \int v_{ext}(\vec{r}) \rho'(\vec{r}) d\vec{r} \geq E_0 \]

- If we knew what this functional \( E_v[\rho'(\vec{r})] \) looks like as a function of \( \rho' \), then we will have a simple approach to quantum mechanics in which we do not have to deal with the many body complexity. We just minimize \( E_v[\rho'(\vec{r})] \) with respect to \( \rho' \).

- The proof of the 2\textsuperscript{nd} Hohenberg-Kohn theorem can be done through the variational principle. If we have a certain \( \rho' \), that determines uniquely the ground state wave function \( \Psi' \) to the many body Schrödinger equation and an external potential that is different from \( v_{ext} \)

- If we take the expectation value of our Hamiltonian with this external potential \( v_{ext} \) and the \( \Psi' \) that comes from \( \rho' \) we can show that:

\[
\langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{T} + \hat{V}_{\text{ee}} + v_{ext} | \Psi' \rangle = \int \rho' v_{ext} + F[\rho'] \geq E_0
\]
The independent electron approximation

- We have a new equation in terms of the charge density – but we don’t know what \( F[\rho'(\vec{r})] \) is – if we knew it, most of the quantum mechanics problems will be trivially solved.

- Kohn-Sham proposed to find an approximation to this functional.

\[
F[\rho(\vec{r})] = \langle \Psi | \hat{T} + \hat{V}_{e-e} | \Psi \rangle
\]

- Suppose we are given \( \rho \), we need to find the many body wave function \( \psi \) for the external potential that corresponds to this charge density. To do that, we invent a problem in which electrons do not interact with each other (this way we get rid of the (difficult to account for) 2-body electrostatic repulsion in the Schrödinger equation.
Kohn-Sham (non-interacting) electrons

- Suppose there is a system of electrons (Kohn-Sham electrons) that do not interact – the K-S electrons feel in the Schrödinger equation only the external potential and kinetic energy.

- For a given $\rho$, there will be non-interacting set of electrons whose ground state charge density is identical to $\rho$. From $\rho$, one computes $V_{\text{ext}}$, then through the many body non-interacting electron Schrödinger equation one computes the wave function $\psi$, from that one computes the ground state charge density which is identical to the charge density that we deal with ($\rho$).

- We call this potential the Kohn-Sham potential: that is such that the ground state of the Schrödinger equation for non-interacting electrons in that K-S potential will give us a wave function and a ground state that leads to a charge density identical to the charge density we deal with.
Kohn-Sham electrons

- We want those non-interacting electrons to feel a potential that is such that their ground state is going to give us a charge density that is identical to the charge density that we start with – and we call this external potential the Kohn-Sham potential.

- So there is going to be this set of Kohn-Sham non-interacting electrons and there is going to be a potential that is called the Kohn-Sham potential that is such that the ground state of the Schrödinger equation for non-interacting electrons (without electron-electron interaction) in that Kohn-Sham potential will give us a wave function and a ground state that leads to a charge density identical to the one we are dealing here. And what do we do with this?

- For the Schrödinger equation of non interacting electrons we know what is the exact solution (the Slater determinant).
Kohn-Sham electrons

- For the non-interacting set of electrons we can solve everything exactly. We can calculate what is the kinetic energy of this set.

- We thus decompose the density functional into different terms. We extract from $F[\rho'(\vec{r})]$ two terms that are very large but know how to calculate. Hopefully, what is left will be something that is small and we can find a numerical approximation for it.

- The two terms we will extract from $F[\rho'(\vec{r})]$ contain most of the physics of our problem and the smaller term that is left we will approximate with something simple. The approximation Kohn-Sham found works very and that helped to make DFT a very practical and useful method.
Kohn-Sham electrons

- The 1st physical large term that they extracted is the quantum kinetic energy
  \[ T_s[n(r)] \] not of the real system but the quantum kinetic energy of the non-interacting problem. From a given charge density there is a set of Kohn-Sham non-interacting electrons that lives in a potential such that they have the same ground state charge density and their kinetic energy is the kinetic energy of the Slater determinant (sum of simple particle terms).

- For a charge density there is a defined quantum kinetic energy which is not the true quantum kinetic energy of the system but it is the quantum kinetic energy of (the associated system of) the non-interacting electrons.

- They also defined the Hartree electrostatic energy of a charge density distribution. The charge density distribution of each infinitesimal volume is interacting with each other infinitesimal volume with electrostatic interaction

\[ \varepsilon^H = \frac{1}{2} \int \rho(x) \mathcal{U}^H(x) \, dx. = \frac{1}{2} \int \frac{\rho(x)\rho(x')}{\|x - x'\|} \, dx \, dx' \]
What we are left with is what is called the exchange correlation term.

\( F[n(r)] \) is in principle an exact quantity – we are now able to define a quantum kinetic energy term that is an exact quantity (not the quantum kinetic energy of the true system) plus another well defined term (Hartree energy) plus a third term that we do not know.

The advantage of the decomposition of \( F[n(r)] \) in 3 terms is that the first 2 terms capture the complexity of our system and so once the exchange correlation is approximated, our problem is well defined.

The universal density functional plus the charge density in the field of the external potential minimizes the new variational principle that comes from the 2nd Hohenberg-Kohn theorem.

\[
E_v[\rho'(\vec{r})] = F[\rho'(\vec{r})] + \int v_{\text{ext}}(\vec{r}) \rho'(\vec{r}) d\vec{r}.
\]

\[
F[n(r)] = T_s[n(r)] + E_H[n(r)] + E_{xc}[n(r)]
\]
The variational principle

\[ E_v[\rho'(\vec{r})] = F[\rho'(\vec{r})] + \int v_{\text{ext}}(\vec{r}) \rho'(\vec{r}) d\vec{r} \]

\[ F[n(\vec{r})] = T_s[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] \]

- \( E_v[\rho'(\vec{r})] \) with the constraint that the number of the electrons be equal to \( N \), should be minimum.

\[ \frac{\delta}{\delta \rho(\vec{x})} \left[ \mathcal{E}_v[\rho] - \mu \left( \int \rho(\vec{x}) d\vec{x} - N^{el} \right) \right] = 0 \]

- This variational principle leads to a set of Euler-Lagrange equations – i.e. the conditions that need to be satisfied by the charge density.

- These are two equivalent approaches to the quantum problem: the variational principle gives you a differential equation, or you have a differential equation that you can re-write it as a variational principle (minimization problem).
The Kohn-Sham Equations

The Kohn-Sham Equations

\[ \delta \left[ F(n(r)) + \int v(r)n(r) \, dr - \mu \left( \int n(r) \, dr - N \right) \right] = 0 \]

\[ \frac{\delta F[n(r)]}{\delta n(r)} + v(r) = \mu. \quad \rightarrow \quad \frac{\delta T_s[n(r)]}{\delta n(r)} + v_{KS}(r) = \mu. \]

\[ v_{KS}(r) \equiv v(r) + \int \frac{n(r')}{|r - r'|} \, dr' + v_{xc}(r); \quad v_{xc}(r) \equiv \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \]

Taking the variation with respect to the charge density and imposing the Lagrange multiplier constraint leads to the following:

\[ \frac{\delta T_s[n(r)]}{\delta n(r)} + v_{KS}(r) = \mu. \]

The charge density needs to satisfy this set of equations: the ‘functional derivative’ of the non-interacting quantum kinetic energy plus a number of terms that contain the external potential, the Hartree interaction and the exchange correlation need to be equal to the Lagrange multiplier that fixes the number of electrons to be \( N \). We often call the KS-potential, the effective potential: \( U^{\text{eff}}(x; \rho) \)
Kohn-Sham orbitals

\[ \frac{\delta T_s[n(r)]}{\delta n(r)} + v_{KS}(r) = \mu. \]

where

\[ v_{KS}(r) \equiv v(r) + \int \frac{n(r')}{|r - r'|} \, dr' + v_{xc}(r); \quad v_{xc}(r) \equiv \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \]

- We are not able to calculate this functional derivative because the quantum kinetic energy of the non-interactive system is written as a Slater determinant. We are not able to explicitly calculate the functional derivative of the kinetic energy with respect to the charge density of the non-interacting electrons.

- But we are able to calculate the derivative of the non-interactive electron kinetic energy with respect to the orbitals that describe the Kohn-Sham electrons. Remember that these independent Kohn-Sham electrons have an exact solution which is a Slater determinant and we know there is a trivial many body wave function composed of single particle orbitals.
The independent non-interacting electrons

- The independent non-interactive electron kinetic energy is now \(-\frac{1}{2} \nabla^2\).

- For a given \(\rho\), we consider the Hamiltonian for an independent (single-particle) electron as:

\[ H^{\text{sp}} = U^{\text{eff}}(x; \rho) + \frac{p^2}{2} \]

with:

\[ U^{\text{eff}}(x; \rho) = U^{H}(x; \rho) + U^{xc}(x; \rho) + U^{\text{ext}}(x). \]

- The expectation of this Hamiltonian (energy of the single particle – not of our real system) is:

\[ \langle \psi^{\text{sp}} | H^{\text{sp}} | \psi^{\text{sp}} \rangle = T^s + E^{\text{eff}} \]

where the kinetic energy (of non-interacting independent electrons) is:

\[ T^s = \langle \psi^{\text{sp}} \left| -\frac{1}{2} \nabla^2 \right| \psi^{\text{sp}} \rangle \]

and

\[ E^{\text{eff}}[\rho] = \langle \psi^{\text{sp}} | U^{\text{eff}} | \psi^{\text{sp}} \rangle = \int \rho(x) U^{\text{eff}}(x; \rho) \, dx. \]
Minimization of the total (single-electron) energy with the constraint $N^\text{el}=1$ gives:

$$\frac{\delta T^s[\rho]}{\delta \rho} + U^\text{eff}(\mathbf{x}; \rho) = \mu.$$  

which is the same Eq as for the multielectron system.

The electron density obtained from the solution of the system of non interacting particles governed by the Hamiltonian

$$H^\text{sp} = U^\text{eff}(\mathbf{x}; \rho) + \frac{p^2}{2},$$

with:

$$U^\text{eff}(\mathbf{x}; \rho) = U^H(\mathbf{x}; \rho) + U^\text{xc}(\mathbf{x}; \rho) + U^\text{ext}(\mathbf{x}).$$

is the same as that for the original system of interacting particles since it satisfies the same equation.

We know from the first DFT theorem that this density is a unique solution. We can therefore replace the original multiparticle problem with the new single-particle one which is much easier to deal with.
The single particle solutions are obtained by the variational problem:

\[
\Pi = \langle \psi^{\text{sp}} | \mathcal{H}^{\text{sp}} | \psi^{\text{sp}} \rangle - \epsilon \left( \langle \psi^{\text{sp}} | \psi^{\text{sp}} \rangle - 1 \right)
\]

\[
\psi_{I}^{\text{sp}} = \sum_{n=1}^{N_{\text{basis}}} c_{In} \varphi_{n}, \quad n = 1, \ldots, N_{\text{basis}}
\]

The total charge density based on the occupied orbitals for \(N_{\text{el}}\) electrons is:

\[
\rho(x) = \sum_{I \in \text{filled}} \rho_{I}(x) = \sum_{I \in \text{filled}} \sum_{n=1}^{N_{\text{basis}}} \|c_{nI}\|^2 \|\varphi_{n}(x)\|^2
\]
The independent non-interacting electrons

- The kinetic energy term can now be evaluated as:

\[ T^s = \sum_{I \in \text{filled}} \left\langle \psi_{I}^{\text{sp}} \left| -\frac{1}{2} \nabla^2 \right| \psi_{I}^{\text{sp}} \right\rangle \]

- The electronic energy of the multielectron interacting system is then given as follows:

\[ \mathcal{E} = T^s + \mathcal{E}^{\text{ext}} + \mathcal{E}^{\text{H}} + \mathcal{E}^{\text{xc}} \]

\[ = \sum_{I \in \text{filled}} \left\langle \psi_{I}^{\text{sp}} \left| -\frac{1}{2} \nabla^2 \right| \psi_{I}^{\text{sp}} \right\rangle + \int \rho(x) U^{\text{ext}}(x; \rho) \, dx \]

\[ + \frac{1}{2} \int \rho(x) U^{\text{H}}(x; \rho) \, dx + \mathcal{E}^{\text{xc}}, \]
Exchange correlation term

- We can modify the kinetic energy term as follows:

\[
\mathcal{E} = \sum_{I \in \text{filled}} \left\langle \psi_I^{\text{sp}} \left| -\frac{1}{2} \nabla^2 + U^\text{eff} \right| \psi_I^{\text{sp}} \right\rangle - \int \rho(x) U^\text{eff} (x; \rho) \, dx \\
+ \int \rho(x) U^\text{ext} (x) \, dx + \frac{1}{2} \int \rho(x) U^\text{H} (x; \rho) \, dx + \mathcal{E}^{\text{xc}}
\]

where:

\[
U^\text{eff} (x; \rho) = U^\text{H} (x; \rho) + U^{\text{xc}} (x; \rho) + U^\text{ext} (x).
\]

- Using the single electron orbitals, we can simply write the total electronic energy as:

\[
\mathcal{E} = \sum_{I \in \text{filled}} \epsilon_I - \mathcal{E}^\text{H} - \int \rho U^{\text{xc}} (x; \rho) \, dx + \mathcal{E}^{\text{xc}} (\rho).
\]
**Exchange correlation term**

- The total electronic energy of the multielectron system is then given as follows:

\[
E = \sum_{I \in \text{filled}} \epsilon_I - E^H - \int \rho U^{xc}(\mathbf{x}; \rho) \, d\mathbf{x} + E^{xc}(\rho).
\]

- At the end of this complex formulation, we obtain a set of Kohn-Sham equations that are the differential equations that the electrons must satisfy to satisfy the variational principle.

- In the Kohn-Sham equations there is an exchange correlation term that we do not know. It is formally defined as the functional derivative of the exchange correlation energy with respect to the charge density. We will need an approximation for this term.

\[
v^{xc}(\mathbf{r}) \equiv \frac{\delta E^{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}
\]
Here are the Kohn-Sham equations:

\[
\left[ -\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \hat{H}_{KS} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})
\]

\[
v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}', \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}
\]

\[
n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2.
\]

These equations describe not the true electrons in the system but the Kohn-Sham non-interacting electrons.

The K-S electrons have their own orbitals $\Psi_i$ that will give us a ground state charge density that if the exchange correlation functional was exact will be not only the same ground state energy of the interacting electrons but it will also be the exact solution of the problem.
**Kohn-Sham equations**

\[
\left[ -\frac{1}{2} \nabla^2 + v_H(r) + v_{xc}(r) + v_{ext}(r) \right] \psi_i(r) = \hat{H}_{KS} \psi_i(r) = \epsilon_i \psi_i(r)
\]

\[v_H(r) = \int \frac{n(r')}{|r - r'|} \, dr', \quad v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}\]

\[n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2.\]

- These equations look a lot like the Schrödinger equation and like the Hartree-Fock equations. The Kohn-Sham electron \(i\) feels a quantum kinetic energy operator, \(-\frac{1}{2} \nabla^2\)

  It feels a Hartree operator \(v_H(r)\), the external potential and the exchange correlation potential.

- If we knew what the exact exchange correlation potential will be, we will have an exact solution to the problem. Fortunately, we are able to come up with a good approximation for this term.
Finding the ground state from the K-S equations is not very different from finding the ground state of the Hartree-Fock equation. However, as we will see the exchange term in the K-S equations is much simpler than the exchange term of the Hartree-Fock equations. Recall that in the Hartree-Fock equation, the exchange term in a complex expression in which the orbital to be computed is inside an integral differential operator.

\[
\begin{align*}
&\left[ -\frac{1}{2} \nabla_i^2 + \sum_{I} V(\vec{R}_I - \vec{r}_i) \right] \phi_\lambda (\vec{r}_i) + \\
&\sum_{\mu} \int \phi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \phi_\mu (\vec{r}_j) d\vec{r}_j \phi_\lambda (\vec{r}_i) - \\
&\sum_{\mu} \int \phi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \phi_\lambda (\vec{r}_j) d\vec{r}_j \phi_\mu (\vec{r}_i) = \varepsilon \phi_\lambda (\vec{r}_i)
\end{align*}
\]
The Kohn-Sham equations are simpler to solve, they tend to be more accurate and that’s what adds to their success.

If we had the exact correlation potential, everything will be exact in this formulation.

We will find Kohn-Sham independent electrons that are the ground electrons for that charge density that is ultimately equal to the charge density of the interacting electrons in the given external potential.
It can be shown that the total energy of the system can now be computed as a sum of: a kinetic energy term, a Hartree term, the exchange correlation functional and the interaction of the external potential with the charge density. It is given as follows:

\[
E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2} \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) \, d\mathbf{r} + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] + \int v_{ext}(\mathbf{r}) n(\mathbf{r}) \, d\mathbf{r}
\]

where

\[
E_H[n(\mathbf{r})] = \frac{1}{2} \iint \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2
\]
Total electronic energy

- Usually if you have independent electrons, the total energy of the system is trivially the sum of each of the single particle energies. In this case, is more complex and the total energy of the system cannot be really written as such and has other terms that depend on the charge density.

- This is actually different from the sum of the eigenvalues that will be the sum of the expectation values:

  \[ E[\{\Psi_i\}] \neq \sum_i \varepsilon_i = \sum_i \langle \Psi_i | T + V_{KS} | \Psi_i \rangle \]

  where \( T = -\frac{1}{2} \nabla_i^2 \) is the quantum kinetic energy of the single particle orbitals.

- If you want to calculate the total energy of the system even if made of independent particles, you cannot sum just the single particle orbitals. You have to deal with the expression given in the earlier slide.
Kohn-Sham equations

➢ Note because of the complex expression for the energy, we cannot find out the equivalent of the Koopmans’ theorems for Hartree-Fock.

➢ At the end these single particle energies are not physically meaningful – they are not giving the total energy of the system by taking the sum over all of them.

\[ E[\{\Psi_i\}] \neq \sum_i \varepsilon_i = \sum_i <\Psi_i|T+V_{KS}|\Psi_i> \]

➢ The only thing that remains for this to become a practical algorithm is to find an approximation to the exchange correlation term \( E_{xc}[n(r)] \) for any arbitrary charge density. To do that we go back to the Thomas-Fermi idea.

➢ We are going to do a local density approximation (LDA) for the exchange correlation functional.
An LDA approximation for the exchange functional

- Consider an inhomogeneous charge density distribution that changes values and then drops to zero. We can calculate the exchange correlation energy for this charge density distribution by decomposing it in infinitesimal volumes of constant charge density. Then we make a LDA – that is, the contribution to the overall exchange correlation energy of this non-homogeneous charge can be broken down and each infinitesimal volume will give its own contribution to the total exchange correlation energy.

- The true exchange correlation functional is ultra non-local and it cannot be decomposed into terms that independently sum up. In principle cannot do this but in practice is a good approximation.
An LDA approximation for the exchange functional

- What we need to do is to find out for each density what is the \( E_{xc}[n(r)] \) for the homogeneous electron gas that is at that density.

- This is something that with advanced computation techniques we can find almost exactly.

- If we know we had homogeneous charge density \( \rho_1 \) everywhere, we will know what will be the charge density per unit volume, we can find \( E_{xc}[n(r)] \) not only for charge density \( \rho_1 \) but for any other value.

- For the non-homogeneous problem, we only need to construct the overall exchange by summing up these different pieces. This is what Ceperley and Alder did (1980).
An LDA approximation for the exchange functional

- They found out the exact solution for the exchange correlation functional for the homogeneous gas (e.g. for a system you have electrons homogeneously -- so the charge density is the same everywhere).

- These homogeneous-gas electrons interact so you can calculate the energy of these interacting electron problem exactly as a function of the density. You change the density in the volume and you find out what is the energy and then you can calculate for any of this density what is the Kohn-Sham kinetic energy, you can find out the Hartree electrostatic energy so you find out numerically for the specific case of the homogeneous gas what is the exchange correlation energy.
Exchange correlation

- For the homogeneous gas case (that does not depend on \( r \)), people found out what is the exchange correlation energy as a function of \( r_s \) where \( r_s \) is the radius of a sphere that contains 1 electron – inverse quantity with respect to the density.

- Using quantum Monte Carlo calculations they solved the interacting Schrödinger equation problem but for the specific case of an electron gas that has homogeneous density. They were able to do that for various densities and so now we have a function for the homogeneous problem.

A homogeneous system is completely described by its density \( n=\frac{N_e}{\Omega} \), which can be characterized by the parameter \( r_s \) defined as the radius of the sphere containing in average 1 electron:

\[
\frac{4\pi}{3} r_s^3 = \frac{\Omega}{N_e} = \frac{1}{n} \quad \text{or} \quad r_s = \left( \frac{3}{4\pi n} \right)^{1/3}
\]
For the non-homogeneous problem we take a local density approximation and we say that the overall exchange correlation energy is given by an integral over all the infinitesimal volumes and each infinitesimal volume will have its own density and will contribute at that density with its own value $E_{xc}[n(r)]$.

This is exactly what Thomas-Fermi did for the Quantum Kinetic Energy. However, we now do this LDA for a term which is much smaller in our problem. Kohn-Sham did it for what is left from the universal functional once we have taken out the quantum kinetic energy and the electrostatic energy of the non-interacting electrons.
The Perdew-Zunger parametrization

At this time, DFT becomes a practical algorithm since we have an expression for the exchange correlation term (1980).

This approach works especially well for solids – the valence electrons in a solid are much less structured than the electrons in a molecule that need to drop to zero so the charge density in a solid overall varies less dramatically as a function of space than it does in atoms and molecules.

This is what is summarized for the exchange correlation energy by Perdew and Zunger (1981) – they suggested an interpolation of the numerical data as a function of the charge density.
The Perdew-Zunger parametrization

\[ E_{XC}[n(r)] = \int dr \, e_{XC}[n(r)] \, n(r) \]

\[ \approx \int dr \left[ e_{X}^{\text{hom}}(n(r)) + e_{C}^{\text{hom}}(n(r)) \right] n(r) \]

\[ e_{X}^{\text{hom}}(n) = -\left(81/64\pi \right)^{1/3} n^{1/3}(r) \]

\[ e_{C}^{\text{hom}}(n) = \begin{cases} 
-0.1423(1 + 1.0529\sqrt{r_{s}} + 0.3334r_{s})^{-1} & \text{if } r_{s} \geq 1, \\
-0.0480 + 0.0311\ln r_{s} - 0.0116r_{s} + 0.002 & \text{if } r_{s} < 1.
\end{cases} \]

\[ r_{s} := \left(4\pi n(r)/3\right)^{-1/3} \quad \text{Wigner-Seitz radius} \]

- Marvin Cohen (1982) wrote the first electronic structure codes that were able to solve the density function equations for a periodic solid (in particular Si).

- Here \( e_{xc}[\rho] \) is the exchange correlation energy per electron in a uniform density field. The exchange correlation potential introduced earlier is then:

\[ U^{xc}(x) = \rho(x) \frac{\delta e^{xc}(\rho[x])}{\delta \rho} + e^{xc}(\rho[x]) \]
Cowen calculated the energy $E$ of the system as a function of the lattice parameter. He took Si in its diamond structure (FCC lattice with 2 basis atoms). To compute the lattice parameter, they located where the minimum of the energy is (1% error). Similarly, they computed the 2nd derivative of the energy at the equilibrium point and that gave them the bulk modulus (5-10% error).

FIG. 5. Total-energy curves of the seven phases of Si as a function of the atomic volume normalized to $\Omega_{\text{expt}}$ (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the $\beta$-tin phase ($c/a = 0.552$).
They also considered Si in the β-tin phase and they computed the lattice parameter in Si. From the Maxwell construction we can find out what is the pressure in which we will have a transition from diamond to β-tin. All high pressure phases of Si were constructed and the results were remarkably close to experiments.

DFT has become since the 80’s better and better in solving these problems and in computing the exchange correlation energy. The Kohn-Sham approximation is however still very good.
Generalized gradient approximations

- We tried to guess what is the energy of the inhomogeneous system by starting for what we knew for the homogeneous electron gas – so we can now introduce in the problem the gradient of the density.

- **Using the gradient actually is much worst.** There is a miracle in LDA (local density approximation) in which the actual expression of the local density approximation satisfies symmetry and scaling properties of what will be the exact exchange correlation functional.

- When introducing gradients, symmetries and scaling properties were not taken care of and the gradient approximations were much worst. You need to introduce gradients in ways that satisfy these forms.

- There is a generalized exchange correlation function done by Perdue (PBE-GGA approximation). There are important improvements but little on the top of the top of the major work in the1960’s.
Generalized gradient approximations

- Hybrid functionals have been developed in the chemistry community.

- DFT while in theory is self-interaction corrected, in practice it is not. Thus why a certain amount of non-local Hartree-Fock exchange is weighted in the GGAs (recall that Hartree-Fock is self-interaction corrected).

- This works well for atoms and molecules but it is more complex.
Most electrons in materials are tightly bound core electrons that remain close to the nucleus and do not participate in bonding.

The electron density in the core experiences rapid fluctuations between regions of very high and very low density, and the LDA becomes quite unreliable there.

These rapid fluctuations also mean that we must choose a very large basis set of wave functions below to realistically capture the density field.

\[
\Pi = \langle \psi^{\text{SP}} | \mathcal{H}^{\text{SP}} | \psi^{\text{SP}} \rangle - \epsilon \left( \langle \psi^{\text{SP}} | \psi^{\text{SP}} \rangle - 1 \right)
\]

\[
\psi^{\text{SP}}_I = \sum_{n=1}^{N_{\text{basis}}} c_{In} \varphi_n, \quad n = 1, \ldots, N_{\text{basis}}
\]

The fact that core electrons do not contribute to bonding means that we can only solve for the electronic structure of the valence electrons as they interact to form bonds.
Introduction to Pseudopotentials

- Away from the core, where valence electrons exist, the variations in the electron density become much less severe and a reduced basis set of wave functions can be used.

- We cannot completely neglect the core electrons. They interact electrostatically with the valence electrons, effectively screening some of the Coulomb potential of the atomic nucleus.

- We must also incorporate exchange/correlation effects between the valence & core electrons.

- Incorporating these effects means replacing the naked Coulomb potential in \( U_{\text{ext}} \) with a pseudopotential.

- We are solving a modified Schrödinger equation for only the valence electrons, where \( U_{\text{ext}} \) has changed due to the presence of the core electrons.

- Note that we also need a screened Coulomb interaction between nuclei (pair potential)
This modification is approximated by a pseudopotential.

The simplest pseudopotential is the empty-core pseudopotential of Ashcroft:

\[ U^{\text{empty}}(r) = \begin{cases} 
0 & \text{for } r < r_{\text{core}}, \\
-z\frac{e^2}{r} & \text{for } r \geq r_{\text{core}},
\end{cases} \]

The approach is to define a core radius within which the potential is taken to be identically zero.

Outside of the core, the potential is the Coulomb attraction between an electron and a point charge of +ez, where z is the valence of the atom (i.e. the difference between the number of protons in the nucleus and the number of electrons in the core).
Empty Core Pseudopotential

- \( r \) is the distance between the electron and the center of the nucleus. \( r_{\text{core}} \) is chosen so that the lowest-energy s-state in the presence of the isolated pseudopotential has the experimentally known energy of the valence s-state for the element.

- Al can be modeled as having only 3 electrons in the presence of the Al pseudopotential, and Cu only one.

- Pseudopotentials are significantly weaker than the Coulomb potential, which explains why valence electrons in metals behave essentially as free electrons.

- It also explains why the LDA works reasonably well for the \( E^{xc} \) contribution; a weak potential means relatively slow variations in \( \rho(x) \).

\[
U^{\text{empty}}(r) = \begin{cases} 
0 & \text{for } r < r_{\text{core}}, \\
-ze^2/r & \text{for } r \geq r_{\text{core}}, 
\end{cases}
\]
Evanescent Core Pseudopotential

- A more realistic pseudopotential is the “evanescent core” pseudopotential.

\[ U_{ec}(r, Z) = -\frac{e^2 z_Z}{B_Z} \left\{ \frac{1}{y} [1 - (1 + b_Z y) \exp (-a_Z y)] - A_Z \exp (-y) \right\} \]

- It is suitable for the description of simple metals and takes the analytical form where \( y = r/B_Z \) and the constants \( A_Z \) and \( b_Z \) are given in terms of parameter \( a_Z \).

- The valence of an ion with atomic number \( Z \) is denoted by \( z_Z \). Two parameters, \( B_Z \) and \( a_Z \), completely determine the potential for atomic number \( Z \), and can be found by fitting to known properties of simple metals.

- The main advantage over the empty core potential is the smooth functional form which permits a simple closed-form expression for Fourier transform. The utility of Fourier transforms in DFT of solids will become clear in a follow up lecture.
Nonlocal Pseudopotential

- In more accurate implementations of DFT, the pseudopotentials are typically of nonlocal form.

- The potential at \( \mathbf{x} \) depends on the electron density everywhere.

\[
U^\text{ext}(\mathbf{x}) = \int v(\mathbf{x}, \mathbf{x}') \rho(\mathbf{x}') \, d\mathbf{x}'
\]

- We will revisit the consequence of this in another lecture.