

1 *ab initio* Calculations

In condensed matter physics, the basic study object we face is a manybody system with the order of 10^{23} electrons and atoms. Each electron/atom has kinetic energy, two electrons/atoms have a long-ranged Coulomb repulsive interaction of form $1/r$, also an electron and an atom has a long-ranged Coulomb attractive interaction. In order to solve the quantum dynamics of it, we need to solve the eigen-problem with the manybody Hamiltonian:

$$\mathcal{H} = T_e + T_i + V_{ee} + V_{ii} + V_{ei} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{ij} \frac{e^2}{|r_i - r_j|} + \sum_i \frac{P_i^2}{2M} + \frac{1}{2} \sum_{ij} \frac{Z^2 e^2}{|R_i - R_j|} - \sum_{ij} \frac{Ze^2}{|r_i - R_j|}, \quad (1)$$

with the total state space $\mathbb{H} \sim \bigotimes_{i=1}^{10^{23}} \mathbb{H}_i$. Solving such an exponentially complex problem is absolutely impossible. So people use different approximation techniques to minimize the complexity. One legitimate approximation is the **Born-Oppenheimer approximation**, which treats the system adiabatically so that we can ignore the energy of atoms and makes the electrons moving in an effective external ionic potential field. Then such Hamiltonian is reduced into

$$\mathcal{H} = T_e + V_{ion} + V_{ee}, \quad (2)$$

where V_{ion} is the effective external ionic potential field that is periodic at most cases. This periodicity is promised by the periodic space structure of the lattice background, which in turn gives us a good quantum number called quasimomentum k . By labeling every electron wavefunction with k , one can form a set of Bloch waves $u_{n\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} c_{n\mathbf{k}}(\mathbf{r})$. Then, by using another approximation called the **tight-binding approximation**, one can continue to form a set of local orbital basis called a **Wannier state** at each lattice site: $w_n(\mathbf{R}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} u_{n\mathbf{k}}(\mathbf{r})$. Eventually, one can write the reduced many-electron Hamiltonian into a second-quantized form dressed in Wannier representation:

$$\mathcal{H} = \sum_{\nu\lambda} \sum_{\sigma} \int d\mathbf{r} \left[\frac{\hbar^2}{2m} \nabla \psi_{\nu\sigma}^{\dagger}(\mathbf{r}) \nabla \psi_{\lambda\sigma}(\mathbf{r}) + \psi_{\nu\sigma}^{\dagger}(\mathbf{r}) V_{ion}(\mathbf{r}) \psi_{\lambda\sigma}(\mathbf{r}) \right] + \frac{1}{2} \sum_{\nu\lambda\beta\alpha} \sum_{\sigma\sigma'} \iint d\mathbf{r} d\mathbf{r}' \psi_{\nu\sigma}^{\dagger}(\mathbf{r}) \psi_{\lambda\sigma'}^{\dagger}(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_{\beta\sigma'}(\mathbf{r}') \psi_{\alpha\sigma}(\mathbf{r}), \quad (3)$$

where $\nu, \lambda, \beta, \alpha$ are orbital indices and σ is spin index, so that $\psi_{\nu\sigma}(\mathbf{r})^{\dagger}$ represents the creation of one electron in the ν th occupied Wannier orbital at coordinate \mathbf{r} with spin σ .

ab initio calculations try to directly solve the Schrodinger equation related to this Hamiltonian.

2 Free Electron Gas

We quickly go through some basic results of the free electron gas.

A free electron gas is the easiest model in solid state theory. Its Hamiltonian is just $\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m}$. That is, we abandon all the messy terms in Eq. 1, but only leave the kinetic energy of electrons. This model can be solved exactly.

In zero-temperature case, one has the step-like Fermi-Dirac distribution: $f_{\mathbf{p}\sigma} = \Theta(\mu_0 - \frac{p^2}{2m})$. Then by giving the density of homogeneous electron gas, one can determine the Fermi momentum $p_F = \hbar(3\pi^2 n_e)^{1/3}$ and single-electron radius $r_e = 1.92 \frac{\hbar}{p_F}$. The dimensionless ratio $r_s = r_e/a_0$ against 1 describes the physical density of the gas. $r_s \ll 1$ corresponds to dense limit then we get a Wigner crystal and $r_s \gg 1$ corresponds to dilute limit then we get a Fermi gas. Between the two edge of the spectrum is a Fermi liquid. One can further get the zero-temperature chemical potential $\mu_0 = (3\pi^2)^{2/3} \frac{\hbar^2}{2m} n_e^{2/3}$, it is usually of eV order. And the total energy $E_0 = \frac{3}{5} N \mu_0$ and the ground state pressure $P_0 = \frac{2}{5} n_e \mu_0$.

In finite-temperature case, one has the Fermi-Dirac distribution: $f_{\mathbf{p}\sigma} = \frac{1}{e^{\beta(\epsilon_{\mathbf{p}} - \mu)} + 1}$. By using the trick of Sommerfeld expansion, one can perturbatively deal with all the thermal observables of the Fermi integral form

$$I = \int_0^\infty f(\epsilon) i(\epsilon) d\epsilon = \int_0^\mu i(\epsilon) d\epsilon + \frac{\pi^2}{6\beta^2} i'(\epsilon) + \frac{7\pi^4}{360\beta^4} i'''(\epsilon) + \dots \quad (4)$$

So the finite-temperature chemical potential has the low-temperature form $\mu(n_e, T) \approx \mu(n_e, 0) \left(1 - \frac{\pi^2}{12} (T/T_F)^2 \right)$.

The above content is default as treated in zero-temperature case.

3 Hartree-Fock Approximation

Hartree-Fock approximation is a wavefunction based variational method to deal with the Hamiltonian in Eq. 3. It assumes that the ground state energy is a functional of the ground state wavefunction $E = E[\Psi]$, so that one need to do the variation to the energy functional respect to some constraint to find the approximated ground state wavefunction and ground state energy. One so has a corresponding function space. The accuracy of this method is determined by the choice of the trial function space.

For Hartree-Fock, such function space is chosen statically by the **Slater determinant space**. By using second-quantized Fermionic creation operator, such Slater state can be naturally written as a non-interacting Fermi ball in momentum space:

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\psi(\mathbf{r}_1, \sigma_1)\rangle_1 & |\psi(\mathbf{r}_2, \sigma_2)\rangle_1 & \cdots & |\psi(\mathbf{r}_N, \sigma_N)\rangle_1 \\ |\psi(\mathbf{r}_1, \sigma_1)\rangle_2 & |\psi(\mathbf{r}_2, \sigma_2)\rangle_2 & \cdots & |\psi(\mathbf{r}_N, \sigma_N)\rangle_2 \\ \cdots & \cdots & \cdots & \cdots \\ |\psi(\mathbf{r}_1, \sigma_1)\rangle_N & |\psi(\mathbf{r}_2, \sigma_2)\rangle_N & \cdots & |\psi(\mathbf{r}_N, \sigma_N)\rangle_N \end{vmatrix} = \prod_{\mathbf{p} \leq \mathbf{k}_F} \prod_{\sigma} a_{\mathbf{p}\sigma}^{\dagger} |0\rangle. \quad (5)$$

Also, transform the two-body interacting term into momentum space, one gets the form

$$V_{ee} = \frac{e^2}{2V} \sum_{\mathbf{q} \neq 0} \sum_{\mathbf{k}\mathbf{k}'} \sum_{\sigma\sigma'} \frac{4\pi}{q^2} a_{\mathbf{k}+\mathbf{q},\sigma}^{\dagger} a_{\mathbf{k}'-\mathbf{q},\sigma'}^{\dagger} a_{\mathbf{k}'\sigma'} a_{\mathbf{k}\sigma}. \quad (6)$$

Average out this with the Slater states, one may use the Wick theorem to determine the average of the string operator $\langle \Psi | a_{\nu}^{\dagger} a_{\lambda}^{\dagger} a_{\beta} a_{\alpha} | \Psi \rangle = (\delta_{\nu\alpha} \delta_{\lambda\beta} - \delta_{\nu\beta} \delta_{\lambda\alpha}) n_{\alpha} n_{\beta}$, one then divides the electron-electron interaction into two different terms: $V_{ee} = \frac{1}{2} \sum_{\nu\lambda} \sum_{\sigma\sigma'} (U_{\nu\lambda}^{\sigma\sigma'} - J_{\nu\lambda}^{\sigma\sigma'})$, where

$$U_{\nu\lambda}^{\sigma\sigma'} = \iint d\mathbf{r} d\mathbf{r}' |\psi_{\nu\sigma}(\mathbf{r})|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\psi_{\lambda\sigma'}(\mathbf{r}')|^2, \quad (7)$$

is the direct Coulomb repulsion and

$$J_{\nu\lambda}^{\sigma\sigma'} = \iint d\mathbf{r} d\mathbf{r}' \psi_{\nu\sigma}^*(\mathbf{r}) \psi_{\lambda\sigma'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_{\nu\sigma}(\mathbf{r}') \psi_{\lambda\sigma'}(\mathbf{r}) \quad (8)$$

is the so-called **exchange potential**. It is no more but the direct consequence of the Pauli principle, an effective attraction by exchanging a hole. For the kinetic and external potential part, it is easy by just replace the field operators into orbital wavefunctions. Then one reaches the corresponding Hartree-Fock energy functional E_{HF} . Do the variation respect to the ψ^* s under the constraint of the normalization condition $\int d\mathbf{r} |\psi_{\nu\sigma}(\mathbf{r})|^2 = 1$. We eventually get the single-particle **Hartree-Fock equations**:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ion}(\mathbf{r}) + \sum_{\lambda\sigma'} \int d\mathbf{r}' n_{\lambda\sigma'}(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_{\nu\sigma}(\mathbf{r}) - \sum_{\lambda\sigma'} \int d\mathbf{r}' \psi_{\lambda\sigma'}^*(\mathbf{r}') \psi_{\nu\sigma}(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_{\lambda\sigma'}(\mathbf{r}) = \epsilon_{\nu\sigma} \psi_{\nu\sigma}(\mathbf{r}). \quad (9)$$

One can do the ab initio calculation by solving these equations iteratively.

By putting into a free electron plane wave ansatz $\psi_{\mathbf{p}} = \frac{e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}}{\sqrt{V}}$ (that is the non-interacting first-order approximation), one can derive the usual kinetic energy $T_e = \frac{p^2}{2m}$ and the external potential $V_{ion} = -e^2 n_e \int \frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}|}$

which cancels the direct Coulomb repulsion term $U_{dir} = e^2 n_e \int \frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}|}$, and the Lindhart-type exchange spectrum:

$$J_{\text{ex}}(\mathbf{p}) = -\frac{e^2 p_F}{\pi \hbar} \left(1 + \frac{(p_F^2 - p^2)}{2pp_F} \ln \left| \frac{p + p_F}{p - p_F} \right| \right). \quad (10)$$

Intergrate them out, one gets the renowned total Hartree-Fock energy density: $\epsilon_{\text{HF}} = \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} \right) \text{Ry}$.

The total Hartree-Fock energy spectrum over that of the free electron gas is a function of $x = p/p_F$: $\epsilon_{\text{HF}}(\mathbf{p})/\epsilon_F = x^2 - 0.663r_s F(x)$, where $F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$ is the Lindhart spectrum function. One can then calculate the bandwidth of Hartree-Fock level:

$$\Delta_{\text{HF}} = \epsilon_{\text{HF}}(x=1) - \epsilon_{\text{HF}}(x=0) = \epsilon_F(1 + 0.331r_s). \quad (11)$$

The obvious limitation of Hartree-Fock approximation is threefold:

1. The effective mass of an electron near Fermi surface in Hartree-Fock level is $\frac{1}{m^*} = \frac{1}{p_F} \left(\frac{\partial \epsilon(\mathbf{p})}{\partial \mathbf{p}} \right)_{p \rightarrow p_F} \propto \ln|1-x|$, so at Fermi surface the electron is actually massless, which is not consistent with experiment. It implies that at every point on the 2D Fermi surface, the band structure is a Dirac cone, which is obvious crude since this statement is only true for a single Fermi point in 1D.
2. The heat capacity in Hartree-Fock level is $C_V \sim \frac{T}{|\ln T|}$, $T \rightarrow 0$, which is not consistent with experimental linear behavior. The unphysical logarithm arises from the long-ranged nature of the Coulomb potential.
3. The cohesive energy of some metals (like group-IA) in Hartree-Fock level is of poor prediction with experiment. It is always a little higher. So there must be higher-order effects not included.

It should be noticed that Hartree-Fock method does not include any correlations between electrons, since it assumes a static Slater state which is composed by single electron orbital wavefunctions. In fact, this is just the first-order approximation of the electron-electron interaction. In real case, this decomposition cannot be done due to correlations between electrons. Thus, what Hartree-Fock implies is that at any moment the wavefunction configuration is well-behaved so that each electron feels exactly an effective field generated by other electrons, which is exactly what Hartree-Fock equations mean. The single-particle image can be defined through **Koopmans' theorem**: the Hartree-Fock single-particle energy ϵ_ν is the energy required to add a particle in the previously unoccupied orbital ν , which can be further treated as a variational approximation to the system's first ionization potential. For higher-order correlations, a perturbative way is to do the manybody perturbation from the uniform electron gas ground state, as pointed out by Gell-Mann and Brueckner (GB1957), a more accurate expression of the Hartree-Fock energy density is (valid for $r_s \leq 1$)

$$\epsilon_{\text{HF}} = \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.062 \ln r_s - 0.096 + \mathcal{O}(r_s) \right) \text{Ry}. \quad (12)$$

4 Thomas-Fermi-Dirac Method

Thomas-Fermi-Dirac method is an advanced version of Hartree-Fock approximation by recast it into a density based language, which can be viewed as a prelude of DFT. At first, Thomas and Fermi rewrote the energy into a functional of a slowly varying electronic ground state density neglecting both exchange and correlation effects:

$$E[n] = T + V_{ion} + U_{dir} = \frac{3}{10}(3\pi^2)^{2/3} \int d\mathbf{r} n(\mathbf{r})^{5/3} + \int d\mathbf{r} V_{ion}(\mathbf{r})n(\mathbf{r}) + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (13)$$

Here the ground state density $n(\mathbf{r}) = \langle \Psi | \sum_{\nu\sigma} \psi_{\nu\sigma}^\dagger \psi_{\nu\sigma} | \Psi \rangle$. Further, Dirac involved the Hartree-Fock exchange term: $J_{ex} = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} n(\mathbf{r})^{4/3}$. Thus, by doing the variation of $E[n] = T + V_{ion} + U_{dir} - J_{ex}$ respect to $n[\mathbf{r}]$ under the constraint of the total particle number $\int d\mathbf{r} n(\mathbf{r}) = N$, one achieves the Thomas-Fermi-Dirac equations:

$$\frac{1}{2}(3\pi^2)^{2/3} n(\mathbf{r})^{2/3} + V_{ion}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \left(\frac{3}{\pi} \right)^{1/3} n(\mathbf{r})^{1/3} - \mu = 0. \quad (14)$$

The limitation of Thomas-Fermi-Dirac is twofold:

1. It does not show the shell structure of atoms, so effects like Friedel oscillation and density oscillation cannot be seized.
2. It gives rise to the infinite density at the nucleus, which is obviously unphysical.

5 Density Functional Theory

Upon the above considerations, the **Density Functional Theory (DFT)** is born.

5.1 Hohenberg-Kohn Theorems

The foundation of DFT is the Hohenberg-Kohn theorems. The Hohenberg-Kohn theorem states: for an arbitrary inhomogeneous electron gas,

1. there exists a universal functional of the ground state electron density, $F[n(\mathbf{r})] = \langle \Psi | T + V_{ee} | \Psi \rangle$, called the **Hohenberg-Kohn functional**, such that the total energy functional $E[n(\mathbf{r})] = \int d\mathbf{r} V_{ion}(\mathbf{r})n(\mathbf{r}) + F[n(\mathbf{r})]$ gives a one-to-one map between the Hamiltonians/ground state wavefunctions and the ground state electron density, regardless whether the ground state is degenerate or not;
2. under the constraint of a given particle number, the corresponding electron density minimizes the energy functional through variation is the correct ground state electron density, combined with 1, we get $\min_n \{E[n(\mathbf{r})], \int d\mathbf{r} n(\mathbf{r}) = N\} \leftrightarrow \{E_0, |\Psi\rangle\}$.

For the first statement, in the nondegenerate case, we can easily show that there exists a one-to-one functional map between the external potential $V_{ion}(\mathbf{r})$ and the ground state electron density by using proof of contradiction.

This conclusion directly relates to the fact that the ground state wavefunction is a unique functional of electron density, since when $V_{ion}(\mathbf{r})$ is fixed, the full Hamiltonian is fixed, then the ground state wavefunction is determined. Consequently, it is legitimate to use electron density as an argument to represent the ground state information. This also directly points out that we can construct a universal functional $F[n(\mathbf{r})]$ for any particle numbers. Then the total energy is a functional of the ground state electron density. In the degenerate case, things are complexier, but this statement is still valid by using the **Levy-Lieb functional** instead.

The Levy-Lieb functional is defined as $L[n(\mathbf{r})] = \min_{\Psi \rightarrow n} \langle \Psi | T + V_{ee} | \Psi \rangle$, whose domain is now $D_L = \{n(\mathbf{r}) | \int d\mathbf{r} n(\mathbf{r}) = N\}$. Recall the domain of Hohenberg-Kohn functional is $D_{HK} = \{n(\mathbf{r}) | V_{ion}[n(\mathbf{r})] = V_{ion}(\mathbf{r})\}$. It can be shown that $D_{HK} \subset D_L$, since in the latter there may exist some densities that cannot be realized by any external potential. Then the ground state energy is just

$$E_0 = \min_{\Psi \rightarrow n} \langle \Psi | T + V_{ee} + V_{ion} | \Psi \rangle = \min_n \left[\min_{\Psi \rightarrow n} \langle \Psi | T + V_{ee} | \Psi \rangle + \int d\mathbf{r} V_{ion}(\mathbf{r})n(\mathbf{r}) \right] = \min_n E[n(\mathbf{r})], \quad (15)$$

which need not to care whether the ground state is degenerate or not.

For the second statement, it may seem trivial at first. However, one should pay special attention to the fact that the possible ground state electron density is defined through every given external potential, but now it is defined through every fixed particle numbers. So we should use Levy-Lieb functional to prove this. We can view each electron density defined by a fixed particle number as if **realized** by a certain

external potential, then by the ground state uniqueness theorem, each energy functional contains a possible external potential has only one ground state. So for the real external potential with fixed particle number, there must exist one density that fits it, which coincides with the minimal energy functional. The key factor is that the domain of Hohenberg-Kohn functional is a subset of that of the Levy-Lieb functional.

Now, the mission is transformed to find the correct electron density to minimize the energy functional with the constraint of the particle number, that is to do the following variation with respect to a Lagrange multiplier: $\delta(E[n(\mathbf{r})] - \epsilon(\int d\mathbf{r}n(\mathbf{r}) - N)) = 0$.

Unlike Hartree-Fock, the accuracy of DFT is determined by the choice of the trial density functional, not density itself. Since density is a universal manybody observable, it cannot cause errors. That is to say, if $F[n(\mathbf{r})]$ is formed exactly, then DFT can solve the inhomogeneous electron gas exactly. So the errors is caused by the explicit form of the universal functional.

One can first separate out the direct Coulomb interaction from $F[n(\mathbf{r})]$: $F[n(\mathbf{r})] = U_{dir}[n(\mathbf{r})] + G[n(\mathbf{r})]$, where $U_{dir}[n(\mathbf{r})]$ is the third term in Thomas-Fermi functional. The latter, which can be written as

$$G[n(\mathbf{r})] = T + \frac{1}{2} \int \int d\mathbf{r}d\mathbf{r}' \frac{C_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (16)$$

where matrix $C_2 = n(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}') - n(\mathbf{r})n(\mathbf{r}')$. This term is the so-called **exchange-correlation potential**. Note here it is insintrically exact many-body potential, not like Hartree-Fock. We then can define an energy density functional as the density of G , $g[n(\mathbf{r})]$. Note that g can have an arbitrary global gauge transformation, which does not affect physics.

In the [original paper](#) of Hohenberg and Kohn, they explicitly studied two approximate cases. The first case is the gas of almost constant density: $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, where $\tilde{n}(\mathbf{r})/n_0 \ll 1$ and $\int \tilde{n}(\mathbf{r})d\mathbf{r} = 0$. In this case, the electron density is almost constant, thus we can express any density functional by $\tilde{n}(\mathbf{r})$: $G[n(\mathbf{r})] = G[n_0(\mathbf{r})] + \int d\mathbf{r}d\mathbf{r}'K(\mathbf{r} - \mathbf{r}')\tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}') + \int d\mathbf{r}d\mathbf{r}'d\mathbf{r}''L(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}')\tilde{n}(\mathbf{r}'') + \dots$.

Note that since the translation symmetry the linear expansion is zero. We only focus on the second-order expansion. The kernel of it is denoted as $K(\mathbf{r})$. HK showed that K can be expressed by electronic polarizability $\alpha = \frac{\epsilon-1}{\epsilon}$. To see this one should first review the former Thomas-Fermi screening formalism. The result is that $K(k) = \frac{2\pi}{k^2} \frac{1-\alpha(k)}{\alpha(k)}$, where $\alpha(k) = \left[1 + \frac{k^2}{k_{extTF}^2} S(k)\right]^{-1}$, where $k_{TF} = \frac{1}{a_0} \sqrt{\frac{2.434}{r_s}}$ is the Thomas-Fermi screening constant, and $S(k) = \left[\frac{1}{2} + \frac{k_F}{2k} \left(1 - \frac{k^2}{4k_F^2} \ln \left| \frac{k+2k_F}{k-2k_F} \right| \right)\right]^{-1}$. Expand this expression one can formulate a **Gradient Expansion Approximation(GEA)** of $G[n(\mathbf{r})]$, the corresponding expand coefficient can be expressed explicitly by dielectric function. It can be noted that $k = k_F$ is a singularity of the kernel, which reveals the fact of Friedel oscillation that cannot be captured by the previous methods.

Standing on this foundation, we can march to the second case in which we consider the gas of slowly varying density: $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$, $r_0 \rightarrow \infty$. Since $1/r_0 \rightarrow 0$, we can expand the energy density by gradient, and because of the rotational symmetry, only scalars can appear. After eliminating all the total derivative terms, the expansion coefficient of each scalars $g_\mu^\nu(n)$ (where the subscript counts the gradient orders and the superscript counts the times of density occurs) can be expressed explicitly by the expansion coefficient

of the dielectric function. HK pointed out that when such method is applied to the first case, a finite density at the nucleus and correct Friedel oscillations in the charge density corresponding to shell structure appears, which cannot be obtained through Hartree-Fock.

5.2 Kohn-Sham Method

Kohn and Sham formulated a scheme to calculate $G[n(\mathbf{r})]$. one first express the kinetic term in the energy functional as the non-interacting form $T = \frac{3}{10}(3\pi^2)^{2/3} \int d\mathbf{r}[n(\mathbf{r})]^{5/3}$ in Thomas-Fermi method, and put the errors all into the exchange-correlation term. Do the variation, one gets the **Kohn-Sham equations**:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}[n(\mathbf{r})] \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (17)$$

where $V_{eff}[n(\mathbf{r})] = V_{ion}[n(\mathbf{r})] + \frac{1}{2} \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V_{xc}[n(\mathbf{r})]$, $V_{xc}[n(\mathbf{r})] = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$, and the density is just the direct sum of each single-particle density: $n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$. It should be pointed out that this is only for iteration: the single-particle wavefunctions appear here is only fake. DFT does not care about the single-particle wavefunctions, but only the manybody density. One can then assume an ansatz density, construct the effective potential and find a new density through the Kohn-Sham equations. Iterating it until the energy is within an error threshold. What Kohn-Sham method surpasses Hartree-Fock method is that it must include the correlation effects, which can be non-local at most times. So the only task left is to find a correct form of the exchange-correlation energy functional $E_{xc}[n(\mathbf{r})]$.

5.3 LDA, GGA and NDA

Here are two famous method determine the explicit form of the exchange-correlation energy functional.

The starting point is **Local Denisty Approximation(LDA)**. This approximation is valid for both a slowly varying density $r_s/r_0 \ll 1$ and a high enough density $r_s/a_0 \ll 1$. For LDA, one can write the exchange-correlation functional as

$$E_{xc}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r})], \quad (18)$$

here the density $\epsilon_{xc}[n(\mathbf{r})]$ is assumed to be known from the exchange-correlation energy density of a homogeneous electron gas, where the exchange energy density is of the form which Dirac has derived $\epsilon_x = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n(\mathbf{r})^{1/3}$, and the correlation energy density need numerical calculation, which depends on different parametrizations. In the first case, one can further do GEA to expand the higher-order corrections respect to the gradient of ground state density, the coefficient is determined by dielectric function just like what HK has shown. In the second case, since the density is so high, the errors of the exchange-correlation interaction can be neglected compared to the kinetic term, so this procedure is still valid. By using LDA, one actually can do a rather accurate calculation to a random inhomogeneous electron gas with local correlations, since one can divide the atoms and molecules into three regions:

1. A core region near the atomic nucleus, where the density is very high, so the approximation is valid;

2. A bulk region contained the main body of the charge distribution, where the density is slowly varying, so the approximation is valid;
3. A surface region where the wavefunctions of atoms and molecules overlap, here the density is rapidly varying and not very high, so the approximation is not valid. This region contributes to the main error of LDA.

Generalized Gradient Approximation(GGA) is a natural improvement of LDA. For the density that are not that slowly varying, we can further include the first-order gradient of the density into the functional, i.e. $E_{xc}[n(\mathbf{r})] = \int d\mathbf{r}n(\mathbf{r})\epsilon_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})]$.

The above considerations is only valid for local correlations. For stronger correlated electron gas, where the correlations are non-local, we can use **Non-local Density Approximation(NDA)** to first separate out the exchange term from the exchange-correlation term, assuming it is of the Hartree-Fock form, then suggest a LDA-type form of the correlation term: $E_{xc}[n(\mathbf{r})] = E_{ex}^{HF}[n((r))] + \int d\mathbf{r}n(\mathbf{r})\epsilon_c[n(\mathbf{r})]$.

Like Koopmans' theorem for Hartree-Fock, there exists the **Janak's theorem** states that the single-particle energy ϵ_i appears in Kohn-Sham equations is equals to the highest occupied state's eigenvalue, that is the first ionization energy.

5.4 Applications

Here we conclude two applications listed by Kohn and Sham.

The first application is to calculate the correct low-temperature form of the heat capacity. Here we first generalize the above formalism to finite-temperature case. For finite-temperature systems, the main functional is the grand canonical potential functional:

$$\Omega[n(\mathbf{r})] = \int d\mathbf{r}n(\mathbf{r})V_{ion}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + G[n(\mathbf{r})] - \mu \int d\mathbf{r}n(\mathbf{r}). \quad (19)$$

We write the universal functional $G[n(\mathbf{r})]$ into the familiar form: $G[n(\mathbf{r})] = G_s[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})]$, where $G_s[n(\mathbf{r})] = T_s[n(\mathbf{r})] - TS_s[n(\mathbf{r})]$ is the free version of a non-interacting electron gas. Again one can use LDA to approximate the exchange-correlation term and do the same iteration procedure. Note one more difference is that now the density is $n(\mathbf{r}) = \sum_{i=1}^N \frac{|\psi_i(\mathbf{r})|^2}{e^{\beta(\epsilon_i - \mu)} + 1}$.

The finite-temperature entropy can be expressed as

$$S[n(\mathbf{r})] = S_s[n(\mathbf{r})] + \int d\mathbf{r}n(\mathbf{r}) \frac{\partial \epsilon_{xc}}{\partial T}, \quad (20)$$

which implies the low-temperature heat capacity $C_V = \gamma T, T \rightarrow 0$, where γ can be expressed as single-particle DOS. This is correct with the experiment, which cannot be obtained by Hartree-Fock.

The second application is to calculate the susceptibility. Consider a (spin) moment function $m(\mathbf{r})$ with the corresponding (magnetic) field $H(\mathbf{r})$, then the energy functional is

$$E[n(\mathbf{r}), m(\mathbf{r})] = \int d\mathbf{r}[n(\mathbf{r})V_{ion}(\mathbf{r}) - m(\mathbf{r})H(\mathbf{r})] + \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + G[n(\mathbf{r}), m(\mathbf{r})], \quad (21)$$

now the universal functional is also a functional of the moment. Under perturbative expansion, it can be expanded towards the second-order moment term, where the kernel is denoted as $G(\mathbf{r}, \mathbf{r}'; n(\mathbf{r}))$. For weak field, we have

$$-H(\mathbf{r}) + \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}'; n(\mathbf{r}))m(\mathbf{r}') = 0, \quad (22)$$

further we have the (spin) susceptibility:

$$\chi[n(\mathbf{r})] = \frac{1}{V} \frac{\partial}{\partial H} \int d\mathbf{r} m(\mathbf{r}) = \int d\mathbf{r} d\mathbf{r}' G^{-1}(\mathbf{r}, \mathbf{r}'; n(\mathbf{r})). \quad (23)$$

For the inverse kernel $G^{-1}(\mathbf{r}, \mathbf{r}'; n(\mathbf{r}))$, one can again separate it as the free term plus the exchange-correlation term, the latter can be further determined through the same procedure.

5.5 Conclusion

The above formalism, including the foundation of HK theorem and the KS equations, is called the Density Functional Theory (DFT). DFT is the modern version of calculating the many-electron system from the first principle computation. Note that there is an intrinsic difference between the Hartree-Fock formalism and DFT. The difference is threefold.

1. In the general spirit sector, Hartree-Fock uses the ground state wavefunction as its building block; but DFT uses the ground state density as its building block.
2. In the physical sector, Hartree-Fock is a static formalism excludes correlations between electrons, but DFT is a dynamical formalism includes correlations between electrons.
3. In the computation sector, the core approximation of Hartree-Fock is to average the two-body electron string operator by plane waves through Wick theorem, and thus reduce it to an exchange operator but ignore the correlation effect, one then get an explicit Lindhard-type form. Then, one get a well-defined single particle energy. But in DFT, there is actually no approximation of the interaction part formally, so it includes non-local correlation effect. There is no single particle image at all, since one deal with the manybody density, not the single-body wavefunction. Only when the iterating is turned on do we care about the single-body wavefunction. All the approximation is stored in the exchange-correlation functional, which needs a prior ansatz form.

We may list a table to show the main differences of these ab initio calculations.

Table 1 Conclusion.

Method	Interaction	Solvability?	Base	Single/Many-body?	Correlations?
Free Electron Gas	No interaction	Exact	-	Single-body	No
Hartree-Fock	Direct Coulomb repulsion+exchange attraction	First-order	Wavefunction	Single-body	No
Thomas-Fermi-Dirac	Direct Coulomb repulsion+exchange attraction	First-order	Homogeneous density	Many-body	No
DFT	Direct Coulomb repulsion+exchange-correlation interaction	Theoretically exact	Inhomogeneous density	Many-body	Yes
LDA	DFT level	Perturbatively exact	Slowly varying density	DFT level	Local correlations
GGA	DFT level	Perturbatively exact	More varied than LDA	DFT level	Local correlations
NDA	DFT level	Perturbatively exact	LDA level	DFT level	Non-local correlations

6 References

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