Lecture on First-principles Computation (3): The Interacting Homogeneous Electron Gas

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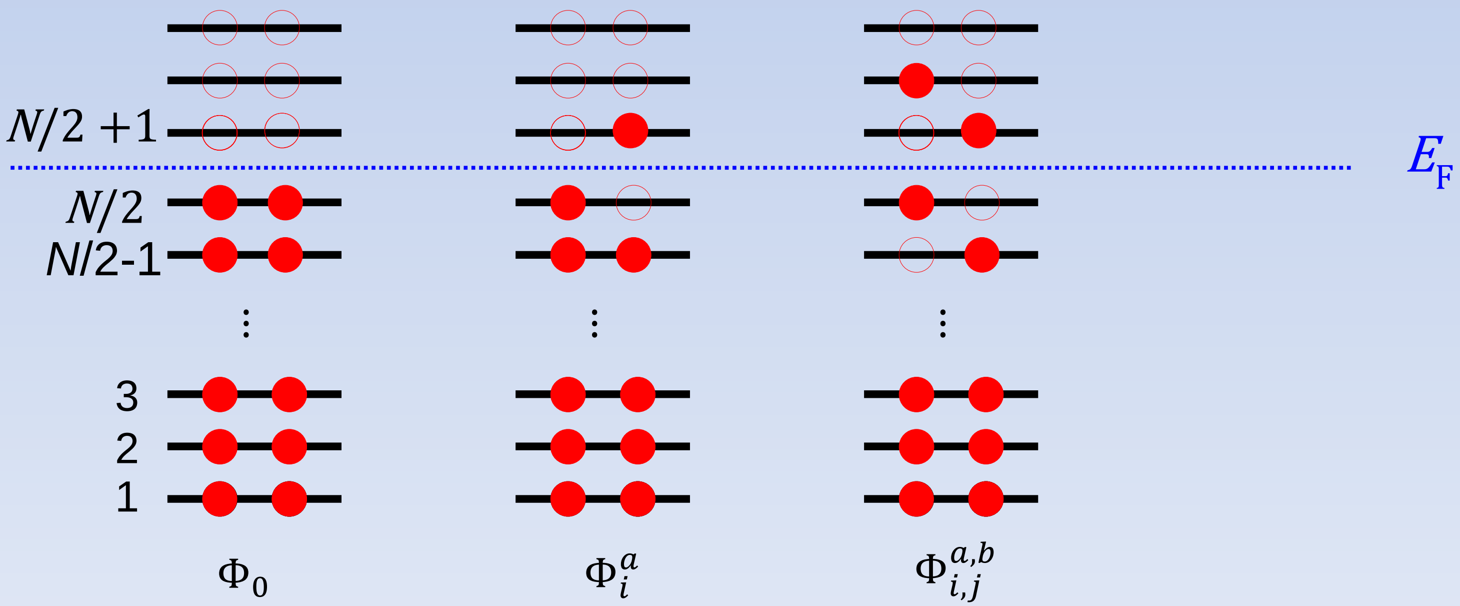
Second quantization of quantum mechanics

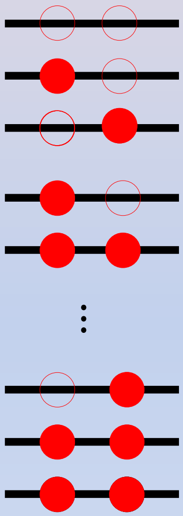
Under the independent particle (e.g., Hartree-Fock) approximation, the ground-state wave function of many-fermion system is a single Slater determinant:

$$\Phi_0 = \frac{1}{\sqrt{N!}} \det[\varphi_1, \varphi_2, \cdots, \varphi_{N-1}, \varphi_N]$$

$$\Phi_1 = \frac{1}{\sqrt{N!}} \det[\varphi_1, \varphi_2, \cdots, \varphi_{N-1}, \varphi_{N+1}]$$



Occupation representation



$$\Phi = \frac{1}{\sqrt{N!}} \det\left[\varphi_{l_1}, \varphi_{l_2}, \cdots, \varphi_{l_N}\right]$$

Under the occupation representation:

$$|\Phi\rangle = |n_1, n_2, \cdots, n_\infty\rangle, \qquad n_i = 0,1$$

For example,

$$|\Phi_0\rangle = |\underbrace{1,1,\cdots,1}_{N},0,\cdots,0\ \rangle$$

For every single-particle orbital *i*, one can define a pair of creation and annihilation operators:

$$\left[c_i, c_j^\dagger\right]_+ = \delta_{ij}, \qquad \left[c_i, c_j\right]_+ = \left[c_i^\dagger, c_j^\dagger\right]_+ = 0$$

Creation and annihilation operators

$$c_j|1\rangle_{j'} = \delta_{jj'}|0\rangle_j \qquad c_j|0\rangle_{j'} = 0$$

$$c_j^\dagger|1\rangle_{j'} = 0, \qquad c_j^\dagger|0\rangle_{j'}=\delta_{jj'}|1\rangle_j$$

$$\left[c_j, c_{j'}^\dagger\right]_+ = \delta_{jj'}, \qquad [c_j, c_{j'}]_+ = \left[c_j^\dagger, c_{j'}^\dagger\right]_+ = 0$$

Particle number operator:

$$\hat{n}_j|n\rangle_j = c_j^\dagger c_j|n\rangle_j = n|n\rangle_j$$

Particle number operators commute with each other,

$$\hat{n}_i\hat{n}_j = \hat{n}_j\hat{n}_i$$

The Fock space

Define a vacuum state, which contains no particles:

$$c_j|\mathrm{Vac}\rangle = 0, \qquad \text{for } j = 1,2,\cdots,\infty$$

All single-particle states: $c_j^\dagger|\mathrm{Vac}\rangle$, $j = 1,2,\cdots,\infty$

All two-particle states: $c_i^\dagger c_j^\dagger|\mathrm{Vac}\rangle$, $j < i$

N-particle ground-state: $\prod_{j\leq N} c_j^\dagger|\mathrm{Vac}\rangle$

The essence of second quantization is, within the Fock space, express the many-body Hamiltonian in terms of creation and annihilation operators.

Second-quantized form of the Coulomb interaction

$$\hat{V}_{ee} = \frac{1}{2}\sum_{i\neq j}^{N} \frac{1}{|\hat{\boldsymbol{r}}_\mathrm{i} - \hat{\boldsymbol{r}}_\mathrm{j}|} = \frac{1}{2}\int d\boldsymbol{r}d\boldsymbol{r}' \frac{\hat{n}(\boldsymbol{r})\hat{n}(\boldsymbol{r}') - \hat{n}(\boldsymbol{r})\delta(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta\,(\boldsymbol{r} - \hat{\boldsymbol{r}}_i) = \sum_{\boldsymbol{k}=0}^{\infty}\sum_{i=1}^{N} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)} = \sum_{\mathbf{k}=0}^{\infty} \hat{\rho}_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

where $\hat{\rho}_{\boldsymbol{k}} = \sum_{i=1}^{N} e^{-i\boldsymbol{k}\cdot\hat{\boldsymbol{r}}_i}$

$$\hat{V}_{ee} = \frac{1}{2}\sum_{\boldsymbol{k}} \frac{4\pi}{k^2}\left(\hat{\rho}_{\boldsymbol{k}}^{\dagger}\hat{\rho}_{\boldsymbol{k}} - \hat{N}\right) \qquad \hat{N} = \int d\boldsymbol{r}\hat{n}(\boldsymbol{r})$$

The ***k***=0 term cancel out the positive charge background.

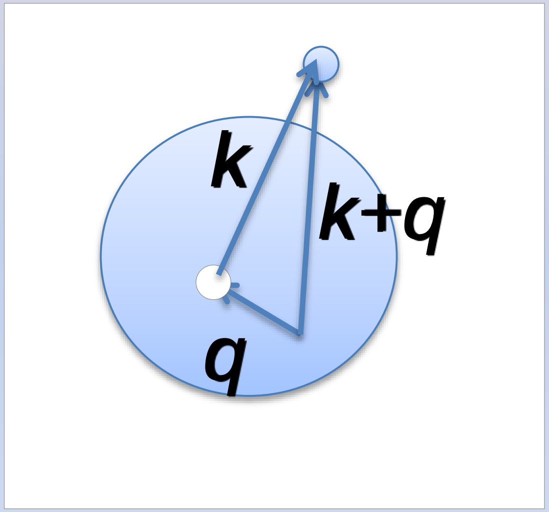
The Hamiltonian of interacting HES

$$\hat{H} = \sum_{\boldsymbol{k},\sigma} \frac{k^2}{2\mathrm{m}} \hat{c}^{\dagger}_{\boldsymbol{k}\sigma} \hat{c}_{\boldsymbol{k}\sigma} + \frac{1}{2} \sum_{\mathbf{k}} \frac{4\pi}{k^2} \left(\hat{\rho}^{\dagger}_{\boldsymbol{k}} \hat{\rho}_{\boldsymbol{k}} - \hat{N} \right)$$

$\hat{\rho}_k$ can be expressed in terms of creation and annihilation operators:

$$\hat{\rho}_{\boldsymbol{k}} = \sum_{\boldsymbol{q},\sigma} \hat{c}^{\dagger}_{\boldsymbol{q}\sigma} \hat{c}_{\boldsymbol{q}+\boldsymbol{k}\sigma}$$

$$\hat{\rho}^{\dagger}_{\boldsymbol{k}} = \sum_{\boldsymbol{q},\sigma} \hat{c}^{\dagger}_{\boldsymbol{q}+\boldsymbol{k}\sigma} \hat{c}_{\boldsymbol{q}\sigma}$$



$\hat{\rho}_{\boldsymbol{k}}$: the summation of all particle-hole pairs with a total momentum of ***k***

$$\langle \Phi_0 \mid \hat{\rho}_{\boldsymbol{k}} \mid \Phi_0 \rangle = N \delta_{\boldsymbol{k},0}$$

The ground-state energy of interacting HES

$$\hat{H} = \sum_{\boldsymbol{k},\sigma} \frac{k^2}{2\mathrm{m}} \hat{c}^{\dagger}_{\boldsymbol{k}\sigma} \hat{c}_{\boldsymbol{k}\sigma} + \frac{1}{2} \sum_{\boldsymbol{k}} \frac{4\pi}{k^2} \left(\hat{\rho}^{\dagger}_{\boldsymbol{k}} \hat{\rho}_{\boldsymbol{k}} - \hat{N} \right) = \hat{H}_0 + \hat{H}'$$

$$\hat{H}_0 \left| \Phi_0 \right\rangle = \mathrm{E}_0^{(0)} \left| \Phi_0 \right\rangle, \qquad |\Phi_0\rangle = \prod_{\mathrm{k} \le k_F, \sigma} \hat{\mathrm{c}}^{\dagger}_{\boldsymbol{k}\sigma} |\mathrm{Vac}\rangle$$

Compute the ground-state energy by the perturbation theory：

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \cdots$$

$$E_0^{(0)} = \langle \Phi_0 \mid \hat{H}_0 \mid \Phi_0 \rangle \qquad E_0^{(1)} = \langle \Phi_0 \mid \hat{H}' \mid \Phi_0 \rangle$$

$$E_0^{(2)} = \sum_{n>0} \frac{\mid \langle \Phi_0 \mid \hat{H}' \mid \Phi_n \rangle \mid^2}{E_0^{(0)} - E_n^{(0)}} \qquad \ldots\ldots$$

The zero-th order term of the ground-state energy

$$\hat{H} = \sum_{\boldsymbol{k},\sigma} \frac{k^2}{2\mathrm{m}} \hat{c}^\dagger_{\boldsymbol{k}\sigma} \hat{c}_{\boldsymbol{k}\sigma} + \frac{1}{2} \sum_{\boldsymbol{k}} \frac{4\pi}{k^2} \left(\hat{\rho}^\dagger_{\boldsymbol{k}} \hat{\rho}_{\boldsymbol{k}} - \hat{N} \right) = \hat{H}_0 + \hat{H}'$$

$$\hat{H}_0 \left| \Phi_0 \right\rangle = \mathrm{E}_0^{(0)} \left| \Phi_0 \right\rangle, \qquad |\Phi_0\rangle = \prod_{\mathrm{k} \le k_F, \sigma} \hat{\mathrm{c}}^\dagger_{\boldsymbol{k}\sigma} |\mathrm{Vac}\rangle$$

$$E_0^{(0)} = \langle \Phi_0 \mid \hat{H}_0 \mid \Phi_0 \rangle = \sum_{\boldsymbol{k}\sigma} \frac{k^2}{2\mathrm{m}} \langle \Phi_0 \mid \hat{c}^\dagger_{\boldsymbol{k}\sigma} \hat{c}_{\boldsymbol{k}\sigma} \mid \Phi_0 \rangle$$

$$= 2 \sum_{k \le k_F} \frac{k^2}{2\mathrm{m}} = 2 \frac{V}{8\pi^3} \int_0^{k_F} d^3 k \, \frac{k^2}{2\mathrm{m}}$$

$$= \frac{V}{2\mathrm{m}\pi^2} \int_0^{k_F} k^4 \, dk = V \frac{k_F^5}{10\mathrm{m}\pi^2} = Vn \frac{3}{5} \epsilon_\mathrm{F} = N \frac{3}{5} \epsilon_\mathrm{F}$$

Kinetic energy per electron: $E_0^{(0)}/N = \frac{3}{5} \epsilon_\mathrm{F}$

On the density of HES

For HES with density *n,* it is convenient to introduce an dimensionless average inter-electronic distance: $\boldsymbol{r_s}$.

$$\frac{4\pi}{3} r_s^3 a_0^3 = \frac{1}{n}$$

a_0: Bohr radius

$r_s < 1$: high density electron gas

$$k_F = (3\pi^2 n)^{1/3} = \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s a_0}$$

$$E_0^{(0)}/N = \frac{3}{5}\frac{k_F^2}{2\mathrm{m}} = \frac{2.21}{r_s^2}[Ryd]$$

Rydberg atomic unit:

$$\hbar = 2\mathrm{m} = a_0 = 1$$

1 Ryd = 13.6 eV = 0.5 Hartree

The first-order term: the exchange energy

$$\widehat{H}' = \frac{1}{2}\sum_{\boldsymbol{k}} \frac{4\pi}{k^2}\left(\hat{\rho}_{\mathbf{k}}^{\dagger}\hat{\rho}_{\mathbf{k}} - \widehat{N}\right) = \frac{1}{2}\sum_{\boldsymbol{k}} \frac{4\pi}{k^2} \sum_{\boldsymbol{q},\boldsymbol{q}',\sigma,\sigma'} c_{\boldsymbol{q}+\mathbf{k}\sigma}^{\dagger}\, c_{\boldsymbol{q}'-\boldsymbol{k}\sigma'}^{\dagger} c_{\boldsymbol{q}'\sigma'} c_{\boldsymbol{q}\sigma}$$

$$E_0^{(1)} = \langle \Phi_0 \mid \widehat{H}' \mid \Phi_0 \rangle = \frac{1}{2}\sum_{\mathbf{k}} \frac{4\pi}{k^2} \sum_{\mathbf{q},\mathbf{q}',\sigma,\sigma'} \langle \Phi_0 \mid c_{\mathbf{q}+\mathbf{k}\sigma}^{\dagger} c_{\mathbf{q}'-\mathbf{k}\sigma'}^{\dagger} c_{\mathbf{q}'\sigma'} c_{\mathbf{q}\sigma} \mid \Phi_0 \rangle$$

$$= -\frac{1}{2}\sum_{\boldsymbol{k}} \frac{4\pi}{k^2} \sum_{\boldsymbol{q},\sigma} \langle c_{\mathbf{q}+\mathbf{k}\sigma}^{\dagger} c_{\mathbf{q}+\mathbf{k}\sigma} \rangle_0 \, \langle c_{\mathbf{q}\sigma}^{\dagger} c_{\mathbf{q}\sigma} \rangle_0$$

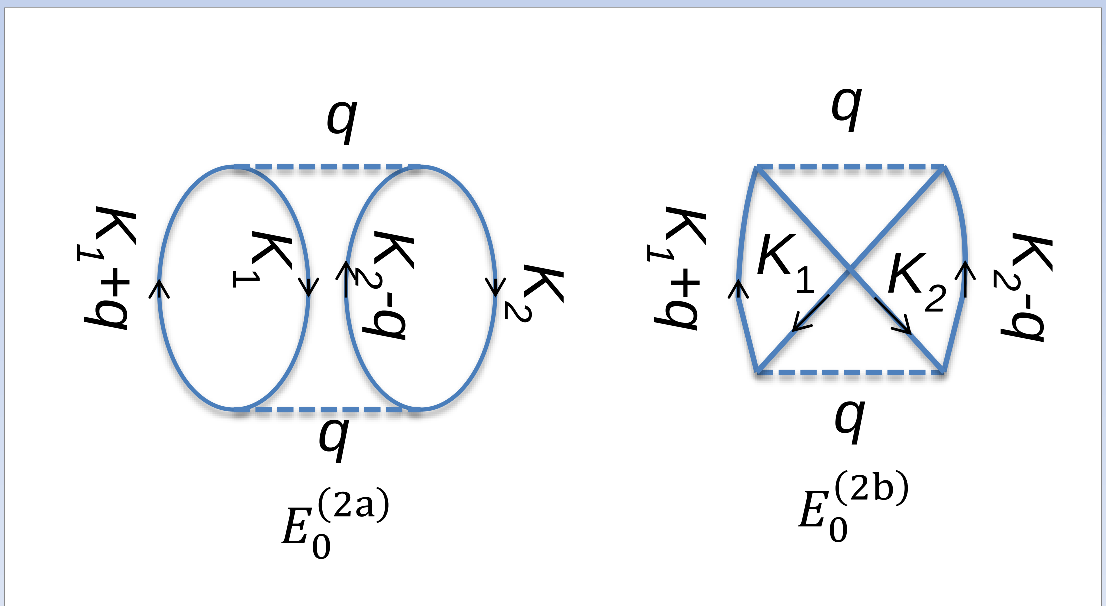
$$= -\sum_{\mathbf{k}} \frac{4\pi}{k^2} \sum_{\boldsymbol{q}} \theta\left(k_F - \mid \mathbf{k} + \mathbf{q} \mid\right)\theta(k_F - q) = -N\left(\frac{3}{4\pi}\right) k_F$$

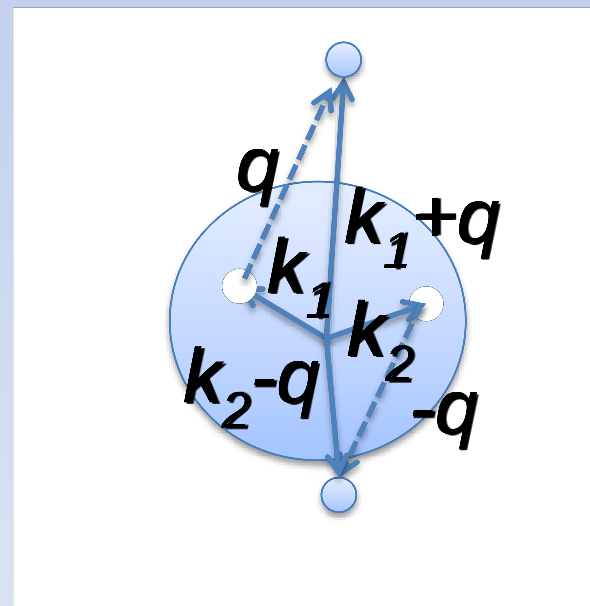
The Hartree-Fock ground-state energy of HES:

$$E_{\mathrm{HF}}/N = \left(E_0^{(0)} + E_0^{(1)}\right)/N = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} [Ryd]$$

The correlation energy: the second-order perturbation term

$$E_0^{(2)} = \sum_{n>0} \frac{|\langle \Phi_0 \mid \hat{H}' \mid \Phi_n \rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \sum_{\boldsymbol{k_1},\boldsymbol{k_2},\boldsymbol{q}} \frac{\langle \Phi_0 \mid \hat{H}' \mid \Phi_{\boldsymbol{k_1},\boldsymbol{k_2}}^{\boldsymbol{k_1+q},\boldsymbol{k_2-q}} \rangle \langle \Phi_{\boldsymbol{k_1},\boldsymbol{k_2}}^{\boldsymbol{k_1+q},\boldsymbol{k_2-q}} \mid \hat{H}' \mid \Phi_0 \rangle}{\epsilon_{\boldsymbol{k_1}} + \epsilon_{\boldsymbol{k_2}} - \epsilon_{\boldsymbol{k_1+q}} - \epsilon_{\boldsymbol{k_2-q}}}$$





The computation of the second-order perturbation term

The 2nd-order Coulomb term：

$$\frac{E_0^{(2a)}}{N}=-\frac{3}{8\pi^5}\int\frac{d^3q}{q^4}\int_{|\boldsymbol{k_1}+\boldsymbol{q}|>1}d^3k_1\int_{|\boldsymbol{k_2}-\boldsymbol{q}|>1}d^3k_2\frac{\theta(1-k_1)\theta(1-k_2)}{q^2+\boldsymbol{q}\cdot(\boldsymbol{k_1}-\boldsymbol{k_2})}$$

Divergence！

The 2nd-order exchange term：

$$\frac{E_0^{(2b)}}{N}=\frac{3}{16\pi^5}\int\frac{d^3q}{q^2}\int_{|\boldsymbol{k_1}+\boldsymbol{q}|>1}d^3k_1\int_{|\boldsymbol{k_2}-\boldsymbol{q}|>1}d^3k_2\frac{\theta(1-k_1)\theta(1-k_2)}{|\,\boldsymbol{q}+\boldsymbol{k_1}-\boldsymbol{k_2}\,|^2\left(q^2+\boldsymbol{q}\cdot(\boldsymbol{k_1}-\boldsymbol{k_2})\right)}$$

$$=0.046\ [Ryd]$$

The random-phase approximation (RPA)

- In an interacting many-electron system, the long-range Coulomb force between electrons gets screened. The electrons together with their screening cloud become quasiparticles, which interact via short-range forces.
(Bohm & Pines, 1953; Hubbard, 1957).

- Adding up the most divergent terms to infinite order, one obtains a finite value (Gell-Mann & Brueckner, 1957)

$$E_0^{\mathrm{c,RPA}} = 0.062\ln(r_s) - 0.142 + \cdots \quad \text{for } r_s \ll 1$$

Ground-state energy of 3D HES:

$$E_0(r_s) = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} - 0.096 + 0.062\ln(r_s) + \cdots [Ryd]$$

Reference book

- 1. Gerald D. Mahan, Many-particle Physics, Chapter 5
- 2. A. L. Fetter & J. D. Wallecka,
- "Quantum Theory of Many-Particle Systems", Chapter 1
- 3. N. W. Aschcroft & N. D. Mermin,
  "Solid State Physics", Chapter 2
- 4. P. W. Anderson, "Concepts in Solids", Chapter 2
- 5. 李正中，《固体理论》第四章

Homework II

Please show the second-order direct term of the ground-state energy of the 3-dimensional HES is diverging, while the second-order exchange term not. Please discuss what happens for 2-dimensional HES.