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

任新国 (Xinguo Ren)

中国科学技术大学
量子信息重点实验室
Key Laboratory of Quantum Information, USTC

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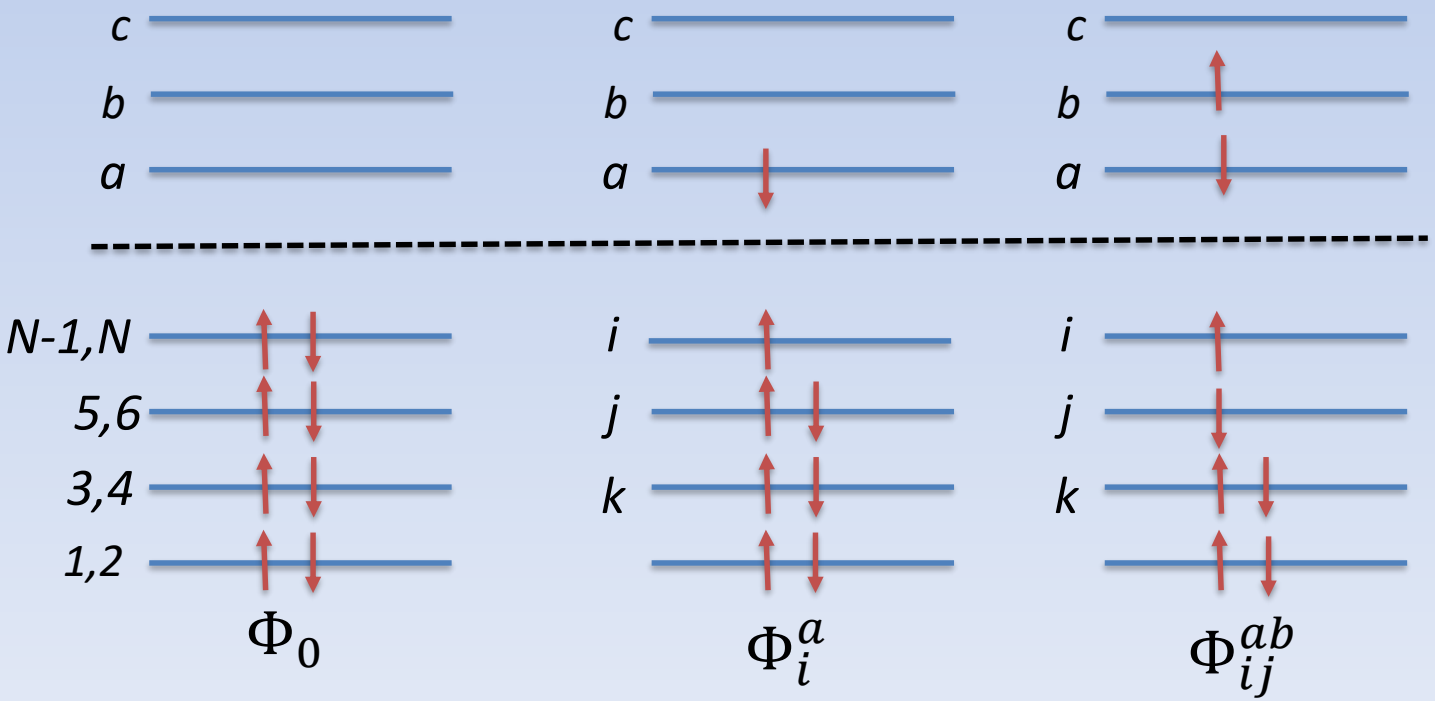
Second quantization of quantum mechanics

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

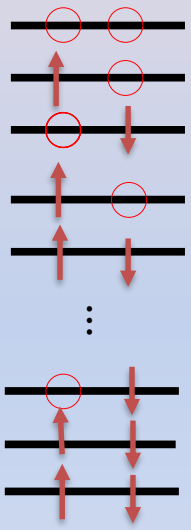
$$\Phi_0 = \frac{1}{\sqrt{N!}}\det[\varphi_1, \varphi_2, \cdots, \varphi_{N-1}, \varphi_N]$$

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

…… All possible Slater determinants form a many-particle basis set.



Occupation representation



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

Under the occupation representation:

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

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

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

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

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

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.

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

$$|Vac\rangle = |0\rangle_1|0\rangle_2|0\rangle_3\cdots = \prod_j|0\rangle_j$$

All single-particle states: $c_j^+|Vac\rangle = |0\rangle_1|0\rangle_2\cdots|1\rangle_j\cdots,\ j = 1,2,\cdots,M$

All two-particle states: $c_i^+c_j^+|Vac\rangle = |0\rangle_1|0\rangle_2\cdots|1\rangle_j\cdots|1\rangle_i\cdots,\ \mathrm{i} < j = 1,2,\cdots,M$

N-particle states: $\prod_j^N c_j^+|Vac\rangle$ (Creating N particles out of M states.)

The Hilbert space formed by all these states with different particle numbers are called Fock space. The essence of second quantization is to express, within the Fock space, the many body Hamiltonian in terms of creation and annihilation operators.

Second-quantized form of the Coulomb interaction

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

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

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

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

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

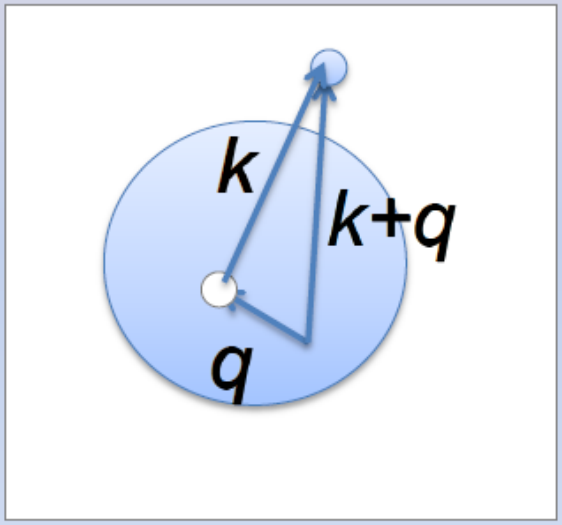
The Hamiltonian of interacting HES

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

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

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

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



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

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

The ground-state energy of interacting HES

$$\hat{H} = \sum_{\boldsymbol{k},\sigma} \frac{k^2}{2\mathrm{m}} \hat{c}^{\dagger}_{\boldsymbol{k}\sigma} \hat{c}_{\boldsymbol{k}\sigma} + \frac{1}{2} \sum_{\boldsymbol{k}\neq 0} \frac{4\pi}{k^2} \left(\hat{\rho}^{\dagger}_{\boldsymbol{k}} \hat{\rho}_{\boldsymbol{k}} - \hat{N} \right) = \hat{H}_0 + \hat{H}'$$

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

Compute the ground-state energy by the perturbation theory:

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

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

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

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

$$\hat{H} = \sum_{\boldsymbol{k},\sigma} \frac{k^2}{2\mathrm{m}} \hat{c}^{\dagger}_{\boldsymbol{k}\sigma} \hat{c}_{\boldsymbol{k}\sigma} + \frac{1}{2} \sum_{\boldsymbol{k}\neq 0} \frac{4\pi}{k^2} \left(\hat{\rho}^{\dagger}_{\boldsymbol{k}} \hat{\rho}_{\boldsymbol{k}} - \hat{N} \right) = \hat{H}_0 + \hat{H}'$$

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

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

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

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

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

$$\hat{H}' = \frac{1}{2}\sum_{\boldsymbol{k}\neq 0}\frac{4\pi}{k^2}\left(\hat{\rho}_{\mathbf{k}}^{\dagger}\hat{\rho}_{\mathbf{k}} - \hat{N}\right) = \frac{1}{2}\sum_{\boldsymbol{k}\neq 0}\frac{4\pi}{k^2}\sum_{\boldsymbol{q},\boldsymbol{q}',\sigma,\sigma'} c_{\boldsymbol{q}+\mathbf{k}\sigma}^{\dagger}\, c_{\boldsymbol{q}'-\boldsymbol{k}\sigma'}^{\dagger} c_{\boldsymbol{q}'\sigma'} c_{\boldsymbol{q}\sigma}$$

$$E_0^{(1)} = \langle \Phi_0 \mid \hat{H}' \mid \Phi_0 \rangle = \frac{1}{2}\sum_{\mathbf{k}\neq 0}\frac{4\pi}{k^2}\sum_{\mathbf{q},\mathbf{q}',\sigma,\sigma'} \langle \Phi_0 \mid c_{\mathbf{q}+\mathbf{k}\sigma}^{\dagger} c_{\mathbf{q}'-\mathbf{k}\sigma'}^{\dagger} c_{\mathbf{q}'\sigma'} c_{\mathbf{q}\sigma} \mid \Phi_0 \rangle$$

$$= -\frac{1}{2}\sum_{\boldsymbol{k}\neq 0}\frac{4\pi}{k^2}\sum_{\boldsymbol{q},\sigma} \langle c_{\mathbf{q}+\mathbf{k}\sigma}^{\dagger} c_{\mathbf{q}+\mathbf{k}\sigma}\rangle_0 \langle c_{\mathbf{q}\sigma}^{\dagger} c_{\mathbf{q}\sigma}\rangle_0$$

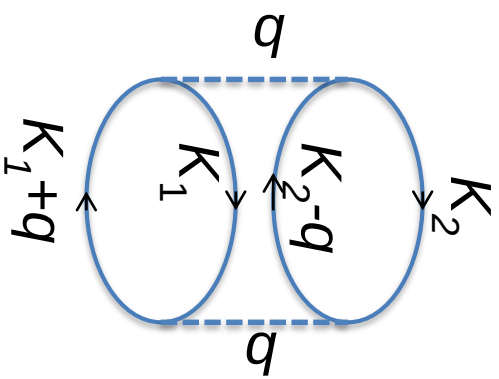
$$= -\sum_{\mathbf{k}\neq 0}\frac{4\pi}{k^2}\sum_{\boldsymbol{q}} \theta\left(k_F - \mid \mathbf{k}+\mathbf{q} \mid\right)\theta(k_F - q) = -N\left(\frac{3}{4\pi}\right)k_F$$

The Hartree-Fock ground-state energy of HES:

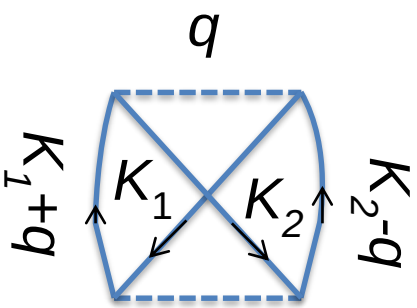
$$E_{\mathrm{HF}}/N = \left(E_0^{(0)} + E_0^{(1)}\right)/N = \frac{2.21}{r_s^2} - \frac{0.916}{r_s}[Ryd]$$

The correlation energy: the second-order perturbation term

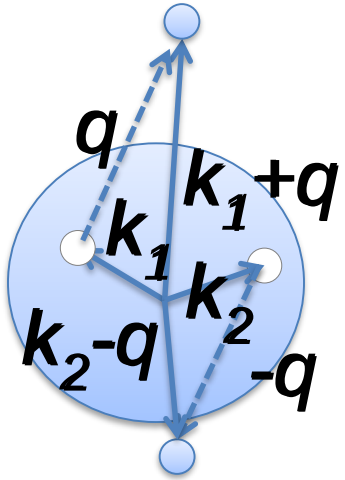
$$E_0^{(2)} = \sum_{n>0} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_n \rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \sum_{k_1,k_2,q} \frac{\langle \Phi_0 | \hat{H}' | \Phi_{k_1,k_2}^{k_1+q,k_2-q} \rangle \langle \Phi_{k_1,k_2}^{k_1+q,k_2-q} | \hat{H}' | \Phi_0 \rangle}{\epsilon_{k_1} + \epsilon_{k_2} - \epsilon_{k_1+q}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



$E_0^{(2a)}$



$E_0^{(2b)}$



The computation of the second-order perturbation term

The 2nd-order Coulomb term:

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

Divergence!

The 2nd-order exchange term:

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

$= 0.046\ [Ryd]$

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