

Simulator of photoemission angular distribution for experiments (SPADExp)

1. Hartree-Fock-Slater equation

Hiroaki Tanaka (ISSP / Graduate School of Science, the Univ. of Tokyo)

April 27, 2022

Abstract

Plane waves for photoelectron wave functions are modified by atomic potentials. Here, we explain Hartree-Fock-Slater (HFS) equations to obtain self-consistent atomic potentials.

Contents

1	Atomic units	1
2	Exchange-correlation terms in free electron gas	1
3	HFS equation	3
4	Thomas-Fermi potential	4

1 Atomic units

The following arguments use **the atomic unit**, in which the following physical constants are omitted.

- **Electron mass** $m = 9.109 \times 10^{-31}$ kg
- **Bohr radius** $a_0 = 0.5292$ Å
- **Elementary charge** $e = 1.602 \times 10^{-19}$ C
- **Dirac constant** $\hbar = 1.054 \times 10^{-34}$ J · s

Values in the SI unit is from Ref. [1]. Therefore, the units of energy and wavevector become $E_h = 27.2114$ eV and $1/a_0 = 1.890$ Å⁻¹, respectively. Since Ref. [2] uses Ryberg ($E_h/2$) as the unit, coefficients may be different twice.

2 Exchange-correlation terms in free electron gas

In the HFS equations, the exchange-correlation term is approximated by the local density approximation (LDA). Here we calculate the term in free electron gas with number density n .

In a three-dimensional space with large enough volume V , wavefunctions of free-electron gases $\psi_{\mathbf{k}}(\mathbf{r})$ and eigenenergies $E(\mathbf{k})$ become

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}, \quad E(\mathbf{k}) = \frac{1}{2} |\mathbf{k}|^2. \quad (1)$$

We represent the Fermi wavevector by k_F , and using that the number density coefficient in the reciprocal space is $1/(2\pi)^3$, we obtain the following relationship;

$$n = 2 \times \frac{4}{3} \pi k_F^3 \cdot \frac{1}{(2\pi)^3} = \frac{k_F^3}{3\pi^2}. \quad (2)$$

We solve the above equation w.r.t. k_F , and then get

$$k_F = (3\pi^2 n)^{1/3}. \quad (3)$$

We calculate the exchange-correlation term where $|\mathbf{k}| < k_F$ region is occupied by the Hartree-Fock approximation. Here we calculate the term for only one spin direction.

$$E_{xc} = -\frac{1}{2} \sum_{i,j} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_j(\mathbf{r}_1) \psi_i(\mathbf{r}_2) \quad (4)$$

$$= -\frac{1}{2V^2} \sum_{i,j} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{i(\mathbf{k}_j - \mathbf{k}_i) \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \quad (5)$$

using $\mathbf{r}_3 = \mathbf{r}_1 - \mathbf{r}_2$ as a new integral variable,

$$= -\frac{1}{2V} \sum_{i,j} \int d^3\mathbf{r}_3 \frac{1}{|\mathbf{r}_3|} e^{i(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}_3} \quad (6)$$

in the polar coordinate system with principal axis parallel to $\mathbf{k}_j - \mathbf{k}_i$,

$$= -\frac{1}{2V} \sum_{i,j} \int_0^\infty r_3^2 dr_3 \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi \frac{1}{r_3} e^{iKr_3 \cos \theta} \quad (K = |\mathbf{k}_j - \mathbf{k}_i|) \quad (7)$$

$$= -\sum_{i,j} \frac{\pi}{iKV} \int_0^\infty (e^{iKr_3} - e^{-iKr_3}) dr_3 \quad (8)$$

Adding a convergence factor $e^{-\eta r}$, finally we get

$$= -\sum_{i,j} \frac{2\pi}{K^2 V}. \quad (9)$$

Next, we calculate the sum w.r.t. \mathbf{k}_j with fixed \mathbf{k}_i ,

$$E_{xc} = -\frac{2\pi}{V} \sum_i \int_{|\mathbf{k}_j| < k_F} d^3\mathbf{k}_j \frac{1}{K^2} \cdot \frac{V}{(2\pi)^3} \quad (10)$$

in polar coordinate system with principal axis parallel to \mathbf{k}_i ,

$$= -\frac{1}{4\pi^2} \sum_i \int_0^{k_F} k_j^2 dk_j \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi \frac{1}{k_i^2 + k_j^2 - 2k_i k_j \cos \theta} \quad (k_i = |\mathbf{k}_i|, k_j = |\mathbf{k}_j|) \quad (11)$$

$$= -\frac{1}{2\pi} \sum_i \frac{1}{k_i} \int_0^{k_F} dk_j k_j (\log |k_i + k_j| - \log |k_i - k_j|) \quad (12)$$

Using

$$\int_0^b x \log |x + a| dx = \left[\frac{1}{2} x^2 \log |x + a| - \frac{1}{4} x^2 + \frac{a}{2} x - \frac{a^2}{2} \log |x + a| \right]_0^b \quad (13)$$

$$= \frac{b^2 - a^2}{2} \log |b + a| - \frac{1}{4} b^2 + \frac{ab}{2} + \frac{a^2}{2} \log |a|, \quad (14)$$

we get

$$E_{xc} = -\frac{1}{2\pi} \sum_i \frac{1}{k_i} \left[\frac{k_F^2 - k_i^2}{1} (\log |k_F + k_i| - \log |k_F - k_i|) + k_F k_i \right] \quad (15)$$

$$= -\frac{k_F}{2\pi} \sum_i \left(1 + \frac{k_F^2 - k_i^2}{2k_F k_i} \log \left| \frac{k_i + k_F}{k_i - k_F} \right| \right). \quad (16)$$

At last we take the summation w.r.t \mathbf{k}_i ,

$$E_{xc} = -2k_F \int_0^{k_F} k_i^2 dk_i \left(1 + \frac{k_F^2 - k_i^2}{2k_F k_i} \log \left| \frac{k_i + k_F}{k_i - k_F} \right| \right) \cdot \frac{V}{(2\pi)^3} \quad (17)$$

$$= -\frac{k_F^4 V}{12\pi^3} + \frac{V}{8\pi^3} \int_0^{k_F} dk_i k_i (k_i^2 - k_F^2) (\log |k_i + k_F| - \log |k_i - k_F|) \quad (18)$$

Using

$$\int_0^b x(x^2 - a^2) \log |x + a| dx = \left[\left(\frac{1}{4}x^4 - \frac{a^2}{2}x^2 \right) \log |x + a| - \frac{1}{16}x^4 + \frac{a}{12}x^3 + \frac{a^2}{8}x^2 - \frac{a^3}{4}x + \frac{a^4}{4} \log |x + a| \right]_0^b \quad (19)$$

$$= \frac{(b^2 - a^2)^2}{4} \log |b + a| + \frac{1}{48}(-3b^4 + 4ab^3 + 6a^2b^2 - 12a^3b) - \frac{a^4}{4} \log |a|, \quad (20)$$

we get

$$E_{xc} = -\frac{k_F^4 V}{12\pi^3} - \frac{k_F^4 V}{24\pi^3} = -\frac{k_F^4 V}{8\pi^3}. \quad (21)$$

Electron with the other spin has the same energy, so the exchange-correlation term per one electron becomes

$$e_{xc} = 2E_{xc} \times \frac{1}{nV} = -\frac{3k_F}{4\pi}. \quad (22)$$

The exchange-correlation potential becomes twice because the energy is half to avoid double counting. Therefore, the exchange-correlation potential in the LDA approximation is

$$V_{xc} = 2e_{xc} = -3 \left(\frac{3n}{8\pi} \right)^{1/3}. \quad (23)$$

3 HFS equation

The HFS equation is obtained by averaging the Hartree-Fock equation along the angle direction. Since the potential becomes spherically isotropic, the wavefunctions can be separated by radial functions and spherical harmonics;

$$\psi(\mathbf{r}) = \frac{P_{nl}(r)}{r} Y_{lm}(\theta, \varphi). \quad (24)$$

Here, the HFS equation of $P_{nl}(r)$ becomes

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) \right] P_{nl}(r) = E_{nl} P_{nl}(r). \quad (25)$$

The potential $V(r)$ is the sum of nucleus potential, Hartree term, and Fock term;

$$V(r) = -\frac{Z}{r} + \frac{1}{r} \int_0^r \sigma(r') dr' + \int_r^\infty \frac{\sigma(r')}{r'} dr' - 3 \left(\frac{3\rho(r)}{8\pi} \right)^{1/3} \quad (26)$$

$$\sigma(r) = \sum_{nl} w_{nl} (P_{nl}(r))^2 \quad (27)$$

$$\rho(r) = \frac{\sigma(r)}{4\pi r^2}, \quad (28)$$

where w_{nl} is the occupation number of each orbital, Z is the atomic number. There are given as input paramters. $\sigma(r)$ is the number density integrated along the angle direction, and $\rho(r)$ is the number density per unit volume. When the atomic potential $V(r)$ becomes self-consistent, that potential is the solution.

4 Thomas-Fermi potential

When we try to obtain self-consistent potential in the HFS equation, the initial potential is given by the Thomas-Fermi potential. We put the atomic nucleus with charge Z at the coordinate origin, and consider Z electrons around it. We represent the potential and electron density by $V(r)$ and $\rho(r)$, respectively. Also, we suppose the relationship electron gases $\rho(r) = k_F(r)^3/3\pi^2$ similar to electron gases.

The Fermi level, determined by the potential and Fermi wavevector, should be isotropically uniform, so the relationship

$$E_F = \frac{1}{2}k_F(r)^2 + V(r) = \text{const.} = 0 \quad (29)$$

hold. We represent k_F as a function of $\rho(r)$, and using $V(r) = -\phi(r)$ where $\phi(r)$ is the electric field, then we get

$$E_F = \frac{1}{2}(3\pi^2\rho(r))^{2/3} - \phi(r). \quad (30)$$

Combining it with the Poisson equation of the electric field

$$\Delta\phi(r) = 4\pi\rho(r) \quad (\rho(r) \text{ は電子の個数密度であることに注意}), \quad (31)$$

then we get

$$\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} (\phi(r) + E_F) = \frac{4}{3\pi} (2(\phi(r) + E_F))^{3/2}. \quad (32)$$

We define a function $f(r)$ by

$$f(r) = \frac{r}{Z}(\phi(r) + E_F). \quad (33)$$

In the limit $r \rightarrow 0$, $\phi(r) \rightarrow Z/r$ should be dominant, so $f(r) \rightarrow 1$. On the other hand, in the limit $r \rightarrow \infty$ electron density and the potential becomes zero so $f(r) \rightarrow 0$. Using $f(r)$, we get

$$\frac{1}{r} \frac{d^2}{dr^2} f(r) = \frac{4}{3\pi} r^{-3/2} Z^{1/2} (2f(r))^{3/2} \quad (34)$$

$$\iff \frac{d^2}{dr^2} f(r) = \frac{2^{7/2} Z^{1/2}}{3\pi} \frac{1}{r^{1/2}} f(r)^{3/2}. \quad (35)$$

To obtain simple coefficients by the scaling $r = \mu x$, using $g(x) = f(r) = f(\mu x)$ we get

$$\frac{1}{\mu^2} \frac{d^2}{dx^2} g(x) = \frac{2^{7/2} Z^{1/2}}{3\pi} \frac{1}{(\mu x)^{1/2}} g(x)^{3/2} \quad (36)$$

$$\frac{d^2}{dx^2} g(x) = \frac{2^{7/2} Z^{1/2}}{3\pi} \frac{\mu^{3/2}}{x^{1/2}} g(x)^{3/2} \quad \therefore \mu = \left(\frac{3\pi}{2^{7/2} Z^{1/2}} \right)^{2/3} = \frac{1}{2Z^{1/3}} \left(\frac{3\pi}{4} \right)^{2/3}. \quad (37)$$

Using this scaling, the equation to solve becomes

$$\frac{d^2}{dx^2} g(x) = \frac{g(x)^{3/2}}{\sqrt{x}}, \quad (38)$$

and the Thomas-Fermi potential is obtained by the following equation;

$$V(r) = -\frac{Z}{r} g(r/\mu), \quad V(\mu x) = -\frac{Z}{\mu x} g(x). \quad (39)$$

References

- [1] <https://physics.nist.gov/cuu/Constants/index.html>
- [2] Herman and Skillman “Atomic Structure Calculations”, 1963.