Homework 4

November 1, 2019

1 The Exchange Energy of a Uniform Electron Gas

The exchange energy term (自旋轨道, r 包括自旋) is that:

$$E_{\text{exc}} = -\frac{1}{2}\sum_i \sum_j \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r'} \frac{\phi_i^*(\boldsymbol{r})\phi_j^*(\boldsymbol{r'})\phi_i(\boldsymbol{r'})\phi_j(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r'}|} \tag{1.1}$$

If we take the interaction term as pertubation to the original system, so the base wave function of the system is plane wave:

$$\phi(\boldsymbol{r}) = \frac{1}{\sqrt{V}}\exp(i\boldsymbol{k}\boldsymbol{r}) \tag{1.2}$$

The exchange term can be write as (相同自旋才有交换作用, 对自旋求和相当于乘 2, 利用库伦势场– 汤川势的傅里叶变换, 下面开始 r 不包括自旋):

$$\begin{aligned} E_{\text{exc}} &= -\frac{1}{2V^2}\sum_\sigma \sum_{\boldsymbol{k}} \sum_{\boldsymbol{k'}} \int \mathrm{d}\boldsymbol{r}\, e^{i(\boldsymbol{k'}-\boldsymbol{k})\boldsymbol{r}} \int \mathrm{d}\boldsymbol{r'} \frac{e^{i(\boldsymbol{k}-\boldsymbol{k'})\boldsymbol{r'}}}{|\boldsymbol{r}-\boldsymbol{r'}|} \\ &= -\frac{1}{V^2}\sum_{\boldsymbol{k}} \sum_{\boldsymbol{k'}} \int \mathrm{d}\boldsymbol{r}\, 4\pi e^{i(\boldsymbol{k'}-\boldsymbol{k})\boldsymbol{r}} \frac{e^{i(\boldsymbol{k}-\boldsymbol{k'})\boldsymbol{r}}}{|\boldsymbol{k}-\boldsymbol{k'}|^2} \\ &= -\frac{4\pi}{V}\sum_{\boldsymbol{k}} \sum_{\boldsymbol{k'}} \frac{1}{|\boldsymbol{k}-\boldsymbol{k'}|^2} \end{aligned} \tag{1.3}$$

Under quasicontinuous approximation, we have that:

$$\sum_{\boldsymbol{k}} \to \frac{V}{(2\pi)^3}\int_0^{k_f} k^2 \mathrm{d}k \int_0^{\pi} \mathrm{d}\theta \sin\theta \int_0^{2\pi} \mathrm{d}\varphi \tag{1.4}$$

Therefore,

$$E_{\text{exc}} = -\frac{1}{\pi}\sum_{\boldsymbol{k}} \int_0^{k_f} k'^2 \mathrm{d}k' \int_0^{\pi} \mathrm{d}\theta \frac{\sin\theta}{k^2+k'^2+2kk'\cos\theta} \tag{1.5}$$

Take $k_f = (3\pi^2\rho)^{1/3}$, then we can get E_{exc}/N. I just take the result from wiki:

$$\frac{E_{\text{exc}}}{N} = -\frac{0.916}{\left(\frac{3}{4\pi n}\right)^{1/3}} \tag{1.6}$$

2 Correlated Quantum Chemistry Methods

End-to-end Symmetry Preserving Inter-atomic Potential Energy Model for Finite and Extended Systems.
The authors proposed a well-developed compuatational technique – DeePMD-kit. Deep Potential is to employ deep learning techniques and realize an inter-atomic potential energy model that is general and accurate. The key component is to apply symmetry-invariant properties of a potential energy model by assigning a local reference frame and a local environment to each atom.
They do the following experiment:

1. The DeepPotential Model for the small molecular system.
2. The DeepPotential Model for MoS2 and Pt system.
3. The DeepPotential Model for Co, Cr, Fe, Mn, Ni, HEA system.
4. The DeepPotential Model for the TiO2 system, which contains 3 different polymorphs.

This paper is quite interesting, because it combines symmetry in many body quantum systems and machine learning. Because I am not an expert in machine learning, I cannot express the calculation in detail. If you are interested in this paper, just download and run the code.

$$R_{ij} = \sum_{m,n} \langle m, n | \sigma_i m, \sigma_j, n \rangle$$