

Density Functional Theory

Principle and Applications

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前言

DFT is widely used in physics, to calculate the band structure of many body system. However, few people truly know how it works. This note summaries opinions on Wei's group meeting.

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第一章 Density Functional Theory

There are two very important theorems in DFT, proposed by Hohenberg and Kohn in 1964.[1] However, very few people know the value of these two theorems. Actually, they even do not understand them correctly.

1.1 HK Theorem 1: The Density as Basic Variable

Given an external potential $v(r)$, we can obtain all information of the system by solving many-body Schrodinger equation.¹ Especially, we can get the ground state Ψ and also the corresponding electron density

$$n(r) \equiv (\Psi, \psi^\dagger \psi \Psi),$$

where the ψ is field operator. We can believe that $n(r)$ (ground state electron density) can be uniquely determined by $v(r)$, so $n(r)$ is a functional of $v(r)$.

How is the inversion? HK shows that $v(r)$ can be also a unique functional of $n(r)$, apart from a trivial additive constant.

¹Here, I even do not understand the meaning of many-body Schrodinger equation.

Before proving it, let me say it clearly. Normally we come from a external potential to get electron density. Is it superising that different potentials can only lead to different electron density? Maybe you would say, different potentials must lead to different ground state wave function, thus the ground state electron density. However, you should notice that, the information in $n(r)$ is highly reduced compared with many body wave function Ψ . One obvious evidence is that Ψ is a function of all particle's coordinates, but $n(r)$ only contains 3 spacial degrees of freedom. How can you prove that two different GSWFs must lead to different GS electron density?

This theorem just tell you the answer to the question above. $n(r)$ is decided by a unique $v(r)$. Any $v'(r)$ that nontrivially differs from $v(r)$ will not lead to $n(r)$. Once you know one $n(r)$ is the electron density of some physical system, you can determine the external potential $v(r)$ of the system uniquely!

However, you must treat this theorem carefully. You can not arbitrarily construct a $n(r)$, and say, there must be a unique $v(r)$ corresponding to it. No, it is wrong! Hk theorem only tells you that, only the $n(r)$ from real physical system uniquely corresponds to a $v(r)$. No one has proved that an arbitrary function $n(r)$ is permitted by real world. Thus, we can imagine a set, which contains all possible $n(r)$ that comes from real system. Imagine another set, contains the external potentials of these systems. HK 1 tells you that there is a one-to-one map between these two set. We give these permitted $n(r)$ a name — v -representable $n(r)$.

Now, $v(r)$ is a functional of $n(r)$. $v(r)$ determine the whole system, so the many-body WF is also the functional of $n(r)$. Everything is functional of $n(r)$! We can also conclude that, the information in many-body WF is highly redundant. We only need $n(r)$ to sketch everything.

Next, I will give a proof of HK theorem 1. The proof proceeds by reduction to absurdity.....(See [1]) There is another assumption: the ground state is non-degenerate.

1.2 HK Theorem 2: The Variational Principle

To illustrate this theorem, it is convenient to define some new functionals first. Since Ψ is a functional of $n(r)$, T and U are both universal operator independent of $v(r)$, we can define a functional

$$F[n(r)] \equiv (\Psi, (T + U)\Psi).$$

This functional does not depend explicitly on $v(r)$. In other word, even though some $n'(r)$ is NOT the correct GS electron density of the system defined by $v(r)$, we can put it into F to calculate.

$F[n(r)]$ is a universal functional, valid for any number of particles and any external potential.

Now, for a given system with $v(r)$, we can define another functional, named energy functional

$$E_v[n(r)] \equiv \int v(r)n(r)dr + F[n].$$

This energy functional depend explicitly on $v(r)$. You can put any $v(r)$ and any $n(r)$ (of course v -representable) here. However, it is obvious that only when you put the correct $n(r)$ that corresponds to $v(r)$, the $E_v[n(r)]$ represents the ground state energy of the system $v(r)$.

Now, if we fix the external potential and the particle number, HK theorem 2 tells us that, $E_v[n(r)]$ assumes its minimum value if and only if we put in the correct $n(r)$.

First, let me emphasize that HK2 is based on HK1. Without HK1, you can even not define $F[n]$ and $E_v[n]$. Second, if we temporarily forget about GSWF, and only care about $v(r)$ and $n(r)$ as its solution, HK2 says that the energy will increase if the solution is not the right one.

Let's try to prove HK2. Suppose we have another $n'(r)$, we want to show that

$$E_v[n'(r)] > E_v[n(r)].$$

According to HK1, since $n'(r)$ is also v -representable, there exists a unique $v'(r)$ corresponding to it. The system with $v'(r)$ will have a GSWF Ψ' different from Ψ . Since $v(r)$ system is non-degenerate, quantum variational theory tells us

$$\epsilon_v(\Psi') > \epsilon_v(\Psi),$$

where ϵ_v is the energy of different WF. By definition, both $\epsilon_v[\Psi]$ and $E_v[n(r)]$ are the GS energy of the $v(r)$ system, so they must equal. The question is whether

$$(\Psi', (T + U + V)\Psi') \equiv \epsilon_v(\Psi') = E_v[n'(r)] \equiv \int v(r)n'(r)dr + F[n'(r)]$$

exists.^{2 3}

²这里我想先停顿一下。这里的关键在于理解这样一件事：把 A 系统的波函数放入 B 系统中，和把 A 系统的电子密度放入 B 系统中是否具有相同的含义。如果是放入 A 系统中，由于波函数和电子密度是一一对应的（HK1 可以保证），是一样的。但是，现在放进去的是 B 系统，在 B 系统中，这两个物理量并不能保证一定是关联的。

³当我再次回顾 HK1 的证明时，发现其可以在 A 系统计算 V_B 的均值。那么，这里的问题也很好理解了。我们换个角度，即不在 B 系统中考虑问题，而单独在 A 系统考虑问题。对于一个波函数为 Ψ' ，电子密度为 $n'(r)$ 的 A 系统，我们大可以计算一个形式为 $v(r)$ 的观测量，这个观测量可以和外势能 $v'(r)$ 毫无关系，但是我们仍然可以计算它。显然，在 A 系统中， Ψ' 和 $n'(r)$ 都有明确的意义——表示基态。那么不管以哪种方式计算可观测量结果都是相同的。

HK2 provide a possible way to calculate the GS electron density without solving a many-body Schrodinger equation. it requires merely the minimization of a functional of the three-dimensional density function. However, there are two difficulties.

- (1) Conceptual difficulty. The minimization must be taken among all the v -representable $n(r)$. However, we do not have such a set before we solve the many-bady system. We do not even know whether $n(r)$ set is continuous or not.
- (2) Technical difficulty. We do not know the form of $F[n]$. We can guess, we can do pertubation, we can refine the form again and again until it works!

第二章 Energy Band

2.1 Bloch Theorem

When the external potential has periodicity, the solution to the Schrodinger equation has the following property,

$$\psi(\mathbf{r} + \mathbf{R}_n) = e^{i\mathbf{k} \cdot \mathbf{R}_n} \psi(\mathbf{r}).^1 \quad (2.1)$$

Equivalently, we can write the wave function as

$$\psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{R}_n} u(\mathbf{r}),$$

where $u(\mathbf{r})$ is a periodic function, $u(\mathbf{r} + \mathbf{R}_n) = u(\mathbf{r})$.

Proof of the Bloch Theorem

Define translation operations T_α as

$$T_\alpha f(\mathbf{r}) = f(\mathbf{r} + \mathbf{a}_\alpha), \alpha = 1, 2, 3,$$

where $f(\mathbf{r})^2$ is any given function, and \mathbf{a}_α is the primitive translation vectors of the lattice. It can be easily shown that T_1, T_2 and T_3 commute with each other. Any translation vectors $\mathbf{R}_m = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3$ can be seen as the effect of $T_1^{m_1} T_2^{m_2} T_3^{m_3}$.

¹注意这里对 \mathbf{k} 还没有做出任何限制。

²在不引起歧义的情况下，矢量不用粗体了。

The Hamiltonian of a single electron in lattice is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r). \quad (2.2)$$

where $V(r)$ is a periodical function.

$$\begin{aligned} T_\alpha H f(r) &= \left[-\frac{\hbar^2}{2m}\nabla_{r+a_\alpha}^2 + V(r+a_\alpha) \right] f(r+a_\alpha) \\ &= \left[-\frac{\hbar^2}{2m}\nabla_r^2 + V(r) \right] f(r+a_\alpha) \\ &= H T_\alpha f(r). \end{aligned} \quad (2.3)$$

From 2.3 we can get the commutation relations

$$[H, T_\alpha] = 0. \quad (2.4)$$

Thus, we can select the common eigenstates of the four operators.

$$\begin{cases} H\psi &= E\psi, \\ T_1\psi &= \lambda_1\psi, \\ T_2\psi &= \lambda_2\psi, \\ T_3\psi &= \lambda_3\psi. \end{cases} \quad (2.5)$$

To determine the eigenvalues λ_α , we introduce a periodical boundary conditions

$$\psi(r) = \psi(r + N_\alpha a_\alpha). \quad (2.6)$$

$$\psi(r + N_\alpha a_\alpha) = T_\alpha^{N_\alpha} \psi(r) = \lambda_\alpha^{N_\alpha} \psi(r) \equiv \psi(r),$$

which gives $\lambda_\alpha = e^{2\pi i l_\alpha / N_\alpha}$, where l_α is integers. Introducing vector \mathbf{k} of the reciprocal lattice,

$$\mathbf{k} = \frac{l_1}{N_1} \mathbf{b}_1 + \frac{l_2}{N_2} \mathbf{b}_2 + \frac{l_3}{N_3} \mathbf{b}_3,$$

where b_j satisfy $a_i b_j = 2\pi \delta_{ij}$, then $\lambda_\alpha = e^{i\mathbf{k} \cdot \mathbf{a}_\alpha}$.

$$\begin{aligned} \psi(r + R_m) &= T_1^{m_1} T_2^{m_2} T_3^{m_3} \psi(r) = \lambda_1^{m_1} \lambda_2^{m_2} \lambda_3^{m_3} \psi(r) \\ &= e^{i\mathbf{k} \cdot (m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3)} \psi(r) = e^{i\mathbf{k} \cdot R_m} \psi(r). \end{aligned} \quad (2.7)$$

So far we have proved the Bloch theory and known the meaning of \mathbf{k} .³

2.2 Two cases

There are two cases that can be used to understand the energy band. The first one is free electron approximation, the other is tight binding approximation. You will see that the perturbation theory is of great importance in these two cases. It provides a nice way to understand the energy.

2.2.1 Free Electron Approximation

One dimensional case

Regard V_0 as the zero order approximation, and $V(x) - V_0$ as perturbation.

$$\psi_k^0(x) = \frac{1}{\sqrt{L}} e^{ikx},$$

with $E_k^0 = \frac{\hbar^2 k^2}{2m} + V_0$. k here is a wavevector of the electron, rather than the wavevector defined in the Bloch theorem. So k here can be chosen any real number. After introducing periodical boundary condition, $k = \frac{l}{N} \frac{2\pi}{a}$, where l can be any integer, NOT only in the first Brillouin zone.

The perturbation theory shows that, the first and second corrections are

$$E_k^{(1)} = \langle k | \Delta V | k \rangle, \quad (2.8)$$

$$E_k^{(2)} = \sum_{k' \neq k} \frac{|\langle k' | \Delta V | k \rangle|^2}{E_k^0 - E_{k'}^0}, \quad (2.9)$$

$$\psi_k^{(1)} = \sum_{k' \neq k} \frac{\langle k' | \Delta V | k \rangle}{E_k^0 - E_{k'}^0} \psi_{k'}^0. \quad (2.10)$$

³这里的 \mathbf{k} 称为简约波矢，它并不代表粒子的真正波矢。从欧拉函数的周期性可以看出， \mathbf{k} 只需要取第一布里渊区的点即可得到所有平移矢量的本征值。我们应该明白，同一个 \mathbf{k} 可能有很多简并态，它们对应不同的能量。

For one-dimensional free electron gas, it can be easily shown that

$$\langle k'|V(x)|k\rangle = \begin{cases} V_n, & \text{if } k' = k + 2\pi n/a; \\ 0, & \text{if otherwise.} \end{cases} \quad (2.11)$$

$V_n = \frac{1}{a} \int_0^a \exp(-i2\pi n\xi/a) V(\xi) d\xi$ is the n -th Fourier coefficient of $V(x)$.

$$\psi_k = \psi_k^0 + \psi_k^{(1)} = \frac{1}{\sqrt{L}} e^{ikx} \left\{ 1 + \sum_n \frac{V_n}{\frac{\hbar^2}{2m} [k^2 - (k + \frac{2\pi n}{a})^2]} e^{2\pi i n x/a} \right\} \quad (2.12)$$

To the first order, ψ_k takes the form of Bloch theorem. Obviously, the free electron wavevector appears to be the same as Bloch vector in the first Brillouin zone.

$$E_k^{(2)} = \sum_n \frac{|V_n|^2}{\frac{\hbar^2}{2m} [k^2 - (k + 2\pi n/a)^2]}. \quad (2.13)$$

When $k = -n\pi/a$, $E_k^{(2)} \rightarrow \infty$. It can be seen from 2.10 that, the first order correction contains the zero-order wave function of other wavevectors. The energy difference is smaller, the weight is larger. When there are degenerate states, the result diverges. So for the wavevector k' at or near $k = -n\pi/a$, non-degenerate perturbation theory no longer works. We need to use degenerate perturbation theory. In the degenerate perturbation theory, we only care about the states which has very small energy difference compared to $|V_n|$ because of their large weight.

The idea of degenerate perturbation theory is linear combination. Because two or more states have very approaching energies, they have approaching weights and no longer can be seen as perturbations. We just assume the true state as linear combination of them, and determine the linear coefficients by Schrodinger equation.

2.2.2 Tight Binding Approximation

参考文献

- [1] Pierre Hohenberg and Walter Kohn. Inhomogeneous electron gas. *Physical review*, 136(3B):B864, 1964.