Lecture VII : Planewave expansion

I. PLANEWAVES

In the previous lecture, we arrived at the Kohn-Sham equation system which needs to be solved self-consistently. In shorthand notation, the Kohn-Sham system may be written as

$$\left[\hat{T}_s + V_{eff}\right]\phi_i = \epsilon_i\phi_i \tag{1}$$

where $\hat{T}_s$ is the single-particle kinetic energy, V_{eff} is the effective potential which contains the external, Hartree and exchange-correlation parts and ϕ_i and ϵ_i are the Kohn-Sham orbitals and eigenvalues. Just as for the Hartree-Fock equation system, it is very difficult if not impossible to solve the above equation in real space. Instead, a viable method is to expand each of the Kohn-Sham orbitals in a suitable basis, converting the real space equation in Eq. 1 into a matrix equation in coefficient space. A matrix equation is far easier to solve than a real-space equation.

A planewave expansion of the Kohn-Sham orbitals can be achieved as follows :

$$\phi_i(\vec{r}) = \sum_{\vec{q}} c_{i,\vec{q}}\frac{1}{\sqrt{\Omega}}\exp(i\vec{q}\cdot\vec{r}) \equiv \sum_{\vec{q}} c_{i,\vec{q}}|\vec{q}\rangle \tag{2}$$

where $c_{i,\vec{q}}$ are the expansion coefficients and the normalization constant $1/\sqrt{\Omega}$ is chosen so as to satisfy the definition of the Kronecker-δ

$$\langle\vec{q}'|\vec{q}\rangle = \frac{1}{\Omega}\int_\Omega d\vec{r}\exp(-i\vec{q}'\cdot\vec{r})\exp(i\vec{q}\cdot\vec{r}) = \delta_{\vec{q},\vec{q}'} \tag{3}$$

In order to convert Eq. 1 into a matrix equation, we insert Eq. 2 into Eq. 1, multiply from the left by $\langle\vec{q}'|$ and integrate in real space

$$\sum_{\vec{q}}\langle\vec{q}'|\hat{H}_{eff}|\vec{q}\rangle c_{i,\vec{q}} = \epsilon_i\sum_{\vec{q}}\langle\vec{q}'|\vec{q}\rangle c_{i,\vec{q}} = \epsilon_i c_{i,\vec{q}} \tag{4}$$

Eq. 5 is a matrix equation which may be written as

$$\bar{H}C = \epsilon_i C \tag{5}$$

where $\bar{H}$ is the Hamiltonian in matrix representation and C is a vector of coefficients. In the planewave representation, the kinetic energy term assumes an extremely simple, diagonal form

$$\langle\vec{q}'| - \frac{1}{2}\nabla^2|\vec{q}\rangle = \frac{1}{2}|\vec{q}|^2\delta_{\vec{q}\vec{q}'} \tag{6}$$

For the potential part of the effective Hamiltonian, the Fourier transform is the natural way to proceed since the planewave basis is essentially the same object as the exponentials used while writing down the Fourier transform of operators. The effective potential, V_{eff} has the periodicity of the lattice and therefore the only allowed Fourier components are those with the wavevectors in the reciprocal space of the crystal. We thus have

$$V_{eff}(\vec{r}) = \sum_m V_{eff}(\vec{G}_m)\exp(i\vec{G}_m\cdot\vec{r}) \tag{7}$$

where

$$V_{eff}(\vec{G}) = \frac{1}{\Omega_{cell}}\int_{\Omega_{cell}} V_{eff}(\vec{r})\exp(-i\vec{G}\cdot\vec{r})d\vec{r} \tag{8}$$

and the index m has been attached to the reciprocal space vector so as to make the summation easier. If we now insert Eq. 8 into Eq. 4, we have

$$\langle\vec{q}'|V_{eff}|\vec{q}\rangle = \sum_m\langle\vec{q}'|V_{eff}(\vec{G}_m)|\vec{q}\rangle\exp(i\vec{G}_m\cdot\vec{r}) \tag{9}$$

$$\equiv \sum_m\langle\vec{q}'|V_{eff}(\vec{G}_m)|\vec{q}+\vec{G}_m\rangle = \sum_m V_{eff}(\vec{G}_m)\langle\vec{q}'|\vec{q}+\vec{G}_m\rangle = \sum_m V_{eff}(\vec{G}_m)\delta_{\vec{q}'-\vec{q},\vec{G}_m} \tag{10}$$

Thus, the matrix elements of the effective potential are only nonzero for those wavevectors that differ by a reciprocal lattice vector. In order to switch completely to the representation in terms of the $\vec{G}_m$'s, we make the definitions $\vec{q} = \vec{k} + \vec{G}_m$ and $\vec{q}' = \vec{k} + \vec{G}_{m'}$. Written this way, $\vec{q}$ and $\vec{q}'$ differ manifestly by a reciprocal lattice vector. The sum over $\vec{q}$ in Eq. 4 is then converted into a sum over m. Then for a given $\vec{k}$, the Schrödinger-like equation is given by

$$\sum_m \langle \vec{k} + \vec{G}_{m'} | \hat{H}_{eff} | \vec{k} + \vec{G}_m \rangle c_{i,m} = \epsilon_i c_{i,m'} \tag{11}$$

In accord with the Bloch theorem, the $\vec{k}$-dependence in Eq. 11 may be incorporated into the Hamiltonian

$$\sum_m H_{m'm}(\vec{k}) c_{i,m}(\vec{k}) = \epsilon_i(\vec{k}) c_{i,m'}(\vec{k}) \tag{12}$$

where

$$H_{m'm}(\vec{k}) = \frac{1}{2} |\vec{k} + \vec{G}_m|^2 \delta_{m'm} + V_{eff}(\vec{G}_m - \vec{G}_{m'}) \tag{13}$$

Since the Hamiltonian is now labeled by $\vec{k}$, the coefficients and energies are also labeled by $\vec{k}$. As seen in Eq. 13, the effective potential depends on the difference between two reciprocal lattice vectors. This follows straightforwardly from the presence of the Krönecker delta in its definition in Eq. 10. Next, let's look at the planewave representation of each term in the total energy (which ill be useful later) and the potential one by one.

II. HARTREE TERM IN PLANEWAVES

In order to find the Fourier representation of the Hartree term, we start by expanding the two densities in the definition as a Fourier sum

$$\frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} = \frac{1}{2} \sum_{\vec{G},\vec{G}'} \int \int d\vec{r} d\vec{r}' \frac{n(\vec{G})n(\vec{G}')}{|\vec{r} - \vec{r}'|} e^{-i\vec{G}\cdot\vec{r}} e^{-i\vec{G}'\cdot\vec{r}'}$$

$$= \frac{1}{2} \sum_{\vec{G},\vec{G}'} \int \int d\vec{u} d\vec{r}' \frac{n(\vec{G})n(\vec{G}')}{|\vec{u}|} e^{-i\vec{G}\cdot\vec{u}} e^{-i(\vec{G}+\vec{G}')\cdot\vec{r}'}$$

$$= \pi \sum_{\vec{G},\vec{G}'} n(\vec{G})n(\vec{G}') \int d\vec{r}' e^{-i(\vec{G}+\vec{G}')\cdot\vec{r}} \int \int u^2 du(-d\cos\theta) \frac{e^{-iGu\cos\theta}}{u}$$

$$= \pi \sum_{\vec{G},\vec{G}'} n(\vec{G})n(\vec{G}')\Omega_{cell}\delta_{\vec{q}\vec{q}'} \int u^2 \frac{e^{-iGu\cos\theta}}{-iGu^2}\Big|_1^{-1} du$$

$$= \pi\Omega_{cell} \sum_{\vec{G}} n(\vec{G})n(-\vec{G}) \int \frac{e^{iGu} - e^{-iGu}}{-iG} du$$

$$= \pi\Omega_{cell} \sum_{\vec{G}} n(\vec{G})n(-\vec{G}) \frac{e^{iGu} - e^{-iGu}}{G^2}\Big|_0^\infty \tag{14}$$

$$= \pi\Omega_{cell} \sum_{\vec{G}} n(\vec{G})n(-\vec{G}) \lim_{\eta\to 0} \frac{e^{iG(u+i\eta)} - e^{-iG(u-i\eta)}}{G^2}$$

$$= 2\pi\Omega_{cell} \sum_{\vec{G}} n(\vec{G})n(-\vec{G}) \tag{15}$$

where a *regulator* has been employed in order to take the complex integral. One final simplification comes from the fact that $n(\vec{r}) = n(-vr)$. This reflects in the Fourier components of n in the following manner :

$$n(\vec{r}) = \sum_{\vec{G}} n(\vec{G}) e^{-i\vec{G}\cdot\vec{r}} \tag{16}$$

On the other hand

$$n(-\vec{r}) = \sum_{\vec{G}} n(\vec{G})e^{i\vec{G}\cdot\vec{r}} = \sum_{\vec{G}} n(-\vec{G})e^{-i\vec{G}\cdot\vec{r}}. \tag{17}$$

Comparing Eq. 16 and Eq. 17, we obtain the following relation between the Fourier components

$$n(\vec{G}) = n(-\vec{G}) \tag{18}$$

Thus, the Fourier representation of the Hartree energy term is

$$\frac{1}{2} \int \int d\vec{r}d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} = 2\pi\Omega_{cell} \sum_{\vec{G}} \frac{n(\vec{G})^2}{G^2} \tag{19}$$

By a similar argument, the Hartree potential in the effective potential of Eq. 12 may be written in the Fourier representation as

$$V_H(\vec{G}) = 4\pi \frac{n(\vec{G})}{G^2} \tag{20}$$

Notice the absence of the volume factor in this case. This comes from the fact that there is one forward Fourier transform in this case which brings a factor of $\frac{1}{\Omega}$ which is cancelled by the Ω coming from the definition of the Krönecker delta.

III.   EXCHANGE-CORRELATION TERM IN PLANEWAVES

The exchange-correlation term is written in the form of an integral of the product of two functions. The Fourier transform then takes a particularly simple form, namely a convolution

$$\int d\vec{r}n(\vec{r})\epsilon_{xc}(\vec{r}) = \sum_{\vec{G},\vec{G}'} \int d\vec{r}n(\vec{G})e^{-i\vec{G}\cdot\vec{r}}\epsilon_{xc}(\vec{G}')e^{-i\vec{G}'\cdot\vec{r}}$$

$$= \Omega_{cell} \sum_{\vec{G},\vec{G}'} \delta_{\vec{G},-\vec{G}'} n(\vec{G})\epsilon_{xc}(\vec{G}')$$

$$= \Omega_{cell} \sum_{\vec{G}} n(-\vec{G})\epsilon(\vec{G}) = \Omega_{cell} \sum_{\vec{G}} n(\vec{G})\epsilon_{xc}(\vec{G}) \tag{21}$$

Following once again a similar argument for the exchange-correlation potential, we have

$$V_{xc}(\vec{G}) = \sum_{\vec{G}'} n_{xc}(\vec{G} - \vec{G}')\frac{d\epsilon_{xc}}{dn}(\vec{G}') + \epsilon_{xc}(\vec{G}) \tag{22}$$

IV.   THE EXTERNAL POTENTIAL — STRUCTURE AND FORM FACTORS

Let the crystal be composed of different species of atoms each labeled $\kappa = 1, \cdots n_{sp}$. For each κ, there are n^κ identical atoms at positions $\vec{\tau}_{\kappa,j}$ in the unit cell. The ionic potential (the external potential) may then be written as a superposition of isolated atom potentials,

$$V_{ne}(\vec{r}) = \sum_{\kappa=1}^{n_{sp}} \sum_{j=1}^{n_\kappa} \sum_{\vec{T}} V^\kappa(\vec{r} - \vec{\tau}_{\kappa,j} - \vec{T}). \tag{23}$$

If we now consider the Fourier transform of such a function as in Eq. 23, this derivation follows :

$$V(\vec{G}) = \frac{1}{\Omega}\int_\Omega d\vec{r}\, V(\vec{r})\exp(i\vec{G}\cdot\vec{r}) = \frac{1}{\Omega}\sum_{\kappa=1}^{n_{sp}}\sum_{j=1}^{n_\kappa}\int_\Omega d\vec{u}\, V^\kappa(\vec{u})\exp(i\vec{G}\cdot(\vec{u}+\vec{\tau}_{\kappa,j}))\underbrace{\sum_{\vec{T}}\exp(i\vec{G}\cdot\vec{T})}_{N_{cell}}$$

$$= \frac{1}{\Omega_{cell}}\underbrace{\sum_{\kappa=1}^{n_{sp}}}_{n_{sp}}\int_\Omega d\vec{u}\, V^\kappa(\vec{u})\exp(i\vec{G}\cdot\vec{u})\sum_{j=1}^{n_\kappa}\exp(i\vec{G}\cdot\vec{\tau}_{\kappa,j})$$

$$\equiv \sum_{\kappa=1}^{n_{sp}}\frac{\Omega^\kappa}{\Omega_{cell}}S^\kappa(\vec{G})V^\kappa(\vec{G}) \tag{24}$$

where

$$V^\kappa(\vec{G}) = \frac{1}{\Omega^\kappa}\int_\Omega V^\kappa(\vec{r})\exp(i\vec{G}\cdot\vec{r})d\vec{r} \tag{25}$$

is the form factor and

$$S^\kappa(\vec{G}) = \sum_{j}^{n^\kappa}\exp(i\vec{G}\cdot\vec{\tau}_{\kappa,j}) \tag{26}$$

is the structure factor. When separated in this way, the Fourier transform of the external potential reduces to the Fourier transform of the isolated atomic potential (to be approximated later by a pseudopotential) and a sum of planewaves which impose the periodicity.

Eq. 24 is particularly useful if the function is spherically symmetric since the Fourier transform of a spherically symmetric function is also spherically symmetric. Let $f(\vec{r}) = f(r)$ for an arbitrary function, f. The Fourier transform is

$$f(\vec{G}) = -\frac{1}{\Omega}\int r^2 f(r)\exp(i\vec{G}\cdot\vec{r})dr d\phi d\cos\theta$$

$$= -\frac{2\pi}{\Omega}\int r^2 f(r)\frac{\exp(iGr\cos\theta)}{iGr}\Big|_0^\pi dr$$

$$= -\frac{4\pi}{\Omega}\int r^2 f(r)\frac{\exp(-iGr)-\exp(iGr)}{iGr}dr$$

$$= \frac{4\pi}{\Omega}\int r^2 j_0(|\vec{G}|r)f(r)dr \equiv f(|\vec{G}|) \tag{27}$$

We thus have

$$V^\kappa(\vec{G}) = V^\kappa(|\vec{G}|)\int_0^\infty dr\, r^2 j_0(|\vec{G}|r)V^\kappa(r) \tag{28}$$

V. CALCULATION OF THE ELECTRON DENSITY

After the Kohn-Sham equations have been solved, the density needs to be calculated. Remember the fact that we have a different system of Kohn-Sham equations for each $\vec{k}$. For the final expression of the energy and the density, we have to conduct a summation of all these $\vec{k}$ points over the first Brillioun zone. Thus, for the density,

$$n(\vec{r}) = \frac{1}{N_k}\sum_{\vec{k},i}n_{i,\vec{k}}\quad where\quad n_{i,\vec{k}}(\vec{r}) = |\phi_{i,\vec{k}}| \tag{29}$$

where the index i runs over the occupied states. For the planewave basis, we obtain rather straightforwardly the folloing expression for $n_{i,\vec{k}}(\vec{r})$

$$n_{i,\vec{k}} = \frac{1}{\Omega}\sum_{mm'}c_{im}^*(\vec{k})c_{im'}(\vec{k})e^{i(\vec{G}_{m'}-\vec{G})\cdot\vec{r}} \tag{30}$$

which yields

$$n_{i\vec{k}}(\vec{G}) = \frac{1}{\Omega} \sum_m c^*_{i,m}(\vec{k}) c_{i,m''}(\vec{k}) \tag{31}$$

where m'' is defined as the index of the vector $\vec{G}_{m''} = \vec{G}_m + \vec{G}$. Although it is a straightforward operation, obtaining the density through the use of coefficients of the Kohn-Sham orbitals requires $N^2_{\vec{G}}$ operations. If, on the other hand, once we know the coefficients of the Kohn-Sham orbitals and convert them directly to a real space grid using efficient FFT algorithms, this only takes $N_{\vec{G}} \log N_{\vec{G}}$ operations. If we know the real-space density, we can also compute V_{xc} and E_{xc} in real space easily. In summary, it is more advantegous to use $n(\vec{G})$ to calculate the Hartree potential whereas for V_{xc} we use the real space density.

VI.   THE PLANEWAVE CUTOFF

If you have run a PW-DFT code before, you will have seen that there is a parameter in the input file that allows you to specify an energy cutoff. This cutoff is necessary because we cannot possible have a complete expansion in terms of infinitely many planewaves. However, one can show that the contribution of the higher frequency planewaves are less than those of lower frequency planewaves. It is thus a viable option to introduce sum sort of a cutoff and take only those wavevectors that satisfy

$$\frac{1}{2}|\vec{G}|^2 < E_{cut}. \tag{32}$$

What this cutoff should be depends upon the system and a convergence study should be made before deciding what's the appropriate cutoff.

We must keep in mind while talking about the efficiency of the FFT approach that the density requires a maximum Fourier component that has twice the frequency of that of the Kohn-Sham orbitals. Moreover, the FFT grid needs to be a regular parallelepiped whereas the $E_c ut$ in Eq. 32 defines a sphere. Thus, the FFT has some reduntant kpoints which somewhat slow down the calculation, however it's still efficient enough to justify its use.