

Computation of Energy Bands

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1 Density Functional Theory (DFT)

1.1 Hohenberg-Kohn Theorem

Theorem 1.1. (Hohenberg-Kohn)

- 1 The ground state energy of a spinless system consisting of identical fermions is uniquely determined by the number density $n(\mathbf{r})$;
- 2 The energy functional $E[n]$ takes a minimum for correct ground state density when the number of particles remains the same.

The proof is a simple application of variational principle. Theorem 1.1-1 tells that the ground state number density of electrons determines all properties in ground state, including wave function. While the second one gives a method to achieve the ground state number density n .

Hohenberg-Kohn theorem is the foundation of DFT, but the explicit form of functionals remain unknown.

1.2 Kohn-Sham Equations

In DFT, to solve a many body system can be reduced to solve the Kohn-sham equation for a single electron. Under adiabatic approximation, we can ignore the kinetic term of the nuclear, and the system Hamiltonian is

$$H[n] = T[n] + V[n] + V_{\text{ext}}. \quad (1)$$

The main point of Kohn-Sham equations is to define exchange energy $E_x = V - V_0$ and correlation energy $E_c = T - T_0$, where V_0 and T_0 are potential and kinetic energy terms of free electrons and $E_{xc} = E_x + E_c$. Doing variation to n , and we achieve

$$\left(-\frac{1}{2}\nabla^2 + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{ext}} + V_{xc}\right)\psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r}). \quad (2)$$

The complexity has now been included in exchange-correlation energy V_{xc} :

$$V_{xc} = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (3)$$

Mention that E_i in Kohn-Sham equation isn't the real energy of the single electron, and ψ_i isn't the real wave function either, but in fact it is the wave function of a quasi-particle satisfying the KS equation, which satisfies the condition that sum of the square-norm of wave function equals to the real density of electrons.

What's more, Kohn-Sham equation is strict except the adiabatic approximation. But E_{xc} is still unknown and needs to be approximated.

When solving the Kohn-Sham equation, more approximations are needed. For kinetic term of Hamiltonian, it can be either non-relativistic or relativistic (especially for heavy atoms). When it comes to potential term, common ones are pseudo-potentials and muffin-tin approximation. While for exchange-correlation energy E_{xc} , we might use local density approximation (LDA/LSDA), general gradient approximation (GGA) and so on.

The wave function can be expanded with different bases as well:

- atomic orbitals: Slater type, Gaussian type, numerical;
- orthogonal plane wave (OPW);
- full potential linearised augmented plane wave (FLAPW), augmented spherical wave (ASW);
- etc.

Theoretically, any complete basis can be used to expand the wave function. However, in practice we require the basis satisfying the following properties to simplify computation:

- complete and orthogonal,
- similar to the atomic orbital, in order to decrease the number of basis in computation,
- has simple forms and is easy to compute multi-centre integral.

Assume a basis $|\phi_i\rangle$ is chosen, we can expand the wave function as $|\psi\rangle = \sum_i C_i |\phi_i\rangle$. Then solving Schrödinger equation $H|\psi\rangle = E|\psi\rangle$ is reduced to find the coefficient C_i . Left multiply $\langle\phi_i|$ to the Schrödinger equation gives the linear equation of C_i , and let the determinant to be zero we get

$$\det |\langle\phi_j|H|\phi_i\rangle - E\langle\phi_j|\phi_i\rangle| = 0 \quad (4)$$

Eigenvalue as energy and eigenfunction is obtained once H_{ij} and S_{ij} is computed.

2 Linear Combination of Atomic Orbitals (LCAO) Method

Consider the Schrödinger's equation of a single electron in solid:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi_n^{\mathbf{k}}(\mathbf{r}) = E_n^{\mathbf{k}}\psi_n^{\mathbf{k}}(\mathbf{r}) \quad (5)$$

The lattice potential can be described by linear combination of atomic potential field:

$$V(\mathbf{r}) = \sum_l \sum_a V^{la}(\mathbf{r} - \mathbf{R}_l - \mathbf{t}_a), \quad (6)$$

where \mathbf{R}_l is the lattice vector and \mathbf{t}_a is the position vector of the a -th atom in the l -th primitive cell. Further extend the wave function with Bloch wave functions:

$$\begin{aligned} \phi_j^{\mathbf{k}}(\mathbf{r}) &= \frac{1}{\sqrt{N}} \sum_{l,a} e^{i\mathbf{k} \cdot \mathbf{R}_l} \phi_j^{la}(\mathbf{r} - \mathbf{R}_l - \mathbf{t}_a), \\ \psi_n^{\mathbf{k}} &= \sum_j A_{n,j} \phi_j^{\mathbf{k}}(\mathbf{r}). \end{aligned} \quad (7)$$

j represents the orbital and N is the number of lattices in unit volume. It needs mentioning that ϕ is not necessarily orthogonal for atoms at different lattice points. Substitute it into Schrödinger's equation and define $H_{j,j'}(\mathbf{k}) = \langle \phi_{j'}^{\mathbf{k}} | H | \phi_j^{\mathbf{k}} \rangle$, $S_{j,j'}(\mathbf{k}) = \langle \phi_{j'}^{\mathbf{k}} | \phi_j^{\mathbf{k}} \rangle$. Finally we achieve

$$\sum_j A_{n,j} (H_{j',j} - E_n^k S_{j',j}) = 0. \quad (8)$$

Hence we need to solve a secular equation to get $A_{n,j}$. Nevertheless, there is a main difficulty that we may face integration of multi-centres. For instance, $\langle \phi_{j'}^{\mathbf{k}} | \frac{1}{r_{j,j'}} | \phi_j^{\mathbf{k}} \rangle$. Such integrals will take a long time, and seem unsolvable considering the computing ability when LCAO was initially developed. Hence there raises some approximation methods.

2.1 Slater-Koster Tight-Binding (TB) Method

The name "tight-binding" suggests that this model can describe electrons tightly bound to the atom to which they belong. Following Slater-Koster (SK), these assumptions are made:

- We consider only the nearest neighbours when calculate interaction;
- On site and two-centre integrals are viewed as parameters and fitted with accurate theoretical or experimental results at points in momentum space with high symmetry;
- Three or more centres integrals are neglected.
- $S_{ij} = \delta_{ij}$.

Under such approximation, we just need to diagonalize the Hamiltonian to achieve band structure.

2.2 Gaussian Type Orbitals (GTOs) and Orthogonalized LCAO (OLCAO) Method

We can use Gaussian type orbitals to expand the radial wave function:

$$u_{nlm}(\mathbf{r}) = [\sum_j A_{nl}^j r^l e^{(-\alpha_j r^2)}] Y_{lm}(\theta, \phi). \quad (9)$$

The choice of $\{\alpha_j\}$ remains a problem. From experience, an effective way is to determine α_{\min} and α_{\max} , and extend them to a geometrical sequences of length N . α_{\min} should be neither too small to make the integral unstable, nor too large to make the wave function too local, which may influence the accuracy. Typically α_{\min} can be selected between 0.1 and 0.5, while α_{\max} can be between 10^6 and 10^9 , which rely on sizes of atoms.^[1]

Different from Slater orbitals, most integrations can be analytically written with GTOs. One exception is the integral

$$I = \langle s_A | \frac{e^{-\alpha r_C^2}}{r_C} | s_B \rangle, \quad (10)$$

which can still be expressed with error function $\text{erf}(t) = \frac{2}{\sqrt{\pi}} \int_0^t e^{-r^2} dr$. If we have chosen appropriate $\{\alpha_j\}$, the remaining calculation will be much easier and more accurate.

3 Orthogonal Plane Wave (OPW) and Augmented Plane Wave (APW) Method

3.1 Plane Wave Basis

Expand the wave function by the plane wave basis:

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{N\Omega}} \sum_{\mathbf{K}} C(\mathbf{k} - \mathbf{K}) e^{i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{r}} \quad (11)$$

then we get

$$\sum_{\mathbf{K}} [(\mathbf{k} + \mathbf{K})^2 - E_n(k)] \delta_{\mathbf{K}\mathbf{K}'} + V(\mathbf{K}' - \mathbf{K}) C(\mathbf{k} - \mathbf{K}) = 0 \quad (12)$$

in which

$$V(\mathbf{K}' - \mathbf{K}) = \frac{1}{N\Omega} \int d\mathbf{r} V(\mathbf{r}) e^{-i(\mathbf{K}' - \mathbf{K}) \cdot \mathbf{r}} \quad (13)$$

The drawback of plane wave basis is its slow convergence. For the wave function close to the nucleus which oscillates drastically, a huge number of plane wave basis is required. In general we set a cut-off energy:

$$E_c = \hbar^2 K_m^2 / 2m.$$

3.2 Orthogonal Plane Wave Basis

Define the orthogonal plane wave basis using core states of atoms:

$$|\chi_{\mathbf{k}+\mathbf{K}}\rangle = |\mathbf{k} + \mathbf{K}\rangle + \sum_c a_c \phi_c(\mathbf{k}, \mathbf{r}) \quad (14)$$

which is orthogonal to the core states: $\langle \phi_c(\mathbf{k}, \mathbf{r}) | \chi_{\mathbf{k}+\mathbf{K}} \rangle = 0$, and expansion coefficients are obtained from this condition: $a_c = -\langle \phi_c(\mathbf{k}, \mathbf{r}) | \mathbf{k} + \mathbf{K} \rangle$.

Orthogonal plane wave is the plane wave subtracts its projection to the core state, and is orthogonal to core states. It behaves like the plane wave when far away from the nucleus, and oscillates drastically like core states when close to the nucleus.

Expand the wave function by the orthogonal plane wave basis $|\chi_{\mathbf{k}+\mathbf{K}}\rangle$:

$$|\psi_{\mathbf{k}}\rangle = \sum_{\mathbf{K}} C(\mathbf{k} + \mathbf{K}) |\chi_{\mathbf{k}+\mathbf{K}}\rangle \quad (15)$$

Then we have:

$$\det |\langle \chi_{\mathbf{k}+\mathbf{K}'} | H | \chi_{\mathbf{k}+\mathbf{K}} \rangle - E_{\mathbf{k}} \langle \chi_{\mathbf{k}+\mathbf{K}'} | \chi_{\mathbf{k}+\mathbf{K}} \rangle| = 0 \quad (16)$$

Since core states are tightly bounded, we can assume that they are also eigenstates of the real Hamiltonian, $H\phi_c = E_c\phi_c$, and then we obtain:

$$\det \left| \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K}^2 \delta_{\mathbf{K}\mathbf{K}'} + \sum_{\mathbf{K}} \langle \mathbf{k} + \mathbf{K}' | U | \mathbf{k} + \mathbf{K} \rangle) \right| = 0 \quad (17)$$

in which

$$U = V + \sum_c (E(\mathbf{k}) - E_c) |\phi_c\rangle \langle \phi_c| \quad (18)$$

is the effective potential.

The orthogonalization leads to an effective repulsive potential, and partly cancels the attractive potential of the nucleus.

In practice the coefficient $a_c = -\langle \phi_c(\mathbf{k}, \mathbf{r}) | \mathbf{k} + \mathbf{K} \rangle$ is difficult to compute. The main error of OPW comes from the fact that $|\phi_c\rangle$ isn't eigenstates of the real Hamiltonian.

3.3 Pseudo Potential

The construction of the pseudo potential is almost identical to OPW, while the difference is that we assume $|\phi_c\rangle$ and $|\phi_v\rangle$ to be the eigenstate of the real Hamiltonian:

$$\begin{aligned} H|\phi_c\rangle &= E_c|\phi_c\rangle \\ H|\phi_v\rangle &= E_v|\phi_v\rangle \end{aligned} \tag{19}$$

and replace the plane wave by the pseudo wave function: $|\phi_v\rangle = |\psi_v^{ps}\rangle + \sum_c a_{vc}|\phi_c\rangle$, From the orthogonality of $|\phi_c\rangle$ and $|\phi_v\rangle$, we get the coefficient $a_{vc} = -\langle\phi_c|\psi_v^{ps}\rangle$. Then it's easy to obtain the equation $|\psi_v^{ps}\rangle$ satisfies:

$$(T + V^{ps} - E_v)|\psi_v^{ps}\rangle = 0 \tag{20}$$

In which

$$V^{ps} = V + \sum_c (E_v - E_c)|\phi_c\rangle\langle\phi_c| \tag{21}$$

is the pseudo potential. Observe that E_v is the real energy of the valence band, but not the pseudo energy. (If we solve this equation by expanding $|\psi_v^{ps}\rangle$ using plane wave basis, then $|\phi_v\rangle$ is nothing but the linear combination of orthogonal plane wave $|\chi_{\mathbf{k}+\mathbf{K}}\rangle$.)

The accuracy of Pseudo potential method is usually lower than all-electron method, and since the core states are excluded, we can't calculate their properties. The quality of results relies heavily on the pseudo potential, which requires experience and plenty of tests. Norm-conserving pseudo potential(NSPP) and Ultra-soft pseudo potential (USPP) is often adopted in practice.

Pseudo potential is adopted in order to smooth the potential around the nucleus, since plane wave can't efficiently expand the drastically oscillating function. However, this problem can be solved by adopting more reasonable basis without smoothing the potential. This is the augmented plane wave method.

3.4 Augmented Plane Wave Method

First we introduce the concept of Muffin-tin ball. The lattice potential can be divided into two parts. One is the spheres centered around each nucleus (in which the potential is the superposition of the center atom and atoms close to the center), and the other one is the region between these spheres in which the potential is a constant.

The augmented plane wave basis consists of two parts based on the Muffin-tin ball. In the ball the wave function is the linear combination of atomic orbitals, and outside the ball is plane wave:

$$\phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}, E) = \begin{cases} \sum_{l,m} A_{lm}^{\alpha, \mathbf{k}+\mathbf{G}} u_l^{\alpha}(\mathbf{r}, E) Y_{lm}(\mathbf{r}), & r < R; \\ \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}, & r > R. \end{cases} \quad (22)$$

$u_l^{\alpha}(\mathbf{r}, E)$ is the radial wave function of isolated atoms, which is obtained by solving radial Schrödinger equation. But since there isn't the boundary condition of $\psi \rightarrow 0$ when $r \rightarrow \infty$, the eigenvalue E can change continuously, which all correspond to a solution of the radial equation. The linear combination coefficient A is determined by the continuous condition on the Muffin-tin ball.

The Schrödinger equation we have to solve is in fact a transcendental equation, since the atomic radial wave function depends on E . In practice we have the iterate on E , and update the radial wave function. This makes the algorithm slow, and more efficient algorithm is proposed like LAPW.

4 Application: Energy Band Structure of Silicon

4.1 By Tight-Binding Method

We can generally discuss $A_m B_{8-m}$ -like semi-conductors ($m = 2, 3, 4$) with diamond cubic crystal structure. From quantum mechanics, we know the orbital wave function of electron can be written as

$$\phi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta, \varphi). \quad (23)$$

Here only four orbitals on valence shell, s, p_x, p_y, p_z , are considered. For s-orbital, $l = m = 0$. For p-orbital, $l = 1$, and we can do linear combination of $m = -1, 0, 1$ to represent them with x (respectively, y, z):

$$\phi(\mathbf{r})_{n,1} = \sqrt{\frac{3}{4\pi}} R_{n,1}(r) \frac{x \text{ (respectively, } y, z)}{r} \quad (24)$$

We denote them as p_x, p_y and p_z orbitals. With s and p orbitals, the interaction matrices can be written as $V_{ss\sigma} := \langle s | H | s \rangle$, $V_{sp\sigma} := \langle s | H | p \rangle$, $V_{pp\sigma} := \langle p_x | H | p_x \rangle$, $V_{pp\pi} := \langle p_y | H | p_y \rangle = \langle p_z | H | p_z \rangle$. Assume u, v, w

are direction cosines, and $\mathbf{r}_{n,n'} = r(u, v, w)$, then with simple integration, we arrive at ^[2]

$$\begin{aligned}
E_{s,s} &= V_{ss\sigma} \\
E_{s,x} &= uV_{sp\sigma} \\
E_{x,x} &= u^2V_{pp\sigma} + (1 - u^2)V_{pp\pi} \\
E_{x,y} &= uv(V_{pp\sigma} - V_{pp\pi}) \\
E_{x,z} &= uw(V_{pp\sigma} - V_{pp\pi})
\end{aligned} \tag{25}$$

Go back to the crystal. An A atom together with four neighbouring B atoms forms a regular tetrahedron, and the position of the four B atoms relevant to A is $\mathbf{d}_1 = \frac{1}{4}(1, 1, 1)$, $\mathbf{d}_2 = \frac{1}{4}(1, -1, -1)$, $\mathbf{d}_3 = \frac{1}{4}(-1, 1, -1)$ and $\mathbf{d}_4 = \frac{1}{4}(-1, -1, 1)$. Now we can write explicitly the Hamiltonian in an 8×8 matrix:

$$H = \begin{pmatrix} H^{AA} & H^{AB} \\ H^{BA} & H^{BB} \end{pmatrix} \tag{26}$$

H^{AA} and H^{BB} are diagonalized and

$$H^{AB} = \begin{pmatrix} E_{ss}g_1 & E_{sp}g_2 & E_{sp}g_3 & E_{sp}g_4 \\ -\bar{E}_{sp}g_2 & E_{xx}g_1 & E_{xy}g_4 & E_{xy}g_3 \\ -\bar{E}_{sp}g_3 & E_{xy}g_4 & E_{xx}g_1 & E_{xy}g_2 \\ -\bar{E}_{sp}g_4 & E_{xy}g_3 & E_{xy}g_2 & E_{xx}g_1 \end{pmatrix} \tag{27}$$

where

$$\begin{aligned}
E_{ss} &= V_{ss\sigma}, \quad E_{sp} = \frac{1}{\sqrt{3}}V_{sp\sigma}, \quad \bar{E}_{sp} = \frac{1}{\sqrt{3}}\bar{V}_{sp\sigma} \\
E_{xx} &= \frac{1}{3}V_{pp\sigma} + \frac{2}{3}V_{pp\pi}, \quad E_{xy} = E_{xz} = \frac{1}{3}V_{pp\sigma} - \frac{1}{3}V_{pp\pi} \\
g_1(\mathbf{k}) &= e^{i\mathbf{k} \cdot \mathbf{d}_1} + e^{i\mathbf{k} \cdot \mathbf{d}_2} + e^{i\mathbf{k} \cdot \mathbf{d}_3} + e^{i\mathbf{k} \cdot \mathbf{d}_4}, \\
g_1(\mathbf{k}) &= e^{i\mathbf{k} \cdot \mathbf{d}_1} + e^{i\mathbf{k} \cdot \mathbf{d}_2} - e^{i\mathbf{k} \cdot \mathbf{d}_3} - e^{i\mathbf{k} \cdot \mathbf{d}_4}, \\
g_1(\mathbf{k}) &= e^{i\mathbf{k} \cdot \mathbf{d}_1} - e^{i\mathbf{k} \cdot \mathbf{d}_2} + e^{i\mathbf{k} \cdot \mathbf{d}_3} - e^{i\mathbf{k} \cdot \mathbf{d}_4}, \\
g_1(\mathbf{k}) &= e^{i\mathbf{k} \cdot \mathbf{d}_1} - e^{i\mathbf{k} \cdot \mathbf{d}_2} - e^{i\mathbf{k} \cdot \mathbf{d}_3} + e^{i\mathbf{k} \cdot \mathbf{d}_4}.
\end{aligned} \tag{28}$$

With experienced parameters taken from Xie's book ^[3], a simple python program gives the band structure of Silicon with this method as below:

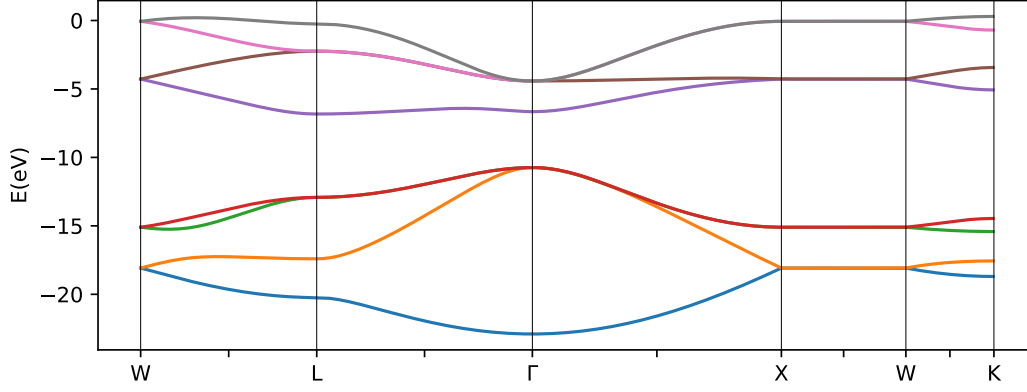


Figure 1: Energy band structure of Si by Tight-Binding

The Silicon should have indirect band gap, while in Fig.1 it does not. The biggest drawback of such method is that we consider all the orbital wave functions are orthogonal. $S_{j'j}$ is actually roughly 0.5 for the nearest atoms. Of course, $S_{j'j}$ can be parametrized in the same way as $H_{j'j}$, which will introduce many more new parameters.

4.2 By Orthogonal Plane Wave Method

Here we use Cambridge Sequential Total Energy Package (CASTEP)^[4] from the software Materials Studio. In this package, electronic wave functions are expanded with plane wave basis. We choose GGA as approximation of exchange-correlation functionals and ultrasoft pseudo potentials to calculate the band structure as well as density of states of Silicon. Comparing Fig.1 with Fig.2, it can be observed that their valence bands are quite similar, while conductive bands are not. The indirect band gap occurs in Fig.2.

We also put the result by OpenMX in Fig.3, which is based on DFT, norm-conserving pseudo potentials and pseudo-atomic localized basis functions. Higher the energy is, the more different the corresponding energy band results of these two packages are. For the important several lowest conductive bands, answers of the two methods fit well.

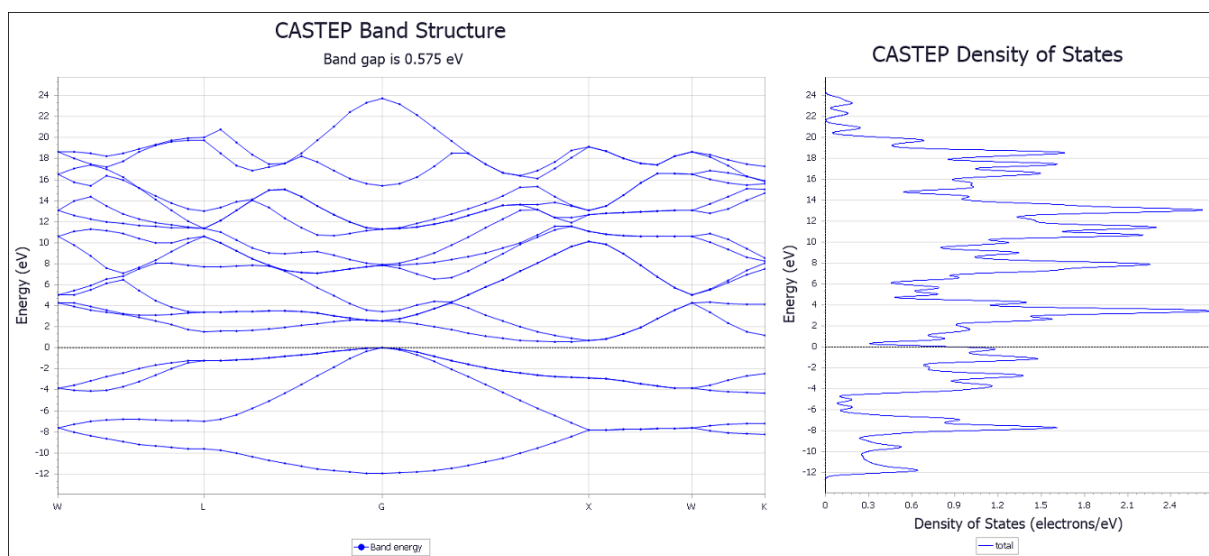


Figure 2: Energy band structure of Si by CASTEP

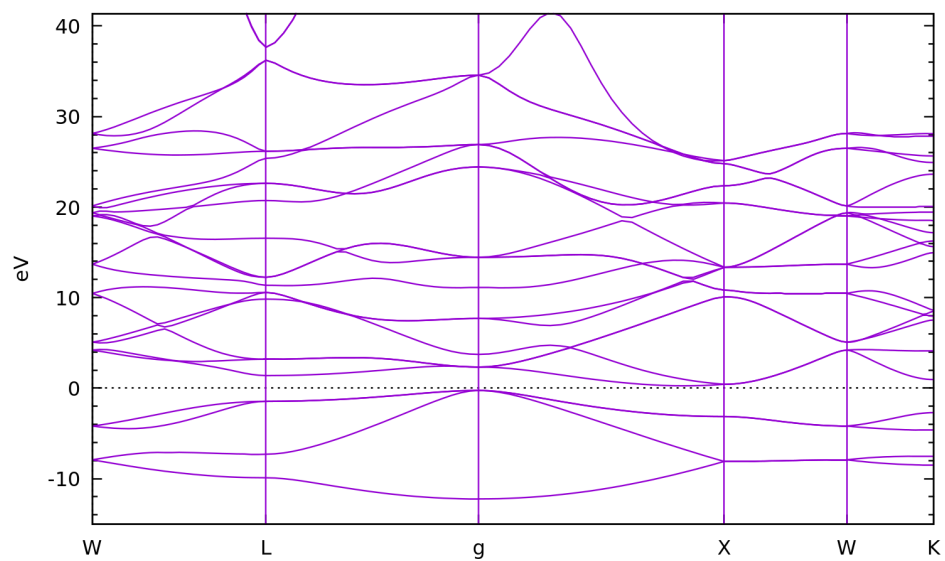


Figure 3: Energy band structure of Si by OpenMX

5 Group Theory in Solid State Physics

5.1 32 Point Groups and 230 space groups

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5.2 Space Group Operators

Elements of space group can be seen as operators which operate on wave functions. For simplicity we only consider point groups here, ignoring the translation.

We define the point group operator as

$$T(\alpha)f(\mathbf{r}) = f(\alpha^{-1}\mathbf{r}) \quad (29)$$

It's easy to prove that $T(\alpha)$ commutes with H , since ∇^2 and $V(\mathbf{r})$ is unchanged under space group operation:

$$\begin{aligned} T(\alpha)H\phi &= \left[-\frac{\hbar^2}{2m}\nabla_{\alpha^{-1}\mathbf{r}^2} + V(\alpha\mathbf{r})\right]\phi(\alpha^{-1}\mathbf{r}) \\ &= \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]T(\alpha)\phi(\mathbf{r}) \\ &= HT(\alpha)\phi \end{aligned} \quad (30)$$

This leads to the conclusion that ϕ and $T(\alpha)\phi$ have the same energy eigenvalue, which leads to the energy degeneracy.

5.3 The Symmetry of $E(k)$

It's easy to prove that under a space group operator $\{\alpha|t\}$, the wave vector of a Bloch function change from \mathbf{k} to $\alpha\mathbf{k}$, with a phase factor undetermined:

$$\psi_{n,\alpha\mathbf{k}}(\mathbf{r}) = \lambda\{\alpha|t\}\psi_{n,\mathbf{k}}(\mathbf{r}), \quad |\lambda|^2 = 1 \quad (31)$$

Since $\{\alpha|t\}$ commutes with H , the Bloch function of \mathbf{k} and $\alpha\mathbf{k}$ have the same energy eigenvalue, i.e

$$E(\mathbf{k}) = E(\alpha\mathbf{k}) \quad (32)$$

in which α can correspond to any elements from the space group (has bigger symmetry than the lattice. Only for simple space group, the crystal and the lattice have the symmetry).

5.4 The Star and the Group of the Wave Vector

The star of a wave vector \mathbf{k} is defined to be the set of different $\alpha\mathbf{k}$, where α go through point group of the lattice.

The group of a wave vector \mathbf{k} is the set of elements β in the point group which satisfy $\beta\mathbf{k} = \mathbf{k} + \mathbf{G}$.

The above two sets satisfy the following relation:

$$|\text{point group}| = |\text{group of } \mathbf{k}| \times |\text{star of } \mathbf{k}| \quad (33)$$

What's more, the dimension of irreducible representations of group of wave vector \mathbf{k} equals the degeneracy of energy bands at \mathbf{k} .

5.5 The symmetry of the wave function

A Bloch function only changes its periodic part when applied by elements in the group of the wave vector, and Bloch functions from different energy band has different transformation properties, which is called the symmetry of the wave function.

As a result, the periodic part of Bloch functions can serve as the basis for irreducible representations of the space group.

Here we see an example of the simple cubic lattice. The Γ point is defined as $\mathbf{k} = (0, 0, 0)$. The point group of SC is O_h , and the group of Γ is also O_h . By the tight binding method, the wave function is of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_m e^{i\mathbf{k} \cdot \mathbf{R}_m} \phi(\mathbf{r} - \mathbf{R}_m) \quad (34)$$

at Γ point,

$$\psi_{\square}(\mathbf{r}) = \sum_m \phi(\mathbf{r} - \mathbf{R}_m) \quad (35)$$

For the s band, we have

$$\begin{aligned} T(\beta)\psi_{\square}^s(\mathbf{r}) &= \sum_m \phi_s(\beta^{-1}\mathbf{r} - \mathbf{R}_m) \\ &= \sum_m \phi_s(\beta^{-1}(\mathbf{r} - \mathbf{R}_m)) \quad (\text{since the sum includes all lattices}) \\ &= \sum_m \phi_s(\mathbf{r} - \mathbf{R}_m) \quad (\text{since the } s \text{ wave function is spherical}) \\ &= \psi_{\square}^s(\mathbf{r}) \end{aligned} \quad (36)$$

This shows that when operating by O_h , $\psi_{\square}^s(\mathbf{r})$ remains unchanged, which corresponds to unit representation of O_h , and is denoted by Γ_1 . For the p band,

$$T(\beta)\psi_{\square}^{p_i}(\mathbf{r}) = \sum_m \phi_{p_i}(\beta^{-1}(\mathbf{r} - \mathbf{R}_m)) \quad (37)$$

When operating by O_h , p_x, p_y, p_z orbit are determined by their spherical harmonic part, which can be reduced to x, y, z . This corresponds to the 3-dimension representation of O_h , and is denoted by Γ_{15} .

The Δ axis can be treated similarly. The group of the wave vector is now C_{4v} . The s and p_x band corresponds to the unit representation, denoted by Δ_1 , while p_y, p_z band correspond to the 2-dimension representation denoted by Δ_5 .

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