Plane wave basis band simulation

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1 Perturbation in a quantum well state

Let us consider a one-dimensional (1D) quantum well expressed as follows:

$$V(x) = \begin{cases} 0 & (0 \leq x \leq a) \\ V_0 & (else) \end{cases} \tag{1}$$

The Schrödinger equation of this system is expressed as follows:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)|\psi_n^{(0)}\rangle = H_0\,|\psi_n^{(0)}\rangle = E_n^{(0)}\,|\psi_n^{(0)}\rangle\,. \tag{2}$$

We expressed the wavefunction as $|\psi_n^{(0)}\rangle$, in which the notation (0) represents that the wavefunction is for the system without perturbation, and n is the quantum number. In a quantum mechanics class, you may have learned how to get the analytic solution for the quantum well system. The solution is given as follows:

$$|\psi_n^{(0)}\rangle = \psi_n^{(0)}(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) \quad (0 \leq x \leq a, n = 1, 2, \dots) \tag{3}$$

$$E_n^{(0)} = \frac{n^2\pi^2\hbar^2}{2m_0 a}. \tag{4}$$

The solutions of the Schrödinger equation compose a complete system: in other words, any shape of a function in this region can be expressed by the linear combination of the solutions, as follows:

$$\begin{aligned} |\psi\rangle &= c_1\,|\psi_1^{(0)}\rangle + c_2\,|\psi_2^{(0)}\rangle + c_3\,|\psi_3^{(0)}\rangle + \cdots \\ &= \sum_{n=1}^{\infty} c_n\,|\psi_n^{(0)}\rangle. \end{aligned} \tag{5}$$

Practically, the wavefunctions with the high quantum number are cut to calculate the low energy state. Thus, we limit n to be $n \leq N$:

$$|\psi\rangle = \sum_{n=1}^{N} c_n\,|\psi_n^{(0)}\rangle. \tag{6}$$

We assume that a perturbation potential $\Delta V(x)$ is applied to the quantum well state. Let us consider a perturbation in the quantum well. The Schrödinger equation for the perturbated system is expressed as follows:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) + \Delta V(x)\right)|\psi\rangle = (H_0 + \Delta V(x))\,|\psi\rangle = E\,|\psi\rangle \tag{7}$$

As the wavefunctions in (unperturbed) quantum well state compose a complete system, the wavefunctions after the perturbation should be expressed by eq. 6. Therefore, let us insert eq. 6 to eq. 7:

$$(H_0 + \Delta V(x)) \sum_{n=1}^{N} c_n \left|\psi_n^{(0)}\right\rangle = E \sum_{n=1}^{N} c_n \left|\psi_n^{(0)}\right\rangle. \tag{8}$$

Our task is to get proper combinations of c_n and corresponding energies. Firstly, let us multiply $\langle\psi_1^{(0)}|$ on both side of eq. 8.

$$\left\langle\psi_1^{(0)}\right| (H_0 + \Delta V(x)) \sum_{n=1}^{N} c_n \left|\psi_n^{(0)}\right\rangle = E \left\langle\psi_1^{(0)}\right| \sum_{n=1}^{N} c_n \left|\psi_n^{(0)}\right\rangle \tag{9}$$

$$\therefore \sum_{n=1}^{N} c_n \left\langle\psi_1^{(0)}\right| H_0 \left|\psi_n^{(0)}\right\rangle + \sum_{n=1}^{N} c_n \left\langle\psi_1^{(0)}\right| \Delta V(x) \left|\psi_n^{(0)}\right\rangle = E \sum_{n=1}^{N} c_n \left\langle\psi_1^{(0)}|\psi_n^{(0)}\right\rangle. \tag{10}$$

Using the orthogonality of the wave functions ($\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{mn}$), the right side of eq. 10 is calculated to be

$$E \sum_{n=1}^{N} c_n \left\langle\psi_1^{(0)}|\psi_n^{(0)}\right\rangle = Ec_1. \tag{11}$$

The first term on the left side of eq. 10 is calculated using eq. 2 and the orthogonality as follows:

$$\begin{aligned} \sum_{n=1}^{N} c_n \left\langle\psi_1^{(0)}\right| H_0 \left|\psi_n^{(0)}\right\rangle &= \sum_{n=1}^{N} c_n E_n^{(0)} \left\langle\psi_1^{(0)}|\psi_n^{(0)}\right\rangle \\ &= c_1 E_1^{(0)}. \end{aligned} \tag{12}$$

For the second term on the left side of eq. 10, we will use the following simplified expression :

$$\left\langle\psi_m^{(0)}\right| \Delta V(x) \left|\psi_n^{(0)}\right\rangle = V_{m,n} \tag{13}$$

Combining eqs. 11, 12, and 13, eq. 10 is transformed as follows:

$$c_1 E_1^{(0)} + \sum_{n=1}^{N} c_n V_{1,n} = Ec_1. \tag{14}$$

Secondly, let us multiply $\langle\psi_2^{(0)}|$ on both side of eq.8. Following the same process, we will get the following equation:

$$c_2 E_2^{(0)} + \sum_{n=1}^{N} c_n V_{2,n} = Ec_2. \tag{15}$$

Then, let us multiply $\langle\psi_m^{(0)}|$ $(1 \leq m \leq N)$. We get the following equation:

$$c_m E_m^{(0)} + \sum_{n=1}^{N} c_m V_{m,n} = Ec_m. \tag{16}$$

Repeating the same calculation for all the $\langle\psi_m^{(0)}|$ $(1 \leq m \leq N)$, we get N-th equations like eq. 16. All the equations can be summarized in a matrix form as follows:

$$\begin{pmatrix} E_1^{(0)} + V_{1,1} & V_{1,2} & V_{1,3} & \cdots & V_{1,N} \\ V_{2,1} & E_2^{(0)} + V_{2,2} & V_{2,3} & \cdots & V_{2,N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ V_{N,1} & V_{N,2} & V_{N,3} & \cdots & E_N^{(0)} V_{N,N} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix} \tag{17}$$

Equation 17 is an eigenequation, which the perturbated system should satisfy. $E_n^{(0)}$ is the energy states of the unperturbed system, expressed in eq. 4. Thus, we know the values. Using the characteristics of bra and kets, $V_{n,m}$ is expressed as follows:

$$\begin{aligned} V_{mn} &= \langle\psi_m^{(0)}|\,\Delta V(x)\,|\psi_n^{(0)}\rangle & (18)\\ &= \int_0^a \psi_m^{(0)*}(x)\Delta V(x)\psi_n^{(0)}(x). & (19)\end{aligned}$$

As $\psi_n^{(0)}(x)$ is the wavefunction in the unperturbed system, expressed by eq. 3, $V_{m,n}$ can be calculated by the integration if the perturbation potential ΔV is given. Therefore, all the elements in the matrix in eq. 17 can be calculated.

Diagonalization is a well-known method of getting the solution for the matrix from eigenequation. Diagonalizing the matrix yields the eigenenergy and eigenstates of the perturbed system. In this way, the electronic state under the perturbed potential can be calculated using the unperturbed states.

2 Using plane waves as the basis

In the case of the quantum well state, we used the solutions of the unperturbed system as the basis to express the wave functions. In this section, we will start from a system without any potential. In this system, the wave function is expressed by plane waves. We will consider the periodic potential as a perturbation and express the electronic states using the plane waves as the basis set. Basically, we will repeat the same discussion as the previous section using the different basis set.

Although an unperturbed system does not have a periodicity (as there is no potential), we will consider a 1D periodic potential as the perturbation. Therefore, we consider the Broch condition from the beginning. If the potential is periodic with the periodicity of a, the wave function should satisfy the following Broch condition:

$$\begin{aligned} \psi(x) &= e^{iKx}u_k(x), & (20)\\ u_k(x) &= u_k(x+a), & (21)\\ -\pi/a &\le K \le \pi/a. & (22)\end{aligned}$$

The Schrödinger equation of the unperturbed system is expressed as follows:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)|\psi_n^{(0)}\rangle = H_0\,|\psi_n^{(0)}\rangle = E_n^{(0)}\,|\psi_n^{(0)}\rangle\,. \quad (23)$$

The solution of eq. 23 satisfying the Broch condition is expressed as follows:

$$\begin{aligned} \psi_n^{(0)}(x) &= |\psi_n^{(0)}\rangle = e^{iKx}e^{ik_nx} & (24)\\ E_n^{(0)} &= \frac{\hbar^2}{2m}(K+k_n)^2 & (25)\end{aligned}$$

Here, $k_n = \frac{2\pi n}{a}, n = 0, \pm1, \pm2, \ldots$. We will use eq. 24 as the basis set, as follows:

$$|\psi\rangle = \sum_{n=-N}^{N} c_n\,|\psi_n^{(0)}\rangle. \quad (26)$$

Let us consider a potential $V(x)$ ($V(x+a) = V(x)$). The Schrödinger equation is expressed as follows:

$$\begin{aligned} (H_0 + V(x))\,|\psi\rangle &= E\,|\psi\rangle & (27)\\ \therefore (H_0 + V(x))\sum_{n=-N}^{N} c_n\,|\psi_n^{(0)}\rangle &= E\sum_{n=-N}^{N} c_n\,|\psi_n^{(0)}\rangle & (28)\end{aligned}$$

Let us multiply $\langle\psi_m^{(0)}|$ on both sides:

$$\sum_{n=-N}^{N} c_n \langle\psi_m^{(0)}|H_0|\psi_n^{(0)}\rangle + \sum_{n=-N}^{N} c_n \langle\psi_m^{(0)}|V(x)|\psi_n^{(0)}\rangle = E \sum_{n=-N}^{N} c_n \langle\psi_m^{(0)}|\psi_n^{(0)}\rangle \tag{29}$$

The first term can be converted using eq. 23 and the orthogonality as follows:

$$\begin{aligned}\sum_{n=-N}^{N} c_n \langle\psi_m^{(0)}|H_0|\psi_n^{(0)}\rangle &= \sum_{n=-N}^{N} c_n E_n^{(0)} \langle\psi_m^{(0)}|\psi_n^{(0)}\rangle \\ &= c_m E_m^{(0)}.\end{aligned} \tag{30}$$

We will simplify the second term using the following expression:

$$\begin{aligned}V_{m,n} = \langle\psi_m^{(0)}|V(x)|\psi_n^{(0)}\rangle &= \int_0^a e^{-iKx} e^{-ik_m x} V(x) e^{iKx} e^{ik_n x} \\ &= \int_0^a e^{-ik_m x} V(x) e^{ik_n x}.\end{aligned} \tag{31}$$

Note that $V_{m,n}$ does not depend on K. The right side of eq. 29 can be converted using the orthogonality as follows:

$$E \sum_{n=-N}^{N} c_n \langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = E c_m \tag{32}$$

To summarize, eq. 29 is simplified to be

$$c_m E_m^{(0)} + \sum_{n=-N}^{N} c_n V_{m,n} = E c_m. \tag{33}$$

Repeating the same process for all the m ($-N \le m \le N$) yields $2N+1$ equations. The equations are summarized in a matrix form as follows:

$$\begin{pmatrix} E_{-N}^{(0)} + V_{-N,-N} & V_{-N,-N+1} & V_{-N,-N+2} & \cdots & V_{-N,N} \\ V_{-N+1,-N} & E_{-N+1}^{(0)} + V_{-N+1,-N+1} & V_{-N+1,-N+2} & \cdots & V_{-N+1,N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ V_{N,-N} & V_{N,-N+1} & V_{N,-N+2} & \cdots & E_N^{(0)} V_{N,N} \end{pmatrix} \begin{pmatrix} c_{-N} \\ c_{-N+1} \\ \vdots \\ c_N \end{pmatrix} = E \begin{pmatrix} c_{-N} \\ c_{-N+1} \\ \vdots \\ c_N \end{pmatrix} \tag{34}$$

If the potential is given, we can calculate all the matrix components. We can get the eigen energies for a K by diagonalizing the matrix. We can draw the band structure by plotting the eigenenergies for various K ($-\pi/a \le K \le \pi/a$).

3 Plane wave basis: 2D case

We will extend the discussion of plane wave basis for 2D periodic potential with the lattice vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$. The Broch condition for 2D lattice is expressed as follows:

$$\psi(\boldsymbol{r}) = e^{i\boldsymbol{K}\cdot\boldsymbol{r}} u_{\boldsymbol{k}}(\boldsymbol{r}), \tag{35}$$

where $\boldsymbol{r} = (x, y)$, $\boldsymbol{K} = (K_x, K_y)$, and $\boldsymbol{K}$ in the first Brillouin zone (BZ). $u_{\boldsymbol{k}}(\boldsymbol{r})$ is a periodic function, which satisfies $u_{\boldsymbol{k}}(\boldsymbol{r}) = u_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{R})$, where $\boldsymbol{R} = i\boldsymbol{a}_1 + j\boldsymbol{a}_2$ (i and j are the integers). The Schrödinger equation for the unperturbed 2D system is expressed as follows:

$$\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}\right) |\psi_{n,m}^{(0)}\rangle = H_0 \, |\psi_n^{(0)}\rangle = E_n^{(0)} \, |\psi_{n,m}^{(0)}\rangle \, . \tag{36}$$

The wave function satisfying the Broch condition is expressed as follows:

$$u_{\boldsymbol{k}}(\boldsymbol{r}) = \exp\{i(n\boldsymbol{b}_1 + m\boldsymbol{b}_2)\cdot\boldsymbol{r}\}. \tag{37}$$

Here, n and m are integers, and $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ are the reciprocal vectors defined as follows:

$$\begin{aligned}
\boldsymbol{b}_1 &= \frac{2\pi}{V}\boldsymbol{a}_2 \times \boldsymbol{a}_3, && (38)\\
\boldsymbol{b}_2 &= \frac{2\pi}{V}\boldsymbol{a}_3 \times \boldsymbol{a}_1, && (39)\\
\boldsymbol{a}_3 &= (0,0,1), V = \boldsymbol{a}_3 \cdot \boldsymbol{a}_1 \times \boldsymbol{a}_2. && (40)
\end{aligned}$$

Note that the reciprocal vectors and lattice vectors satisfies the following relation:

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij}. \tag{41}$$

To summarize, the wavefunction for the 2D system without potential is expressed as follows:

$$|\psi^{(0)}_{n,m}\rangle = \psi^{(0)}_{n,m}(\boldsymbol{r}) = e^{i\boldsymbol{K}\cdot\boldsymbol{r}}e^{i(n\boldsymbol{b}_1+m\boldsymbol{b}_2)\cdot\boldsymbol{r}} \tag{42}$$

The eigenenergy is calculated from the Schrödinger equation :

$$E^{(0)}_{n,m} = \frac{\hbar^2}{2m}(\boldsymbol{K} + n\boldsymbol{b}_1 + m\boldsymbol{b}_2)^2. \tag{43}$$

We will use the linear combination of eq. 42for expressing the states in a perturbated system:

$$|\psi\rangle = \sum_{n=-N}^{N}\sum_{m=-M}^{M} c_{n,m}\,|\psi^{(0)}_{n,m}\rangle \tag{44}$$

Note that because of 2D, we have two quantum numbers, n and m. We limit the number of bases to $|n| \neq N$ and $|m| \neq M$.

Let us consider a 2D potential, expressed by $V(\boldsymbol{r})$ ($V(\boldsymbol{r}+\boldsymbol{R}) = V(\boldsymbol{r})$). The Schrödinger equation is expressed as follows:

$$\begin{aligned}
(H_0 + V(\boldsymbol{r}))\,|\psi\rangle &= E\,|\psi\rangle && (45)\\
\therefore (H_0 + V(\boldsymbol{r}))\sum_{n=-N}^{N}\sum_{m=-M}^{M} c_{n,m}\,|\psi^{(0)}_{n,m}\rangle &= E\sum_{n=-N}^{N}\sum_{m=-M}^{M} c_{n,m}\,|\psi^{(0)}_{n,m}\rangle\,. && (46)
\end{aligned}$$

Multiplying $\langle\psi^{(0)}_{n',m'}|$ on both sides yields the following equation:

$$\sum_{all\ n,m} c_{n,m}\,\langle\psi^{(0)}_{n',m'}|H_0|\psi^{(0)}_{n,m}\rangle + \sum_{all\ n,m} c_{n,m}\,\langle\psi^{(0)}_{n',m'}|V(\boldsymbol{r})|\psi^{(0)}_{n,m}\rangle = E\sum_{all\ n,m} c_{n,m}\,\langle\psi^{(0)}_{n',m'}|\psi^{(0)}_{n,m}\rangle\,. \tag{47}$$

The first term is calculated as follows:

$$\begin{aligned}
\sum_{all\ n,m} c_{n,m}\,\langle\psi^{(0)}_{n',m'}|H_0|\psi^{(0)}_{n,m}\rangle &= \sum_{all\ n,m} c_{n,m}E^{(0)}_{n,m}\,\langle\psi^{(0)}_{n',m'}|\psi^{(0)}_{n,m}\rangle && (48)\\
&= E^{(0)}_{n',m'}c_{n',m'}. && (49)
\end{aligned}$$

We will express the following expression for the second term:

$$\begin{aligned}
V_{(n',m'),(n,m)} &= \langle\psi^{(0)}_{n',m'}|V(\boldsymbol{r})|\psi^{(0)}_{n,m}\rangle && (50)\\
&= \int e^{-i\boldsymbol{K}\cdot\boldsymbol{r}}e^{-i(n'\boldsymbol{b}_1+m'\boldsymbol{b}_2)\cdot\boldsymbol{r}}V(\boldsymbol{r})e^{i\boldsymbol{K}\cdot\boldsymbol{r}}e^{i(n\boldsymbol{b}_1+m\boldsymbol{b}_2)\cdot\boldsymbol{r}}d\boldsymbol{r} && (51)\\
&= \int e^{-i((n'-n)\boldsymbol{b}_1+(m'-m)\boldsymbol{b}_2)\cdot\boldsymbol{r}}V(\boldsymbol{r})d\boldsymbol{r} && (52)
\end{aligned}$$

Note that $V_{(n',m'),(n,m)}$ is independent on $\boldsymbol{K}$. The right side is calculated as follows:

$$E \sum_{all\ n,m} c_{n,m} \langle \psi^{(0)}_{n',m'} | \psi^{(0)}_{n,m} \rangle = E c_{n',m'}. \tag{53}$$

To summarize, eq. 47 is simplified to be

$$E^{(0)}_{n',m'} c_{n',m'} + \sum_{all\ n,m} c_{n,m} V_{(n',m'),(n,m)} = E c_{n',m'}. \tag{54}$$

By repeating the same process for all the combination of n and m, we get $(2N+1) \times (2M+1)$ equations (remind that $-N \leq n \leq N$ and $-M \leq m \leq M$).

$$\begin{pmatrix} E^{(0)}_{-N,-M} + V_{(-N,-M),(-N,-M)} & V_{(-N,-M),(-N,-M+1)} & \cdots & V_{(-N,-M),(N,M)} \\ V_{(-N,-M+1),(-N,-M)} & E^{(0)}_{-N,-M+1} + V_{(-N,-M+1),(-N,-M+1)} & \cdots & V_{(-N,-M+1)(N,M)} \\ V_{(-N,-M+2),(-N,-M)} & V_{(-N,-M+2)(-N,-M+1)} & \cdots & V_{(-N,-M+2),(N,M)} \\ \vdots & \vdots & \vdots & \vdots \\ V_{(-N,M),(-N,-M)} & V_{(-N,M)(-N,-M+1)} & \cdots & V_{(-N,M),(N,M)} \\ V_{(-N+1,-M),(-N,-M)} & V_{(-N+1,-M),(-N,-M+1)} & \cdots & V_{(-N+1,-M)(N,M)} \\ \vdots & \vdots & \vdots & \vdots \\ V_{(N,M),(-N,-M)} & V_{(N,M),(-N,-M+1)} & \cdots & E^{(0)}_{N,-M} + V_{(N,M),(N,M)} \end{pmatrix} \begin{pmatrix} c_{-N,-M} \\ c_{-N,-M+1} \\ c_{-N,-M+2} \\ \vdots \\ c_{-N,M} \\ c_{-N+1,-M} \\ \vdots \\ c_{N,M} \end{pmatrix} = \mathrm{E} \begin{pmatrix} c_{-N,-M} \\ c_{-N,-M+1} \\ c_{-N,-M+2} \\ \vdots \\ c_{-N,M} \\ c_{-N+1,-M} \\ \vdots \\ c_{N,M} \end{pmatrix} \tag{55}$$

If the 2D potential is given, we can calculate all the components of the matrix. Diagonalizing the matrix allows us to get the eigen energies for a $\boldsymbol{K}$. By plotting the eigenenergies for various $\boldsymbol{K}$ ($\boldsymbol{K}$ in BZ), we can draw the band structure.