第十次作业

截止时间：2020. 5. 15（周五）17:00

姓名：陈 稼 霖
学号：45875852
成绩：________

第 1 题 ((15.1) ‡Nearly Free Electron Model) 得分: ________. Consider an electron in a weak periodic potential in one dimension $V(x) = V(x+a)$. Write the periodic potential as

$$V(x) = \sum_G e^{iGx} V_G$$

where the sum is over the reciprocal lattice $G = 2\pi n/a$, and $V_G^* = V_{-G}$ assure that the potential $V(x)$ is real.

(a) Explain why for k near to a Brillouin zone boundary (such as k near π/a) the electron wave-function should be taken to be

$$\psi = Ae^{ikx} + Be^{i(k+G)x} \tag{15.14}$$

where G is a reciprocal lattice vector such that $|k|$ is close to $|k+G|$.

(b) For an electron of mass m with k exactly at a zone boundary, use the above form of the wavefunction to show that the eigenenergies at this wavevector are

$$E = \frac{\hbar^2 k^2}{2m} + V_0 \pm |V_G|$$

where G is chosen so $|k| = |k+G|$.

- ▷ Give a qualitative explanation of why these two states are separated in energy by $2|V_G|$.
- ▷ Give a sketch (don't do a full calculation) of the energy as a function of k in both the extended and the reduced zone schemes.

(c) * Now consider k close to, but not exactly at, the zone boundary. Give an expression for the energy $E(k)$ correct to order $(\delta k)^2$ where δk is the wavevector difference from k to the zone boundary wavevector.

- ▷ Calculate the effective mass of electron at this wavevector.

解: (a) 因为在布里渊区边界处，波矢为k的电子和波矢为$k+G$的电子具有相近的能量，所以当使用微扰理论时，能量的二阶修正项的分母趋于0，此时必须采用简并微扰理论。在由$|k\rangle$和$|k+G\rangle$组成的子希尔伯特空间中，求解哈密顿矩阵

$$H = \begin{pmatrix} E_0 & V_G \\ V_G^* & E_0 \end{pmatrix} \tag{1}$$

的本征函数，就会得到其本征函数是两个波函数$|k\rangle = e^{ikx}$，$|k+G\rangle = e^{i(k+G)x}$的线性组合.

(b) ▷ 定性的解释：在布里渊区边界处，状态$|k\rangle$和$|k+G\rangle$简并，周期性势场作为一种微扰存在，将这两个能级的简并去除了.
定量的解释：本征态的能量可通过求解哈密顿的本征值得到. 在布里渊区边界处，电子的哈密顿矩阵的各个矩阵元为

$$\langle k|H|k\rangle = \frac{\hbar^2 k^2}{2m} + V_0, \tag{2}$$

$$\langle k+G|H|k+G\rangle = \frac{\hbar^2 (k+G)^2}{2m} + V_0, \tag{3}$$

$$\langle k|H|k+G\rangle = V_G, \tag{4}$$

$$\langle k+G|H|k\rangle = V_G^*. \tag{5}$$

因此哈密顿矩阵为

$$H = \begin{pmatrix} \frac{\hbar^2 k^2}{2m} + V_0 & V_G \\ V_G^* & \frac{\hbar^2 (k+G)^2}{2m} + V_0 \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2}{2m}\left(-\frac{\pi}{a}\right)^2 + V_0 & V_G \\ V_G^* & \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 \end{pmatrix}. \tag{6}$$

哈密顿矩阵的特征方程为

$$\begin{aligned}|H-EI|=&\begin{vmatrix}\frac{\hbar^2}{2m}\left(-\frac{\pi}{a}\right)^2+V_0-E & V_G\\ V_G^* & \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2+V_0-E\end{vmatrix}\\=&E^2-2\left[\frac{\hbar^2}{2m}\left(-\frac{\pi}{a}\right)^2+V_0\right]E+\left[\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2+V_0\right]^2-|V_G|^2=0.\end{aligned}\tag{7}$$

解得哈密顿矩阵的本征值即为

$$E=\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2+V_0\pm|V_G|.\tag{8}$$

▷ 简约布里渊区和拓展布里渊区的色散关系如图1.

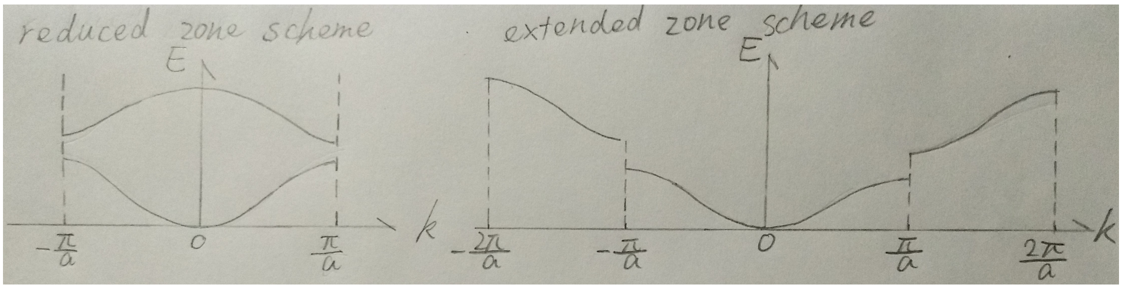

图 1: 简约布里渊区和拓展布里渊区的色散关系.

(c) 当波矢k与布里渊区边界相差δk，哈密顿矩阵为

$$H=\begin{pmatrix}\frac{\hbar^2k^2}{2m}+V_0 & V_G\\ V_G^* & \frac{\hbar^2(k+G)^2}{2m}+V_0\end{pmatrix}=\begin{pmatrix}\frac{\hbar^2}{2m}\left(-\frac{\pi}{a}+\delta k\right)^2+V_0 & V_G\\ V_G^* & \frac{\hbar^2}{2m}\left(\frac{\pi}{a}+\delta k\right)^2+V_0\end{pmatrix}.\tag{9}$$

哈密顿矩阵的特征方程为

$$\begin{aligned}|H-EI|=&\begin{vmatrix}\frac{\hbar^2}{2m}\left(-\frac{\pi}{a}+\delta k\right)^2+V_0-E & V_G\\ V_G^* & \frac{\hbar^2}{2m}\left(\frac{\pi}{a}+\delta k\right)^2+V_0-E\end{vmatrix}\\=&E^2+2\left\{\frac{\hbar^2}{2m}\left[\left(\frac{\pi}{a}\right)^2+(\delta k)^2\right]+V_0^2\right\}E\\&+\left\{\frac{\hbar^2}{2m}\left[\left(\frac{\pi}{a}\right)^2-2\left(\frac{\pi}{a}\right)\delta k+(\delta k)^2\right]+V_0\right\}\left\{\frac{\hbar^2}{2m}\left[\left(\frac{\pi}{a}\right)^2+2\left(\frac{\pi}{a}\right)\delta k+(\delta k)^2\right]+V_0\right\}-|V_G|^2=0.\end{aligned}\tag{10}$$

$$\Longrightarrow\left\{E-\frac{\hbar^2}{2m}\left[\left(\frac{\pi}{a}\right)^2+(\delta k)^2\right]-V_0\right\}^2=\left(\frac{\hbar^2}{2m}2\frac{\pi}{a}\delta k\right)^2+|V_G|^2.\tag{11}$$

解得本征能量为

$$E=\frac{\hbar^2}{2m}\left[\left(\frac{\pi}{a}\right)^2+(\delta k)^2\right]+V_0\pm\sqrt{\left(\frac{\hbar^2}{2m}2\frac{\pi}{a}\delta k\right)^2+|V_G|^2}.\tag{12}$$

将上式做级数展开并保留到二阶项得

$$\begin{aligned}E=&\frac{\hbar^2}{2m}\left[\left(\frac{\pi}{a}\right)^2+(\delta k)^2\right]+V_0\pm|V_G|\left[1\pm2\left(\frac{\hbar^2}{2m}\frac{\pi}{a}\delta k\right)^2\right]\\=&\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2+V_0\pm|V_G|^2+\frac{\hbar^2}{2m}(\delta k)^2\left[1\pm\frac{\hbar^2}{m}\left(\frac{\pi}{a}\right)^2\frac{1}{|V_G|}\right].\end{aligned}\tag{13}$$

▷ 电子的有效质量为

$$m^* = \frac{\hbar^2(\delta k)^2}{2E(\delta k)} = \frac{\hbar^2\,(\delta k)^2}{2\left\{\frac{\hbar^2}{2m}(\delta k)^2\left[1\pm\frac{\hbar^2}{m}\left(\frac{\pi}{a}\right)^2\frac{1}{|V_G|}\right]\right\}} = m\left[1\pm\frac{\hbar^2}{m}\left(\frac{\pi}{a}\right)^2\frac{1}{|V_G|}\right].$$

□

第 2 题 ((15.2) Periodic Functions) 得分: ________. Consider a lattice of points $\{\boldsymbol{R}\}$ and a function $\rho(\boldsymbol{x})$ which has the periodicity of the lattice $\rho(\boldsymbol{x}) = \rho(\boldsymbol{x}+\boldsymbol{R})$. Show that ρ can be written as

$$\rho(\boldsymbol{x}) = \sum_{\boldsymbol{G}} \rho_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{x}}$$

where the sum is over points $\boldsymbol{G}$ in the reciprocal lattice.

解: 由函数$\rho(\boldsymbol{x})$的周期性，有

$$\rho(\boldsymbol{x}) = \frac{1}{N}\sum_{\boldsymbol{R}}\rho(\boldsymbol{x}+\boldsymbol{R}). \tag{14}$$

对$\rho(\boldsymbol{x}+\boldsymbol{R})$做傅里叶变换得

$$\begin{aligned}\rho(\boldsymbol{x}) =& \frac{V}{N}\sum_{\boldsymbol{R}}\int\frac{d\boldsymbol{k}}{(2\pi)^3}\rho_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot(\boldsymbol{x}+\boldsymbol{R})}\\ =&\frac{V}{N}\int\frac{d\boldsymbol{k}}{(2\pi)^3}\rho_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\sum_{\boldsymbol{R}}e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\\ =&\frac{V}{N}\int\frac{d\boldsymbol{k}}{(2\pi)^3}\rho_k e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\frac{(2\pi)^3}{v}\sum_{\boldsymbol{G}}\delta^3(\boldsymbol{k}-\boldsymbol{G})\\ =&\sum_{\boldsymbol{G}}\rho_{\boldsymbol{G}e^{i\boldsymbol{G}\cdot\boldsymbol{x}}}.\end{aligned} \tag{15}$$

□

第 3 题 ((15.3) Tight binding Bloch Wavfunctions) 得分: ________. Analogous to the wavefunction introduced in Chapter 11, consider a tight-binding wave ansatz of the form

$$|\psi\rangle = \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}}|\boldsymbol{R}\rangle$$

where the sum is over the points $\boldsymbol{R}$ of a lattice, and $|\psi\rangle$ is the ground-state wavefunction of a electron bound to a nucleus on site $\boldsymbol{R}$. In real space this ansatz can be expressed as

$$\psi(\boldsymbol{r}) = \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\varphi(\boldsymbol{r}-\boldsymbol{R}).$$

Show that this wavefunction is of the form required by Bloch' theorem (i.e., show it is a modified plane wave).

解: 上述的波函数可化为

$$\psi(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\sum_{\boldsymbol{R}}e^{i\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{r})}\varphi(\boldsymbol{r}-\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u(\boldsymbol{r}), \tag{16}$$

其中

$$u(\vec{r}) \equiv \sum_{\boldsymbol{R}}e^{i\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{r})}\varphi(\boldsymbol{r}-\boldsymbol{R}). \tag{17}$$

因为当将$\boldsymbol{r}$平移一个晶格基矢，$\boldsymbol{r}\rightarrow\boldsymbol{r}+\boldsymbol{a}$

$$u(\vec{r}+\boldsymbol{a})=\sum_{\boldsymbol{R}}e^{i\boldsymbol{k}\cdot[(\boldsymbol{R}-\boldsymbol{a})-\boldsymbol{r}]}\varphi(\boldsymbol{r}-(\boldsymbol{R}-\boldsymbol{a}))=\sum_{\boldsymbol{R}-\boldsymbol{a}}e^{i\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{r})}\varphi(\boldsymbol{r}-\boldsymbol{R}),\tag{18}$$

根据平移群的性质，将群内的所有矢量与一个晶格基矢相减，得到的仍然是原先的平移群，$\boldsymbol{R}-\boldsymbol{a}\rightarrow\boldsymbol{R}$，故

$$u(\vec{r}+\boldsymbol{a})=\sum_{\boldsymbol{R}}e^{i\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{r})}\varphi(\boldsymbol{r}-\boldsymbol{R})=u(\vec{r}),\tag{19}$$

$u(\vec{r})$是一个以$\boldsymbol{a}$为周期的周期函数，故$\psi(\boldsymbol{r})$满足布洛赫定理要求的形式. □

第 4 题 ((15.4) *Nearly Free Electrons in Two Dimensions) 得分: ________. Consider the nearly free electron model for a square lattice with lattice constant a. Suppose the periodic potential is given by

$$\begin{aligned}V(x,y)=&2V_{10}[\cos(2\pi x/a)+\cos(2\pi y/a)]\\&+4V_{11}[\cos(2\pi x/a)\cos(2\pi y/a)]\end{aligned}$$

(a) Use the nearly free electron model to find the energies of states at wavevector $\boldsymbol{G}=(\pi/a,0)$.

(b) Calculate the energies of the states at wavevector $\boldsymbol{G}=(\pi/a,\pi/a)$. (Hint: You should write down a 4 by 4 secular determinant, which looks difficult, but a actually factors nicely. Make use of adding together rows or columns of the determinant before trying to evaluate it!)

解: (a) $\boldsymbol{G}$处于x方向上的布里渊区边界，y方向上的布里渊区中心，故其能量应当等于一维周期势场中布里渊区边界处的能量，其能量应为

$$E=\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\pm|V_{\boldsymbol{G}}|,\tag{20}$$

其中

$$\begin{aligned}|V_{\boldsymbol{G}}|=&|\langle(-\pi/a,0)|V(x,y)|(\pi/a,0)\rangle|\\=&\left|\frac{1}{a^2}\int_{-a/2}^{a/2}dx\int_{-a/2}^{a/2}dy\,(e^{-i\pi x/a})^*\{2V_{10}[\cos(2\pi x/a)+\cos(2\pi y/a)]+4V_{11}[\cos(2\pi x/a)\cos(2\pi y/a)]\}e^{i\pi x/a}\right|\\=&|V_{10}|\,.\end{aligned}\tag{21}$$

(b) 状态$|(\pi/a,\pi/a)\rangle$和状态$|(\pi/a,-\pi/a)\rangle,|(-\pi/a,-\pi/a)\rangle,|(-\pi/a,\pi/a)\rangle$简并，在以这四个状态依次为基矢组成的子希尔伯特空间中，如式21那样，用

$$H_{i,j}=\langle\psi_i|H|\psi_j\rangle\tag{22}$$

我们可以算出哈密顿矩阵的各个矩阵元，从而得到哈密顿矩阵为

$$H=\begin{pmatrix}\varepsilon&V_{10}&V_{11}&V_{10}\\V_{10}&\varepsilon&V_{10}&V_{11}\\V_{11}&V_{10}&\varepsilon&V_{10}\\V_{10}&V_{11}&V_{10}&\varepsilon\end{pmatrix},\tag{23}$$

其中$\varepsilon=\frac{\hbar^2}{2m}\left[\left(\frac{\pi}{a}\right)^2+\left(\frac{\pi}{a}\right)^2\right]$为自由电子的能量. 这一哈密顿矩阵的特征方程为

$$|H-EI|=\begin{vmatrix}\varepsilon-E&V_{10}&V_{11}&V_{10}\\V_{10}&\varepsilon-E&V_{10}&V_{11}\\V_{11}&V_{10}&\varepsilon-E&V_{10}\\V_{10}&V_{11}&V_{10}&\varepsilon-E\end{vmatrix}=0.\tag{24}$$

对这一行列式做如下操作：用第一行减去第三行，用第二行减去第四行，得到

$$\begin{vmatrix} \varepsilon - E - V_{11} & 0 & V_{11} - \varepsilon + E & 0 \\ 0 & \varepsilon - E - V_{11} & 0 & V_{11} - \varepsilon + E \\ V_{11} & V_{10} & \varepsilon - E & V_{10} \\ V_{10} & V_{11} & V_{10} & \varepsilon - E \end{vmatrix} = 0. \tag{25}$$

然后再将第三列加到第一列，将第四列加到第二列，得到

$$\begin{aligned} &\begin{vmatrix} 0 & 0 & V_{11} - \varepsilon + E & 0 \\ 0 & 0 & 0 & V_{11} - \varepsilon + E \\ \varepsilon - E + V_{11} & 2V_{10} & \varepsilon - E & V_{10} \\ 2V_{10} & \varepsilon - E + V_{11} & V_{10} & \varepsilon - E \end{vmatrix} \\ =&(V_{11} - \varepsilon + E)^2[(\varepsilon - E + V_{11})^2 - 4V_{10}^2] = 0. \end{aligned} \tag{26}$$

解得本征能量为

$$E_1 = E_2 = \varepsilon - V_{11}, \quad E_3 = \varepsilon + V_{11} - 2V_{10}, \quad E_4 = \varepsilon + V_{11} + 2V_{10}. \tag{27}$$

□

第 5 题 ((15.6) Kronig-Penney Model*) 得分: ________. Consider electrons of mass m in a so-called "delta-function comb" potential in one dimension

$$V(x) = aU \sum_n \delta(x - na)$$

(a) Argue using the Schrodinger equation that in-between delta functions, an eigenstate of energy E is always of a plane wave form $e^{iq_E x}$ with

$$q_E = \sqrt{2mE}/\hbar.$$

Using Bloch's theorem conclude that we can write an eigenstate with energy E as

$$\psi(x) = e^{ikx} u_E(x)$$

where $u(E)$ is a periodic function defined as

$$u_E(x) = A \sin(q_E x) + B \cos(q_E x) \quad 0 < x < a$$

and $u_E(x) = u_E(x + a)$ defines u outside of this interval.

(b) Using continuity of the wavefunction at $x = 0$ derive

$$B = e^{-ika}[A \sin(q_E a) + B \cos(q_E a)],$$

and using the Schrodinger equation to fix the discontinuity in slope at $x = 0$ derive

$$q_E A - e^{ikx} q_E [A \cos(q_E a) - B \sin(q_E a)] = 2maUB/\hbar^2$$

Solve these two equations to obtain

$$\cos(ka) = \cos(q_E a) + \frac{mUa}{\hbar^2 q_E} \sin(q_E a)$$

The left-hand side of this equation is always between -1 and 1, but the right-hand side is not. Conclude that there must be values of E for which there are no solutions of the Schrodinger equation — hence concluding there are gap in the spectrum.

(c) For small values of the potential U show that this result agrees with the prediction of the nearly free electron model (i.e., determine the size of the gap at the zone boundary).

解: (a) 在两个delta势之间，由于势能为0，所以薛定谔方程为

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)=E, \tag{28}$$

这是典型的波动方程的形式，其波函数必为平面波的形式：

$$\psi(x)=\alpha e^{iq_Ex}+\beta e^{-iq_Ex}=A\sin(q_Ex)+B\cos(q_Ex). \tag{29}$$

其中$q_E=\sqrt{2mE}/\hbar$. 根据布洛赫定理，波函数可化为这样的形式

$$\psi(x)=e^{ikx}u_E(x), \tag{30}$$

其中$u_E(x)$是以a为周期的函数. 故

$$\psi(x+a)=e^{ik(x+a)}u_E(x+a)=e^{ik(x+a)}u_E(x)=e^{ika}\psi(x). \tag{31}$$

且$u_E(x)$也具有如下的形式：

$$u_E(x)=\frac{\psi(x)}{e^{ikx}}=\alpha e^{i(q_E-k)x}+\beta e^{-i(q_E+k)x}=A'\sin((q_E-k)x)+B'\cos((q_E-k)x). \tag{32}$$

(b) 根据u的周期性，其在$x=0$处的函数值应当等于在$x=a$处的函数值

$$u_E(0)=B=u_E(a)=e^{-ika}[A\sin(q_Ea)+B\cos(q_Ea)]. \tag{33}$$

波函数的导数为

$$\psi(x)=Aq_E\cos(q_Ex)-Bq_E\sin(q_Ex). \tag{34}$$

在$x=0$处对薛定谔方程两边关于x进行积分，得到

$$\begin{aligned}\int_{0^-}^{0^+}dx\,\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)=&-\frac{\hbar^2}{2m}[\psi'(0^+)-\psi'(0^-)]=-\frac{\hbar^2}{2m}[\psi'(0^+)-e^{-ika}\psi'(a^-)]\\ =&-\frac{\hbar^2}{2m}[Aq_E-e^{-ika}(Aq_E\cos(q_Ea)-Bq_E\sin(q_Ea))]\\ =&\int_{0^-}^{0^+}aU\sum_n\delta(x-na)\psi(x)\,dx \qquad (35)\\ =&aUB. \qquad (36)\end{aligned}$$

$$\Longrightarrow q_EA-e^{-ika}q_E[A\cos(q_Ea)-B\sin(q_Ea)]=-\frac{2maUB}{\hbar^2}. \tag{37}$$

将式34代入式36，消去A和B，可得

$$\cos(ka)=\cos(q_Ea)+\frac{mUa}{\hbar^2q_E}\sin(q_Ea). \tag{38}$$

上式左侧的取值范围为$[-1,1]$，而右侧则可能在这一范围之外，因此当E取某些值时，薛定谔方程无解而产生带隙.

(c) 在布里渊区边界$k=\frac{\pi}{a}$附近，$q_E\approx k+\delta$，上式化为

$$-1=\cos(\pi+\delta a)+\frac{mUa}{\hbar^2(\frac{\pi}{a}+\delta)}\sin(\pi+\delta a). \tag{39}$$

上式右边关于δ展开并保留到二阶项，得

$$-1=-1+\frac{1}{2}(\delta a)^2-\frac{mUa}{\hbar^2\pi}(1+\frac{\delta a}{\pi})\delta a, \tag{40}$$

$$\Longrightarrow\delta=0\text{或}\approx\frac{2mUa}{\hbar^2\pi}. \tag{41}$$

电子的能量为

$$E=\frac{\hbar^2}{2m}\left(\frac{\pi}{a}+\delta\right)^2\approx E_0\text{或}\approx E_0+2U_0. \tag{42}$$

其中

$$V_G=\frac{1}{a}\int_{-a/2}^{a/2}dx\,e^{-iGx}V(x)e^{iGx}=U. \tag{43}$$

带隙$2\left|U\right|=2\left|V_G\right|$与用进自由电子计算得到的一致.

□