Problem 1. Bloch's theorem   Prove Bloch's theorem by operating with the translation operator on $H\psi$ and using the periodic symmetry of the potential. Show furthermore that $T_{\mathbf{R}}T_{\mathbf{R}'} = T_{\mathbf{R}'}T_{\mathbf{R}} = T_{\mathbf{R}+\mathbf{R}'}$; the translation operators commute with themselves.

Solution.   Bloch's theorem is given by (8.6) of Ashcroft & Mermin:

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

Additionally, $H\psi(\mathbf{r})$ is given by (4.1):

$$H\psi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right)\psi(\mathbf{r}).$$

According to (4.5) in the lecture notes, the action of the translation operator is $T_{\mathbf{R}}f(\mathbf{r}) = f(\mathbf{r}+\mathbf{R})$. Operating on $H\psi$ yields [1, p. 134]

$$
\begin{aligned}
T_{\mathbf{R}}(H\psi) &= H(\mathbf{r}+\mathbf{R})\psi(\mathbf{r}+\mathbf{R}) \\
&= \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}+\mathbf{R})\right)\psi(\mathbf{r}+\mathbf{R}) \\
&= \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right)\psi(\mathbf{r}+\mathbf{R}) \\
&= H(\mathbf{r})\psi(\mathbf{r}+\mathbf{R}) \\
&= HT_{\mathbf{R}}\psi,
\end{aligned}
$$

since $U(\mathbf{r}) = U(\mathbf{r}+\mathbf{R})$ for all $\mathbf{R}$ in a Bravais lattice according to p. 35 of the lecture notes. Thus we have shown

$$T_{\mathbf{R}}H = HT_{\mathbf{R}};$$

that is, H and $T_{\mathbf{R}}$ commute.

Note also that

$$T_{\mathbf{R}}T_{\mathbf{R}'}f(\mathbf{r}) = T_{\mathbf{R}}f(\mathbf{r}+\mathbf{R}') = f(\mathbf{r}+\mathbf{R}'+\mathbf{R}) = f(\mathbf{r}+\mathbf{R}+\mathbf{R}') = T_{\mathbf{R}'}f(\mathbf{r}+\mathbf{R}) = T_{\mathbf{R}'}T_{\mathbf{R}}f(\mathbf{r})$$

and that

$$T_{\mathbf{R}+\mathbf{R}'}f(\mathbf{r}) = f(\mathbf{r}+\mathbf{R}+\mathbf{R}'),$$

so we have shown that

$$T_{\mathbf{R}}T_{\mathbf{R}'} = T_{\mathbf{R}'}T_{\mathbf{R}} = T_{\mathbf{R}+\mathbf{R}'}. \qquad \square$$

Since H and $T_{\mathbf{R}}$ commute and the $T_{\mathbf{R}}$s commute with each other, they can be simultaneously diagonalized. We can apply (4.8) of the lecture notes:

$$H\psi = E\psi, \qquad\qquad\qquad T_{\mathbf{R}}\psi = c(\mathbf{R})\psi. \tag{2}$$

Now applying what we have just proven about the $T_{\mathbf{R}}$s,

$$c(\mathbf{R})c(\mathbf{R}')\psi = T_{\mathbf{R}}T_{\mathbf{R}'}\psi = T_{\mathbf{R}+\mathbf{R}'}\psi = c(\mathbf{R}+\mathbf{R}')\psi \quad\implies\quad c(\mathbf{R})c(\mathbf{R}') = c(\mathbf{R}+\mathbf{R}'). \tag{3}$$

From Ashcroft & Mermin (4.1), any position vector $\mathbf{R}$ on the Bravais lattice can be written

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3,$$

where the n_i are integers. So using Eq. (3), we can write

$$c(\mathbf{R}) = c(n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3) = c(n_1\mathbf{a}_1)c(n_2\mathbf{a}_2)c(n_3\mathbf{a}_3) = c(\mathbf{a}_1)^{n_1}c(\mathbf{a}_2)^{n_2}c(\mathbf{a}_3)^{n_3}. \tag{4}$$

We define the numbers k_i such that (4.10) of the lecture notes is satisfied:

$$c(\mathbf{a}_i) = e^{2\pi i k_i},$$

where $\mathbf{a}_i$ are the primitive vectors of the lattice. Applying this to Eq. (4),

$$c(\mathbf{R}) = (e^{2\pi i k_1})^{n_1}(e^{2\pi i k_2})^{n_2}(e^{2\pi i k_3})^{n_3} = e^{2\pi i (k_1 n_1 + k_2 n_2 + k_3 n_3)} = e^{i\mathbf{k}\cdot\mathbf{R}}, \tag{5}$$

where

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3$$

from Ashcroft & Mermin (5.6) is any vector on the reciprocal lattice (with primitive vectors $\mathbf{b}_i$), and we have applied their (4.8),

$$\mathbf{k}\cdot\mathbf{R} = 2\pi((k_1 n_1 + k_2 n_2 + k_3 n_3).$$

Putting Eq. (5) together with Eq. (2) and the definition of $T_\mathbf{R}$, we have

$$\psi(\mathbf{r} + \mathbf{R}) = T_\mathbf{R}\psi(\mathbf{r}) = c(\mathbf{R})\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r}),$$

which is Bloch's theorem [1, pp. 134–135].   □

Problem 2.   Another proof of Bloch's theorem   A more elegant way to prove Bloch's theorem is to note that the translation operator can be written

$$T_\mathbf{R} = e^{-i\mathbf{p}\cdot\mathbf{R}/\hbar},$$

where $\mathbf{p} = -i\hbar\nabla$ is the momentum operator. By multiplying by the bra $\langle\mathbf{k}|$ (an eigenfunction of momentum), show that either $\langle\mathbf{k}|\psi\rangle = 0$, or $c(\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}$.

Solution.   We will proceed in a similar manner as before. Adapting (4.1) of the lecture notes to Dirac notation, we have

$$H\,|\psi\rangle = \left(\frac{\mathbf{p}^2}{2m} + U(\mathbf{r})\right)|\psi\rangle.$$

Multiplying by $T_\mathbf{R}$ on the left,

$$T_\mathbf{R}H\,|\psi\rangle = e^{-i\mathbf{p}\cdot\mathbf{R}/\hbar}\left(\frac{\mathbf{p}^2}{2m} + U(\mathbf{r})\right)|\psi\rangle$$

$$= \left(\frac{\mathbf{p}^2}{2m}e^{-i\mathbf{p}\cdot\mathbf{R}/\hbar} + U(\mathbf{r}+\mathbf{R})\right)|\psi\rangle$$

$$= \left(\frac{\mathbf{p}^2}{2m}e^{-i\mathbf{p}\cdot\mathbf{R}/\hbar} + U(\mathbf{r}-\mathbf{R})\right)|\psi\rangle$$

$$= HT_\mathbf{R}\,|\psi\rangle,$$

where we have used

$$T_\mathbf{R}U(\mathbf{r}) = U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r}-\mathbf{R}) = U(\mathbf{r})T_\mathbf{R},$$

which is the unitarity of the translation operator [2, p. 45], and the fact that $U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r}) = U(\mathbf{r}-\mathbf{R})$.

Since $\mathbf{k}$ is a momentum eigenstate, define $\mathbf{k} = (k_1, k_2, k_3)$ for constant k_i such that $\mathbf{p}\,|\mathbf{k}\rangle = \hbar\mathbf{k}\,|\mathbf{k}\rangle$. Then

$$T_{\mathbf{R}}\,|\mathbf{k}\rangle = e^{-i\mathbf{p}\cdot\mathbf{R}/\hbar}\,|\mathbf{k}\rangle = e^{-i\mathbf{k}\cdot\mathbf{R}}\,|\mathbf{k}\rangle\,.$$

The proof that $T_{\mathbf{R}}T_{\mathbf{R'}} = T_{\mathbf{R'}}T_{\mathbf{R}} = T_{\mathbf{R}+\mathbf{R'}}$ from 1 still applies in the new interpretation, as does the simultaneous diagonalization of H and $T_{\mathbf{R}}$. Writing (4.8) of the lecture notes in Dirac notation,

$$H\,|\psi\rangle = E\,|\psi\rangle\,, \qquad\qquad T_{\mathbf{R}}\,|\psi\rangle = c(\mathbf{R})\,|\psi\rangle\,.$$

Multiplying the second of these equations by $\langle\mathbf{k}|$ on the left,

$$c(\mathbf{R})\,\langle\mathbf{k}|\psi\rangle = \langle\mathbf{k}|c(\mathbf{R})|\psi\rangle = \langle\mathbf{k}|T_{\mathbf{R}}|\psi\rangle = \langle\mathbf{k}|e^{i\mathbf{k}\cdot\mathbf{R}}|\psi\rangle = e^{i\mathbf{k}\cdot\mathbf{R}}\,\langle\mathbf{k}|\psi\rangle\,,$$

which implies

$$c(\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \quad\text{or}\quad \langle\mathbf{k}|\psi\rangle = 0$$

as we wanted to show. $\square$

Problem 4. One-dimensional band Consider a one-dimensional system which is filled up to the first Brillouin zone boundary at $k = \pi/a$, and assume that there is a small gap produced by a single Fourier component of the lattice potential $U = U_{K=2\pi/a}$ (small meaning that $U/E_{K/2}^0 \ll 1$). Considering momenta close to the zone boundary, show that a good approximation for the energy dispersion of the bands is

$$E = E_0\left(1 \pm \sqrt{\frac{U^2}{E_0^2} + 4x^2}\right)$$

where $E_0 = E_{K/2}^0$ and $k = \pi(1+x)/a$, with $x \ll 1$.

Evaluate the change in electronic energy

$$E_{\text{elec}} = \sum_{k\text{ occ.}} [E(k; U_K) - E(k; U_K = 0)]$$

to leading order in U/E_0. (Hint: the result is non-analytic—don't try a Taylor series in U.)

Solution. As evaluated in 5(a),

$$E^{\pm} = \frac{E_{\mathbf{k}}^0 + E_{\mathbf{k}-2\pi/a}^0}{2} \pm \sqrt{\left(\frac{E_{\mathbf{k}}^0 - E_{\mathbf{k}-2\pi/a}^0}{2}\right)^2 + \left|U_{2\pi/a}\right|^2}\,.$$

Sine $E_{\mathbf{k}}^0 = \hbar^2 k^2/2m$ from p. 42 of the lecture notes, $E_{\mathbf{k}}^0 = E_{-\mathbf{k}}^0$. As $k \to \pi/a$, $E_{\mathbf{k}}^0 \to E_{\pi/a}^0 = E_0$ and $E_{\mathbf{k}-2\pi/a}^0 \to E_{-\pi/a} = E_0$. So $E_{\mathbf{k}}^0 \approx E_{\mathbf{k}-2\pi/a}^0 \approx E_0$, and

$$E^{\pm} = E_0 \pm \sqrt{\left(\frac{E_{\mathbf{k}}^0 - E_{\mathbf{k}-2\pi/a}^0}{2}\right)^2 + U^2}\,.$$

Now applying $E_{\mathbf{k}}^0 = \hbar^2 k^2 / 2m$,

$$
\begin{aligned}
E^{\pm} &= E_0 \pm \sqrt{\left(\frac{\hbar^2}{4m}\right)^2 \left[k^2 - \left(k - \frac{2\pi}{a}\right)^2\right]^2 + U^2} \\
&= E_0 \pm \sqrt{\left(\frac{\hbar^2}{4m}\right)^2 \left(\frac{4\pi}{a}k - \frac{4\pi^2}{a^2}\right)^2 + U^2} \\
&= E_0 \pm E_0 \sqrt{\left(\frac{\hbar^2}{4m}\right)^2 \frac{1}{E_0^2} \left(\frac{4\pi}{a}k - \frac{4\pi^2}{a^2}\right)^2 + \frac{U^2}{E_0^2}} \\
&= E_0 \pm E_0 \sqrt{\left(\frac{\hbar^2}{4m}\right)^2 \left(\frac{2ma^2}{\hbar^2\pi^2}\right)^2 \left(\frac{4\pi}{a}k - \frac{4\pi^2}{a^2}\right)^2 + \frac{U^2}{E_0^2}} \\
&= E_0 \pm E_0 \sqrt{\frac{a^4}{\pi^4} \left(\frac{4\pi}{a}k - \frac{4\pi^2}{a^2}\right)^2 + \frac{U^2}{E_0^2}} \\
&= E_0 \pm E_0 \sqrt{\left(\frac{4a}{\pi}k - 4\right)^2 + \frac{U^2}{E_0^2}} \\
&= E_0 \pm E_0 \sqrt{4\left(\frac{a}{\pi}k - 1\right)^2 + \frac{U^2}{E_0^2}} \\
&= E_0 \pm E_0 \sqrt{\frac{U^2}{E_0^2} + 4x^2},
\end{aligned}
$$

where we have used $x = ka/\pi - 1$. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\square$

We approximate the sum as an integral from $k = -\pi/a$ to $k = \pi/a$:

$$
E_{\text{elec}} = \frac{L}{2\pi} \int_{-\pi/a}^{\pi/a} dk \left(E_0 \pm E_0 \sqrt{\frac{U^2}{E_0^2} + 4x^2} - E_0 \mp E_0 \sqrt{4x^2}\right) = \pm \frac{L}{2\pi} E_0 \int_{-\pi/a}^{\pi/a} dk \left(\sqrt{\frac{U^2}{E_0^2} + 4x^2} - 2x\right),
$$

where L is the one-dimensional volume. Transforming the variable of integration from k to x using $dk/dx = \pi/a$, we have

$$
E_{\text{elec}} = \pm \frac{L}{2a} E_0 \int_{-2}^{0} dx \left(\sqrt{\frac{U^2}{E_0^2} + 4x^2} - 2x\right).
$$

For the first term,

$$
\begin{aligned}
\int_{-\pi/a}^{\pi/a} dk \sqrt{\frac{U^2}{E_0^2} + 4x^2} &= \frac{U}{E_0} \int_{-2}^{0} dx \sqrt{1 + 4\frac{E_0^2}{U^2}x^2} \\
&= \frac{U}{E_0} \left[\sqrt{1 + 16\frac{E_0^2}{U^2}} + \frac{1}{4}\frac{U}{E_0} \sinh^{-1}\left(4\frac{E_0}{U}\right)\right] \\
&= \sqrt{\frac{U^2}{E_0^2} + 16} + \frac{1}{4}\frac{U^2}{E_0^2} \sinh^{-1}\left(4\frac{E_0}{U}\right).
\end{aligned}
$$

For the second,

$$
-2 \int_{-2}^{0} x = 4.
$$

So we have

$$E_{\text{elec}} = \pm \frac{L}{2a} E_0 \left[\sqrt{\frac{U^2}{E_0^2} + 16} + \frac{1}{4}\frac{U^2}{E_0^2} \sinh^{-1}\left(4\frac{E_0}{U}\right) + 4 \right].$$

Taylor expanding with Mathematica, we have

$$E_{\text{elec}} = \pm \frac{L}{2a} E_0 \left\{ 4 + 4 + \frac{1}{8}\frac{U^2}{E_0^2} + \frac{1}{8}\frac{U^2}{E_0^2} \left[\ln(64) - 2\ln\left(\frac{U}{E_0}\right) \right] + 4 \right\}$$

$$= \pm \frac{L}{2a} \left[12E_0 + \frac{1}{8}\frac{U^2}{E_0} \left[1 + \ln(64) - 2\ln\left(\frac{U}{E_0}\right) \right] \right]$$

which is to second order in U/E_0.

Problem 5. Some one-dimensional chemistry Consider a diatomic lattice of two atoms labeled A and B in a lattice with period a, at the positions $\pm a(1-\delta)/4$ in a one-dimensional array with overall period a.

5(a) Using the NFE approximation valid for momenta near the zone boundary $k \to \pi/a$, show that the solution of Eq. (4.47) leads to

   (i) a gap on the zone boundary of $2|U_{2\pi/a}|$, and

   (ii) wavefunctions that satisfy $c_k^\pm / c_{k-2\pi/a}^\pm = \pm U/|U|$ as $k \to \pi/a$.

Solution. Equation (4.47) is
$$\begin{pmatrix} E_{\mathbf{k}}^0 - E & U_{\mathbf{K}} \\ U_{\mathbf{K}}^* & E_{\mathbf{k-K}}^0 - E \end{pmatrix} \begin{pmatrix} c_{\mathbf{k}} \\ c_{\mathbf{k-K}} \end{pmatrix} = 0.$$

According to p. 43 of the lecture notes, the Brillouin zone boundary is at $\mathbf{K}/2$, so $\mathbf{K} = 2\pi/a$. Then Eq. (4.47) is
$$\begin{pmatrix} E_{\mathbf{k}}^0 - E & U_{2\pi/a} \\ U_{2\pi/a}^* & E_{\mathbf{k}-2\pi/a}^0 - E \end{pmatrix} \begin{pmatrix} c_{\mathbf{k}} \\ c_{\mathbf{k-K}} \end{pmatrix} = 0$$

which implies that the determinant of the 2×2 matrix is 0 [1, p. 158]:

$$\begin{aligned} 0 &= \begin{vmatrix} E_{\mathbf{k}}^0 - E & U_{2\pi/a} \\ U_{2\pi/a}^* & E_{\mathbf{k}-2\pi/a}^0 - E \end{vmatrix} \\ &= (E_{\mathbf{k}}^0 - E)(E_{\mathbf{k}-2\pi/a}^0 - E) - |U_{2\pi/a}|^2 \\ &= E^2 - (E_{\mathbf{k}}^0 + E_{\mathbf{k}-2\pi/a}^0)E + E_{\mathbf{k}}^0 E_{\mathbf{k}-2\pi/a}^0 - |U_{2\pi/a}|^2. \end{aligned}$$

Solving for E using the quadratic equation yields

$$E^\pm = \frac{E_{\mathbf{k}}^0 + E_{\mathbf{k}-2\pi/a}^0}{2} \pm \sqrt{\left(\frac{E_{\mathbf{k}}^0 - E_{\mathbf{k}-2\pi/a}^0}{2}\right)^2 + |U_{2\pi/a}|^2}.$$

Applying $E_{\mathbf{k}}^0 = \hbar^2 k^2/2m$ from p. 42 of the lecture notes, this is

$$E^\pm = \frac{\hbar^2}{4m} \left[k^2 + \left(k - \frac{2\pi}{a}\right)^2 \right] \pm \sqrt{\left(\frac{\hbar^2}{4m}\right)^2 \left[k^2 - \left(k - \frac{2\pi}{a}\right)^2 \right]^2 + |U_{2\pi/a}|^2}. \tag{6}$$

At the zone boundary $k = \pi/a$, and

$$
\begin{aligned}
E^{\pm} &= \frac{\hbar^2}{4m}\left[\left(\frac{\pi}{a}\right)^2 + \left(\frac{\pi}{a} - \frac{2\pi}{a}\right)^2\right] \pm \sqrt{\left(\frac{\hbar^2}{4m}\right)^2\left[\left(\frac{\pi}{a}\right)^2 - \left(\frac{\pi}{a} - \frac{2\pi}{a}\right)^2\right]^2 + \left|U_{2\pi/a}\right|^2} \\
&= \frac{\hbar^2}{4m}\left(2\frac{\pi^2}{a^2}\right) \pm \sqrt{\left|U_{2\pi/a}\right|^2} \\
&= \frac{\hbar^2}{2m}\frac{\pi^2}{a^2} \pm \left|U_{2\pi/a}\right|.
\end{aligned}
$$

Then the gap is

$$
E^{+} - E^{-} = \left(\frac{\hbar^2}{2m}\frac{\pi^2}{a^2} + \left|U_{2\pi/a}\right|\right) - \left(\frac{\hbar^2}{2m}\frac{\pi^2}{a^2} - \left|U_{2\pi/a}\right|\right) = 2\left|U_{2\pi/a}\right|
$$

as we wanted to show. □

At $k = \pi/a = K/2$, the energy levels are given by (4.49) in the lecture notes,

$$
E^{\pm}(K/2) = E^0_{K/2} \pm |U_K|. \tag{7}
$$

The leading corrections in U for two energy levels are given by Ashcroft & Mermin (9.22),

$$
(E - E^0_{\mathbf{k}})c_{\mathbf{k}} = U_{\mathbf{K}}c_{\mathbf{k}-\mathbf{K}}, \qquad\qquad (E - E^0_{\mathbf{k}-\mathbf{K}})c_{\mathbf{k}-\mathbf{K}} = U_{-\mathbf{K}}c_{\mathbf{k}} = U^*_{\mathbf{K}}c_{\mathbf{k}},
$$

where $c_{\mathbf{k}}$ and $c_{\mathbf{k}-\mathbf{K}}$ are the coefficients of the wavefunctions. Substituting $k = \pi/a$ and $K = 2\pi/a$ and Eq. (7) into the first of these expressions, we find

$$
U_{2\pi/a}c^{\pm}_{k-2\pi/a} = (E^{\pm} - E^0_{\pi/a})c^{\pm}_k = [(E^0_{\pi/a} \pm |U_{2\pi/a}|) - E^0_{\pi/a}]c^{\pm}_k = \pm|U_{2\pi/a}|c^{\pm}_k
$$

which implies

$$
\frac{c^{\pm}_k}{c^{\pm}_{k-2\pi/a}} = \pm\frac{U_{2\pi/a}}{|U_{2\pi/a}|} \tag{8}
$$

as desired [1, p. 159]. □

5(b) Hence show that the probability density for the electronic states at $k = \pi/a$ take the form

$$
\left|\psi^{+}(r)\right|^2 \propto \cos^2\left(\frac{\pi x}{a} + \frac{\phi}{2}\right), \qquad\qquad \left|\psi^{-}(r)\right|^2 \propto \sin^2\left(\frac{\pi x}{a} + \frac{\phi}{2}\right). \tag{9}
$$

Solution. The wavefunctions are given by (4.38) in the lecture notes,

$$
\psi_k(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}}e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}}.
$$

With $k = \pi/a$, this gives us

$$
\begin{aligned}
\psi^{+}(r) &= c^{+}_k e^{ikx} + c^{+}_{k-2\pi/a}e^{i(k-2\pi/a)x} = c^{+}_k(e^{i\pi x/a} + e^{-i\pi x/a}) = 2c^{+}_k\cos\left(\frac{\pi x}{a}\right), \\
\psi^{-}(r) &= c^{-}_k e^{ikx} - c^{-}_{k-2\pi/a}e^{i(k-2\pi/a)x} = c^{-}_k(e^{i\pi x/a} - e^{-i\pi x/a}) = 2ic^{-}_k\sin\left(\frac{\pi x}{a}\right),
\end{aligned}
$$

where we have used Eq. (8). Then

$$
\begin{aligned}
\left|\psi^{+}(r)\right|^2 &= -2\left|c^{+}_k\right|^2\cos^2\left(\frac{\pi x}{a}\right) \propto \cos^2\left(\frac{\pi x}{a} + \frac{\phi}{2}\right), \\
\left|\psi^{-}(r)\right|^2 &= 2\left|c^{-}_k\right|^2\sin^2\left(\frac{\pi x}{a}\right) \propto \sin^2\left(\frac{\pi x}{a} + \frac{\phi}{2}\right),
\end{aligned}
$$

where we have included a phase shift $\phi/2$ in order to account for the complex coefficient. □

5(c) Show that the potential can be written

$$U_{2\pi/a} = \sin\left(\frac{\pi\delta}{2}\right)\left(U_{2\pi/a}^A + U_{2\pi/a}^B\right) - i\cos\left(\frac{\pi\delta}{2}\right)\left(U_{2\pi/a}^A - U_{2\pi/a}^B\right), \tag{10}$$

where

$$U_{2\pi/a}^{A,B} = \frac{N}{V}\int dr\, e^{-2\pi ir/a}U^{A,B}(r).$$

Solution. Since $U(\mathbf{r})$ is a sum of atomic potentials located at the positions of the atoms, it can be written as Ashcroft & Mermin (9.31):

$$U(\mathbf{r}) = \sum_{\mathbf{R}}\left[U^A(\mathbf{r}-\mathbf{R}-\mathbf{d}_A) + U^B(\mathbf{r}-\mathbf{R}-\mathbf{d}_B)\right]$$

$$= \sum_{\mathbf{R}}\left[U^A\left(\mathbf{r}-\mathbf{R}-\frac{a}{4}(1-\delta)\right) + U^B\left(\mathbf{r}-\mathbf{R}+\frac{a}{4}(1-\delta)\right)\right], \tag{11}$$

where $\mathbf{d}_A$ and $\mathbf{d}_B$ are the positions of the atoms. The momentum components of the potential are given by (4.20) in the lecture notes:

$$U_{\mathbf{G}} = \frac{N}{V}\int_{\text{unit cell}} d\mathbf{r}\, e^{-i\mathbf{G}\cdot\mathbf{r}}U(\mathbf{r}).$$

Feeding in Eq. (11) and $K = 2\pi/a$,

$$U_K = \frac{N}{V}\int_{\text{unit cell}} dr\, e^{-iKr}\sum_{R}\left[U^A\left(r-R-\frac{a}{4}(1-\delta)\right) + U^B\left(r-R+\frac{a}{4}(1-\delta)\right)\right]$$

$$= \frac{N}{V}\left[\int_{\text{all space}} dr\, e^{-iKr}U^A\left(r-\frac{a}{4}(1-\delta)\right) + \int_{\text{all space}} dr\, e^{-iKr}U^B\left(r+\frac{a}{4}(1-\delta)\right)\right].$$

Let $r' = r \mp a(1-\delta)/4$. Then

$$U_K = \frac{N}{V}\int_{\text{all space}} dr'\, e^{-iKr'}\left[e^{-iKa(1-\delta)/4}U^A(r') + e^{-iKa(1+\delta)/4}U^B(r')\right].$$

Renaming $r' \to r$ and applying $K = 2\pi/a$, we have

$$U_{2\pi/a} = \frac{N}{V}\int_{\text{all space}} dr\, e^{-i2\pi r/a}\left[e^{-i2\pi(1-\delta)/4}U^A(r) + e^{-i2\pi(1+\delta)/4}U^B(r)\right]$$

$$= e^{-i\pi/2}\frac{N}{V}\int_{\text{all space}} dr\, e^{-i2\pi r/a}\left[e^{i\pi\delta/2}U^A(r) - e^{-i\pi\delta/2}U^B(r)\right]$$

$$= i\frac{N}{V}\left[\int dr\, e^{-i\pi(2r/a+\delta/2)}U^B(r) - \int dr\, e^{-i\pi(2r/a-\delta/2)}U^A(r)\right]$$

$$= i\frac{N}{V}\left[e^{-i\pi\delta/2}\int dr\, e^{-2\pi ir/a}U^B(r) - e^{i\pi\delta/2}\int dr\, e^{-2\pi ir/a}U^A(r)\right]$$

$$= i\left[e^{-i\pi\delta/2}U_{2\pi/a}^B - e^{i\pi\delta/2}U_{2\pi/a}^A\right]$$

$$= \frac{i}{2}\left[e^{-i\pi\delta/2}(U_{2\pi/a}^A + U_{2\pi/a}^B - U_{2\pi/a}^A + U_{2\pi/a}^B) - e^{i\pi\delta/2}(U_{2\pi/a}^A + U_{2\pi/a}^B + U_{2\pi/a}^A - U_{2\pi/a}^B)\right]$$

$$= \frac{i}{2}(e^{-i\pi\delta/2} - e^{i\pi\delta/2})\left(U_{2\pi/a}^A + U_{2\pi/a}^B\right) - \frac{i}{2}(e^{-i\pi\delta/2} + e^{i\pi\delta/2})\left(U_{2\pi/a}^A - U_{2\pi/a}^B\right)$$

$$= \sin\left(\frac{\pi\delta}{2}\right)\left(U_{2\pi/a}^A + U_{2\pi/a}^B\right) - i\cos\left(\frac{\pi\delta}{2}\right)\left(U_{2\pi/a}^A - U_{2\pi/a}^B\right)$$
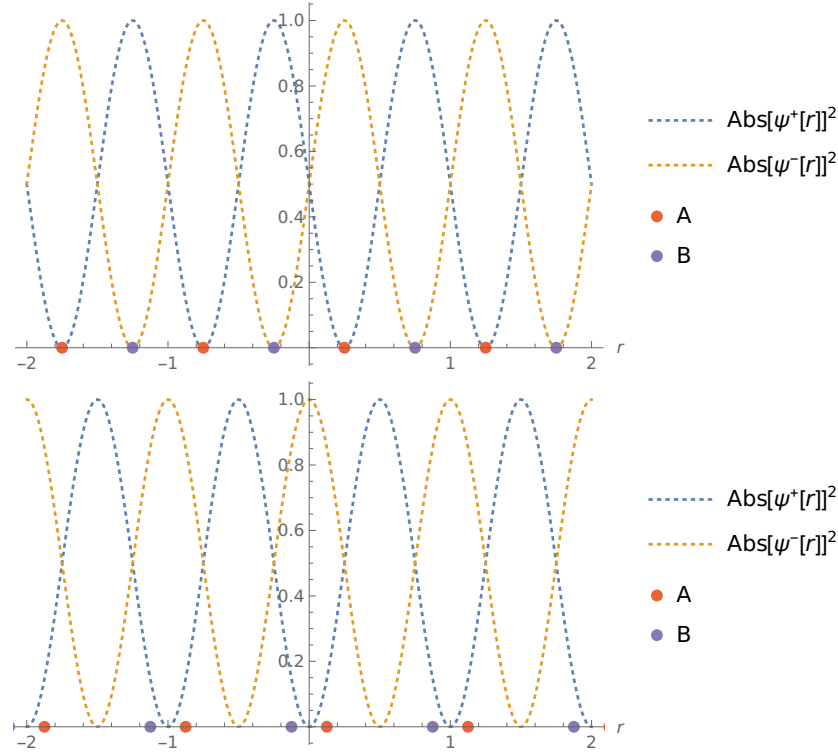
as we wanted to show. $\square$

Figure 1: Plot of charge densities for the highest filled electron state, $|\psi^-(r)|^2$ (gold dotted line), and the lowest empty electron state (blue dotted line), $|\psi^+(r)|^2$, along with A atoms (red dots) and B atoms (violet dots). The charge densities are given by Eq. (9) with (top) $\delta = 0$, $U_A \neq U_B$, $\phi = n\pi/2$ for n odd; and with (bottom) $\delta = 1/8$, $U_A = U_B$, $\phi = n\pi/2$ for n even. The top (bottom) panel demonstrates an ionic (a covalent) solid.

5(d) The system contains an average of one electron per atom, or equivalently two electrons per unit cell. Discuss the values of the energy gaps and plot the charge densities corresponding to the highest filled electron state and the lowest empty electron state in the two cases:

(i) $\delta = 0$, $U_A \neq U_B$;

(ii) identical atoms, $U_A = U_B$, and $\delta \neq 0$.

Explain how this provides a simple model of either an *ionic* or *covalent* solid.

Solution. We know that the energy gap is $2|U_{2\pi/a}|$. In the first case, substituting $\delta = 0$ into Eq. (10) gives us

$$U_{2\pi/a} = \sin(0)\left(U_{2\pi/a}^A + U_{2\pi/a}^B\right) - i\cos(0)\left(U_{2\pi/a}^A - U_{2\pi/a}^B\right) = -i\left(U_{2\pi/a}^A - U_{2\pi/a}^B\right)$$

so the energy gap is

$$2|U_{2\pi/a}| = 2\left|U_{2\pi/a}^A - U_{2\pi/a}^B\right|.$$

The charge density corresponding to the highest filled electron state is $|\psi^-(r)|^2$, and that corresponding to the lowest empty electron state is $|\psi^+(r)|^2$. When $\delta = 0$, the atoms are uniformly spaced so $\phi = n\pi/2$ with n an odd integer. Figure (1) (top) shows the positions of the atoms A and B as well as $|\psi^\pm(r)|^2$ from Eq. (9). The A atoms (red dots) have positions $a(1-\delta)/4$, and the B atoms (violet dots) have positions $-a(1-\delta)/4$. In the figure $|\psi^-(r)|^2$ is shown by a dotted gold line and $|\psi^+(r)|^2$ by a dotted blue line. The charge densities show that the electron in a particular state is localized near one atom. This is representative of an *ionic* solid, which has one electron "donated" to the more positive ion.

In the second case, substituting $U_A = U_B$ into Eq. (10) yields

$$U_{2\pi/a} = \sin\left(\frac{\pi\delta}{2}\right)\left(U^A_{2\pi/a} + U^A_{2\pi/a}\right) - i\cos\left(\frac{\pi\delta}{2}\right)\left(U^A_{2\pi/a} - U^A_{2\pi/a}\right) = 2\sin\left(\frac{\pi\delta}{2}\right)U^A_{2\pi/a},$$

so the energy gap is

$$2\left|U_{2\pi/a}\right| = 4\left|\sin\left(\frac{\pi\delta}{2}\right)U^A_{2\pi/a}\right|.$$

When $\delta \neq 0$, the atoms are not uniformly spaced so $\phi = n\pi/2$ with n an even integer. The charge densities for this scenario are shown in Fig. (1) (bottom), with $\delta = 1/8$. Here the charge densities show that the electron in a particular state is localized between the ions. This is a model of a *covalent* solid, which has one or more electrons "shared" between ions of similar charge.

Problem 6.   Tight binding for BCC and FCC lattices   Show that the tight-binding band structure for a body-centered cubic lattice (include only the hopping to the eight nearest neighbors) is

$$E(\mathbf{k}) = \epsilon_0 + 8t\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right),$$

and for the face-centered cubic lattice (twelve nearest neighbors)

$$E(\mathbf{k}) = \epsilon_0 + 4t\left[\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_z a}{2}\right)\cos\left(\frac{k_x a}{2}\right)\right].$$

Solution.   The band energy in the tight-binding description is given by (4.57) in the lecture notes,

$$E(\mathbf{k}) = \epsilon_0 + t\sum_{\boldsymbol{\rho}} e^{-i\mathbf{k}\cdot\boldsymbol{\rho}}.$$

In a BCC lattice of spacing a, the eight nearest neighbors of the origin are located at

$$\boldsymbol{\rho} \in \frac{a}{2}\{(1,1,1),\ (-1,-1,-1),\ (1,1,-1),\ (-1,-1,1),\ (1,-1,1),\ (-1,1,-1),\ (-1,1,1),\ (1,-1,-1)\}.$$

So the band energy is

$$\begin{aligned}
E(\mathbf{k}) &= \epsilon_0 + t\Big(e^{-ia(k_x+k_y+k_z)/2} + e^{-ia(-k_x-k_y-k_z)/2} + e^{-ia(k_x+k_y-k_z)/2} + e^{-ia(-k_x-k_y+k_z)/2} \\
&\qquad + e^{-ia(k_x-k_y+k_z)/2} + e^{-ia(-k_x+k_y-k_z)/2} + e^{-ia(-k_x+k_y+k_z)}/2 + e^{-ia(k_x-k_y-k_z)/2}\Big) \\
&= \epsilon_0 + t\left(e^{-iak_x/2} + e^{iak_x/2}\right)\left(e^{-iak_y/2} + e^{iak_y/2}\right)\left(e^{-iak_z/2} + e^{iak_z/2}\right) \\
&= \epsilon_0 + t\left[2\cos\left(\frac{k_x a}{2}\right)\right]\left[2\cos\left(\frac{k_y a}{2}\right)\right]\left[2\cos\left(\frac{k_z a}{2}\right)\right] \\
&= \epsilon_0 + 8t\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right)
\end{aligned}$$

as we wanted to show. $\square$

In an FCC lattice of spacing a, the twelve nearest neighbors of the origin are located at [1, p. 182]

$$\begin{aligned}
\boldsymbol{\rho} \in \frac{a}{2}\{&(1,1,0),\ (-1,-1,0),\ (1,-1,0),\ (-1,1,0),\ (1,0,1),\ (-1,0,-1), \\
&(1,0,-1),\ (-1,0,1),\ (0,1,1),\ (0,-1,-1),\ (0,1,-1),\ (0,-1,1)\}.
\end{aligned}$$

So the band energy is

$$
\begin{aligned}
E(\mathbf{k}) = \epsilon_0 + t \Big(& e^{-ia(k_x+k_y)/2} + e^{-ia(-k_x-k_y)/2} + e^{-ia(k_x-k_y)/2} + e^{-ia(-k_x+k_y)/2} \\
& + e^{-ia(k_x+k_z)/2} + e^{-ia(-k_x-k_z)/2} + e^{-ia(k_x-k_z)}/2 + e^{-ia(-k_x+k_z)/2} \\
& + e^{-ia(k_y+k_z)/2} + e^{-ia(-k_y-k_z)/2} + e^{-ia(k_y-k_z)}/2 + e^{-ia(-k_y+k_z)/2} \Big) \\
= \epsilon_0 + t \Big[& \left(e^{-iak_x/2} + e^{iak_x-/2} \right) \left(e^{-iak_y/2} + e^{iak_y/2} \right) + \left(e^{-iak_x/2} + e^{iak_x-/2} \right) \left(e^{-iak_z/2} + e^{iak_z/2} \right) \\
& + \left(e^{-iak_y/2} + e^{iak_y-/2} \right) \left(e^{-iak_z/2} + e^{iak_z/2} \right) \Big] \\
= \epsilon_0 + t \Big\{ & \left[2\cos\left(\frac{k_x a}{2}\right) \right] \left[2\cos\left(\frac{k_y a}{2}\right) \right] + \left[2\cos\left(\frac{k_x a}{2}\right) \right] \left[2\cos\left(\frac{k_z a}{2}\right) \right] + \left[2\cos\left(\frac{k_y a}{2}\right) \right] \left[2\cos\left(\frac{k_z a}{2}\right) \right] \Big\} \\
= \epsilon_0 + 4t \Big[& \cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_z a}{2}\right)\cos\left(\frac{k_x a}{2}\right) \Big]
\end{aligned}
$$

as desired. $\qquad\square$

Problem 7. Pseudopotential Show that $\langle \chi | f_n \rangle = 0$ if we choose $\beta_n = \langle f_n | \mathbf{k} \rangle$.

The pseudopotential is not unique. Show that the valence eigenvalues of a Hamiltonian $H + V_R$ are the same for any operator of the form

$$
V_R \phi = \sum_n \langle F_n | \phi \rangle \, f_n, \tag{12}
$$

where the F_n are *arbitrary* functions.

Solution. Equation (4.59) of the lecture notes defines the basis vectors

$$
|\chi_{\mathbf{k}}\rangle = |\mathbf{k}\rangle - \sum_n \beta_n \, |f_{n\mathbf{k}}\rangle .
$$

If we choose $\beta_n = \langle f_n | \mathbf{k} \rangle$ and multiply on the left by $\langle f_n |$, then

$$
\langle f_n | \chi \rangle = \langle f_n | \mathbf{k} \rangle - \sum_m \langle f_m | \mathbf{k} \rangle \langle f_n | f_m \rangle = \langle f_n | \mathbf{k} \rangle - \sum_m \langle f_m | \mathbf{k} \rangle \, \delta_{mn} = \langle f_n | \mathbf{k} \rangle - \langle f_n | \mathbf{k} \rangle = 0.
$$

Since $\langle \chi | f_n \rangle = \langle f_n | \chi \rangle^*$, we have shown that if $\beta_n = \langle f_n | \mathbf{k} \rangle$ then

$$
\langle \chi | f_n \rangle = 0 \tag{13}
$$

as desired. $\qquad\square$

Let E' be the valence eigenvalues of $H + V_R$, where ψ is the valence wavefunction. We want to show that

$$
(H + V_R) |\psi\rangle = E' |\psi\rangle
$$

for any V_R given by Eq. (12). Applying the Schrödinger equation $H |\psi\rangle = E |\psi\rangle$ yields

$$
V_R |\psi\rangle = (E' - E) |\psi\rangle .
$$

Multiplying on the left by $\langle \phi |$ and applying Eq. (12),

$$
\langle \phi | V_R | \psi \rangle = \langle \phi | (E' - E) | \psi \rangle \quad \implies \quad \sum_n \langle F_n | \phi \rangle^* \langle f_n | \psi \rangle = (E' - E) \langle \phi | \psi \rangle \quad \implies \quad 0 = E' - E \tag{14}
$$

since ψ and f_n are orthogonal, but ψ and ϕ are not. We know this since $|\psi\rangle$ can be written as a linear combination of $|\chi\rangle$ by (4.60) of the lecture notes,

$$|\psi_k\rangle = \sum_{\mathbf{G}} \alpha_{\mathbf{k}-\mathbf{G}} |\chi_{\mathbf{k}-\mathbf{G}}\rangle,$$

and we showed in Eq. (13) that $\langle\chi|f_n\rangle = 0$. On the contrary, (4.62) shows that ϕ and ψ cannot be orthogonal since

$$|\psi\rangle = |\phi\rangle - \sum_n \langle f_n|\phi\rangle |f_n\rangle.$$

Equation (14) holds for any F_n. So we have shown that the valence eigenvalues E' are the same for arbitrary F_n. $\qquad\square$

Problem 8. Hartree–Fock theory for the two-level atom Show that the Hartree–Fock total energy Eq. (4.83) applied to the two-level atom model of Sec. 4.2.1 gives exactly the direct and exchange energy calculated in Eq. (4.75).

Solution. Equation (4.83) is

$$\langle H \rangle_\Psi = \sum_i \langle i|(T + U_{\text{ion}})|i\rangle + \frac{1}{2} \sum_{i,j} \left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle \, \delta_{\sigma_i \sigma_j} \right).$$

For the two-level atom, $i, j \in \{1, 2\}$. So we have

$$\langle H \rangle_\Psi = \langle 1|(T + U_{\text{ion}})|1\rangle + \langle 2|(T + U_{\text{ion}})|2\rangle$$
$$+ \frac{1}{2} \left(\langle 12|\frac{e^2}{r_{12}}|12\rangle - \langle 12|\frac{e^2}{r_{12}}|21\rangle \, \delta_{\sigma_1 \sigma_2} + \langle 21|\frac{e^2}{r_{21}}|21\rangle - \langle 21|\frac{e^2}{r_{21}}|12\rangle \, \delta_{\sigma_1 \sigma_2} \right). \quad (15)$$

since $\delta_{\sigma_i \sigma_i} = 1$.

Using (4.76) in the lecture notes, the direct energy is

$$\langle 12|V|12\rangle = \langle 12|\frac{e^2}{r_{12}}|12\rangle = \int d\mathbf{r}\, d\mathbf{r}' \, |\psi_1(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\psi_2(\mathbf{r})|^2 = \int d\mathbf{r}'\, d\mathbf{r} \, |\psi_1(\mathbf{r})|^2 \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\psi_2(\mathbf{r}')|^2 = \langle 21|\frac{e^2}{r_{21}}|21\rangle,$$

where we have simply interchanged $\mathbf{r}$ and $\mathbf{r}'$. Similarly, using (4.77) in the lecture notes, the exchange energy is

$$\langle 21|V|12\rangle = \langle 21|\frac{e^2}{r_{21}}|12\rangle$$
$$= \int d\mathbf{r}\, d\mathbf{r}' \, \psi_2^*(\mathbf{r})\psi_1^*(\mathbf{r}') \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_1(\mathbf{r})\psi_2(\mathbf{r}')$$
$$= \int d\mathbf{r}'\, d\mathbf{r} \, \psi_2^*(\mathbf{r}')\psi_1^*(\mathbf{r}) \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_1(\mathbf{r}')\psi_2(\mathbf{r})$$
$$= \langle 12|\frac{e^2}{r_{12}}|21\rangle.$$

From p. 53 of the lecture notes, $E_i = \langle i|(T + U_{\text{ion}})|i\rangle$. Finally, Eq. (15) can be written

$$\langle \Psi|H|\Psi\rangle = E_1 + E_2 + \langle 12|V|12\rangle + \langle 21|V|12\rangle$$

which has the same direct and exchange energy as (4.75) in the lecture notes. $\qquad\square$

Problem 9. Hartree–Fock equations Evaluate the energy in the form

$$\langle H \rangle_\Psi = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

with the determinantal wavefunction of Eq. (4.82) using an orthonormal set of orbitals ψ_i.

Show that by minimizing with respect to the ψ_i^* one obtains the Hartree–Fock equations

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U_{\text{ion}}(\mathbf{r}) + U_{\text{coul}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) - \sum_j \int d\mathbf{r}' \, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r})\delta_{\sigma_i \sigma_j} = \epsilon_i \psi_i(\mathbf{r}),$$

and that the total energy can be written

$$\langle H \rangle_\Psi = \sum_i \epsilon_i - \frac{1}{2} \sum_{i,j} \left(\langle ij| \frac{e^2}{r_{ij}} |ij\rangle - \langle ij| \frac{e^2}{r_{ij}} |ji\rangle \, \delta_{\sigma_i \sigma_j} \right).$$

Solution. Equation (4.82) is

$$\Psi_{\text{HF}} = \begin{vmatrix} \psi_1(\mathbf{r}_1,\sigma_1) & \cdots & \psi_1(\mathbf{r}_N,\sigma_N) \\ \vdots & & \vdots \\ \psi_N(\mathbf{r}_1,\sigma_1) & \cdots & \psi_N(\mathbf{r}_N,\sigma_N) \end{vmatrix}$$

The determinant for an $n \times n$ matrix can be expressed using the formula

$$\det(A) = \sum_{\tau \in S_n} \text{sgn}(\tau) \prod_{i=1}^n A_{i,\tau(i)} = \sum_{\rho \in S_n} \text{sgn}(\rho) \prod_{i=1}^n A_{\sigma(i),i},$$

where S_n is the set of all permutations of the matrix elements and sgn is the sign function of the permutation [3]. Since the elements of Ψ_{HF} have the positions and spins of the electrons as their argument, we may permute by interchanging electrons. Because of the antisymmetry of fermions as shown in (4.70) of the lecture notes, we pick up a minus sign every time two fermions are interchanged. There are N electrons with $N!$ possible permutations. This is represented by

$$\Psi_{\text{HF}} = \sum_{\tau \in S_n} \text{sgn}(\tau)\psi_1(\mathbf{r}_{\tau(1)},\sigma_{\tau(1)})\cdots\psi_N(\mathbf{r}_{\tau(N)},\sigma_{\tau(N)}).$$

The electronic Hamiltonian is given by (4.67) of the lecture notes:

$$H_{\text{elec}} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m}\nabla_i^2 + U_{\text{ion}}(\mathbf{r}_i) + U_{\text{coul}}(\mathbf{r}_i) \right),$$

where by (4.68) and (4.78),

$$U_{\text{ion}}(\mathbf{r}) = \sum_I \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}, \qquad\qquad U_{\text{coul}}(\mathbf{r}) = e^2 \sum_{j \neq i} \int d\mathbf{r}' \, \frac{|\psi_j(\mathbf{r}')|^2}{\mathbf{r} - \mathbf{r}'}.$$

Only one term of the Hamiltonian involves particle interactions. Let $H_{\text{elec}} = H_0 + H_{\text{int}}$ such that

$$H_0 = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m}\nabla_i^2 + \sum_I \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} \right) = \sum_{i=1}^N (T + U_{\text{ion}}), \qquad H_{\text{int}} = \sum_{i=1}^N U_{\text{coul}}(\mathbf{r}_i) = \sum_{j \neq i} \int d\mathbf{r}' \, \frac{e^2}{r_{ij}}.$$

For the first term, note that

$$\langle\Psi|H_0|\Psi\rangle = \int d\mathbf{r}_1\cdots d\mathbf{r}_N\,\Psi^*H_0\Psi = \sum_{\tau\in S_n}\sum_{\rho\in S_n}\text{sgn}(\tau)\text{sgn}(\rho)\int\prod_{i=1}^{N}d\mathbf{r}_i\,\psi_i^*(\mathbf{r}_{\tau(i)},\sigma_{\tau(i)})H_0\psi_i(\mathbf{r}_{\rho(i)},\sigma_{\rho(i)}).$$

The ψ_i are orthonormal, so we must have $\rho = \tau$ for nonzero terms. Since $\text{sgn}(\rho) = \pm 1$, $[\text{sgn}(\rho)]^2 = 1$. This means we can write

$$\langle\Psi|H_0|\Psi\rangle = \sum_{\tau\in S_n}\int\prod_{i=1}^{N}d\mathbf{r}_i\,\psi_i^*(\mathbf{r}_{\tau(i)},\sigma_{\tau(i)})H_0\psi_i(\mathbf{r}_{\tau(i)},\sigma_{\tau(i)}).$$

Since there are $N!$ possible permutations of the electrons, which are indistinguishable, we can further write

$$\langle\Psi|H_0|\Psi\rangle = N!\sum_{i=1}^{N}\int d\mathbf{r}_i\,\psi_i^*(\mathbf{r}_i,\sigma_i)(T+U_{\text{ion}})\psi_i(\mathbf{r}_i,\sigma_i) = N!\sum_{i=1}^{N}\langle i|(T+U_{\text{ion}})|i\rangle. \tag{16}$$

For the second term of the Hamiltonian, note that

$$\langle\Psi|H_{\text{int}}|\Psi\rangle = \int d\mathbf{r}_1\cdots d\mathbf{r}_N\,\Psi^*H_{\text{int}}\Psi$$

$$= \sum_{\tau\in S_n}\sum_{\rho\in S_n}\text{sgn}(\tau)\text{sgn}(\rho)\int d\mathbf{r}_1\cdots d\mathbf{r}_N\prod_{i=1}^{N}\prod_{j=1}^{N}\psi_i^*(\mathbf{r}_{\tau(i)},\sigma_{\tau(i)})H_{\text{int}}\psi_j(\mathbf{r}_{\rho(j)},\sigma_{\rho(j)}).$$

Feeding in H_{int}, we have

$$\langle\Psi|H_{\text{int}}|\Psi\rangle = \sum_{i=1}^{N}\sum_{j\neq i}\sum_{\tau\in S_n}\sum_{\rho\in S_n}\text{sgn}(\tau)\text{sgn}(\rho)\int d\mathbf{r}_1\cdots d\mathbf{r}_N\prod_{i=1}^{N}\prod_{j=1}^{N}\psi_i^*(\mathbf{r}_{\tau(i)},\sigma_{\tau(i)})\frac{e^2}{r_{ij}}\psi_j(\mathbf{r}_{\rho(j)},\sigma_{\rho(j)}).$$

Since $j\neq i$, interchanging i and j gives a minus sign so long as the electrons have the same spin; if they do not, the term is 0. Accounting for the $N(N-1)/2$ possible pairs of N electrons and their indistinguishability, which gives us $(N-2)!$ identical terms in the sum, we can write

$$\langle\Psi|H_{\text{int}}|\Psi\rangle = \frac{N!}{2}\sum_{i=1}^{N}\sum_{j\neq i}\int d\mathbf{r}_i\,d\mathbf{r}_j\,\psi_i^*(\mathbf{r}_i,\sigma_i)\psi_j^*(\mathbf{r}_j,\sigma_j)\frac{e^2}{r_{ij}}\left[\psi_i(\mathbf{r}_i,\sigma_i)\psi_j(\mathbf{r}_j,\sigma_j) - \delta_{\sigma_i\sigma_j}\psi_j(\mathbf{r}_j,\sigma_j)\psi_i(\mathbf{r}_i,\sigma_i)\right]$$

$$= \frac{N!}{2}\sum_{i,j}\left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle\,\delta_{\sigma_i\sigma_j}\right), \tag{17}$$

where we have included $i = j$ terms in the sum since they are 0.

Feeding Eqs. (16) and (17) into the expectation value, we find

$$\langle\Psi|H|\Psi\rangle = \langle\Psi|(H_0+H_{\text{int}})|\Psi\rangle = N!\left[\sum_i\langle i|(T+U_{\text{ion}})|i\rangle + \frac{1}{2}\sum_{i,j}\left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle\,\delta_{\sigma_i\sigma_j}\right)\right].$$

Since there are N indistinguishable electrons, clearly $\langle\Psi|\Psi\rangle = N!$. So we have the total energy

$$\langle H\rangle_\Psi = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \sum_i\langle i|(T+U_{\text{ion}})|i\rangle + \frac{1}{2}\sum_{i,j}\left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle\,\delta_{\sigma_i\sigma_j}\right)$$

as we wanted to show [4]. $\qquad\square$

For the minimization procedure, let $\psi_i \to \psi_i + \delta\psi_i$ for all ψ_i. We know $\langle i|j\rangle = \delta_{ij}$ is a constraint on the system, so we use the method of Lagrange multipliers ϵ_{ij} to minimize the Lagrangian [5]:

$$L = \langle H\rangle_\Psi - \sum_{i,j} \epsilon_{ij}(\langle i|j\rangle - \delta_{ij}).$$

To simplify this procedure, we will postulate that the constraint $\langle i|i\rangle = 1$ is sufficient to minimize the Lagrangian, and that the more general condition follows from this procedure. Let ϵ_i be the Lagrange multipliers such that

$$L = \langle H\rangle_\Psi - \sum_i \epsilon_i(\langle i|i\rangle - 1) = \sum_i \langle i|(T + U_{\text{ion}})|i\rangle + \frac{1}{2}\sum_{i,j}\left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle\,\delta_{\sigma_i\sigma_j}\right) - \sum_i \epsilon_i(\langle i|i\rangle - 1).$$

Now we feed in the variations $|i\rangle \to |i\rangle + |\delta i\rangle$. To $\mathcal{O}(\delta)$, this gives us

$$L \to L + \delta L$$

$$= \sum_i (\langle i| + \langle\delta i|)(T + U_{\text{ion}})(|i\rangle + |\delta i\rangle) + \frac{1}{2}\sum_{i,j}(\langle ij| + \langle i\,\delta j| + \langle\delta i\,j|)\frac{e^2}{r_{ij}}(|ij\rangle + |i\,\delta j\rangle + |\delta i\,j\rangle)$$

$$- \frac{1}{2}\sum_{i,j}\delta_{\sigma_i\sigma_j}(\langle ij| + \langle i\,\delta j| + \langle\delta i\,j|)\frac{e^2}{r_{ij}}(|ji\rangle + |j\,\delta i\rangle + |\delta j\,i\rangle) - \sum_i \epsilon_i[(\langle i| + \langle\delta i|)(\langle i| + \langle\delta i|) - 1].$$

Subtracting the Lagrangian yields

$$\delta L = \sum_i (\,\langle\delta i|(T + U_{\text{ion}})|i\rangle + \langle i|(T + U_{\text{ion}})|\delta i\rangle)$$

$$+ \frac{1}{2}\sum_{i,j}(\,\langle\delta i\,j|\frac{e^2}{r_{ij}}|ij\rangle + \langle i\,\delta j|\frac{e^2}{r_{ij}}|ij\rangle + \langle ij|\frac{e^2}{r_{ij}}|\delta i\,j\rangle + \langle ij|\frac{e^2}{r_{ij}}|i\,\delta j\rangle)$$

$$- \delta_{\sigma_i\sigma_j}\frac{1}{2}\sum_{i,j}(\,\langle\delta i\,j|\frac{e^2}{r_{ij}}|ji\rangle + \langle i\,\delta j|\frac{e^2}{r_{ij}}|ji\rangle + \langle ij|\frac{e^2}{r_{ij}}|\delta j\,i\rangle + \langle ij|\frac{e^2}{r_{ij}}|j\,\delta i\rangle)$$

$$- \sum_i \epsilon_i(\langle\delta i|i\rangle + \langle i|\delta i\rangle).$$

Since $r_{ij} = r_{ji}$ and we can relabel indices, we note that

$$\langle\delta i\,j|\frac{e^2}{r_{ij}}|ij\rangle = \left(\langle ij|\frac{e^2}{r_{ij}}|\delta i\,j\rangle\right)^*, \qquad\qquad \langle\delta i\,j|\frac{e^2}{r_{ij}}|ij\rangle = \langle i\,\delta j|\frac{e^2}{r_{ij}}|ij\rangle.$$

Then we have

$$\delta L = \left[\sum_i \langle\delta i|(T + U_{\text{ion}})|i\rangle + \sum_{i,j}\left(\langle\delta i\,j|\frac{e^2}{r_{ij}}|ij\rangle - \delta_{\sigma_i\sigma_j}\langle\delta i\,j|\frac{e^2}{r_{ij}}|ji\rangle\right) - \sum_i \epsilon_i\,\langle\delta i|i\rangle\right] + \text{c.c.}.$$

Using integral notation, this is

$$
\begin{aligned}
\delta L = &\left[\sum_i \int d\mathbf{r}\, \delta\psi_i^*(\mathbf{r})(T + U_{\text{ion}})\psi_i(\mathbf{r}) \right.\\
&+ \sum_{i,j} \iint d\mathbf{r}\, d\mathbf{r}'\, \delta\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left\{\psi_i(\mathbf{r})\psi_j(\mathbf{r}') - \delta_{\sigma_i\sigma_j}\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\right\}\\
&\left. - \sum_i \epsilon_i \int d\mathbf{r}\, \delta\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \right] + \text{c.c.}\\
= &\int d\mathbf{r}\, \delta\psi_i^*(\mathbf{r})\left\{ \left[\sum_i (T + U_{\text{ion}}) + e^2 \sum_{i,j}\int \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} - \sum_i \epsilon_i \right]\psi_i(\mathbf{r}) \right.\\
&\left. - \sum_{i,j}\delta_{\sigma_i\sigma_j}\int d\mathbf{r}'\, \psi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_j(\mathbf{r})\psi_i(\mathbf{r}') \right\} + \text{c.c.}\\
= &\int d\mathbf{r}\, \delta\psi_i^*(\mathbf{r})\left\{ \left[\sum_i \left(-\frac{\hbar^2}{2m}\nabla^2 + U_{\text{ion}}(\mathbf{r}) + U_{\text{coul}}(\mathbf{r}) - \epsilon_i \right) \right]\psi_i(\mathbf{r}) \right.\\
&\left. - \sum_{i,j}\delta_{\sigma_i\sigma_j}\int d\mathbf{r}'\, \psi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_j(\mathbf{r})\psi_i(\mathbf{r}') \right\} + \text{c.c.}
\end{aligned}
$$

Since $\delta\psi_i^*$ is an arbitrary variation, this expression must hold when $\epsilon_i = 0$ for all i. This gives us the equations

$$
\left(-\frac{\hbar^2}{2m}\nabla^2 + U_{\text{ion}}(\mathbf{r}) + U_{\text{coul}}(\mathbf{r}) \right)\psi_i(\mathbf{r}) - \sum_j \int d\mathbf{r}'\, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r})\delta_{\sigma_i\sigma_j} = \epsilon_i\psi_i(\mathbf{r}) \tag{18}
$$

as we wanted to show [4]. $\qquad\square$

We showed that the total energy is

$$
\begin{aligned}
\langle H \rangle_\Psi &= \sum_i \langle i|(T + U_{\text{ion}})|i\rangle + \frac{1}{2}\sum_{i,j}\left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle\, \delta_{\sigma_i\sigma_j} \right)\\
&= \sum_i \langle i|(T + U_{\text{ion}})|i\rangle + \sum_{i,j}\left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle\, \delta_{\sigma_i\sigma_j} \right) - \frac{1}{2}\sum_{i,j}\left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle\, \delta_{\sigma_i\sigma_j} \right).
\end{aligned}
$$

Note that

$$
\sum_{i,j}\langle ij|\frac{e^2}{r_{ij}}|ij\rangle = \sum_{i,j}\iint d\mathbf{r}\, d\mathbf{r}'\, \psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_i(\mathbf{r})\psi_j(\mathbf{r}') = \sum_i \iint d\mathbf{r}\, \psi_i^*(\mathbf{r})U_{\text{coul}}\psi_i(\mathbf{r}) = \sum_i \langle i|U_{\text{coul}}|i\rangle\,,
$$

$$
\sum_{i,j}\langle ij|\frac{e^2}{r_{ij}}|ji\rangle = \sum_{i,j}\iint d\mathbf{r}\, d\mathbf{r}'\, \psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_j(\mathbf{r})\psi_i(\mathbf{r}').
$$

So we have

$$\langle H \rangle_\Psi = \sum_i \langle i|(T + U_{\text{ion}} + U_{\text{coul}})|i\rangle - \sum_{i,j} \iint d\mathbf{r}\, d\mathbf{r}'\, \psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r} - \mathbf{r}'|}\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\delta_{\sigma_i\sigma_j}$$

$$- \frac{1}{2}\sum_{i,j}\left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle\,\delta_{\sigma_i\sigma_j}\right)$$

$$= \sum_i \langle i|\epsilon_i|i\rangle - \frac{1}{2}\sum_{i,j}\left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle\,\delta_{\sigma_i\sigma_j}\right)$$

$$= \sum_i \epsilon_i - \frac{1}{2}\sum_{i,j}\left(\langle ij|\frac{e^2}{r_{ij}}|ij\rangle - \langle ij|\frac{e^2}{r_{ij}}|ji\rangle\,\delta_{\sigma_i\sigma_j}\right)$$

as we wanted to show.   □

Problem 10.   Band structure in the Hartree–Fock approximation   Using Eq. (4.91), calculate the density of states near the Fermi energy to leading order in $(E - E_F)/E_F$. If this result were physically correct, what would be the temperature dependence of the electronic specific heat at low temperature?

Solution.   Equation (4.91) from the lecture notes is

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} - \frac{2e^2 k_F}{\pi}F(k/k_F)$$

where by (4.92),

$$F(x) = \frac{1}{2} + \frac{1 - x^2}{4x}\ln\left|\frac{1 + x}{1 - x}\right|.$$

Making this substitution gives us

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} - \frac{2e^2 k_F}{\pi}\left(\frac{1}{2} + \frac{1 - k^2/k_F^2}{4k/k_F}\ln\left|\frac{1 + k/k_F}{1 - k/k_F}\right|\right) \tag{19}$$

Then $E_F = \epsilon(\mathbf{k}_F)$ is

$$E_F = \frac{\hbar^2 k_F^2}{2m} - \frac{2e^2 k_F}{\pi}\left(\frac{1}{2} + \frac{1 - k_F^2/k_F^2}{4k_F/k_F}\ln\left|\frac{1 + k_F/k_F}{1 - k_F/k_F}\right|\right) = \frac{\hbar^2 k_F^2}{2m} - \frac{e^2 k_F}{\pi},$$

so

$$\frac{E - E_F}{E_F} = \frac{\dfrac{\hbar^2 k^2}{2m} - \dfrac{2e^2 k_F}{\pi}F(k/k_F)}{\dfrac{\hbar^2 k_F^2}{2m} - \dfrac{e^2 k_F}{\pi}} - 1 = \frac{\dfrac{\hbar^2}{2m}\left(\dfrac{k}{k_F}\right)^2 - \dfrac{2e^2}{\pi k_F}F(k/k_F)}{\dfrac{\hbar^2}{2m} - \dfrac{e^2}{\pi k_F}} - 1.$$

The first term will be close to 1, and thus $(E - E_F)/E_F$ will be very small, when $x = k/k_F \to 1$.

From (4.34), the density of states can be found by

$$g(E) = 2\frac{4\pi k^2}{(2\pi)^3/V}\frac{dk}{dE}.$$

From our Eq. (19), we have

$$\frac{dE}{dk} = \frac{\hbar^2}{m}k - \frac{e^2 k_F}{\pi k} + \frac{e^2}{2\pi}\left(1 + \frac{k_F^2}{k^2}\right)\ln\left|\frac{1 + k/k_F}{1 - k/k_F}\right|.$$

Then the density of states is

$$g(E) = 2\frac{4\pi k^2}{(2\pi)^3/V}\left[\frac{\hbar^2}{m}k - \frac{e^2 k_F}{\pi k} + \frac{e^2}{2\pi}\left(1 + \frac{k_F^2}{k^2}\right)\ln\left|\frac{1 + k/k_F}{1 - k/k_F}\right|\right]^{-1} \approx \frac{2Vk^2}{\pi e^2}\left[\left(1 + \frac{k_F^2}{k^2}\right)\ln\left|\frac{1 + k/k_F}{1 - k/k_F}\right|\right]^{-1},$$

where the leading order term in the denominator is the logarithmic divergence.

I cannot figure out how to write $g(E)$ in terms of E and E_F, so based on $E \propto k^2$ to leading order I will guess that

$$g \sim \frac{E}{\ln|E|}$$

and attempt to determine the proportionality of the specific heat using a heuristic argument.

The specific heat can be calculated from Eq. (2.15) in the lecture notes:

$$c_v = \int dE\, Eg(E)\frac{\partial f(E)}{\partial T}.$$

From (2.17),

$$\frac{df}{dT} = \frac{e^y}{(e^y + 1)^2}\left(\frac{y}{T} + \frac{1}{k_B T}\frac{d\mu}{dT}\right) = \frac{e^y}{(e^y + 1)^2}\frac{y}{T}$$

where $y = (E - \mu)/k_B T$. At low temperature, $d\mu/dT \approx 0$ and the chemical potential $\mu = E_F$. This approximation is valid below the degeneracy temperature $k_B T \approx E_F$ [6, pp. 167–168]. Since $g(E)$ is sharply peaked near $k = k_F$ or $E = E_F$, we can write $y \approx (E - E_F)/E_F$ with little error. Further, we can say the behavior of $g(E)$ is like a delta function that picks out $k_B T \approx E$. Expanding to leading order in y, which we know is small,

$$\frac{df}{dT} \approx \frac{y}{4T}.$$

Assuming this argument is at all legitimate, the behavior of c_v is like

$$c_v \sim \int dE\, E\delta(E - T)\frac{E}{\ln(E)}\frac{y}{T} \sim \frac{T^2}{\ln|T|}\frac{y}{T} \sim \frac{T}{|\ln T|},$$

which is in agreement with Ashcroft & Mermin [1, p. 337].

Problem 11. Ferromagnetism in the HF approximation Previously, we considered the unpolarized spin state, which is a paramagnet. Now consider a fully spin polarized state at the same density: the Hartree–Fock Slater determinant corresponds to singly occupying each state in the Fermi sphere. In analogy to Eq. (4.93), compute the total energy of the spin polarized state, and show that this is lower in energy than the unpolarized state if $r_s > 5.45$ in the Hartree–Fock approximation.

Solution. Equation (4.93) is

$$E = N\left(\frac{3}{5}\frac{\hbar^2 k_F^2}{2m} - \frac{3}{4}\frac{e^2 k_F}{\pi}\right) = N\left(\frac{3}{5}(k_F a_B)^2 - \frac{3}{2\pi}k_F a_B\right)\text{Ry}, \tag{20}$$

where we have used the definition of the Rydberg in (4.87):

$$1\,\text{Ry} = \frac{\hbar^2}{2m a_B^2} = \frac{e^2}{2a_B},$$

where a_B is the Bohr radius.

The exchange term of the Hartree-Fock equations (4.84) in the lecture notes is

$$\sum_j \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r})\delta_{\sigma_i\sigma_j},$$

which is nonzero only for electrons of the same spin. This means we can write an expression like Eq. (20) for electrons of each spin state:

$$E_\uparrow = N_\uparrow\left(\frac{3}{5}(k_\uparrow a_B)^2 - \frac{3}{2\pi}k_\uparrow a_B\right)\text{Ry}, \qquad E_\downarrow = N_\downarrow\left(\frac{3}{5}(k_\downarrow a_B)^2 - \frac{3}{2\pi}k_\downarrow a_B\right)\text{Ry}. \qquad (21)$$

Here, $k_\uparrow$ and $k_\downarrow$ are the wave vectors corresponding to the highest energy states occupied by spin up and by spin down electrons, respectively.

The total energy is the sum of the energies for each spin state: $E = E_\uparrow + E_\downarrow$. The total electron density is the sum of the densities of spin up and of spin down electrons:

$$n = \frac{N}{V} = \frac{N_\uparrow}{V} + \frac{N_\downarrow}{V} = \frac{4k_\uparrow^3/3}{(2\pi)^3} + \frac{4k_\downarrow^3/3}{(2\pi)^3} = \frac{k_\uparrow^3}{6\pi^2} + \frac{k_\downarrow^3}{6\pi^2} = \frac{k_F}{3\pi^2}. \qquad (22)$$

For a fully spin polarized state, either $N_\uparrow$ or $N_\downarrow$ is 0 and the other N; that is, all electrons are in the same spin state. Say $N_\downarrow = N$ and $N_\uparrow = 0$. Then $E = E_\downarrow$, and

$$\frac{k_\downarrow^3}{6\pi^2} = \frac{k_F}{3\pi^2} \implies k_\downarrow = 2^{1/3}k_F.$$

Making these substitutions in Eq. (21), we have [1, pp. 682–683]

$$E = N\left(\frac{3}{5}(2^{1/3}k_F a_B)^2 - \frac{3}{2\pi}2^{1/3}k_F a_B\right)\text{Ry}$$

$$= N\left(\frac{2^{2/3}3}{5}(k_F a_B)^2 - \frac{2^{1/3}3}{2\pi}k_F a_B\right)\text{Ry}$$

$$= N\left(\frac{2^{2/3}3}{5}\frac{\hbar^2 k_F^2}{2m} - \frac{2^{1/3}3}{4}\frac{e^2 k_F}{\pi}\right). \qquad (23)$$

Call the energy for the spin unpolarized state E_{par}, and the energy for the fully polarized state E_{fer}. Using Ashcroft & Mermin (2.22),

$$k_F = \frac{(9\pi/4)^3}{r_s} \approx \frac{1.92}{r_s},$$

we have

$$E_{\text{par}} = N\left[\frac{3}{5}\left(1.92\frac{a_B}{r_s}\right)^2 - \frac{3}{2\pi}1.92\frac{a_B}{r_s}\right]\text{Ry}, \qquad E_{\text{fer}} = N\left[\frac{2^{2/3}3}{5}\left(1.92\frac{a_B}{r_s}\right)^2 - \frac{2^{1/3}3}{2\pi}1.92\frac{a_B}{r_s}\right]\text{Ry}$$

Then $E_{\text{fer}} < E_{\text{par}}$ can be written as

$$\frac{2^{2/3}3}{5}\left(1.92\frac{a_B}{r_s}\right)^2 - \frac{2^{1/3}3}{2\pi}1.92\frac{a_B}{r_s} < \frac{3}{5}\left(1.92\frac{a_B}{r_s}\right)^2 - \frac{3}{2\pi}1.92\frac{a_B}{r_s},$$

which is equivalent to

$$0 > (2^{2/3}-1)\frac{3}{5}\left(1.92\frac{a_B}{r_s}\right)^2 - (2^13-1)\frac{3}{2\pi}1.92\frac{a_B}{r_s} \approx 1.299\left(\frac{a_B}{r_s}\right)^2 - 0.238\frac{a_B}{r_s}.$$

The solutions of the quadratic equation are 0 and

$$\frac{a_B}{r_s} < \frac{0.238 + 0.238}{2 \times 1.299} \approx 0.183,$$

which is equivalent to

$$\frac{r_s}{a_B} > 5.45.$$

Thus, we have shown that $r_s/a_B > 5.45 \implies E_{\text{fer}} < E_{\text{par}}$.   □

Problem 12. Thomas–Fermi screening Check the formulae in Eq. (4.133) and Eq. (4.134). Supposing that the potential $v_{\text{ext}} = Q/r$, show that the induced charge density is then of the form

$$\delta n(r) \propto \frac{e^{-r/\xi}}{r}$$

and identify the screening length ξ.

Solution. Equation (4.133) is

$$\delta n(\mathbf{q}) = -\frac{v_{\text{ext}}(\mathbf{q})}{\frac{4\pi e^2}{q^2}\left(1 + \frac{q^2}{q_{TF}^2}\right)},$$

and (4.124) is

$$q_{TF}^2 = \frac{4}{\pi}\frac{me^2}{\hbar^2}k_F.$$

We must Fourier transform v_{ext} to get an expression in terms of $\mathbf{q}$. From Ashcroft & Mermin (17.52),

$$v_{\text{ext}}(\mathbf{r}) = \frac{Q}{r} \quad \implies \quad v_{\text{ext}}(\mathbf{q}) = \frac{4\pi Q}{q^2}.$$

Then

$$\delta n(\mathbf{q}) = \frac{4\pi Q/q^2}{\frac{4\pi e^2}{q^2}\left(1 + q^2 \frac{\pi}{4}\frac{\hbar^2}{me^2 k_F}\right)} = \frac{4\pi Q/q^2}{\frac{4\pi e^2}{q^2} + \frac{\pi^2 \hbar^2}{mk_F}} = \frac{Q}{e^2 + \frac{\pi\hbar^2}{4mk_F}q^2}.$$

The inverse Fourier transform is

$$\delta n(r) = \int \frac{d\mathbf{q}}{(2\pi)^3} e^{-i\mathbf{q}\cdot\mathbf{r}} \frac{Q}{e^2 + \frac{\pi\hbar^2}{4mk_F}|\mathbf{q}|^2}$$

$$= Q \int \frac{dq}{(2\pi)^3} \int_0^\pi d\theta \int_0^{2\pi} d\phi\, e^{-iqr\cos\theta} \frac{q^2 \sin\theta}{e^2 + \frac{\pi\hbar^2}{4mk_F}q^2}$$

$$= 4\pi Q \int_0^\infty \frac{dq}{(2\pi)^3} \frac{\sin(qr)}{qr} \frac{q^2}{e^2 + \frac{\pi\hbar^2}{4mk_F}q^2}$$

$$= 4\pi \frac{Q}{r} \int_0^\infty \frac{dq}{(2\pi)^3} \frac{x\sin x}{e^2 r^2 + \frac{\pi\hbar^2}{4mk_F}x^2}$$

$$= \frac{2\pi^2}{\pi\hbar^2/4mk_F} \frac{Q}{(2\pi)^3 r} \exp\left(-\frac{er}{\sqrt{\pi\hbar^2/4mk_F}}\right)$$

$$= \frac{mk_F Q}{\pi^2 \hbar^2} \frac{1}{r} \exp\left(-\frac{r}{q_{TF}}\right)$$

where we have defined $x = qr$. Then $\xi = q_{TF}$.   □

Problem 13.   Generalized one-dimensional band theory   Consider a 1D solid, lattice constant a, made of "building blocks" $(-a/2 < x < a/2)$ that scatter plane waves with a reflection coefficient r and transmission coefficient t $(|r|^2 + |t|^2 = 1)$. The energy of the plane wave is written as $\epsilon = \hbar^2 K^2/2m$. In the solid, the building blocks are stacked together indefinitely in the x direction.

13(a)   Write the solution to the Schrödinger equation in the solid $\psi(x)$ as a linear combination of $\psi_r(x)$ and $\psi_l(x)$, and use Bloch's theorem to relate the wavefunction at each side of the building block (the same theorem applies to the gradient ψ'):

$$\psi(x + a) = e^{ika}\psi(x), \qquad\qquad \psi'(x + a) = e^{ika}\psi'(x).$$

Hence, show

$$\cos(ka) = \frac{t^2 - r^2}{2t}e^{iKa} + \frac{1}{2t}e^{-iKa}.$$

Solution.   Referring to the diagrams, we can write

$$\psi_l(x) = \begin{cases} e^{iKx} + re^{-iKx} & x \leq -\frac{a}{2}, \\ te^{iKx} & x \geq \frac{a}{2}; \end{cases} \qquad\qquad \psi_r(x) = \begin{cases} te^{-iKx} & x \leq -\frac{a}{2}, \\ e^{-iKx} + re^{iKx} & x \geq \frac{a}{2}; \end{cases}$$

and the gradients

$$\psi_l'(x) = \begin{cases} iK\left(e^{iKx} - re^{-iKx}\right) & x \leq -\frac{a}{2}, \\ iKte^{iKx} & x \geq \frac{a}{2}; \end{cases} \qquad\qquad \psi_r'(x) = \begin{cases} -iKte^{-iKx} & x \leq -\frac{a}{2}, \\ iK\left(-e^{-iKx} + re^{iKx}\right) & x \geq \frac{a}{2}. \end{cases}$$

Inside the barrier,

$$\psi(x) = A\psi_l + B\psi(\mathbf{r}) \qquad -\frac{a}{2} \leq x \leq \frac{a}{2}.$$

Using Bloch's theorem Eq. (1), we can write the boundary conditions [1, p. 147]

$$\psi(x + a) = e^{ika}\psi(x), \qquad\qquad \psi'(x + a) = e^{ika}\psi'(x),$$

Imposing the first condition on the boundary at $x = -a/2$, we find

$$Ate^{iKa/2} + Be^{-iKa/2} + Bre^{iKa/2} = e^{ika}\left(Ae^{-iKa/2} + Are^{iKa/2} + Bte^{iKa/2}\right)$$

$$B + (At + Br)e^{iKa} = e^{ika}\left[A + (Ar + Bt)e^{iKa}\right]$$

$$B\left[1 + re^{iKa} - te^{iKa}e^{ika}\right] = A\left[e^{ika} + re^{iKa}e^{ika} - te^{iKa}\right]$$

$$B = e^{ika}\frac{1 + re^{iKa} - te^{iKa}e^{-ika}}{1 + re^{iKa} - te^{iKa}e^{ika}}A.$$

Imposing the second gives us

$$iK\left(Ate^{iKa/2} - Be^{-iKa/2} + Bre^{iKa/2}\right) = iKe^{ika}\left(Ae^{-iKa/2} - Are^{iKa/2} - Bte^{iKa/2}\right)$$

$$-B + (At + Br)e^{iKa} = e^{ika}\left[A + (-Ar + Bt)e^{iKa}\right]$$

$$B\left[-1 + re^{iKa} + te^{iKa}e^{ika}\right] = A\left[e^{ika} - re^{iKa} - te^{iKa}e^{ika}\right]$$

$$B = e^{ika}\frac{1 - re^{iKa} - te^{iKa}e^{-ika}}{-1 + re^{iKa} + te^{iKa}e^{ika}}A.$$

Equating both expressions for B, we have

$$\frac{1 + re^{iKa} - te^{iKa}e^{-ika}}{1 + re^{iKa} - te^{iKa}e^{ika}} = \frac{1 - re^{iKa} - te^{iKa}e^{-ika}}{-1 + re^{iKa} + te^{iKa}e^{ika}}$$

$$\left(1 + re^{iKa} - te^{iKa}e^{-ika}\right)\left(-1 + re^{iKa} + te^{iKa}e^{ika}\right) = \left(1 - re^{iKa} - te^{iKa}e^{-ika}\right)\left(1 + re^{iKa} - te^{iKa}e^{ika}\right).$$

The left side is

$$-1 + re^{iKa} + te^{iKa}e^{ika} - re^{iKa} + r^2e^{2iKa} + rte^{2iKa}e^{ika} + te^{iKa}e^{-ika} - rte^{2iKa}e^{-ika} - t^2e^{2iKa},$$

and the right side is

$$1 + re^{iKa} - te^{iKa}e^{ika} - re^{iKa} - r^2e^{2iKa} + rte^{2iKa}e^{ika} - te^{iKa}e^{-ika} - rte^{2iKa}e^{-ika} + t^2e^{2iKa}.$$

So the equality becomes

$$0 = 1 - te^{iKa}e^{ika} - r^2e^{2iKa} - te^{iKa}e^{-ika} + t^2e^{2iKa}$$

$$= 1 - te^{iKa}\left(e^{ika} + e^{-ika}\right) + (t^2 - r^2)e^{2iKa}$$

$$= 1 - 2te^{iKa}\cos(ka) + (t^2 - r^2)e^{2iKa}$$

or

$$\cos(ka) = \frac{t^2 - r^2}{2t}e^{iKa} + \frac{1}{2t}e^{-iKa}$$

as we wanted to show. $\qquad\square$

13(b) If the transmission coefficient is $t = |t|e^{i\delta}$, it can be shown that $r = \pm i|r|e^{i\delta}$. Use this result to eliminate r and show

$$\frac{\cos(Ka + \delta)}{|t|} = \cos(ka).$$

Solution. Feeding the coefficients and $1 = |t|^2 + |r|^2$ into the previous result, we have

$$\cos(ka) = \frac{e^{2i\delta}(|t|^2 + |r|^2)}{2|t|e^{i\delta}}e^{iKa} + \frac{1}{2|t|e^{i\delta}}e^{-iKa}$$

$$= \frac{e^{2i\delta}}{2|t|e^{i\delta}}e^{iKa} + \frac{1}{2|t|e^{i\delta}}e^{-iKa}$$

$$= \frac{e^{i(\delta + Ka)}}{2|t|} + \frac{e^{-i(\delta + Ka)}}{2|t|}$$

$$= \frac{\cos(Ka + \delta)}{|t|}$$

as we wanted to show. $\qquad\square$

13(c) Since $|t| < 1$, this result shows there are values of K (and hence ϵ) for which no Bloch states exist. Demonstrate this by sketching the left-hand side as a function of K (or preferably ϵ). Use your sketch to illustrate the behavior for

(i) strong scattering, and

(ii) weak scattering.

Explain why, in general, electron bands tend to get wider and their gaps narrower as the electron energy increases.
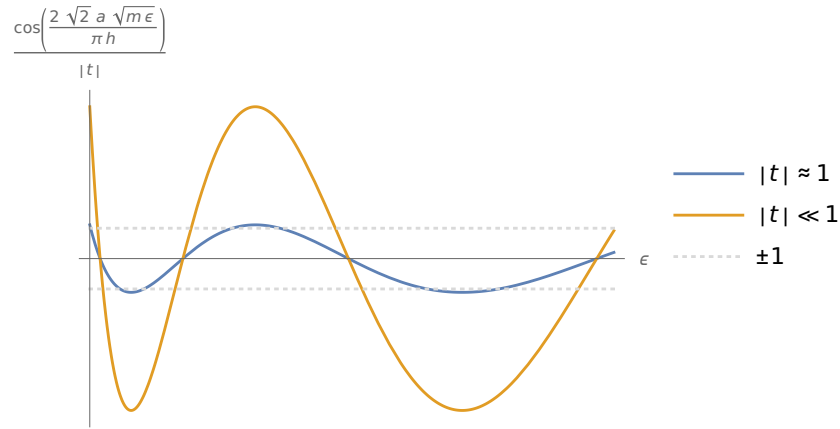
Figure 2: Plot of Eq. (24) with $\delta = 0$ as a function of ϵ. Strong (weak) scattering is shown as the blue (gold) curve. The ranges of ϵ for which the curves are between the light gray dashed lines are regions in which Bloch states exist.

Solution. Figure 2 shows

$$\frac{1}{|t|}\cos\left(\frac{a\sqrt{2m\epsilon}}{\hbar} + \delta\right) \tag{24}$$

as a function of ϵ. In the figure, the phase $\delta = 0$. No Bloch states exist in the regions in which

$$\frac{\cos(Ka + \delta)}{|t|} > 1 \quad \text{or} \quad \frac{\cos(Ka + \delta)}{|t|} < -1.$$

Strong scattering (blue curve) is associated with $|r|$ near 1 and small $|t|$, with the majority of the wave being being reflected. Weak scattering (gold curve) is associated with small $|r|$ and $|t|$ near 1, with the majority of the wave being transmitted. The regions with no existing Bloch states are narrower for strong scattering [1, p. 149].

This model suggests the electron bands and gaps both tend to widen as electron energy increases. However, in general we expect the bands to widen and the gaps to narrow. This is because the higher-energy atomic orbitals have larger radii; hence, there is a higher degree of overlap between high-energy orbitals of adjacent atoms than between low-energy orbitals of adjacent atoms. As this degree of overlap increases, the degree of "non-overlap" decreases. Since the bands represent the overlapping regions of space and the gaps represent the non-overlapping regions, the bands widen and the gaps narrow.

References

[1] N. W. Ashcroft and N. D. Mermin, "Solid State Physics". Harcourt College Publishers, 1976.

[2] J. J. Sakurai, "Modern Quantum Mechanics". Addison-Wesley Publishing Company, revised edition, 1994.

[3] Wikipedia contributors, "Leibniz formula for determinants." From Wikipedia, the Free Encyclodia. https://en.wikipedia.org/wiki/Leibniz_formula_for_determinants.

[4] T. H. Kim, "An iterative technique for solving the n-electron Hamiltonian: The Hartree-Fock method",.

[5] E. W. Weisstein, "Lagrange Multiplier." From MathWorld—A Wolfram Web Resource. https://mathworld.wolfram.com/LagrangeMultiplier.html.

[6] L. D. Landau and E. M. Lifshitz, "Statistical Physics", volume 5. Pergamon Press, 2nd edition, 1970.