ECE 456 - Problem Set 3 (Part 1)

David Lenfesty
lenfesty@ualberta.ca

Phillip Kirwin
pkirwin@ualberta.ca

2021-03-31

Problem 1

(a) (i) The matrix equation is

$$[\hat{H}]\{\phi\} = E\{\phi\},$$

where $[\hat{H}]$ is an N-by-N matrix with $[\hat{H}]_{nm} = 0$ except for the following elements:

$$[\hat{H}]_{nn} = 2t_0 + U_n$$
$$[\hat{H}]_{n,n\pm1} = -t_0$$
$$[\hat{H}]_{0,N} = [\hat{H}]_{N,0} = -t_0,$$

with $t_0 = \hbar^2/(2ma^2)$ and $U_n = U(na)$. The N-vector $\{\phi\}$ has elements ϕ_n which each represent the value of the eigenvector at the point $na = x_n$.

(ii) The expression of the wave function $\phi(x)$ as a sum of basis functions is as below:

$$\phi(x) = \sum_{n=1}^{N} \phi_n u_n(x)$$

The derived matrix equation:

$$[\hat{H}]_u\{\phi\} = [S]_u\{\phi\}$$

Where $[\hat{H}]_u$ is a matrix with the elements:

$$H_{nm} = \int u_n^*(x)\hat{H}u_m(x)dx$$

and $[S]_u$ is a matrix with the elements:

$$S_{nm} = \int u_n^*(x)u_m(x)dx$$

$[\hat{H}]_u$ and $[S]_u$ are both of size N-by-N. The elements of $\{\phi\}$, ϕ_n, are the expansion coefficients of $\phi(x)$.

(b) (i) code:

```
%constants
E1 = -13.6;
R = 0.074;
a0 = 0.0529;

%matrix elements
R0 = R/a0;

a = 2*E1*(1-(1+R0)*exp(-2*R0))/R0;
b = 2*E1*(1+R0)*exp(-R0);
s = exp(-R0)*(1+R0+(R0^2/3));

%matrices
H_u = [E1 + a, E1*s+b; E1*s+b, E1 + a];
S_u = [1, s; s, 1];

%find eigenvalues and eigenvectors
[vectors,energies] = eig(inv(S_u)*H_u);
```

The bonding and antibonding eigenenergies are $\boxed{-32.2567\,\text{eV}}$ and $\boxed{-15.5978\,\text{eV}}$ respectively.

(ii) Neglecting normalization, we have the following expressions for $\phi_B(z)$ and $\phi_A(z)$:

$$\phi_B(z) = u_L(z) + u_R(z)$$
$$\phi_A(z) = u_L(z) - u_R(z).$$

We obtain the following plot:

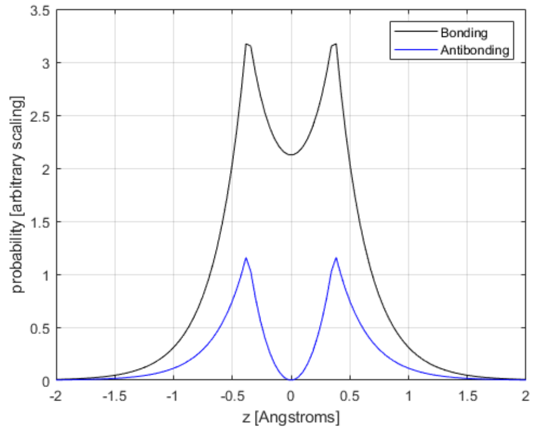

Figure 1. *non-normalized probability densities for bonding and antibonding solutions.*

Problem 2

(a) (i)

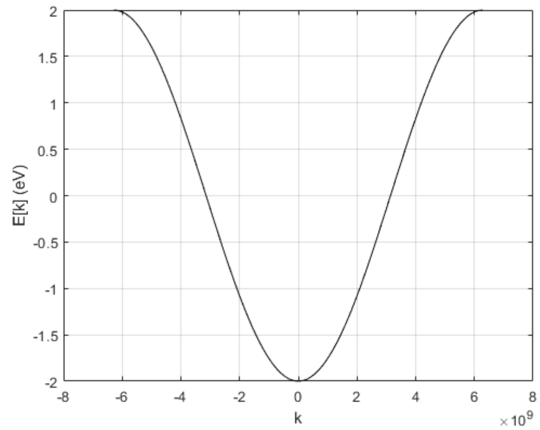

Figure 2. *Energy vs. wave vector relationship.*

(ii) Energy values from -2 eV to 2 eV are allowed.

(iii) The vector $\{\phi\}$, which is of length N, and has elements n is:

$$\{\phi\} = Ce^{ik\cdot na}$$

$$\{\phi\} = \begin{bmatrix} Ce^{ika} \\ Ce^{ik2a} \\ \vdots \\ C_A e^{ikNa} \end{bmatrix}$$

The corresponding wave function is:

$$\phi(x) = \sum_{n=1}^{N} Ce^{ik\cdot na} u_n(x)$$

There is one wave function and thus one energy level for each value of k. This means that there is one electronic state per k.

(b) (i)

$$\{\phi\} = \begin{bmatrix} C_A e^{ika} \\ C_B e^{ika} \\ C_A e^{ik2a} \\ C_B e^{ik2a} \\ \vdots \\ C_A e^{ikNa} \\ C_B e^{ikNa} \end{bmatrix}$$

(ii)

$$\phi(x) = \sum_{n=1}^{N} C_A e^{ikna} u_{nA}(x) + C_B e^{ikna} u_{nB}(x)$$

(iii) $[h(k)]$ is of size 2-by-2. Thus there will be two values of $E(k)$ for a fixed k. This also means there are two $\phi(x)$ for each k.

(c) (i)

$$\phi_2 + 2\phi_3 + \phi_4 = E\phi_1$$
$$\phi_1 + \phi_3 + 2\phi_4 = E\phi_2$$
$$2\phi_1 + \phi_2 + \phi_4 = E\phi_3$$
$$\phi_1 + 2\phi_2 + \phi_3 = E\phi_4$$

(ii)

$$\phi_2 + 2\phi_3 + \phi_0 = E\phi_1$$
$$\phi_1 + \phi_3 + 2\phi_4 = E\phi_2$$
$$2\phi_5 + \phi_2 + \phi_4 = E\phi_3$$
$$\phi_5 + 2\phi_6 + \phi_3 = E\phi_4$$

(iii) A generalized form of the nth equation is:

$$E\phi_n = \phi_{n-1} + \phi_{n+1} + 2\phi_{n+2}$$

(iv)

$$ECe^{ikna} = Ce^{ik(n+1)a} + Ce^{ik(n-1)a} + 2Ce^{ik(n+2)a}$$
$$E = e^{ika} + e^{-ika} + 2e^{2ika}$$
$$E(k) = 2e^{2ika} + 2\cos(ka) \quad (1)$$

(v) Imposing the repeating boundary conditions $\phi_{n+4} = \phi_n$, We obtain the following relationship:

$$Ce^{ikna} = Ce^{ik(n+4)a}$$
$$1 = e^{i4ka}$$

For this to hold, $4ka$ must be some multiple of 2π, and this mean $k = \frac{\pi}{2a} \cdot integer$.

(vi) Using the E-k relationship from equation 1, we know that k must always be real, so the $2\cos(ka)$ portion of the E-k relationship must be real. As well, if we substitute in the equation for k we obtained in part (v), we get the following (partial) expression:

$$2e^{i2ka} = 2e^{i\pi \cdot integer}$$

Which we know will always be real (with a value of ± 2).

(vii) Since $e^{2\pi n} = 1$, we have:

$$\phi_n(k + \frac{2\pi}{a}) = Ce^{i(k+\frac{2\pi}{a})\cdot nA} = Ce^{ik\cdot nA}$$
$$\phi_n(k + \frac{2\pi}{a}) = \phi_n(k).$$

Therefore wavefunctions for which k is separated by $\frac{2\pi}{a}$ are equivalent, and we only need consider the range $k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$.

Problem 3

(a) Given the geometry and interaction rules stated, the interaction matrices $[H]_{nm}$ are zero except for

$$[H]_{nn} = \begin{bmatrix} E_0 & t_i \\ t_i & E_0 \end{bmatrix}$$
$$[H]_{n,m*} = \begin{bmatrix} t_A & 0 \\ 0 & t_B \end{bmatrix}$$

where $m*$ corresponds to any of the four nearest neighbor square-shaped unit cells to cell n. For cell n, let cell a be above, cell b be to the right, cell c be below, and cell d be to the left. Given that each cell is spaced a length a apart, the associated phase factors for nonzero H_{nm}, $e^{i\vec{k}\cdot(\vec{d_m}-\vec{d_n})}$, are then:

$$\begin{aligned} (n): &\quad 1 \\ (a): &\quad e^{ik_y a} \\ (b): &\quad e^{ik_x a} \\ (c): &\quad e^{-ik_y a} \\ (d): &\quad e^{-ik_x a} \end{aligned}$$

with $\vec{k} = k_x\hat{x} + k_y\hat{y}$. The Bloch matrix then follows:

$$\begin{aligned} [h(\vec{k})] &= \sum_m [H]_{nm} e^{i\vec{k}\cdot(\vec{d_m}-\vec{d_n})} \\ &= \begin{bmatrix} E_0 + t_A\left(e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a}\right) & t_i \\ t_i & E_0 + t_B\left(e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a}\right) \end{bmatrix} \\ &= \begin{bmatrix} E_0 + 2t_A\left(\cos(k_x a) + \cos(k_y a)\right) & t_i \\ t_i & E_0 + 2t_B\left(\cos(k_x a) + \cos(k_y a)\right) \end{bmatrix} \end{aligned}$$

(b) To find the E-$\vec{k}$ relationship in terms of cosine functions, we must first find h_0 in terms of trigonometric functions. We will require the following trigonometric identities to do so:

$$\sin(\alpha \pm \beta) = \sin(\alpha)\cos(\beta) \pm \sin(\beta)\cos(\alpha) \tag{2}$$

$$\cos(\alpha \pm \beta) = \cos(\alpha)\cos(\beta) \mp \sin(\alpha)\sin(\alpha) \tag{3}$$

$$1 = \sin^2(\theta)\cos^2(\theta), \tag{4}$$

as well as the following general sine/cosine properties:

$$\begin{aligned} \cos(\theta) &= \cos(-\theta) \\ \sin(\theta) &= -\sin(-\theta). \end{aligned} \tag{5}$$

First we can rewrite the exponentials in h_0 using Euler's identity:

$$h_0 = -t_c\left(1 + \cos(-k_x a - k_y b) + i\sin(-k_x a - k_y b) + \cos(-k_x a + k_y b) + i\sin(-k_x a + k_y b)\right)$$

Using identities (2) and (3), we can expand this relationship further.

$$h_0 = -t + c\big(1 + \cos(-k_x a)\cos(-k_y b) - \sin(-k_x a)\sin(-k_y b) + i\sin(-k_x a)\cos(-k_y b) + i\sin(-k_y b)\cos(-k_x a)$$
$$+ \cos(k_y b)\cos(k_x a) + \sin(k_y b)\sin(k_x a) + i\sin(k_y b)\cos(k_x a) - i\sin(k_x a)\cos(k_y b)\big)$$

Here we can use the properties from (5) to reduce this equation. Since $|h_0|^2 = h_0 h_0^*$, we also obtain a simple expression for h_0^*.

$$h_0 = -t_c\left(1 + 2\cos(k_x a)\cos(k_y b) - 2i\sin(k_x a)\cos(k_y b)\right)$$
$$h_0^* = -t_c\left(1 + 2\cos(k_x a)\cos(k_y b) + 2i\sin(k_x a)\cos(k_y b)\right)$$

We can now find $|h_0|^2 = h_0 h_0^*$:

$$h_0 h_0^* = 1 + 4\cos(k_x a)\cos(k_y b) + 4\cos^2(k_y b)$$

From this, we can finally obtain an expression for $E(\vec{k})$:

$$E(\vec{k}) = E_0 \pm t_c\sqrt{1 + 4\cos(k_x a)\cos(k_y b)4\cos^2(k_y b)} \tag{6}$$

Problem 4

(a) We can substitute (from the assignment) equation (24) into equation (23):

$$\sum_k i\hbar\frac{\delta}{\delta t}c_k(t)\phi_k(x)e^{-i[E(k)/\hbar]t} = \sum_k c_k(t)\hat{H}_0\phi(x)e^{-i[E(k)\ \hbar]t} \tag{7}$$
$$+ \sum_k c_k(t)U_s(x,t)\phi_k(x)e^{-i[E(k)/\hbar]t} \tag{8}$$

We can partially evaluate the derivative on the left hand side:

$$\frac{\delta}{\delta t}c_k(t)\phi_k(t)e^{-i[E(k)/\hbar]t} = \frac{\delta c_k(t)}{\delta t}\phi_k(t)e^{-i[E(k)/\hbar]t} - \frac{i}{\hbar}c_k(t)E(k)\phi_k(x)e^{-i[E(k)/\hbar]t}$$

Expanding the rightmost term out into the summation, we get the expression $\sum_k c_k(t)E(k)\phi_k(x)e^{-i[E(k)/\hbar]t}$. Since $\hat{H}_0\phi_k(x) = E(k)\phi_k(x)$, we can see that this cancels out the term with $\hat{H}_0$ in our first substition (8), and we get the final differential equation:

$$\sum_k c_k(t)U_s(x,t)\phi_k(x)e^{-i[E(k)/\hbar]t} = \sum_k i\hbar\frac{\delta c_k(t)}{\delta t}\phi_k(x)e^{-i[E(k)/\hbar]t}$$

(b)

$$\sum_k c_k(t)\left[\int \phi^*_{k_f}(x)U_s(x,t)\phi_k(x)\,dx\right]e^{-i[E(k)/\hbar]t} = \sum_k i\hbar\frac{\partial c_k(t)}{\partial t}\left[\int \phi^*_{k_f}(x)\phi_k(x)\,dx\right]e^{-i[E(k)/\hbar]t}$$
$$\sum_k c_k(t)I_{k_f k}e^{-i[E(k)/\hbar]t} = \sum_k i\hbar\frac{\partial c_k(t)}{\partial t}\delta_{k_f k}e^{-i[E(k)/\hbar]t}$$
$$\sum_k c_k(t)I_{k_f k}e^{-i[E(k)/\hbar]t} = i\hbar\frac{\partial c_k(t)}{\partial t}e^{-i[E(k)/\hbar]t}$$

where $I_{k_f k}$ is as defined in the assignment and $\delta_{k_f k}$ is the Kronecker delta.

(c) Starting with the initial equation

$$\sum_k c_k(t)I_{k_f k}e^{-i[E(k)/\hbar]t} = i\hbar\frac{\delta c_{k_f}(t)}{\delta t}e^{-i[E(k_f)/\hbar]t}$$

Since we approximated that $c_k = 1$, only when $k = k_i$, and 0 otherwise, we can simplify the sum on the left hand side to a single element, and divide out the exponentials.

$$I_{k_f k_i}e^{i[-E(k_i)+E(k_f)/\hbar]t} = i\hbar\frac{\delta c_k(t)}{\delta t}$$

Defining a new symbol $\Lambda = [E(k_f) - E(k_i)]/\hbar$, we can simplify the equation to it's final form.

$$I_{k_f k_i}e^{i\Lambda t} = i\hbar\frac{\delta c_k(t)}{\delta t} \tag{9}$$

(d)

$$\int\frac{\partial c_{k_f}(t)}{\partial t} = \frac{1}{i\hbar}I_{k_f k_i}\int e^{i\Lambda t}$$
$$c_{k_f}(t) = \frac{1}{i\hbar}I_{k_f k_i}\frac{1}{i\Lambda}e^{i\Lambda t} + C$$
$$c_{k_f}(t) = \frac{1}{i\hbar}I_{k_f k_i}e^{i\Lambda t/2}\left[\frac{1}{i\Lambda}e^{i\Lambda t/2} + Ce^{-i\Lambda t/2}\right]$$

Let $C = -\frac{1}{i\Lambda}$. We then have:

$$c_{k_f}(t) = \frac{1}{i\hbar}I_{k_f k_i}e^{i\Lambda t/2}\frac{1}{i\Lambda}\left[e^{i\Lambda t/2} - e^{-i\Lambda t/2}\right]$$
$$c_{k_f}(t) = \frac{1}{i\hbar}I_{k_f k_i}e^{i\Lambda t/2}\frac{\sin(\Lambda t/2)}{\Lambda/2}.$$

(e)