

ECE 456 - Problem Set 3 (Part 1)

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TOTAL: $\frac{25}{25}$

Well done, David and Phillip!

-Adan

Problem 1

Q1: 20/60

- (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:

$$[\hat{H}]_{nn} = 2t_0 + U_n$$

$$[\hat{H}]_{n,n\pm 1} = -t_0$$

$$[\hat{H}]_{0,N} = [\hat{H}]_{N,0} = -t_0,$$

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:

```

1 %constants
2 E1 = -13.6;
3 R = 0.074;
4 a0 = 0.0529;
5
6 %matrix elements
7 R0 = R/a0;
8
9 a = 2*E1*(1-(1+R0)*exp(-2*R0))/R0;
10 b = 2*E1*(1+R0)*exp(-R0);
11 s = exp(-R0)*(1+R0+(R0^2/3));
12
13 %matrices
14 H_u = [E1 + a, E1*s+b; E1*s+b, E1 + a];
15 S_u = [1, s; s, 1];
16
17 %find eigenvalues and eigenvectors
18 [vectors, energies] = eig(inv(S_u)*H_u);

```

The bonding and antibonding eigenenergies are -32.2567 eV and -15.5978 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:

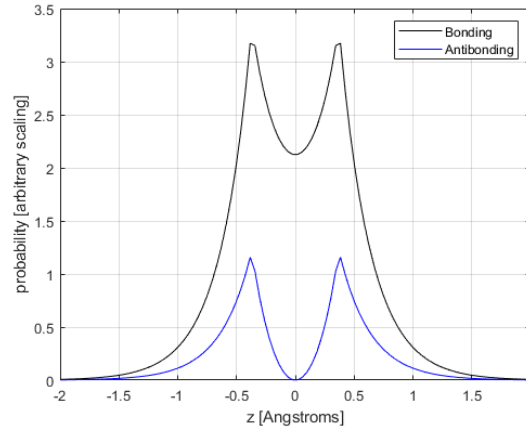


Figure 1. *non-normalized probability densities for bonding and antibonding solutions.*

Problem 2

Q2: 13/13

(a) (i)

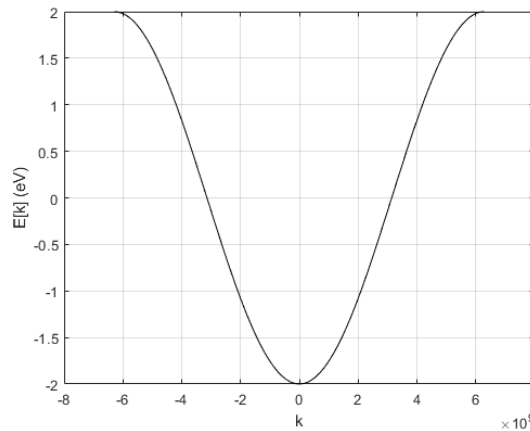


Figure 2. Energy vs. wave vector relationship.

(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:

$$\{\phi\} = C e^{ik \cdot na}$$

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

The corresponding wave function is:

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

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 n th 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 $k = \frac{\pi}{2a} \cdot \text{integer}$.

(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:

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

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 $k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$.