ECE 456 - Problem Set 3 (Part 1)

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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:

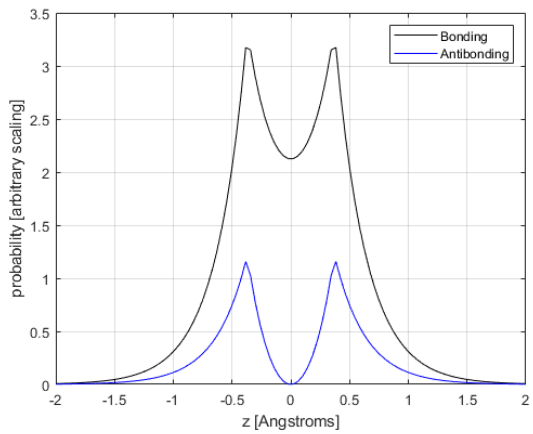

Figure 1. *non-normalized probability densities for bonding and antibonding solutions.*

Problem 2

(a) (i)

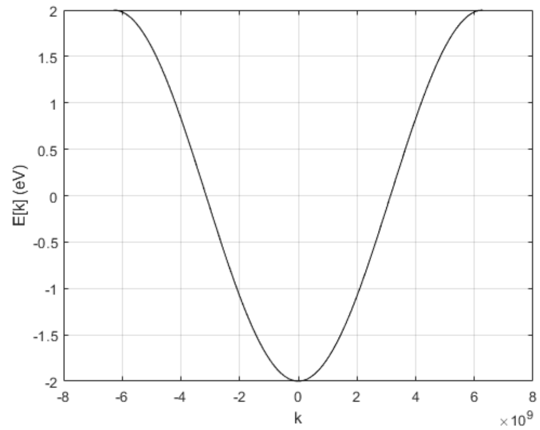

Figure 2. *Energy vs. wave vector relationship (note: not discretized to account for N)*

(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:

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

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)

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

(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)

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

(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:

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

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