

Problem 1

Using the tight-binding model, compute the energy band formed by atomic s-orbitals in a square lattice of constant a , with a single atom basis (the s-level atomic energy and the overlap integrals, respectively) are considered to be known).

a) Plot the energy band (ϵ_q versus q) in 3D.

```
clc
clear
close all

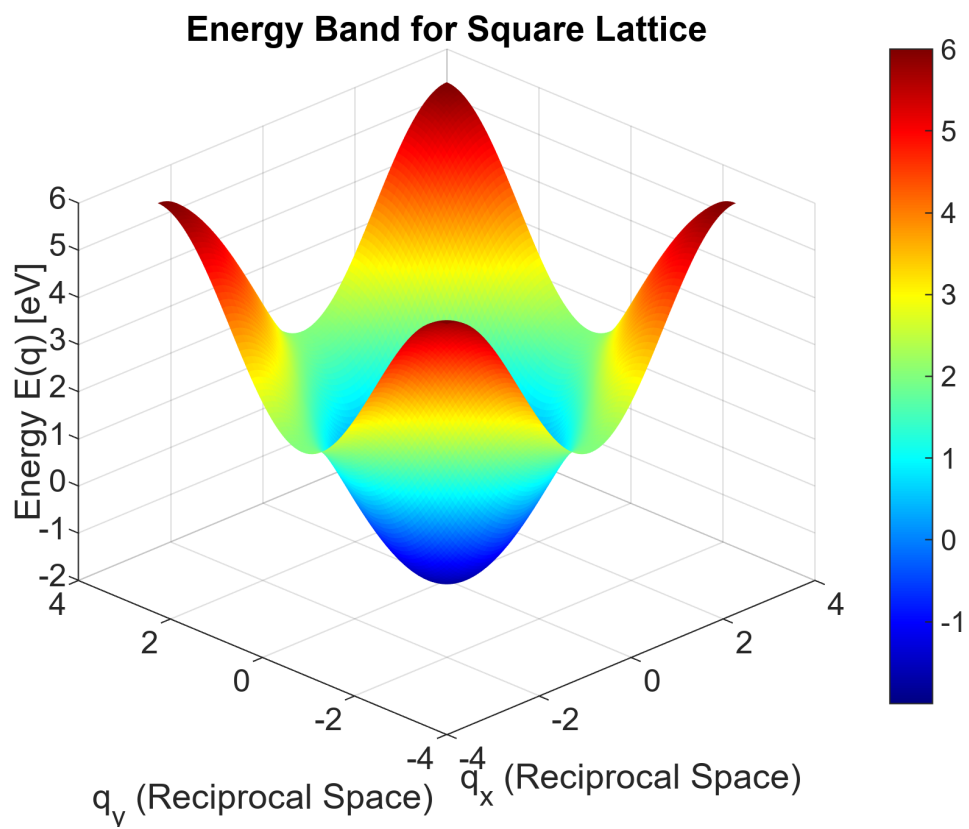
qx = linspace(-pi, pi, 100); % k_x space
qy = linspace(-pi, pi, 100); % k_y space

% I searched for typical values for Es and gamma in different papers
% From what I remember in class, gamma is negative
Es = 2; % eV
gamma = -1; % eV

[QX, QY] = meshgrid(qx, qy);

E_k = Es + 2*gamma * cos(QX) + 2*gamma * cos(QY);

figure;
surf(QX, QY, E_k, 'EdgeColor', 'none'); % 3D surface plot
xlabel('q_x (Reciprocal Space)', 'FontSize', 12);
ylabel('q_y (Reciprocal Space)', 'FontSize', 12);
zlabel('Energy E(q) [eV]', 'FontSize', 12);
title('Energy Band for Square Lattice', 'FontSize', 20);
colormap jet;
colorbar;
grid on;
view([-45, 30]); % Adjust viewing angle for better visualization
set(gca, 'FontSize', 12);
```



b) Plot the energy vs q along certain directions: going from M to Γ , then from Γ to X , then from X back to M (This will be a 2D plot.)

```
M = [pi, pi];
X = [pi, 0];
Gamma = [0, 0];

k_MG = [linspace(M(1), Gamma(1), 100)', linspace(M(2), Gamma(2), 100)'];
k_GX = [linspace(Gamma(1), X(1), 100)', linspace(Gamma(2), X(2), 100)'];
k_XM = [linspace(X(1), M(1), 100)', linspace(X(2), M(2), 100)'];

E_MG = Es + 2*gamma * cos(k_MG(:,1)) + 2*gamma * cos(k_MG(:,2));
E_GX = Es + 2*gamma * cos(k_GX(:,1)) + 2*gamma * cos(k_GX(:,2));
E_XM = Es + 2*gamma * cos(k_XM(:,1)) + 2*gamma * cos(k_XM(:,2));

figure;

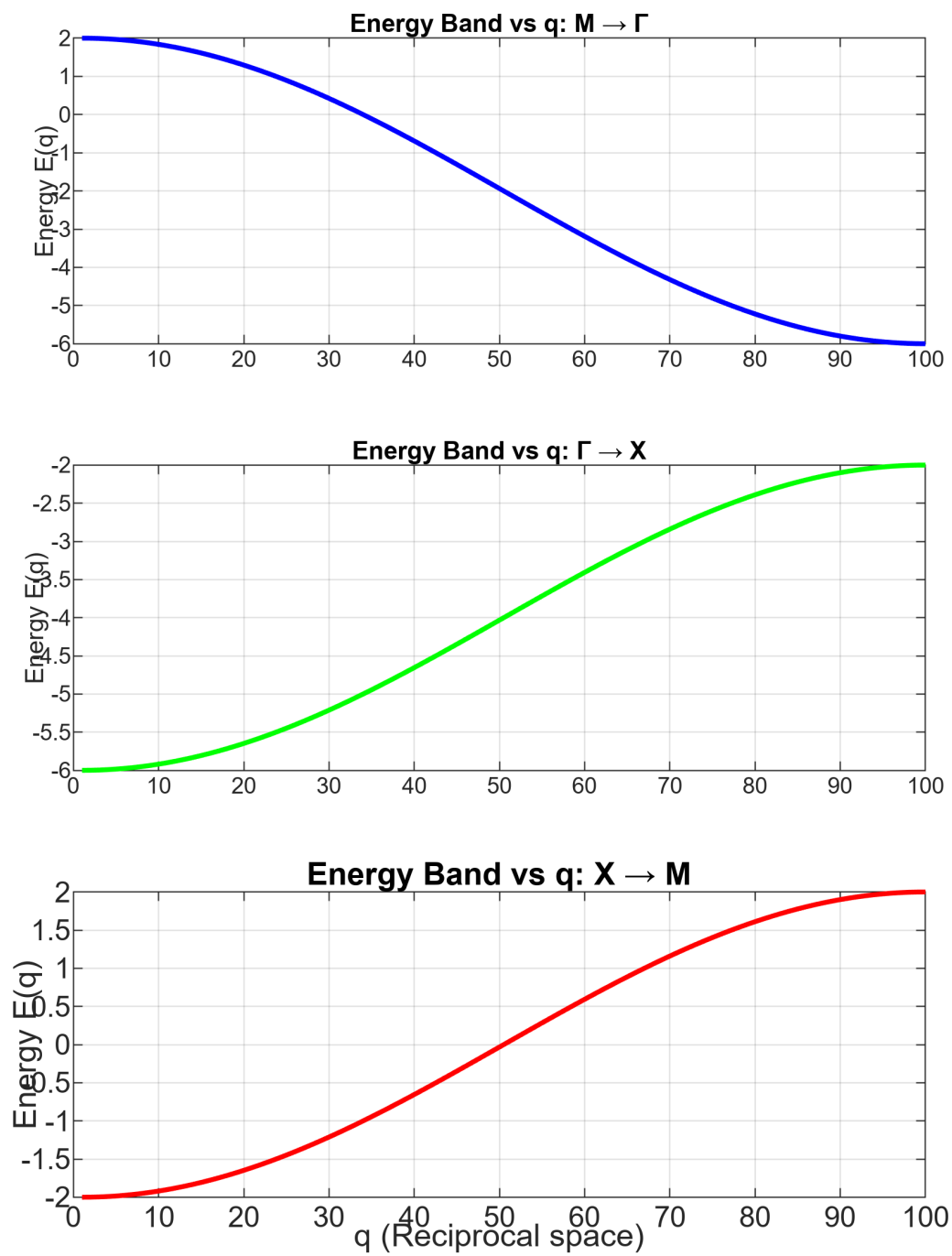
% M -> Gamma
subplot(3,1,1);
plot(E_MG, 'b', 'LineWidth', 2);
title('Energy Band vs q: M  $\rightarrow$   $\Gamma$ ');
ylabel('Energy E(q)');
grid on;

% Gamma -> X
subplot(3,1,2);
plot(E_GX, 'g', 'LineWidth', 2);
title('Energy Band vs q:  $\Gamma$   $\rightarrow$  X');
ylabel('Energy E(q)');
grid on;

% X -> M
subplot(3,1,3);
plot(E_XM, 'r', 'LineWidth', 2);
title('Energy Band vs q: X  $\rightarrow$  M');
xlabel('q (Reciprocal space)');
ylabel('Energy E(q)');
grid on;

% Adjust layout for better readability
sgtitle('Energy Dispersion in Square Lattice', 'FontSize', 16);
set(gca, 'FontSize', 12);
set(gcf, 'Position', [100, 100, 600, 800]);
```

Energy Dispersion in Square Lattice



Problem 2

Using the tight-binding (LCAO) approach, compute the energy band formed by atomic s-orbitals in an fcc lattice with a monoatomic basis. Plot the energy vs q along L - Γ - X - U - Γ

```
gamma1 = -1;

Gamma = [0, 0, 0];
X = [2*pi, 0, 0];
L = [pi, pi, pi];
U = [2*pi, pi, 0];
% Since a cancels out when calculating the energy, plus we don't have a
% value to set it to, I'm going to leave it out of this solution.

k_LG = [linspace(L(1), Gamma(1), 100); linspace(L(2), Gamma(2), 100);
linspace(L(3), Gamma(3), 100)];
k_GX = [linspace(G(1), X(1), 100); linspace(Gamma(2), X(2), 100);
linspace(Gamma(3), X(3), 100)];
k_XU = [linspace(X(1), U(1), 100); linspace(X(2), U(2), 100); linspace(X(3), U(3),
100)];
k_UG = [linspace(U(1), Gamma(1), 100); linspace(U(2), Gamma(2), 100);
linspace(U(3), Gamma(3), 100)];

E_LG = 2 * gamma1 * (cos(k_LG(1,:)) + cos(k_LG(2,:)) + cos(k_LG(3,:)));
E_GX = 2 * gamma1 * (cos(k_GX(1,:)) + cos(k_GX(2,:)) + cos(k_GX(3,:)));
E_XU = 2 * gamma1 * (cos(k_XU(1,:)) + cos(k_XU(2,:)) + cos(k_XU(3,:)));
E_UG = 2 * gamma1 * (cos(k_UG(1,:)) + cos(k_UG(2,:)) + cos(k_UG(3,:)));

figure;
hold on;
grid on;
% L -> Gamma
subplot(2, 2, 1);
plot(E_LG, 'b', 'LineWidth', 2);
title('Energy Band vs q: M  $\rightarrow$   $\Gamma$ ');
ylabel('Energy E(q)');

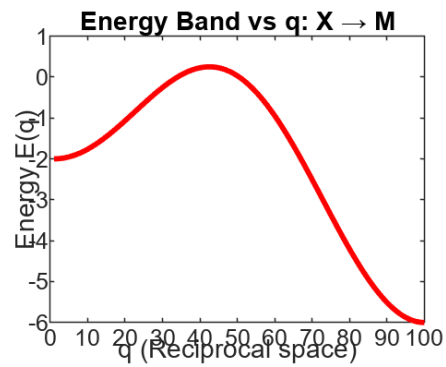
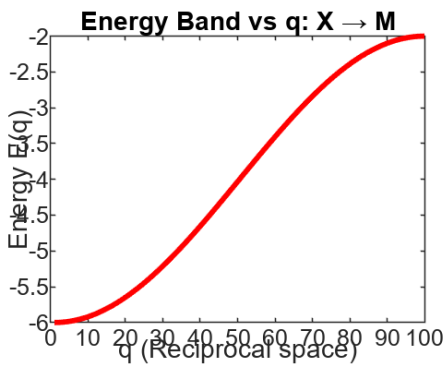
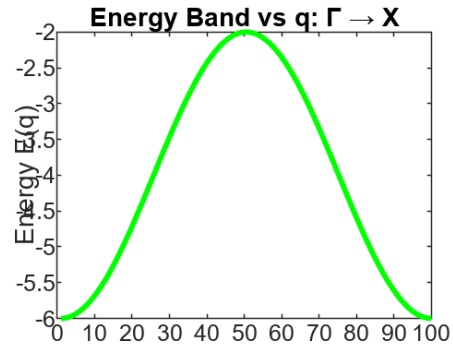
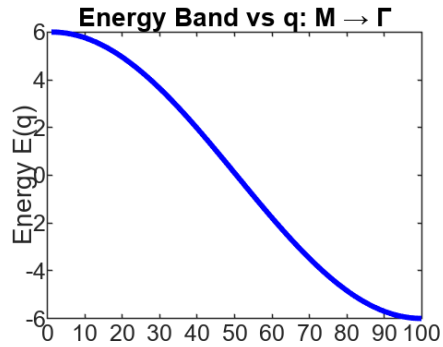
% Gamma -> X
subplot(2, 2, 2);
plot(E_GX, 'g', 'LineWidth', 2);
title('Energy Band vs q:  $\Gamma$   $\rightarrow$  X');
ylabel('Energy E(q)');

% X -> U
subplot(2, 2, 3);
plot(E_XU, 'r', 'LineWidth', 2);
title('Energy Band vs q: X  $\rightarrow$  M');
xlabel("q (Reciprocal space)");
ylabel('Energy E(q)');
```

```

% U -> Gamma
subplot(2, 2, 4);
plot(E_UG, 'r', 'LineWidth', 2);
title('Energy Band vs q: X → M');
xlabel("q (Reciprocal space)");
ylabel('Energy E(q)');

```



Problem 3

Redo the “Mock 1D NaCl” problem that we did in class. A 1D chain consists of alternating Na and Cl atoms, with the spacing between Na and Cl them being a . If Na contributes its s orbital (energy E_s) and Cl contributes its p_x orbital (energy E_p) to the formation of this fictitious crystal, with the magnitude of the overlap integral denoted as E_{sp} , answer the following:

a) What is the lattice period?

The lattice period is the smallest region that can be used for symmetry for the entire crystal, so it ends when we start at an Na atom and ends at an Na atom (or with a Cl atom). Since the spacing between each alternating atom is a , it takes $2a$ to reach an Na atom from the start.

$$\text{period} = 2a$$

b) How many atoms are in the basis?

Just like in class, there are two atoms in the basis. One chlorine and one sodium atom.

c) How many bands will form

Each orbital forms a band, and since there are two atoms, each contributing one orbital, two bands will form.

d) Calculate and graph the energy dispersions for all the bands across the Brillouin zone.

The nearest neighbors for any atom are both at distance a apart. We start with solving the determinant for

$$\det \begin{pmatrix} E_s - E & E_{sp}(e^{ika} + e^{-ika}) \\ E_{sp}(e^{ika} + e^{-ika}) & E_{p_x} - E \end{pmatrix} = 0$$

and using Euler's formula, the matrix can be rewritten as;

$$\det \begin{pmatrix} E_s - E & 2E_{sp}\cos(ka) \\ 2E_{sp}\cos(ka) & E_{p_x} - E \end{pmatrix} = 0$$

solving for the values of E_k gives us the equation

$$E_s E_{p_x} - E(E_s + E_{p_x}) + E^2 - 4E_{sp}^2 \cos^2(ka) = 0$$

but we can then set it up in the quadratic formula;

$$E^2 - E(E_s + E_{p_x}) + (E_s E_{p_x} - 4E_{sp}^2 \cos^2(ka)) = 0$$

$$E(k) = \frac{E_s + E_{p_x} \pm \sqrt{(E_s + E_{p_x})^2 - 4(E_s E_{p_x} - 4E_{sp}^2 \cos^2(ka))}}{2}$$

Since the s-orbital, p_x -orbital, and overlap energies are all constant throughout the entire crystal, the energy only depends on the cosine term.

$$E(k) \propto \pm \sqrt{\cos^2(k)} \propto \pm \cos(k), \quad \frac{-\pi}{2a} < k < \frac{+\pi}{2a}$$

To properly graph this, I'll set the energies to simple integers

```
clc
clear
close all

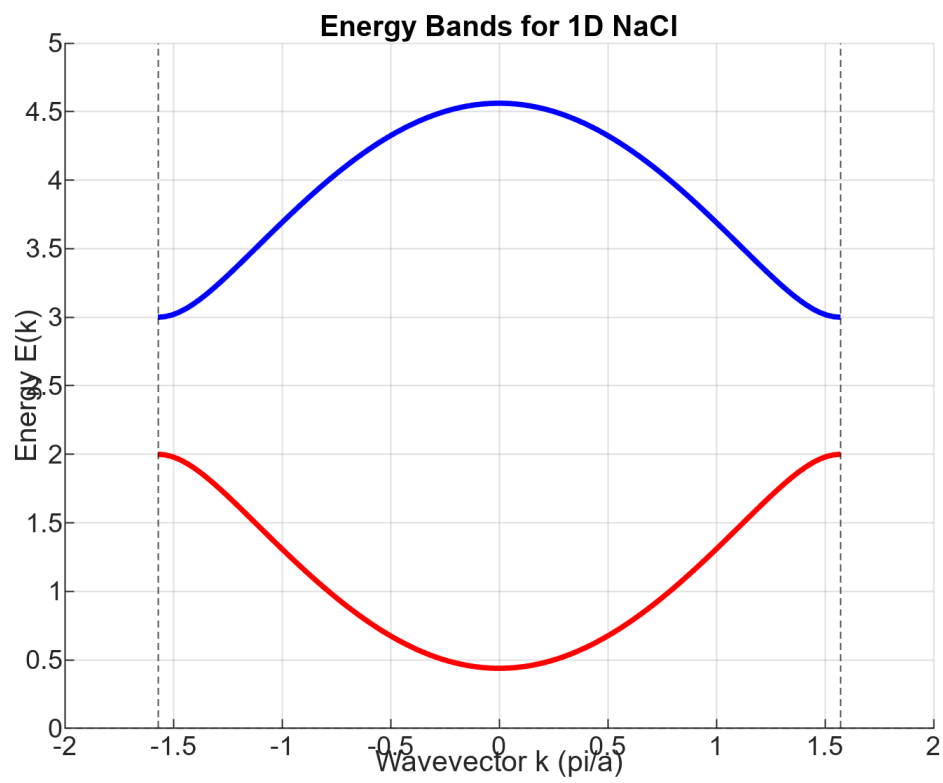
Es = 2;
Epx = 3; % this orbital is higher in energy
Esp = 1;

k = linspace(-pi/2, pi/2, 100);

% This is an even more simplified equation than above
E_plus = (Es + Epx) / 2 + sqrt(((Es - Epx))^2 + 16 * Esp^2 * cos(k).^2) / 2;
E_minus = (Es + Epx) / 2 - sqrt(((Es - Epx))^2 + 16 * Esp^2 * cos(k).^2) / 2;

hold on;
grid on;
plot(k, E_plus, 'b', 'LineWidth', 2); % Upper band
plot(k, E_minus, 'r', 'LineWidth', 2); % Lower band

xlabel('Wavevector k (pi/a)');
ylabel('Energy E(k)');
title('Energy Bands for 1D NaCl');
yline(0, '--k'); % Reference energy line
xline(-pi/2, '--k'); % Brillouin Zone boundary
xline(pi/2, '--k'); % Brillouin Zone boundary
hold off;
```

Problem 4

One of the simplest conjugated polymers is polyacetylene, whose structure is shown below. The double bonds are known to be slightly shorter than the single bonds (this phenomenon is called dimerization). Polyacetylene can be modeled as a solid with a onedimensional Bravais lattice along the x-axis.

a) What is the lattice period (from the picture)?

c, not $d_1 + d_2$

b) What are the atoms that constitute the basis? (The basis—a periodically repeated unit—is called a monomer in the case of polymeric chains). The hydrogen atom contributes to bonding with one electron in its 1s orbital, while C is in group 4, and contributes with 4 electrons distributed over its 2s and 2p orbitals (a total of 4 orbitals).

Drawing attached

c) How many bands will form? When the chain is formed, carbon's 2s orbital and two of its three 2p orbitals form the bonds C-C and C-H that are located in the plane of the picture (the so-called sigma-bonds). In addition, each of the carbon atoms has an extra pz orbital, perpendicular to the plane of the paper, which overlap sideways and form the weaker pi bond.

The pz orbital is what contributes to these bands, so two bands will form, one from each pz orbital from the two carbon atoms per basis.

d) Assuming that two of the bands are formed by the carbon pz orbitals alone, use a simple nearest-neighbor tight-binding model to calculate the bandstructure of these two bands. Also, plot the calculated bandstructure within the first Brillouin zone.

```
clc
clear
close all

% We can model this as 1D even though the carbons bond at an angle,
% so we can approximate c = d1 + d2

Ep = 3;
gamma_1 = -2;
gamma_2 = -3;
d1 = 1.5;
d2 = 1.3;
c = d1 + d2;

k = linspace(-pi/c, pi/c, 100); % really -pi/c to pi/c, but we have c in our cosine,
                                % so it cancels out

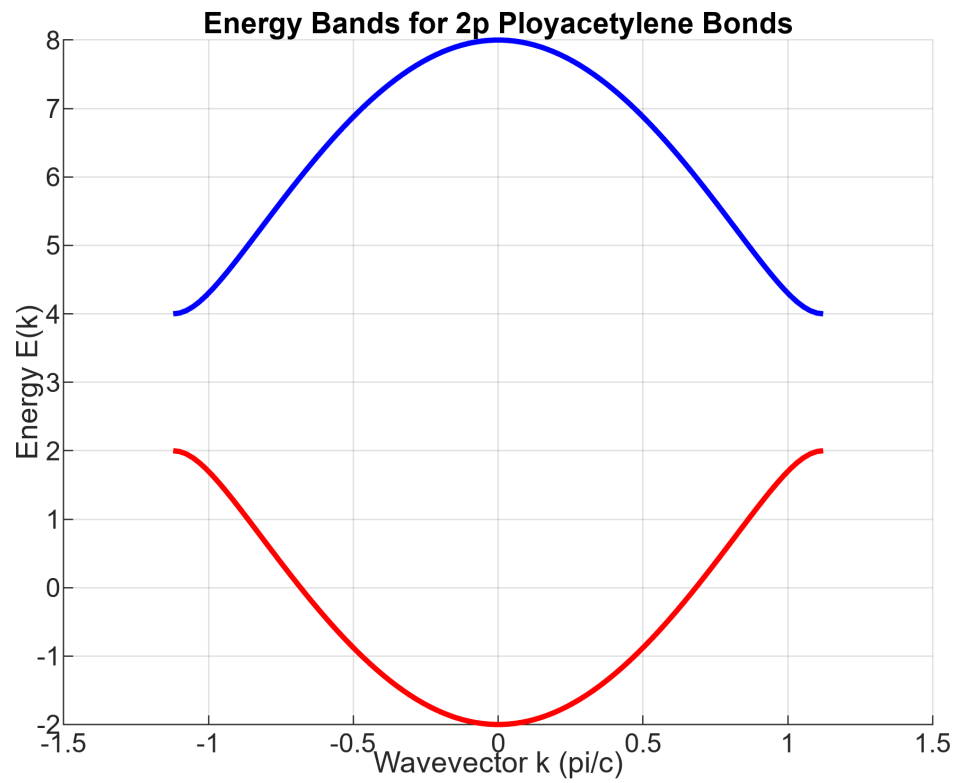
E_plus = Ep + sqrt(gamma_1^2 + gamma_2^2 + 2 * gamma_2 * gamma_1 * cos(k * c));
E_minus = Ep - sqrt(gamma_1^2 + gamma_2^2 + 2 * gamma_2 * gamma_1 * cos(k * c));

hold on;
grid on;
```

```

plot(k, E_plus, 'b', 'LineWidth', 2); % Upper band
plot(k, E_minus, 'r', 'LineWidth', 2); % Lower band
title("Energy Bands for 2p Ployacetylene Bonds");
xlabel('Wavevector k (pi/c)');
ylabel('Energy E(k)');

```



Problem 5

a)

```
clc;
clear;
close all;

% Define Constants
ao = 5.292e-11;
a = 3 * ao;
gamma1 = -2;

kx = linspace(-4*pi/a, 4*pi/a, 150); % Extending beyond first BZ
ky = linspace(-4*pi/a, 4*pi/a, 150);
[KX, KY] = meshgrid(kx, ky);

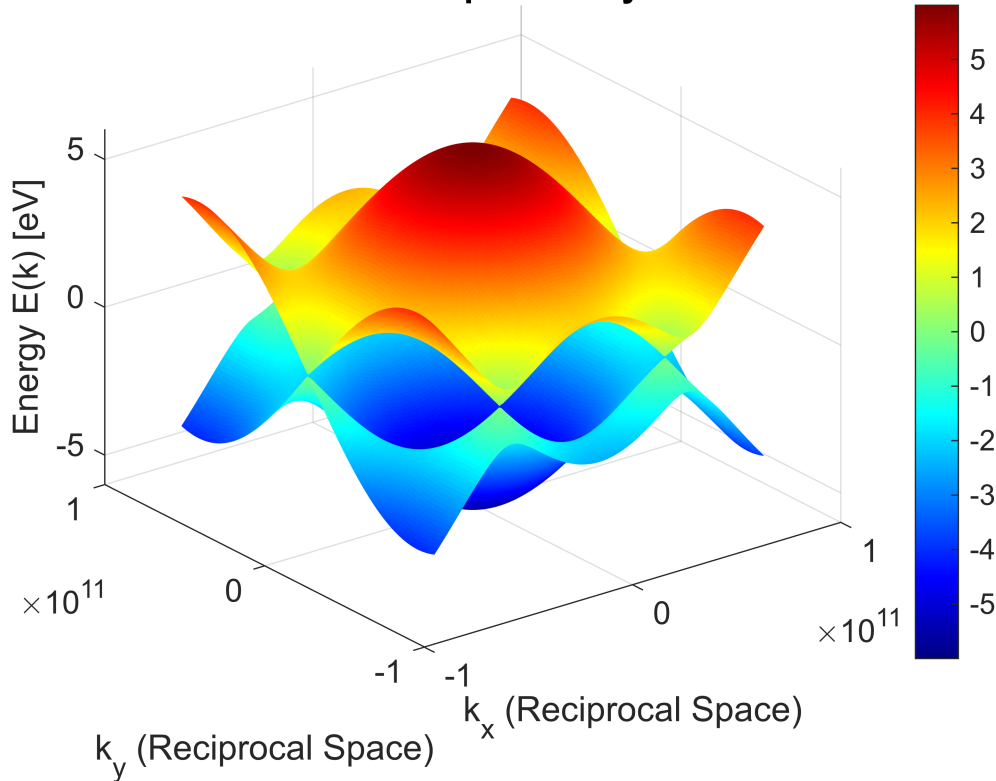
E_plus = gamma1 * sqrt(1 + 4*cos(sqrt(3)*ao*KY/2) .* cos(ao*KX/2) + 4*cos(ao*KX/2).^2);
E_minus = -gamma1 * sqrt(1 + 4*cos(sqrt(3)*ao*KY/2) .* cos(ao*KX/2) + 4*cos(ao*KX/2).^2);

figure;
hold on;
grid on;

% Upper and Lower Bands
surf(KX, KY, E_plus, 'EdgeColor', 'none'); % Upper  $\pi^*$  band
surf(KX, KY, E_minus, 'EdgeColor', 'none'); % Lower  $\pi$  band

xlabel('k_x (Reciprocal Space)', 'FontSize', 12);
ylabel('k_y (Reciprocal Space)', 'FontSize', 12);
zlabel('Energy E(k) [eV]', 'FontSize', 12);
title('Band Structure of Graphene Beyond First BZ', 'FontSize', 14);
colormap jet;
colorbar;
view(3);
set(gca, 'FontSize', 12);
```

Band Structure of Graphene Beyond First BZ



b)

```
K = [2*pi/(3*ao), 2*pi/(sqrt(3)*ao)];
Gamma = [0, 0];
M = [0.5, 0];

k_KG = [linspace(K(1), Gamma(1), 100)', linspace(K(2), Gamma(2), 100)'];
k_GM = [linspace(Gamma(1), M(1), 100)', linspace(Gamma(2), M(2), 100)'];
k_MK = [linspace(M(1), K(1), 100)', linspace(M(2), K(2), 100)'];

E_KG = gamma1 * sqrt(1 + 4*cos(sqrt(3)*ao*k_KG(:,2)/2) .* cos(ao*k_KG(:,1)/2) +
4*cos(ao*k_KG(:,1)/2).^2);
E_GM = gamma1 * sqrt(1 + 4*cos(sqrt(3)*ao*k_GM(:,2)/2) .* cos(ao*k_GM(:,1)/2) +
4*cos(ao*k_GM(:,1)/2).^2);
E_MK = gamma1 * sqrt(1 + 4*cos(sqrt(3)*ao*k_MK(:,2)/2) .* cos(ao*k_MK(:,1)/2) +
4*cos(ao*k_MK(:,1)/2).^2);

figure;

% M -> Gamma
subplot(3,1,1);
plot(E_KG, 'b', 'LineWidth', 2);
title('Energy Band vs q: K → Γ');
ylabel('Energy E(q)');
grid on;
```

```

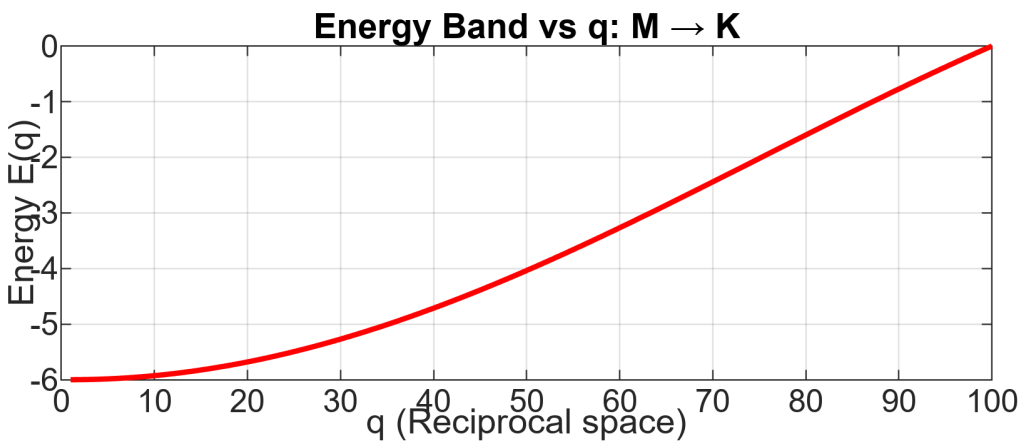
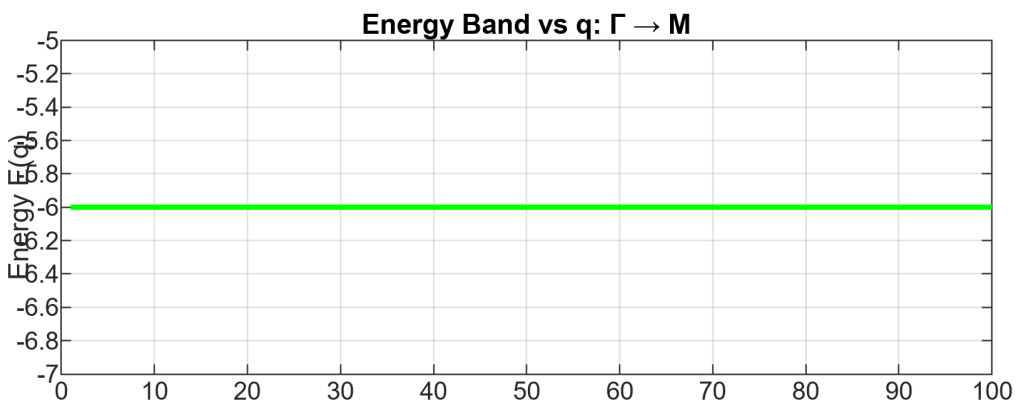
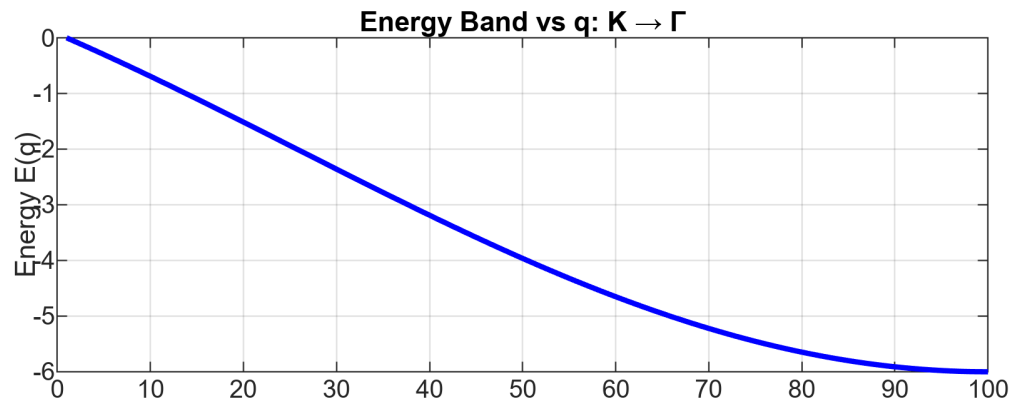
% Gamma -> X
subplot(3,1,2);
plot(E_GM, 'g', 'LineWidth', 2);
title('Energy Band vs q:  $\Gamma \rightarrow M$ ');
ylabel('Energy E(q)');
grid on;

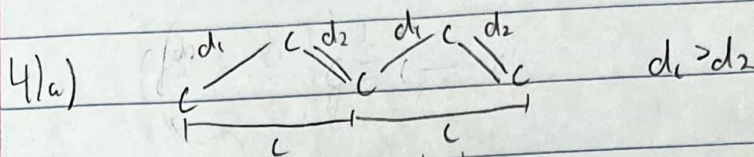
% X -> M
subplot(3,1,3);
plot(E_MK, 'r', 'LineWidth', 2);
title('Energy Band vs q:  $M \rightarrow K$ ');
xlabel("q (Reciprocal space)");
ylabel('Energy E(q)');
grid on;

% Adjust layout for better readability
sgtitle('Energy Dispersion in Square Lattice', 'FontSize', 16);
set(gca, 'FontSize', 12);
set(gcf, 'Position', [100, 100, 600, 800]);

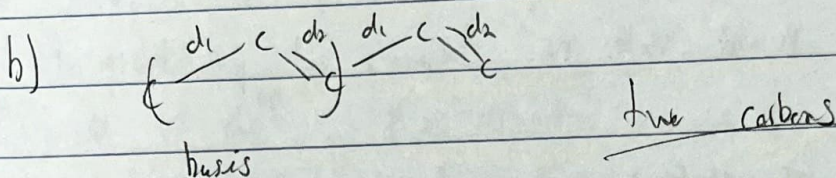
```

Energy Dispersion in Square Lattice





lattice period c , NOT d_1 or d_2



c) 2 bands, one from each p_z π -bond

d)
$$\det \begin{bmatrix} \epsilon_p - \epsilon_k & \gamma_1 e^{ikd_1} + \gamma_2 e^{-ikd_2} \\ \gamma_1^* e^{-ikd_1} + \gamma_2^* e^{ikd_2} & \epsilon_p - \epsilon_k \end{bmatrix} = 0$$

$$(\epsilon_p - \epsilon_k)(\epsilon_p - \epsilon_k) - (\gamma_1 e^{ikd_1} + \gamma_2 e^{-ikd_2})(\gamma_1^* e^{-ikd_1} + \gamma_2^* e^{ikd_2}) = 0$$

$$\epsilon_p^2 - 2\epsilon_p \epsilon_k + \epsilon_k^2 - (|\gamma_1|^2 + |\gamma_2|^2 + \gamma_1^* \gamma_2 e^{-ik(d_1+d_2)} + \gamma_1 \gamma_2^* e^{ik(d_1+d_2)}) = 0$$

$$\epsilon_k^2 - \epsilon_k(2\epsilon_p) + (\epsilon_p^2 - |\gamma_1|^2 - |\gamma_2|^2 - \gamma_1^* \gamma_2 e^{-ik(d_1+d_2)} - \gamma_1 \gamma_2^* e^{ik(d_1+d_2)}) = 0$$

$$\epsilon_k \pm \sqrt{(2\epsilon_p)^2 - 4 \left(\epsilon_p^2 - |\gamma_1|^2 - |\gamma_2|^2 - \gamma_1^* \gamma_2 e^{-ik(d_1+d_2)} - \gamma_1 \gamma_2^* e^{ik(d_1+d_2)} \right)}$$

$$\epsilon_k \pm \sqrt{4\epsilon_p^2 - 4\epsilon_p^2 + 4(|\gamma_1|^2 + |\gamma_2|^2 + \gamma_1^* \gamma_2 e^{-ik(d_1+d_2)} + \gamma_1 \gamma_2^* e^{ik(d_1+d_2)})}$$

$$\epsilon_k \pm \sqrt{(|\gamma_1|^2 + |\gamma_2|^2 + \gamma_1^* \gamma_2 e^{-ik(d_1+d_2)} + \gamma_1 \gamma_2^* e^{ik(d_1+d_2)})}$$

I believe gamma is real for this purpose, but I think you

said in class it can also be complex

$$\gamma_1 \gamma_2^* e^{-ik(d_1+d_2)} + \gamma_1^* \gamma_2 e^{ik(d_1+d_2)} = 2\gamma_1 \gamma_2 \cos(k(d_1+d_2))$$

I forgot to put back in

$$\epsilon_k = \epsilon_p \pm \sqrt{|\gamma_1|^2 + |\gamma_2|^2 + 2\gamma_1 \gamma_2 \cos(k(d_1+d_2))}$$

from research, $d_1 \approx 1.45 \text{ \AA}$, $d_2 \approx 1.37 \text{ \AA}$, $\gamma_1 \approx 2.5 \text{ eV}$, $\gamma_2 \approx 3 \text{ eV}$