QM Problems

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1   A. Solid Argon With LJ Potential

1.1   Lattice Parameters

From the general expression of the Lennard-Jones potential

$$V(r) = 4\epsilon \left(\left(\frac{\sigma}{r}\right)^1 2 - \left(\frac{\sigma}{r}\right)^6 \right) \tag{1}$$

We can easily find the minimum finding the zero of the first derivative.

$$r_0 = 2^{\frac{1}{6}} \sigma \tag{2}$$

and, substituting it into the potential expression we find

$$V(r_0) = -\epsilon \tag{3}$$

From these two expressions we can deduce $\sigma = \frac{3.758}{2^{\frac{1}{6}}}$Åand $\epsilon = 99.55 cm^{-1}$

1.2   Crystal Structures

Knowing the expression for the Lennard-Jones potential we can derive an approximate value of the energy of different lattice structures by numerically summing the potential energy contributions of the neighbours.
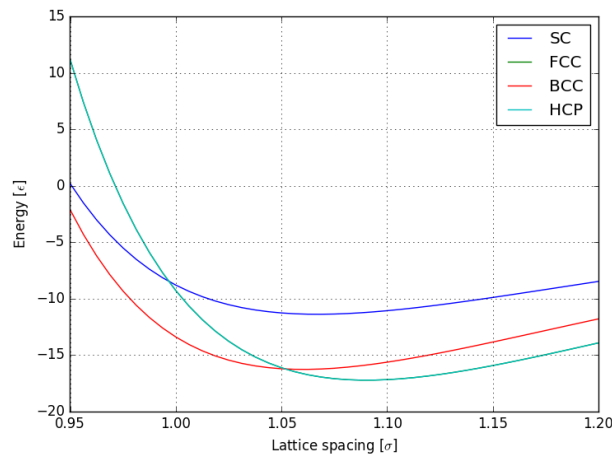

Figure 1: *Energy of the atoms in the lattice as a function of the lattice spacing for four possible lattices: Simple Cubic (Blue), Face Centered (Green), Body Centered (Red), hexagonal Cenered (Light blue)*

Doing so for the 14^3 closest neighbours we found the following values for the required structures

	spacing	energy
sc	1.066σ	-11.36ϵ
bcc	1.069σ	-16.45ϵ
fcc	1.090σ	-17.2160ϵ
hcp	1.090σ	-17.2192ϵ

We thus found that the energetically favorable configuration is the hcp one by a factor of 0.01% with respect to the fcc. This is in agreement with re results found in the litterature refcrystal. In the same reference it is also pointed out that despite hcp configuration being lower in energy, the one that more easily appears in nature is the fcc one. We here try to justify such a result without considering, as done in refcrystal, impurities.

We tried instead to consider the behaviour of the energy in the minimum when some random noise is present in the lattice, displacing the positions of the atoms. We looked at the behaviour of the energy as a function of the amplitude of the noise averaging over 10^4 different realizations of the system with a Gaussian random displacement of amplitude d.
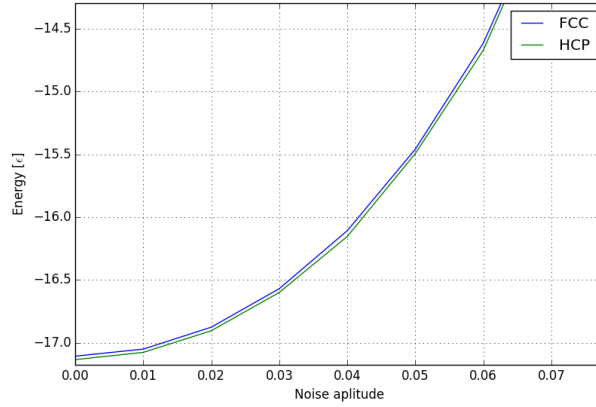

Figure 2: *Energy of the minima obtained above for FCC and HCP lattices as a function of the amplitude of a random noise displacing the atoms positions*

We can see that there is no crossing between the two energies and thus it the fact that the "fcc" structure is prefererred in nature cannot be explained in this way.

1.3   Spectrum of the FCC

In the case of the hcp configuration the cell can be easily identified through the three vectors shown in Fig.(??). Their coordinates are

$$R_1 = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \qquad\qquad R_2 = \begin{bmatrix} \frac{1}{2} \\ \frac{\sqrt{3}}{2} \\ 0 \end{bmatrix} \qquad\qquad R_0 = \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2\sqrt{3}} \\ \sqrt{\frac{2}{3}} \end{bmatrix}$$

and that of the corresponding reciprocal lattice vectors can be constructed from those above and their coordinates are

$$G_1 = \begin{bmatrix} \frac{2\pi}{3} \\ \frac{2\pi}{\sqrt{3}} \end{bmatrix} \qquad\qquad\qquad G_2 = \begin{bmatrix} \frac{2\pi}{3} \\ -\frac{2\pi}{\sqrt{3}} \end{bmatrix}$$

From this we can construct the Brillouin zone which corresponds to the Wigner-Seitz cell in K-space

The $2P_x, 2P_y$, and 2S orbitals undergo SP_2 hybridization and the electrons form strong covalent sigma bonds with the neighbouring sites. So it is sufficient to consider only the P_z orbitals in the tight binding calculation

From Bloch's theorem it follows that our wave function will be of the form

$$\begin{aligned}
|\psi\rangle &= \sum_R \exp(iKR)(\exp(ika_1)c_1 |R,1\rangle + \exp(ika_1)c_2 |R,2\rangle) && (4) \\
|\psi\rangle &= \sum_R \exp(i\vec{K}\vec{R})(b_1 |R,1\rangle + b_2 |R,2\rangle) && (5)
\end{aligned}$$

Where $\vec{R} = n\vec{R1} + m\vec{R2}$ with $m, n \in Z$

We solve the Eigenvalue problem and project onto the kets corresponding to the cell R =(0,0)

$$\begin{aligned}
\langle 0,1| H |\psi\rangle &= E \langle 0,1| |\psi\rangle && (6) \\
\langle 0,2| H |\psi\rangle &= E \langle 0,2| |\psi\rangle && (7)
\end{aligned}$$

Expanding the above equation gives us two linear equations in two variables.

$$\begin{aligned}
(E - e_c)b_1 + t(1 + \exp(-ikR_1) + \exp(-ikR_2))b_2 &= 0 && (8) \\
t(1 + \exp(ikR_1)b_1 + \exp(ikR_2)) + (E - e_c)b_2 &= 0 && (9)
\end{aligned}$$

from this we find that the band structure is

$$E = e_c \pm t\sqrt{(1 + \cos(\vec{k}\vec{R_1}) + \cos(\vec{k}\vec{R_2}))^2 + (\sin(\vec{k}\vec{R_1}) + \sin(\vec{k}\vec{R_2}))^2} \qquad (10)$$

From the Eigenvalues we can eventually find the dependence of the b_1, b_2 factors in the wave function on the parameters of the system as

$$b_1 = \sqrt{\frac{1}{1+a}} \qquad b_2 = \sqrt{\frac{a}{1+a}} \qquad\qquad (11)$$

where

$$a = \frac{1 + e^{i\vec{k}\vec{R_1}} + e^{i\vec{k}\vec{R_2}}}{1 + e^{-i\vec{k}\vec{R_1}} + e^{-i\vec{k}\vec{R_2}}}$$

Assuming the value of t = -2.5 and measuring our energy from e_c we obtain the plot shown below

Figure 3: 3d plot of the band structure of Graphene

We observe the existence of Dirac cones,at the points where the two bands touch with linear dispersion. To see this more clearly we plot The Energy along the line $K_y = \frac{K_x}{\sqrt{3}}$

Figure 4: 2d plot of Graphene spectrum along the $K_y = \frac{Kx}{\sqrt{3}}$

We then numerically calculated the density of states as a function of the energy obtaining the function plotted below

Figure 5: Density of states against Energy

We can see the linear dependence of $n(E)$ for $E \sim 0$. To see instead the behavior on the function around the divergence we decided to plot it as a function of $y_1 := \log(E - E_0)$ for $E > E_0$ and $y_2 := \log(E_0 - E)$ for $E < E_0$. Where $E_0 = 2.479$ is the Energy that maximizes the density of states.

Figure 6: DOS against $\log(E - E_0)$

We can here observe near linear behavior for $y_i \to -\infty$. This clearly shoes the logarithmic dependence of the divergence.

2 Boron-Nitride Model

Figure 7: BN hexagonal mono layer sheet

The unit cell, lattice vectors and reciprocal lattice vectors are equivalent to that of graphene and are written below Fig.(7). Their coordinates are

$$R_1 = \begin{bmatrix} \frac{3}{2} \\ \frac{\sqrt{3}}{2} \end{bmatrix} \qquad\qquad R_2 = \begin{bmatrix} \frac{3}{2} \\ \frac{-\sqrt{3}}{2} \end{bmatrix}$$

and that of the corresponding reciprocal lattice vectors can be constructed from those above and their coordinates are

$$G_1 = \begin{bmatrix} \frac{2\pi}{3} \\ \frac{2\pi}{\sqrt{3}} \end{bmatrix} \qquad\qquad G_2 = \begin{bmatrix} \frac{2\pi}{3} \\ -\frac{2\pi}{\sqrt{3}} \end{bmatrix}$$

From this we can construct the Brillouin zone which corresponds to the Wigner-Seitz cell in K-space

From Bloch's theorem it follows that our wave function will be of the form

$$|\psi\rangle \quad = \quad \sum_R \exp(iKR)(\exp(ika_1)c_1 |R,1\rangle + \exp(ika_1)c_2 |R,2\rangle) \tag{12}$$

$$|\psi\rangle \quad = \quad \sum_R \exp(i\vec{K}\vec{R})(b_1 |R,1\rangle + b_2 |R,2\rangle) \tag{13}$$

Where $\vec{R} = n\vec{R1} + m\vec{R2}$ with $m,n \in Z$
We solve the Eigenvalue problem and project onto the kets corresponding to the cell R =(0,0)

$$\langle 0,1| H |\psi\rangle \quad = \quad E \langle 0,1| |\psi\rangle \tag{14}$$

$$\langle 0,2| H |\psi\rangle \quad = \quad E \langle 0,2| |\psi\rangle \tag{15}$$

Writing explicitly the above equations gives us two linear equations in two variables.

$$(E - e_c + \frac{\Delta}{2})b_1 + t(1 + \exp(-ikR_1) + \exp(-ikR_2))b_2 \quad = \quad 0 \tag{16}$$

$$t(1 + \exp(ikR_1)b_1 + \exp(ikR_2)) + (E - e_c - \frac{\Delta}{2})b_2 \quad = \quad 0 \tag{17}$$

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from this we find that the band structure is

$$E = e_c \pm \sqrt{\frac{\Delta^2}{4} + t^2((1 + \cos(\vec{k}\vec{R_1}) + \cos(\vec{k}\vec{R_2}))^2 + t^2((\sin(\vec{k}\vec{R_1}) + \sin(\vec{k}\vec{R_2}))^2} \qquad (18)$$

assuming the value of t = -2.5 and measuring our energy from e_c and $\Delta = 6.1$(i.e the difference in first ionization energies between Boron and nitrogen) we obtain the plot shown below

Figure 8: 3d plot of the band structure of Boron Nitride

We do not observe the existence of Dirac cones. plotting The Energy along the line $K_y = \frac{K_x}{\sqrt{3}}$ we observe a band gap of roughly 5ev

Figure 9: 2d plot of Boron Nitride lowest band along the $K_y = \frac{K_x}{\sqrt{3}}$

Figure 10: Density of states

3 Boron, Carbon, Nitrogen Model

Figure 11: *The structure of the system under examination. Atoms are shown as: Black-Carbon, Blue-Boron, Red-Nitrogen. Light gray lines are drown just to emphasize the honeycomb structure of the cells.*

The cell, since the lattice is, as before, honeycomb-shaped is identified by the two vectors used up to know, just scaled by a common factor that doesn't affect the physics, as shown in Fig.(11). Their coordinates are

$$R_1 = \begin{bmatrix} 3 \\ \sqrt{3} \end{bmatrix} \qquad\qquad R_2 = \begin{bmatrix} 3 \\ -\sqrt{3} \end{bmatrix}$$

and that of the corresponding reciprocal lattice vectors can be constructed from those above and their coordinates are

$$G_1 = \begin{bmatrix} \frac{\pi}{3} \\ \frac{\pi}{\sqrt{3}} \end{bmatrix} \qquad\qquad G_2 = \begin{bmatrix} \frac{\pi}{3} \\ -\frac{\pi}{\sqrt{3}} \end{bmatrix}$$

From this we can construct the Brillouin zone which corresponds to the Wigner-Seitz cell in K-space

From Bloch's theorem it follows that our wave function will be of the form

$$|\psi\rangle = \sum_R \exp(i\vec{K}\vec{R})(b_1\,|R,1\rangle + b_2\,|R,2\rangle + b_3\,|R,3\rangle + b_4\,|R,4\rangle + b_5\,|R,5\rangle + b_6\,|R,6\rangle + b_7\,|R,7\rangle + b_8\,|R,8\rangle) \tag{19}$$

Where $\vec{R} = n\vec{R1} + m\vec{R2}$ with $m, n \in Z$

We solve the Eigenvalue problem and project onto the kets corresponding to the cell R =(0,0)

This brings us to an Hamiltonian representation of the following form

$$\begin{pmatrix}
e_c & 0 & -t_{CN} & 0 & -t_{CN}e^{-i\vec{k}\vec{R}_1} & 0 & -t_{CN}e^{-i\vec{k}\vec{R}_2} & 0 \\
0 & e_C & 0 & -t_{CB}e^{i\vec{k}\vec{R}_2} & 0 & -t_{CB} & 0 & -t_{CB}e^{i\vec{k}\vec{R}_1} \\
-t_{CN} & 0 & e_N & -t_{NB} & 0 & 0 & 0 & -t_{NB} \\
0 & -t_{CB}e^{-i\vec{k}\vec{R}_2} & -t_{NB} & e_B & -t_{NB} & 0 & 0 & 0 \\
-t_{CB}e^{i\vec{k}\vec{R}_1} & 0 & 0 & -t_{NB} & e_N & -t_{NB} & 0 & 0 \\
0 & -t_{CB} & 0 & 0 & -t_{NB} & e_B & -t_{NB} & 0 \\
-t_{CB}e^{i\vec{k}\vec{R}_2} & 0 & 0 & 0 & 0 & -t_{NB} & e_N & -t_{NB} \\
0 & -t_{CB}e^{-i\vec{k}\vec{R}_1} & -t_{NB} & 0 & 0 & 0 & -t_{NB} & e_B
\end{pmatrix}$$

The matrix is then numerically solved using the parameters found in the literature $e_C = 11eV$, $e_B = 9eV$, $e_N = 14eV$, $t_{NB} = 2.1eV$, $t_{CB} = 2.3eV$, $tt_{CN} = 2.2eV$ finding the following 2D shape for the lower band

Figure 12: *surface plot of the lowest band structure of Carbon-Boron-Nitrogen model*

We can see the expected periodicity of the Brillouin zone.

To see the properties of the bands we look at their behavior along the $\pi/6$ line as we have done for the two previous models.

Figure 13: Plot of CBN Model spectrum along the $K_y = \frac{Kx}{\sqrt{3}}$. The first 8 bands are here shown

As expected the bands do not cross, and no Dirac cones are formed.