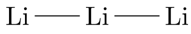
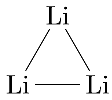
Problem 1: LCAO - The Li_3 molecule

Here we shall consider two possible configurations of the molecule:



(linear)



(cyclic)

The linear configuration

The Hamiltonian matrix is given by

$$\hat{H} = \begin{pmatrix} 0 & t & 0 \\ t & 0 & t \\ 0 & t & 0 \end{pmatrix} \tag{1}$$

so the secular equation is

$$\begin{vmatrix} E & t & 0 \\ t & E & t \\ 0 & t & E \end{vmatrix} = 0 \tag{2}$$

Using the cofactor expansion, this reads

$$\begin{aligned} E\left(E^2 - t^2\right) + t\left(-Et\right) &= 0 \\ E^3 - 2Et^2 &= 0 \\ E\left(E + t\sqrt{2}\right)\left(E - t\sqrt{2}\right) &= 0 \\ E &= 0, \pm t\sqrt{2} \end{aligned} \tag{3}$$

The cyclic configuration

We have

$$\hat{H} = \begin{pmatrix} 0 & t & t \\ t & 0 & t \\ t & t & 0 \end{pmatrix} \tag{4}$$

so

$$\begin{aligned} \begin{vmatrix} E & t & t \\ t & E & t \\ t & t & E \end{vmatrix} &= 0 \\ E\left(E^2 - t^2\right) + t\left(t^2 - Et\right) + t\left(t^2 - Et\right) &= 0 \\ E^3 - 3Et^2 + 2t^3 &= 0 \\ \left(E + t\right)^2\left(E - 2t\right) &= 0 \\ E &= 2t, t, t \end{aligned} \tag{5}$$

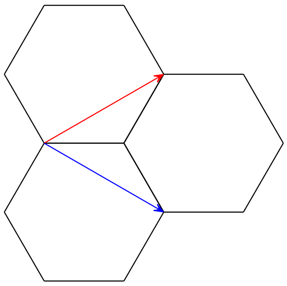
Which configuration is taken?

Noting that $t < 0$, we can see that

- In the linear configuration, the three valence electrons occupy the $+t\sqrt{2}, +t\sqrt{2}, 0$ levels, respectively, giving a total energy of $2t\sqrt{2}$
- In the cyclic configuration, the valence electrons occupy the $2t, 2t, -t$ levels, respectively, giving a total energy of $3t$.

Since $t < 0$, the configuration with lower energy is the **cyclic configuration**, so this one is taken by the molecule as it is more stable.

Problem 2: Reciprocal Lattice of a Honeycomb Lattice



I am still not good with tikz and chemfig, please pardon the simple drawing.

The red arrow represents the lattice vector $\boldsymbol{a}_1$, while the blue arrow represents $\boldsymbol{a}_2$. With the zero of coordinate taken to be where both arrows originate, we have

$$\boldsymbol{a}_1 = \frac{a}{2}\left(\sqrt{3}, 1\right), \qquad \boldsymbol{a}_2 = \frac{a}{2}\left(\sqrt{3}, -1\right) \tag{6}$$

Let the reciprocal lattice vectors be

$$\boldsymbol{b}_1 = (p, q), \qquad \boldsymbol{b}_2 = (x, y) \tag{7}$$

The condition for reciprocal lattice vector,

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij} \tag{8}$$

gives us four equations to solve simultaneously:

$$\begin{aligned} \frac{a}{2}\left(p\sqrt{3} + q\right) &= 2\pi \\ \frac{a}{2}\left(x\sqrt{3} - y\right) &= 2\pi \\ \frac{a}{2}\left(x\sqrt{3} + y\right) &= 0 \\ \frac{a}{2}\left(p\sqrt{3} - q\right) &= 0 \end{aligned} \tag{9}$$

From the latter two we find that

$$\begin{aligned} q &= p\sqrt{3} \\ y &= -x\sqrt{3} \end{aligned} \tag{10}$$

Putting these into the rest, we obtain

$$\begin{aligned} p &= \frac{2\pi}{a\sqrt{3}} \\ x &= \frac{2\pi}{a\sqrt{3}} \end{aligned} \tag{11}$$

Finally, putting these into (10) we obtain

$$\begin{aligned} q &= \frac{2\pi}{a} \\ y &= -\frac{2\pi}{a} \end{aligned} \tag{12}$$

The reciprocal lattice vectors are thus

$$\boldsymbol{b}_1 = \frac{2\pi}{a\sqrt{3}}\left(1, \sqrt{3}\right), \qquad \boldsymbol{b}_2 = \frac{2\pi}{a\sqrt{3}}\left(1, -\sqrt{3}\right) \tag{13}$$