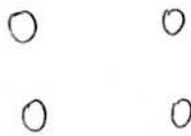


Answers To HW Assignment #2

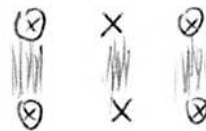
1 (a) Random adsorption does not lead to diffraction, but produces a diffuse smear, which partially interferes with the substrate pattern. When an ordered monolayer is finally formed, one sees additional spots due to adsorbate diffraction. With $\theta = 1/4$, the spots, on average, have $1/2$ the spacing of the substrate reflexes.

(b) When an overlayer is ordered only in one direction, a diffraction pattern will appear in that direction only for the adsorbate. The substrate pattern in the orthogonal direction will be smeared out.

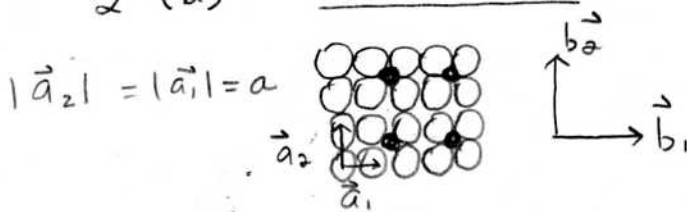
Substrate



Substrate + Adsorbate



2 (b) Real Lattice



$$\vec{b}_1 = 2\vec{a}_1 \quad (\text{c.n.} = 4)$$

$$\vec{b}_2 = 2\vec{a}_2 \quad \theta = \frac{a_1 \times a_2}{b_1 \times b_2} = \frac{1}{4}$$

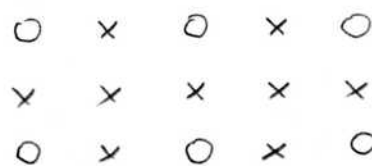
$$G = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix} \Rightarrow G^* = \frac{1}{|G|} \begin{pmatrix} G_{22} & -G_{21} \\ -G_{12} & G_{11} \end{pmatrix} = \frac{1}{4} \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$$

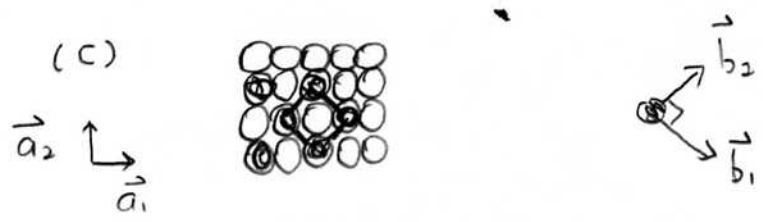
$$G^* = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$$

$$|\vec{b}_1^*| = 1/2 |\vec{a}_1^*| = 1/2 a^*$$

$$|\vec{b}_2^*| = 1/2 |\vec{a}_2^*| = 1/2 a^*$$

Inverse Net





$$\vec{b}_1 = \vec{a}_1 - \vec{a}_2 \quad b_1^2 = 2a^2$$

$$\vec{b}_2 = \vec{a}_1 + \vec{a}_2 \quad b_2^2 = 2a^2$$

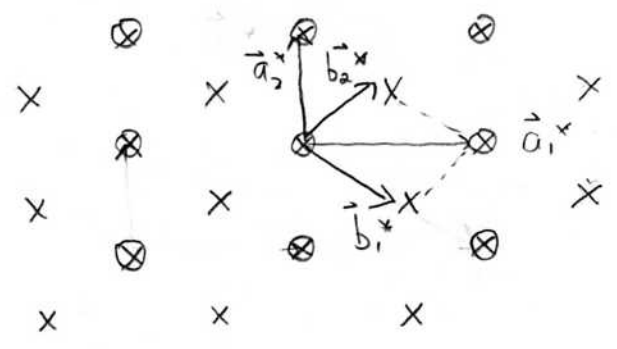
$$G = \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \Rightarrow G^* = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} = \begin{pmatrix} 1/2 & -1/2 \\ 1/2 & 1/2 \end{pmatrix}$$

$$\vec{b}_1^* = \frac{1}{2} (\vec{a}_1^* - \vec{a}_2^*)$$

$$\vec{b}_2^* = \frac{1}{2} (\vec{a}_1^* + \vec{a}_2^*)$$

Inverse Net

$$\Theta = \frac{a_1 \times a_2}{b_1 \times b_2} = \frac{a^2}{(\sqrt{2})^2 a^2} = \frac{1}{2}$$



(h) (fcc 110)



$$\vec{b}_1 = 2\vec{a}_1 \quad \vec{b}_2 = \vec{a}_2$$

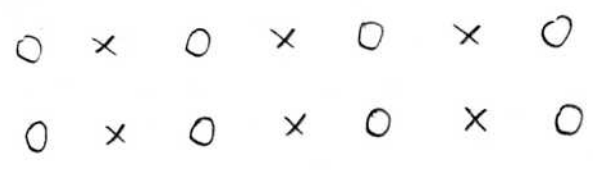
$$\Theta = \frac{a_1 \times a_2}{2a_1 \times a_2} = \frac{1}{2} \text{ of } \text{to layer}$$

$$G = \begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix}$$

$$G^* = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix} = \begin{pmatrix} 1/2 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\vec{b}_1^* = \frac{1}{2} \vec{a}_1^* \quad \vec{b}_2^* = \vec{a}_2^*$$

Inverse Net

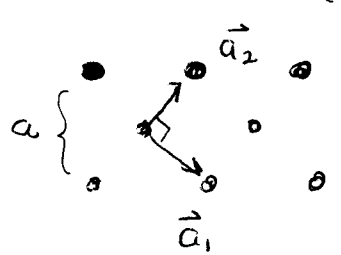


$$|\vec{a}_2| = a$$

$$|\vec{a}_1| = \frac{\sqrt{2}a}{2} = a/\sqrt{2}$$

$$a_2^* = a^* \quad a_1^* = \sqrt{2} a^*$$

3. a, c fcc(100)



$$|\vec{a}_2| = |\vec{a}_1| = \frac{\sqrt{2}}{2} a$$

$$a_2^* = a_1^* = \sqrt{2} a^*$$

$$\vec{a}_1^* + \vec{a}_2^* = 2a^* \hat{i} \quad \leftarrow$$

$$-\vec{a}_1^* + \vec{a}_2^* = 2a^* \hat{j}$$

⇓

$$\vec{b}_1^* = \frac{1}{2} (\vec{a}_1^* + \vec{a}_2^*) - \frac{1}{2} (-\vec{a}_1^* + \vec{a}_2^*)$$

$$= \frac{3}{4} \vec{a}_1^* + \frac{1}{4} \vec{a}_2^*$$

$$\vec{b}_2^* = \frac{1}{4} \vec{a}_1^* + \frac{3}{4} \vec{a}_2^*$$

$$G^* = \begin{pmatrix} 3/4 & 1/4 \\ 1/4 & 3/4 \end{pmatrix}$$

$$G = \frac{1}{\frac{9}{16} - \frac{1}{16}} \begin{pmatrix} 3/4 & -1/4 \\ -1/4 & 3/4 \end{pmatrix} = \begin{pmatrix} 3/2 & -1/2 \\ -1/2 & 3/2 \end{pmatrix}$$

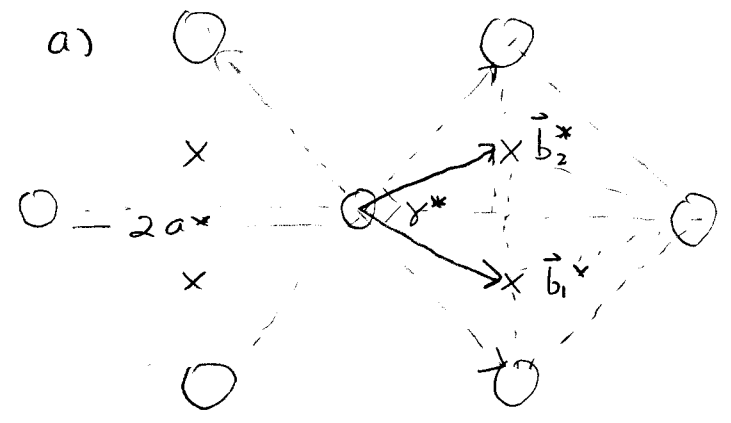
$$\vec{b}_1 = \frac{3}{2} \vec{a}_1 - \frac{\vec{a}_2}{2} \quad \vec{b}_2 = -\frac{1}{2} \vec{a}_1 + \frac{3}{2} \vec{a}_2$$

but $\vec{a}_1 = \frac{1}{2} a \hat{i} - \frac{1}{2} a \hat{j} \quad \vec{a}_2 = \frac{1}{2} a \hat{i} + \frac{1}{2} a \hat{j}$

$$\vec{b}_1 = \frac{3}{2} \left[\frac{a}{2} \hat{i} - \frac{a}{2} \hat{j} \right] - \frac{1}{2} \left[\frac{a}{2} \hat{i} + \frac{a}{2} \hat{j} \right]$$

$$\vec{b}_1 = \frac{a}{2} \hat{i} - a \hat{j}$$

LEED

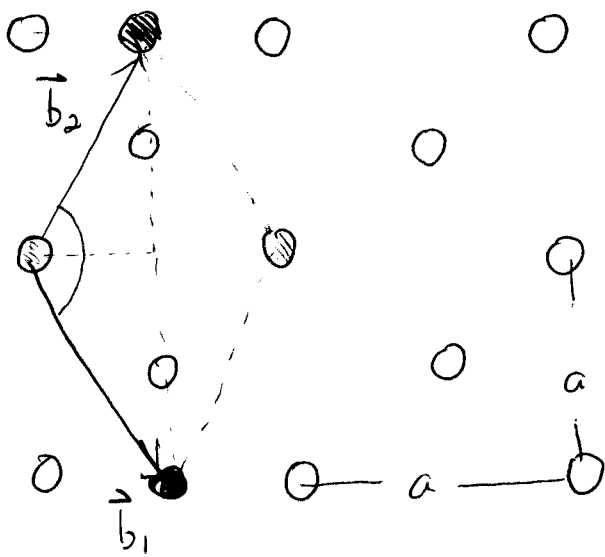


$$\vec{b}_1^* = a^* \hat{i} - \frac{a^*}{2} \hat{j}$$

$$\vec{b}_2^* = a^* \hat{i} + \frac{a^*}{2} \hat{j}$$

Similarly $\vec{b}_2 = \frac{a}{2} \vec{i} + a \vec{j}$

Regular Lattice



○ - substrate

⊗ - overlayer

⊙ - new adsorbate

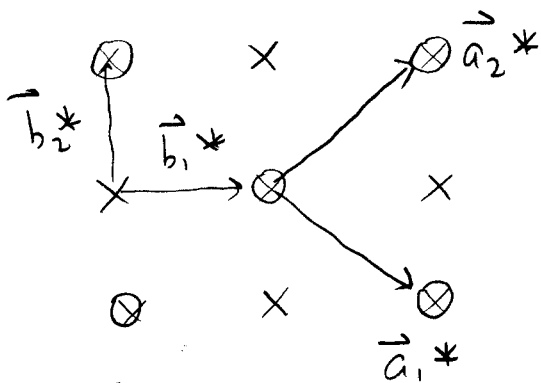
$$\frac{\gamma}{2} = \tan^{-1} 2 = 63.43^\circ$$

$$\gamma = 126.87^\circ$$

\vec{b}_1, \vec{b}_2 unit cell $a \times 2a$

(c)

LEED



$$\vec{b}_1^* = \frac{1}{2} (\vec{a}_1^* + \vec{a}_2^*)$$

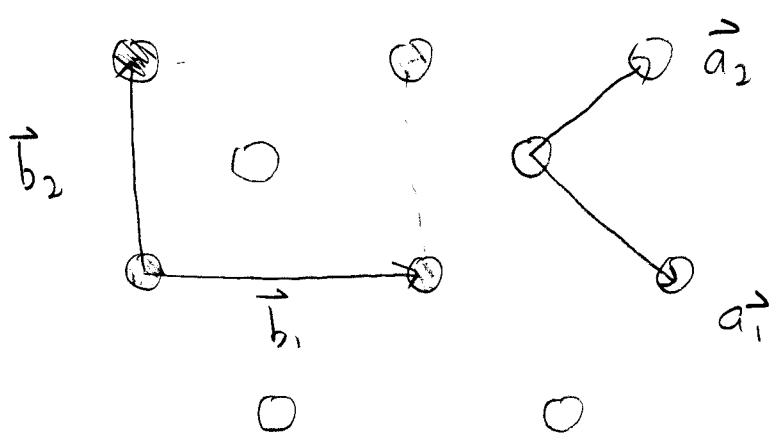
$$\vec{b}_2^* = \frac{1}{2} (-\vec{a}_1^* + \vec{a}_2^*)$$

$$G^* = \begin{pmatrix} 1/2 & 1/2 \\ -1/2 & 1/2 \end{pmatrix}$$

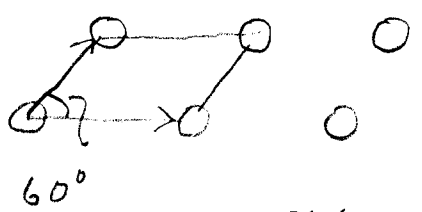
$$\Rightarrow G = 2 \begin{pmatrix} 1/2 & 1/2 \\ -1/2 & 1/2 \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$$

$$\vec{b}_1 = \vec{a}_1 + \vec{a}_2 \quad \vec{b}_2 = -\vec{a}_1 + \vec{a}_2$$

Regular Lattice



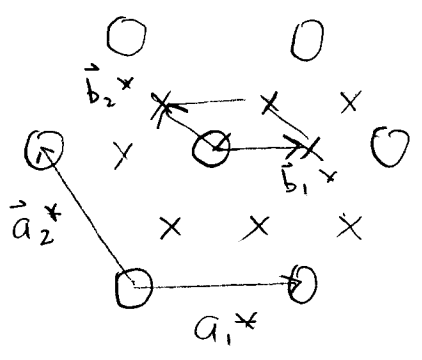
g, i
fcc (111)



← regular lattice
 $a_1 = a_2 = a/\sqrt{2}$

$$\angle(a_1, a_2) = 60^\circ$$

(g) LEED

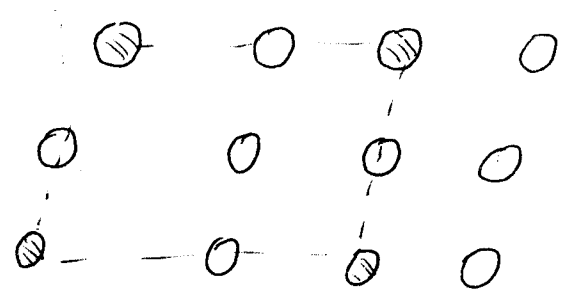


$$\therefore \angle(a_1^*, a_2^*) = 120^\circ$$

$$\vec{b}_1^* = \frac{1}{2} \vec{a}_1^* \quad \vec{b}_2^* = \frac{1}{2} \vec{a}_2^*$$

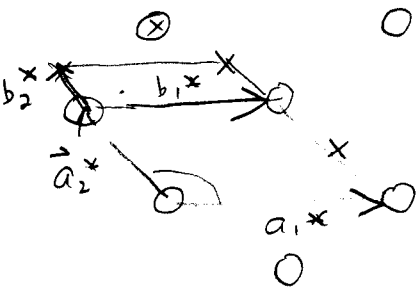
$$G^* = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \Rightarrow G = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$$

$$\therefore \vec{b}_1 = 2\vec{a}_1 \quad \vec{b}_2 = 2\vec{a}_2$$



LEED

(i)



$$\vec{b}_1^* = \vec{a}_1^*$$

$$\vec{b}_2^* = \frac{1}{2} \vec{a}_2^*$$

$$G^* = \begin{pmatrix} 1 & 0 \\ 0 & 1/2 \end{pmatrix}$$

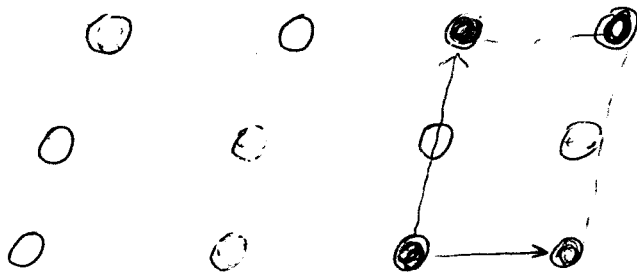
$$G = \frac{1}{1/2} \begin{pmatrix} 1/2 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}$$

$$\angle (\vec{a}_1^*, \vec{a}_2^*) = 120^\circ$$

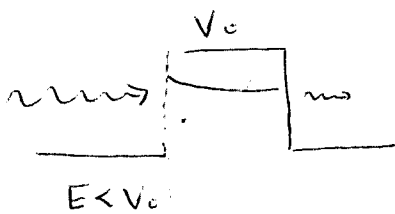
$$\angle (a_1, a_2) = 60^\circ$$

$$\angle (b_1^*, b_2^*) = 120^\circ$$

$$\vec{b}_1 = \vec{a}_1 \quad \vec{b}_2 = 2\vec{a}_2$$



(4) According to quantum mechanics, the transmission fraction under a rectangular barrier of height V_0 and width d is given by



$$T = \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sinh^2(Kd)}$$

$$K = \sqrt{2m(V_0 - E)/\hbar^2}$$

For $Kd \gg 1$: $\sinh Kd = \frac{e^{Kd} + e^{-Kd}}{2} \approx \frac{1}{2} e^{Kd}$

$$\therefore T = \frac{4E(V_0 - E)}{4E(V_0 - E) + \frac{V_0^2}{4} \exp(2Kd)}$$

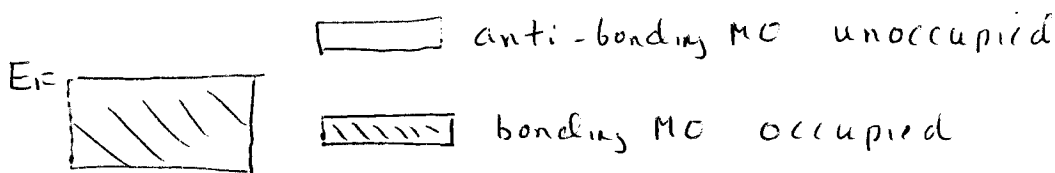
Ignoring the first term in the denominator leads to

$$T \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2Kd}$$

For electrons at the Fermi level, the pre-exponential factor does not change upon scanning the surface.

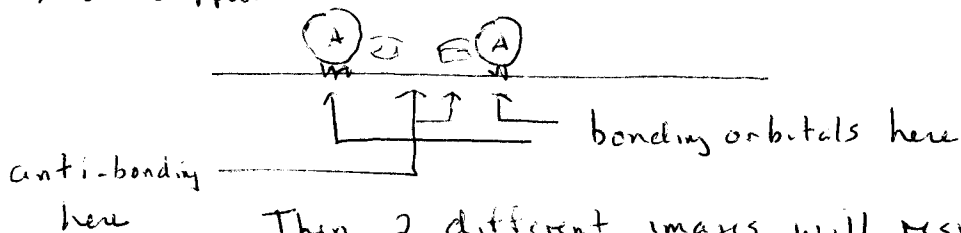
$$\therefore T \propto e^{-2Kd}$$

5. Assume that the orbitals of the adsorbate and the Fermi level of the substrate are like this:



Then, the bonding orbitals can be imaged by STM if the polarity is such that the electrons flow from them to the tip, whereas the anti-bonding orbitals require a polarity such that tip electrons flow into them.

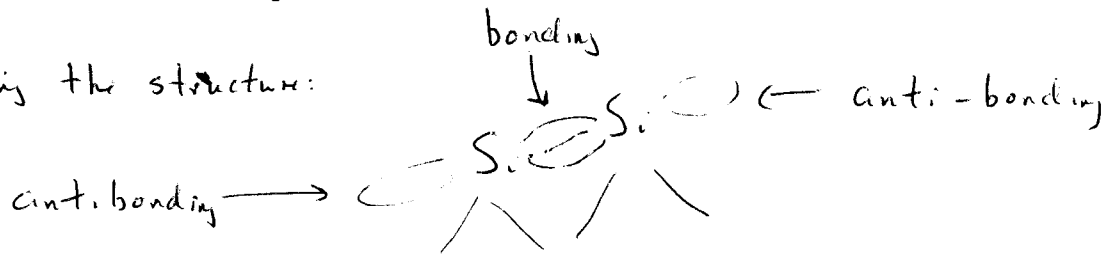
Also suppose:



Then 2 different images will result

6. Just like LEED, STM images smear out with enhanced motion.
7. Similar to my answer to 5. The bonding orbital will be imaged if electrons can flow out of it, so that the tip must be biased positively. The anti-bonding orbital will be imaged if electrons flow into it, so that the tip must be biased negatively.

Assuming the structure:



the images may look like this:



8. Two peaks: ← these CO moieties are not isolated molecules but part of the $Rh(CO)_2$ system.

We can think of the vibrations of $Rh(CO)_2$ as a set of normal modes, two of which involve C-O motions in some manner. The modes need not have the same frequency.

Per mode
$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$
 ← reduced mass affected by isomeric substitution

