Utrecht University
Solids & Solid Surfaces
Tuesday, January 31st, 2017
Time: 13:30 - 16:30

Read the questions carefully. Answer the questions in the spaces provided on the question sheets. If you run out of room for an answer, continue on the back of the page.

Name and student number: ____________________________________

Good luck!

- Calculators, graphical or otherwise, are not allowed.
- Please note that you can earn a maximum of 75 points (which will correspond to a 10.0).
- Not each question is worth the same number of points. Suggestion: save the most difficult/time consuming questions for last.
- The following relations might be helpful:

$$\begin{aligned} e^{-x} &\approx 1 - x \text{ for small } x \\ \sin(x) &\approx x \text{ for small } x \\ \cos(2a) &= 2\cos^2 a - 1 \\ e^{ia} + e^{-ia} &= 2\cos(a) \\ \cos(\pi/2 + a) &= -\sin(a) \end{aligned} \tag{1}$$

Question 1: **Creating and characterizing an electronic Lieb lattice** .... *21 points*

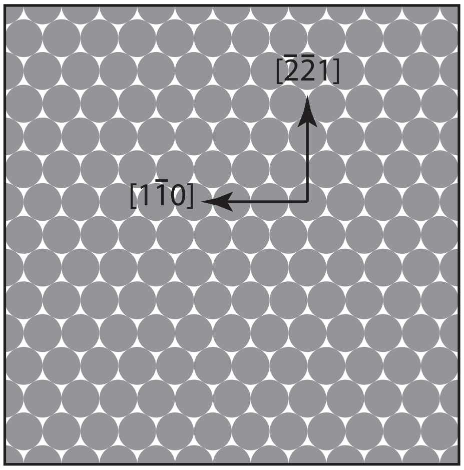

Figure 1: The surface of a particular Cu crystal.

(a) (2 points) Figure 1 shows part of a specific surface of a Cu crystal. Cu has a face-centered-cubic crystal structure. Give the Miller indices of this plane.

Answer: Cu(111) (2 points)

(b) (2 points) Indicate the $[1\bar{1}0]$ and $[\bar{2}\bar{2}1]$ directions in the figure.

Answer: See Figure 1. One point for each correct direction (other origins can be used, as well as other close-packed and open directions).

(c) (1 point) How many equivalent $[1\bar{1}0]$ directions are there in this plane? Explain your answer in the next question.

Answer: 6 (1 point)

(d) (3 points) Explain your answer to the previous question.

Answer: The surface has 6-fold rotational symmetry (3 points). Alternatively, a sketch can be used.

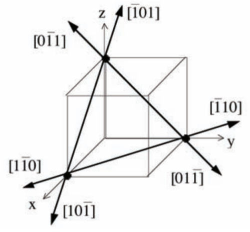

Figure 2: The 6 $[1\bar{1}0]$ type directions of the Cu(111) surface.

(e) (2 points) This particular Cu surface exhibits an electronic surface state with an energy close to the Fermi level. What is the physical reason a surface state can exist?

Answer: The surface breaks translational symmetry in the direction perpendicular to the surface. This allows solutions of the Schrödinger equation with imaginary wave vectors (2 points).

(f) (3 points) Sketch the shape of a surface state wave function along a line from the bulk to the surface to the vacuum above the surface.

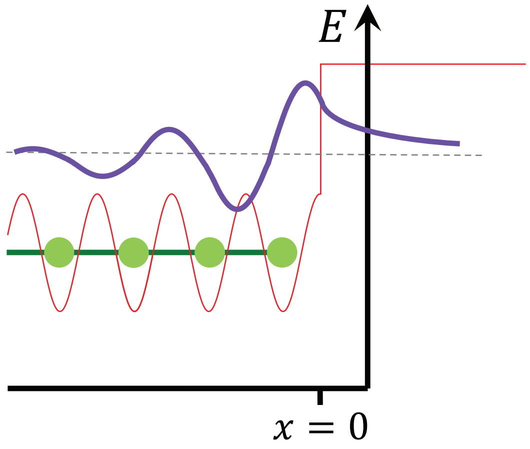

Figure 3: Sketch of the shape of a surface state wave function along the line from the bulk to the surface to the vacuum above the surface.

1 point for exponentially decaying function above the surface, 1 point for wave nature in the crystal, 1 point for exponential damping of the wave inside the crystal.

The surface state can be thought of as a 2D free electron gas. Picture the surface state electrons as waves. The electrons in the surface state are scattered by adsorbates that are located on top of this surface. If there are multiple adsorbates, one can get constructive- and destructive interference. If there is constructive (destructive) interference, the amplitude of the wave function is enhanced (reduced) locally. An enhanced (reduced) amplitude implies a higher (lower) probability to find an electron at these locations. Hence, by positioning adsorbates with atomic scale accuracy, the surface state electrons can be confined to regions of choice. This opens up the possibility to create lattices of electrons. In class, I showed how the Manoharan group at Stanford used this approach to engineer a honeycomb lattice of electrons.

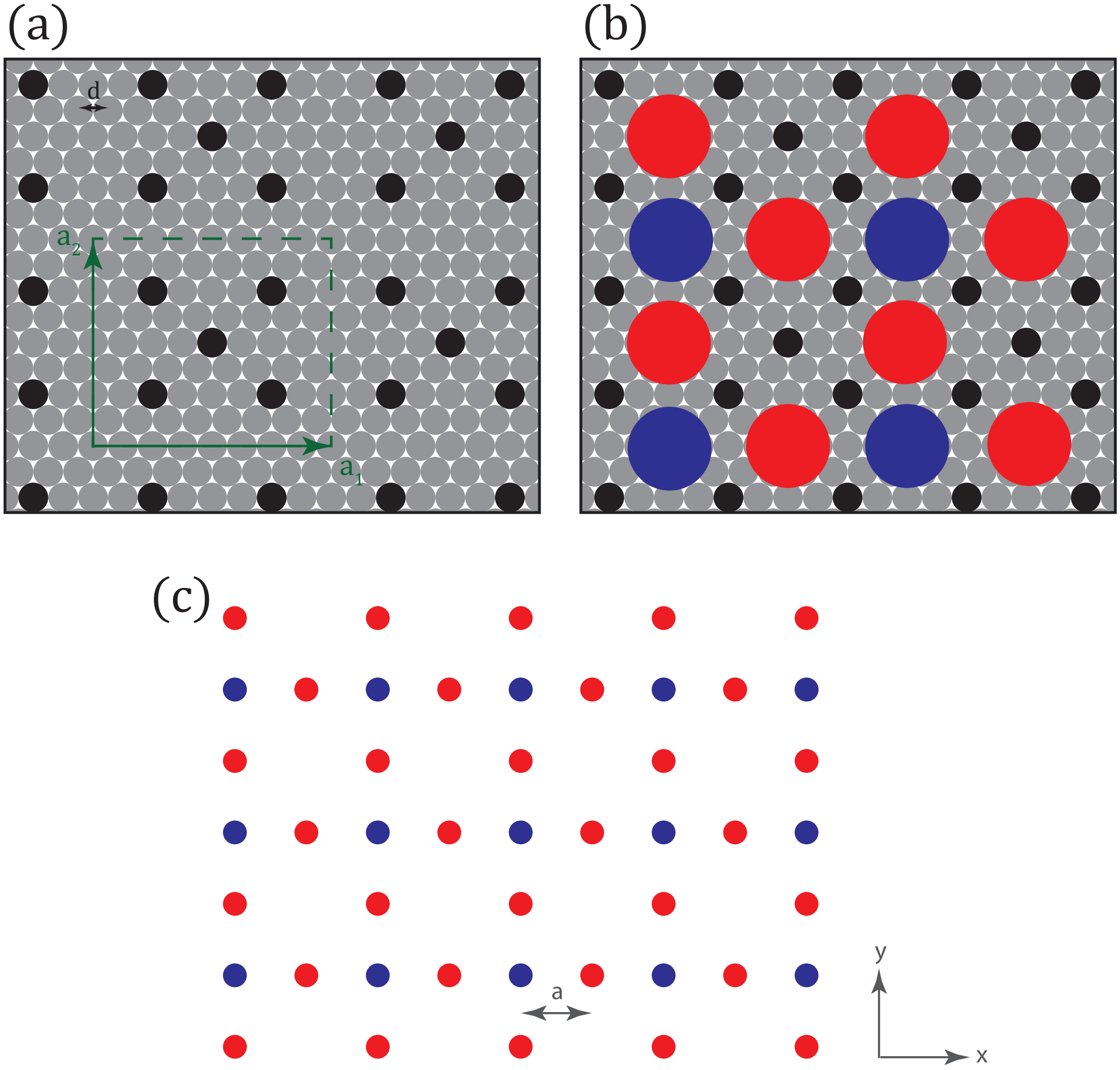

Figure 4: **(a)** CO molecules (black) adsorbed on top of a Cu surface (gray). **(b)** The CO molecules confine the electrons to the regions indicated in blue and red. These are called corner and edge sites respectively. **(c)** Larger piece of the electron lattice with CO molecules and Cu surface omitted for clarity.

(g) (2 points) Consider the arrangement of CO molecules shown in Figure 4a. Indicate the unit cell in Figure 4a.

Answer: See the green dashed line in Figure 4a. Other options are possible. 2 points for the correct unit cell.

The CO molecules confine the electrons to the regions shown in Figure 4b. There are two nonequivalent sites: one with 4 neighbors (corner sites, indicated in blue) and one with two neighbors (edge sites, indicated in red). Hence, the arrangement of CO molecules shown in Figure 4a effectively generates the electron configuration shown in Figure 4c. The lattice in Figure 4c is known as the Lieb lattice. Until recently, it was only studied theoretically.

(h) (6 points) Given that the basis vectors in real-space electron lattice are $\boldsymbol{a_1} = (2a, 0)$ and $\boldsymbol{a_2} = (0, 2a)$, determine the basis vectors of the reciprocal space unit cell. textbfHint: $\boldsymbol{a_i} \cdot \boldsymbol{b_j} = 2\pi\delta_{i,j}$.

Answer: Use the fact that reciprocal space unit vectors have to be perpendicular to the real-space ones.

$$\begin{aligned}
\boldsymbol{a_1} \cdot \boldsymbol{b_1} \cdot &= 2\pi \\
\boldsymbol{a_1} \cdot \boldsymbol{b_2} \cdot &= 0 \\
\boldsymbol{a_2} \cdot \boldsymbol{b_1} \cdot &= 0 \\
\boldsymbol{a_2} \cdot \boldsymbol{b_2} \cdot &= 2\pi
\end{aligned}$$

Using these relations (2 points), immediately gives:

$$\begin{aligned}
\boldsymbol{b_1} &= \left(\frac{\pi}{a}, 0\right) \\
\boldsymbol{b_2} &= \left(0, \frac{\pi}{a}\right)
\end{aligned}$$

1 point for each correct vector component.

Question 2: **The electronic structure of the Lieb lattice** .... *44 points*

In the following, you will perform a tight-binding calculation on the Lieb lattice to investigate its band structure.

(a) (2 points) On which two principles is tight-binding based?

Answer:

- Linear combination of atomic orbitals model (1 point)
- Variational principle (1 point)

(b) (5 points) Consider the case that each site in the unit cell contributes one *s*-orbital to bonding. The simplest wave function for this system is given by

$$\psi(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{R} e^{i\boldsymbol{k}\boldsymbol{R}} \left[c_1\phi_1(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{r}_1) + c_2\phi_2(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{r}_2) + c_3\phi_3(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{r}_3)\right] \tag{2}$$

Give the meaning of the following terms:

- $\frac{1}{\sqrt{N}}$
  Answer: Normalization factor. (1 point)
- $\sum_R$
  Answer: Sum over all lattice sites of the crystal. (1 point)
- $e^{i\boldsymbol{k}\boldsymbol{R}}$
  Answer: Coefficient to indicate the contribution of all wave function at site $\boldsymbol{R}$. (1 point)
- c_i
  Answer: Coefficient to indicate the contribution of wave function i. (1 point)
- $\phi_i(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{r}_i)$
  Answer: Wave function centered on atom i located at site $\boldsymbol{r}_i$ of lattice site $\boldsymbol{R}$. (1 point)

(c) (2 points) How many electronic bands will you find from the tight-binding calculation?

Answer: Because the unit cell contains 3 atoms. (2 points)

(d) (10 points) Show that a tight-binding calculation on the Lieb lattice, taking into account only interaction between nearest neighbors, gives rise to the following matrix equation

$$\begin{pmatrix} \alpha - E(\boldsymbol{k}) & \beta\left(1+e^{i\boldsymbol{k}\boldsymbol{a_2}}\right) & 0 \\ \beta\left(1+e^{-i\boldsymbol{k}\boldsymbol{a_2}}\right) & \alpha - E(\boldsymbol{k}) & \beta\left(1+e^{-i\boldsymbol{k}\boldsymbol{a_1}}\right) \\ 0 & \beta\left(1+e^{i\boldsymbol{k}\boldsymbol{a_1}}\right) & \alpha - E(\boldsymbol{k}) \end{pmatrix} \times \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \tag{3}$$

Answer: In the following, $\boldsymbol{r}$ and $\boldsymbol{r}_i$ are omitted to keep the notation concise.

The variational theorem, in combination with the nearest neighbor approximation, results in a 3×3 matrix. Diagnoal elements are simply $\alpha - E$ (1 point). Atom 1 has 2 neighbors (both of type 2). One of these is located in the same unit cell ($\boldsymbol{R} = \boldsymbol{R'}$) and one in ($\boldsymbol{R} = \boldsymbol{R'} + \boldsymbol{a_2}$). Hence, for the first row, second column, the entry should be $\beta(1 + \exp[i\boldsymbol{ka2}])$. 1 point for the correct number of neighbors/terms and 1 point for the correct expression. Since atom 1 only has neighbors of type 2, the entry in the first row, third column should be 0 (0.5 point). Same arguments apply to the other off-diagonal elements.

(e) (6 points) Show that the matrix equation given in the previous question leads to the following bands.

$$E = \alpha \text{ and } E(\boldsymbol{k})_\pm = \alpha \pm 2\beta\sqrt{\cos^2\left(\frac{\boldsymbol{k}\boldsymbol{a_1}}{2}\right) + \cos^2\left(\frac{\boldsymbol{k}\boldsymbol{a_2}}{2}\right)} \tag{4}$$

Answer: This matrix equation can be solved by setting the determinant equal to zero (1 point). This gives

$$(\alpha - E(\boldsymbol{k})) \begin{vmatrix} \alpha - E(\boldsymbol{k}) & \beta\left(1+e^{-i\boldsymbol{k}\boldsymbol{a_1}}\right) \\ \beta\left(1+e^{i\boldsymbol{k}\boldsymbol{a_1}}\right) & \alpha - E(\boldsymbol{k}) \end{vmatrix} - \beta\left(1+e^{-i\boldsymbol{k}\boldsymbol{a_2}}\right) \begin{vmatrix} \beta\left(1+e^{i\boldsymbol{k}\boldsymbol{a_2}}\right) & 0 \\ \beta\left(1+e^{i\boldsymbol{k}\boldsymbol{a_1}}\right) & \alpha - E(\boldsymbol{k}) \end{vmatrix} = 0$$

$$\begin{aligned} (\alpha - E(\boldsymbol{k}))\left[(\alpha - E(\boldsymbol{k}))^2) - \beta^2\left(1+e^{-i\boldsymbol{k}\boldsymbol{a_1}}\right)\left(1+e^{i\boldsymbol{k}\boldsymbol{a_1}}\right)\right] \\ -\beta\left(1+e^{-i\boldsymbol{k}\boldsymbol{a_2}}\right)\left[\beta\left(1+e^{i\boldsymbol{k}\boldsymbol{a_2}}\right)(\alpha - E(\boldsymbol{k}))\right] = 0 \end{aligned}$$

(2 points) Divide both sides by $(\alpha - E(\boldsymbol{k}))$. This gives the solution $E = \alpha$. (1 points)

$$\begin{aligned} (\alpha - E(\boldsymbol{k}))^2 - \beta^2\left(1+e^{-i\boldsymbol{k}\boldsymbol{a_1}}\right)\left(1+e^{i\boldsymbol{k}\boldsymbol{a_1}}\right) - \beta^2\left(1+e^{-i\boldsymbol{k}\boldsymbol{a_2}}\right)\left(1+e^{i\boldsymbol{k}\boldsymbol{a_2}}\right) = 0 \\ (\alpha - E(\boldsymbol{k}))^2 - \beta^2(2 + 2\cos(\boldsymbol{k}\boldsymbol{a_1})) - \beta^2(2 + 2\cos(\boldsymbol{k}\boldsymbol{a_2})) = 0 \end{aligned}$$

Use the trigonometric relation $\cos(2a) = 2\cos^2 a - 1$, rearrange and take the square root to find equation 4 (2 points).

(f) (4 points) For the solution $E = \alpha$, show that the coefficients $c_2 = 0$.

Answer: Insert $E = \alpha$ into equation 3 (1 points). This gives

$$\begin{pmatrix} 0 & \beta\left(1+e^{i\boldsymbol{k}\boldsymbol{a_2}}\right) & 0 \\ \beta\left(1+e^{-i\boldsymbol{k}\boldsymbol{a_2}}\right) & 0 & \beta\left(1+e^{-i\boldsymbol{k}\boldsymbol{a_1}}\right) \\ 0 & \beta\left(1+e^{i\boldsymbol{k}\boldsymbol{a_1}}\right) & 0 \end{pmatrix} \times \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \tag{5}$$

(2 points) Focus on the first line to find

$$c_1 \cdot 0 + c_2 \cdot \beta\left(1+e^{i\boldsymbol{k}\boldsymbol{a_2}}\right) + c_3 \cdot 0 = 0$$

This immediately gives $c_2 = 0$. (1 points)

(g) (3 points) Using the fact that $c_2 = 0$, explain why the band $E = \alpha$ does not depend on $\boldsymbol{k}$, i.e. why the band is flat.

Answer: $c_2 = 0$ implies that the wave function on atom 2, i.e. the corner atom, is zero (1 point). If only interactions between nearest-neighbors are included, atoms 1 and 3 do not interact (1 point). This band therefore corresponds to a collection of completely localized states (1 point).

(h) (5 points) We will now focus on the dispersion relation at the corners of the Brillouin zone. One of these is located at $(\pi/2a, \pi/2a)$. Recall that $\boldsymbol{a_1} = (2a, 0)$ and $\boldsymbol{a_2} = (0, 2a)$. Show that the dispersion relation (equation 4) at this point can be approximated as

$$E(\boldsymbol{k}) = \alpha \pm 2\beta a\sqrt{\Delta k_x^2 + \Delta k_y^2} \tag{6}$$

where $\Delta\boldsymbol{k} = (\Delta k_x, \Delta k_y)$ is the deviation from the Brillouin zone boundary, i.e. $\boldsymbol{k} = \left(\frac{\pi}{2a} + \Delta k_x, \frac{\pi}{2a} + \Delta k_y\right)$. We are interested in the dispersion close to the Brillouin zone boundary, i.e. in small values of Δk_x and Δk_y.

Hint: A Taylor expansion is not required.

Answer: Insert the substitution $\boldsymbol{k} = \left(\frac{\pi}{2a} + \Delta k_x, \frac{\pi}{2a} + \Delta k_y\right)$, together with the definition of $\boldsymbol{a_1}$ and $\boldsymbol{a_2}$, into equation 4 (2 points). This gives

$$\begin{aligned} E(\boldsymbol{k})_\pm &= \alpha \pm 2\beta\sqrt{\cos^2\left(\frac{\pi}{2} + \Delta k_x a\right) + \cos^2\left(\frac{\pi}{2} + \Delta k_y a\right)} \\ &= \alpha \pm 2\beta\sqrt{\sin^2(a\Delta k_x) + \sin^2(a\Delta k_y)} \\ &= \alpha \pm 2a\beta\sqrt{\Delta k_x^2 + \Delta k_y^2} \end{aligned}$$

where we used $\cos(\pi/2 + a) = -\sin(a)$ and $\sin(x) \approx x$ for small x. (3 points)

(i) (3 points) Focusing on the band structure at the corners of the Brillouin zone, do the electrons in the Lieb Lattice have a dispersion relation more like free electrons or more like those in graphene. Explain.

Answer: Graphene has a linear dispersion close to the Fermi energyi i.e. the energy depends linearly on momentum (1 point). We see from equation 6 that the dispersion of the Lieb lattice close to the Fermi level is linear, similar to graphene. (2 points)

(j) (4 points) Equation 4 gives the energies as a function of wave vector. Figure 5 shows the band structure of the Lieb lattice. Using this graph, sketch the density of states of the Lieb Lattice.

Answer: See Figure 5. 2 point for δ-type peak, 2 points for side bands.

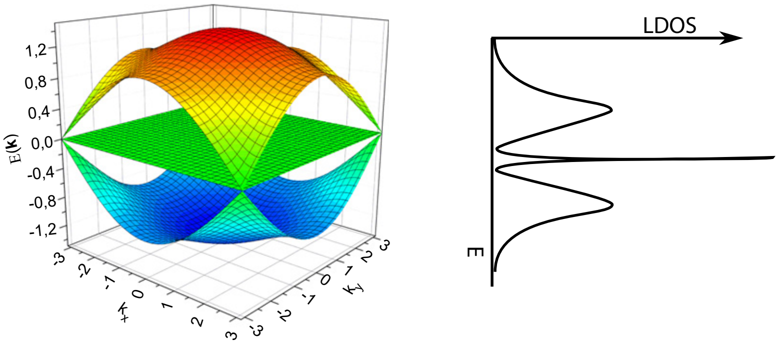

Figure 5: Band structure of the Lieb lattice, including nearest-neighbor interactions only, as given by equation 4.

Question 3: **Characterizing the Lieb lattice** . . . . *10 points*

(a) (6 points) A scanning tunneling microscope (STM) can be used to image surfaces with high (often atomic) resolution. Explain how an STM works. The following elements should be included in your explanation: the physical basis of the technique, why you can get high spatial resolution, how an image of the surface is constructed.

Answer: The scanning tunneling microscope uses the quantum mechanical tunneling effect. When the distance between two potential wells is small, and the barrier between them is finite, there is a finite probability for an electron to tunnel through the barrier, i.e. to go from one potential well to the other (2 points, a sketch similar to Figure 7.8 in the reader is also worth 2 points). The tunnel current depends exponentially on the distance between the two wells: $I(d) \propto e^{-2\kappa d}$ (1 point). The decay constant κ is on the order of 1 Å^{-1}. Hence, the current changes by a factor $e^2 (\approx 10)$ when the distance changes by 1Å(1 point). The tip is approached to the surface until a given set-point current is detected. The tip is then raster-scanned over the surface while a feedback mechanism adjusts the tip-height such that the tunnel current is kept constant (2 points).

(b) (4 points) Sketch the differential conductance spectrum (measured using a scanning tunneling microscope) at a corner site of the Lieb lattice (blue circle in Figure 4, respectively). **Hint:** Use the fact that for the flat band $c_2 = 0$. In addition, you should take equation 6 into account.

Answer: For the flat band $c_2 = 0$. This implies that at the corner site (i.e. at site 2), the amplitude of the wave functions contributing to the flat band at these sites, and therefore the density of states , is zero (2 points). Equation 6 shows that the energy depends linearly on $\boldsymbol{k}$. Hence, the differential conductance spectrum at the corner site (which is proportional to the density of states, 1 point) depends linearly on voltage (1 point).