# CHEMISTRY 448/548 Winter 2009

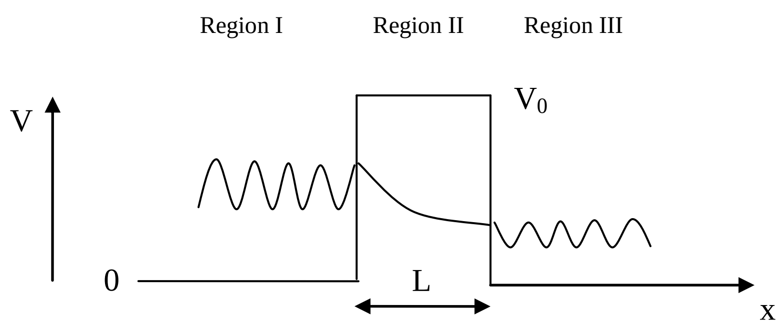
## Assignment #2 (75 pts)

## Due Jan. 26th

**SHOW WORKING FOR FULL CREDIT AND ALL WORK MUST BE NEAT AND READABLE OR YOU WILL LOSE POINTS !**

**PLOTS SHOULD BE CAREFULLY DONE AND LABELED ON GRAPH (NOT QUADRILLE) PAPER OR COMPUTER PLOTTED. SUBMIT (ABBREVIATED) TABLES OF NUMBERS THAT GO INTO THE PLOT.**

1. (20 pts) We can model the operation of an STM by the transmission of a particle-wave through a 1-D potential energy barrier, height $V_0$ and width L.




For an electron mass *m* and energy *E*, the wavefunctions in each region are:

$$\psi_I(x) = Ae^{+ikx} + Be^{-ikx}$$
$$\psi_{II}(x) = Ce^{-\kappa x} + De^{+\kappa x}$$
$$\psi_{III}(x) = Fe^{+ikx}$$

where $k = \sqrt{\dfrac{8\pi^2 mE}{h^2}}$ and $\kappa = \sqrt{\dfrac{8\pi^2 m(V_0 - E)}{h^2}}$

The transmission probability, $T = \left|\dfrac{F^2}{A^2}\right| = \dfrac{1}{1 + [(k^2+\kappa^2)^2 \sinh^2(\kappa L)]/4(\kappa k)^2}$

(a) Plot the transmission (tunneling) probability of an electron as a function of energy for a barrier that is 2 eV high and 10 Å wide for energies up to 2 eV. At what energy is the probability 0.05? Use a spreadsheet, Mathcad or similar. (7 pts)

Note: The relationship $(h^2 / 8\pi^2 m) = 3.88$ eV Å$^{-2}$ makes things easier.

Solution:

We have $k = \sqrt{\dfrac{8\pi^2 mE}{h^2}}$ and $\kappa = \sqrt{\dfrac{8\pi^2 m(V_0 - E)}{h^2}}$

so, using units of eV and Å

$k = \sqrt{\dfrac{E}{3.88}}$ and $\kappa = \sqrt{\dfrac{(V_0 - E)}{3.88}}$

Setting

$$T = 1 \Big/ (1 + AB/C)$$

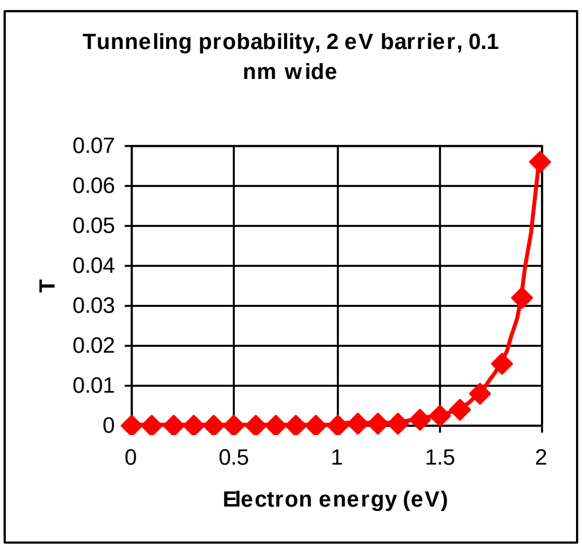
with

$A = (k^2 + \kappa^2)^2$, $B = \sinh^2(\kappa L)$ and $C = 4(k\kappa)^2$

For $V_0 = 2$ eV and $L = 10$ Å, the first few rows of the spreadsheet are:

| E | k | kappa | A | B | C | AB/C | T |
|---|---|---|---|---|---|---|---|
| 0.001 | 0.016054 | 0.7177786 | 0.26570305 | 429027.975 | 0.000531 | 214621298 | 4.659E-09 |
| 0.1 | 0.16054 | 0.6997791 | 0.26570305 | 299324.937 | 0.050484 | 1575394.41 | 6.348E-07 |
| 0.2 | 0.227038 | 0.6811149 | 0.26570305 | 206076.242 | 0.095653 | 572434.007 | 1.747E-06 |
| 0.3 | 0.278064 | 0.6619247 | 0.26570305 | 140392.367 | 0.135509 | 275279.15 | 3.633E-06 |
| 0.4 | 0.321081 | 0.6421613 | 0.26570305 | 94553.9956 | 0.17005 | 147740.618 | 6.769E-06 |
| 0.5 | 0.358979 | 0.62177 | 0.26570305 | 62887.1905 | 0.199277 | 83849.5873 | 1.193E-05 |

and the plot is:



The energy for which T = 0.05 is 1.96 eV

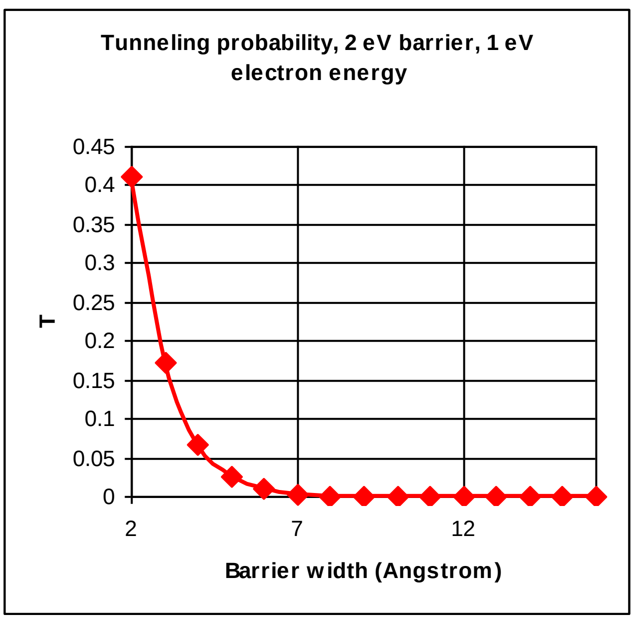
| E | k | kappa | A | B | C | AB/C | T |
|---|---|---|---|---|---|---|---|
| 1.9558 | 0.70998 | 0.1067322 | 0.26570305 | 1.64307882 | 0.022969 | 19.0069173 | 0.0499827 |

(b) Plot the transmission (tunneling) probability of an electron as a function of barrier width (from 2 to 15 Å) for a barrier that is 2 eV high and an electron with 1 eV of energy. At what energy is the probability 0.15? (7 pts)

Solution:

Repeating the calculation for these conditions produces:

| L | k | kappa | A | B | C | AB/C | T |
|---|---|---|---|---|---|---|---|
| 2 | 0.507673 | 0.5076731 | 0.26570305 | 1.43765107 | 0.265703 | 1.43765107 | 0.410231 |
| 3 | 0.507673 | 0.5076731 | 0.26570305 | 4.76985207 | 0.265703 | 4.76985207 | 0.1733147 |
| 4 | 0.507673 | 0.5076731 | 0.26570305 | 14.0179666 | 0.265703 | 14.0179666 | 0.0665869 |
| 5 | 0.507673 | 0.5076731 | 0.26570305 | 39.563889 | 0.265703 | 39.563889 | 0.0246525 |



The barrier width for which T = 0.15 is 3.16 Å.

| L | k | kappa | A | B | C | AB/C | T |
|---|---|---|---|---|---|---|---|
| 3.156 | 0.507673 | 0.5076731 | 0.26570305 | 5.67052346 | 0.265703 | 5.67052346 | 0.1499133 |

(c) Assume that the tunneling current is proportional to $T$ and that the barrier width can be equated to the tip-sample distance. What is the ratio of the currents for a barrier that is 2 eV high for an electron with an energy of 1 eV when the tip is moved from 5 Å to 6 Å away from the surface? (3 pts)

Solution:

If the current $i$ is proportional to $T$, then $I = (i_{5Å} / i_{6Å}) = (T_{5Å} / T_{6Å})$

So, we simply put in the appropriate values from the calculation in (b):

| L | T | I |
|---|---|---|
| 5 | 0.024652 | **2.7385284** |
| 6 | 0.009002 | |

$(i_{5Å} / i_{6Å}) = 2.74$

(d) Repeat the calculation in (c) for a proton instead of an electron. Does a proton tunneling microscope seem like a good idea? (3 pts)

Solution:

The only thing to change here is that we swap the mass of a proton for the mass of an electron which goes into $k$ and $\kappa$.

$m_p = 1.673 \times 10^{-27}$ kg and $m_e = 9.109 \times 10^{-31}$ kg

$k$ and $\kappa$ will change by a factor of $(m_p / m_e)^{1/2}$.

| L | k | kappa | A | B | C | AB/C | T | I |
|---|---|---|---|---|---|---|---|---|
| 5 | 21.75689 | 21.756887 | 896286.8361 | 7.707E+93 | 896286.8 | 7.707E+93 | 1.297E-94 | **7.9E+18** |
| 6 | 21.75689 | 21.756887 | 896286.8361 | 6.091E+112 | 896286.8 | 6.091E+112 | 1.642E-113 | |

The extremely small values of T mean that it will be impossible to measure a tunneling current.

2. (20 pts) We can approximately represent the potential between the atom in the tip of an AFM and one in the sample by a Lennard-Jones 12-6 type of potential.

$$V(z) = 4\varepsilon[(\sigma/z)^{12} - (\sigma/z)^{6}]$$

a) Derive an analytical expression that links σ with the value of $z$ at the minimum of the curve ($z_e$) and show that $\sigma = 0.891\, z_e$. (4 pts)

Solution :

$$V(z) = 4\varepsilon[(\sigma/z)^{12} - (\sigma/z)^{6}]$$

The minimum in V will occur at $z = z_e$ when

$$dV/dz = 0 = 4\varepsilon\,(1/z_e)\,[-12\,(\sigma/z_e)^{12} + 6\,(\sigma/z_e)^{6}]$$

so

$$12\,(\sigma/z_e)^{12} = 6\,(\sigma/z_e)^{6}$$

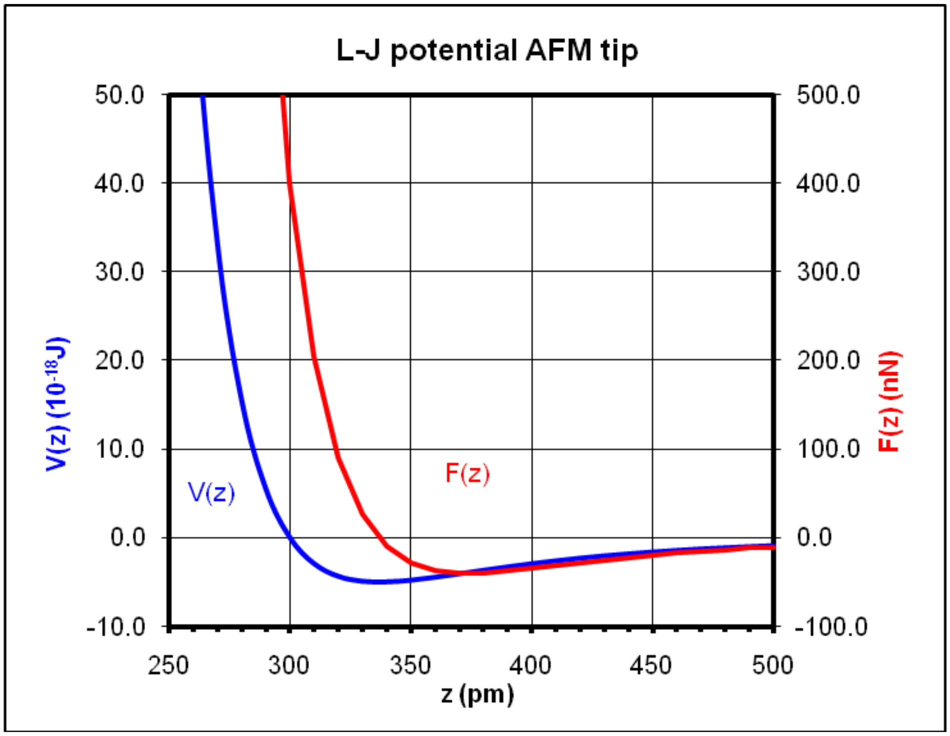
$$\sigma = (½)^{1/6}\, z_e = 0.891$$

b) Suppose for a Si tip and a Si sample $\varepsilon = 5.00 \times 10^{-18}$ J and $\sigma = 300$ pm. Calculate V(z) from z = 250 pm to 500 pm and check that the value of $z_e$ agrees with that calculated in (a). Use a spreadsheet or similar. Make sure to use a small enough grid of points and adjust the y-axis to be able to see the minimum in the curve. (8 pts)

Solution:

Putting in values for V(z) – the first few rows of the spreadsheet.

| | | | |
|---|---|---|---|
| **LJ for AFM** | | | |
| **Si** | **σ** | **300** | **pm** |
| | **ze = 0.981 * σ** | **337** | **pm** |
| | **epsilon** | **5.00E-18** | **J** |
| | | | |
| **z (pm)** | **V (10-18J)** | **sigma/z** | **F(nN)** |
| 250 | 118.60 | 1.20E+00 | 7126.18 |
| 260 | 64.18 | 1.15E+00 | 4051.42 |
| 270 | 33.18 | 1.11E+00 | 2310.99 |
| 280 | 15.51 | 1.07E+00 | 1313.27 |
| 290 | 5.53 | 1.03E+00 | 735.93 |
| 300 | 0.00 | 1.00E+00 | 400.00 |




The calculated curve minimizes near 335 pm and

$z_e = \sigma\ / 0.891 = 337$ pm

c) Derive an analytical expression for the force F(z) (nN) between the tip atom and surface atom and make a plot of the force between the same z values. Again make sure to use a small enough grid of points and adjust the y-axis to be able to see the minimum in the curve. (8 pts)

Solution :

Force = -dV/dz which we have already found.

$F = -dV/dz = \ 4\varepsilon\ (1/\ z\ )\ [\ 12\ (\sigma/z)^{12}\ -\ 6\ (\sigma/z)^{6}\ ]$

See plot above. Notice the plot crosses the x-axis at 337 pm ($z_e$).

3. (20 pts) Suppose an fcc(110) surface undergoes a reconstruction that is labeled as (2x3). The LEED pattern shows "extra" spots in the (2x3) reconstruction relative to the ideal (110) pattern.

(a) Draw the real space unit mesh vectors for fcc(110) (1x1) and fcc(110) (2x3) surfaces. Label them with ($\underline{a}$ , $\underline{b}$) and ($\underline{a}_s$ , $\underline{b}_s$) notations. (6 pts)

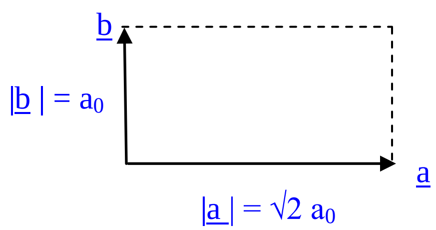
Solution:

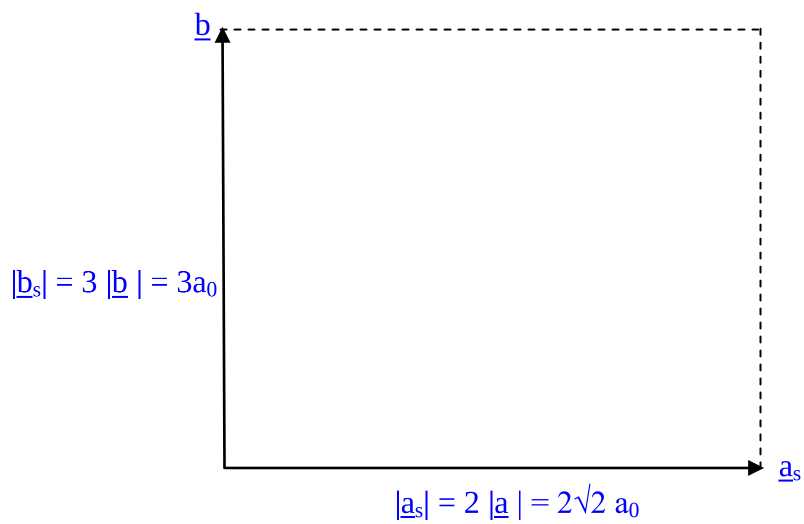
fcc(110) (1x1)

Mesh vectors are rectangular with lengths $|\underline{a}| = \sqrt{2}\, a_0$ and $|\underline{b}| = a_0$.

fcc(110) (2x3)

Mesh vectors are rectangular with $|\underline{a}_s| = 2\,|\underline{a}| = 2\sqrt{2}\, a_0$ and $|\underline{b}_s| = 3\,|\underline{b}| = 3a_0$




b) Draw the LEED patterns expected for the ideal and reconstructed for spots with (hk) indices $-1 \leq h,k \leq 1$ at normal electron beam incidence i.e. the (00) spot will be in the middle of the diagram. Show any extra spots that appear in the (2x3) pattern as a different symbol. Plot both to the same scale and make the relative dimensions accurate and label them with ($\underline{a^*}$ , $\underline{b^*}$) and ($\underline{a^*}_s$ , $\underline{b^*}_s$) notations. (10 pts)

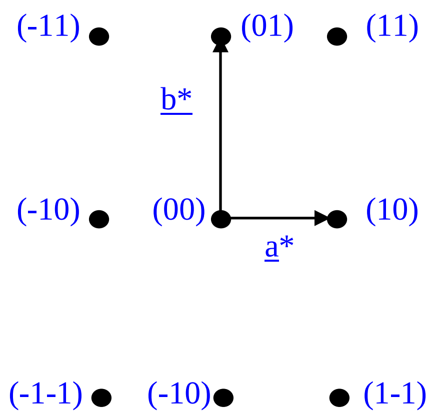
Solution:

Fcc(110) (1x1) $|\underline{a^*}| = 2\pi / |\underline{a}| = 2\pi / \sqrt{2}\, a_0$

$|\underline{b^*}| = 2\pi / |\underline{b}| = 2\pi / a_0$.

So, $|\underline{a^*}| / |\underline{b^*}| = 1 / \sqrt{2}$ and $\underline{a}^*$ is perpendicular to $\underline{b}$ , $\underline{b}^*$ is perpendicular to $\underline{a}$

The LEED pattern will look like below (the absolute size is arbitrary). Notice that the reciprocal mesh means that the long real vectors produce short reciprocal vectors.



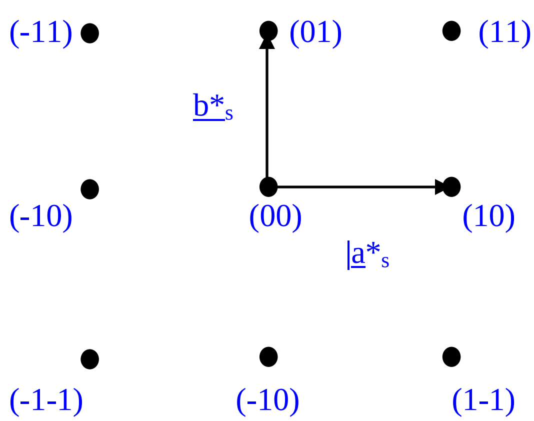

Fcc(110) (2x3) $\quad |\underline{a}^*_s| = 2\pi / |\underline{a}_s| = 2\pi / 2\sqrt{2}\ a_0$

$|\underline{b}^*_s| = 2\pi / |\underline{b}_s| = 2\pi / 3\ a_0$.

So, $|\underline{a}^*_s| / |\underline{b}^*_s| = 3 / 2\sqrt{2} = 1.06$ and $\underline{a}_s^*$ is perpendicular to $\underline{b}_s$, $\underline{b}_s^*$ is perpendicular to $\underline{a}_s$

There are two ways to index this LEED pattern.

The first is to index it without regard to the clean surface. In this case the spots are labeled (10), (01) etc as before, but with new vectors that are almost the same length.




The second is to treat the (2x3) as a new pattern relative to the clean (1x1) pattern. In this case the “new” spots from the (2x3) surface have non-integer indices because the new reciprocal mesh vectors are a fraction of those of the clean surface.

Fcc(110) (2x3) $|\underline{a}^*_s| = 2\pi / |\underline{a}_s| = 2\pi / 2\sqrt{2}\, a_0$

$|\underline{b}^*_s| = 2\pi / |\underline{b}_s| = 2\pi / 3\, a_0.$

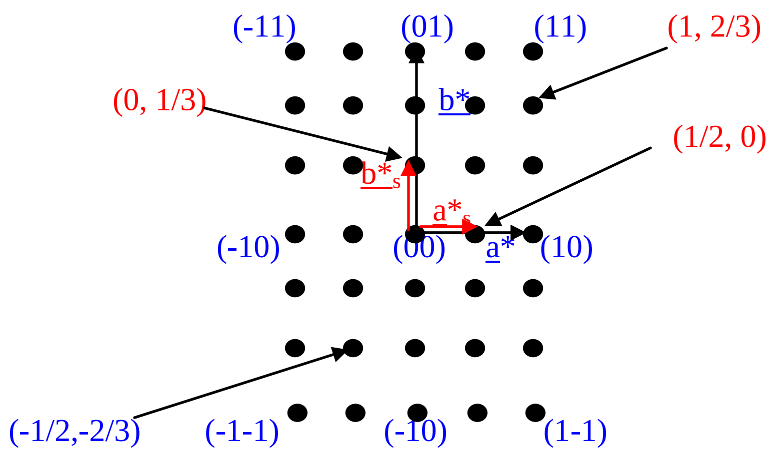
Fcc(110) (1x1) $|\underline{a}^*| = 2\pi / |\underline{a}| = 2\pi / \sqrt{2}\, a_0$

$|\underline{b}^*| = 2\pi / |\underline{b}| = 2\pi / a_0.$

$|\underline{a}^*_s| / |\underline{a}^*| = (2\pi / 2\sqrt{2}\, a_0) / (2\pi / \sqrt{2}\, a_0) = 1/2$

$|\underline{b}^*_s| / |\underline{b}^*| = (2\pi / 3\, a_0) / (2\pi / a_0) = 1/3$

And the pattern is then (new spots shown in red):




c) Describe qualitatively what will happen to the LEED pattern if i) the electron energy is reduced ii) the angle of incidence is set at 45º to the surface. (4 pts)

Solution :

i) At a lower energy, the electron wavelength is smaller, hence the separation between spots increases and the pattern will expand.

ii) The pattern will shift by 45º, and will no longer be centered on the (00) spot.