Utrecht University
Exam Structure of Matter
Monday, April 18th, 2016
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 83 points.
- Not each question is worth the same number of points.
- Questions have been ordered by subject, not by difficulty. Suggestion: save the most difficult/time consuming questions for last.
- The following relations might be helpful:

$$\begin{aligned}\cos(2a) &= 2\cos^2 a - 1\\ \cos(a+b) &= \cos(a)\cos(b) - \sin(a)\sin(b)\\ \cos(a-b) &= \cos(a)\cos(b) + \sin(a)\sin(b)\\ e^{ik} + e^{-ik} &= 2\cos(k)\end{aligned}$$

Question 1: **Atomic Physics** . . . . *14 points*

(a) (1 point) When going down a group in the periodic table, the size of an atom decreases

A. True

B. False ← Correct Answer

(b) (1 point) When crossing a period of the periodic table from left to right , the size of atoms increases

A. True

B. False ← Correct Answer

(c) (3 points) Calculate how many electrons the 'shell' with main quantum number $n = 4$ can accommodate.

Answer: The number of electrons in a shell is given by $2n^2$ (1 point). Hence, the shell with $n = 4$ accommodates 32 electrons (2 points). Also correct $4s^2 4p^6 4d^{10} 4f^{14}$.

(d) (2 points) Give the electron configuration of F ($Z = 9$)

Answer: $1s^2 2s^2 2p^5$

(e) (2 points) Give the electron configuration of Fe ($Z = 26$

Answer: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

(f) (5 points) The electron affinity (E_a) of atom A is defined as the energy difference between the neutral atom and the anion:

$$E_a = E(A) - E(A^-) \tag{1}$$

The electron affinity of an element is determined in a large part by the energy of the lowest empty orbital of the ground state atom. The energy of this orbital is related to the effective nuclear charge of the atom. In which part of the periodic table do you expect to find the atoms with the highest electron affinity? Explain.

Answer: At the top right, i.e. around F (1 point). The energy of the orbitals decreases with increasing effective nuclear charge (2 points). The effective nuclear charge increasing when crossing a period of the periodic table from left to right (1 point). The effective charge decreases when going down a group of the periodic table (1 point).

Question 2: **Molecular Physics** . . . . *26 points*

(a) (1 point) Give the correct order of magnitude of the energy associated with a covalent bond

A. 1 eV ← Correct Answer
B. 0.1 eV
C. 0.01 eV
D. 0.001 eV

(b) (1 point) Give the correct order of magnitude of the energy associated with an ionic bond

A. 1 eV ← Correct Answer
B. 0.1 eV
C. 0.01 eV
D. 0.001 eV

(c) (1 point) Give the correct order of magnitude of the energy associated with a van der Waals interaction

A. 1 eV
B. 0.1 eV
C. 0.01 eV ← Correct Answer
D. 0.001 eV

(d) (1 point) Give the correct order of magnitude of the energy associated with a hydrogen bond

A. 1 eV
B. 0.1 eV ← Correct Answer
C. 0.01 eV
D. 0.001 eV

(e) (2 points) Which two principles form the basis of tight-binding calculations?

Answer:

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

(f) (4 points) Consider the reaction between butadiene (C_4H_6)and an electrophile (HBr), as indicated in Figure 1 below. The electrophile can attack at one of the central carbon atoms *or* at a terminal carbon atom. As indicated in the figure, the product of the reaction depends on where the HBr attacks the butadiene. The rate of a chemical reaction is proportional to the barrier height (ΔE), which is defined as the energy difference between the species with the highest energy (the so-called transition state, structures indicated in the figure) and the reactant (in this case butadiene). The energy of butadiene is $E_{butadiene} = 4\alpha + 4.48\beta$ (**there is no need to calculate this again!**). Recall that both α and β are negative. The energy of a H atom within the Hückel approximation is zero. Assume that there are no changes in the $\sigma-$orbitals.

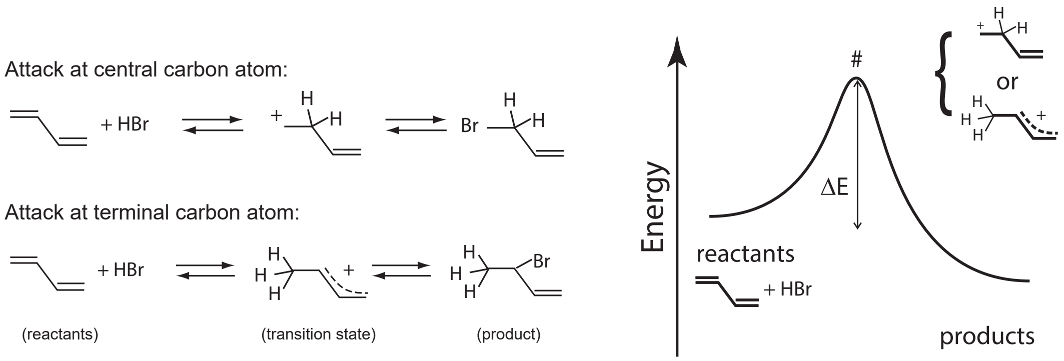

Figure 1: Electrophilic addition reaction of butadiene. Two possible reaction pathways, including the reaction intermediates (transition states) are indicated.

Look at the structure of the transition states. For each transition state, indicate how many carbon atoms are part of the π-conjugated system.

Answer: For the reaction shown at the top: 2 carbon atoms (cf. ethylene) (2 points). For the reaction shown at the bottom: 3 carbon atoms (2 points).

(g) (16 points) Use a Hückel calculation to estimate ΔE (the barrier height) for the two different pathways indicated in Figure 1 **and** state what is the expected dominant product of the chemical reaction. **Hint:** Recall that Hückel calculations are done on π-conjugated molecules.

Answer: The barrier height corresponds to the energy difference between the transition state (see the Figure) and the starting material, i.e. butadiene:

$$\Delta E = E_{trans} - E_{butadiene} \quad \text{(1 point)}$$

For attack at the central carbon atom, the π-system consists of only the two right most carbon atoms. There are two π-electrons (1 point). Within the Hückel approximation, the transition state of the top reaction is identical to ethylene. Recall or calculate that the energy of ethylene is $E_{TS1} = 2\alpha + 2\beta$ (3 points). Calculation is done by equating the secular determinant to zero and solving for the energy.

$$\begin{vmatrix} \alpha - E_{TS1} & \beta \\ \beta & \alpha - E_{TS1} \end{vmatrix} = 0$$

Hence, for the top reaction the activation barrier is: $\Delta E_1 = -2\alpha - 2.48\beta$. (2 points)

For attack at the terminal carbon atom, the π-system consists of three carbon atoms. Within the Hückel approximation, the transition state of the bottom reaction is identical equivalent to a chain of three atoms

$$\begin{vmatrix} \alpha - E_{TS2} & \beta & 0 \\ \beta & \alpha - E_{TS2} & \beta \\ 0 & \beta & \alpha - E_{TS2} \end{vmatrix} = 0 \quad \text{(1 point)}$$

Hence

$$(\alpha - E)\left[(\alpha - E)^2 - \beta^2\right] - \beta^2(\alpha - E) = 0$$

Solving this equation (by dividing both slides by $(\alpha - E)$), yields three states. These have energies $E_{\pm} = \alpha \pm \sqrt{2}\beta$, and $E = \alpha$ (3 points). There are two π-electrons (note the positive charge, 2 points). The Hückel energy of the second transition state is therefore $E_{TS2} = 2\alpha + 2\sqrt{2}\beta$ (1 point). Hence, for the bottom reaction the activation barrier is: $\Delta E_2 = -2\alpha - 1.66\beta$ (2 points).

As $\Delta E_2 < \Delta E_1$, attack at the terminal carbon atom is preferred and the product of the bottom reaction will be most abundant (2 points).

Question 3: **Condensed Matter Physics 1** . . . . *11 points*

(a) (4 points) Consider a two-dimensional crystal (i.e. not a quasicrystal). Which rotational symmetries can the unit cell of such a crystal have?

Answer: 2, 3, 4, and 6-fold rotational symmetry (1 point for each correct answer).

(b) (2 points) Explain why only the rotational symmetries given under a are allowed.

Answer: Only unit cells with these symmetries can fill all of space continuously (2 points).

(c) (1 point) Consider a line of lattice points A-O-B, separated by distance a (indicated in blue). Rotate the entire row by $\theta = +2\pi/n$ and $\theta = -2\pi/n$ (orange and green lines), with point O kept fixed. If the rotation over $\theta = +2\pi/n$ corresponds to a symmetry operation of the lattice, lattice points A is moved to lattice point C . Similarly, rotation over $\theta = -2\pi/n$ maps lattice point B to D.

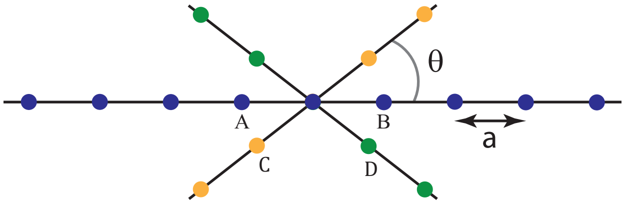

Figure 2: Line of lattice points (blue). Rotations over $\theta = +2\pi/n$ and $\theta = -2\pi/n$ result in orange and green lines, respectively.

Without calculating: what is the distance between **C** and **D** if the rotation corresponds to a symmetry operation of the lattice?

Answer: An integer number times the lattice spacing (1 point).

(d) (4 points) Calculate the restrictions this imposes on n.

Answer: The distance between **C** and **D** can be expressed in terms of the angle θ

$$2a\cos\theta = ma(1\text{ point})$$

This gives $\cos\theta = \frac{m}{2}$. Since $-1 \leq \cos\theta \leq 1$, $m = -2, -1, 0, 1, 2$ (1 point), yielding $\theta = 180^o, 120^o, 90^o, 60^o$, respectively (1 point). n is therefore restricted to 2,3,4, and 6 (1 point).

Question 4: **Condensed Matter Physics 2** . . . . *24 points*

Consider a 2D square lattice with a two-atom basis shown in the figure below.

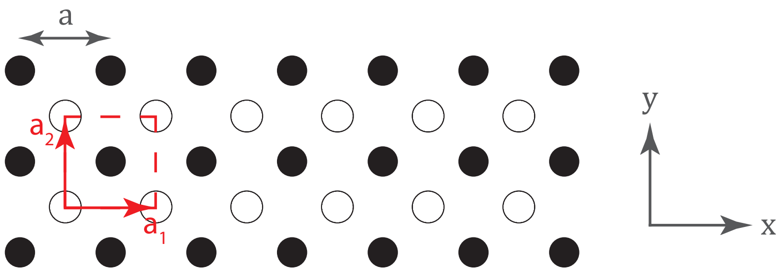

Figure 3: 2D square lattice. Atoms are indicated by black circles.

(a) (4 points) Indicate a unit cell AND the corresponding unit cell vectors in Figure 3.

Answer: See Figure 3. 2 points for a correct unit cell. 1 points per correct lattice vector.

(b) (4 points) In case each atom contributes one s-orbital that contributes to bonding. The simplest LCAO wave function for this system is given by

$$\psi_t(x) = \frac{1}{\sqrt{N}} \sum_n e^{i\boldsymbol{k}\boldsymbol{R}} \left[c_1\psi_1(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{\tau}_1) + c_2\psi_2(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{\tau}_2)\right] \tag{2}$$

Give the meaning of each term/factor in this expression for the wave function. **Answer:**

- $1/\sqrt{N}$: normalization factor (1 point).
- $\sum_n e^{i\boldsymbol{k}\boldsymbol{R}}$: phase factor. Allows the wave function to have different values at different unit cells (1 point).
- c_i: coefficient or weighing factor of each state within the unit cell (1 point).
- $\psi_i(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{\tau}_i)$: wave function centered on atom i that is located at position $\boldsymbol{\tau}_i$ in unit cell $\boldsymbol{R}$ (1 point).

(c) (1 point) How many electronic bands will you find when you perform a tight-binding calculation with this wave function?

Answer: 2 (1 point).

(d) (15 points) Show that the band structure for a square lattice with a two-atomic basis, as calculated using tight-binding, with nearest neighbor interactions only, is given by

$$E(\boldsymbol{k}) = \alpha \pm 4\beta \cos\left(\frac{\boldsymbol{k}\cdot\boldsymbol{a_1}}{2}\right)\cos\left(\frac{\boldsymbol{k}\cdot\boldsymbol{a_2}}{2}\right)$$

Use $\alpha_1 = \alpha_2$

Answer: The dispersion relation is found by calculating the expectation value of the energy (2 points). Since there are two orbitals per unit cell, this results in a 2×2 matrix:

$$\begin{vmatrix} \alpha - E & \beta\left(1 + e^{-i\boldsymbol{ka_1}} + e^{-i\boldsymbol{ka_2}} + e^{-i\boldsymbol{k}(\boldsymbol{a_1}+\boldsymbol{a_2})}\right) \\ \beta\left(1 + e^{i\boldsymbol{ka_1}} + e^{i\boldsymbol{ka_2}} + e^{i\boldsymbol{k}(\boldsymbol{a_1}+\boldsymbol{a_2})}\right) & \alpha - E \end{vmatrix} = 0$$

Total number of points for the correct matrix: 6. (2 points for 2×2 matrix, 2 points for having the correct number of terms on the off-diagonal (= number of nearest neighbors), and 2 points for correctness of the off-diagonal terms.

Evaluate the determinant

$$(\alpha - E)^2 - \beta^2\left(1 + e^{-i\boldsymbol{ka_1}} + e^{-i\boldsymbol{ka_2}} + e^{-i\boldsymbol{k}(\boldsymbol{a_1}+\boldsymbol{a_2})}\right)\left(1 + e^{i\boldsymbol{ka_1}} + e^{i\boldsymbol{ka_2}} + e^{i\boldsymbol{k}(\boldsymbol{a_1}+\boldsymbol{a_2})}\right) = 0$$

$$(\alpha - E)^2 - \beta^2(4 + 4\cos(\boldsymbol{ka_1}) + 4\cos(\boldsymbol{ka_1}) + 2\cos[k(\boldsymbol{a_1}+\boldsymbol{a_2})] + 2\cos[k(\boldsymbol{a_1}-\boldsymbol{a_2})]) = 0$$

$$(\alpha - E)^2 - \beta^2\left(4 + 4\cos(\boldsymbol{ka_1})\cos(\boldsymbol{ka_2}) + 4\cos(\boldsymbol{ka_1}) + 4\cos(\boldsymbol{ka_1})\right) = 0$$

$$\begin{aligned}(\alpha - E)^2 - 4\beta^2(1 + (2\cos^2(\boldsymbol{ka_1}/2) - 1)(2\cos^2(\boldsymbol{ka_2}/2) - 1) \\ + (2\cos^2(\boldsymbol{ka_1}/2) - 1) + (2\cos^2(\boldsymbol{ka_2}/2) - 1)) = 0\end{aligned}$$

$$(\alpha - E)^2 - 16\beta^2\cos^2\left(\frac{\boldsymbol{k}\cdot\boldsymbol{a_1}}{2}\right)\cos^2\left(\frac{\boldsymbol{k}\cdot\boldsymbol{a_2}}{2}\right) = 0$$

Rearranging the last expression directly gives the requested result (7 points for correct algebra).

Question 5: **Soft Condensed Matter** . . . . *8 points*

(a) (8 points) Structures with a significant degree of disorder are typically described using a radial distribution function, such as shown in Figure 4. Describe the origin of the different features seen in this plot.

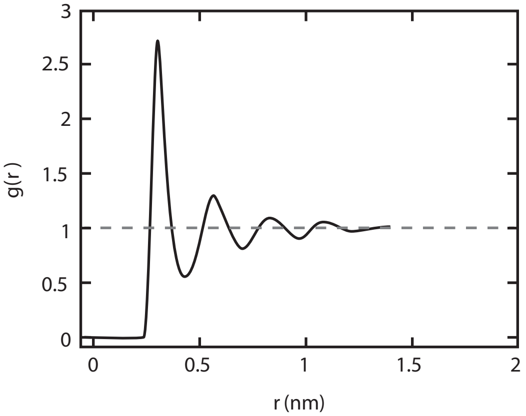

Figure 4: Radial distribution function.

Answer:

- **$g(r) = 0$ for very small r.**
  $g(r)$ represents the probability to find a particle at a distance r from another particle. For very small distances, the particles would overlap. The probability for this to happen is zero.
- **There is a pronounced maximum in $g(r)$ for the first coordination shell.**
  For short distances, the interparticle distances are correlated. Hence, nearest neighbor particles are most likely to be found at a distance that corresponds (approximately) to the minimum of the interparticle potential. This 'shell' of particles around the center particle is known as the first *coordination shell.* In case of a hard sphere model, the maximum would occur near $r = 2a$. The result of the correlation is that on this length scale the local density is much higher than the global density, causing $g(r) \gg 1$.
- **There are undulations in $g(r)$ for larger r.**
  Upon continuing past the first coordination shell, the probability first decreases before reaching a second maximum for the second coordination shell. This process is repeated several times. As the correlations between particle positions decrease with increasing r, the magnitude of the undulations in $g(r)$ become smaller with increasing r.
- **$g(r) \to 1$ for $r \to \infty$**
  Since the volume element ($dV = 4\pi\, r^2\, dr$) grows in size as r increases, the local

density at large values of r will eventually mimic that of the global density. Thus at large r, $g(r)$ tends to a value of unity, implying that the probability of finding a second particle center is no better or worse than the random odds associated with an average density of particles

(2 points for each correct answer.)