Utrecht University
Exam Structure of Matter
Tuesday, March 6th, 2018
Time: 13:30 - 16:30

Name and student number: ____________________

Good luck!

- Please pay attention to your hand-writing. If we cannot read your answers, we cannot award points.
- In your answers, do not immediately start with equations. Also draw conclusions from the calculations you have done.
- Calculators, graphical or otherwise, are not allowed.
- Please note that you can earn a maximum of 61 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:

$$\begin{aligned}
\cos(2a) &= 2\cos^2 a - 1 \\
\cos(a+b) &= \cos(a)\cos(b) - \sin(a)\sin(b) \\
\cos(a-b) &= \cos(a)\cos(b) + \sin(a)\sin(b) \\
e^{ik} + e^{-ik} &= 2\cos(k) \\
\int_{-\infty}^{\infty} f(x)\delta(x-x_0)\,dx &= f(x_0)
\end{aligned}$$

Question 1: **Atomic Physics** . . . . *10 points*

(a) (2 points) Give the electron configuration of Si ($Z = 14$)

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

(b) (2 points) Give the electron configuration of Ag ($Z = 47$)

Answer: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^9$

(c) (6 points) Electronegativity is a property of atoms that describes the tendency of an atom to attract electron density towards itself. An atom's electronegativity is affected by both its atomic number and the distance at which its valence electrons reside from the nucleus. The higher the associated electronegativity number, the more an element or compound attracts electrons towards it. Describe how the electronegativity changes when crossing a period of the periodic table, as well as how it changes when going down a group **AND** explain.

Answer: The further to the right in the periodic table, the higher the effective nuclear charge that the electrons in the valence shell experience (2 points). Hence, the electronegativity increases when crossing a period of the periodic table (1 point). As you go down a group in the periodic table, there are more and more 'core' electrons available. The more of these are available, the more efficient the shielding. Hence, the effective nuclear charge that the valence electrons experience becomes smaller as you go down a group (2 points). The electronegativity therefore decreases when going down a group (1 point).

Question 2: **Molecular Physics 1** . . . . *12 points*

Vision begins with the photoisomerization of retinal (one of the many forms of vitamin A). The reaction is shown in Figure 1 below. Upon adsorption of a photon, there is a rotation about one of the C-C double bonds. For the aficionados: When the 11-cis-retinal chromophore absorbs a photon it isomerizes from the 11-cis state to the all-trans state. In this question, you will explore how adsorption of a photon can lead to such an isomerization.

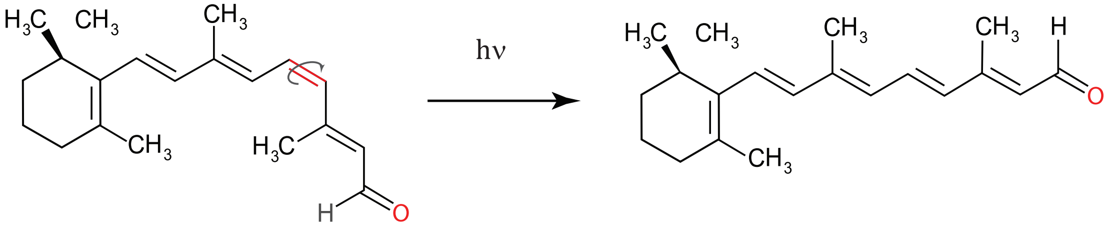

Figure 1: The first step in vision is a chemical reaction, the photoisomerization of retinal.

Consider the simplest model system with C-C double bonds: ethylene (C_2H_4). Rotation over the C-C double bond involves breaking the π-bond, which is energetically unfavorable. Consequently, C-C double bonds, i.e. C atoms bound by a σ and a π orbital are structurally rigid and for all intents and purposes rotations about such bonds do not occur at room temperature.

For ethylene (and retinal) to isomerize, the π-bond therefore has to be broken, such that part of the molecule can (freely) rotate about the remaining σ bond. Within the framework of Hückel calculations this implies a bond order of zero. The bond order between atoms i and j, is given by:

$$b = \sum_{k=1}^{K} n_k c_i^k c_j^k \tag{1}$$

n_k indicates the number of electrons in orbital k. The sum runs over all occupied orbitals. Assume that in your Hückel calculation you only have to take into account the double bond that undergoes isomerization.

(a) (5 points) Give the matrix corresponding to the simplified retinal system, compute the energies of the molecular orbitals **AND** draw the MO diagram.

Answer: The calculation is essentially a calculation on ethylene. The corresponding determinant is given by

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \tag{2}$$

(2 points). Hence, $E = (\alpha - E)^2 - \beta^2 = 0$. This gives $E_{\pm} = \alpha \pm \beta$ (1 point). This gives the following MO diagram

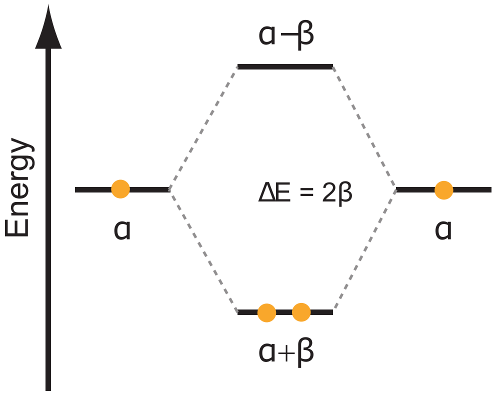

Figure 2: MO diagram of ethylene. 1 points for the two levels and correct energies, 1 point for a correct occupation of the levels.

(b) (2 points) What happens physically upon adsorption of a photon?

Answer: An electron is promoted from the HOMO to the LUMO level (2 points).

(c) (5 points) Calculate the π bond order in the ground and excited state of ethylene. Comment on the feasibility of isomerization.

Answer: First the values of the coefficients $c_{1,2}$ have to be calculated for both HOMO and LUMO. This can be done by inserting the eigenvalues found in the previous question in the matrix equation, which is given here for the sake of completeness

$$\begin{pmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{pmatrix} \times \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{3}$$

Together with the normalization requirement this gives for the HOMO $c_1 = c_2 = \frac{1}{\sqrt{2}}$ and for the LUMO $c_1 = \frac{1}{\sqrt{2}} = -c_2$ (2 points). We therefore find the following bond orders

- For the ground state: $b = 2 \times \frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}} = 1$
- For the excited state: $b = 1 \times \frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}} + 1 \times \frac{1}{\sqrt{2}}\frac{-1}{\sqrt{2}} = 0$

(2 points) Hence, upon adsorption of a photon the $\pi-$bond order is reduced from 1 to 0. Just the C-C σ-bond is left, over which the molecule can to first order rotate freely. In the excited state isomerization of retinal is expected to be possible (1 points)

Question 3: **Molecular Physics 2** . . . . *5 points*

(a) (2 points) Describe the concept of orbital hybridization.

Answer: Orbital hybridization of an atom describes the mixing of atomic orbitals into new so-called hybrid orbitals that have (nearly) the same symmetry as the local surrounding of the atom (2 points).

(b) (3 points) Consider the molecules shown in Figure 3. C, H and N atoms are indicated in black, white and blue, respectively. N has atomic number $Z = 7$. For each molecule, indicate if the N atom is hybridized, and if so, how. **Hint**: consider the number of valence electrons. All of these need to be accommodated.

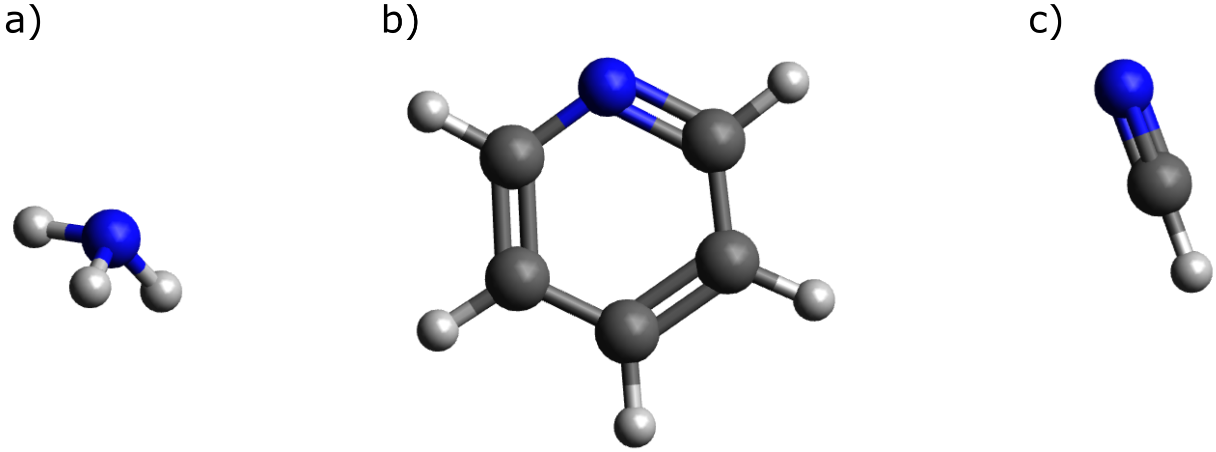

Figure 3: Three-dimensional form of 3 nitrogen containing molecules.

Answer: The nitrogen atoms in a,b, and c are sp^3,sp^2, and sp hybridized, respectively (1 point for each correct answer).

Question 4: **Condensed Matter Physics** . . . . *26 points*

You will perform a tight-binding calculation of crystalline Lithium. Only interactions with nearest neighbors have to be taken into account. Each atom contributes one $2s$ orbital and one electron.

Lithium forms crystals with a body centered cubic (bcc) Bravais lattice, see Figure 4. The primitive lattice vectors for a bcc lattice with lattice constant a are

$$\boldsymbol{a_1} = \frac{a}{2}\left(\hat{x} + \hat{y} - \hat{z}\right) \tag{4}$$

$$\boldsymbol{a_2} = \frac{a}{2}\left(-\hat{x} + \hat{y} + \hat{z}\right) \tag{5}$$

$$\boldsymbol{a_3} = \frac{a}{2}\left(\hat{x} - \hat{y} + \hat{z}\right) \tag{6}$$

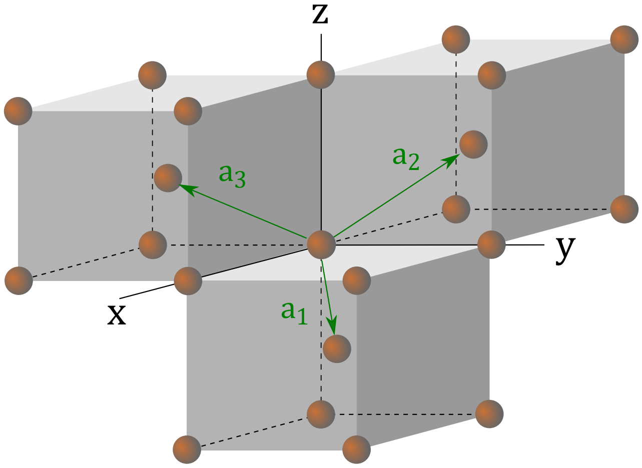

Figure 4: Part of a lithium crystal. Unit vectors defined above are indicated.

(a) (5 points) Determine the reciprocal space unit cell of Lithium

Answer: The reciprocal space lattice vectors can be calculated from either of the following equations:

$$\boldsymbol{b_i} \cdot \boldsymbol{a_j} = 2\pi\delta_{i,j} \tag{7}$$

or

$$\boldsymbol{b_1} = 2\pi\frac{\boldsymbol{a_2} \times \boldsymbol{a_3}}{\boldsymbol{a_1} \cdot (\boldsymbol{a_2} \times \boldsymbol{a_3})} \tag{8}$$

2 points for a correct equation. This gives

$$\begin{aligned}
\boldsymbol{b_1} &= 2\pi \frac{\boldsymbol{a_2} \times \boldsymbol{a_3}}{\boldsymbol{a_1} \cdot (\boldsymbol{a_2} \times \boldsymbol{a_3})} && (9)\\
&= 2\pi \frac{a/2(-1,1,1) \times a/2(1,-1,1)}{a/2(1,1,-1) \cdot (a/2(-1,1,1) \times a/2(1,-1,1))} && (10)\\
&= 2\pi \frac{a^2/4(2,2,0)}{a^3/2} && (11)\\
&= \frac{2\pi}{a}(1,1,0) && (12)
\end{aligned}$$

and similarly $\boldsymbol{b_2} = \frac{2\pi}{a}(0,1,1)$ and $\boldsymbol{b_3} = \frac{2\pi}{a}(1,0,1)$. 1 point for each correct answer.

(b) (2 points) The Wigner-Seitz cell in reciprocal space has a special name. What is that name?

Answer: Brillouin zone (2 points).

(c) (3 points) How many nearest neighbor atoms does each Lithium atom have? Indicate them in a drawing.

Answer: 8 (1 point). 2 points for the drawing.

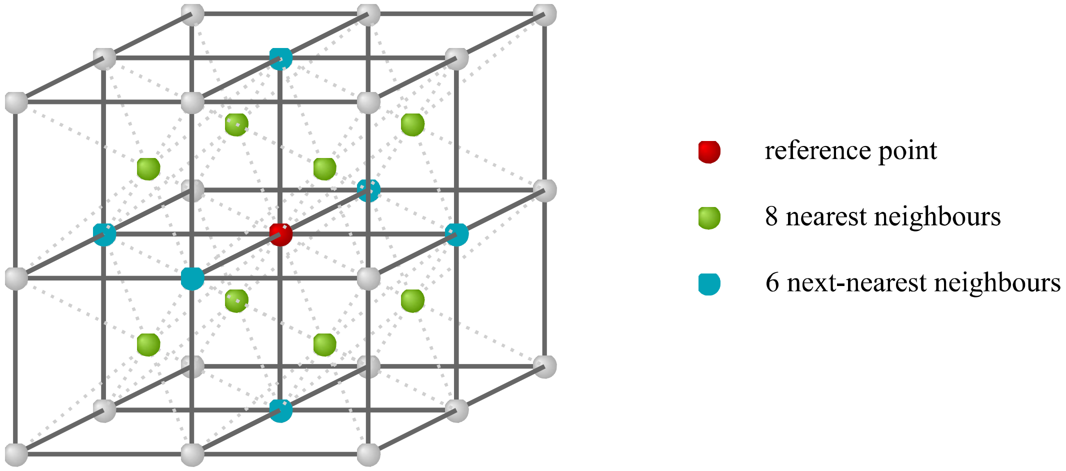

Figure 5: Nearest neighbors are indicated in green

(d) (12 points) Show that a nearest-neighbor tight-binding calculation results in the following dispersion relation

$$E(\boldsymbol{k}) = \alpha + 8\beta \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) \tag{13}$$

Answer: Evaluate the expectation value of the energy (2 points),

$$E(\boldsymbol{k}) = \sum_{\boldsymbol{R}} e^{i(\boldsymbol{R}-\boldsymbol{R}')\boldsymbol{k}} \int \psi_{\boldsymbol{R}'} | \hat{H} | \psi_{\boldsymbol{R}} \, dx \tag{14}$$

9 terms remain, 1 on-site term, and 8 for the interactions between nearest neighbors (2 points):

$$\begin{aligned} E(\boldsymbol{k}) = \alpha + \beta e^{i\boldsymbol{k}\boldsymbol{a_1}} + \beta e^{i\boldsymbol{k}\boldsymbol{a_2}} + \beta e^{i\boldsymbol{k}\boldsymbol{a_3}} + \beta e^{-i\boldsymbol{k}\boldsymbol{a_1}} + \beta e^{-i\boldsymbol{k}\boldsymbol{a_2}} + \beta e^{-i\boldsymbol{k}\boldsymbol{a_3}} + \\ \beta e^{i\boldsymbol{k}(\boldsymbol{a_1}+\boldsymbol{a_2}+\boldsymbol{a_3})} + \beta e^{-i\boldsymbol{k}(\boldsymbol{a_1}+\boldsymbol{a_2}+\boldsymbol{a_3})} \end{aligned} \tag{15}$$

3 points for the correct expression. Using the definitions of the primitive lattice vectors, (a_i), this can be written as

$$\begin{aligned} E(\boldsymbol{k}) = \alpha + \beta e^{ik_x a/2} e^{ik_y a/2} e^{-ik_z a/2} + \beta e^{-ik_x a/2} e^{ik_y a/2} e^{ik_z a/2} + \beta e^{ik_x a/2} e^{-ik_y a/2} e^{ik_z a/2} + \\ + \beta e^{-ik_x a/2} e^{-ik_y a/2} e^{ik_z a/2} + \beta e^{ik_x a/2} e^{-ik_y a/2} e^{-ik_z a/2} + \beta e^{-ik_x a/2} e^{ik_y a/2} e^{-ik_z a/2} + \\ + \beta e^{ik_x a/2} e^{ik_y a/2} e^{ik_z a/2} + \beta e^{-ik_x a/2} e^{-ik_y a/2} e^{-ik_z a/2} \end{aligned} \tag{16}$$

3 points. Use $e^x = \cos(x) + i\sin(x)$ and $e^{-x} = \cos(x) - i\sin(x)$. This gives

$$E(\boldsymbol{k}) = \alpha + 8\beta \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \tag{17}$$

To see this, focus on e.g. the last two terms in equation (16). The $i\sin(x)$ terms cancel, while the $\cos(x)$ terms add up. 2 points for the correct answer.

(e) (4 points) Given the dispersion relation, explain if lithium is a metal, semiconductor or insulator. Include the term *Fermi level* in your answer.

Answer: A Lithium atom has 1 electron in the $2s$ orbital. Hence, the band given by equation (14) is half full, i.e. the Fermi level is located in the middle of the band (2 points). Since there are empty states immediately above the Fermi level, lithium is a metal (2 points).

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

(a) (3 points) Describe the differences between a crystal, a quasicrystal and an amorphous material.

Answer: In a crystal, the atoms are arranged periodically. A crystal has translational and rotational symmetry (1 point). A quasicrystal only has rotational symmetry but no translational symmetry (1 point). In an amorphous material there is no long-range order (1 point).

(b) (2 points) The Lennard Jones potential which is used to approximate interatomic interactions is given in Equation 18.

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{18}$$

Give the names or briefly describe the phenomena which give rise to the two terms in Equation 18.

Answer: The first term (r^{-12}) describes the Pauli repulsion (1 point) The second term (r^{-6}) term represents the Van der Waals forces (1 point).

(c) (3 points) Figure 6 shows radial distribution functions for a system of Lennard Jones particles in different configurations. Describe the structures of the three different configurations and justify your answer with reference to the features of the g(r) in each case.

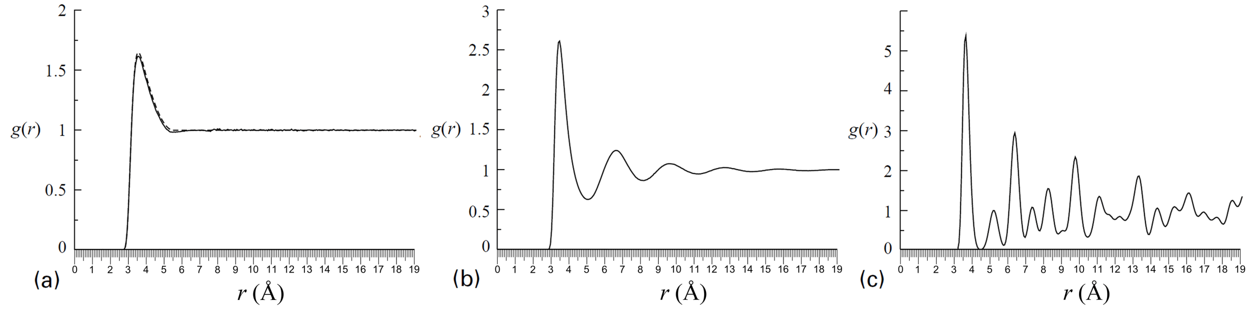

Figure 6: Radial distribution functions for Lennard Jones particles in various states.

Answer:

- (a) Shows particles in a gas phase. At low r, the probability of finding a particle is zero because particles cannot overlap. At distances slightly larger than the particle radius, the positions are correlated in the first coordination shell giving the peak. At larger distances, the particle positions are uncorrelated and the local density tends to the global density.

- (b) Shows particles in a liquid (or glass) phase. At low and high r, the g(r) behaves in the same way for the same reasons as described above. At intermediate distance, there are fluctuations in the g(r) corresponding to successive coordination shells, representing the short range correlations in the liquid phase.
- (c) Shows a crystalline phase. The long range order in the structure yields well defined peaks and troughs corresponding to the well defined positions of the particles on the lattice. At large r, the g(r) will either tend to the global density or fluctuate periodically about this value depending on the crystal structure (and its relation to the spherically averaged g(r)).