Utrecht University
Exam Structure of Matter
Monday, April 11th, 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 89 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** . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . *13 points*

(a) (2 points) Give the electron configuration of C ($Z = 6$)

(b) (2 points) Give the electron configuration of Ni ($Z = 28$)

(c) (4 points) Explain the variational theorem in words.

(d) (5 points) The radial parts of three wave functions of the hydrogen atom are plotted in Figure 1. Which orbitals are plotted? Explain your answer.

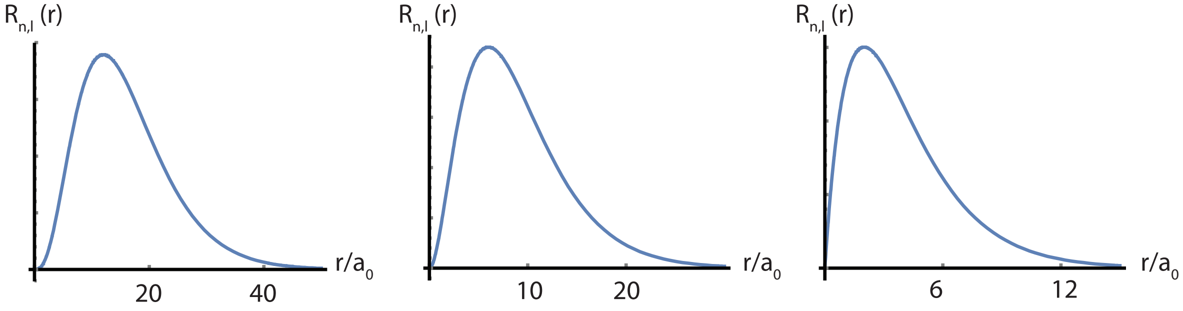

Figure 1: Radial part of three wave functions of the hydrogen atoms.

Question 2: **Molecular Physics 1** . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . *25 points*

Consider the ethyne molecule, $C_2H_2$, shown in Figure 2. The two carbon atoms are said to be *sp-hybridized*. The two C-H bonds are made by the interaction of C *sp*-orbitals with the H orbitals. The three C-C bonds are formed due to overlap of the *sp*-orbitals and the $2p_x$ and $2p_y$ orbitals, respectively.

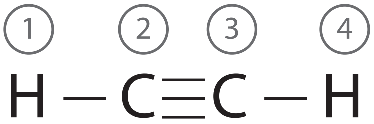

Figure 2: The ethyne molecule. Each line between two atoms indicates a covalent bond. The numbering of the atoms is indicated.

(a) (4 points) Which bonds in the ethyne molecule are $\sigma$-bonds and which bonds are $\pi$-bonds? Use a 3D-sketch to explain your answer.

(b) (3 points) Write down the simplest LCAO wave function for this molecule, taking into account the *sp*-hybridization. You may neglect the C 1*s* orbitals.

(c) (6 points) Explain that the tight-binding determinant of the ethyne molecule can be written as

$$\begin{vmatrix} \alpha_H - E & \beta_{CH} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_{CH} & \alpha_{sp} - E & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha_{sp} - E & 0 & 0 & 0 & \beta_{CC}^{sp} & 0 & 0 & 0 \\ 0 & 0 & 0 & \alpha_p - E & 0 & 0 & 0 & \beta_{CC}^{pp} & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha_p - E & 0 & 0 & 0 & \beta_{CC}^{pp} & 0 \\ 0 & 0 & 0 & 0 & 0 & \alpha_{sp} - E & 0 & 0 & 0 & \beta_{CH} \\ 0 & 0 & \beta_{CC}^{sp} & 0 & 0 & 0 & \alpha_{sp} - E & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta_{CC}^{pp} & 0 & 0 & 0 & \alpha_p - E & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_{CC}^{pp} & 0 & 0 & 0 & \alpha_p - E & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_{CH} & 0 & 0 & 0 & \alpha_H - E \end{vmatrix} = 0 \qquad (1)$$

where $\beta_{CC}^{sp}$, $\beta_{CC}^{pp}$ and $\beta_{CH}$ describe C-C bonds and C-H bonds, respectively. $\alpha_H$, $\alpha_{sp}$ and $\alpha_p$ are the on-site energies of the H atoms, the *sp*-hybrid orbital and *p*-orbitals, respectively.

(d) (7 points) Determine the eigenvalues of the matrix given in equation (1).

(e) (5 points) Using your answer to the previous question, sketch the molecular orbital diagram of the molecule. You do not need to include the single atoms. You may use the following approximations: $\beta_{CC}^{sp} = \beta_{CH} = -5eV$, $\beta_{CC}^{pp} = -3$ eV and $\alpha_s = \alpha_p = -5$ eV, $\alpha_H = -3$ eV. Include the electon occupation. If you have not solved the previous question, explain the general procedure to construct a molecular orbital diagram.

Question 3: **Condensed Matter Physics** ........................................ *40 points*

At pressures below 495 GPa, a crystal of atomic hydrogen atoms is unstable. Instead a crystal of hydrogen *molecules* is formed.

(a) (3 points) What would you have to calculate to demonstrate that the above statement is correct?

Consider an infinite ring of hydrogen atoms with spacing $a$, in which the hopping integral is $\beta$ and the on-site energy (i.e. $\alpha$) is zero. Each atom contributes one $1s$-orbital and one electron. As shown in class, the bandstructure for this system is $E(k) = 2\beta\cos(k)$. Half of the states in the band are occupied, implying that this unperturbed chain of hydrogen atoms is metallic. Suppose we now introduce a distortion of the chain as indicated in Figure 3.

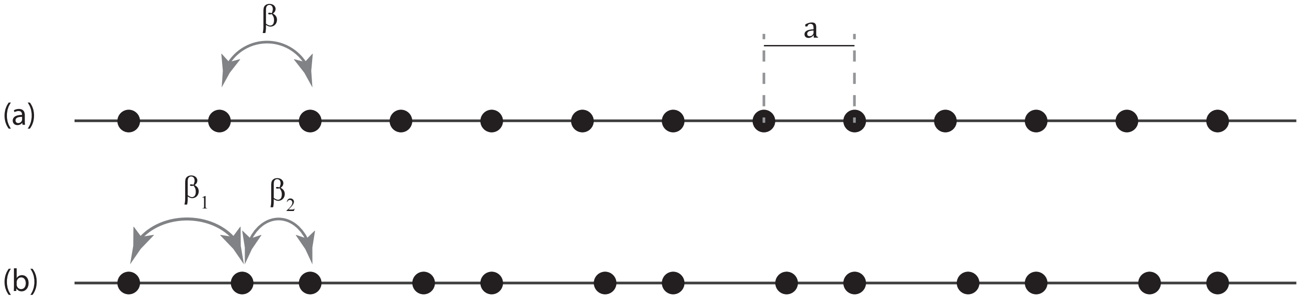

Figure 3: **(a)** A perfect infinite ring in which all nearest neighbor bond lengths are identical. The distance between nearest neighbors is $a$. **(b)** A distorted infinite ring in which every second atoms is moved to the right. Note that this resembles a collection of hydrogen molecules.

(b) (3 points) Indicate a unit cell and a lattice vector of the disorted chain. Give the lattice vector in terms of the lattice constant of the undistorted chain.

(c) (3 points) Do you expect the interactions between the nearest neighbors, indicated by $\beta_1$ and $\beta_2$ to be the same or different? Explain.

(d) (3 points) How does the unit cell of the two chains compare in reciprocal space?

(e) (12 points) The simplest LCAO wave function for the distorted chain is given by

$$\phi_t(x) = \frac{1}{\sqrt{N}} \sum_{n}^{N} e^{ink} \left[ c_1 \psi_1(x - n2a - \boldsymbol{r}_1) + c_2 \psi_2(x - n2a - \boldsymbol{r}_2) \right] \tag{2}$$

Using this wave function, show that a tight-binding calculation of the distorted chain, taking into account interactions between nearest neighbors only, results in the following energy bands:

$$E(k) = \pm\sqrt{(\beta_1 - \beta_2)^2 + 4\beta_1\beta_2 \cos^2(k)} \tag{3}$$

(f) (4 points) Sketch the band structure of the distorted chain.

(g) (9 points) In the remainder of this question you may assume that for the distorted chain $\beta_1 \approx 0$, $\beta_2 = 2\beta$, where $\beta$ is the interaction between neighbors in the perfect chain. Calculate the total energy for each chain and comment on the relative stability.

(h) (3 points) Do you expect a crystal of hydrogen molecules, i.e. the distorted chain, to be a metal or an insulator? Explain.

Question 4: **Soft Condensed Matter** . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . *11 points*

(a) (3 points) Consider the molecules shown in Figure (4). Which of these molecules could exhibit liquid crystal behavior? Explain your answer.

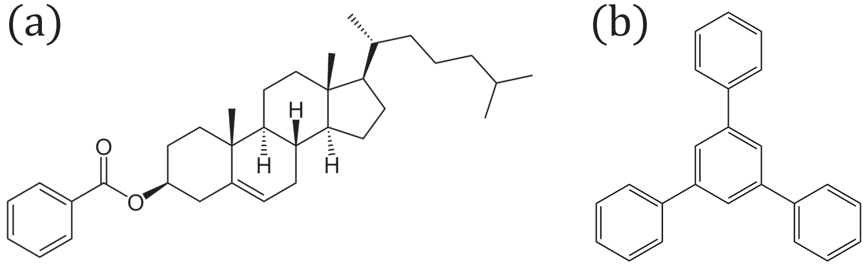

Figure 4: Chemical structure of two different types of molecules

Liquid crystals have been discussed in the reader using a schematic similar to that shown in Figure 5. In this question you will quantify the degree of order in a nematic phase.

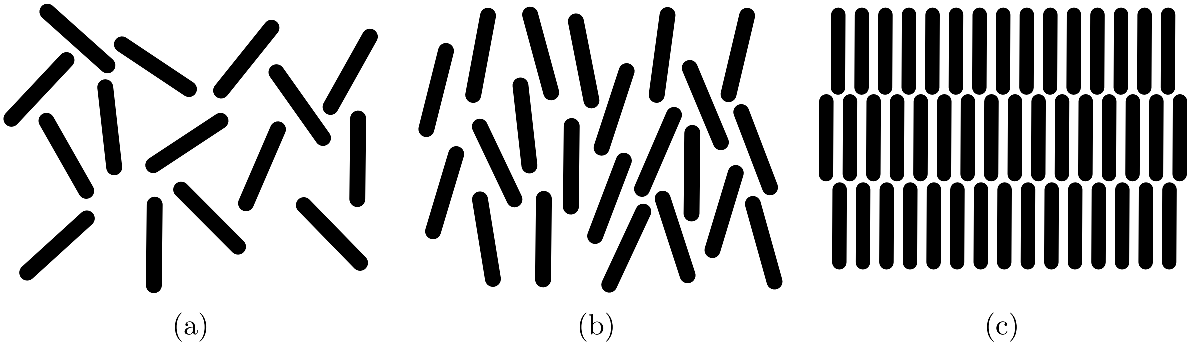
(a) (b) (c)

Figure 5: Liquid Crystal Phases: (a) Isotropic: No ordering. (b) Nematic: Some degree of orientational order but no translational order. (c) Crystal: full orientational and translational order.

(b) (8 points) In order to quantify the degree of orientational ordering in a system of rodlike particles (for example elongated organic molecules), it is helpful to think about the orientational distribution function $f(\theta)$. This function describes the probability of finding a particle orientated at an angle $\theta$ relative to the nematic director, $\hat{n}$. Due to the head/tail symmetry of a rodlike particle, the function need only be considered over the $\theta$ range $[-\pi/2, \pi/2]$.

The conventional descriptor for the order in a system is the scalar order parameter, $S$, which is defined as:

$$S = \frac{1}{2} < 3\cos^2\theta - 1 >= \frac{1}{2}\int (3\cos^2\theta - 1) f(\theta) dA. \tag{4}$$

The integration is carried out over half of the unit sphere, since each orientation corresponds to a point on this hemisphere. By considering the form of $S$ and the images of the phases in Figure 5, define the range of $S$ and identify the possible values it can take for the different phases.