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 ($Z = 6$)
Answer: $[\mathrm{C}] = 1s^2 2s^2 p^2$

(b) (2 points) Give the electron configuration of Ni ($Z = 28$)
Answer: $[\mathrm{Ni}] = 1s^2 2s^2 p^6 3s^2 3p^6 4s^2 3d^8$

(c) (4 points) Explain the variational theorem in words.
Answer: The expectation value of the energy (1 point) as calculated using some wave function (1 point) is always larger than the true ground state energy (2 points).

(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.

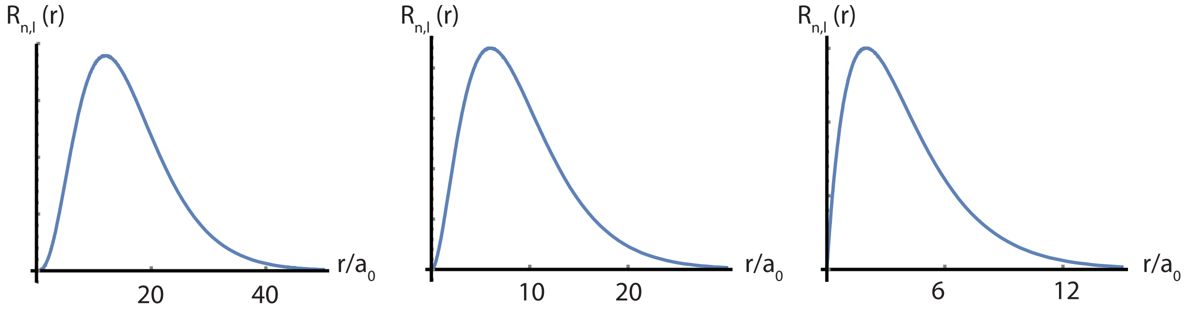


Figure 1: Radial part of three wave functions of the hydrogen atoms.

Answer: From left to right: $4f$, $3d$ and $2p$ (1 point for each correct answer). Each state has a radial node at the position of the nucleus. Hence, the wave functions cannot correspond to an s-orbital (1 point). There is just one radial node (at the origin), while the maximum is located at different distances from the nucleus. The states must therefore correspond to $4f$, $3d$ and $2p$, respectively (1 point).

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.

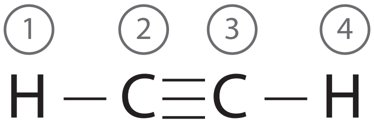


Figure 2: The ethyne molecule. Each line between two atoms indicates a covalent bond. The numbering of the atoms is indicated.

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

Answer: There is 1 $\sigma-$bond between the C atoms (1 point), as well as two $\pi-$bonds (1 point). The C-H bonds are $\sigma-$bonds (1 point). 1 Point for the figure.

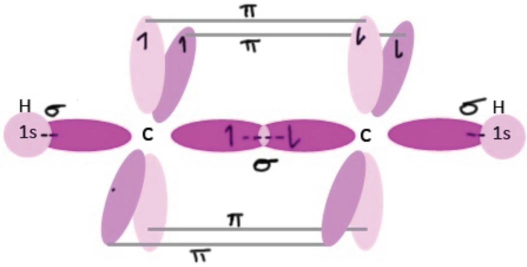


Figure 3: The ethyne molecule. Each line between two atoms indicates a covalent bond. The numbering of the atoms is indicated.

(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.

$$\psi = c_1H^1_{1s} + c_2\psi_1 + c_3\psi_2 + c_4C^2_{2px} + c_5C^2_{2py} + c_6\psi_3 + c_7\psi_4 + c_8C^3_{2px} + c_9C^3_{2py} + c_{10}H^4_{1s} \quad (1)$$

with $\psi_{1,2} = \frac{1}{\sqrt{2}}\left[C^2_{2s} \pm C^2_{2pz}\right]$ and $\psi_{3,4} = \frac{1}{\sqrt{2}}\left[C^2_{2s} \pm C^2_{2pz}\right]$. The superscripts denote the atom number as given in Figure 2. 2 points for the correct hybrid orbitals, 1 point for the rest.

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

$$\begin{vmatrix}
\alpha_H - E & \beta_{CH} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\beta_{CH} & \alpha_{sp} - E & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \alpha_{sp} - E & 0 & 0 & 0 & \beta_{CC}^{sp} & 0 & 0 & 0 \\
0 & 0 & 0 & \alpha_p - E & 0 & 0 & 0 & \beta_{CC}^{pp} & 0 & 0 \\
0 & 0 & 0 & 0 & \alpha_p - E & 0 & 0 & 0 & \beta_{CC}^{pp} & 0 \\
0 & 0 & 0 & 0 & 0 & \alpha_{sp} - E & 0 & 0 & 0 & \beta_{CH} \\
0 & 0 & \beta_{CC}^{sp} & 0 & 0 & 0 & \alpha_{sp} - E & 0 & 0 & 0 \\
0 & 0 & 0 & \beta_{CC}^{pp} & 0 & 0 & 0 & \alpha_p - E & 0 & 0 \\
0 & 0 & 0 & 0 & \beta_{CC}^{pp} & 0 & 0 & 0 & \alpha_p - E & 0 \\
0 & 0 & 0 & 0 & 0 & \beta_{CH} & 0 & 0 & 0 & \alpha_H - E
\end{vmatrix} = 0 \qquad (2)$$

where β_{CC}^{sp}, β_{CC}^{pp} and β_{CH} describe C-C bonds and C-H bonds, respectively. α_H, α_{sp} and α_p are the on-site energies of the H atoms, the sp-hybrid orbital and p-orbitals, respectively.

Answer: The LCAO wave function contains 10 functions, resulting in a 10 × 10 TB matrix (1 point). Because of symmetry, the interaction between the H $1s$ and C_{2p} states is zero (1 point). One of the $sp-$hybrid orbitals on each C atom point towards the other C, resulting in bonding interaction of β_{CC}^{sp}(1 point). The other $sp-$hybrid orbitals point towards the H atoms (β_{CH}, 1 point). The $2p$ states on each C atom form two $\pi-$bonds. Interaction strength: β_{CC}^{pp} (1 point). The on-site energy of the $sp-$hybrid orbitals is $\alpha_{sp} = (\alpha_{2s} + \alpha_{2p})/2$ (1 point).

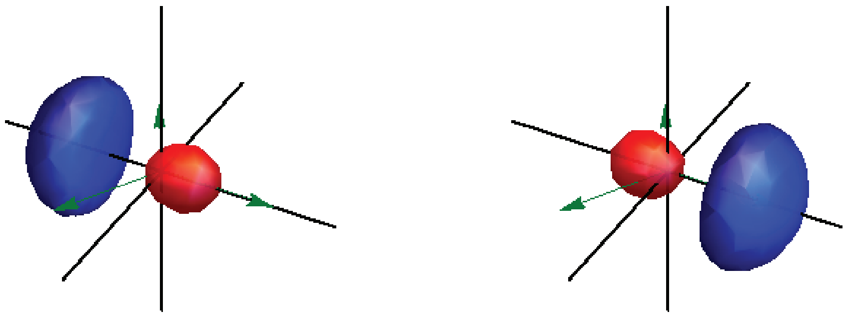


Figure 4: The two $sp-$hybrid orbitals.

(d) (7 points) Determine the eigenvalues of the matrix given in equation (2).

Answer: The determinant in equation (2) can be rearranged to block-diagonal form. The determinant reduces to 3 different 2 × 2 determinants (1 point for each correct determinant):

$$\begin{vmatrix} \alpha_H - E & \beta_{CH} \\ \beta_{CH} & \alpha_{sp} - E \end{vmatrix} = 0 \tag{3}$$

$$\begin{vmatrix} \alpha_{sp} - E & \beta_{CC}^{sp} \\ \beta_{CC}^{sp} & \alpha_{sp} - E \end{vmatrix} = 0 \tag{4}$$

$$\begin{vmatrix} \alpha_p - E & \beta_{CC}^{pp} \\ \beta_{CC}^{pp} & \alpha_p - E \end{vmatrix} = 0 \tag{5}$$

The determinants (3) and (5) occur twice. This can be rationalized from the fact that there are two C-H and two C-C $\pi-$bonds (1 point). The solutions are

- For equation (3)

$$E^2 - (\alpha_H + \alpha_{sp})E + \alpha_H\alpha_{sp} - \beta_{CH}^2 = 0$$

$$E = \frac{\alpha_H + \alpha_{sp}}{2} \pm \sqrt{\left(\frac{\alpha_H - \alpha_{sp}}{2}\right)^2 + \beta_{CH}^2} \tag{6}$$

- For equation (4)

$$(\alpha_{sp} - E)^2 - (\beta_{CC}^{sp})^2 = 0$$

$$E = \alpha_{sp} \pm \beta_{CC}^{sp} \tag{7}$$

- For equation (5)

$$(\alpha_p - E)^2 - (\beta_{CC}^{pp})^2 = 0$$

$$E = \alpha_p \pm \beta_{CC}^{pp} \tag{8}$$

1 point for each correct solution. Solutions (6) and (8) occur twice (because of degeneracy) (1 point).

(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.

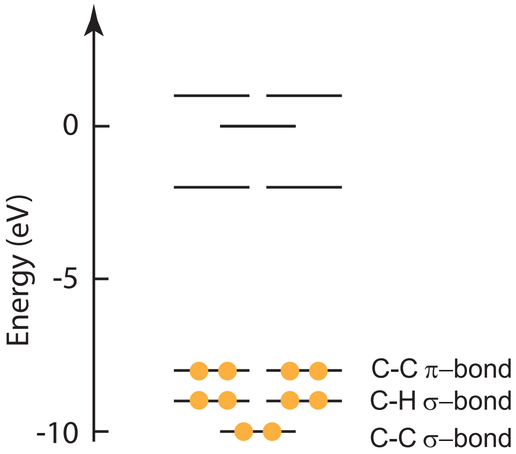


Figure 5: Molecular orbital diagram of ethyne. Orange circles represent electrons.

Answer: See Figure 5. 2 points for the correct order, 2 points for correctly indicating the degeneracies, 1 point for the correct occupation of the states.

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?

Answer: One should calculate the energy of the distorted and undistorted chains. The more stable configuration will have the lowest energy (3 points).

Consider an infinite ring of hydrogen atoms with spacing a, in which the hopping integral is β and the on-site energy (i.e. α) is zero. Each atom contributes one $1s$-orbital and one electron. As shown in class, the bandstructure for this system is $E(k) = 2\beta\cos(ka)$. 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 6.

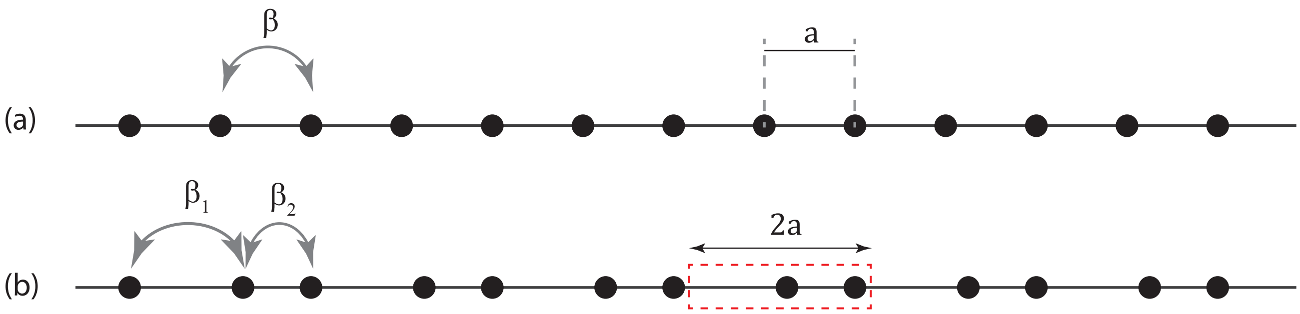


Figure 6: **(a)** A perfect infinite ring in which all nearest neighbor bond lengths are identical. The distance between nearest neighbors is a. **(b)** A distorted infinite ring in which every second atoms is moved to the right. Note that this resembles a collection of hydrogen molecules.

(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.

Answer: See the red box in Figure 6 (3 points). Other unit cells are possible.

(c) (3 points) Do you expect the interactions between the nearest neighbors, indicated by β_1 and β_2 to be the same or different? Explain.

Answer: β_1 and β_2 will be different (1 point). They represent the interaction between neighboring atoms, which is strongly distance dependent. In the distorted chain $\beta_1 < \beta_2$ (2 points).

(d) (3 points) How does the unit cell of the two chains compare in reciprocal space?
Answer: In real space, the unit cell of the distorted chain is twice as large as that of the undistorted chain. Hence, it is twice as small in reciprocal space (3 points).

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

$$\phi_t(x) = \frac{1}{\sqrt{N}} \sum_{n}^{N} e^{ink} \left[c_1 \psi_1(x - n2a - \vec{r}_1) + c_2 \psi_2(x - n2a - \vec{r}_2) \right] \tag{9}$$

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:

$$E(k) = \pm\sqrt{(\beta_1 - \beta_2)^2 + 4\beta_1\beta_2 \cos^2(ka)} \tag{10}$$

Answer: The dispersion relation can be found by evaluating the expectation value of the energy using the wave function given in equation (9) (2 point).

$$E(k) = \sum_{n=1} e^{i(n-n')k} \langle c_1\psi_1 + c_2\psi_2 | \hat{H} | c_1\psi_1 + c_2\psi_2 \rangle \tag{11}$$

This results in a matrix equation. In the limit of nearest-neighbor interactions only, this matrix becomes

$$\begin{vmatrix} \alpha - E & \beta_2 + \beta_1 e^{2inka} \\ \beta_2 + \beta_1 e^{-2inka} & \alpha - E \end{vmatrix} = 0 \tag{12}$$

(6 points for the correct matrix).

$$\begin{aligned} (\alpha - E)^2 - \left(\beta_2 + \beta_1 e^{2inka}\right)\left(\beta_2 + \beta_1 e^{-2inka}\right) &= 0 \\ (\alpha - E)^2 - \left(\beta_2^2 + \beta_1^2 + 2\beta_1\beta_2\cos(2ka)\right) &= 0 \end{aligned}$$

One finds:

$$\begin{aligned} E &= \alpha \pm \frac{1}{2}\sqrt{4\alpha^2 - 4(\alpha^2 - (\beta_2^2 + \beta_1^2 + 2\beta_1\beta_2\cos(2ka)))} \\ &= \alpha \pm \sqrt{\beta_2^2 + \beta_1^2 + 2\beta_1\beta_2\cos(2ka)} \\ &= \alpha \pm \sqrt{(\beta_1 - \beta_2)^2 + 4\beta_1\beta_2\cos^2(ka)} \end{aligned}$$

where in the last step we used the relation $\cos(2a) = 2\cos^2 a - 1$. (4 points for the correct answer.)

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

Answer: There are two bands (1 point) with cosine like dispersion, plus and minus branches (2 points). The edge of the first Brillouin zone is at $\pi/2a$ (1 point).

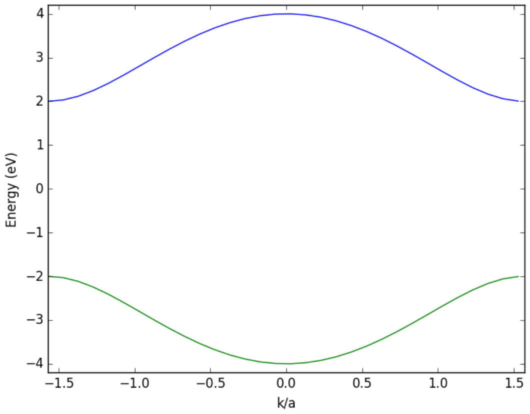


Figure 7: Band structure of the distorted chain of H atoms.

(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 β is the interaction between neighbors in the perfect chain. Calculate the total energy for each chain and comment on the relative stability.

Answer: In a tight-binding calculation, the total energy is the sum of the electron energies (2 points). Since the $k-$point spacing is small, one can simply integrate the dispersion relation over the range of occupied states. This gives

For the undistorted chain:

Half of the states of the single band are occupied, hence the $k-$vector of the Fermi level is $\pi/2a$ (2 points).

$$\begin{aligned} E_u &= \int_{-\pi/2}^{\pi/2} 2\beta\cos(ka)\,dk \\ &= \frac{2\beta}{a}\left[\sin(ka)\right]_{-\pi/2}^{\pi/2a} \\ &= \frac{4\beta}{a} \end{aligned}$$

1 point for the correct answer.

For the distorted chain:

The bottom band is completely occupied, hence the $k-$vector of the Fermi level is $\pi/2a$ (2 points).

$$\begin{aligned}
E_d &= \int_{-\pi/2}^{\pi/2} \sqrt{(\beta_1-\beta_2)^2+4\beta_1\beta_2\cos^2(ka)}\,dk \\
&= \int_{-\pi/2}^{\pi/2a} \sqrt{(\beta_2)^2}\,dk \\
&= \int_{-\pi/2}^{\pi/2a} 2\beta\,dk \\
&= \frac{2\pi\beta}{a}
\end{aligned}$$

1 point for the correct answer. We made use of the simplifications given in the question. Since β is negative, the distorted chain has a lower energy i.e. it is more stable (1 point).

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

Answer: An insulator (1 point). The system has only completely occupied and empty bands separated by a considerable band gap (2 points).

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

(a) (3 points) Consider the molecules shown in Figure (8). Which of these molecules could exhibit liquid crystal behavior? Explain your answer.

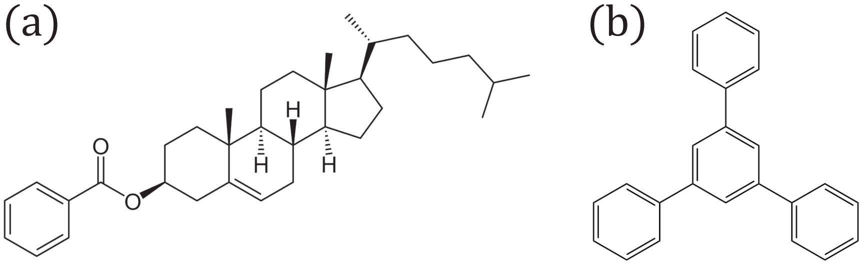
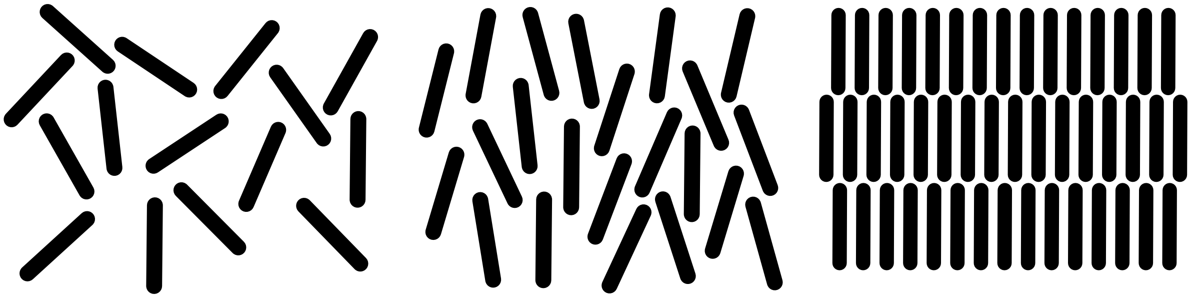


Figure 8: Chemical structure of two different types of molecules

Answer: The molecule shown in (a) (1 point). For a molecule to exhibit liquid crystal behavior, the molecule should have an anisotropic shape (2 points). Typically, they have a dipole moment or are easily polarizable.

Liquid crystals have been discussed in the reader using a schematic similar to that shown in Figure 9. In this question you will quantify the degree of order in a nematic phase.



(a) (b) (c)

Figure 9: 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 θ 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 θ range $[-\pi/2, \pi/2]$.

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

$$S = \frac{1}{2} < 3\cos^2\theta - 1 >= \frac{1}{2}\int (3\cos^2\theta - 1) f(\theta) dA. \tag{13}$$

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 9, define the range of S and identify the possible values it can take for the different phases.

Answer: Based on equation (13), S can vary from -0.5 to 1 (1 point). In a crystal, all particles are perfectly aligned, so $f(\theta) = \delta(\theta - \theta_0)$. In a liquid, the particles are all randomly oriented so $f(\theta)$ is a constant. For a liquid crystal, $f(\theta)$ is a narrow peak centred at 0. (1 point for each correct answer).

- $S < 0$ corresponds to a oblate nematic phase (extreme case is $S = -0.5$ which is a phase where the particle orientation vectors have no z component but random x and y components) which is not a commonly observed phase.
- $S = 0$ corresponds to the isotropic liquid:

$$\begin{aligned} S &= \frac{1}{2}\int (3\cos^2\theta - 1) f(\theta) dA && (14)\\ &= \frac{C}{2}\int_0^{2\pi}\int_0^{\pi/2} (3\cos^2\theta - 1)\sin\theta \, d\theta \, d\phi && (15)\\ &= \frac{C}{2}\int_0^1 (3u^2 - 1) du && (16)\\ &= \frac{C}{2}\left[u^3 - u\right]_0^1 && (17)\\ &= 0 && (18)\end{aligned}$$

  Where the substitution $u = \cos\theta$ has been made.
- $0 < S < 1$ corresponds to prolate nematic phases with increasing degrees of order.
- $S = 1$ corresponds to the crystal.

$$\begin{aligned} S &= \frac{1}{2}\int (3\cos^2\theta - 1) f(\theta) dA && (19)\\ &= \frac{1}{2}\int (3\cos^2\theta - 1)\delta(\theta - \theta_0) dA && (20)\\ &= \frac{1}{2}\left(3\cos^2(0) - 1\right) && (21)\\ &= 1 && (22)\end{aligned}$$

1 point for each correct answer.