Übungen - Molecular and Solid State Physics

Mid-Term Exam April 28, 2026

Name:	
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Instructor:	

Additonal information

Be: 4 protons

$\sum_1^n n = \frac{n(n+1)}{2}$; $\qquad \binom{n}{k} = \frac{n!}{k!\,(n-k)!}$

c = 3 x 10^{10} cm/s

h = 6.626 x10^{-34} Js

1 amu = 1.66x10^{-27} kg

Please note: if the total score is >50 points, it will be cut down to 50 points.

Question 1: Simple molecules (18 points)

Consider a Be_2 molecules. Beryllium (Be) has 4 protons, 4 electrons, and 5 neutrons.

a) Write down the **many-particle Hamiltonian** for Be_2, *without* using the Born-Oppenheimer approximation. **(30% of the points)**
Indicate what coordinates the wave function depends on.
How many terms are there in total, in the Hamiltonian?

$$\hat{H} = -\sum_{i=1}^{8} \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{\alpha=A,B} \frac{\hbar^2}{2M_{\mathrm{Be}}}\nabla_\alpha^2 - \sum_{i=1}^{8}\sum_{\alpha=A,B} \frac{4e^2}{4\pi\varepsilon_0\,|\mathbf{r}_i - \mathbf{R}_\alpha|} + \sum_{i<j}^{8} \frac{e^2}{4\pi\varepsilon_0\,|\mathbf{r}_i - \mathbf{r}_j|} + \frac{16e^2}{4\pi\varepsilon_0\,|\mathbf{R}_A - \mathbf{R}_B|}$$

coordinates the wave function depends: $\psi(\vec{R}_\alpha; \vec{r}_i)$

$\sum_i^8 \frac{\hbar}{2m_e}\nabla_i^2 = \mathbf{8};$ $\qquad \sum_{\alpha=A;B} \frac{\hbar}{2M_{Be}}\nabla_\alpha^2 = \mathbf{2};$

$\sum_i^8 \frac{1}{4\pi\epsilon_0}\sum_{\alpha=A;B}\frac{4e^2}{|\vec{r}_i-\vec{R}_\alpha|} = \mathbf{16};$

$\frac{1}{4\pi\epsilon_0}\sum_{i<j}^8 \frac{e^2}{|\vec{r}_i-\vec{r}_j|} = \binom{8}{2} = \mathbf{28}$ $\qquad ; \frac{16e^2}{4\pi\epsilon_0}\cdot\frac{1}{|\vec{R}_A-\vec{R}_B|} = \mathbf{1}$

tot = 55 terms

b) Write down the molecular-orbital Hamiltonian for a **single electron** in Be_2.
How many terms are in this Hamiltonian? **(20% of the points)**

$$\hat{h} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{4e^2}{4\pi\varepsilon_0|\mathbf{r} - \mathbf{R}_A|} - \frac{4e^2}{4\pi\varepsilon_0|\mathbf{r} - \mathbf{R}_B|}$$

tot = 3 terms

c) Calculate the total energy of the bonding and antibonding orbitals of Be_2 using: **(10% of the points)**
- overlap integral S: 0.43
- resonance integral β: -7.0 eV
- on-site energy ϵ: -9.3 eV

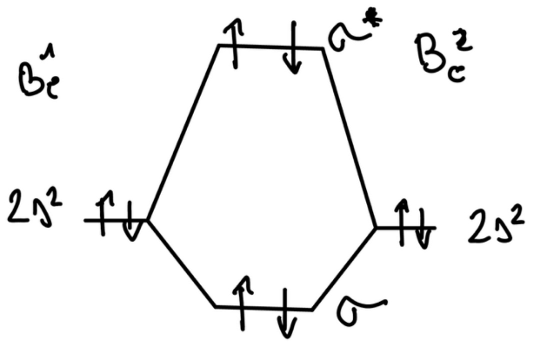
$$\boldsymbol{E_\sigma = \frac{\epsilon-\beta}{1+S} = -11.4\ eV} \qquad \boldsymbol{E_\sigma = \frac{\epsilon+\beta}{1-S} = -4\ eV}$$

d) A molecular orbital wavefunction (MO-wavefunction) can be constructed for the Hamiltonian in b) by a linear combination of atomic orbitals. Write down the **general Ansatz for the MO-wavefunction** using atomic orbitals. **(25% of the points)**

$\boldsymbol{\phi(\vec{r}) = \sum c_i AO_i(\vec{r})}$ **AO:= Atomic Orbitals**

e) Using a **minimal basis**, draw the molecular orbital scheme of Be_2 (a qualitative sketch of the orbital energies as function of the energy). In this approximation, would Be_2 be stable?

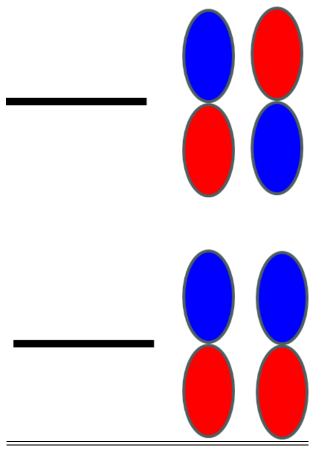
(15% of the points)



No, it would not be stable, the energy of Be atoms at infinite distance is lower that the Be_2, this is because the antibonding orbitals increases the energy of the system more than the binding ones decrease it.

Question 2: Large Molecules (18 points)

The figure below shows the two pi-orbitals of ethene (C_2H_4).

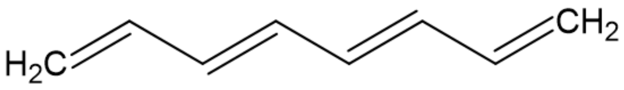


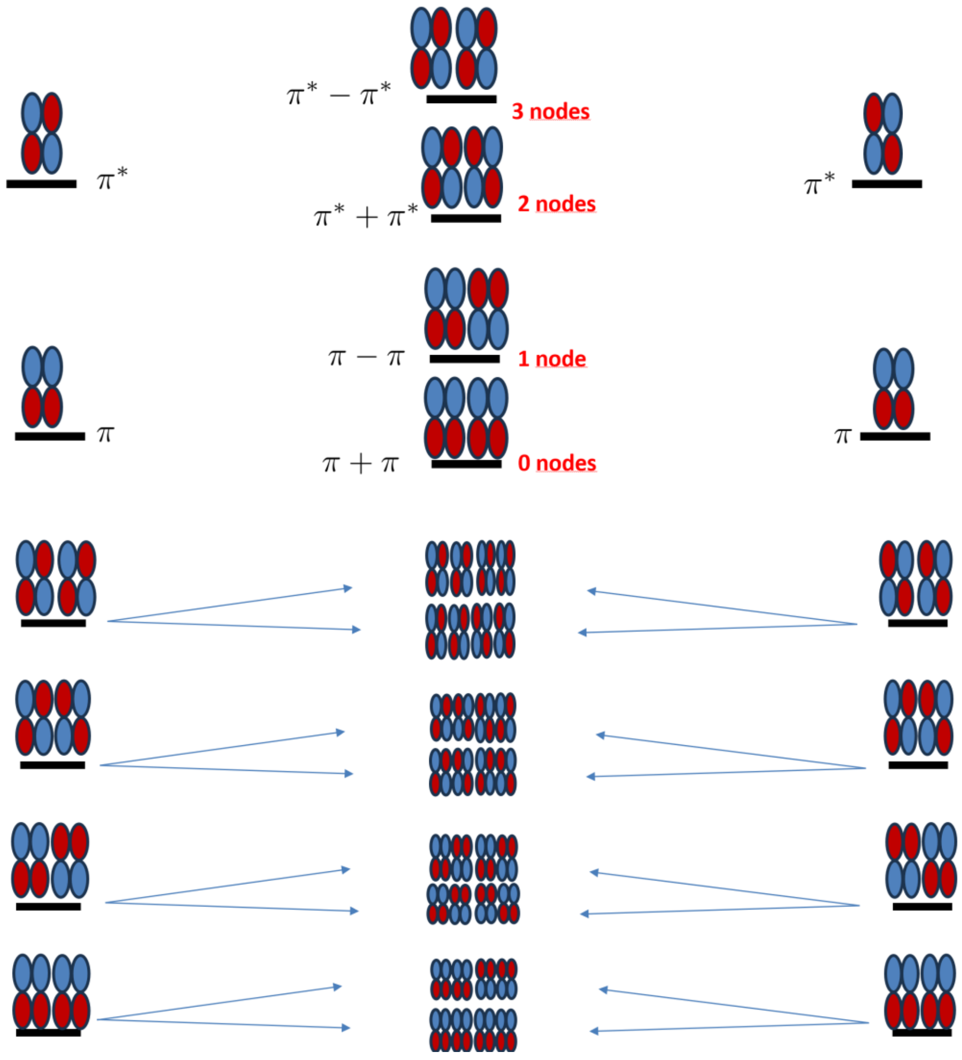
a) Indicate which one is the bonding and which one is the antibonding orbital, and explain why. **(30% of the points)**

Antibonding (up), Bonding (down). The upper is antibonding because there is a nodal plane btw the atoms, while the lower is binding because there is no nodal plane.

b) Using the ethene orbitals as basis, draw the molecular orbital scheme for 1,3,5-7-octatetrane (a conjugated organic molecule with **8** carbons). Here you can see the Lewis formula for octatetrane.

(40% of the points)





c) Write the the Hückel matrix for this molecule. How many molecular orbitals are obtained from solving the Hückel model for this molecule?

(30% of the points)

$$\begin{pmatrix}
\alpha - E & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\
\beta & \alpha - E & \beta & 0 & 0 & 0 & 0 & 0 \\
0 & \beta & \alpha - E & \beta & 0 & 0 & 0 & 0 \\
0 & 0 & \beta & \alpha - E & \beta & 0 & 0 & 0 \\
0 & 0 & 0 & \beta & \alpha - E & \beta & 0 & 0 \\
0 & 0 & 0 & 0 & \beta & \alpha - E & \beta & 0 \\
0 & 0 & 0 & 0 & 0 & \beta & \alpha - E & \beta \\
0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha - E
\end{pmatrix}$$

There are molecular 8 orbitals

Question 3: Vibrational and rotational levels of HCl^{35} (18 points).

Vibrational transition from ν_0 to ν_1 ~2886.00 cm^{-1}
Line spacing of the rotational spectrum: 21.20 cm^{-1}
Atomic masses: Cl^{35} = 34.96 amu, H = 1 amu, D= 2.014 amu

a) Using the rigid rotor model, calculate the moment of inertia (**I**), the equilibrium bond length (**R_0**) and the rotational constant (**B**).

(30% of the points)

$B = \frac{21.20}{2} = 10.60\ cm^{-1}$ $\qquad$ $I = \frac{\hbar^2}{2\tilde{B}} = \frac{\hbar^2}{2B \cdot hc} = \frac{h}{8\pi^2 Bc} = 2.64 \cdot 10^{-47} kg \cdot m^2$

$R_0 = \sqrt{I/\mu} = 1.28\ A$

b) Using the harmonic approximation, calculate the effective spring constant (**k_{eff}**) and the natural frequency (**ν**). **(25% of the points)**

$f = \nu \cdot c = 8.65 \cdot 10^{13} Hz$ $\qquad$ $k_{eff} = \mu \cdot (2\pi f)^2 = 481\ N/m$

c) If now I replace H with D (deuterium), assuming that the nature of the bond is unchanged, how would the effective spring constant (k_{eff}) and the natural frequency (**ν**) change?

(25% of the points)

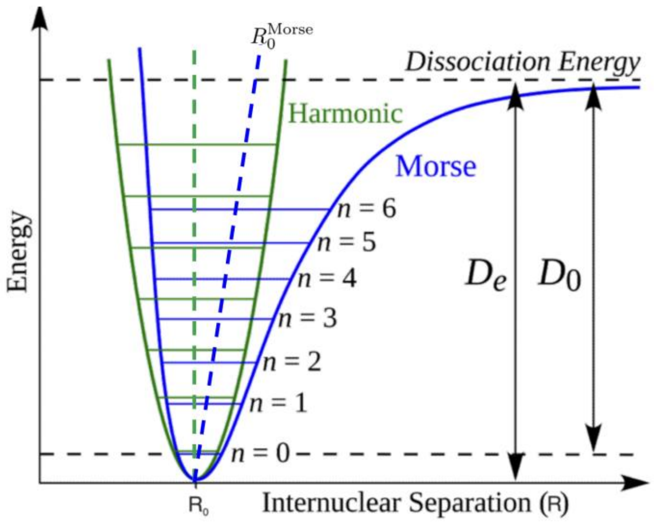
the effective spring constant would not change: it is defined by the bond potential, which in turn, is calculated using the Hamiltonian that not depend on the masses of the element involved.

The natural frequency instead changes: $\omega \propto \frac{1}{\sqrt{\mu}} \rightarrow \frac{\omega_D}{\omega_H} = \sqrt{\frac{\mu_H}{\mu_D}} = \sqrt{\frac{0.9722}{1.892}} = 0.717$

$$\nu_D = 0.717\nu_H = 6.18 \cdot 10^{13} Hz$$

d) Sketch the Morse potential for HCl, mark the equilibrium distance, and indicate what would be the energy needed for dissociating the HCl molecule.

(20% of the points)



The energy needed to dissociate the molecule is D_0