PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 11 EXERCISE CLASSES (25 - 29 March 2019)

The Sample Questions are designed to serve several purposes. They either review what you have learnt in previous courses, supplement our discussions in lectures, or closed related to the questions in an upcoming Problem Set. Students should be able to do the homework problems independently after attending the exercise class. **You should attend one exercise class session.** You are encouraged to think about (or work out) the sample questions before attending exercise class and ask the TA questions.

Progress: In Week 10, we discussed LCAO-MO for solving the electronic part of the molecular problem and the emergence of bonding. Based on MO's and Pauli exclusion principle, we can understand much about bonding in molecules. In addition to H_2^+ ion and H_2, we also used LCAO for "AB" molecules consisting of two different atoms. Filling in MO's following the Pauli Exclusion Principle gives the bond order. Some atoms, carbon in particular, needs the idea of hybridized orbitals (sp, sp^2, sp^3) in forming bonds with other atoms, giving the directional property of bonding and affecting the structure of important solids. These hybridized orbitals emerge rather naturally when we include several atomic states from carbon into LCAO. Another application of LCAO is an understanding of the delocalizing behavior of π-electrons in benzene (Hückel theory). We will then move on to vibrational and rotational motions and molecular spectrum.

SQ24 - Angle between sp^3 hybridized orbitals
SQ25 - H_3^+? Can two electrons bring three protons together?
SQ26 - Spring constant of a bond: Two-balls-and-a-spring and diatomic molecules

SQ24 **Angle between sp^3 hybridized orbitals** (Related to Problem 6.4)

The existence of CH_4 led us to the picture of sp^3 hybridization. It is also the key to understand the diamond structure and the crystal structure of semiconductors such as silicon and GaAs. Let's consider sp^3 hybridization in carbon. It involves the combination of one $2s$ atomic orbital and three $2p$ atomic orbitals in a carbon atom. The four sp^3 hybridized orbitals form a tetrahedron. We aim at finding the angle between two such hybridized orbitals. Formally, we should write

$$\begin{aligned}
\xi_1 &= a_1\psi_{2s} + b_1\psi_{2p_x} + c_1\psi_{2p_y} + d_1\psi_{2p_z} \\
\xi_2 &= a_2\psi_{2s} + b_2\psi_{2p_x} + c_2\psi_{2p_y} + d_2\psi_{2p_z} \\
\xi_3 &= a_3\psi_{2s} + b_3\psi_{2p_x} + c_3\psi_{2p_y} + d_3\psi_{2p_z} \\
\xi_4 &= a_4\psi_{2s} + b_4\psi_{2p_x} + c_4\psi_{2p_y} + d_4\psi_{2p_z} \qquad (1)
\end{aligned}$$

where ψ_{2s} and ψ_{2p} are normalized atomic orbitals belonging to the **same atom**. We know that $a_i = 1/\sqrt{4}$ for the reason that the s-orbital has equal share in ξ_i's. These ξ_i's should be normalized and orthogonal to each other. This is sufficient to fix the coefficients (after one takes a certain direction for one of the ξ's). In class notes, we wrote down a common form of Eq. (1).

TA: Here we aim at finding the angle between two hybridized orbitals. Without loss of generality, we take two of the four orbitals out and put them on the x-z plane with one pointing along the z-axis. These two hybridized orbitals can be taken as ξ_1 and ξ_2 and they have the form:

$$\xi_1 = \frac{1}{\sqrt{4}}\psi_{2s} + d_1\psi_{2p_z}$$

$$\xi_2 = \frac{1}{\sqrt{4}}\psi_{2s} + b_2\psi_{2p_x} + d_2\psi_{2p_z} \tag{2}$$

ξ_1 points at the z-direction. Using the concept that hybridized orbitals are normalized and mutually orthogonal, **determine** d_1, b_2, and d_2. Hence, **find** the angle between ξ_1 and ξ_2. This is the angle between two bonds in CH_4 and in diamond structure (solid state physics). The angle should be very familiar to students who did General Chemistry courses.

SQ25 **H_3^+? Can two electrons bring three protons together?**

H_3^+ is a very famous ion. For the astronomy fans, it is the most prevalent molecular ion in interstellar space. It is believed to be important in star formation. Can we understand why it can be there using the Hückel Theory, which is a form of LCAO. [In class notes, we discuss benzene using the same method.]

We take the structure of H_3^+ to be triangular in the form of $[\triangle]^+$, with a proton (hydrogen nucleus) at each vertex. There are two electrons wandering around, waiting to be filled into molecular orbitals formed by three hydrogen 1s atomic orbitals.

Thinking about linearly combining the hydrogen $1s$ centered at each vertex (and thinking about doing a variational calculation), a 3×3 determinant problem comes out. Following the Hückel Theory (and think like a physicist), the diagonal terms in the determinant are $\alpha - E$, with α being the $1s$ energy (called on-site energy with "on-site" referring to diagonal element H_{ii}). The off-diagonal elements are β with $\beta < 0$ for the non-zero H_{ij} between nearest neighboring centers. Obviously S_{ij} is set to zero for $i \neq j$.

Set up the determinant and **solve** for the energies of the three MOs. Hence, **fill in** the electrons and **find** the energy of the triangular $[\triangle]^+$. **Compare** this energy with the energy 2α corresponding to two separate hydrogen atoms plus a proton far far away and **argue** that binding into $[\triangle]^+$ lowers the energy.

[Remarks: H_3^+ is a famous MO problem. Pearson (J. Chem. Phys **16**, 502 (1948)) studied a linear structure $[H{-}H{-}H]^+$ and H_3 in the same approach. It will be an easy reading for you. A paper by Walsh *et al.* (J. Chem. Phys. **18**, 1070 (1950)) entitled *Molecular Orbitals for H_3^+* used a two-electron trial wavefunction. Interested students will appreciate how QM can be extended in different ways. A standard way to study a molecule or molecular ion is through its spectrum. The infrared spectrum of H_3^+ was studied by T. Oka in Chicago (Phys. Rev. Lett. **45**, 531 (1980)). Oka reviewed research on H_3^+ in his article *Chemistry, astronomy and physics of H_3^+* in Phil. Trans. R. Soc. A **370**, 4991 (2012). Professor MC Chan, an expert in quantum chemistry and spectroscopy in the Chemistry Department, had his PhD research supervised by Oka. Research interest on H_3^+ continues up to these days, mostly for its relevance to astronomy and astrophysics.]

SQ26 **Spring constant of a bond - two-balls-and-a-spring and diatomic molecules**

For two balls connected by a spring, the characteristic frequency (normal mode frequency) of the relative motion is $\omega = \sqrt{k/\mu}$, where k is the spring constant and μ is the reduced mass. Quantum mechanically, this becomes the angular frequency of a harmonic oscillator problem. Applying this idea to diatomic molecules, it is expected that something unusual will occur when EM wave of the right ω is incident upon the molecules.

For $^{75}Br^{19}F$, where the superscript indicates the number of nucleons (protons plus neutrons) in the nucleus and thus the mass, something unusual is observed at 380 cm^{-1}. Note that spectroscopists like to use the wave number. **Estimate the spring constant** of the bond. [Hint: For Br (and F), the mass can be taken as 75 amu (19 amu) (atomic mass unit), where 1 amu corresponds to 1.661×10^{-27} Kg.]