PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 13 EXERCISE CLASSES (27 - 31 April 2020)

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. **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.

Where are we? The electronic part of the molecular problem gives the bonding in compounds. LCAO-MO is an effective and physically transparent idea of understanding bonding. We discussed the *sp* hybrid orbitals. We will do the sp^2 and sp^3 hybrid orbitals and the Hückel theory of π-electrons.

After working out the electronic part, there is a curve $E_{el}(R)$ that shows a preferred bond length at $R = R_0$ such that $E_{el}(R_0)$ is a minimum. Near the minimum, the profile $E_{el}(R)$ looks like a parabola (harmonic oscillator) and the curvature gives the force (spring) constant K of the bond. The next step is to include the nuclei motions - rotational and vibrational motions. The rotational motion is related to a rigid 3D rotor (angular parts of a 3D problem) and the vibrational motion is related to a harmonic oscillator problem (radial part). These two problems were solved previously. We can copy and apply results to understand molecular spectrum. At the end, for molecular states in the lowest electronic state, the possible energies are

$$E^{(molecule)} = E_{el}(R_0) + (n + \frac{1}{2})\hbar\omega + \frac{\ell(\ell+1)\hbar^2}{2I} \tag{1}$$

where the second term gives the vibrational levels with $\omega = \sqrt{K/\mu}$ being the characteristic angular frequency of the bond (spring) with μ the reduced mass of the two atoms (diatomic molecule), and the third term gives the rotational levels with $I \approx \mu R_0^2$ being the moment of inertia related to the bond length. It is important to realize that the energy scales are very different. The difference of electronic terms (first term to the next curve of $E_{el}(R)$) is of the order several eV to 10 eV (visible to UV). The vibrational term (second term) is 1% of the first term and thus of the order 0.01 eV to 0.1 eV (IR). The rotational term (third term) is another 1%. Thus, it is of the order of 10^{-4} to 10^{-3} eV (microwave to far IR). Finally, transitions between the allowed molecular energy levels give molecular spectrum. There are selection rules. Details of molecular spectrum will be discussed in class.

SQ30 - sp^3 hybrid orbitals: Angle between sp^3 hybrid orbitals
SQ31 - Almost all molecules are in the lowest vibrational level at room temperature
SQ32 - Rotational Spectrum

SQ30 sp^3 hybridization: Angle between sp^3 hybrid orbitals

The existence of CH_4 led us to 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 one $2s$ atomic orbital and three $2p$ atomic orbitals in a carbon atom. The result is that the four sp^3 hybridized orbitals form a tetrahedron. We aim at finding the angle between two such hybridized orbitals.

Here, the logic follows that in *sp* hybridization. Formally, we write the four hybrid orbitals as

$$\xi_1 = a_1\psi_{2s} + b_1\psi_{2p_x} + c_1\psi_{2p_y} + d_1\psi_{2p_z}$$

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

where ψ_{2s} and ψ_{2p} are normalized atomic orbitals belonging to the same (carbon) atom. We know that $a_i = 1/\sqrt{4}$ for the reason that the s-orbital will not bias any of the hybrid orbitals. Then, these ξ_i's should be made **normalized and orthogonal to each other**. We have the freedom to assign in which direction one of these ξ's points at. After that, the normalized and orthogonal requirements are sufficient to fix the coefficients.

TA: Without loss of generality, 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:

$$
\begin{aligned}
\xi_1 &= \frac{1}{\sqrt{4}}\psi_{2s} + d_1\psi_{2p_z} \\
\xi_2 &= \frac{1}{\sqrt{4}}\psi_{2s} + b_2\psi_{2p_x} + d_2\psi_{2p_z} \qquad (3)
\end{aligned}
$$

Determine d_1, b_2, d_2 by requiring ξ_1 and ξ_2 to be normalized and orthogonal to each other. Hence, **find the angle** between ξ_1 and ξ_2 by (i) simply observing from the coefficients where ξ_2 points at; and (ii) by invoking the angular dependence in the wavefunctions ψ_{2p_x} and ψ_{2p_z} and finding the angle at which ξ_2 is a maximum (extremum).

The result is the angle between two bonds in CH_4 and in diamond structure (solid state physics). The angle should be very familiar to students taken General Chemistry courses.

SQ31 **Almost all diatomic molecules are in the lowest $n = 0$ vibrational state at room temperature - Thermal physics at work**

Look at Eq. (1). The first term is a constant referring to the minimum point of the curve $E_{el}(R)$ obtained by, say, LCAO. We focus on the second term for the vibrational (harmonic oscillator) levels here. For diatomic molecules, ω often falls into the infrared (IR) range of about $\hbar\omega \sim 0.5$ eV. Room temperature (300 K) corresponds to 1/40 eV. Here is a question making use of your thermal/statistical physics. Given a large collection of molecules in thermal equilibrium at 300 K, what is the fraction of them in $n = 0$, $n = 1$, $n = 2$,... levels.

(a) An important result in statistical physics is that the probability of finding a molecule to be in an energy ϵ_n is **proportional** to $\exp(-\epsilon_n)/kT$ and hence it is given by

$$
f_n = \frac{e^{-\epsilon_n/kT}}{\sum_{n=0}^{\infty} e^{-\epsilon_n/kT}} \qquad (4)
$$

where the denominator is called the partition function, which normalizes the probability. Applying the result to the second term (harmonic oscillator), **show that the probability of finding a molecule to be in the $n = 0$ vibrational ground state** is

$$
f_0 = 1 - e^{-\hbar\omega/kT} \qquad (5)
$$

(b) Spectroscopic data are often given in cm^{-1} (it is related to the wavelength and thus the photon frequency ν and thus angular frequency ω). Given that the characteristic frequency for $H^{35}Cl$ is 2990.94 cm^{-1}, i.e., there is an intense line observed right there for $H^{35}Cl$, **find the fraction of molecules in the $n = 0$ vibrational ground state**.

(c) Use the given characteristic frequency to **estimate the force constant** of $H^{35}Cl$.

SQ32 **Rotational Spectrum**

Given that almost all molecules are in the $n = 0$ vibrational level at room temperature and the characteristic frequency is 2990.94 cm^{-1} (that big) for $H^{35}Cl$, microwave (or far IR for some molecules) cannot excite them to $n = 1$ level. However, something does happen when microwave is incident upon the molecules. This is related to the third term in Eq. (1). The selection rule is $\Delta\ell = \pm 1$. Thus, molecules (all in $n = 0$) at $\ell = 0$ can absorb a photon to go to $\ell = 1$, and those in $\ell = 1$ to $\ell = 2$, and so on.

(a) **Show** that the third term in Eq. (1) would give a series of lines of equal spacing $\hbar^2/I$.

(b) It is observed that the microwave spectrum of $H^{35}Cl$ consists of equally spaced lines of separation of 6.350×10^{11} Hz. **Estimate the bond length** R_0 of $H^{35}Cl$.