PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 12 EXERCISE CLASSES (20 - 24 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.

Progress: In Week 11, we discussed the energetics of ionic bond, the difficulties in the full QM molecular problem, and the Born-Oppenheimer approximation. In Week 12, we will discuss LCAO in solving the electronic part of the simplest problem of H_2^+ molecular ion, and the result is the emergence of bonding and anti-bonding molecular orbitals (MO's). The LCAO-MO idea explains much of molecules (and solids), including σ and π bonds, hybridization, Hückel theory of delocalization of π-electrons in benzene (and in solids).

SQ28 - Overlap integral $S(R)$ for H_2^+ molecular ion: R-dependence and exact evaluation
SQ29 - Why do Diatomic molecules have only one vibrational model? General rules? Classical mechanics helps.

SQ28 **Normalizing ψ_+ LCAO wavefunction in H_2^+ ion and evaluating $S(R)$ for nuclei at a separation R.**

In the electronic part of H_2^+ molecular ion problem, **one electron** is under the influence of **two protons**. Each separation R of the two protons gives a separate QM problem. When considering the ground state of H_2^+, we would think by physical sense that "Ah! The electron is on A-side atomic ground state. But...the electron can also be on B-side. We couldn't tell. So...we form a linear superposition of these two possibilities." And this results in the following wavefunction, which is the essential of LCAO (Linear Combination of Atomic Orbitals) to describe molecular orbitals (MOs).

(a) **Any separation R.** We may write down the bonding MO as

$$\psi_+(\mathbf{r}) = C_A\psi_{1s,A} + C_B\psi_{1s,B} \tag{1}$$

and then do a variational calculation. Here $\psi_{1s,A}$ and $\psi_{1s,B}$ are the **normalized** 1s atomic orbitals for the nuclei located at $\mathbf{R}_A$ and $\mathbf{R}_B$, respectively. You may regard A to be on the left and B on the right (without loss of generality).

For H_2^+, the problem is easier. The symmetry of the problem tells us that what you will call the A-side would be another person's B-side (e.g. someone behind the white board) as both sides correspond to a hydrogen nucleus (proton). This symmetry appears in the form of $U(\mathbf{r})$ that the electron sees. By this symmetry argument, we expect $|C_A|^2 = |C_B|^2$ and hence the bonding MO (with $C_A = C_B = C_+$) can be written as

$$\psi_+(\mathbf{r}) = C_+(\psi_{1s,A} + \psi_{1s,B}) \tag{2}$$

without doing any variational calculations, where C_+ is a normalization constant to be determined. This argument is valid for any separation R, but **the normalization constant C_+ will depend on R**, as shown below.

TA: **Show that** the normalization constant C_+ is in general given by

$$C_+ = \frac{1}{\sqrt{2(1+S)}} \,, \tag{3}$$

where the number S is an integral given by

$$S(R) = \int d^3r \; \psi^*_{1s,A}(\mathbf{r})\psi_{1s,B}(\mathbf{r}) = \int d^3r \; \psi^*_{1s,B}(\mathbf{r})\psi_{1s,A}(\mathbf{r}) = \int d^3r \; \psi^*_{1s}(\mathbf{r}-\mathbf{R}_A)\psi_{1s}(\mathbf{r}-\mathbf{R}_B) \tag{4}$$

with the integrals taken over all space. The 1s wavefunction is real for hydrogen atom. This is the S_{ji} when we turn TISE in a matrix. The last term in Eq. (4) gives the explicit form of $S(R)$, with $R = |\mathbf{R}_A - \mathbf{R}_B|$. This integral is called the **Overlap Integral**. It should be clear that, since the two atomic orbitals are **centered at different nuclei**, S **is in general nonzero** and it is a function of R.

(b) **Draw schematically a diagram** with the two 1s atomic orbitals (exponentially decaying from a location x_A (just consider x-coordinates for simplicity) and another decaying from x_B). **Illustrate and explain** that for large separations $R = |x_A - x_B|$, the integral vanishes, i.e., $S = 0$. For smaller R where the two 1s orbitals come closer, **sketch the integrand** in S and **illustrate** that S is nonzero.

(c) The integral $S(R)$ can be evaluated exactly, but the mathematics is tedious. The answer (in atomic units) is simple though. It is

$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right), \tag{5}$$

where R is the inter-nuclear separation (measured in the Bohr radius a_0). **Plot** $S(R)$ as a function of R. **Evaluate** $S(R)$ at $R = 2$ (meaning twice the Bohr radius), say. [Note that $R = 2$ is close to the equilibrium separation in H_2^+.]

(d) **Show** the other (odd) linear combination

$$\psi_-(\mathbf{r}) = C_-(\psi_{1s,A} - \psi_{1s,B}) \tag{6}$$

has a different normalization constant C_-.

(e) **This part is OPTION for exam purposes. It is only for the TA to show off. Evaluate the integral** $S(R)$. Try to use a method that is easier for students to follow. This is meant to illustrate that H_2^+ ion is simple enough for LCAO integrals to be calculated exactly.

[Remark: The same method of evaluating $S(R)$ can be applied to evaluate the other two integrals $J(R)$ and $K(R)$ in the LCAO-MO calculation for H_2^+, as given in Appendix A (optional) of class notes.]

SQ29 **Why do diatomic molecules have only one vibrational mode? General rules? Classical Mechanics helps.**

(a) There are many empirical rules for chemistry students to remember. One of them is the "$3N-5$" rule for a **linear molecule**. What does it say? It says that for a molecule making consisting of N **atoms** and the molecule is **linear in shape like a rod**, there are $(3N-5)$ vibration normal modes. [Recall in classical mechanics, you did the vibrational normal modes problem with balls connected by springs.] A diatomic molecule is certainly linear in shape, like a dumbbell with atom A and atom B at the two ends.

TA: For a diatomic molecule, $N = 2$ and therefore there are 6 degrees of freedom (each atom has 3 coordinates), **explain what those "5" are about** and that the only remaining vibrational mode has the normal mode (angular) frequency given by $\omega = \sqrt{k/\mu}$, where k is the spring constant and μ is the reduced mass.

TA: Hence, **explain** why there are in general $(3N-5)$ vibrational modes after taking care of the center-of-mass and rotational degrees of freedom **for a linear molecule with N atoms**.

(b) The quantum mechanics of the vibrational motion in a diatomic molecule is therefore that of a harmonic oscillator of angular frequency ω. It is expect that something unusual will occur when EM wave of the right ω is incident upon the molecule. For the molecule $^{75}\mathrm{Br}^{19}\mathrm{F}$, 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.]

(c) The famous or now infamous molecule CO_2 (CO_2 is blamed for its impact on climate, but it is just a molecule) is a **linear molecule**. So there are 4 vibrational modes. **Google** them and **sketch** the 4 vibrational modes. [Note: The point here is NOT to solve for the normal modes (although classical mechanics balls-and-springs can give the answers), but illustrate why there are 4 modes and what they are.]

(d) There is also the "$3N-6$" rule (so many rules) for non-linear molecules. **Explain why** there are $(3N-6)$ vibrational modes after taking care of the CM and rotational motions.

(e) The three atoms in a water molecule do not line up linearly, but extended an angle between H-O-H. **Google** the vibrational modes of a H_2O molecule and **sketch** the 3 vibrational modes.

[Remarks: The topics of degrees of freedom, CM and relative motions, normal modes and oscillators are typical in classical mechanics courses. I hope that you understand why they are there and that they are useful in understanding QM of molecules, greenhouse gases, and climate change.]