PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 10 EXERCISE CLASSES (18 - 22 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 9, we discussed the energetics of ionic bond, the full QM molecular problem, Born-Oppenheimer approximation, 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).

SQ22 - Overlap integral $S(R)$ for H_2^+ molecular ion: R-dependence and exact evaluation
SQ23 - LCAO for atomic orbitals from two atoms differ much in energy

SQ22 **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 constitutes a separate QM problem. When considering the ground state of H_2^+, by physical sense we would think "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)!

(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 a 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.

For H_2^+, the problem is easier. The symmetry of the problem informs 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 comes from the form of $U(\mathbf{r})$ of what the electron sees. Thus, simply by symmetry argument, we expect $C_A = C_B$ (more formally $|C_A|^2 = |C_B|^2$) and hence the bonding MO can be written as

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

where C_+ is a normalization constant to be determined. This argument is valid regardless of the 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. [Note that hydrogen 1s state has real wavefunction.] This is the S_{ji} in turning TISE into a big matrix. The last term gives the long form of what $S(R)$ is about, with $R = |\mathbf{R}_A - \mathbf{R}_B|$. This integral is called the **Overlap Integral**. **Point out clearly** 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 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 $S = 0$. Similarly, for smaller R where the two 1s orbitals come closer, **sketch the integrand** in S and **illustrate** that S is nonzero.

(c) It turns out that the integral $S(R)$ can be evaluated exactly. Although the mathematics is tedious, the answer (in atomic units) is simple. It is

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

where R is the inter-nuclear separation (in units of 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) **This part is optional 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.

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

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

has a different normalization constant C_-.

[Remark: The same method of evaluating $S(R)$ can be applied to evaluate the other two integrals $J(R)$ and $K(R)$ in the discussion of LCAO-MO.]

SQ23 **LCAO for atomic orbitals from two atoms differ much in energy - ionic character of bonding - Think like a physicist**

This SQ is a sketchy and qualitative way to think about LCAO and its results. The point is to illustrate that simply 2×2 matrix mathematics can do a lot of things (c.f. Problem Set 1).

Hydrogen 1s atomic orbital has an energy of $E_{H,1s} = -13.6$ eV. Fluorine 2p atomic orbital has an energy of $E_{F,2p} = -18.7$ eV. The point is that they are off by a big energy difference of ~ 5 eV.

Let's consider a hydrogen atom and a fluorine atom come together to form HF. [**Remark: HF is a highly dangerous compound when it meets moisture. It will lead to**

blindness and it will eat into your bone! So it is safer to study its quantum mechanics than using it.] As they come closer, electrons see the potential energy functions of the two nuclei instead of one. In any case, we have a Hamiltonian $\hat{H}$. Now we want to set up schematically LCAO to consider the formation of molecular orbitals. A sensible minimal choice is to invoke hydrogen's 1s (one electron is there ready for bonding) and one 2p-state from fluorine (there is one 2p-state with a lonely electron waiting to form bond). It doesn't matter which 2p-state it is. It is because when two atoms form a bond, there is a special direction corresponding to the line joining the two nuclei. We can call this line (direction) whatever we like. If we call it the z-direction, then it is $2\mathrm{p}_z$ that matters and there is a lone electron in there ready for bonding. **So the situation becomes one electron is hydrogen 1s and one electron in fluorine 2p and they come together to form a bond.** Now, we can imagine that we form a linear combination

$$\psi = C_H\, \psi_{H,1s} + C_F\, \psi_{F,2p} \tag{7}$$

and use it as a trial wavefunction for a variational calculation. The end result is a 2×2 matrix equation of the form (sketchy here, but the physics is right)

$$\begin{pmatrix} E_{H,1s} & \Delta \\ \Delta^* & E_{F,2p} \end{pmatrix} \begin{pmatrix} c_H \\ c_F \end{pmatrix} = E \begin{pmatrix} c_H \\ c_F \end{pmatrix} \tag{8}$$

As the difference $(E_{H,1s} - E_{F,2p}) \approx 5$ eV, it is usually much bigger than $|\Delta|$. Eq. (8) is the equation that should come to an educated mind when two atoms come together to form a bond.

Solve for the two molecular orbitals. In particular, **show** that the bonding orbital (the one of lower energy) is dominated by Fluorine (i.e. Fluorine in character), while the anti-bonding molecular orbital (the one of higher energy) is dominated by hydrogen (i.e., hydrogen in character). [Recall: For matrix of the form in Eq. (8), "*The lower energy state pushes the higher one higher, and the higher energy state pushes the lower one lower*".]

As there are two electrons waiting to form bond, they go into the bonding state. **Show that** forming HF could indeed lower the energy. **Discuss** that the resulting state has a strong ionic character with the electrons having a heavy weighting to be on the fluorine side, thus forming what is called a F^- ion.

[Remark: For a 1D analogy, it is a shallow well and a deeper well come together for a molecule.]