PHYS3022 Applied Quantum Mechanics Problem Set 6 Due: 2 May 2020 (Saturday). "T+2 = 4 May 2020"

To submit your homework, **email your work** *to* **cuhkphys3022@gmail.com by 23:00 on the due date**. *TA will send you a reply confirming receipt of your work.*

Please work out the steps of the calculations in detail. Discussions among students are highly encouraged, yet it is expected that we do your homework independently.

6.0 **Reading Assignment.** For atom-light interaction, we discussed (stimulated) absorption, stimulated emission and spontaneous emission within the electric dipole mechanism, based on the time-dependent perturbation theory. We focused on the results on transition probabilities (rates), selection rules, the frequency must be right, Einstein's A and B coefficients, spontaneous emission, life time of excited states, and the ideas behind 3-level and 4-level lasers. Chapters in *Modern Physics* (e.g. by Taylor, Zafiratos, Dubson; and by Harris) give the big picture and physical ideas. The discussions in *Introduction to Quantum Mechanics* by Griffiths and *An Introduction to Theory and Applications of Quantum Mechanics* by Yariv are more technical. The coverage in atomic physics and transitions are sufficient to take you through serious studies on molecular and solid state physics.

We started to discuss the Physics of Molecules. The first part introduces the general QM problem of a molecule and the very clever Born-Oppenheimer approximation, which separates the molecular QM problem into two parts. The electronic part takes the nuclei as fixed (in principle should try different nuclei separations). The results include a preferred separation (bond length) and the the electronic wavefunction provides the chemical bond, which in turn gives the spring that models a bond about which the nuclei vibrate and rotate. The electronic part is usually handled by LCAO (linear combination of atomic orbitals). See the chapter on molecules in *Modern Physics* (e.g. by Taylor, Zafiratos, Dubson; and by Harris) for physics contents. We treated the QM in LCAO more completely. The discussion on MO follows that in *Physical Chemistry* by McQuarrie and *Quantum Chemistry and Spectrocopy* by Engel.

6.1 The form of $|a_2(t)|^2$ for transitions from state 1 to a group of final states

Background: In class, we obtained the following expression for the probability $|a_2(t)|^2$ of finding an atom in state 2 given that it was initially in an initial state 1, when a z-polarized incident EM waves, i.e., with $\vec{\mathcal{E}}_0 = \mathcal{E}_0 \hat{z}$, interact with the atom:

$$\begin{aligned} |a_2(t)|^2 &= e^2 \mathcal{E}_0^2 \, |z_{21}|^2 \, \frac{\sin^2[\frac{1}{2\hbar}(E_2 - E_1 - \hbar\omega)t]}{(E_2 - E_1 - \hbar\omega)^2} \\ &= \frac{e^2 \mathcal{E}_0^2}{\hbar^2} \, |z_{21}|^2 \, \frac{\sin^2[\frac{1}{2}(\omega_{21} - \omega)t]}{(\omega_{21} - \omega)^2} \end{aligned} \tag{1}$$

where $\omega_{21} = (E_2 - E_1)/\hbar$ is set by the energy difference between the initial state "1" and final state "2". Eq. (1) works for **monochromatic light** of angular frequency ω polarized in the $\hat{z}$-direction for a transition **from one initial state "1" to one final state "2"**. It is the starting point for deriving several other results.

One thing we did in class notes was the case of a **non-monochromatic light source** with a spread in the angular frequencies. In that case, we summed up their contributions to $|a_2(t)|^2$ and found

$$|a_2(t)|^2 = \frac{\pi e^2}{\epsilon_0 \hbar^2} |z_{21}|^2 \, t \, U(\omega_{21}) \tag{2}$$

and hence the transition probability per unit time (rate) per atom as

$$\lambda_{1\to 2} = \frac{\pi e^2}{\epsilon_0 \hbar^2} |z_{21}|^2 \, U(\omega_{21}) \tag{3}$$

where $U(\omega_{21})$ is the energy density of the incident energy right at the frequency ω_{21} defined by $(E_2 - E_1)/\hbar$. In going from Eq. (1) to Eq. (2), we looked at the time-dependent function in Eq. (1) as a function of ω for a fixed ω_{21} (i.e. given two states). The factor in front of $U(\omega_{21})$ in Eq. (3) is related to Einstein's B coefficient.

Your Action: Let's start from Eq. (1) again. We consider the case of a **monochromatic incident light** (single frequency) at ω with energy density $U(\omega)$. In many real systems, it so happens that starting from **an initial state** "1", the **transitions can go to a group of final states**. This will be the case of many degenerate final states. This happens readily in a solid. This is the physical scenario for you to work out here.

In this case, the time-dependent function in Eq. (1) can be regarded as a function of ω_{21} at fixed ω (and time t). Make a sketch of that function as a function of ω_{21}. The physical scenario under consideration implies that there is a spread in ω_{21} among the possible final states. There is a function called the **density of state** $g(\omega_{21})$ with $g(\omega_{21})d\omega_{21}$ giving the number of states with the quantity $(E_2 - E_1)/\hbar$ falling within the interval ω_{21} to $\omega_{21} + d\omega_{21}$. By summing up the contributions from possible transitions (possible final states and many of them), **derive** an expression for $|a_2(t)|^2$ and **show** that the answer is linear in time t. Hence, **obtain** an expression for $\lambda_{1\to group\ of\ states}$ and **show** that the answer picks up $g(\omega)$ (i.e., the number of states with $(E_2 - E_1)/\hbar$ right at the incident frequency $\hbar\omega$. [Remark: The answer is another popular form of what is called the Fermi Golden rule.]

6.2 Selection rule of transitions between harmonic oscillator states - Molecular vibrational states

Within the electric dipole mechanism, the $\vec{E}$-field in the EM waves interacts with the electric dipole moment $\vec{\mu}$ in the atom, giving the $\hat{H}'$ term. Thus,

$$a_2(t) \propto (\vec{\mu})_{fi} = \int \psi^*_{final}(\mathbf{r}) \, \vec{\mu} \, \psi_{initial}(\mathbf{r}) \, d^3r \tag{4}$$

where we emphasized that it is the **electric dipole moment matrix element** that matters and $\vec{\mu}$ is the electric dipole moment (a vector).

This expression is general. It can be applied to different forms of initial and final states. Here, let's consider the initial and final states being 1D **harmonic oscillator states** with the oscillator centered at $x = x_0$. Such state carries a quantum number n. Practically, we need to consider transitions between one harmonic oscillator state ψ_n and another state $\psi_{n'}$ in molecular physics. In an earlier Problem Set we did integrals of x and x^2 between harmonic oscillator states. You may make use of those results here without repeating the calculations.

The **Physical Situation** is: Let's say there is a negatively charged ion sitting at $x = 0$ (fixed) and a positively charged ion at $x = x_0$ at equilibrium (bottom of the oscillator's $U(x)$). So there is an electric dipole moment $\vec{\mu}_0 = qx_0\hat{x}$ at equilibrium separation. The ion will oscillate about $x = x_0$ and so $\vec{\mu}(x)$ for $x \approx x_0$ can be written as an expansion

$$\mu(x \approx x_0) = \mu_0 + \left.\frac{d\mu}{dx}\right|_{x=x_0} (x - x_0) \tag{5}$$

The vector sign is omitted because in 1D it is understood to be along the $\hat{x}$-direction.

(a) In Eq. (4), the initial and final states for harmonic oscillator energy eigenstate ψ_n and $\psi_{n'}$. Substituting Eq. (5) into Eq. (4), there are two terms. **Evaluate** the first term due to μ_0 and **comment on its contribution to inducing a transition from ψ_n to $\psi_{n'}$.**

(b) Consider the contribution of the second term in Eq. (5) and **obtain the selection rule** on Δn for an allowed transition. [You may use the results of integrals involving harmonic oscillator states in previous problem sets.]

(c) Consider the results in part (b), **comment on whether a transition from ψ_n to $\psi_{n'}$ is allowed or not if** $(d\mu/dx)_{x=x_0} = 0$.

[Important remarks: **Results in (a), (b) and (c) are important in IR spectroscopy of molecules.** They are related to the transitions between vibrational states and how to extract the oscillator's spring constant from molecular spectrum. Part (a) says that a molecule with a **fixed and constant electric dipole moment** will not absorb in IR range (usually harmonic oscillator states have energy difference in the infrared). Parts (b) and (c) say that the condition for possible transitions between vibrational states due to an incident EM wave is that **the molecules' electric dipole moment must be changing as the atoms vibrate**, as quantified by $(d\mu/dx)_{x=x_0}$ which must not be zero. Take this with you. This result can be generalized to normal modes of all molecules, i.e., normal mode oscillations in which the electric dipole moment of the molecule changes while the atoms are oscillating can lead to transitions between oscillator states. Since the normal modes are usually in IR frequency range, such modes are called IR active. CO_2 has such modes and it absorbs (and then emits) IR and makes it the bad guy responsible for global warming. H_2O also has such modes. We are also fortunate that O_2 and N_2 (the most abundance in the atmosphere) have $(d\mu/dx)_{x=x_0} = 0$ (obviously) so that they are not greenhouse gases. A further remark is that Eq. (4) can also be applied to transitions between rotational states, where $\psi_{initial}$ and ψ_{final} are $Y_{\ell,m_\ell}(\Theta,\Phi)$'s and $\vec{\mu}$ in between is a vector that can be specified by two angles with respect to the coordinate axes.]

6.3 Ionic Bond Energetics – KBr.

Let's practice the energetic consideration of the ionic bonds for the case of KBr.

(a) **Search** for the values of the ionization energy and electron affinity.

(b) **Estimate** the critical separation below which the transfer of an electron from a K atom to a Br atom becomes energetically favorable. This is the separation that energy consideration breaks even.

(c) **What** is the electrostatic energy (i.e. including contributions from ionization energy, electron affinity, and Coulomb interaction between ions) at the equilibrium separation r_0, where r_0 is known to be 0.282 nm (or 2.82 Å) for KBr.

(d) The experimental value of the dissociation energy (or binding energy) for KBr is about 3.97 eV. Is it different from the value obtained in (c). Explain why?

(e) Now, including schematically the strong repulsion at short distances, **sketch** $U(r)$ as a function of the separation between the ions r.

(f) The repulsive part of the potential energy function can be represented quite generally as $E_{repulsion} = b/r^n$, where b and n are constants (n usually refers to some high power representing a steep repulsive part of the potential energy function). Using the known values of the equilibrium separation and dissociation energy for KBr, estimate the value of b (units?) and the power n. [Remark: The value of n so obtained reflects how steep the repulsive part of $U(r)$ is.]

6.4 **HF bonding: Closely related to SQ23 but now with numbers**

Background: We discussed the bonding in H_2^+ molecular ion and H_2 molecule. We also discussed the bonding in HF qualitatively. If we call the line joining the two atoms the x-direction, then the bonding in HF is governed by how the hydrogen $1s$ atomic orbital (AO) and the fluorine $2p_x$ form MO's and filling two electrons (one from hydrogen and one from fluorine) into the MO's. Since hydrogen is very different from fluorine, it is typical of a diatomic molecule with the two AO's involved in LCAO having very different energies. You did some 2×2 matrix math before and now let's put it to practice use.

In considering bonding in HF, we can start with a linear combination (LCAO)

$$\psi = c_H \psi_{H,1s} + c_F \psi_{F,2p} \equiv c_H \psi_1 + c_F \psi_2 \tag{6}$$

and use it as a trial wavefunction for a variational calculation. The results give a set of equations

$$\begin{aligned} c_H(H_{11} - ES_{11}) + c_F(H_{12} - ES_{12}) &= 0 \qquad (7) \\ c_H(H_{12} - ES_{12}) + c_F(H_{22} - ES_{22}) &= 0 \qquad (8) \end{aligned}$$

and hence the values of E can be obtained by

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{9}$$

Eq. (9) can be used to get the two values of E and Eqs. (7) and (8) can be used to find c_H and c_F for each allowed value of E. So far, it is completely general (as discussed under variational method).

Your actions start here. Let's put in the numbers for HF. We have $S_{11} = 1$ and $S_{22} = 1$ because the AO's are normalized. For HF, $H_{11} = -13.6$ eV and $H_{22} = -18.6$ eV. Formally, there may be some other terms (in the formula) in H_{ii}, but the energy of the atomic orbital will dominate. These numbers are related to the ionization energies of hydrogen $1s$ electron and fluorine $2p$ electron. For the other parameters, take $S_{12} = 0.30$ and $H_{12} = -8.35$ eV.

(a) **Find** the energies E_{lower} and E_{upper} for the bonding and anti-bonding molecular orbitals.

(b) For E_{lower} (the bonding MO), **find** the ratio c_H/c_F. Hence, using the normalization condition of bonding MO ψ_{lower} to **find** c_H and c_F and hence **find** the normalized LCAO ψ_{lower}.

(c) For E_{upper} (the antibonding MO), **do the same** as in part (b) to find the normalized LCAO ψ_{upper}.

(d) Filling in the electrons, **write down** formally the two-electron ground state wavefunction for HF. **Comment and connect the answer** to the ionic character of the bonding.

6.5 **The Hückel Molecular Orbital Theory for the π electrons in Benzene (1931) and Delocalization Energy**

We outlined the physics of the π-electron in benzene in class notes. Here, you will fill in a bit of details. Like the hydrogen atom problem (Schrödinger 1926), the successful applications to the physics of molecules (bonding) are among the early triumphs of quantum mechanics. Benzene (C_6H_6) is the best example showing how simple QM can explain its electronic structure. It is a planar molecule with 6 carbon atoms forming a ring. The skeleton is formed by six σ bonds in a plane, using sp^2 hybrid orbitals. This gives a hexagonal ring with nearby bonds making an angle of 120°. All these are quantum mechanics (LCAO basically). Here, we explore another beautiful

QM application to benzene so as to understand the behavior of the remaining six p_z electrons or the π-electrons.

Let the plane of the benzene hexagonal framework be the x-y plane. These are strong bonds (good overlaps between the sp^2 hybrid orbitals). For each carbon atom, there is one lonely electron in the $2p_z$ orbital, pointing out of the x-y plane. We will focus on the molecular orbitals (MO's) formed by these six $2p_z$ orbitals. **The problem is to study how these 6 atomic p_z orbitals form the additional bonds on top of the strong σ-bonds framework**. Mulliken developed the MO theory in 1927. Erich Hückel developed/applied the MO theory to treat the bonding of these π electrons around 1930. His Hückel Molecular Orbital Theory is highly successful and essential for the understanding of many organic molecules. Hückel also learned quantum mechanics from Max Born while he was in Göttingen. He worked with Peter Debye (also in Göttingen) for his doctoral thesis. [Born and Debye are both Nobel Laureates, one in physics and one in chemistry.]

Let's label these $2p_z$ atomic orbitals by ϕ_1, ϕ_2, ϕ_3, ϕ_4, ϕ_5, ϕ_6 in a cyclic way around the ring. Naturally, we could study how these p_z orbitals form bonds by constructing a trial wavefunction

$$\psi = \sum_{n=1}^{6} c_n \phi_n = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6. \tag{10}$$

The result is a 6×6 determinant to solve for the six values of the energy and one can find the set of coefficients for each energy and thus ψ for each energy. "Six (atomic orbitals) in and six (MO's) out" - no more and no less. That's formal.

(a) **To think like a physicist**, we go by **physical sense** and we don't care about the details in the integrals H_{ij} and the overlap integrals S_{ij}. We expect the "on-site" terms H_{ii} should be important. We don't care about how to integrate it out and just represent it by a symbol α. Carbon 2 is quite far away from Carbon 4,5,6 and it is closer to only Carbon 1 and Carbon 3. Therefore, we only include H_{21} and H_{23} and call them β. More generally, we let $H_{ij} = \beta$ for **nearest-neighboring** Carbon i and Carbon j and $H_{ij} = 0$ otherwise. **This is often referred to as including only the nearest-neighbor interaction – a very useful approximation in physics.** Note that β is an energy and it is usually **negative**.

For the overlap integral, we even take the simplest possible approximation of $S_{ii} = 1$ and $S_{ij} = 0$ for $i \neq j$.

Write down an equation of the form of a determinant equation $|6 \times 6| = 0$ that is to be solved for the 6 energies of the molecular orbitals. [Remark: You have written down the 6×6 structure by physical sense. Consult class notes if necessary.]

(b) **Solve the energies** of the six MO's. Try it, how to handle determinants? Don't be scared.

(c) **Make a sketch of the energies** by lining them up, with the one with the lowest energy at the bottom and the highest energy at the top. (Recall: β is usually negative.)

(d) **Sketch** a picture with the 6 electrons filled into the MO's according to the Pauli Exclusion Principle so as to attain the lowest possible energy. Hence **find** the total π-electronic energy E_π(benzene) by adding up the energies of the electrons.

(e) Once upon a time, it was thought that the benzene molecule consists of alternating double and single bonds (there are two configurations). **Sketch** a picture of benzene in this form. Now **set up** the 6×6 determinant again for this picture of a benzene molecule (simply by physical sense). **Solve for the energies** of the six molecular orbitals. **Fill in** the electrons and **find** the total π-electronic energy in this case. Again, β is usually negative.

(f) Compare the results of part (d) and part (e). **Evaluate the difference** E_π(benzene) minus the energy in part (e). It is called the **delocalization energy**. You might have heard of the term in secondary school chemistry. [For benzene, the delocalization energy, i.e., **the energy lowered (gained) by delocalizing the π electrons**, is about -150 kJ mol^{-1} (recall this is the unit that chemists used for energies). The minus sign is there to mean that the delocalized case has a lower energy.]

(g) HOMO and LUMO. **HOMO** is the short-hand for **highest occupied molecular orbital** and **LUMO** is the short-hand for **lowest unoccupied molecular orbitals. Find** the HOMO-LUMO gap. In your sketch in part (d), **indicate** the energy between LUMO and HOMO.

Remark: Nowadays, many scientists study the optical properties of organic molecules, in particular related to controlling the absorption or emission of light at some preferred wavelength and to solar energy applications. The LUMO-HOMO energy difference is an important parameter. In solids (which can be regarded as very big molecules), this LUMO-HOMO energy difference becomes the band gap in a semiconductor or insulator.

(h) (Optional and harder - NO Bonus Points but educational) - Find the wavefunctions of the six MO's, i.e., solve for the six eigenvectors c_n $(n = 1, ..., 6)$ for each of the six MO energies. This will give you a sense of how the electrons in the (filled) lower energy MO's spread out over the benzene and why we put a circle inside the benzene symbol.

[Remarks: (i) Now go back to parts (a) to (f) again and appreciate how simply QM considerations and clever approximations can bring out deep physics in the molecular world. (ii) We see that delocalizing the electrons leads to lower energy. It can be extended to a solid, in which the delocalization of electrons leads to extended wavefunctions of electrons (called Bloch states). For example, consider 3 square wells, 4 square wells,..., 10 square wells, etc. The benzene picture can be seen as a way to understand the **metallic bond**. (iii) What you just did for benzene is called the **Hückel theory of molecular orbitals**. (iv) The same approach can be applied to other aromatic (structure of a ring) molecules. (v) Reference: E. Hückel, Zeitschrift für Physik **70**, 204-286 (1931) (a classic paper on QM of benzene).]