PHYS3022 Applied Quantum Mechanics Problem Set 6 Due: 2 April 2019 (Tuesday)
"T+2 = 4 April 2019"

All problem sets should be handed in not later than 5pm on the due date. Drop your assignments in the PHYS3022 box outside Rm.213.
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.

Progress: We discussed the physics of molecules. The Born-Oppenheimer approximation separates the electronic problem and the nuclei motions in a clever way. The electronic part becomes a problem similar to multi-electron atoms. It can be treated in an independent particle approximation. To solve the electronic problem, LCAO gives a powerful and conceptually transparent method. The formation of molecular orbitals (MO) allows the understanding of bonding when electrons are fill into the MO's according to the Pauli Principle. The MO concept can be applied to understand many other molecules. LCAO is also essential to understanding the idea of sp, sp^2 and sp^3 hybridization. The LCAO approach also describes the behavior of the π-electrons in benzene and other conjugated molecules (such as butadiene). In these contexts, it is called the Hückel theory. With the chemical bond(s) formed by the electrons, the nuclei motions come back into consideration. They consist of vibrational motion and rotational motion. The full description of a molecular state, including the electronic, vibrational, and rotational parts. Molecular spectrum comes from transitions between molecular states. One can extract useful information (band length and bond strength) from rotational spectrum, and vibrational-rotational spectrum. This forms a good and essential story of the quantum physics of molecules at the undergraduate level.

Reading: Essential phenomena are covered in the chapters on molecules in *Modern Physics* (e.g. by Taylor, Zafiratos, Dubson; and by Harris). Our QM treatment is deeper than those in typical modern physics and quantum physics books. With your undergraduate QM background, it is easy to read standard Physical Chemistry or Quantum Chemistry textbooks. Good discussions on MO theory can be found in *Physical Chemistry* and *Quantum Chemistry* by McQuarrie, and *Quantum Chemistry and Spectrocopy* by Thomas Engel. For those insisting on reading physics books only, see *Physics of Atoms and Molecules* by Bransden and Joachain (1000+ pages), which takes you from the undergraduate level to the postgraduate level both in QM and in atomic/molecular physics. For those who don't want to see equations but like to know the physics of chemistry, see *Absolutely Small* by Michael Fayer for an accurate narration.

6.1 H_2^+ molecular ion: Molecular Orbitals approach

We did the H_2^+ molecular ion problem both qualitatively and quantitatively in class and in class notes. Here, it is your turn to work it out, again. For two nuclei labelled A and B (left or right if you like) and one electron, the Hamiltonian for the single-electron problem with fixed nuclei can be written in atomic units as

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \tag{1}$$

The terms are: kinetic energy of electron, electron sees nucleus A, electron sees nucleus B, and nucleus-nucleus interaction. The last term is a constant for a given nucleus-nucleus separation R. You may rewrite $\hat{H}$ in the full SI units to work out the problem.

Background: In class notes, we used the combination

$$\psi = c_A\psi_A + c_B\psi_B \tag{2}$$

for a variational calculation and obtained a 2×2 matrix problem. Here, ψ_A is the 1s atomic orbital centered at A and ψ_B is the 1s atomic orbital centered at B, respectively. We have saved the coordinates of the electron, e.g. $\psi_A(\mathbf{r})$, for simplicity (laziness). The bonding and anti-bonding molecular orbitals are obtained. The result is a bonding molecular orbital (MO) when $c_A = c_B$ and an anti-bonding MO when $c_A = -c_B$.

Action: Making use of (2×2 or any size) matrix properties, (or by the symmetry of the problem given that both sides have a proton), the coefficients must have $|c_A| = |c_B|$. Therefore, the eigenvectors must be of the form

$$\psi_\pm = c_\pm \left(\psi_A \pm \psi_B\right) \tag{3}$$

In mathematical thoughts, using the two functions in Eq. (3) to express $\hat{H}$, the matrix will be diagonalized. This is our starting point.

(a) **Find** the normalization constants $c_\pm$ in terms of the overlap integral $S(R)$. [Hint: See class notes]

(b) Hence, **find** the energies $E_\pm$, more formally $E_\pm(R)$, which are simply the **expectation values** of $\hat{H}$ with respect to the normalized ψ_+ and ψ_-, respectively. For example,

$$E_+ = \int \psi_+^* \, \hat{H} \, \psi_+ \, d^3r \tag{4}$$

and there is an analogous expression for E_-.

Express the answer in terms of integrals such as J and K without evaluating them.

[Remark: You may want to compare results with the two energies obtained by observing the 2×2 matrix problem as given in class notes.]

(c) Expressions for $J(R)$, $K(R)$, and $S(R)$ are given in class notes. **Plot them out** and **combine them** properly to illustrate the behavior of $E_\pm(R)$ as a function of R.

6.2 HF bonding: Closely related to SQ23 but now with numbers

Background: The bonding in HF is governed by how the hydrogen $1s$ atomic orbital (AO) and the fluorine $2p_x$ (or p_y or p_z, doesn't matter) 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 case in which the two AO's in LCAO are of very different energies. You did the 2×2 matrix problem in which the two diagonal elements are different in Problem Set 1. In SQ23, this form is used to understand MO formation in HF qualitatively. Read SQ23 as a preparation.

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

$$\psi = c_H \psi_{H,1s} + c_F \psi_{F,2p} \equiv c_H \psi_1 + c_F \psi_2 \tag{5}$$

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

$$\begin{aligned} c_H(H_{11} - ES_{11}) + c_F(H_{12} - ES_{12}) &= 0 \qquad (6) \\ c_H(H_{12} - ES_{12}) + c_F(H_{22} - ES_{22}) &= 0 \qquad (7) \end{aligned}$$

and hence the values of E can be obtained by

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{8}$$

Eq. (8) can be used to get the two values of E and Eqs. (6) and (7) 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).

We now put in numbers. 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 LCAO ψ_{lower}.

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

(d) Filling in the electrons, **write down** formally the two-electron ground state wavefunction for HF.

6.3 sp^3 hybridization - Key to understanding semiconductor structure

sp^3 hybridization is key to understand CH_4 and the structure of many semiconductors. We live in a semiconductor world (your computer, your phone).

In discussing sp^2 hybridization, we put one hybridized orbital in the z-direction and then worked out a second one and showed that the angle between them is 120°. This is completely general as we could always put two directions (two vectors) onto a plane. The angle between two sp^3 hybridized orbitals can be evaluated in a similar procedure.

Back to class notes on sp^3 hybridization. The four sp^3 hybridized orbitals are written in a more "symmetric" form, with each one carrying some share of s, p_x, p_y and p_z atomic orbitals. The form is often used in solid state physics. It is because diamond (carbon), silicon, germanium, and GaAs have the same crystal structure dictated by sp^3 hybridization at the local (atomic) level.

(a) [Referring to class notes] **Write** down the four hybridized orbitals. Pick (any) one and **show that** it is properly normalized.

(b) Orthogonality is a concept that should be handled carefully in QM. It is not tested by eye (being 90° between eac other in space). For example, the sp^2 hybridized orbitals are orthogonal but they have 120° between them. Instead, **orthogonality** is defined by an integral (or inner product) between two hybridized orbitals. Pick any two of the sp^3 orbitals and **show that they are orthogonal** in the quantum mechanical sense.

(c) Pick any two and **find the angle** between them. [You may use the mathematical sense that the p-atomic states are like unit vectors pointing in different directions.]

(d) (This is harder artistically.) Take the hybridized orbital with coefficients 1/2, 1/2, 1/2 for p_x, p_y and p_z components and think of it as pointing towards the $(+1, +1, +1)$ direction in Cartesian coordinates. In a similar way, **draw** the four orbitals to illustrate the standard relative orientations of the orbitals.

Remark: To consolidate what you did here, refer to a picture of the diamond structure and GaAs structure. Inspect how the sp^3 hybridized orbitals from each atom propagate to become a crystal structure. The bonds formed the hybridized orbitals are strong (carbon is very hard). This covers a part on bonding and crystal structure in solid state physics. See, e.g., C. Kittel, *Introduction to Solid State Physics.*

6.4 π-bond in ethene C_2H_4 - Warming up for benzene

Consider C_2H_4. After invoking sp^2 hybridization, each carbon is bonded to two hydrogen and the other carbon. These bonds are strong and they form the strong framework/skeleton and govern the 120° structure between bonds. We can call the plane of the framework the x-y plane. Here, we consider the rest of the story.

For each carbon, there is one electron in the $2p_z$ orbital that is not involved in bonding so far. With two carbon, these $2p_z$ orbitals will form another bond which is called the π-bond. So, these two electrons are called the π electrons. We apply LCAO again to these two $2p_z$ orbitals to form the π-bond. The approach is more often called the Hückel Theory.

We construct LCAO using the two $2p_z$ AOs of the two carbon atoms as

$$\psi = c_A \psi_{A,2p_z} + c_B \psi_{B,2p_z} \tag{9}$$

This is exactly the same form as in Eq. (5) and thus Eq. (8) also applies here. Next, we use the Hückel Theory. Its spirit is to retain the most important parameters in Eq. (8). Namely, $S_{11} = 1$, $S_{22} = 1$, but $S_{12} \approx 0$. Then H_{11} is dominated by the atomic $2p$ energy α (following chemistry notations), so $H_{11} = H_{22} = \alpha$. Note $H_{11} = H_{22}$ because they are both carbon atom's $2p_z$ AOs. The only thing remains is H_{12}. We simply put $H_{12} = \beta$, representing how the two $2p_z$ AO's couple in the presence of $\hat{H}$.

(a) Apply the Hückel Theory to the π electrons in ethene and **find** the energies of the two molecular orbitals in terms of α and β. Note that $\beta < 0$.

(b) Hence, **fill in the two electrons** according to the Pauli Principle and **find** the total energy of the two π electrons.

(c) The case of no bonding refers to $H_{12} = 0$. **Find** the total energy of the two π electrons in this case.

(d) Hence, compare results and **find** the amount of energy lowered by forming the π-bond.

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

The application of the Hückel Theory to ethene in Problem 6.4 is rather trivial. A more interesting application is benzene. Here, you will complete the calculation as already outlined in class notes. 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 QM. 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. For each carbon atom, there is one lonely electron in the $2p_z$ orbital. 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 backbone**. 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 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 (c.f. Eq. (8)) to solve for the six values of the energy and one can find the set of coefficients for each value of the energies and thus ψ for every energy. "Six (atomic orbitals) in and six (MO's) out" - no more and no less. That's formal and it follows from the variational method.

(a) **To think like a physicist**, we go by **physical sense** and we don't care about the details in the many 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.** A remark is 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. See class notes if necessary.]

(b) **Solve the energies** of the 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 lowest energy one at the bottom and the highest energy one 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 molecular orbitals. **Fill in** the electrons and **find** the total π-electronic energy in this case.

(f) Compare the results of part (d) and part (e). [Recall that β is usually negative.] **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!) Thus, allowing the electrons to delocalize leads to 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 energy gap in a semiconductor or insulator.

(h) (Optional - NO Bonus Points but educational) - Find the wavefunctions of the six MO's, i.e., solve for 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).]