

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Chemistry

5.61 Quantum Mechanics

Fall 2013

Problem Set #8

Reading Assignment: McQuarrie 9.1-9.5, 10.1-10.5)

(● = Easier ■ = More Challenging ◆ = Most Challenging)

1. ■ In class, we discussed the MO picture of H_2^+ and found simple solutions for the energies of the σ and σ^* orbitals in terms of a few integrals. After significant effort, these integrals can all be worked out:

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

$$H_{12} = e^{-R} \left(\frac{1}{R} - \frac{1}{2} - \frac{7}{6} R - \frac{1}{6} R^2 \right)$$

$$\varepsilon = -\frac{1}{2} + e^{-2R} \left(1 + \frac{1}{R} \right)$$

- a. Plot these functions as a function of the distance, R , between the two hydrogen nuclei. Which terms are attractive? Which ones decay most quickly with distance? Also, note that ε is the average energy of a 1s electron on hydrogen atom A. Why is this energy not exactly equal to the energy of a hydrogen 1s electron?
- b. Plot the energies of the σ and σ^* orbitals as a function of R . What is the equilibrium bond length for H_2^+ in this approximation? What is the binding energy? Compare these to the experimental values of 1.06 Å and 2.8 eV, respectively. How does the sum of the MO energies, $E_\sigma + E_{\sigma^*}$ vary with distance?
- c. In other chemistry classes, you may have been taught that the strength of a chemical bond is proportional to the overlap of the atomic orbitals involved. Based on your results above, how accurate is this approximation for H_2^+ ? When does it break down?
2. ● In class we discussed matrix mechanics, which we will use with increasing frequency in the remainder of the course. The following problems provide practice in the mechanics of the use of this notation. Suppose ψ and ϕ are a wavefunctions composed of a linear combination of three orthonormal basis functions ψ_1 , ψ_2 and ψ_3 :

$$\psi = \sqrt{2}\psi_2 - 5\psi_3$$

$$\phi = \sqrt{6}\psi_1 + i\psi_2$$

- a. How would we express ψ and ϕ in matrix mechanics? That is, what are the vectors Ψ and Φ ?
- b. What are Ψ^\dagger and Φ^\dagger ?
- c. Normalize Ψ and Φ .

- Compute the inner products $\psi^\dagger \cdot \phi$ and $\phi^\dagger \cdot \psi$. Do you notice any relationship between these two numbers?
- Are these two states orthogonal?
- From the information given, can you tell which wavefunction has more nodes?
- For each of the following matrices, decide whether the matrix could or could not represent the Hamiltonian for this system. For matrices that could not be the Hamiltonian, explain why not.

$$\begin{pmatrix} 1 & -1 \\ -1 & 2 \end{pmatrix} \quad \begin{pmatrix} -1 & -1 \\ -1 & -2 \end{pmatrix} \quad \begin{pmatrix} 1 & i \\ i & 2 \end{pmatrix} \quad \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 & -i \\ 0 & 2 & 0 \\ i & 0 & 3 \end{pmatrix} \quad \begin{pmatrix} 1 & 2 & 2 \\ 0 & -1 & 1 \\ 0 & 0 & 3 \end{pmatrix} \quad \begin{pmatrix} i & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2i \end{pmatrix}$$

$$\begin{pmatrix} 1 & -1 & 0 & 0 \\ -1 & 2 & 0 & 0 \\ 0 & 0 & -3 & 1 \\ 0 & 0 & 1 & -1 \end{pmatrix} \quad \begin{pmatrix} 1 & -i & 1 & 1 \\ -i & 2 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 2 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}$$

- /◆ In this problem we want to approximate the strength of a two electron bond between two atoms (A and B) with different electronegativities. Approximate the molecular orbitals as linear combinations of one valence orbital on A and another on B

$$\psi \equiv c_1 \phi_A + c_2 \phi_B$$

For simplicity, assume that the atomic orbitals are approximately orthogonal

$$S \equiv \int \phi_A \phi_B d\tau \approx 0.$$

- We now want to approximate the energy of the AB bond for a fixed atom A bonding to different partners B with varying electronegativity. To this end, Fix the electronegativity of atom A (ϵ_A) and allow the electronegativity of B (ϵ_B) to vary freely. Finally, assume the coupling matrix element is independent of the electronegativity and (arbitrarily) equal to 1

$$V \equiv \int \phi_A \hat{H} \phi_B d\tau \approx 1$$

Within this model, compute the binding energy of the lowest MO as a function of ϵ_B . That is to say, compute the difference in energy between the lowest MO and the lowest AO as you vary the electronegativity of atom B. What electronegativity produces the strongest AB bond? Does this agree with your chemical intuition? You may wish to look up a few A-B bond strengths to substantiate your argument.

- The model above is missing electron-electron interactions. Qualitatively speaking, how would you expect the results of part a. to

change if you included electron-electron interactions at the level of the independent particle model (IPM)? Be as specific as you can in your answer. For example, will the bond get stronger or weaker? Will the optimal electronegativity change?

4. ◆ Consider the MO picture of the one-electron bond in HeH^{+2} . We will write the molecular orbitals as linear combinations of the $1s$ functions on each nucleus:

$$\psi = c_1 1s_H + c_2 1s_{\text{He}}$$

- Work out the eigenvalue equation that you would solve for the molecular orbitals in HeH^{+2} . You do not need to evaluate any integrals here, but please simplify your expression as much as possible otherwise.
 - For simplicity we will assume at this point that the $1s$ orbitals on the two nuclei are orthogonal. What are the molecular orbital eigenvalues for HeH^{+2} in this case? Once again, you need not evaluate any integrals to obtain your final expression. It may prove useful to write your expressions in terms of the energy gap ($\Delta = \epsilon_H - \epsilon_{\text{He}}$) and the off-diagonal coupling (H_{12}).
 - It is quite complicated to work out a general formula for the probability of finding an electron on He as a function of Δ and H_{12} . Without necessarily working out the whole formula, show that the probability of finding the electron on He is larger than the probability of finding the electron on H. [Hint: you will need to use the fact that $\epsilon_H > \epsilon_{\text{He}}$]. Does this agree with your chemical intuition?
 - How do you expect Δ and H_{12} to change if you change the bond distance, R ? Construct approximate functions $\Delta(R)$ and $H_{12}(R)$ that account qualitatively for the expected dependence on R and the known $R=0$ and $R=\infty$ limits of each term.
 - Given your forms of $\Delta(R)$ and $H_{12}(R)$, plot the MO energy of HeH^{+2} as a function of R . How does the charge on He change with distance? Why does this happen?
5. ■ Unsaturation (i.e. the existence of stable multiple bonds) is an extremely important phenomenon for the chemistry of carbon. However, it is comparatively rare for silicon even though C and Si have the same valence shell. In this problem, we develop an explanation for this based on MO theory. Consider the ethylene molecule ($\text{H}_2\text{C}-\text{CH}_2$) oriented in the x - y plane. At equilibrium, the MO Hamiltonian for the carbon p_z orbitals is

$$\mathbf{H}_{\text{C-C}} = \begin{pmatrix} -10.9 & -0.8 \\ -0.8 & -10.9 \end{pmatrix}$$

Answer the following questions. In preparing your answer it may prove useful to know the following data:

	Silicon	Carbon
Electronegativity	1.90	2.55
Atomic Radius	1.46 Å	0.91 Å

- a. Consider the two molecules $\text{H}_2\text{Si-SiH}_2$ and $\text{H}_2\text{Si-CH}_2$ at their respective equilibrium geometries. Of the eight matrices below, one represents the Hamiltonian for the p_z orbitals in $\text{H}_2\text{Si-SiH}_2$, while another represents $\text{H}_2\text{C-SiH}_2$. Which is which? Justify your answer.

$$\begin{pmatrix} -8.9 & -1.0 \\ -1.0 & -8.9 \end{pmatrix} \quad \begin{pmatrix} -8.9 & -0.4 \\ -0.4 & -8.9 \end{pmatrix} \quad \begin{pmatrix} -12.3 & -0.4 \\ -0.4 & -12.3 \end{pmatrix} \quad \begin{pmatrix} -12.3 & -1.0 \\ -1.0 & -12.3 \end{pmatrix}$$

$$\begin{pmatrix} -10.9 & -0.5 \\ -0.5 & -9.0 \end{pmatrix} \quad \begin{pmatrix} -10.9 & -0.6 \\ -0.6 & -12.2 \end{pmatrix} \quad \begin{pmatrix} -10.9 & -1.0 \\ -1.0 & -9.1 \end{pmatrix} \quad \begin{pmatrix} -10.9 & -0.9 \\ -0.9 & -12.4 \end{pmatrix}$$

- b. Based on your answer to part A, how do you expect the strength of the π bonds in $\text{H}_2\text{Si-SiH}_2$ and $\text{H}_2\text{Si-CH}_2$ to compare to the strength of the π bond in ethylene? Justify your answer.

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