

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Chemistry

5.61 Quantum Mechanics

Fall 2013

Problem Set #7

Reading Assignment: McQuarrie 9.1-9.5, 10.1-10.5, Matlab and Linear Algebra Handouts

(● = Easier ■ = More Challenging ◆ = Most Challenging; 🍏 = Computer)

1. ●/🍏 Later in the course, we will find a very useful connection between quantum mechanical eigenvalue problems and matrix eigenvalue problems. To prepare for that, we want to practice using a computer to solve a not-so-simple matrix eigenvalue problem. Use your favorite software package to compute the eigenvalues and eigenvectors of the following matrix:

$$\begin{pmatrix} \alpha & \beta & 0 & 0 & \beta \\ \beta & \alpha & \beta & \beta & 0 \\ 0 & \beta & \alpha & \beta & 0 \\ 0 & \beta & \beta & \alpha & \beta \\ \beta & 0 & 0 & \beta & \alpha \end{pmatrix}$$

Be careful to make sure your eigenvectors are orthonormal. Compare the results to the eigenvectors you get for the matrix:

$$\begin{pmatrix} \alpha & \beta & 0 & 0 & 0 \\ \beta & \alpha & 0 & 0 & 0 \\ 0 & 0 & \alpha & \beta & \beta \\ 0 & 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \beta & \alpha \end{pmatrix}$$

What differences do you see in the eigenvectors? [Note: if you use Matlab, it will prove useful to write each of these matrices as α times the identity matrix plus β times another matrix. Call this other matrix \mathbf{M} . You will then need to convince yourself that the eigenvectors of the full matrix are the same as the eigenvectors of \mathbf{M} .]

2. ◆ As you have been taught in your earlier chemistry classes, the s and p orbitals are not the most appropriate way to think about atomic orbitals in, say, methane. Instead, it is useful to consider sp^3 hybrid orbitals:

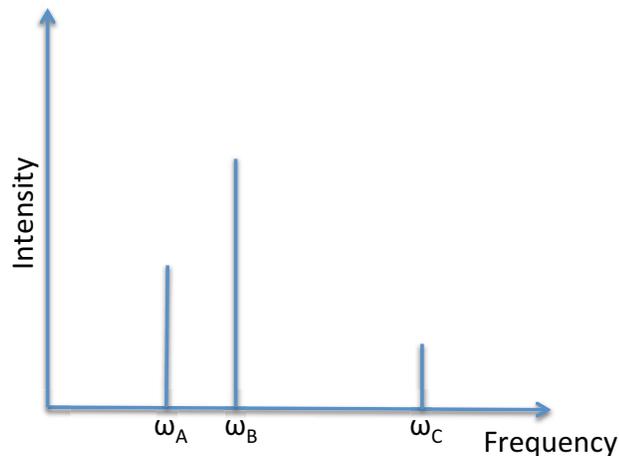
$$\psi_1(\mathbf{r}) = \frac{1}{2} [2s(\mathbf{r}) + 2p_x(\mathbf{r}) + 2p_y(\mathbf{r}) + 2p_z(\mathbf{r})]$$

$$\psi_2(\mathbf{r}) = \frac{1}{2} [2s(\mathbf{r}) - 2p_x(\mathbf{r}) - 2p_y(\mathbf{r}) - 2p_z(\mathbf{r})]$$

$$\psi_3(\mathbf{r}) = \frac{1}{2} [2s(\mathbf{r}) + 2p_x(\mathbf{r}) - 2p_y(\mathbf{r}) - 2p_z(\mathbf{r})]$$

$$\psi_4(\mathbf{r}) = \frac{1}{2} [2s(\mathbf{r}) - 2p_x(\mathbf{r}) + 2p_y(\mathbf{r}) - 2p_z(\mathbf{r})]$$

- a. Just as $\{2s, 2p_x, 2p_y, 2p_z\}$ are orthonormal, the sp^3 hybrid orbitals above are also orthonormal. Go one step toward proving this by showing that ψ_1 is normalized and that ψ_1 and ψ_2 are orthogonal to each other. Note that it is possible to do this without computing any integrals.
- b. Show that for a hydrogen atom the sp^3 hybrid orbitals are degenerate with eigenvalue $E_{sp^3} = -3.4$ eV. Note that it is possible to do this without computing any integrals.
- c. The salient difference between the sp^3 orbitals and the s and p orbitals is that each of the sp^3 orbitals points in a particular direction, whereas the hydrogenic orbitals are directionless. For ψ_1 compute the average value of z and show that $\langle \hat{z} \rangle < 0$, so that ψ_1 “points” in the $-z$ direction. Hint: You will want to use reflection symmetry to prove that all but two of the $4 \times 4 = 16$ integrals are zero.
3. ■ Suppose you have a potential for which the selection rules dictate that there are only three allowed transitions at frequencies ω_A , ω_B and ω_C respectively. The spectrum for one electron in this potential looks like this:



- a. Now, suppose you have two *non-interacting* electrons in this potential. What will the allowed transitions be? What will the frequencies of these transitions be?
- b. Based on your answers to part a., draw the spectrum for two electrons in this potential.
- c. Now suppose the electrons interact weakly. Sketch how the electron-electron repulsion will change your spectrum. Justify your sketch noting what changes you expect to see in the selection rules and the transition energies.
4. ■ For two electrons, the total z component of the spin angular momentum for the system is

$$\hat{S}_{z,total} = \hat{S}_{z1} + \hat{S}_{z2}$$

while the total spin operator is given by:

$$\hat{S}_{total}^2 = \hat{S}_{x,total}^2 + \hat{S}_{y,total}^2 + \hat{S}_{z,total}^2 = (\hat{S}_{x1} + \hat{S}_{x2})^2 + (\hat{S}_{y1} + \hat{S}_{y2})^2 + (\hat{S}_{z1} + \hat{S}_{z2})^2$$

- a. Show that both

$$\Psi_{\alpha\beta} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 2s\beta(1) \\ 1s\alpha(2) & 2s\beta(2) \end{vmatrix} \equiv \frac{1}{\sqrt{2}} (1s\alpha(1)2s\beta(2) - 2s\beta(1)1s\alpha(2))$$

and

$$\Psi_{\beta\alpha} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\beta(1) & 2s\alpha(1) \\ 1s\beta(2) & 2s\alpha(2) \end{vmatrix} \equiv \frac{1}{\sqrt{2}} (1s\beta(1)2s\alpha(2) - 2s\alpha(1)1s\beta(2))$$

are antisymmetric. Show also that $\Psi_{\alpha\beta}$ and $\Psi_{\beta\alpha}$ are eigenfunctions of $\hat{S}_{z,total}$. What are the eigenvalues in each case?

- Show that, while $\Psi_{\alpha\beta}$ and $\Psi_{\beta\alpha}$ cannot be written in the form $\Psi_{space} \Psi_{spin}$ yet the combinations $\Psi_{\alpha\beta} \pm \Psi_{\beta\alpha}$ can both be cast in the form $\Psi_{space} \Psi_{spin}$.
- Verify that the total spin operator can be re-written in terms of raising and lowering operators:

$$\hat{S}_{total}^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_{1z}\hat{S}_{2z} + (\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+})$$

- Show that neither $\Psi_{\alpha\beta}$ nor $\Psi_{\beta\alpha}$ is an eigenfunction of \hat{S}_{total}^2 . That is to say, show that neither of these wavefunctions is a total spin eigenstate.
- Finally, show that the combinations $\Psi_{\alpha\beta} \pm \Psi_{\beta\alpha}$ are eigenfunctions of both $\hat{S}_{z,total}$ and \hat{S}_{total}^2 .
- Note that $\Psi_{\alpha\beta}$, $\Psi_{\beta\alpha}$ and $\Psi_{\alpha\beta} \pm \Psi_{\beta\alpha}$ are all degenerate states within the noninteracting electron picture. Comment on why your work above shows that $\Psi_{\alpha\beta} \pm \Psi_{\beta\alpha}$ are more realistic eigenstates of the Hamiltonian.

- /■ Consider a universe where the electron has spin 5/2 instead of spin 1/2.
 - Draw the periodic table (up to Halfnium) in this alternate universe.
 - What elements would be “noble gases”? Which would be alkali earth elements? What elements would be in the same period as carbon?
 - What would the bond order of He_2 be in this universe? What about O_2 ?
 - What would the equivalent of the octet rule be in this alternate universe? [Note: you could spend a *lot* of time answering this last question. It is intended to be fun. When it stops being fun, your answer is long enough.]

- The following concern the independent particle model. You may find the following set of Coulomb and exchange integrals useful (energies in eV) :

$$J_{1s1s} = 17.0 Z \quad J_{1s2s} = 4.8 Z \quad K_{1s2s} = 0.9 Z \quad J_{2s2s} = 3.5 Z$$

$$J_{1s2p} = 6.6 Z \quad K_{1s2p} = 0.5 Z \quad J_{2s2p} = 4.4 Z \quad K_{2s2p} = 0.8 Z$$

$$J_{2p_2p_i} = 3.9 Z \quad J_{2p_2p_k} = 3.5 Z \quad K_{2p_2p_k} = 0.2 Z \quad (i \neq k)$$

- Using the independent particle model discussed in class, what is the energy difference between the $1s^2 2p_x^2$ configuration and the $1s^2 2s^2$ configuration? How do you justify your result?

- b. What is the energy difference between the ground state of Lithium and the spin polarized $1s^{\uparrow}2s^{\uparrow}2p_z^{\uparrow}$ state? Is this energy about the size you expected?
- c. Use the IPM to compute the ionization potential of B: $IP=E(B^+)-E(B)$. Compare your boron result with the ionization potential of Lithium within the IPM. Does this agree with periodic trends?
- d. Finally, compare the ionization potentials computed in part c. with the experimental results [$IP(\text{Li})=5.4$ eV, $IP(\text{B})=8.3$ eV] and the answer you would have gotten if you had assumed the electrons do not interact.
- e. Within the IPM, what is the energy difference between a closed shell $1s^22s^22p_x^2$ configuration and a high spin $1s^22s^{\uparrow}2p_x^{\uparrow}2p_y^{\uparrow}2p_z^{\uparrow}$ configuration for carbon? Does this agree with your intuition?

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