3.23 Electrical, Optical, and Magnetic Properties of Materials
Fall 2007

Homework # 2

Nicolas Poilvert & Nicola Marzari

September 28, 2007

Homework is due on Wednesday September 26th, 5pm

1 The power of spinach

MIT researchers have been able to use the Photosystem 1 in spinach chloroplasts to convert sunlight to energy into a solid-state electronic spinach sandwich device that may one day power laptops and cell phones. What would be the size of the confining region for the electron responsible for the green color of spinach ? (Hint: To study this problem, assume that the electronic transition is from the ground state to the first excited state. You can think at Photosystem 1 as being a 1-d infinite well)

solution:

For a one dimensional infinite well, the energy levels are given by:

$$E_n = \frac{\hbar^2 \pi^2}{2ma^2} n^2 = \frac{h^2}{8ma^2} n^2$$

The ground state is given by $n = 1$ and the first exited state is given by $n = 2$ (Remember the discussion about the negative values of n that are not eigenstates because they lead to the same solution as the ones with positive n. Moreover $n = 0$ would lead to a null wavefunction which is not physical.). From there we find that the energy of the corresponding photon $E = h\nu = \frac{hc}{\lambda}$ (for green light $\lambda \approx 510$nm) is such that:

$$\frac{hc}{\lambda} = E_2 - E_1 = \frac{3h^2}{8ma^2}$$

From this equation, we extract the value for a,

$$a = \sqrt{\frac{3h\lambda}{8mc}}$$

Numerically we find, $a \approx 6.8$Å.

2 Molecular orbitals and the Linear Combinaition of Atomic Orbitals method (LCAO)

Background on LCAO   In this problem, we will be interested in characterizing the two lowest lying molecular orbitals of an electron in the Hydrogen molecule H_2. To find those molecular orbitals, we will use a well-known technique in Quantum Chemistry called the Linear Combinaition of Atomic Orbitals

(LCAO). The spirit of the technique is the following: Imagine that you take two hydrogen atoms far from each other. In that case each atom has one electron, and the wavefunction of each electron is described by a 1s atomic orbital, $\phi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$, where a_0 is the Bohr radius. When one then reduces the distance between the two hydrogen atoms up to atomic dimensions, the ground state wavefunction of each electron is no longer described by a 1s orbital because an electron localized around one of the proton can hop to the second proton of the H_2 molecule. So what is the wavefunction then? The LCAO technique applied to the case of the H_2 molecule consists in writing the total wavefunction of an electron as a linear combinaison of two 1s orbitals, one centered around each proton. The new wavefunction is then called a **molecular orbital** because it spreads over the entire molecule and is not localized around a particular atom. Hence the molecular orbital looks like this:

$$\psi = c_1 \phi_{1s}(1) + c_2 \phi_{1s}(2)$$

where (1) and (2) stand for proton 1 and 2. We can compactly represent this linear combinaison as a 2-dimensional vector in the basis of $\phi_{1s}(1)$ and $\phi_{1s}(2)$ as:

$$\psi = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Expressing the Hamiltonian of an electron Let's call $\hat{H}$ the hamiltonian of a single electron in an H_2 molecule. Since we expressed the electronic wavefunction as a linear combinaition of $\phi_{1s}(1)$ and $\phi_{1s}(2)$ only, we need to find the hamiltonian matrix in the basis formed by those two atomic orbitals if we want to be able to find the eigenenergies (i.e the molecular energies) and the corresponding eigenfunctions (i.e the molecular orbitals). So we see that instead of expressing the hamiltonian in an **infinite and complete** basis, we chose a two-dimensional basis. This is clearly an approximation but if the two basis functions are carrefully chosen, then the eigenfunctions obtained by diagonalizing the hamiltonian matrix in this 2-dimensional basis can be very accurate in describing the "exact" molecular orbitals. Let's define the matrix elements of the hamiltonian as:

$$E_0 = \left\langle \phi_{1s}(1) | \hat{H} | \phi_{1s}(1) \right\rangle = \int \phi_{1s}^*(1) \hat{H} \phi_{1s}(1)$$

which by symmetry is equal to:

$$E_0 = \left\langle \phi_{1s}(2) | \hat{H} | \phi_{1s}(2) \right\rangle = \int \phi_{1s}^*(2) \hat{H} \phi_{1s}(2)$$

and

$$V = \int \phi_{1s}^*(1) \hat{H} \phi_{1s}(2) = \int \phi_{1s}^*(2) \hat{H} \phi_{1s}(1)$$

The off-diagonal elements shown above are in general **complex conjuguate** to each other, because the hamiltonian matrix **must be hermitian**, i.e $\hat{H}^\dagger = \hat{H}$. Using E_0 and V we find that the hamiltonian matrix expressed in the two-dimensional basis of the $\phi_{1s}(1)$ and $\phi_{1s}(2)$ atomic orbitals is:

$$\hat{H} = \begin{pmatrix} E_0 & V \\ V & E_0 \end{pmatrix}$$

The atomic orbitals $\phi_{1s}(1)$ and $\phi_{1s}(2)$ are real and normalized wavefunctions -i.e $\int |\phi_{1s}(1)|^2 = \int \phi_{1s}(1)^2 = 1$ and the same for $\phi_{1s}(2)$- but they are not orthogonal because $\int \phi_{1s}(1)\phi_{1s}(2) = S \neq 0$. In order to find the eigenergies we will have to equate the determinant of the following matrix to zero (This is a generalization of the determinantal eigenvalue equation for **non-orthogonal** basis):

$$\begin{pmatrix} E_0 - \lambda & V - \lambda S \\ V - \lambda S & E_0 - \lambda \end{pmatrix}$$

1. Find the eigenenergies (λ_+ and λ_-) of an electron in an H_2 molecule by solving the determinantal equation above for λ. λ_+ will be the smallest eigenenergy (knowing that **S is positive** and **V is negative**) and λ_- the largest.

   solution:

   If we equate the determinant of the above matrix to zero, we find:

   $$(E_0 - \lambda)^2 - (V - \lambda S)^2 = 0$$

   Now we know that if $x^2 = y^2$, then $x = y$ or $x = -y$. From this we deduce that:

   $$E_0 - \lambda_- = V - \lambda_- S \text{ or } E_0 - \lambda_+ = -(V - \lambda_+ S)$$

   and so we find:

   $$\lambda_- = \frac{E_0 - V}{1 - S} \text{ and } \lambda_+ = \frac{E_0 + V}{1 + S}$$

2. For each of the two possible eigenenergies λ_+ and λ_-, find the corresponding normalized eigenvectors by solving the Schrodinger equation in matrix form (This is a generalization of the matrix eigenvalue equation for **non-orthogonal** basis):

   $$\begin{pmatrix} E_0 - \lambda_\pm & V - \lambda_\pm S \\ V - \lambda_\pm S & E_0 - \lambda_\pm \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

   solution:

   For each of the eigenenergies, we will inject their expression in the above matrix equation:

   for λ_+, we have

   $$\begin{pmatrix} E_0 - \lambda_+ & V - \lambda_+ S \\ V - \lambda_+ S & E_0 - \lambda_+ \end{pmatrix} \begin{pmatrix} c_1^+ \\ c_2^+ \end{pmatrix} = 0$$

   which gives us

   $$\begin{pmatrix} E_0 - \frac{E_0 + V}{1 + S} & V - \frac{E_0 + V}{1 + S} S \\ V - \frac{E_0 + V}{1 + S} S & E_0 - \frac{E_0 + V}{1 + S} \end{pmatrix} \begin{pmatrix} c_1^+ \\ c_2^+ \end{pmatrix} = 0$$

   which when multiplied everywhere by $(1 + S)$ simplifies to

$$\begin{pmatrix} SE_0 - V & V - SE_0 \\ V - SE_0 & SE_0 - V \end{pmatrix} \begin{pmatrix} c_1^+ \\ c_2^+ \end{pmatrix} = 0$$

we then end up with $c_1^+ = c_2^+$. We need now to normalize this eigenvector. To do this let us write explicitly the eigenvector in terms of the basis kets $|\phi_{1s}(1)\rangle$ and $|\phi_{1s}(2)\rangle$:

$$|c^+\rangle = \begin{pmatrix} c_1^+ \\ c_2^+ \end{pmatrix} = c_1^+ |\phi_{1s}(1)\rangle + c_2^+ |\phi_{1s}(2)\rangle$$

To express the corresponding bra $\langle c^+|$, we will take the complex conjuguate of the above ket:

$$\langle c^+| = \left(c_1^+ |\phi_{1s}(1)\rangle + c_2^+ |\phi_{1s}(2)\rangle \right)^\dagger = (c_1^+)^* \langle\phi_{1s}(1)| + (c_2^+)^* \langle\phi_{1s}(2)|$$

If we want the eigenvector to be normalized, we need to impose the following condition: $\langle c^+|c^+\rangle = 1$, which translates into:

$$\left((c_1^+)^* \langle\phi_{1s}(1)| + (c_2^+)^* \langle\phi_{1s}(2)| \right) \left(c_1^+ |\phi_{1s}(1)\rangle + c_2^+ |\phi_{1s}(2)\rangle \right) = 1$$

Expanding this expression and remembering that $\langle\phi_{1s}(1)|\phi_{1s}(2)\rangle = \langle\phi_{1s}(2)|\phi_{1s}(1)\rangle = S$, $\langle\phi_{1s}|\phi_{1s}(1)\rangle = 1$ and $\langle\phi_{1s}(2)|\phi_{1s}(2)\rangle = 1$, we find:

$$|c_1^+|^2 + (c_1^+)^* c_2^+ S + (c_2^+)^* c_1^+ S + |c_2^+|^2 = 1$$

To finish, we will use the fact that for $|c^+\rangle$, we have $c_1^+ = c_2^+$. Knowing this, we see that the above expression reduces to:

$$|c_1^+|^2(2 + 2S) = 1$$

which gives us:

$$c_1^+ = \tfrac{1}{\sqrt{2+2S}}$$

The final answer for the normalized eigenvector $|c^+\rangle$ is:

$$|c^+\rangle = \tfrac{1}{\sqrt{2+2S}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

for λ_-, we have

$$\begin{pmatrix} E_0 - \lambda_- & V - \lambda_- S \\ V - \lambda_- S & E_0 - \lambda_- \end{pmatrix} \begin{pmatrix} c_1^- \\ c_2^- \end{pmatrix} = 0$$

which gives us

$$\begin{pmatrix} E_0 - \frac{E_0 - V}{1-S} & V - \frac{E_0 - V}{1-S}S \\ V - \frac{E_0 - V}{1-S}S & E_0 - \frac{E_0 - V}{1-S} \end{pmatrix} \begin{pmatrix} c_1^- \\ c_2^- \end{pmatrix} = 0$$

which when multiplied everywhere by $(1 - S)$ simplifies to

$$\begin{pmatrix} -SE_0 + V & V - SE_0 \\ V - SE_0 & -SE_0 + V \end{pmatrix} \begin{pmatrix} c_1^- \\ c_2^- \end{pmatrix} = 0$$

we then end up with $c_1^- = -c_2^-$. Following the same procedure as above, we can easily find the expression for the normalized eigenvector $|c^-\rangle$:

$$|c^-\rangle = \tfrac{1}{\sqrt{2-2S}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

3. From the calculations carried out in the previous questions, we see that an electron has two possible states in the H_2 molecule. Because of the spin degeneracy, the ground state of the H_2 molecule consists of the two electrons accupying the lowest energy state with opposite spins. Then what is the total energy of the H_2 molecule? (in its ground state)

   solution:

   The total energy of the H_2 molecule in its ground state is given by:

   $$E_{\text{tot}} = 2\lambda_+ = 2\tfrac{E_0+V}{1+S}$$

4. If $\hat{h}$ is the hamiltonian of an electron in the hydrogen **atom**, then ϕ_{1s} is an eigenfunction (the ground state) of $\hat{h}$ for the eigenvalue ϵ_0 (the ground state energy). Then what is the total energy of two isolated hydrogen atoms? (in their ground state)

   solution:

   You cannot find an easier question than this one in this problem set. The total energy of two isolated hydrogen atom is obviously:

   $$E_{\text{tot}}^{\text{isolated}} = 2\epsilon_0$$

5. If one considers that ϵ_0 is equal to E_0 (this is almost true for the H_2 molecule), can you demonstrate that the formation of a H_2 molecule is favored energetically with respect to two isolated atoms?

solution:
   Let us look at the energy difference between the H_2 molecule and two isolated hydrogen atoms:

$$\Delta E = E_{\text{tot}} - E_{\text{tot}}^{\text{isolated}} = 2\tfrac{E_0+V}{1+S} - 2\epsilon_0$$

Now if we consider that ϵ_0 is close to E_0, we see that:

$$\Delta E = 2\tfrac{V-SE_0}{1+S} < 0$$

So the formation of an hydrogen molecule is energetically favored with respect to two isolated hydrogen atom.

3 The spin of the electron

During the 1920's, physicists realized that in order for them to be able to explain all the experimental results accumulated over the previous 20 years, they needed to give to the electron an intrinsic property, the *spin*. In Quantum mechanics, the spin of the electron is described by a 2 dimensional complex vector like:

$$|\psi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$$

where a and b are complex numbers. *In this exercise, we will consider that the electron spin is described by the following quantum state:*

$$|\psi\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$$

Since the spin is a measurable quantity there are hermitian operators associated with it. We have seen in class the angular momentum operator $\hat{\vec{L}}$, which is a **vectorial operator**, i.e it has 3 coordinates ($\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$) that are actually operators of their own. Now suppose you want to know what is the y projection of the spin of an electron described by the spin vector above ($|\psi\rangle$). For this you need the expression of the y projection of the spin operator $\hat{S}_y$:

$$\hat{S}_y = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$$

Using the principles of Quantum mechanics, answer the following questions:

1. What are the possible measurement results for the y projection of the spin?

   solution:

   According to the postulates of quantum mechanics, the only possible result of the measurement of the physical quantity s is one of the eigenvalues of the corresponding operator $\hat{S}_y$. Thus we need to determine the eigenvalues of $\hat{S}_y$ by solving : $\det(\hat{S}_y - \lambda\hat{I}) = 0$. The second order algebraic equation that we obtain is: $\lambda^2 - 1 = 0$. Solutions are ± 1. Consequently, the possible measurement results are $s_1 = -1$ and $s_2 = 1$.

2. Is $|\psi\rangle$ normalized?

   solution:

   To check whether $|\psi\rangle$ is normalized, we must verify that its norm $\sqrt{\langle\psi|\psi\rangle}$ equals 1:

   $$\sqrt{\langle\psi|\psi\rangle} = \sqrt{\left((\tfrac{1}{\sqrt{2}})^*, (-\tfrac{1}{\sqrt{2}})^*\right) \cdot \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}}$$

   We then find that $\sqrt{\langle\psi|\psi\rangle} = 1$ such that $|\psi\rangle$ is indeed normalized.

3. Is $|\psi\rangle$ an **eigenvector** of the spin operator $\hat{S}_y$?

   solution:

   To check whether $|\psi\rangle$ is an eigenvector of $\hat{S}_y$, we need to determine whether $\hat{S}_y |\psi\rangle = s |\psi\rangle$ where s is one of the eigenvalues calculated before. The matrix product gives us:

   $$\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} \frac{-i}{\sqrt{2}} \\ \frac{-i}{\sqrt{2}} \end{pmatrix}$$

   But this last vector cannot be written as $s |\psi\rangle$ (check it), so $|\psi\rangle$ is **not** an eigenvector of $\hat{S}_y$.

4. What are the eigenvectors of $\hat{S}_y$?

   solution:

   To calculate the first eigenvector of $\hat{S}_y$, we need to solve the equation $\hat{S}_y |u_1\rangle = s_1 |u_1\rangle$. The matrix product gives us:

   $$\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = - \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

   which reduces to a single equation : $x_1 + iy_1 = 0$. Consequently we have $y_1 = -\frac{1}{i}x_1 = ix_1$. Now we want to normalize our vector, so we impose:

   $$\sqrt{\langle u_1|u_1\rangle} = 1 = \sqrt{((x_1)^*, (ix_1)^*) \cdot \begin{pmatrix} x_1 \\ ix_1 \end{pmatrix}}$$

   we then end up with $|x_1| = \frac{1}{\sqrt{2}}$ and so $|u_1\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} \end{pmatrix}$. In the same way we find that the eigenvector associated with the eigenvalue $s_2 = 1$ is $|u_2\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} \end{pmatrix}$

5. Can you express $|\psi\rangle$ in terms of the eigenvectors of $\hat{S}_y$?

   solution:

   The eigenvectors $|u_1\rangle$ and $|u_2\rangle$ form an orthonormal basis set of the spin vector space. As a result, $|\psi\rangle$ can be written as a linear combinaison of $|u_1\rangle$ and $|u_2\rangle$:

   $$|\psi\rangle = \alpha |u_1\rangle + \beta |u_2\rangle$$

   The coefficiants are nothing but the projections of $|\psi\rangle$ onto the corresponding basis vector. For example:

   $$\alpha = \langle u_1|\psi\rangle = \left((\tfrac{1}{\sqrt{2}})^*, (\tfrac{i}{\sqrt{2}})^* \right) \cdot \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$$

so we easily find that $\alpha = \frac{1+i}{2}$. In the same way we find that $\beta = \frac{1-i}{2}$ and we conclude that:

$$|\psi\rangle = \frac{1+i}{2}|u_1\rangle + \frac{1-i}{2}|u_2\rangle$$

6. What would be the probability of obtaining each one of the possible measurement results for the y projection of the spin?

   solution:

   According to the postulates of quantum mechanics, when the physical quantity s (here the y projection of the spin) is measured on a system in the normalized state $|\psi\rangle$, the probability $P(s = s_1)$ of obtaining the measurement result $s = s_1$ is:

   $$P(s = s_1) = |\langle u_1|\psi\rangle|^2 = (\frac{1+i}{2})^*(\frac{1+i}{2}) = \frac{1}{2}$$

   Similarly, the probability $P(s = s_2)$ of obtaining the measurement result $s = s_2$ is:

   $$P(s = s_2) = |\langle u_2|\psi\rangle|^2 = (\frac{1-i}{2})^*(\frac{1-i}{2}) = \frac{1}{2}$$

7. What is the quantum state of the particle after each possible measurement?

   solution:

   Still following the postulates of quantum mechanics, if the result of the measurement is $s = s_1$ the state of the system immediately after the measurement is $|u_1\rangle$ (that is the eigenvector corresponding to the eigenvalue s_1). Similarly, if the result is s_2, the particle goes in the state $|u_2\rangle$.