

**Lecture 14****Question 1.**<sup>1</sup> Atomic term symbol.

(1) Suppose that an atom has 4 electrons in different spatial orbitals. What are the possible values of the total spin quantum number  $S$ ? What is the spin multiplicity in each case?

(2) What atomic terms (include  $J$ ) are possible for the electron configuration  $ns^1nd^1$ ?

(3) What values of  $J$  may occur in the terms (a)  $^1S$ , (b)  $^2P$ , (c)  $^3P$ ? How many states (distinguished by the quantum number  $M_J$ ) belong to each level?

(4) Give the possible terms symbols (include  $J$ ) for  $np^1nd^1$ .

(5) The Zeeman effect is the modification of an atomic spectrum by a strong magnetic field. It arises from the interaction between applied magnetic fields and the magnetic moments due to orbital and spin angular momenta (recall the evidence provided for electron spin by the Stern-Gerlach experiment). Consider a p electron, with  $l = 1$  and  $m_l = 0, \pm 1$ . In the absence of a magnetic field, these three states are degenerate. When a field of magnitude  $B$  is present, the degeneracy is removed, and the state with  $m_l = +1$  moves up in energy by  $\mu B$ , the state with  $m_l = 0$  is unchanged, and the state with  $m_l = -1$  moves down in energy by  $\mu B$ , where the Bohr magneton (unit magnetic moment carried by a spinning electron)  $\mu = e\hbar/2m_e = 9.274 \times 10^{-24} \text{ J T}^{-1}$ . Therefore, a transition between a  $^1S_0$  term and a  $^1P_1$  term consists of three spectral lines in the presence of a magnetic field where, in the absence of the magnetic field, there is only one.

(a) Calculate the splitting in wavenumbers (in  $\text{cm}^{-1}$ ) between the three spectral lines of a transition between a  $^1S_0$  term and a  $^1P_1$  term in the presence of a magnetic field of 2 T (where  $1 \text{ T} = 1 \text{ kg s}^{-2} \text{ A}^{-1}$ ).

(b) Compare the value you calculated in (a) with typical optical transition wavenumbers, such as the middle of the visible spectrum ( $\sim 600 \text{ nm}$ ) and those for the Balmer series (transitions from  $n = 2$  to higher  $n$ , e.g.,  $n = 3$  and  $n = \text{infinity}$ ) of the H atom. Is the line splitting caused by normal Zeeman effect relatively small or relatively large?

**Question 2.** The algebra (No calculus involved!) of a two-electron atom: Slater determinants, spin eigenfunctions, and exchange interactions.

(1) For a single particle, the spin raising and lowering operators are defined as  $\hat{S}_+ = \hat{S}_x + i\hat{S}_y$  and  $\hat{S}_- = \hat{S}_x - i\hat{S}_y$ . For a multielectron system, we always think about the total spin. For a two-electron system, prove that the total spin  $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$  satisfies the following relation

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

(2) Write down the Slater determinant of a He atom in the following states: (a)  $1s^2$ , (b)  $1s^12s^1$ , (c)  $1s^12s^1$ , where  $1s$  and  $2s$  are the  $1s$  and  $2s$  spatial orbitals, and  $\uparrow$  and  $\downarrow$  are the  $\alpha$  and  $\beta$  electrons.

(3) Using the two-electron spin operator in (1) to validate that the Slater determinant of (a)  $1s^2$  is an eigenfunction of the total spin. What is the corresponding eigenvalue and total spin quantum number? What is the spin multiplicity (i.e.,  $2S+1$ , where  $S$  is the quantum number of total spin)?

(4) Is a single Slater determinant for (b)  $1s^12s^1$  an eigenfunction of the total spin? Why?

**Note:** This is why it is simply “illegal” to talk about the spin multiplicity of such an open-shell electronic configuration.

(5) Let us construct eigenfunction of the total spin  $\hat{S}^2$  by considering

(5a) [the Slater determinant of  $1s^12s^1$ ] + [the Slater determinant of  $1s^12s^1$ ]

(5b) [the Slater determinant of  $1s^12s^1$ ] – [the Slater determinant of  $1s^12s^1$ ]

<sup>1</sup> Adapted from Atkins, the 9<sup>th</sup> Ed., Chapter 9 – Exercises 9.23–9.26 and Problem 9.9.

Show that both **(5a)** and **(5b)** are eigenfunctions of the total spin. What is the spin multiplicity of **(5a)**? What is the spin multiplicity of **(5b)**?

**Hint:** First, show that

$$\hat{S}^2 |1s^\uparrow 2s^\downarrow\rangle = \hbar^2 [|1s^\uparrow 2s^\downarrow\rangle + |1s^\downarrow 2s^\uparrow\rangle]$$

and

$$\hat{S}^2 |1s^\downarrow 2s^\uparrow\rangle = \hbar^2 [|1s^\uparrow 2s^\downarrow\rangle + |1s^\downarrow 2s^\uparrow\rangle]$$

based on your work in **(4)**. Next, consider applying  $\hat{S}^2$  on the linear combinations.

**(6) (Optional – For bonus credits)** This question is purely algebraic and does not involve the computation of any integrals. Nevertheless, you will reveal a deep and unique kind of interaction that is purely quantum mechanical – the exchange interactions. Exchange interactions play a vital role in understanding the relative energies of different electronic configurations and the stability of radicals. For instance, the ground-state  $O_2$  is a triplet rather than a singlet state.

**Question:** Please show that the energy expectation for **(5a)** and **(5b)** are different, i.e., they are NOT degenerate. In particular, please show that the energy expectation value for **(5a)** is  $E_{1s} + E_{2s} + J_{1s,2s} - K_{1s,2s}$ , where  $E_{1s}$  is the 1s orbital energy for a single-electron hydrogenic atom with a nuclear charge of +2, and  $E_{2s}$  the 2s single-electron orbital energy.  $J_{1s,2s}$  is an integral (No need to compute the value of integral!) that characterizes the Coulomb repulsion between the 1s and 2s shell.  $K_{1s,2s}$  is an integral, the so-called **exchange** integral, that characterizes a **unique purely quantum mechanical interaction** between the two permutations of the electrons 1s(1)2s(2) and 1s(2)2s(1). For **(5b)**, the energy expectation value is  $E_{1s} + E_{2s} + J_{1s,2s} + K_{1s,2s}$ . Therefore, the energy difference between (5a) and (5b) is given by the exchange interaction  $2K_{1s,2s}$ .

**Note:** You do NOT need to compute the value of any integrals in this question. Simply compute the expectation value based on the definition and the expansion of the Slater determinants. Organize the terms into brackets and analyze the physical meaning of each term. If you do the algebra correctly, the  $J_{1s,2s}$  and  $K_{1s,2s}$  terms naturally arise.

**Hint:** The spin parts (i.e., spin eigenfunctions) also satisfy the orthonormalization condition. Since spin is nothing but a kind of (intrinsic) angular momentum and thus, its eigenfunctions obey the general properties of the angular momentum eigenfunctions as well:  $\langle \alpha(i) | \alpha(i) \rangle = 1$ ,  $\langle \beta(i) | \beta(i) \rangle = 1$ , and  $\langle \alpha(i) | \beta(i) \rangle = \langle \beta(i) | \alpha(i) \rangle = 0$  for electron  $i$ .

## Lecture 15

**Question 3.** Suppose that we do not know the trick of the rising and lowering operators and we are not good at solving the differential equation (which is certainly not trivial for a harmonic potential), then we could use the variational principle to estimate the ground-state energy for a 1D harmonic oscillator. Let us guess a trial function for a 1D harmonic oscillator (with mass  $m$  and angular frequency  $\omega$ ).

**(1)** We want a symmetric function because the harmonic potential  $V(x) = m\omega^2 x^2 / 2$  (in which  $x$  ranges from  $-\infty$  to  $+\infty$ ) is symmetric with respect to the axis  $x = 0$ . In addition, this function should approach zero when  $x$  is infinitely large. Our first guess (a real-valued even function) is:

$$\psi(x) = \frac{A}{x^2 + b^2}$$

where  $A$  is determined by normalization and  $b$  is the variational parameter. What is the variationally best solution to the ground-state energy of a 1D harmonic oscillator by using this trial function? Please compare your result with the exact ground-state energy – what is the percentage error?

**(2)** We like to use real-valued trigonometric functions to represent waves, and thus, our second guess is:

$$\psi(x) = \begin{cases} A\cos(\pi x/a) & \text{for } -a/2 < x < a/2 \\ 0 & \text{otherwise} \end{cases}$$

where  $A$  is determined by normalization and  $a$  is the variational parameter. This guess is inspired by the wavefunction of the particle-in-a-1D-box model in which we shift the range of the box from 0 to  $a$  to  $-a/2$  to  $a/2$ . What is the variationally best solution to the ground-state energy of a 1D harmonic oscillator by using this trial function? Please compare your result with the exact ground-state energy – what is the percentage error?

**Useful integrals:**

$$\int_0^{+\infty} \frac{1}{(x^2 + b^2)^2} dx = \frac{\pi}{4b^3}$$

$$\int_0^{+\infty} \frac{x^2}{(x^2 + b^2)^2} dx = \frac{\pi}{4b}$$

$$\int_0^{+\infty} \frac{x^2}{(x^2 + b^2)^4} dx = \frac{\pi}{32b^5}$$

$$\int_0^{+\infty} \frac{1}{(x^2 + b^2)^4} dx = \frac{5\pi}{32b^7}$$

$$\int_{-\pi/2}^{\pi/2} x^2 \cos^2 x dx = \frac{\pi}{4} \left( \frac{\pi^2}{6} - 1 \right)$$

**Question 4.** Calculate the *effective* (screened) nuclear charge  $Z$  (the variational parameter) and the ground-state energy of a  $\text{Li}^+$  cation variationally by using a simplest two-electron trial function. Spin does not affect the energy for this closed-shell system (in which a pair of spin-up and spin-down electrons occupy the same spatial orbital), and thus we can simply ignore spin in the variational calculation. Compare your result with the experimental ionization energy (from  $\text{Li}^+$  to  $\text{Li}^{3+}$  requires an energy compensation of 198 eV): What is the percentage error?

The two-electron trial wavefunction  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  is the product of the two 1s orbitals of the hydrogenic atom with a nuclear charge of +3:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = 1s(\mathbf{r}_1)1s(\mathbf{r}_2) = \left( \frac{Z^3}{\pi a_0^3} \right) \exp \left[ -\frac{Z(r_1 + r_2)}{a_0} \right]$$

where  $a_0$  is the first bohr radius, and  $r_i$  the separation between electron  $i$  and the origin (located on the nucleus). We can also write the above trial function in atomic units:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = 1s(\mathbf{r}_1)1s(\mathbf{r}_2) = \left( \frac{Z^3}{\pi} \right) \exp[-Z(r_1 + r_2)]$$

in which the distance is in the atomic unit of length (i.e., 1 bohr radius).

**Hint:**

(a) Use atomic units in this question will simplify all the coefficients. In atomic units,  $-\hbar^2/2m = -1/2$ ,  $e^2/(4\pi\epsilon_0) = 1$ ,  $a_0 = 1$  (1 bohr radius), and  $E_{1s}(\text{H}) = -1/2$ . Remember to convert your final energy from atomic units to the SI units (or to eV) when you try to make a comparison

between the computation and the experimentally measured values. One atomic unit (1 a.u.) of energy is equivalent to 27.2 eV.

(b) Rewrite the two-electron Hamiltonian  $\hat{H}$  (with a nuclear charge of +3) in terms of the single-electron Hamiltonians  $\hat{h}_1$  and  $\hat{h}_2$  (i.e., a hydrogenic atom with the nuclear charge being the effective charge  $Z$ ), and thus, the variational parameter  $Z$  is naturally included in  $\hat{H}$ .

(c) Useful integrals:

- The two-electron integral (in atomic units)

$$\langle \psi(\mathbf{r}_1, \mathbf{r}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi(\mathbf{r}_1, \mathbf{r}_2) \rangle = \frac{5}{8} Z$$

where  $|\mathbf{r}_1 - \mathbf{r}_2|$  is the separation between electron 1 and 2.

- Exponential function integral

$$\int_0^{+\infty} x^n e^{-ax} dx = n! \left(\frac{1}{a}\right)^{n+1}$$

### Lecture 16

**Question 5.** Repeat the derivation we covered in class for the Born-Oppenheimer approximation by using a  $\text{H}_2$  molecule as an example. **Use atomic units.** (Please write out the total molecular Hamiltonian, the two nuclear and the two electronic coordinates explicitly.)

### Lecture 17

**Question 6.** Given the following two-level system:

$$\hat{H} = \varepsilon (|1\rangle\langle 1| - |2\rangle\langle 2| + |1\rangle\langle 2| + |2\rangle\langle 1|)$$

where  $|1\rangle$  and  $|2\rangle$  are orthonormal basis and  $\varepsilon$  is a constant with the unit of energy.

(1) Construct the Hamiltonian matrix  $\mathbf{H}$  for this two-level system.

Hint: The matrix elements are determined by  $\langle i|\hat{H}|j\rangle$  using the given basis  $|1\rangle$  and  $|2\rangle$ .

(2) Find the energy levels, i.e., eigenvalues (expressed in terms of  $\varepsilon$ ) and the eigenvectors, i.e., eigenstates (expressed in terms of the combination of the two basis states). Do not forget to normalize each eigenvector (i.e., the length of the vector is normalized to 1).

### Lecture 18

**Question 7.** The MO wavefunction of a linear  $\text{H}_3$  molecule may be modelled by  $\psi = c_A s_A + c_B s_B + c_C s_C$ , in which  $s_i$  denotes the hydrogen 1s orbital of the relevant atom.

Let us use Hückel's approximations for the  $\sigma$  electrons and assume that

$$H_{ij} = \begin{cases} \alpha & (i=j) \\ \beta & (i,j \text{ are neighbours}) \\ 0 & (i,j \text{ are not neighbours}) \end{cases} \quad \text{and the overlap matrix } \mathbf{S} \text{ is an identity matrix } \mathbf{I} \text{ (i.e., we ignore}$$

the orbital overlaps). (a) Solve for the energy levels (in terms of the parameters  $\alpha < 0$  and  $\beta < 0$ ), (b) identify the bonding, anti-bonding, and non-bonding orbitals, and (c) schematically plot the corresponding molecular orbitals (pay attention to the relative size and phase of atomic orbitals).

**Question 8.** The trimethylenemethane radical,  $\cdot\text{C}(\text{CH}_2)_3$ , is stable at low temperature and can be prepared by the photolysis of 4-methylene-1-pyrazoline (reported by P. Dowd, *J. Am. Chem. Soc.*, 1966, 88, 2587). Trimethylenemethane and its derivatives have been postulated to explain the

formation of “rearranged” methylenecyclopropanes in the pyrolyses or photolysis of 4-alkylidene-1-pyrazolines and in the thermal isomerization of methylenecyclopropanes.

Please apply Hückel’s method for the  $\pi$  electrons in  $\cdot\text{C}(\text{CH}_2)_3$ : **(a)** Compute the  $\pi$ -MO energy levels (in terms of the parameters  $\alpha < 0$  and  $\beta < 0$ ), **(b)** identify the bonding, anti-bonding, and non-bonding orbitals, **(c)** schematically plot the corresponding molecular orbitals (pay attention to the relative size and phase of the atomic orbitals), and **(d)** analyze the bond order between **the central carbon (let us label it as atom 1)** and a  $\text{CH}_2$  carbon. Do you expect to have a longer or shorter C-C bond in  $\cdot\text{C}(\text{CH}_2)_3$  as compared to a typical single C-C bond (e.g., in ethane)?

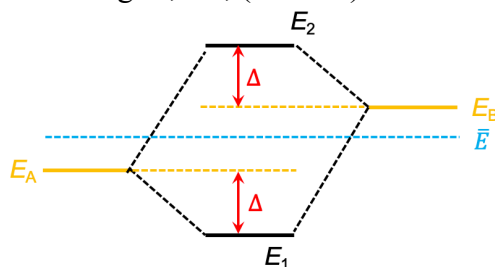
**Question 9. Analyze a single chemical bond in a heteronuclear diatomic molecule AB with a two-by-two determinant under the minimal valence basis.** As a rough approximation, let us ignore the orbital overlap (i.e., set  $S_{AB} = 0$ ) for AB, in which atom A contributes one basis (a real-valued atomic orbital), and atom B contributes one basis (real-valued) as well. We have a two-electron two-center bond. We have four important integrals (which are all  $\leq 0$  at equilibrium geometry or beyond) for this molecule:  $H_{AA}$ ,  $H_{AB}$ ,  $H_{BA}$ , and  $H_{BB}$ . (No need to compute them! Simply use the notations to represent these integrals.)

**(1)** Show that  $H_{AB} = H_{BA}$  with real-valued basis functions.

**(2)** Construct the two-by-two secular determinant and solve for the eigenvalues.

**Note:** The energy eigenvalues are expressed in terms of the integrals  $H_{AA}$ ,  $H_{AB}$ , and  $H_{BB}$ .

**(3)** For a heteronuclear diatomic molecule,  $H_{AA} \neq H_{BB}$ . Let’s approximate  $H_{AA}$  as the valence-shell atomic-orbital energy of atom A (i.e.,  $E_A$ ) and  $H_{BB}$  as the valence-shell atomic-orbital energy of atom B (i.e.,  $E_B$ ). For our convenience, we set  $E_B > E_A$ . Based on **(2)**, please derive the following MO diagram, in which  $\Delta$  is a non-negative constant (at a given finite bond length), and  $\bar{E}$  is the average of the two atomic-orbital energies, i.e.,  $(E_A + E_B)/2$ . What is the expression of  $\Delta$ ?



**(4)** Analyze the following situations by using the quantitative results obtained above.

**(4a)** In order to form a strong bond, do we need a larger value of  $\Delta$  or a smaller value?

**(4b)** If  $E_B \gg E_A$ , that is, if the atomic-orbital energy difference between B and A is huge (in fact, it is so huge that  $H_{BB} - H_{AA} \gg H_{AB}$ ), do you expect a strong or weak bond?

**(4c)** If  $E_B \approx E_A$ , do you expect a strong or weak bond (as compared to (4b))?

**(4d)** The value of  $H_{AB}$  decays to zero with respect to the increase of the interatomic distance  $R_{AB}$ . What are the molecular-orbital energy eigenvalues  $E_1$  and  $E_2$  when  $R_{AB}$  goes to infinity?

**(4e)** As a more refined treatment, we should not ignore the overlap  $S_{AB}$ , since its value is  $\geq 0$  in general. Do you expect that  $E_2 - \bar{E}$  becomes smaller or larger than  $\bar{E} - E_1$  when  $S_{AB} > 0$ ? This is the so-called “closed-shell repulsive effect”, which means the energy increase caused by a doubly occupied antibonding orbital is bigger than the energy stabilization caused by bonding.

**(4f)** We know that the value of the integral  $H_{AB}$  is roughly proportional to the overlap  $S_{AB}$  (if we consider the exchange  $K$  being small). If atomic orbital A and B do not have the same symmetry or they overlap poorly, i.e.,  $S_{AB} = 0$ , do you expect a strong or weak bond?