Chem 332 **Problem Set #5** (due Monday 01 March, in class)

Q1. Suppose an assignment question asks you to give the orbital and spin angular momentum for an atom
[1] in a $^2D_1$ state. Why should you email your instructor to see if there is a misprint in the question?

Q2. The partial term symbols for nickel ($[Ar]4s^2 3d^8$) are ^1S, ^1D, ^1G, ^3P and ^3F.

a) Calculate the J values for each of these states and give the complete term symbols.

[3] **b)** Give the term symbol for the ground state.

Q3. The trial wave function $\psi = c_1 1s_A + c_2 1s_B$ for the H_2^+ molecule ion gives the overlap integral (S), Coulomb integral (J) and exchange integral (K).

a) Why is $S = \int 1s_A 1s_A d\tau = \left(1 + R + \frac{R^2}{3}\right) e^{-R}$ called the **overlap integral**?

b) Show $S \rightarrow 0$ as $R \rightarrow \infty$.

c) Why is $J = \int 1s_A \left(\frac{1}{R} - \frac{1}{r_A}\right) 1s_A d\tau = \left(1 + \frac{1}{R}\right) e^{-R}$ called the **Coulomb integral**?

[5] **d)** Why is $K = \int 1s_A \left(\frac{1}{R} - \frac{1}{r_A}\right) 1s_B d\tau = (1 + R)\, e^{-R}$ called the **exchange integral**?

e) The exchange integral has no classical interpretation. Explain.

Q4. In the treatment of the H_2^+ molecule ion, the trial wave function $\psi = c_1 1s_A + c_2 1s_B$ gives the determinantal equation

$$\begin{vmatrix} H_{AA} - E & H_{AB} - SE \\ H_{AB} - SE & H_{BB} - E \end{vmatrix} = 0$$

with (in atomic units with energies in Hartrees: 1 Hartree = 27.20 eV)

$$H_{AA} = H_{BB} = \int 1s_A \hat{H} 1s_A d\tau = -\frac{1}{2} + J$$

$$H_{AB} = H_{Ba} = \int 1s_A \hat{H} 1s_B d\tau = -\frac{S}{2} + K$$

... page 2

(Q4. cont.)

a) Use the determinantal equation to show the variational energies of H_2^+ are

$$E_- = \frac{H_{AA} - H_{AB}}{1 - S} \qquad E_+ = \frac{H_{AA} + H_{AB}}{1 + S}$$

b) In terms of the overlap, Coulomb and exchange integrals, show

$$E_- = -\frac{1}{2} + \frac{J - K}{1 - S} \qquad E_+ = -\frac{1}{2} + \frac{J + K}{1 + S}$$

[6] **c)** For the energy state E_-, show $c_1 = -c_2$ and

$$\psi_- = \frac{1s_A - 1s_B}{\sqrt{2(1 - S)}}$$

(*hint*: ψ_- is normalized)

d) For the state with energy E_+, show $c_1 = c_2$ and

$$\psi_+ = \frac{1s_A + 1s_B}{\sqrt{2(1 + S)}}$$

(*hint*: ψ_+ is normalized)

Q6. Without actually performing the calculations, explain how the energy expression for H_2^+

$$E_+ = -\frac{1}{2} + \frac{J + K}{1 + S}$$

to calculate:

[2] **a)** the force constant k of the H_2^+ bond

b) the fundamental vibration frequency ν of H_2^+.

Q7. **a)** Is the bond in the H_2^+ molecule ion weaker than the bond in the H_2 molecule? Explain.

[2] **b)** Is the bond length of H_2^+ longer than the bond length of H_2? Explain.

Q8. The trial wave function $\psi = c_1 1s_A + c_2 1s_B$ gives 1.77 eV and 0.132 nm for the dissociation energy and bond length of H_2^+, which are not in very good agreement with the measured values (2.78 eV and 0.106 nm). This treatment is useful, however, to illustrate how a linear combination of atomic orbitals can be used to estimate the wave functions of molecules. Describe how a more accurate quantum mechanical treatment of H_2^+ could be developed. [1]

Chem 332 Assignment #5

Q1 $^{2}D_{1}$ state has $L = 2$

from the spin multiplicity $= 2 = 2S+1$, get $S = 1/2$

for $L = 2$, M values are $-2, -1, 0, 1, 2$

for $S = 1/2$, M_S values are $-1/2, 1/2$

$M_J = M + M_S$, so M_J values range from

$L+S$ to $|L-S|$ $\quad J = \frac{5}{2}, \frac{3}{2}$ for ^{2}D

indicating $J = 5/2$ $\quad$ $^{2}D_{1}$ is a misprint

$$\boxed{\text{the term symbol should be } {}^{2}D_{5/2} \text{ or } {}^{2}D_{3/2}}$$

Q2 as shown in Q1, M_J values range from $-M-M_S$ to $M+M_S$

$$\boxed{{}^{1}S} \text{ has } \left.\begin{array}{l} L=0,\ M=0 \\ 2S+1=1,\ S=0,\ M_S=0 \end{array}\right\} \ J \text{ can only be } 0$$

for the total angular momentum

$(-M-M_S=0$ to $M+M_S=0)$

$$\Rightarrow \boxed{{}^{1}S_{0}}$$

$$\boxed{{}^{1}D} \text{ has } \left.\begin{array}{l} L=2,\ M_S=-2,-1,0,1,2 \\ 2S+1=1,\ S=0,\ M_S=0 \end{array}\right\} \ J=2$$

M_J from $-M-M_S=-2$ to $M+M_S=2$

$$\Rightarrow \boxed{{}^{1}D_{2}}$$

(Q2 cont.)

$$\left(\begin{array}{ccccccc} & S & P & D & F & G & H\cdots \\ L= & 0 & 1 & 2 & 3 & 4 & 5\cdots \end{array}\right)$$

^1G has $L=4$, $M=-4,-3,-2,-1,0,1,2,3,4$

$2S+1=1$, $S=0$, $M_S=0$ $\boxed{^1G_4}$

$M+M_S=M_J$ ranges from -4 to $+4$ $J=4$

$\boxed{^3P}$ has $L=1$, $S=1$

$M=-1,0,1$ $M_S=-1,0,1$

adding M and M_S gives M_J values

The largest J value corresponds to $\vec{L}$ and $\vec{S}$ pointing in the same direction, which gives $J=L+S$

The smallest value of J corresponds to $\vec{L}$ and $\vec{S}$ pointing in opposite directions, which gives $J=|L-S|$

So the possible J values range from:

$L+S,\ L+S-1,\ L+S-2,\ \ldots,\ |L-S|$

Here, with $L=1$ and $S=1$, the J values for ^3P states are:

$L+S=2$ $L+S-1=1$ and $|L-S|=2-2=0$

and the complete term symbols are

$\boxed{^3P_2 \qquad ^3P_1 \qquad ^3P_0}$ (illustrated in the course notes for carbon atoms with $2p^2$)

(Q2 cont.)

$\boxed{{}^3F}$ has $L = 3$, $S = 1$

J values range from $L+S$, $L+S-1$, $L+S-2$, …, $|L-S|$

$\Rightarrow 4, 3, 2$

$$\boxed{{}^3F_4 \quad {}^3F_3 \quad {}^3F_2}$$

b) term symbols for the nickel [Ar] $3s^2 3d^8$ configuration:

${}^1S_0$, ${}^1D_2$, ${}^1G_4$, ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, ${}^3F_4$, ${}^3F_3$, ${}^3F_2$

<u>Hund Rule #1</u> triplets ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, ${}^3F_4$, ${}^3F_3$, ${}^3F_2$ have lower energy than the singlets (higher spin multiplicity)

<u>Hund's Rule #2</u> triplet F states ${}^3F_4$, ${}^3F_3$, ${}^3F_2$ have lower energy than the triplet D states

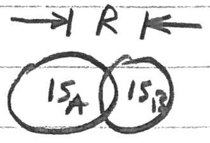
(why? F states have larger orbital angular momentum than D states)

<u>Hund's Rule #3</u> The Ni [Ar] $4s^2 3d^8$ electronic configuration $\Rightarrow$ 3d subshell is <u>more than half full</u>

so the $\boxed{{}^3F_4}$ state (largest J value) is the ground state

(Q3) Our treatment of bonding for the hydrogen molecule ion H_2^+ used the simple, but reasonable, trial wave function

$$\psi_{H2+} = c_1 1s_A + c_2 1s_B$$

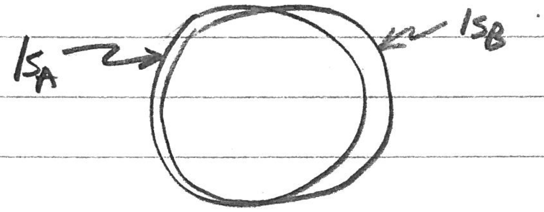


with a 1s atomic orbital centered on proton A and a 1s atomic orbital centered on proton B

a) The overlap integral $S = \int 1s_A \, 1s_B \, d\tau$

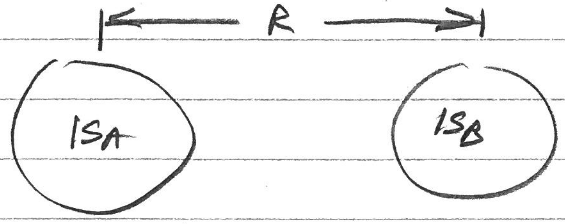
indicates how much of the electron density in the $1s_A$ atomic orbital centered on proton A overlaps the electron density in the $1s_B$ atomic orbital centered on proton B

$R \cong 0$



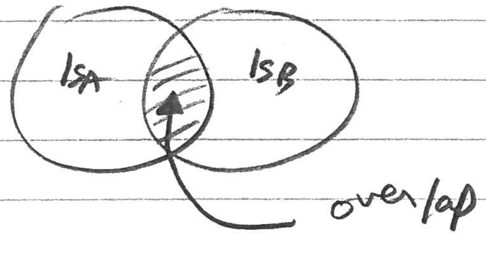
almost complete overlap, $S \cong 1$
(1s orbitals are normalized)

Large R values



almost zero overlap
$S \cong 0$

intermediate R values



overlap integral > 0
< 1

(Q3 cont.)

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

R and $R^2/3$ increase as R increases, but e^{-R} decreases much more rapidly so the exponential term "wins" as $R \rightarrow \infty$ and $S \rightarrow 0$ in this limit no overlap at $R = \infty$

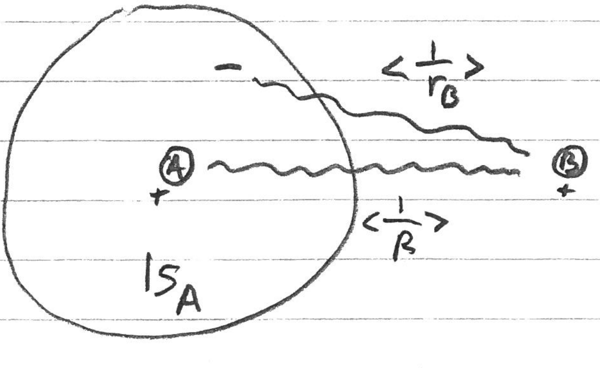
(use l'Hopital's rule or plot S against R to show this)

also, as $R \rightarrow 0$, $S \rightarrow \left(1 + 0 + \frac{0^2}{3}\right) e^{-0} = 1$

complete overlap at $R = 0$

c) $J = \int 1s_A \left(\frac{1}{R} - \frac{1}{r_B}\right) 1s_A \, d\tau \Rightarrow \left\langle \frac{1}{R} - \frac{1}{r_B} \right\rangle$

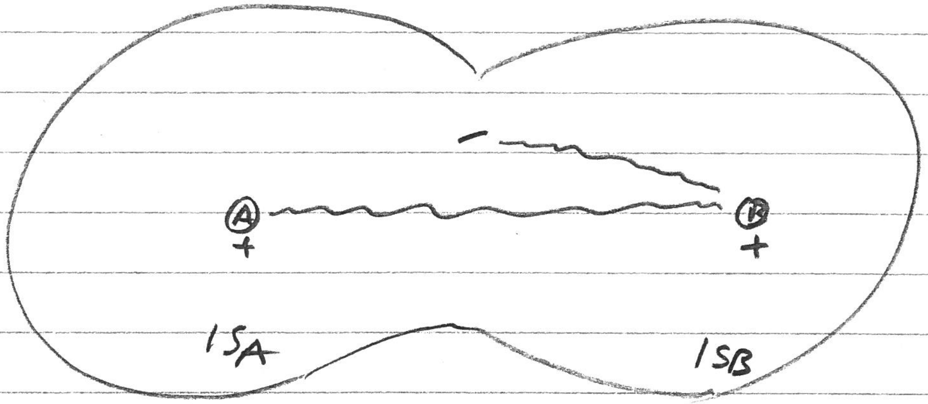
is called the Coulomb integral because it gives the electric potential (Coulomb) energy for the interaction of the electron localized in the $1s_A$ orbital with proton B, and the proton-proton potential energy



(Q3 cont.)

d) $$K = \int \underline{\underline{1s_A}} \left(\frac{1}{R} - \frac{1}{r_A}\right) \underline{\underline{1s_B}} \, d\tau$$

is called the exchange integral because it give the electric potential energy when the electron in H_2^+ is "exchanged" between both proton A (in the $1s_A$ atomic orbital) and proton B (in the $1s_B$ atomic orbital)



e) the exchange integral is "non-classical" because the electron is simultaneously located ("delocalized") in different places: the $1s_A$ and $1s_B$ orbitals

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Q4 a) the secular determinant $$\begin{vmatrix} H_{AA}-E & H_{AB}-SE \\ H_{AB}-SE & \underset{(= H_{AA})}{H_{BB}-E} \end{vmatrix} = 0$$

gives

$$(H_{AA}-E)^2 - (H_{AB}-SE)^2 = 0$$

$$(H_{AA}-E)^2 = (H_{AB}-SE)^2 \qquad \therefore \; H_{AA}-E = \pm(H_{AB}-SE)$$

(Q4 cont.)

b) <u>positive root</u> $H_{AA} - E = +(H_{AB} - SE)$

$$E - SE = H_{AA} - H_{AB}$$

$$E = \frac{H_{AA} - H_{AB}}{1-S} = \frac{-\frac{1}{2} + J - \left(-\frac{S}{2} + K\right)}{1-S}$$

$$= \frac{(S-1)\frac{1}{2} + \cancel{(1-S)}\frac{1}{2} \cancel{-\frac{1}{2}} + J + \cancel{\frac{S}{2}} - K}{1-S}$$

$$E = \boxed{-\frac{1}{2} + \frac{J-K}{1-S} \equiv E_-}$$ (due to the minus signs)

<u>negative root</u> $H_{AA} - E = -(H_{AB} - SE)$

$$E + SE = H_{AA} + H_{AB}$$

$$E = \frac{H_{AA} + H_{AB}}{1+S} = \frac{-\frac{1}{2} + J + \frac{-S}{2} + K}{1+S}$$

$$= \frac{-(1+S)\frac{1}{2} + \cancel{(1+S)}\frac{1}{2} - \cancel{\frac{1}{2}} + J - \cancel{\frac{S}{2}} + K}{1+S}$$

$$= \boxed{-\frac{1}{2} + \frac{J+K}{1+S} \equiv E_+}$$ ("+" signs - due to the "+" signs)

note: as $R \to \infty$, we have a $1s_A$ hydrogen atom and proton B infinitely far away (no interaction)

as $R \to 0$: $S \to 0$, $J \to 0$, $K \to 0$

and $E \to -\frac{1}{2}$ $\left(= -\frac{1}{2}\right.$ Hartree $\left.= -13.60 \text{ eV}\right)$

(Q4 cont.)

c) the trial wave function for H_2^+ is

$$\psi = c_1 1s_A + c_2 1s_B$$

but what are c_1 and c_2 ?

the secular equation gives $(H_{AA} - E)c_1 + (H_{AB} - SE)c_2 = 0$

for energy E_- $\quad (H_{AA} - E_-)c_1 = -(H_{AB} - SE_-)c_2$

$$\left(\cancel{-\frac{1}{2}} + J - \left[\cancel{-\frac{1}{2}} + \frac{J-K}{1-S}\right]\right)c_1 = -\left(\cancel{-\frac{S}{2}} + K - S\left[\cancel{-\frac{1}{2}} + \frac{J-K}{1-S}\right]\right)c_2$$

$$\left(J - \frac{J-K}{1-S}\right)c_1 = -\left(K - S\,\frac{J-K}{1-S}\right)c_2$$

$$\frac{J(\cancel{1}-S)\cancel{-J}+K}{1-S}\,c_1 = -\,\frac{K-\cancel{KS}-SJ+\cancel{SK}}{1-S}$$

$$\cancel{\frac{K-SJ}{1-S}}\,c_1 = -\,\cancel{\frac{K-SJ}{1-S}}\,c_2$$

$$\boxed{c_1 = -c_2} \quad \text{for } E = E_-$$

similarly,

for energy E_+ $\quad (H_{AA} - E_+)c_1 = -(H_{AB} - SE_+)c_2$

$$\left(-\frac{1}{2} + J - \left[-\frac{1}{2} + \frac{J+K}{1+S}\right]\right)c_1 = -\left(-\frac{S}{2} + K - S\left[-\frac{1}{2} + \frac{J+K}{1+S}\right]\right)c_2$$

$$\vdots$$

$$\frac{K-SJ}{1+S}\,c_1 = \frac{K-SJ}{1+S}\,c_2 \qquad \boxed{c_1 = c_2} \text{ for } E = E_+$$

(Q4 cont.)

<u>wave function for $E = E_-$</u> $\quad \psi_- = c_1 1s_A - c_1 1s_B$

$(c_1 = -c_2)$

normalization requirement $\quad 1 = \int \psi_-^* \psi_- \, d\tau$

$$\left(\begin{array}{l} c_1, \psi_- \text{ are real:} \\ c_1^* = c_1 \\ \psi_-^* = \psi \end{array} \right)$$

$$1 = \int (c_1 1s_A - c_1 1s_B)^* (c_1 1s_A - c_1 1s_B) \, d\tau$$

$$= c_1^2 \overset{=1}{\int 1s_A 1s_A \, d\tau} - c_1^2 \overset{=S}{\int 1s_A 1s_B \, d\tau} - c_1^2 \overset{=S}{\int 1s_B^* 1s_A \, d\tau} + c_1^2 \overset{=1}{\int 1s_B^* 1s_B \, d\tau}$$

$$= c_1^2 - c_1^2 S - c_1^2 S + c_1^2$$

$$1 = c_1^2 (2 - 2S) \qquad \boxed{c_1 = \frac{1}{\sqrt{2(1-S)}}}$$

$$\boxed{\psi_- = \frac{1s_A - 1s_B}{\sqrt{2(1-S)}}}$$

d) <u>wave function for $E = E_+$</u> $\quad \psi_+ = c_1 1s_A + c_1 1s_B$

$(c_1 = c_2)$

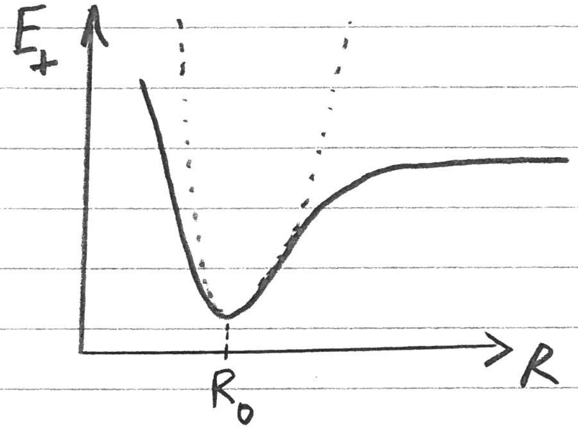
$$1 = \int (c_1 1s_A + c_1 1s_B)^* (c_1 1s_A + c_2 1s_B) \, d\tau$$

$$= c_1^2 + c_1^2 S + c_1^2 S + c_1^2$$

$$1 = c_1^2 (2 + 2S) \qquad \boxed{c_1 = \frac{1}{\sqrt{2(1+S)}}}$$

$$\boxed{\psi_+ = \frac{1s_A + 1s_B}{\sqrt{2(1+S)}}}$$

Q6 The variational treatment of H_2^+ gives the energy of the molecule as a function of the internuclear distance R.



To find the equilibrium bond length R_0,

solve $\frac{dE_+}{dR} = 0$

define $x = R - R_0$ as the displacement of the nuclei from the equilibrium bond length

for a harmonic oscillator, the potential energy is $E_+ = \frac{1}{2} kx^2$ (accurate near $R=R_0$)

$$\frac{dE_+}{dx} = \frac{1}{2} 2kx = kx$$

$$\boxed{\frac{d^2E_+}{dx^2} = \frac{d(kx)}{dx} = k}$$

k is the force constant for the vibration of H_2^+

a) evaluate the force constant by taking the second derivative of E_+ at $R = R_0$

b) vibration frequency $\boxed{\nu_{calc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}}$

can test the accuracy of ψ_+ by comparing ν_{calc} to $\nu_{measured}$

(Q7) H_2^+ molecule ion

one bonding electron

$H\text{---}H^+$

$\sim \frac{1}{2}$ bond

$$\left.\begin{array}{l} R_0 = 0.132\text{ nm} \\ E_+ = -1.77\text{eV} \end{array}\right\}\text{ variational calculation}$$

$$\left.\begin{array}{l} R_0 = 0.106\text{ nm} \\ E_+ = -2.78\text{ eV} \end{array}\right\}\text{ measured}$$

H_2 molecule

two bonding electrons

$H - H$

~ 1 bond

(stronger bond than H_2^+, shorter bond length)

$$\left.\begin{array}{l} R_0 = 0.087\text{ nm} \\ E_+ = 3.15\text{ eV} \end{array}\right\}\text{ variational calculations}$$

$$\left.\begin{array}{l} R_0 = 0.074\text{ nm} \\ E_+ = 4.75\text{ eV} \end{array}\right\}\text{ measured}$$

a) H_2^+ has a longer bond length than H_2

b) H_2^+ has a weaker bond than H_2

"makes sense"

H_2^+ has only one bonding electron, but H_2 has two

(Q8) to improve our $\psi = c_1 1s_A + c_2 1s_B$ variational treatment of H_2^+:

i) treat the nuclear charge ($Z_A = Z_B = 1$) as a variational parameter

ii) include additional atomic orbitals (2s, 2p, ...)

iii) use additional basis set functions (e.g. Gaussians)