Chemistry 691, Final Exam, May 17 2016

1. The positron, designated e^+ has an electric charge of $+1e$, a spin of $\frac{1}{2}$, and has the same mass as an electron. Consider a system consisting of a He atom and a positron. Answer the following questions:

    a. What is the Hamiltonian for the motion of the two electrons and the positron around the He nucleus? (5 pts)

    b. Assume that the electrons and the positron are described by identical $1s$ orbitals with exponent ζ

$$1s(r) = (4\zeta^3)^{1/2}\exp(-\zeta r), \quad \text{where} \int_0^\infty 1s(r)^2 r^2 dr = 1$$

In other words, model the attachment of a positron to the $1s^2$ state of He by placing all three particles in an idential $1s$ orbital. Knowing that

$$\langle 1s| -\frac{1}{2}\nabla^2|1s\rangle = \frac{1}{2}\zeta^2, \quad \langle 1s|\frac{1}{r}|1s\rangle = \zeta, \text{ and } [1s^2|1s^2] = 5\zeta/8$$

estimate the energy of the $\text{He}\cdots e^+$ system. (10 pts)

    c. Suppose you model the He atom (just two electrons, no positron) by placing the two electrons in two $1s$ orbitals with different values of ζ. Call this a $1s1s'$ ground state. In this approximation write down an expression for the properly symmetrized and normalized electronic wavefunction for He. (5 pts)

    d. In this $1s1s'$ approximation, give an expression for the energy of He in terms of the integrals

$$S = \langle 1s|1s'\rangle, \quad h_{1s1s} = \langle 1s|\hat{h}|1s\rangle, \quad h_{1s'1s'} = \langle 1s'|\hat{h}|1s'\rangle, \quad h_{1s1s'} = \langle 1s|\hat{h}|1s'\rangle$$

$$[1s^2|1s'^2] = \int 1s(1)^2|1/r_{12}|1s'(2)^2 d\tau_1 d\tau_2, \text{ and } [1s1s'|1s'1s] = \int 1s(1)1s'(1)|1/r_{12}|1s'(2)1s(2)d\tau_1 d\tau_2$$

Here $\hat{h} = -\frac{1}{2}\nabla^2 - 2/r$. Note that $h_{1s1s'} = h_{1s'1s}$. *Hint:* in the case that $1s' =$1s, the expression should revert to the expression for the energy of the $1s^2$ single determinant He wavefunction. (7 pts)

2. Consider the transition from a ground electronic state of a diatomic molecule ($T_e = 0$, since it's in the ground electronic state) in vibrational level $v'' = 0$ to the v' excited vibrational manifold of an excited electronic state ($T_e = T'_e$). Assume that only the ω_e,

$\omega_e x_e$, B_e, and α_e spectroscopic constants in each state are non-zero (you can neglect all other spectroscopic constants). Assume also that all spectroscopic constants are given in cm^{-1}.

a. Write a general expression for the frequency difference for P-branch and R-branch lines associated with $J'' \to J'$ components of the $v'' = 0 \to v'$ vibrational transition. This expression will be a function of J'', J', v' and the spectroscopic constants in the two electronic states. (8 pts)

b. What is the splitting (in wavenumber units) between the location of the $J'' = 0 \to J' = 1$ R-branch line and the $J'' = 1 \to J' = 0$ P-branch line? (5 pts)

c. Assume that $B_e'' > B_e'$ (in other words the rotational constant in the excited state is less than in the ground state). A "band head" occurs at the value of J where there is a maximum or minimum in the expression in part (a). In which branch will this "band head" occur and at what (approximate) value of J'? (explain your answers). (10 pts)

3. Consider the cyclobutadiene molecule, shown below as symmetric (square) in the left panel and distorted (rectangular) in the right panel. The molecule lies in the yz plane. The
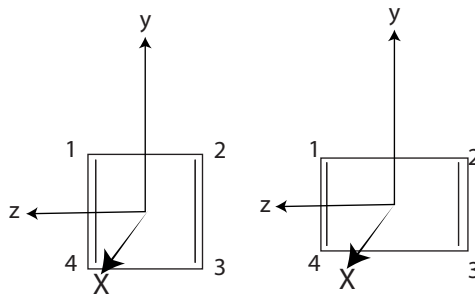
origin of the coordinate system is at the center of the molecule. Each π molecular orbital can be written as

$$\pi_i = \sum_{j=1}^{4} C_{ij} 2p_{zj}$$

where i indicates the orbital and j indicates the atoms as numbered in the figure. The coefficients are normalized as

$$\sum_{j=1}^{4} C_{ij}^2 = 1$$

- In symmetric geometry, the lowest π orbital has energy 2β and coefficients $C_{1j} = 1/2$ (identical for all j).

- The two next highest π orbitals are degenerate, both with energy 0, and coefficients

$$C_{21} = C_{22} = 1/2; \, C_{23} = C_{24} = -1/2$$

$$C_{31} = C_{34} = 1/2; \, C_{32} = C_{33} = -1/2$$

Both these last two orbitals are non-bonding (energy 0). There is a positive overlap between two pairs of $2p_z$ orbitals which is counteracted by a negative overlap between the two other pairs.

- Finally, the highest π orbital has energy -2β and coefficients $C_{41} = 1/2 = C_{43}$; $C_{42} = -1/2 = C_{44}$.

In the distorted (rectangular) geometry, the symmetry of the molecule belongs to the D_{2h} irreducible representation, with character table shown below. Here, C_2 designates a two-fold

TABLE I. Character table for D_{2h} symmetry.

Character	E	$C_2(x)$	$C_2(y)$	$C_2(z)$	i	$\sigma_v(xy)$	$\sigma_v(xz)$	$\sigma_v(yz)$	linear	quadratic	cubic
a_g	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2, y^2, z^2	-
b_{1g}	+1	+1	−1	−1	+1	+1	−1	−1	R_z	xy	-
b_{2g}	+1	−1	+1	−1	+1	−1	+1	−1	R_y	xz	-
b_{3g}	+1	−1	−1	+1	+1	−1	−1	+1	R_x	yz	-
a_u	+1	+1	+1	+1	−1	−1	−1	−1	-	-	xyz
b_{1u}	+1	+1	−1	−1	−1	−1	+1	+1	z	-	-
b_{2u}	+1	−1	+1	−1	−1	+1	−1	+1	y	-	-
b_{3u}	+1	−1	−1	+1	−1	+1	+1	−1	x	-	-

rotation around the indicated axis, i designates inversion $(x, y, z \rightarrow -x, -y, -z)$, and the three σ's are mirror reflections in the indicated planes.

Answer the following questions:

a. What are the characters of the four π_i molecular orbitals? *Hint:* All the molecular orbitals have the same symmetry property of the linear (x, y, z) or quadratic (xy, yz, xz) functions. After making this identification, the symmetry designation of each molecular orbital can be looked up in the above character table. (9 pts)

b. The ground electronic state is a triplet: $\Psi_1 = |\pi_1 \bar{\pi}_1 \pi_2 \pi_3|$. The overall symmetry of this state can be designated by the term symbol ^{2S+1}X where X is the character of the

symmetry of the complete electronic wavefunction (written in upper case, to distinguish from the symmetry of the individual molecular orbitals). What is this term symbol for the ground electronic state. (9 pts)

c. There are also three degenerate singlet states, the first $\Psi_2 = |\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2|$, the second $\Psi_3 = |\pi_1\bar{\pi}_1\pi_3\bar{\pi}_3|$, and the third being the singlet coupled equivalent of $m_s = 0$ component of the ground state, namely $\Psi_4 = 2^{-1/2}[|\pi_1\bar{\pi}_1\pi_2\bar{\pi}_3| - |\pi_1\bar{\pi}_1\bar{\pi}_2\pi_3|]$ What are the term symbols for these states? (7 pts)

4. Consider the electronic ground state of the B atom (5 electrons; $1s^2 2s^2 2p$). The orbital angular momentum $l = 1$ and the spin angular momentum $s = 1/2$. The projection quantum numbers m_l can be 1, 0, or -1 and $m_s = 1/2$ or $-1/2$, We can couple $\vec{l}$ and $\vec{s}$ to get the total angular momentum $\vec{j}$, with $|l - s| \leq j \leq l + s$. The coupled states $|jmls\rangle$ (where m is the projection of j) are linear combinations of the uncoupled state $|lm_lsm_s\rangle$. For simplicity, since l and s are unchanged, we can designate the coupled states as $|jm\rangle$ and the uncoupled states as $|m_lm_s\rangle$. Answer the following questions:

a. The stretched coupled state (both j and m maximal) $|3/2\,3/2\rangle$ is identical to the single uncoupled state $|1\,1/2\rangle$ Determine the expression for the coupled state $|3/2\,1/2\rangle$ as a linear combination of uncoupled states. (10 pts)

b. The coupled state $|1/2\,1/2\rangle$ must be orthogonal to the $|3/2\,1/2\rangle$ coupled state, since they are eigenfunctions of $\hat{j}$ with different eignvalues. Determine an expression for $|1/2\,1/2\rangle$ as a linear combination of uncoupled states. (5 pts)

c. The coupled states are not eigenfunction of $\hat{s}_z$, but the uncoupled states are, since

$$\hat{s}_z|m_lm_s\rangle = m_s|m_lm_s\rangle$$

. Determine then the following matrix elements between coupled states (5 pts each)

$$\langle 3/2\,1/2|\hat{s}_z|3/2\,1/2\rangle$$

and

$$\langle 3/2\,1/2|\hat{s}_z|1/2\,1/2\rangle$$

Chemistry 691, Final Exam - Matlab Part, May 17 2016

1. Under equilibrium conditions, the relative population in rotational level j of a diatomic molecules is defined as

$$p_j(T) = \frac{1}{z_r(T)}(2j+1)\exp[-Bj(j+1)/kT]$$

where the rotational partition function $z_r(T)$ is

$$z_r(T) = \sum_{j=0}^{\infty} p_j(T) = \sum_{j=0}^{\infty}(2j+1)\exp[-Bj(j+1)/kT] \tag{1}$$

Consider a molecule with rotational constant $B = 2$ cm^{-1}. (To convert to temperature multiply B by 1.4388.) Write a Matlab script to carry out the summation in Eq. (??) and then graph $p_j(T)$ as a function of j for T=10, 50, and 100 K. All three curves should be on a single plot. Plot each curve as circles connected with straight lines. Label the x-axis j, and the y-axis P_j.

2. By letting j equal, successively, 1:4 obtain an expression in terms of j of the series

$$\sum_{m=-j}^{j} \frac{(j+m)(j-m)}{(2j-1)(2j+1)}$$

3. a. Consider the cyclobutadiene molecule. Assume that the bond are slightly shifted from
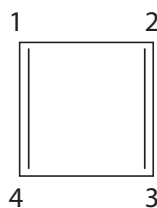
equality, so that bonds 2−3 and 1−4 are shorter, and bonds 1−2 and 3−4, longer, by an infinitesmal δ

$$r_{12} = r_{34} = r_o(1+\delta), \text{ and } r_{12} = r_{34} = r_o(1-\delta)$$

Assume that you can write the coupling between any two adjacent atoms as

$$\beta(r) = \beta(r_o(1+\delta))$$

so that

$$\left.\frac{\partial \beta}{\partial r}\right|_{r=r_o} = \beta_o \delta$$

and

$$\beta(r) = \beta(r_o)(1 + \delta)$$

To make things even simpler let $\beta(r_o) = 1$. *a.* What is the Huckel matrix in the presence of a small bond distortion δr. Then, diagonalize this matrix. What is the total π electron energy as a function of β_o and δ?

b. Then determine the derivative of the total energy of the π electrons with respect to varying δ. Will the molecule be stable with respect to a distortion which lengthens bonds $1-2$ and $3-4$ while shortening the other two?

c. In fact, the π electronic wavefunction of

Chemistry 691   Final Exam (200 pts)   May 7, 2015

Show all work. Conversion factors: 1 eV = 8065 cm^{-1}; 1 hartree=219474.6 cm^{-1} = 27.21165 eV

1 cm^{-1} = 1.4388 K (energy conversion of wavenumbers to degrees K)

1. The table shows line positions (cm-1) and relative intensities for an electronic transition in a diatomic molecule.   Assume that the transition is between rotational levels associated with the ground vibrational levels in both states (v'=0←v"=0).

Line	Intensity
35958.8538	5.85
35964.0636	6.00
35968.9208	5.49
35973.4253	4.25
35977.5773	2.34
35984.8235	2.46
35987.9177	4.69
35990.6594	6.37
35993.0484	7.32
35995.0848	7.50
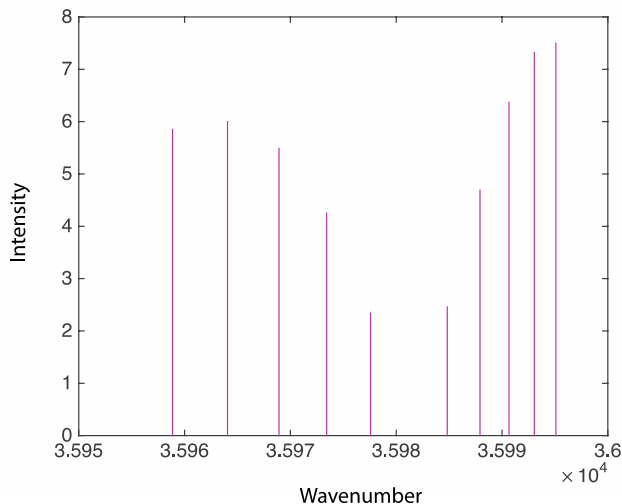
In answering the following questions, ignore the small centrifugal distortion constant.

    a. What is the position (in cm^{-1}) of the R-branch transition out of the j''=2 level? (6 pts)
    b. From the plotted spectrum, estimate the value of T_{00}, the spacing between the v=0 ground vibrational levels of the excited and ground electronic states. (7 pts)
    c. Determine, in terms of T_{00} and the rotational constants in the the v=0 vibrational levels of the excited and ground vibrational states, B_0' and B_0'', the positions of the R-branch lines originating in j''=0, 1, and 2 and the P-branch lines originating in j''= 1 and 2. (10 pts)
    d. Determine the values, in cm^{-1}, of T_{00}, B_0' and B_0''. (7 pts)
    e. The vibrational and anharmonicity constants for the ground and excited electronic states are (in cm^{-1}).

$$\omega_e'' = 2207.0 \text{ cm–1} \qquad \omega_e x_e'' = 16.1$$
$$\omega_e' = 2419.8 \text{ cm–1} \qquad \omega_e x_e' = 23.2$$

Determine the band origin (T_{50}; in cm^{-1}) for the transition from the v"=0 level of the ground electronic state to the v'=5 level of the excited electronic state. (7 pts)

    f. At what temperature will the intensities of the two lowest (in wavenumber) R branch lines be equal? (12 pts)

2. Consider the C_2^+ molecular ion. The ground electronic state has the term symbol $^2\Pi_u$. In this state the vibrational frequency is $\omega_e'' = 2207.0$ cm^{-1}. Answer the following questions:

   a. What should be the Slater determinantal approximation for the wavefunction of the $^2\Pi_u$ state? (7 pts).
   b. Guess, justifying your answer, the Slater determinantal wavefunction, the term symbol, the bond order, and the vibrational frequency of the first excited state of C_2^+. (10 pts)

3. Consider the HF molecule. Assume that the vibrational motion can be approximated as that of a harmonic oscillation with force constant k. The vibrational wavefunctions are

$$|n\rangle = N_n H_n(x)\exp(-ax^2)$$

where $H_n(x)$ is a Hermite polynomial in the variable $x = r - r_e$ and $\alpha = (k\mu)^{1/2}$, with μ being the reduced mass. These vibrational wavefunctions satisfy the relations

$$\langle m|n\rangle = d_{mn} \text{ and } \langle n=1|x|n=0\rangle = (2a)^{-1/2}$$

In the ground electronic state, the dipole moment of HF will depend on r, the bond distance. You can expand this in a power series

$$D(r) = D(r_e) + \left.\frac{dD}{dr}\right|_{r=r_e}(r - r_e) + ...$$

The coefficient of the second term in this power series is called the "dipole derivative". Answer the following questions:

   a. How will the intensity of the infrared $v=1 \leftarrow v=0$ transition depend on the dipole derivative? (7 pts)
   b. The simple freshman chemistry picture of HF is an ionic molecule with fractional charges $+\delta$ and $-\delta$. In this picture, the dipole moment would be
      $$D(r_e) = d'r|_{r=r_e}$$
      The equilibrium internuclear distance of HF is 1.733 bohr and its dipole moment is 0.715 atomic units. Estimate the magnitude of the fractional charge δ. (6 pts)
   c. In this simple picture, estimate the dipole derivative of HF (in units of e/bohr). (6 pts)
   d. Consider now the DF molecule. How will the intensity of the $v=1 \leftarrow v=0$ transition in DF compare with that of HF? In answering this question, approximate the mass of F as 19, the mass of H as 1 and the mass of D as 2. (11 pts)

4. The Slater determinantal wavefunction for the ^{2}D state of the N atom with $M_L=\pm2$ and $M_S=1/2$ is

$$\left|LM_LSM_S\right\rangle = \left|2,\pm2,\tfrac{1}{2}\tfrac{1}{2}\right\rangle = \left|p_{\pm1}\bar{p}_{\pm1}p_0\right|$$

a. Give a similar normalized determinantal wavefunction for the ^{4}S state with $M_S=3/2$, $\left|00\tfrac{3}{2}\tfrac{3}{2}\right\rangle$,   (6 pts)

b. The Cartesian p orbitals are defined in terms of the definite-m orbitals as

$$p_1 = p_z \quad \text{and} \quad p_{\pm1} = \square 2^{-1/2}\left[p_x \pm ip_y\right]$$

Determine determinantal wavefunctions in terms of Cartesian p orbitals for the

$$\left|00\tfrac{3}{2}\tfrac{3}{2}\right\rangle$$

state and for the plus and minus linear combination of the wavefunctions for the $M_L=+2$ and -2 components of the ^{2}D state, namely (10 pts)

$$2^{-1/2}\left[\left|22\tfrac{1}{2}\tfrac{1}{2}\right\rangle + \left|2,-2,\tfrac{1}{2}\tfrac{1}{2}\right\rangle\right]$$

c. Determine the average repulsion energy between the $2p$ electrons in the ^{4}S and ^{2}D states in terms of the two-electron integrals $[x^2|x^2]$, $[x^2|y^2]$, and $[xy|yx]$. (7 pts)

d. Use the result for the ^{2}D state to obtain a relation for the difference between the $[x^2|x^2]$ and $[x^2|y^2]$ Coulomb integrals. *Hint*: we obtained a similar relation in class from treating the C atom. (7 pts)

e. The For C and O, the experimental splitting between the ^{3}P and ^{2}P states is, respectively, ~ 10,000 and ~ 16,000 cm^{-1}. Since N lies in between C and O, we would estimate that the splitting between the ground (highest multiplicity) state and the next state (lower multiplicity but higher L) would be ~ 13,000 cm^{-1}. However, the observed splitting between the ^{4}S and ^{2}D states of N is ~ 19,000 cm^{-1}, much larger. Can you rationalize this observation? (9 pts)

5. Consider the **one**-electron HeH^{2+} molecular ion.

    a. What is the electronic Hamiltonian? (Make sure you give a sketch explaining the various distances). (6 pts)

    b. Write down a simple, normalized LCAO-MO approximation to the wavefunction for HeH^{2+}. (6 pts)

    c. What are the united- and separated-atom limits of the electronic energy of the lowest state of HeH^{2+}? (7 pts)

    d. Now consider the **two**-electron HeH$^+$ ion. What are the united- and separated-atom limits of the electronic energy of the lowest state of HeH$^+$? (9 pts) *Hint*: The first ionization potentials of the lightest atoms (in eV) are:

        H   0.5;   He   24.587; Li   5.391; Be   9.277; B   8.298

    e. The electronic energy of HeH$^+$ at some intermediate values of R are given in the following table.   Estimate the internuclear distance (in bohr) and the dissociation energy D_e (in Hartree) of the HeH$^+$ ion? (11 pts)

R / bohr	Eel / hartree
1.0	–4.9042
1.2	–4.6282
1.4	–4.4061
1.5	–4.3113
1.6	–4.2258
1.8	–4.0782
2.4	–3.7699
3.0	–3.5847
4.0	–3.4070
12.0	–2.9032

6. Imagine an exotic proton, Ħ, with mass 1.0078252 atomic mass units but a charge of only ½ (Z= ½). Consider the exotic Ħ$_2$ molecule (two exotic protons plus an electron; the total charge is zero. Answer the following questions:

    a. What is the electronic energy of Ħ$_2$ (in Hartree) in the united atom and separated atom limits? (9 pts)

    b. Approximate the wave function by the same LCAO-MO function that you used for H$_2^+$, namely

$$1s_g = (1 + S)^{-1/2}[1s(r_a) + 1s(r_b)]$$

where

$$1s = (z^3 / p)^{1/2} \exp(-zr)$$

What would be a reasonable guess for the screening constant ζ? (8 pts)

    c. For this choice of screening constant what would you predict for the kinetic energy and the potential energy of the electron in the united atom and separated atom limits? (10 pts)

Chemistry 691, Mid-Term Exam, April 30 2014. 3 questions total, 100 pts

Conversion factors: 1 Hartree = 219474.6 cm^{-1}= 27.211652 eV ; 1 cm^{-1} = 1.4388 K

1 unified atomic mass unit = 1822.8549 atomic units

For full credit, show all work.

Problem 1

The potential curve of the $^3\Pi$ state of the C_2 molecule is

TABLE I. C_2 V(R).

R/bohr	V(R)/hartree
2.3	-75.79203833
2.4	-75.80255160
2.5	-75.80505208
2.6	-75.80172097
2.7	-75.79424328
39	-75.57802531

(a) Determine R_e for C_2 in the $^3\Pi$ states. (15 pts)

(b) Determine the vibrational frequency (ω_e) in cm^{-1}. (10 pts)

(c) Determine the electronic energy at R_e. (10 pts)

(d) Estimate the dissociation energy D_e in eV.

(e) You want to approximate the potential $V(R)$ by a Morse function

$$V(R) = A\left\{\exp[-2\beta(R - R_e)] - 2\exp[-\beta(R - R_e)]\right\}^2$$

Determine the values of A and β.

Problem 2

Consider the $C_2{}^+$ diatomic molecular ion. Give the term symbols $\left(^{2S+1}\Lambda_{g/u}^{+/-}\right)$ for the states you can have which correspond to the electron occupancy

(a) $|...2\sigma_u^2 3\sigma_g^0 1\pi_u^3|$ (7 pts)

(b) $|...2\sigma_u^2 3\sigma_g^1 1\pi_u^2|$ (7 pts)

Here ... stands for $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$.

(c) What would you predict for the bond-order, vibrational frequencies, and internuclear distances for the answers to part (a)? (10 pts)

Problem 3

For the N atom, the Slater determinantal wavefunction for the ^4S state with $M_S = 3/2$ is

$$\left|^4S_{3/2}\right\rangle = |p_1 p_0 p_{-1}|$$

(a). What is the Slater determinantal wave function for the ^4S state with $M_S = 1/2$? (7 pts)

(b) Express the Slater determinantal wavefunction for the $|^4S_{3/2}\rangle$ state in terms of the Cartesian p orbitals

$$p_{\pm 1} = \mp 2^{-1/2} \left[p_x \pm i p_y\right]$$

and

$$p_0 \equiv p_z$$

Use the convention that (a) all p_x spin-orbitals precede the p_y spin-orbitals which precede the p_z spin-orbitals and (b) an $m_s = 1/2$ (no bar) spin orbital always precedes an $m_s = -1/2$ (bar) spin orbital of the same Cartesian index. (10 pts)

b) Are the determinantal wave function for the $|^4S_{3/2}\rangle$ and the $|^4S_{1/2}\rangle$ states symmetric or antisymmetric with respect to reflection in the xz plane? (7 pts)

c) Determine the expectation value of the electron repulsion operator

$$\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

in the $|^4S_{3/2}\rangle$ state. Just include the effect of this operator in the subspace consisting of the three $2p$ electrons. Give your answer in terms of the integrals $[x^2|x^2] \equiv [2p_x^2|2p_x^2]$, $[x^2|y^2] \equiv [2p_x^2|22p_y^2]$, and $[xy|yx] \equiv [2p_x 2p_y|2p_y 2p_x]$. (7 pts)

Problem 4

On Exam 2, you were given a problem involving the square pyramidal structure for the methane (CH_4) molecule (the four H atoms are coplanar and arranged at the four vertices of a square. Note that the C atom lies above the xy plane). This molecule has C_{4v} symmetry.
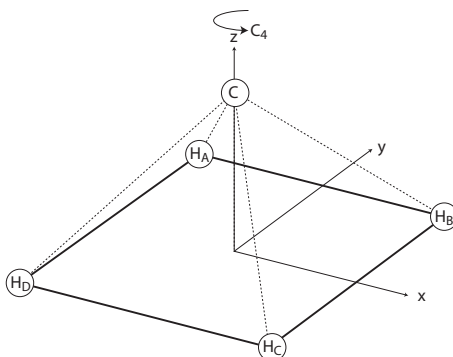

As symmetry elements there are two vertical reflection planes, called σ_v, that bisect two of the vertices of the square, so that hydrogen atoms "A" and "C" lie in one of these planes and hydrogen atoms "B" and "D", in the other. The xz and yz planes constitute another pair of vertical reflection planes, designated σ_d. The σ_v and σ_d pairs of reflection planes are rotated with respect to each other by 45° around the z-axis. Finally, C_2 and C_4 are, respectively, two- and four-fold axes of rotation around the z-axis. The group theoretical character table for C_{4v} is

TABLE II. Character table for C_{4v} symmetry.

Character	E	C_4	C_2	$2\sigma_v$	$2\sigma_d$	quadratic
a_1	+1	+1	+1	+1	+1	$x^2 + y^2$, z^2
a_2	+1	+1	+1	−1	−1	
b_1	+1	−1	+1	+1	−1	$x^2 - y^2$
b_2	+1	−1	+1	−1	+1	xy
e	2	0	−2	0	0	xz, yz

The character table is similar to the C_{2v} character table for the H_2O molecule with the addition of the irreducible representation labelled e. There are two components to this representation which behave like the atomic d orbitals of xz and yz symmetry centered at the origin. When you rotate the d_{xz} orbital around the z axis by $\pi/4$, you get the d_{yz}
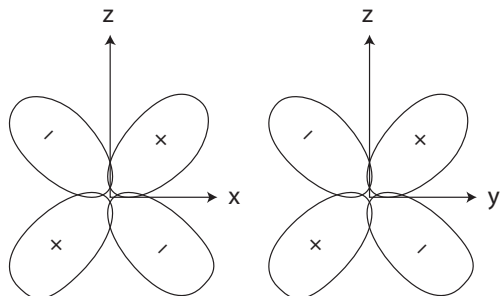
orbital. Similarly $\hat{C}_2 d_{yz} = -d_{xz}$. That's why the character is "0". Also $\hat{\sigma}_v$ reverses those two orbitals, and $\hat{\sigma}_d$ changes one of the orbitals into itself and one into the negative of itself. It is for this reason that d_{xz} and d_{yz} belong to the e irreducible representation. Any other molecular orbitals that belong to the e irreducible representation will occur in pairs.

In the character table, the last column , labelled "quadratic", indicates the irreducible representations for the other three d atomic orbitals, again all centered at the origin.

Similarly the $2p_x$ and $2p_y$ orbitals on the C atom belong to the e irreducible representation. We can specify one of these as e_x and the other as e_y.

Answer the following questions:

(a) You can construct normalized linear combinations of the four $1s$ H orbitals that have 0, 2, or 4 nodes between the 4 H atoms. One of these is

$$\psi_{a_1}^{\mathrm{H}} = [4(1 + 2S)]^{-1/2} (1s_A + 1s_B + 1s_C + 1s_D)$$

As the subscript indicates, this molecular orbital belongs to the a_1 irreducible representation. Write down similar normalized linear combinations for the other H molecular orbitals, indicating to which irreducible representation each of them belongs (a_1, a_2, b_1, b_2, e_x or e_y). You can neglect the overlap between $1s$ orbitals of the H atoms whenever the two atoms are non-adjacent (for example, atoms H_A and H_C). The overlap between adjacent H atoms is designated S. (10 pts)

(b) If you neglect the filled $1s$ and $2s$ orbitals on the C atom, you have remaining a total of 7 atomic orbitals. These can be transformed into 7 molecular orbitals which are linear combinations of the C $2p$ orbitals and the ψ^{H} molecular orbitals, and which belong also to a particular irreducible representation. Labelling each molecular orbitals by its irreducible representation)for example $1b_1$ or $2a_1$) write down expressions for these molecular orbitals, give a simple sketch of these, and indicate whether the orbital is bonding, non-bonding, or

anti bonding, where "bonding" refers to an increase in probability density between the H atoms and the C atom. (10 pts)

(c) What then is the electronic configuration of the square-pyramidal CH_4 molecule? Methane is tetrahedral, not square pyramidal. Can you give a simple explanation why this is. (10 pts)

Problem 5

For a particular diatomic molecule, AB, the vibration-rotation energy levels can be described by the dissociation energy D_e and the spectroscopic constants ω_e, $\omega_e x_e$, B_e and α_e.

(a) The zero of energy corresponds to the separated atoms, A + B. What is the energy of the AB molecule in the $v = 0, j = 3$ vibration-rotation level? (10 pts)

(b) At what frequency, in cm^{-1} will the molecule absorb in the R-branch associated with a vibration-rotation transition from v=0→v=1? Your answer will depend on the spectroscopic constants as well as on the initial rotational angular momentum j. *Hint: determine first the energies of the upper and lower states.* (10 pts)

(c) The intensity of the absorption described in part (b) is proportional to the relative population at temperature T in level j. Let the number R_{56} be the ratio of the intensity of the $R(5)$ line (R-branch transition out of $j = 5$) to the intensity of the $R(6)$ line is R_{56}. In terms of the spectroscopic constants and the number R_{56}, what is the temperature in K? (14 pts)

(d) The dissociation energy and some spectroscopic constants ω_e, B_e and α_e for the H_2 molecule are given in the following table:

TABLE III. Some constants for H_2 (cm^{-1} except for D_e which is in eV).

D_e	ω_e	B_e	α_e
4.7466	4401.21	60.85	–3.06

Determine the values of these constants for the D_2 molecule. (10 pts)

Problem 6

Imagine an exotic proton, $\tilde{H}$, with mass 1.0078252 atomic mass units but a charge of only $1/2$ ($Z = 1/2$). Consider the exotic $\tilde{H}_2$ molecule (two exotic protons plus an electron; the total charge is zero). Answer the following questions:

(a) What is the electronic energy in the united atom and the separated atom limits? (10 pts)

(b) Approximate the wave function using the same LCAO-MO function that you used for H_2^+, namely

$$1\sigma_g = (1 + S)^{-1/2} \left[1s_a(\zeta r_a) + 1s_b(\zeta r_b)\right]$$

where

$$1s = (\zeta^3/\pi)^{1/2} \exp(-\zeta r)$$

What would be a reasonable value of ζ? (10 pts)

(c) For this choice of ζ what would you predict for the kinetic energy and the potential energy of the electron in the limit of $R \to 0$ and $R \to \infty$ (the united atom and separated atom limits). (10 pts)

Chemistry 691, 2010, Take-home, final exam 300 pts total

Problem 1. For the N atom, the Slater determinantal wavefunctions for the ^1D state with $M_L = \pm 2$ are

$$\left|{}^1D_{\pm 2, 1/2}\right\rangle = |p_{\pm 1}\bar{p}_{\pm 1}p_0|$$

Express the wavefunctions for these two states in terms of the Cartesian p orbitals

$$p_{\pm 1} = \mp 2^{-1/2}\left[p_x \pm ip_y\right]$$

and

$$p_0 \equiv p_z$$

When you write these determinants (in simplified notation) use the convention that (a) all p_x spin-orbitals precede the p_y spin-orbitals which precede the p_z spin-orbitals and (b) an $m_s = 1/2$ (no bar) spin orbital always precedes an $m_s = -1/2$ (bar) spin orbital of the same Cartesian index. (15 pts)

b) Take normalized linear combinations to get two functions which are purely real. Are these linear combinations eigenfunctions of the operator for reflection in the xz plane? If so, indicate whether each functions is symmetric or antisymmetric. (10 pts)

c) Determine the expectation value of the electron repulsion operator

$$\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

in these two states. Just include the effect of this operator in the subspace consisting of the three $2p$ electrons. Give your answer in terms of the integrals $[p_x^2|p_x^2]$, $[p_x^2|p_y^2]$, and $[p_xp_y|p_yp_x]$. (25 pts)

Problem 2 Consider the coupling between two angular momenta $\vec{L}_1 = 3/2$ and $\vec{L}_2 = 1$.

a. Write down the expression for the stretched state $|L_1, L_2, J = L_1 + L_2, M = J\rangle$ in terms of the uncoupled states $|L_1, M_1, L_2, M_2\rangle$. (10 pts)

b. Using the appropriate raising and lowering operators to determine the expression for the state $|L_1, L_2, J = L_1 + L_2, M = J - 1\rangle$ in terms of the uncoupled states. (Note that $M = J - 1 = L_1 + L_2 - 1 = 3/2$ here)(15 pts)

c. Now determine an expression for the state $|L_1, L_2, J = L_1 + L_2 - 1, M = J\rangle$ (note that

$M = 3/2$ here) in terms of the uncoupled states. (15 pts)

d. The Condon-Shortley phase convention requires that the overall sign of the wavefunction for the $|L_1, L_2, J = L_1 + L_2 - 1, M = J\rangle$ state $(M = 3/2)$ be chosen so that the matrix element

$$\langle L_1, L_2, J = L_1 + L_2 - 1, M = L_1 + L_2 - 1|\hat{L}_{1z}|L_1, L_2, J = L_1 + L_2, M = L_1 + L_2 - 1\rangle$$

be positive. Determine this matrix element to set the overall sign. Here $\hat{L}_{1z}$ is the operator for the z-component of the angular momentum of the first electron. (15 pts)

Problem 3. The excited ns states of the Na atom, where $n > 3$, lie at increasingly higher energies above the ground $3s$ state. Experimental values for these excitation energies are given in the following Table: The energies of the alkali metals are often fitted to a quantum

TABLE I. Excitation energies of the excited ns states of the Na atom.

n	$E(\text{cm}^{-1})$
4	25739.991
5	33200.675
6	36372.620
7	38012.044
8	38968.51

defect formula (with energies in hartree)

$$E_n = -\frac{0.5}{(n - \delta)^2}$$

where there is a single quantum defect parameter δ for all the ns states of the Na atom.

a. Write a Matlab script to adjust the quantum defect δ to obtain a best fit of the experimental data. (30 pts)

b. Use your result to estimate the ionization potential (in eV) of the Na atom. (15 pts)

Problem 4. Consider the excited state of the N_2 with electron configuration $\ldots 3\sigma_g^2 1\pi_u^3 1\pi_g$.

a. Use the tableau method to determine the allowed electronic states. (20 prs)

b. Give Slater determinantal wavefunctions for each of these states, including explicitly, only the $1\pi_u$ and $1\pi_g$ orbitals. You can use the definite-m $(\pi_{\pm 1})$ rather than Cartesian orbitals $(\pi_x$ and $\pi_y)$. To simplify the notation let the $1\pi_u$ orbitals be designated just π and the $1\pi_g$

orbitals be designated just π^*. Designate each state as $^{2S+1}\Lambda_{g/u}$ and, if a Σ state, indicate the reflection symmetry. (30 pts)

Problem 5. I have attached a table of calculated potential energy curves for the C_2 molecule in a file named `C2_curves.m`. The columns correspond, in order, to the $^1\Sigma_g^+$, $^1\Delta_g$, $^3\Sigma_g^-$, $^1\Pi_u$, and $^3\Pi_u$ states. Write a Matlab script that will

a. Determine and plot the electronic energy, $V_{el}(R)$, of these states as a function of R. (10 pts)

b. Determine the equilibrium value of R and the vibrational frequency in cm^{-1} for each of these states. (15 pts)

c. Suppose you want to fit each of these potential curves by a Morse function

$$V(R) = D_e \left\{ \exp\left[-2\beta\left(R - R_e\right)\right] - 2\exp\left[-\beta\left(R - R_e\right)\right] \right\}$$

Extend your Matlab script to determine the Morse parameters D_e and β for each state. Note that the Morse function, as written, goes to 0 at $R = \infty$, so that you may have to shift the tabulated potential energy curves accordingly. (25 pts)

I want one Matlab script that includes the answer to parts (a)–(c).

Problem 6. Consider the symmetric H_3^+ ion consisting of three protons and two electrons.
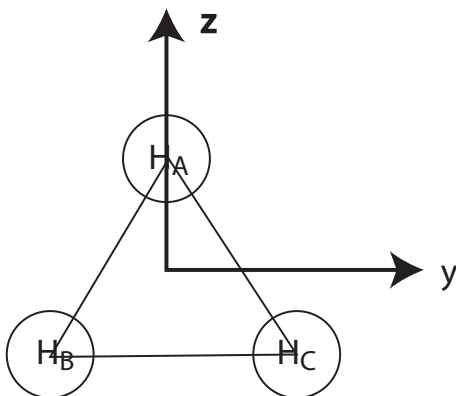
a. Write down the electronic Hamiltonian for this ion. (10 pts)

You can construct molecular orbitals for this ion as linear combinations of H atom $1s$

orbitals. Two of the molecular orbitals are

$$\phi_1 = N_1 \left(1s_a + 1s_b + 1s_c\right)$$

$$\phi_2 = N_2 \left(1s_a - 1s_b\right)$$

b. Determine the normalization constants N_1 and N_2 in terms of the overlap. (10 pts)

$$S = \int 1s_a 1s_b = \int 1s_a 1s_c = \int 1s_b 1s_c$$

c. There is a third molecular orbital

$$\phi_3 = c_a 1s_a + c_b 1s_b + c_c 1s_c$$

Determine the values of the coefficients so that ϕ_3 is normalized and orthogonal to the other two orbitals. (20 pts)

d. Assume that the wavefunction of the electron is $|\phi_1 \bar{\phi}_1|$. Determine an expression for the electronic energy in terms of S and the one-electron integrals T_{aa}, T_{ab}, V_{aaa}, V_{aab}, V_{aba}, and V_{abc} as well as the two-electron integrals $[1s_a^2|1s_a^2]$, $[1s_a^2|1s_b^2]$, $[1s_a^2|1s_a 1s_b]$, $[1s_a^2|1s_b 1s_c]$, and $[1s_a 1s_b|1s_b 1s_a]$, and $[1s_a 1s_b|1s_c 1s_a]$. (30 pts)