

9.1: Solutions

Solutions

1.

a. First determine the eigenvalues:

$$\det = 0$$

$$(-1 - \lambda)(2 - \lambda) - 22 = 0$$

$$-2 + \lambda - 2\lambda + \lambda^2 - 4 = 0$$

$$\lambda^2 - \lambda - 6 = 0$$

$$(\lambda - 3)(\lambda + 2) = 0$$

$$\lambda = 3 \text{ or } \lambda = -2.$$

Next, determine the eigenvectors. First, the eigenvector associated with eigenvalue -2:

$$= -2$$

$$-C_{11} + 2C_{21} = -2C_{11}$$

$$C_{11} = -2C_{21} \text{ (Note: The second row offers no new information, e.g. } 2C_{11} + 2C_{21} = -2C_{21})$$

$$C_{11} + C_{21} = 1 \text{ (from normalization)}$$

$$(-2C_{21}) + C_{21} = 1$$

$$-C_{21} = 1$$

$$C_{21} = -1$$

$$C_{11} = 2$$

$$C_{21} = -1, \text{ and therefore } C_{11} = 2.$$

For the eigenvector associated with eigenvalue 3:

$$= 3$$

$$-C_{12} + 2C_{22} = 3C_{12}$$

$$-4C_{12} = -2C_{22}$$

$$C_{12} = 0.5C_{22} \text{ (again the second row offers no new information)}$$

$$C_{12} + C_{22} = 1 \text{ (from normalization)}$$

$$(0.5C_{22}) + C_{22} = 1$$

$$1.5C_{22} = 1$$

$$C_{22} = 2/3$$

$$C_{12} = 1/3$$

$$C_{22} = 2/3, \text{ and therefore } C_{12} = 1/3.$$

Therefore the eigenvector matrix becomes:

b. First determine the eigenvalues:

$$\det = 0$$

$$\det \det = 0$$

From 1a, the solutions then become -2, -2, and 3. Next, determine the eigenvectors. First the eigenvector associated with eigenvalue 3 (the third root):

$$= 3$$

$$-2 C_{13} = 3 C_{13} \text{ (row one)}$$

$$C_{13} = 0$$

$$-C_{23} + 2 C_{33} = 3 C_{23} \text{ (row two)}$$

$$2 C_{33} = 4 C_{23}$$

$$C_{33} = 2 C_{23} \text{ (again the third row offers no new information)}$$

$$C_{132} + C_{232} + C_{332} = 1 \text{ (from normalization)}$$

$$0 + C_{232} + (2 C_{23})^2 = 1$$

$$5 C_{232} = 1$$

$$C_{23} = \frac{1}{5}, \text{ and therefore } C_{33} = \frac{2}{5}.$$

Next, find the pair of eigenvectors associated with the degenerate eigenvalue of -2. First, root one eigenvector one:

$$-2 C_{11} = -2 C_{11} \text{ (no new information from row one)}$$

$$-C_{21} + 2 C_{31} = -2 C_{21} \text{ (row two)}$$

$$C_{21} = -2 C_{31} \text{ (again the third row offers no new information)}$$

$$C_{112} + C_{212} + C_{312} = 1 \text{ (from normalization)}$$

$$C_{112} + (-2 C_{31})^2 + C_{312} = 1$$

$$C_{112} + 5 C_{312} = 1$$

$$C_{11} =$$

Second, root two eigenvector two:

$$-2 C_{12} = -2 C_{12} \text{ (no new information from row one)}$$

$$-C_{22} + 2 C_{32} = -2 C_{22} \text{ (row two)}$$

$$C_{22} = -2 C_{32} \text{ (again the third row offers no new information)}$$

$$C_{122} + C_{222} + C_{322} = 1 \text{ (from normalization)}$$

$$C_{122} + (-2 C_{32})^2 + C_{322} = 1$$

$$C_{122} + 5 C_{322} = 1$$

$$C_{12} = (1 - 5 C_{322})^{1/2} \text{ (Note: again, two equations in three unknowns)}$$

$$C_{11} C_{12} + C_{21} C_{22} + C_{31} C_{32} = 0 \text{ (from orthogonalization)}$$

Now there are five equations with six unknowns.

Arbitrarily choose $C_{11} = 0$

(whenever there are degenerate eigenvalues, there are not unique eigenvectors because the degenerate eigenvectors span a 2- or more- dimensional space, not two unique directions. One always is then forced to choose one of the coefficients and then determine all the rest; different choices lead to different final eigenvectors but to identical spaces spanned by these eigenvectors).

$$C_{11} = 0 =$$

$$5 C_{312} = 1$$

$$C_{31} =$$

$$C_{21} = -2$$

$$C_{11} C_{12} + C_{21} C_{22} + C_{31} C_{32} = 0 \text{ (from orthogonalization)}$$

$$0 + -2 + C_{32} = 0$$

$$5 C_{32} = 0$$

$$C_{32} = 0, C_{22} = 0, \text{ and } C_{12} = 1$$

Therefore the eigenvector matrix becomes:

2.

$$a. K.E. = \frac{1}{2}mv^2$$

$$K.E. = \frac{1}{2}mv^2$$

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$$K.E. = \frac{1}{2}mv^2$$

$$b. p = mv = ipx + jpy + kpz$$

$$p =$$

where i, j, and k are unit vectors along the x, y, and z axes.

$$c. L_y = z p_x - x p_z$$

$$L_y = z p_x - x p_z$$

3.

First derive the general formulas for r , θ , in terms of x, y, z , and ϕ , and ϕ , in terms of x, y, z . The general relationships are as follows:

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$\tan \phi = \frac{y}{x}$$

First θ , ϕ , and from the chain rule:

$$\frac{\partial}{\partial x} = \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi}$$

$$= \frac{y}{r^2} \frac{\partial}{\partial \theta} + \frac{z}{r^2} \frac{\partial}{\partial \phi}$$

$$= \frac{y}{r^2} \frac{\partial}{\partial \theta} + \frac{z}{r^2} \frac{\partial}{\partial \phi}$$

Evaluation of the many "coefficients" gives the following:

$$\frac{\partial \theta}{\partial x} = \frac{y}{r^2}, \frac{\partial \theta}{\partial y} = -\frac{x}{r^2}, \frac{\partial \theta}{\partial z} = 0$$

$$\frac{\partial \phi}{\partial x} = -\frac{y}{r^2 \sin \theta}, \frac{\partial \phi}{\partial y} = \frac{x}{r^2 \sin \theta}, \frac{\partial \phi}{\partial z} = 0$$

$$\frac{\partial \phi}{\partial x} = -\frac{y}{r^2 \sin \theta}, \frac{\partial \phi}{\partial y} = \frac{x}{r^2 \sin \theta}, \frac{\partial \phi}{\partial z} = 0$$

Upon substitution of these "coefficients":

$$\frac{\partial}{\partial x} = \frac{y}{r^2} \frac{\partial}{\partial \theta} - \frac{y}{r^2 \sin \theta} \frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial y} = -\frac{x}{r^2} \frac{\partial}{\partial \theta} + \frac{x}{r^2 \sin \theta} \frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial r}$$

Next ϕ , θ , and from the chain rule:

$$\frac{\partial}{\partial x} = \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta}$$

$$= -\frac{y}{r^2 \sin \theta} \frac{\partial}{\partial \phi} + \frac{y}{r^2} \frac{\partial}{\partial \theta}$$

$$= -\frac{y}{r^2 \sin \theta} \frac{\partial}{\partial \phi} + \frac{y}{r^2} \frac{\partial}{\partial \theta}$$

Again evaluation of the the many "coefficients" results in:

$$\frac{\partial \phi}{\partial x} = -\frac{y}{r^2 \sin \theta}, \frac{\partial \phi}{\partial y} = \frac{x}{r^2 \sin \theta}, \frac{\partial \phi}{\partial z} = 0$$

$$\frac{\partial \theta}{\partial x} = \frac{y}{r^2}, \frac{\partial \theta}{\partial y} = -\frac{x}{r^2}, \frac{\partial \theta}{\partial z} = 0$$

$$\frac{\partial \theta}{\partial x} = \frac{y}{r^2}, \frac{\partial \theta}{\partial y} = -\frac{x}{r^2}, \frac{\partial \theta}{\partial z} = 0$$

Upon substitution of these "coefficients":

$$= +$$

$$+$$

$$= + -$$

$$= -y + x + 0.$$

Note, these many "coefficients" are the elements which make up the Jacobian matrix used whenever one wishes to transform a function from one coordinate representation to another. One very familiar result should be in transforming the volume element $dx dy dz$ to $r^2 \sin \theta dr d\theta d\phi$. For example:

$$=$$

$$a. L_x =$$

$$L_x =$$

$$-$$

$$L_x = -$$

$$b. L_z = -i$$

$$L_z =$$

$$4.$$

$$B \frac{dB}{dx} \frac{d^2B}{dx^2}$$

$$i. 4x^4 - 12x^2 + 3 \cdot 16x^3 - 24x \cdot 48x^2 - 24$$

$$ii. 5x^4 \cdot 20x^3 \cdot 60x^2$$

$$iii. e^{3x} + e^{-3x} \cdot 3(e^{3x} - e^{-3x}) \cdot 9(e^{3x} + e^{-3x})$$

$$iv. x^2 - 4x + 2 \cdot 2x - 4 \cdot 2$$

$$v. 4x^3 - 3x \cdot 12x^2 - 3 \cdot 24x$$

$B(v.)$ is an eigenfunction of $A(i.)$:

$$(1-x^2) - x B(v.) =$$

$$(1-x^2) (24x) - x (12x^2 - 3)$$

$$24x - 24x^3 - 12x^3 + 3x$$

$$-36x^3 + 27x$$

$$-9(4x^3 - 3x) \text{ (eigenvalue is } -9)$$

$B(iii.)$ is an eigenfunction of $A(ii.)$:

$$B(iii.) =$$

$$9(e^{3x} + e^{-3x}) \text{ (eigenvalue is } 9)$$

$B(ii.)$ is an eigenfunction of $A(iii.)$:

$$x B(ii.) =$$

$$x (20x^3)$$

$$20x^4$$

$$4(5x^4) \text{ (eigenvalue is } 4)$$

$B(i.)$ is an eigenfunction of $A(vi.)$:

$$-2x B(i) =$$

$$(48x^2 - 24) - 2x (16x^3 - 24x)$$

$$48x^2 - 24 - 32x^4 + 48x^2$$

$$-32x^4 + 96x^2 - 24$$

$$-8(4x^4 - 12x^2 + 3) \text{ (eigenvalue is } -8)$$

$B(iv.)$ is an eigenfunction of $A(v.)$:

$$x + (1-x) B(iv.) =$$

$$x(2) + (1-x)(2x - 4)$$

$$2x + 2x - 4 - 2x^2 + 4x$$

$$-2x^2 + 8x - 4$$

$$-2(x^2 - 4x + 2) \text{ (eigenvalue is } -2)$$

5.

6.

7.

8.

i. In ammonia, the only "core" orbital is the N 1s and this becomes an a_1 orbital in C_{3v} symmetry. The N 2s orbitals and 3 H 1s orbitals become 2 a_1 and an e set of orbitals. The remaining N 2p orbitals also become 1 a_1 and a set of e orbitals. The total valence orbitals in C_{3v} symmetry are 3 a_1 and 2e orbitals.

ii. In water, the only core orbital is the O 1s and this becomes an a_1 orbital in C_{2v} symmetry. Placing the molecule in the yz plane allows us to further analyze the remaining valence orbitals as: O 2pz = a_1 , O 2py as b_2 , and O 2px as b_1 . The (H 1s + H 1s) combination is an a_1 whereas the (H 1s - H 1s) combination is a b_2 .

iii. Placing the oxygens of H_2O_2 in the yz plane (z bisecting the oxygens) and the (cis) hydrogens distorted slightly in +x and -x directions allows us to analyze the orbitals as follows. The core O 1s + O 1s combination is an a orbital whereas the O 1s - O 1s combination is a b orbital. The valence orbitals are: O 2s + O 2s = a, O 2s - O 2s = b, O 2px + O 2px = b, O 2px - O 2px = a, O 2py + O 2py = a, O 2py - O 2py = b, O 2pz + O 2pz = b, O 2pz - O 2pz = a, H 1s + H 1s = a, and finally the H 1s - H 1s = b.

iv. For the next two problems we will use the convention of choosing the z axis as principal axis for the $D_{\infty h}$, D_{2h} , and C_{2v} point groups and the xy plane as the horizontal reflection plane in C_s symmetry.

$D_{\infty h}$ D_{2h} C_{2v} C_s

N 1s sg ag a_1 a'

N 2s sg ag a_1 a'

N 2px pxu b_{3u} b_1 a'

N 2py pyu b_{2u} b_2 a'

N 2pz su b_{1u} a_1 a''

9.

a. $Y_n(x) = \sin$

$P_n(x)dx = dx$

The probability that the particle lies in the interval $0 \leq x \leq$ is given by:

$P_n =$

This integral can be integrated to give :

$P_n =$

$P_n =$

$P_n = -\sqrt{f(1,4q,2}$

=

= - Sin

b. If n is even, $\sin = 0$ and $P_n = .$

If n is odd and $n = 1, 5, 9, 13, \dots$ $\sin = 1$

and $P_n = -$

If n is odd and $n = 3, 7, 11, 15, \dots$ $\sin = -1$

and $P_n = +$

The higher P_n is when $n = 3$. Then $P_n = +$

$P_n = + = 0.303$

c. $Y(t) = e^{aY_n e + bY_m e}$

$HY = aY_n E_n + bY_m E_m$

$= |a|^2 E_n + |b|^2 E_m + a^* b e$

$+ b^* a e$

Since a and b are zero,

$= |a|^2 E_n + |b|^2 E_m$ (note the time independence)

d. The fraction of systems observed in Y_n is $|a|^2$. The possible energies measured are E_n and E_m . The probabilities of measuring each of these energies is $|a|^2$ and $|b|^2$.

e. Once the system is observed in Y_n , it stays in Y_n .

f. $P(E_n) = 2 = |c_n|^2$

$c_n = \int_0^L x(L-x) dx$

$= dx$

=

These integrals can be evaluated to give:

$c_n = \int_0^L x(L-x) \sin\left(\frac{n\pi x}{L}\right) dx$

$= \int_0^L x(L-x) \sin\left(\frac{n\pi x}{L}\right) dx$

$c_n = \{$

$-)$

$- ($

$- \cos(np)$

$+ \cos(0))\}$

$c_n = L^{-3} \{- \cos(np) + \cos(np)$

$+ \}$

$c_n =$

$c_n =$

$c_n =)$

$|c_n|^2 =)$

If n is even then $c_n = 0$

If n is odd then $c_n =$

The probability of making a measurement of the energy and obtaining one of the eigenvalues, given by:

E_n is:

$P(E_n) = 0$ if n is even

$P(E_n) =$ if n is odd

$g_n =$

$=$

$=$

$=$

$= 30 \log(h, -L^2 f(x, 2,$

$=$

$=$

$= =$

10.

$= C_i^* e^{C_j}$

Since $= E_j d_{ij}$

$= C_j^* C_j E_j e$

$=$

For other properties:

$= C_i^* e^{C_j}$

but, does not necessarily $= a_{jdij}$ because the Y_j are not eigenfunctions of A unless $[A, H] = 0$.

$= C_i^* C_j e$

Therefore, in general, other properties are time dependent.

11.

a. The lowest energy level for a particle in a 3-dimensional box is when $n_1 = 1$, $n_2 = 1$, and $n_3 = 1$. The total energy (with $L_1 = L_2 = L_3$) will be:

$E_{\text{total}} =$

Note that $n = 0$ is not possible. The next lowest energy level is when one of the three quantum numbers equals 2 and the other two equal 1:

$n_1 = 1, n_2 = 1, n_3 = 2$

$n_1 = 1, n_2 = 2, n_3 = 1$

$n_1 = 2, n_2 = 1, n_3 = 1$.

Each of these three states have the same energy:

$E_{\text{total}} =$

Note that these three states are only degenerate if $L_1 = L_2 = L_3$.

b. $\frac{3}{4} \frac{3}{4} \frac{3}{4} \frac{3}{4} \frac{3}{4} \frac{3}{4}$

$\frac{3}{4}$

$L_1 = L_2 = L_3 \quad L_3^{-1} L_1 = L_2$

For $L_1 = L_2 = L_3$, $V = L_1 L_2 L_3 = L_1^3$,

$E_{\text{total}}(L_1) = 2e_1 + e_2$

$$= +$$

$$= + =$$

$$\text{For } L_3 \neq L_1 = L_2, V = L_1 L_2 L_3 = L_1 L_2 L_3, L_3 = V/L_1 L_2$$

$$E_{\text{total}}(L_1) = 2e_1 + e_2$$

$$= +$$

$$= +$$

$$=$$

$$= =$$

In comparing the total energy at constant volume of the undistorted box ($L_1 = L_2 = L_3$) versus the distorted box ($L_3 \neq L_1 = L_2$) it can be seen that:

£ as long as $L_3 \neq L_1$.

c. In order to minimize the total energy expression, take the derivative of the energy with respect to L_1 and set it equal to zero. $= 0$

$$= 0$$

But since $V = L_1 L_2 L_3 = L_1 L_2 L_3$, then $L_3 = V/L_1 L_2$. This substitution gives:

$$= 0$$

$$= 0$$

$$= 0$$

$$=$$

$$24L_1^6 = 12V^2$$

$$L_1^6 = V^2 \Rightarrow L_1^4 L_3^2$$

$$L_1^2 = L_3^2$$

$$L_3 = L_1$$

d. Calculate energy upon distortion:

$$\text{cube: } V = L^3, L_1 = L_2 = L_3 = (V)^{1/3}$$

$$\text{distorted: } V = L_1 L_2 L_3 = L_1 L_2 L_1 = L_1^3$$

$$L_3 \neq L_1 = L_2 =$$

$$DE = E_{\text{total}}(L_1 = L_2 = L_3) - E_{\text{total}}(L_3 \neq L_1 = L_2)$$

$$= -$$

$$=$$

$$=$$

Since $V = 8\text{\AA}^3$, $V^{2/3} = 4\text{\AA}^2 = 4 \times 10^{-16} \text{ cm}^2$, and $= 6.01 \times 10^{-27} \text{ erg cm}^2$:

$$DE = 6.01 \times 10^{-27} \text{ erg cm}^2$$

$$DE = 6.01 \times 10^{-27} \text{ erg cm}^2$$

$$DE = 0.99 \times 10^{-11} \text{ erg}$$

$$DE = 0.99 \times 10^{-11} \text{ erg}$$

$$DE = 6.19 \text{ eV}$$

12.

a. $H =$ (Cartesian coordinates)

Finding and from the chain rule gives:

$$= y + y, = x + x,$$

Evaluation of the "coefficients" gives the following:

$$y = \cos f, y = -,$$

$$x = \sin f, \text{ and } x = ,$$

Upon substitution of these "coefficients":

$$= \cos f - - ; \text{ at fixed } r.$$

$$= \sin f + = ; \text{ at fixed } r.$$

$$=$$

$$= + ; \text{ at fixed } r.$$

$$=$$

$$= - ; \text{ at fixed } r.$$

$$+ = + + -$$

$$= ; \text{ at fixed } r.$$

So, $H = (\text{cylindrical coordinates, fixed } r)$

$$=$$

The Schrödinger equation for a particle on a ring then becomes:

$$HY = EY$$

$$= EF$$

$$= F$$

The general solution to this equation is the now familiar expression:

$$F(f) = C_1 e^{-imf} + C_2 e^{imf}, \text{ where } m =$$

Application of the cyclic boundary condition, $F(f) = F(f+2\pi)$, results in the quantization of the energy expression: $E =$ where $m = 0, \pm 1, \pm 2, \pm 3, \dots$ It can be seen that the $\pm m$ values correspond to angular momentum of the same magnitude but opposite directions. Normalization of the wavefunction (over the region 0 to 2π) corresponding to $+$ or $-m$ will result in a value of for the normalization constant.

$$\sqrt{F(f)} = e^{imf}$$

$$\frac{1}{\sqrt{2\pi}}$$

$$\frac{1}{\sqrt{2\pi}}$$

$$\frac{1}{\sqrt{2\pi}}$$

$$b. = 6.06 \times 10^{-28} \text{ erg cm}^2$$

$$=$$

$$= 3.09 \times 10^{-12} \text{ erg}$$

$$DE = (22 - 12) 3.09 \times 10^{-12} \text{ erg} = 9.27 \times 10^{-12} \text{ erg}$$

$$\text{but } DE = h\nu = hc/\lambda \text{ So } \lambda = hc/DE$$

$$\lambda =$$

$$= 2.14 \times 10^{-5} \text{ cm} = 2.14 \times 10^3 \text{ Å}$$

Sources of error in this calculation include:

- i. The attractive force of the carbon nuclei is not included in the Hamiltonian.

ii. The repulsive force of the other p-electrons is not included in the Hamiltonian.

iii. Benzene is not a ring.

iv. Electrons move in three dimensions not one.

13.

$$Y(f,0) = \cos 2f.$$

This wavefunction needs to be expanded in terms of the eigenfunctions of the angular momentum operator, L_z . This is most easily accomplished by an exponential expansion of the Cos function.

$$Y(f,0) =$$

=

The wavefunction is now written in terms of the eigenfunctions of the angular momentum operator, L_z , but they need to include their normalization constant, N .

$$Y(f,0) =$$

=

Once the wavefunction is written in this form (in terms of the normalized eigenfunctions of the angular momentum operator having m eigenvalues) the probabilities for observing angular momentums of 0, 2, and -2 can be easily identified as the squares of the coefficients of the corresponding eigenfunctions.

$$P_2 =$$

$$P_{-2} =$$

$$P_0 =$$

14.

$$a. mv^2 = 100 \text{ eV}$$

$$v^2 =$$

$$v = 0.593 \times 10^9 \text{ cm/sec}$$

The length of the N_2 molecule is $2\text{\AA} = 2 \times 10^{-8} \text{ cm}$.

$$v =$$

$$t = = 3.37 \times 10^{-17} \text{ sec}$$

b. The normalized ground state harmonic oscillator can be written as:

$$Y_0 = 1/4e^{-ax^2/2}, \text{ where } a = \text{ and } x = r - r_e$$

Calculating constants;

$$a_{N_2} =$$

$$= 0.48966 \times 10^{19} \text{ cm}^{-2} = 489.66 \text{ \AA}^{-2}$$

$$\text{For } N_2: Y_0(r) = 3.53333\text{\AA}e^{-(244.83\text{\AA}^{-2})(r-1.09769\text{\AA})^2}$$

$$a_{N_2^+} =$$

$$= 0.45823 \times 10^{19} \text{ cm}^{-2} = 458.23 \text{ \AA}^{-2}$$

$$\text{For } N_2^+: Y_0(r) = 3.47522\text{\AA}e^{-(229.113\text{\AA}^{-2})(r-1.11642\text{\AA})^2}$$

$$c. P(v=0) =$$

Let $P(v=0) = I^2$ where $I = \text{integral}$:

$$I = \int$$

$$(3.53333\text{\AA}e^{-(244.830\text{\AA}^{-2})(r-1.09769\text{\AA})^2})dr$$

Let $C_1 = 3.47522\text{\AA}$, $C_2 = 3.53333\text{\AA}$,

$A_1 = 229.113\text{\AA}^{-2}$, $A_2 = 244.830\text{\AA}^{-2}$,

$r_1 = 1.11642\text{\AA}$, $r_2 = 1.09769\text{\AA}$,

$I = C_1 C_2 dr$.

Focusing on the exponential:

$$-A_1(r-r_1)^2 - A_2(r-r_2)^2 = -A_1(r^2 - 2r_1r + r_1^2) - A_2(r^2 - 2r_2r + r_2^2)$$

$$= -(A_1 + A_2)r^2 + (2A_1r_1 + 2A_2r_2)r - A_1r_1^2 - A_2r_2^2$$

Let $A = A_1 + A_2$,

$B = 2A_1r_1 + 2A_2r_2$,

$C = C_1 C_2$, and

$D = A_1r_1^2 + A_2r_2^2$.

$I = Cdr$

$= Cdr$

where $-A(r-r_0)^2 + D' = -Ar^2 + Br - D$

$-A(r^2 - 2r_0r + r_0^2) + D' = -Ar^2 + Br - D$

such that, $2Ar_0 = B$

$-Ar_0^2 + D' = -D$

and, $r_0 =$

$D' = Ar_0^2 - D = A - D = -D$.

$I = Cdr$

$= CeD'dy$

$= CeD'$

Now back substituting all of these constants:

$I = C_1 C_2 \exp$

$I = (3.47522)(3.53333)$

$\cdot \exp$

$\cdot \exp$

$I = 0.959$

$P(v=0) = I_2 = 0.92$, so there is a 92% probability.

15.

a. $E_n =$

$DE = E_{n+1} - E_n$

$=$

$=$

$= 4.27 \times 10^{-13} \text{ erg}$

$DE =$

$l =$

$= 4.66 \times 10^{-4} \text{ cm}$

$$= 2150 \text{ cm}^{-1}$$

$$\text{b. } Y_0 = 1/4e^{-ax^2/2}$$

$$=$$

$$=$$

$$=$$

$$=$$

$$= 1/2e^{-ax^2/2} = 0$$

$$=$$

$$=$$

$$=$$

$$= 21/2$$

$$= 21/21/2$$

$$=$$

$$Dx = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} =$$

$$=$$

$$=$$

$$= 3.38 \times 10^{-10} \text{ cm} = 0.0338 \text{ \AA}$$

$$\text{c. } Dx =$$

The smaller k and m become, the larger the uncertainty in the internuclear distance becomes. Helium has a small m and small attractive force between atoms. This results in a very large Dx . This implies that it is extremely difficult for He atoms to "vibrate" with small displacement as a solid, even as absolute zero is approached.

16.

$$\text{a. } W =$$

$$W =$$

$$e =$$

$$= +$$

$$= +$$

Making this substitution results in the following three integrals:

$$W = +$$

$$+$$

$$= + +$$

$$a$$

$$= 2 + 2 +$$

$$a$$

$$= + +$$

$$W = + a$$

$$\text{b. Optimize } b \text{ by evaluating } = 0$$

$$=$$

$$= - b$$

So, $b =$ or, $b =$,

and, $b =$. Substituting this value of b into the expression for W gives:

$$W = + a$$

$$= + a$$

$$= 2\pi a m + 2\pi a m$$

$$= a m = a m$$

$$= 0.812889106 a m^{-1/3} \text{ which is in error by only } 0.5284\% \text{ !!!!}$$

17.

$$a. H = - + kx^2$$

$$f = a \text{ for } -a < x < a$$

$$f = 0 \text{ for } |x| \geq a$$

$$=$$

$$= a^{-5}$$

$$= a^{-5}$$

$$+ a^{-5}$$

$$= a^{-5}$$

$$+ a^{-5}$$

$$= a^{-5} dx + a^{-5}$$

$$= a^{-5} \int_0^a (a - x) dx$$

$$+ a^{-5} \int_{-a}^0 (a + x) dx$$

$$= a^{-5} + a^{-5}$$

$$= a^{-5}$$

$$= a^{-5}$$

$$= a^{-5}$$

$$= a^{-5} = +$$

b. Substituting $a = b$ into the above expression for E we obtain:

$$E = +$$

$$= km$$

$$c. E = +$$

$$= - + = - + = 0$$

$$= \text{and } 352 = 2mk a^4$$

$$\text{So, } a^4 = , \text{ or } a =$$

$$\text{Therefore } f_{\text{best}} = ,$$

$$\text{and } E_{\text{best}} = + = km.$$

$$d. =$$

$$= = 0.1952 = 19.52\%$$

18.

$$a. H_0 y = y = Y_{l,m}(q, f)$$

$$= 2 l(l+1) Y_{l,m}(q,\phi)$$

$$E = l(l+1)$$

$$b. V = -\frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{4\pi\epsilon_0 r} \cos\theta$$

$$E =$$

$$= -\frac{e^2}{4\pi\epsilon_0 r}$$

Using the given identity this becomes:

$$E = -\frac{e^2}{4\pi\epsilon_0 r} +$$

$$-\frac{e^2}{4\pi\epsilon_0 r}$$

The spherical harmonics are orthonormal, thus $\int Y_{l,m} Y_{l',m'}^* d\Omega = \delta_{l,l'} \delta_{m,m'}$, and $E = 0$.

$$E =$$

$$= -\frac{e^2}{4\pi\epsilon_0 r}$$

Using the given identity this becomes:

$$= -\frac{e^2}{4\pi\epsilon_0 r} +$$

$$-\frac{e^2}{4\pi\epsilon_0 r}$$

$$= -$$

This indicates that the only term contributing to the sum in the expression for E is when $l=1$, and $m=0$, otherwise vanishes (from orthonormality). In quantum chemistry when using orthonormal functions it is typical to write the term as a delta function, for example $\delta_{lm,10}$, which only has values of 1 or 0; $\delta_{ij} = 1$ when $i = j$ and 0 when $i \neq j$. This delta function when inserted into the sum then eliminates the sum by "picking out" the non-zero component. For example,

$$= -\frac{e^2}{4\pi\epsilon_0 r} \delta_{lm,10}, \text{ so}$$

$$E =$$

$$E = 0(0+1) = 0 \text{ and } E = 1(1+1) =$$

Inserting these energy expressions above yields:

$$E = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$c. E = E + E + E + \dots$$

$$= 0 + 0 +$$

$$= -$$

$$a = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$=$$

$$d. a =$$

$$a = \frac{1}{4} \times 12598 \times 10^6 \text{ cm}^{-1} = \frac{1}{4} \times 1.2598 \times 10^7 \text{ cm}^{-1}$$

$$a_H = 0.0987 \text{ Å}^3$$

$$a_{Cs} = 57.57 \text{ Å}^3$$

19.

The above diagram indicates how the SALC-AOs are formed from the 1s, 2s, and 2p N atomic orbitals. It can be seen that there are 3sg, 3su, 1pux, 1puy, 1pgx, and 1pgy SALC-AOs. The Hamiltonian matrices (Fock matrices) are given. Each of these can be diagonalized to give the following MO energies:

$$3sg; -15.52, -1.45, \text{ and } -0.54 \text{ (hartrees)}$$

$$3su; -15.52, -0.72, \text{ and } 1.13$$

$$1pux; -0.58$$

1p_{xy}; -0.58

1p_{gx}; 0.28

1p_{gy}; 0.28

It can be seen that the 3s_g orbitals are bonding, the 3s_u orbitals are antibonding, the 1p_{xu} and 1p_{yu} orbitals are bonding, and the 1p_{gx} and 1p_{gy} orbitals are antibonding.

20.

Using these approximate energies we can draw the following MO diagram:

This MO diagram is not an orbital correlation diagram but can be used to help generate one. The energy levels on each side (C and H₂) can be "superimposed" to generate the reactant side of the orbital correlation diagram and the center CH₂ levels can be used to form the product side. Ignoring the core levels this generates the following orbital correlation diagram.

21.

a. The two F p orbitals (top and bottom) generate the following reducible representation:

D_{3h} E 2C₃ 3C₂ σh 2S₃ 3σv

G_p 2 2 0 0 0 2

This reducible representation reduces to 1A₁' and 1A₂" irreducible representations.

Projectors may be used to find the symmetry-adapted AOs for these irreducible representations.

f_{a1}' =

f_{a2}" =

b. The three trigonal F p orbitals generate the following reducible representation:

D_{3h} E 2C₃ 3C₂ σh 2S₃ 3σv

G_p 3 0 1 3 0 1

This reducible representation reduces to 1A₁' and 1E' irreducible representations.

Projectors may be used to find the symmetry-adapted -AOs for these irreducible representations (but they are exactly analogous to the previous few problems):

f_{a1}' =

f_e' = (1/6)^{-1/2} (2 f₃ – f₄ – f₅)

f_e' = .

c. The 3 P sp² orbitals generate the following reducible representation:

D_{3h} E 2C₃ 3C₂ σh 2S₃ 3σv

G_{sp2} 3 0 1 3 0 1

This reducible representation reduces to 1A₁' and 1E' irreducible representations. Again, projectors may be used to find the symmetry-adapted -AOs for these irreducible representations:

f_{a1}' =

f_e' =

f_e' = .

The leftover P p_z orbital generate the following irreducible representation:

D_{3h} E 2C₃ 3C₂ σh 2S₃ 3σv

G_{pz} 1 1 -1 -1 -1 1

This irreducible representation is A₂"

f_{a2}" = f₉.

Drawing an energy level diagram using these SALC-AOs would result in the following:

22.

a. For non-degenerate point groups, one can simply multiply the representations (since only one representation will be obtained):

$$a_1 \times b_1 = b_1$$

Constructing a "box" in this case is unnecessary since it would only contain a single row. Two unpaired electrons will result in a singlet ($S=0$, $MS=0$), and three triplets ($S=1$, $MS=1$; $S=1$, $MS=0$; $S=1$, $MS=-1$). The states will be: $3B_1(MS=1)$, $3B_1(MS=0)$, $3B_1(MS=-1)$, and $1B_1(MS=0)$.

b. Remember that when coupling non-equivalent linear molecule angular momenta, one simply adds the individual L_z values and vector couples the electron spin. So, in this case ($1p_u 12p_u$), we have ML values of $1+1$, $1-1$, $-1+1$, and $-1-1$ (2 , 0 , 0 , and -2). The term symbol D is used to denote the spatially doubly degenerate level ($ML=\pm 2$) and there are two distinct spatially non-degenerate levels denoted by the term symbol S ($ML=0$). Again, two unpaired electrons will result in a singlet ($S=0$, $MS=0$), and three triplets ($S=1$, $MS=1$; $S=1$, $MS=0$; $S=1$, $MS=-1$). The states generated are then:

$1D$ ($ML=2$); one state ($MS=0$),

$1D$ ($ML=-2$); one state ($MS=0$),

$3D$ ($ML=2$); three states ($MS=1, 0$, and -1),

$3D$ ($ML=-2$); three states ($MS=1, 0$, and -1),

$1S$ ($ML=0$); one state ($MS=0$),

$1S$ ($ML=0$); one state ($MS=0$),

$3S$ ($ML=0$); three states ($MS=1, 0$, and -1), and

$3S$ ($ML=0$); three states ($MS=1, 0$, and -1).

c. Constructing the "box" for two equivalent p electrons one obtains:

ML

MS

2

1

0

1

$|p_1 a p_1 a|$

0

$|p_1 a p_1 b|$

$|p_1 a p_1 b|$,

$|p_1 a p_1 b|$

From this "box" one obtains six states:

$1D$ ($ML=2$); one state ($MS=0$),

$1D$ ($ML=-2$); one state ($MS=0$),

$1S$ ($ML=0$); one state ($MS=0$),

$3S$ ($ML=0$); three states ($MS=1, 0$, and -1).

d. It is not necessary to construct a "box" when coupling non-equivalent angular momenta since vector coupling results in a range from the sum of the two individual angular momenta to the absolute value of their difference. In this case, $3d 14d 1$, $L=4$, 3 , 2 , 1 , 0 , and $S=1, 0$. The term symbols are: $3G$, $1G$, $3F$, $1F$, $3D$, $1D$, $3P$, $1P$, $3S$, and $1S$. The L and S angular momenta can be vector coupled to produce further splitting into levels:

$$J = L + S \dots |L - S|.$$

Denoting J as a term symbol subscript one can identify all the levels and subsequent $(2J + 1)$ states:

3G5 (11 states),

3G4 (9 states),

3G3 (7 states),

1G4 (9 states),

3F4 (9 states),

3F3 (7 states),

3F2 (5 states),

1F3 (7 states),

3D3 (7 states),

3D2 (5 states),

3D1 (3 states),

1D2 (5 states),

3P2 (5 states),

3P1 (3 states),

3P0 (1 state),

1P1 (3 states),

3S1 (3 states), and

1S0 (1 state).

e. Construction of a "box" for the two equivalent d electrons generates (note the "box" has been turned side ways for convenience):

MS

ML

1

0

4

|d_{2a}d_{2b}|

3

|d_{2a}d_{1a}|

|d_{2a}d_{1b}|, |d_{2b}d_{1a}|

2

|d_{2a}d_{0a}|

|d_{2a}d_{0b}|, |d_{2b}d_{0a}|, |d_{1a}d_{1b}|

1

|d_{1a}d_{0a}|, |d_{2a}d_{-1a}|

|d_{1a}d_{0b}|, |d_{1b}d_{0a}|, |d_{2a}d_{-1b}|, |d_{2b}d_{-1a}|

0

|d_{2a}d_{-2a}|, |d_{1a}d_{-1a}|

$|d_{2ad-2b}|, |d_{2bd-2a}|, |d_{1ad-1b}|, |d_{1bd-1a}|, |d_{0ad0b}|$

The term symbols are: 1G, 3F, 1D, 3P, and 1S. The L and S angular momenta can be vector coupled to produce further splitting into levels:

1G₄ (9 states),

3F₄ (9 states),

3F₃ (7 states),

3F₂ (5 states),

1D₂ (5 states),

3P₂ (5 states),

3P₁ (3 states),

3P₀ (1 state), and

1S₀ (1 state).

23.

a. Once the spatial symmetry has been determined by multiplication of the irreducible representations, the spin coupling gives the result:

b. There are three states here :

1.) $|3a_1a_1b_1a|$,

2.) , and

3.) $|3a_1b_1b_1b|$

c. $|3a_1a_3a_1b|$

24.

a. All the Slater determinants have in common the $|1s_a1s_b2s_a2s_b|$ "core" and hence this component will not be written out explicitly for each case.

$$3P(M_L=1, M_S=1) = |p_1a p_0a|$$

$$= |a(pz)a|$$

=

$$3P(M_L=0, M_S=1) = |p_1a p_{-1}a|$$

$$= |aa|$$

=

=

=

$$= -i|pxapya|$$

$$3P(M_L=-1, M_S=1) = |p_{-1}a p_0a|$$

$$= |a(pz)a|$$

=

As you can see, the symmetries of each of these states cannot be labeled with a single irreducible representation of the C_{2v} point group. For example, $|pxapza|$ is xz (B₁) and $|pyapza|$ is yz (B₂) and hence the 3P(M_L=1, M_S=1) state is a combination of B₁ and B₂ symmetries. But, the three 3P(M_L, M_S=1) functions are degenerate for the C atom and any combination of these three functions would also be degenerate. Therefore, we can choose new combinations that can be labeled with "pure" C_{2v} point group labels.

$$3P(xz, M_S=1) = |pxapza|$$

$$= = 3B1$$

$$3P(yx, MS=1) = |pyapxa|$$

$$= = 3A2$$

$$3P(yz, MS=1) = |pyapza|$$

$$= = 3B2$$

Now, we can do likewise for the five degenerate 1D states:

$$1D(ML=2, MS=0) = |p1ap1b|$$

$$= |ab|$$

$$=$$

$$1D(ML=-2, MS=0) = |p-1ap-1b|$$

$$= |ab|$$

$$=$$

$$1D(ML=1, MS=0) =$$

$$=$$

$$=$$

$$1D(ML=-1, MS=0) =$$

$$=$$

$$=$$

$$1D(ML=0, MS=0) =$$

$$=$$

$$+ |ab|)$$

$$=$$

$$+$$

$$+)$$

$$=)$$

Analogous to the three 3P states, we can also choose combinations of the five degenerate 1D states which can be labeled with "pure" C_{2v} point group labels:

$$1D(xx-yy, MS=0) = |pxapxb| - |pyapyb|$$

$$= = 1A1$$

$$1D(yx, MS=0) = |pxapyb| + |pyapxb|$$

$$= = 1A2$$

$$1D(zx, MS=0) = |pzapxb| - |pzbpax|$$

$$= = 1B1$$

$$1D(zy, MS=0) = |pzapyb| - |pzbpaya|$$

$$= = 1B2$$

$$1D(2zz+xx+yy, MS=0) =)$$

$$= 1D(ML=0, MS=0) = 1A1$$

The only state left is the 1S:

$$1S(M_L=0, M_S=0) =$$

=

$$- |ab\rangle$$

=

-

$$-)$$

$$=)$$

Each of the components of this state are A1 and hence this state has

A1 symmetry.

b. Forming symmetry-adapted AOs from the C and H atomic orbitals would generate the following:

The bonding, nonbonding, and antibonding orbitals of CH₂ can be illustrated in the following manner:

c.

d. - e. It is necessary to determine how the wavefunctions found in part a. correlate with states of the CH₂ molecule:

$$3P(xz, M_S=1); 3B1 = sg2s2pxpz \frac{1}{4} \frac{1}{4} \frac{1}{4} \frac{1}{4} \otimes s2n2pps^*$$

$$3P(yx, M_S=1); 3A2 = sg2s2pxpy \frac{1}{4} \frac{1}{4} \frac{1}{4} \frac{1}{4} \otimes s2n2pps$$

$$3P(yz, M_S=1); 3B2 = sg2s2pypz \frac{1}{4} \frac{1}{4} \frac{1}{4} \frac{1}{4} \otimes s2n2ss^*$$

$$1D(xx-yy, M_S=0); 1A1 \frac{1}{4} \frac{1}{4} \frac{1}{4} \frac{1}{4} \otimes s2n2pp2 - s2n2s2$$

$$1D(yx, M_S=0); 1A2 \frac{1}{4} \frac{1}{4} \frac{1}{4} \frac{1}{4} \otimes s2n2spp$$

$$1D(zx, M_S=0); 1B1 \frac{1}{4} \frac{1}{4} \frac{1}{4} \frac{1}{4} \otimes s2n2s^*pp$$

$$1D(zy, M_S=0); 1B2 \frac{1}{4} \frac{1}{4} \frac{1}{4} \frac{1}{4} \otimes s2n2s^*s$$

$$1D(2zz+xx+yy, M_S=0); 1A1 \frac{1}{4} \frac{1}{4} \frac{1}{4} \frac{1}{4} \otimes 2s2n2s^*2 + s2n2pp2 + s2n2s2$$

Note, the C + H₂ state to which the lowest 1A1 (s2n2s₂) CH₂ state decomposes would be sg2s2py₂. This state (sg2s2py₂) cannot be obtained by a simple combination of the 1D states. In order to obtain pure sg2s2py₂ it is necessary to combine 1S with 1D. For example,

$$sg2s2py_2 = - .$$

This indicates that a configuration correlation diagram must be drawn with a barrier near the 1D asymptote to represent the fact that 1A1 CH₂ correlates with a mixture of 1D and 1S carbon plus hydrogen. The C + H₂ state to which the lowest 3B1 (s2ns2pp) CH₂ state decomposes would be sg2spy₂px.

f. If you follow the 3B1 component of the C(3P) + H₂ (since it leads to the ground-state products) to 3B1 CH₂ you must go over an approximately 20 Kcal/mole barrier. Of course this path produces 3B1 CH₂ product. Distortions away from C_{2v} symmetry, for example to C_s symmetry, would make the a₁ and b₂ orbitals identical in symmetry (a'). The b₁ orbitals would maintain their different symmetry going to a'' symmetry. Thus 3B1 and 3A₂ (both 3A'' in C_s symmetry and odd under reflection through the molecular plane) can mix. The system could thus follow the 3A₂ component of the C(3P) + H₂ surface to the place (marked with a circle on the CCD) where it crosses the 3B1 surface upon which it then moves and continues to products. As a result, the barrier would be lowered.

You can estimate when the barrier occurs (late or early) using thermodynamic information for the reaction (i.e. slopes and asymptotic energies). For example, an early barrier would be obtained for a reaction with the characteristics:

and a late barrier would be obtained for a reaction with the characteristics:

This relation between reaction endothermicity or exothermicity and the character of the transition state is known as the Hammond postulate. Note that the C(3P₁) + H₂ → CH₂ reaction of interest here has an early barrier.

g. The reaction C(1D) + H₂ → CH₂ (1A₁) should have no symmetry barrier (this can be recognized by following the 1A₁ (C(1D) + H₂) reactants down to the 1A₁ (CH₂) products).

25.

This problem in many respects is analogous to problem 24.

The 3B1 surface certainly requires a two configuration CI wavefunction; the $s2s2np_x$ ($p2py2sp_x$) and the $s2n2pxs^*$ ($p2s2pxpz$). The 1A1 surface could use the $s2s2n2$ ($p2s2py2$) only but once again there is no combination of 1D determinants which gives purely this configuration ($p2s2py2$). Thus mixing of both 1D and 1S determinants are necessary to yield the required $p2s2py2$ configuration. Hence even the 1A1 surface would require a multiconfigurational wavefunction for adequate description.

Configuration correlation diagram for the reaction $C2H2 + C \rightarrow C3H2$.

26.

a. CCl_4 is tetrahedral and therefore is a spherical top. $CHCl_3$ has C_{3v} symmetry and therefore is a symmetric top. CH_2Cl_2 has C_{2v} symmetry and therefore is an asymmetric top.

b. CCl_4 has such high symmetry that it will not exhibit pure rotational spectra because it has no permanent dipole moment. $CHCl_3$ and CH_2Cl_2 will both exhibit pure rotation spectra.

27.

NH_3 is a symmetric top (oblate). Use the given energy expression,

$$E = (A - B) K^2 + B J(J + 1),$$

$A = 6.20 \text{ cm}^{-1}$, $B = 9.44 \text{ cm}^{-1}$, selection rules $\Delta J = \pm 1$, and the fact that lies along the figure axis such that $\Delta K = 0$, to give:

$$\Delta E = 2B(J + 1) = 2B, 4B, \text{ and } 6B \quad (J = 0, 1, \text{ and } 2).$$

So, lines are at 18.88 cm^{-1} , 37.76 cm^{-1} , and 56.64 cm^{-1} .

28.

To convert between cm^{-1} and energy, multiply by $hc = (6.62618 \times 10^{-34} \text{ J sec})(2.997925 \times 10^{10} \text{ cm sec}^{-1}) = 1.9865 \times 10^{-23} \text{ J cm}$.

Let all quantities in cm^{-1} be designated with a bar,

e.g. $\bar{\nu} = 1.78 \text{ cm}^{-1}$.

a. $hc =$

$R_e =$,

$$m = m_e \times 1.66056 \times 10^{-27} \text{ kg}$$

$$= 1.0824 \times 10^{-26} \text{ kg}.$$

$$hc = hc(\bar{\nu}) = 3.5359 \times 10^{-23} \text{ J}$$

$R_e =$

$$R_e = 1.205 \times 10^{-10} \text{ m} = 1.205 \text{ \AA}$$

$$D_e = D_0 = 6.35 \times 10^{-6} \text{ cm}^{-1}$$

$$w_{exe} = 13.30 \text{ cm}^{-1}.$$

$$D = D_0 + \dots$$

$$= 66782.2 - \dots$$

$$= 65843.0 \text{ cm}^{-1} = 8.16 \text{ eV}.$$

$$a_e = +$$

$$= +$$

$$= + = 0.0175 \text{ cm}^{-1}.$$

$$B_0 = B_e - a_e(1/2), \dots = 1.78 - 0.0175/2$$

$$= 1.77 \text{ cm}^{-1}$$

$$B_1 = B_e - a_e(3/2), \dots = 1.78 - 0.0175(1.5)$$

$$= 1.75 \text{ cm}^{-1}$$

b. The molecule has a dipole moment and so it should have a pure rotational spectrum. In addition, the dipole moment should change with R and so it should have a vibration-rotation spectrum.

The first three lines correspond to $J = 1 \rightarrow 0$, $J = 2 \rightarrow 1$, $J = 3 \rightarrow 2$

$$E = w_e(v + 1/2) - w_{ex}e(v + 1/2)^2 + B_v J(J + 1) - D_e J^2(J + 1)^2$$

$$DE = w_e - 2w_{ex}e - B_0 J(J + 1) + B_1 J(J - 1) - 4D_e J^3$$

$$= -2 - J(J + 1) + J(J - 1) - 4J^3$$

$$= 1885 - 2(13.3) - 1.77J(J + 1) + 1.75J(J - 1) - 4(6.35 \times 10^{-6})J^3$$

$$= 1858.4 - 1.77J(J + 1) + 1.75J(J - 1) - 2.54 \times 10^{-5}J^3$$

$$= 1854.9 \text{ cm}^{-1}$$

$$= 1851.3 \text{ cm}^{-1}$$

$$= 1847.7 \text{ cm}^{-1}$$

29.

The $\text{C}_2\text{H}_2\text{Cl}_2$ molecule has a sh plane of symmetry (plane of molecule), a C_2 axis (\perp to the molecular plane), and inversion symmetry, this results in C_{2h} symmetry. Using C_{2h} symmetry, the modes can be labeled as follows: ν_1 , ν_2 , ν_3 , ν_4 , and ν_5 are g_g , ν_6 and ν_7 are g_u , ν_8 is g_g , and ν_9 , ν_{10} , ν_{11} , and ν_{12} are g_u .

30.

Molecule I Molecule II

$$R_{\text{CH}} = 1.121 \text{ \AA} \quad R_{\text{CH}} = 1.076 \text{ \AA}$$

$$\angle \text{HCH} = 104^\circ \quad \angle \text{HCH} = 136^\circ$$

$$y_{\text{H}} = R \sin(q/2) = \pm 0.8834 \quad y_{\text{H}} = \pm 0.9976$$

$$z_{\text{H}} = R \cos(q/2) = -0.6902 \quad z_{\text{H}} = -0.4031$$

Center of Mass(COM):

clearly, $X = Y = 0$,

$$Z = -0.0986 \quad Z = -0.0576$$

$$a. I_{xx} = -M(Y^2 + Z^2)$$

$$I_{xy} = -2MXY$$

$$I_{xx} = 2(1.121)^2 - 14(-0.0986)^2 \quad I_{xx} = 2(1.076)^2 - 14(-0.0576)^2$$

$$= 2.377 = 2.269$$

$$I_{yy} = 2(0.6902)^2 - 14(-0.0986)^2 \quad I_{yy} = 2(0.4031)^2 - 14(-0.0576)^2$$

$$= 0.8167 = 0.2786$$

$$I_{zz} = 2(0.8834)^2 \quad I_{zz} = 2(0.9976)^2$$

$$= 1.561 = 1.990$$

$$I_{xz} = I_{yz} = I_{xy} = 0$$

b. Since the moment of inertia tensor is already diagonal, the principal moments of inertia have already been determined to be ($I_a < I_b < I_c$):

$$I_{yy} < I_{zz} < I_{xx} \quad I_{yy} < I_{zz} < I_{xx}$$

$$0.8167 < 1.561 < 2.377 \quad 0.2786 < 1.990 < 2.269$$

Using the formula: $A = X$

$$A = \text{cm}^{-1}$$

similarly, $B = \text{cm}^{-1}$, and $C = \text{cm}^{-1}$.

So,

Molecule I Molecule II

$$y \text{ } \bar{A} = 20.62 \text{ } y \text{ } \bar{A} = 60.45$$

$$z \text{ } \bar{B} = 10.79 \text{ } z \text{ } \bar{B} = 8.46$$

$$x \text{ } \bar{C} = 7.08 \text{ } x \text{ } \bar{C} = 7.42$$

c. Averaging $B + C$:

$$B = (B + C)/2 = 8.94 \text{ } B = (B + C)/2 = 7.94$$

$$A - B = 11.68 \text{ } A - B = 52.51$$

Using the prolate top formula:

$$E = (A - B) K^2 + B J(J + 1),$$

Molecule I Molecule II

$$E = 11.68K^2 + 8.94J(J + 1) \text{ } E = 52.51K^2 + 7.94J(J + 1)$$

Levels: $J = 0, 1, 2, \dots$ and $K = 0, 1, \dots, J$

For a given level defined by J and K , there are MJ degeneracies given by: $(2J + 1) \times$

d.

Molecule I Molecule II

e. Assume molecule I is CH_2^- and molecule II is CH_2 . Then,

$$DE = EJ_j(\text{CH}_2) - EJ_i(\text{CH}_2^-), \text{ where:}$$

$$E(\text{CH}_2) = 52.51K^2 + 7.94J(J + 1), \text{ and } E(\text{CH}_2^-) = 11.68K^2 + 8.94J(J + 1)$$

For R-branches: $J_j = J_i + 1$, $DK = 0$:

$$DER = EJ_j(\text{CH}_2) - EJ_i(\text{CH}_2^-)$$

$$= 7.94(J_i + 1)(J_i + 1 + 1) - 8.94J_i(J_i + 1)$$

$$= (J_i + 1)\{7.94(J_i + 1 + 1) - 8.94J_i\}$$

$$= (J_i + 1)\{(7.94 - 8.94)J_i + 2(7.94)\}$$

$$= (J_i + 1)\{-J_i + 15.88\}$$

For P-branches: $J_j = J_i - 1$, $DK = 0$:

$$DEP = EJ_j(\text{CH}_2) - EJ_i(\text{CH}_2^-)$$

$$= 7.94(J_i - 1)(J_i - 1 + 1) - 8.94J_i(J_i + 1)$$

$$= J_i\{7.94(J_i - 1) - 8.94(J_i + 1)\}$$

$$= J_i\{(7.94 - 8.94)J_i - 7.94 - 8.94\}$$

$$= J_i\{-J_i - 16.88\}$$

This indicates that the R branch lines occur at energies which grow closer and closer together as J increases (since the $15.88 - J_i$ term will cancel). The P branch lines occur at energies which lie more and more negative (i.e. to the left of the origin). So, you can predict that if molecule I is CH_2^- and molecule II is CH_2 then the R-branch has a band head and the P-branch does not. This is observed, therefore our assumption was correct: molecule I is CH_2^- and molecule II is CH_2 .

f. The band head occurs when $= 0$.

$$= [(J_i + 1)\{-J_i + 15.88\}] = 0$$

$$= = 0$$

$$= -2J_i + 14.88 = 0$$

$\sqrt{J_i} = 7.44$, so $J = 7$ or 8 .

At $J = 7.44$:

$$DER = (J + 1)\{-J + 15.88\}$$

$$DER = (7.44 + 1)\{-7.44 + 15.88\} = (8.44)(8.44) = 71.2 \text{ cm}^{-1} \text{ above the origin.}$$

31.

a.

D6h

E

2C6

2C3

C2

3C2'

3C2''

i

2S3

2S6

sh

3sd

3sv

A1g

1

1

1

1

1

1

1

1

1

1

1

1

x^2+y^2,z^2

A2g

1

1

1

-1

1

1

-1

B1g

-1

-1

-1

-1

-1

-1

1

1

-1

1

1

-1

E1g

2
1
-1
-2
0
0
2
1
-1
-2
0
0
Rx,Ry
(xz,yz)
E2g
2
-1
-1
2
0
0
2
-1
-1
2
0
0
(x²-y²,xy)
A1u
1
1
1
1
1
1
-1
-1
-1

-1

-1

-1

A2u

1

1

1

1

-1

-1

-1

-1

-1

-1

1

1

z

B1u

1

-1

1

-1

1

-1

-1

1

-1

1

-1

1

B2u

1

-1

1

-1

-1

1

-1

1
-1
1
1
-1
E1u
2
1
-1
-2
0
0
-2
-1
1
2
0
0
(x,y)
E2u
2
-1
-1
2
0
0
-2
1
1
-2
0
0
GC-H
6
0
0
0
0

2
0
0
0
6
2
0

b. The number of irreducible representations may be found by using the following formula:

$n_{\text{irrep}} =$,

where g = the order of the point group (24 for D_{6h}).

$n_{A1g} =$

$$= \{(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1) \\ + (3)(0)(1)+(3)(2)(1)+(1)(0)(1)+(2)(0)(1) \\ + (2)(0)(1)+(1)(6)(1)+(3)(2)(1)+(3)(0)(1)\} \\ = 1$$

$$n_{A2g} = \{(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1) \\ + (3)(0)(-1)+(3)(2)(-1)+(1)(0)(1)+(2)(0)(1) \\ + (2)(0)(1)+(1)(6)(1)+(3)(2)(-1)+(3)(0)(-1)\} \\ = 0$$

$$n_{B1g} = \{(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1) \\ + (3)(0)(1)+(3)(2)(-1)+(1)(0)(1)+(2)(0)(-1) \\ + (2)(0)(1)+(1)(6)(-1)+(3)(2)(1)+(3)(0)(-1)\} \\ = 0$$

$$n_{B2g} = \{(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1) \\ + (3)(0)(-1)+(3)(2)(1)+(1)(0)(1)+(2)(0)(-1) \\ + (2)(0)(1)+(1)(6)(-1)+(3)(2)(-1)+(3)(0)(1)\} \\ = 0$$

$$n_{E1g} = \{(1)(6)(2)+(2)(0)(1)+(2)(0)(-1)+(1)(0)(-2) \\ + (3)(0)(0)+(3)(2)(0)+(1)(0)(2)+(2)(0)(1) \\ + (2)(0)(-1)+(1)(6)(-2)+(3)(2)(0)+(3)(0)(0)\} \\ = 0$$

$$n_{E2g} = \{(1)(6)(2)+(2)(0)(-1)+(2)(0)(-1)+(1)(0)(2) \\ + (3)(0)(0)+(3)(2)(0)+(1)(0)(2)+(2)(0)(-1) \\ + (2)(0)(-1)+(1)(6)(2)+(3)(2)(0)+(3)(0)(0)\} \\ = 1$$

$$n_{A1u} = \{(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1) \\ + (3)(0)(1)+(3)(2)(1)+(1)(0)(-1)+(2)(0)(-1) \\ + (2)(0)(-1)+(1)(6)(-1)+(3)(2)(-1)+(3)(0)(-1)\}$$

$$= 0$$

$$\begin{aligned} nA2u = & \{(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1) \\ & +(3)(0)(-1)+(3)(2)(-1)+(1)(0)(-1)+(2)(0)(-1) \\ & +(2)(0)(-1)+(1)(6)(-1)+(3)(2)(1)+(3)(0)(1)\} \end{aligned}$$

$$= 0$$

$$\begin{aligned} nB1u = & \{(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1) \\ & +(3)(0)(1)+(3)(2)(-1)+(1)(0)(-1)+(2)(0)(1) \\ & +(2)(0)(-1)+(1)(6)(1)+(3)(2)(-1)+(3)(0)(1)\} \end{aligned}$$

$$= 0$$

$$\begin{aligned} nB2u = & \{(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1) \\ & +(3)(0)(-1)+(3)(2)(1)+(1)(0)(-1)+(2)(0)(1) \\ & +(2)(0)(-1)+(1)(6)(1)+(3)(2)(1)+(3)(0)(-1)\} \end{aligned}$$

$$= 1$$

$$\begin{aligned} nE1u = & \{(1)(6)(2)+(2)(0)(1)+(2)(0)(-1)+(1)(0)(-2) \\ & +(3)(0)(0)+(3)(2)(0)+(1)(0)(-2)+(2)(0)(-1) \\ & +(2)(0)(1)+(1)(6)(2)+(3)(2)(0)+(3)(0)(0)\} \end{aligned}$$

$$= 1$$

$$\begin{aligned} nE2u = & \{(1)(6)(2)+(2)(0)(-1)+(2)(0)(-1)+(1)(0)(2) \\ & +(3)(0)(0)+(3)(2)(0)+(1)(0)(-2)+(2)(0)(1) \\ & +(2)(0)(1)+(1)(6)(-2)+(3)(2)(0)+(3)(0)(0)\} \end{aligned}$$

$$= 0$$

We see that $GC-H = A1g \hat{A}E2g \hat{A}B2u \hat{A}E1u$

c. x and $y \nrightarrow E1u$, $z \nrightarrow A2u$, so, the ground state $A1g$ level can be excited to the degenerate $E1u$ level by coupling through the x or y transition dipoles. Therefore $E1u$ is infrared active and \wedge polarized.

d. $(x^2 + y^2, z^2) \nrightarrow A1g$, $(xz, yz) \nrightarrow E1g$, $(x^2 - y^2, xy) \nrightarrow E2g$, so, the ground state $A1g$ level can be excited to the degenerate $E2g$ level by coupling through the $x^2 - y^2$ or xy transitions or be excited to the degenerate $A1g$ level by coupling through the xz or yz transitions. Therefore $A1g$ and $E2g$ are Raman active..

e. The $B2u$ mode is not IR or Raman active.

32.

a. Evaluate the z -component of mfi :

$mfi = \langle 2pz | e | 1s \rangle$, where $y1s = e$, and $y2pz = r \cos \theta e$.

$$mfi = \langle r \cos \theta e | e | r \cos \theta e \rangle$$

$$= \langle r \cos \theta e | e | r \cos \theta e \rangle$$

$$= \cos 2\theta$$

$$= 2p$$

$$= 2p \cos 3\theta \sin 15(p0)$$

$$= 2p$$

$$= = 0.7449$$

b. Examine the symmetry of the integrands for $\langle 2pz | e | x | 1s \rangle$ and $\langle 2pz | e | y | 1s \rangle$. Consider reflection in the xy plane:

Function

Symmetry

2pz

-1

x

+1

1s

+1

y

+1

Under this operation, the integrand of $\langle 2pz | e^x | 1s \rangle$ is $(-1)(1)(1) = -1$ (it is antisymmetric) and hence $\langle 2pz | e^x | 1s \rangle = 0$.

Similarly, under this operation the integrand of $\langle 2pz | e^y | 1s \rangle$ is

$(-1)(1)(1) = -1$ (it is also antisymmetric) and hence $\langle 2pz | e^y | 1s \rangle = 0$.

c. $t_R =$,

$E_i = E_{2pz} = -Z^2$

$E_f = E_{1s} = -Z^2$

$E_i - E_f = Z^2$

Making the substitutions for $E_i - E_f$ and $|mfi|$ in the expression for t_R we obtain:

$t_R =$,

$=$,

$=$,

Inserting $e^2 =$ we obtain:

$t_R =$

$= 25.6289$

$= 25,6289 \times$

$= 1.595 \times 10^{-9} \text{ sec} \times$

So, for example:

Atom

t_R

H

1.595 ns

He+

99.7 ps

Li+2

19.7 ps

Be+3

6.23 ps

Ne+9

159 fs

33.

a. $H = H_0 + \lambda H'(t)$, $H'(t) = V(q(t))$, $H_0|j\rangle = E_k|j\rangle$, $\omega_k = E_k/\hbar$

$i = \hbar$

let $\psi(r,t) = \psi(r)e^{-iE_k t/\hbar}$ and insert into the Schrödinger equation:

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi$$

$$i\hbar \frac{\partial \psi}{\partial t} = 0$$

$$i\hbar \frac{\partial \psi}{\partial t} = 0$$

$$i\hbar \frac{\partial \psi}{\partial t} = i\hbar \frac{\partial \psi}{\partial t}$$

So,

$$\psi = e^{-i(\omega_k)t}$$

Going back a few equations and multiplying from the left by $\langle j|$ instead of $|j\rangle$ we obtain:

$$i\hbar \frac{\partial \psi}{\partial t} = 0$$

$$i\hbar \frac{\partial \psi}{\partial t} = i\hbar \frac{\partial \psi}{\partial t}$$

So,

$$\psi = e^{-i(\omega_k)t}$$

Now, let:

$$c_m = c_m(0) + c_m(1)t + c_m(2)t^2 + \dots$$

$$c_k = c_k(0) + c_k(1)t + c_k(2)t^2 + \dots$$

and substituting into above we obtain:

$$m(0) + m(1)t + m(2)t^2 + \dots = \lambda H'_{mj} e^{-i(\omega_k)t}$$

first order:

$$m(0) = 0 \Rightarrow c_m(0) = 1$$

second order:

$$m(1) =$$

$(n+1)$ st order:

$$m(n) =$$

Similarly:

first order:

$$k(0) = 0 \Rightarrow c_k(0) = 0$$

second order:

$$k(1) =$$

$(n+1)$ st order:

$$k(n) =$$

So,

$$m(1) = c_m(0) \lambda H'_{mj} e^{-i(\omega_k)t} = \lambda H'_{mj}$$

$$c_m(1)(t) =$$

and similarly,

$$k(1) = c_m(0) H'_{km} e^{-i(\omega_k)t} = H'_{km} e^{-i(\omega_k)t}$$

$$c_k(1)(t) = V_{km} =$$

$$m(2) =$$

$$m(2) = H'_{mj} e^{-i(\omega_j)t} + H'_{mm}$$

$$c_m(2) = e^{-i(\omega_j)t} -$$

$$= -$$

$$= -$$

$$= + t -$$

Similarly,

$$k(2) =$$

$$= H'_{kj} e^{-i(\omega_j)t} +$$

$$H'_{km} e^{-i(\omega_k)t}$$

$$c_k(2)(t) = e^{-i(\omega_j)t} -$$

$$- e^{-i(\omega_k)t}$$

$$=$$

$$- h, -e^{-i(\omega_k)t}$$

$$=$$

$$+ h, -e^{-i(\omega_k)t}$$

$$=$$

$$+$$

So, the overall amplitudes c_m , and c_k , to second order are:

$$c_m(t) = 1 + + t +$$

$$-$$

$$c_k(t) = +$$

$$+ e^{-i(\omega_k)t} +$$

b. The perturbation equations still hold:

$$m(n) = ; k(n) =$$

$$\text{So, } c_m(0) = 1 \text{ and } c_k(0) = 0$$

$$m(1) = H'_{mm}$$

$$c_m(1) = V_{mm} =$$

$$k(1) = H'_{km} e^{-i(\omega_k)t}$$

$$c_k(1) = V_{km} =$$

$$=$$

$$m(2) = e^{-i(\omega_j+h)t} V_{mj} e^{-i(\omega_j)t} +$$

$$V_{mm} e^{-i(\omega_j)t}$$

$$c_m(2) = -$$

$$= e^{2ht} - e^{2ht}$$

$$k(2) = e^{-i(\omega_j+h)t} H'_{kj} e^{-i(\omega_k)t} +$$

$$H'_{km} = e^{-i(\omega_k - \omega_m)t}$$

$$c_k(2) = -$$

$$= -$$

Therefore, to second order:

$$c_m(t) = 1 + e^{2i\omega_k t}$$

$$c_k(t) =$$

$$+$$

c. In part a. the $c_k(t)$ grow linearly with time (for $\omega_k = 0$) while in part b. they remain finite for $\hbar > 0$. The result in part a. is due to the sudden turning on of the field.

$$d. |c_k(t)|^2 =$$

$$=$$

$$=$$

$$|c_k(t)|^2 =$$

Now, look at the limit as $\hbar \rightarrow 0^+$:

$$|c_k(t)|^2 \rightarrow 0 \text{ when } E_m = E_k$$

$$\lim_{\hbar \rightarrow 0^+} d(E_m - E_k)$$

So, the final result is the 2nd order golden rule expression:

$$|c_k(t)|^2 = d(E_m - E_k) \lim_{\hbar \rightarrow 0^+}$$

34.

a. $T_{nm} \gg$

evaluating $\langle 1s | V | 2s \rangle$ (using only the radial portions of the 1s and 2s wavefunctions since the spherical harmonics will integrate to unity) where $V = (e^2/r)$, the change in Coulomb potential when tritium becomes He:

$$\langle 1s | V | 2s \rangle = e \int_0^\infty r^2 dr$$

$$\langle 1s | V | 2s \rangle =$$

$$=$$

$$\langle 1s | V | 2s \rangle =$$

$$\langle 1s | V | 2s \rangle =$$

Now,

$$E_n = -\frac{13.6}{n^2}, E_{1s} = -13.6, E_{2s} = -3.4, E_{2s} - E_{1s} =$$

So,

$$T_{nm} = \frac{2\pi}{\hbar} |A_{nm}|^2 = 0.312 \text{ (for } Z = 1)$$

$$b. j_m(r) = j_1(s) = 2e^{-Y_{00}}$$

The orthogonality of the spherical harmonics results in only s-states having non-zero values for A_{nm} . We can then drop the Y_{00} (integrating this term will only result in unity) in determining the value of $A_{1s,2s}$.

$$y_n(r) = y_{2s} = e$$

Remember for $j_1(s)$ $Z = 1$ and for y_{2s} $Z = 2$

$$A_{nm} = e \int_0^\infty r^2 dr$$

$$A_{nm} = e \int_0^\infty r^2 dr$$

$$A_{nm} =$$

We obtain:

$$A_{nm} =$$

$$A_{nm} =$$

$$A_{nm} =$$

$$A_{nm} = -2$$

The transition probability is the square of this amplitude:

$$T_{nm} = = = 0.25 \text{ (for } Z = 1\text{)}.$$

The difference in these two results (parts a. and b.) will become negligible at large values of Z when the perturbation becomes less significant than in the case of $Z = 1$.

35.

is along Z (lab fixed), and is along z (the C-I molecule fixed bond). The angle between Z and z is b :

$$. = e m \cos b = e m D$$

So,

$$I = \langle D | . | D \rangle = \sin b d b d g d a$$

$$= e m \sin b d b d g d a.$$

Now use:

$$D D = *$$

to obtain:

$$I = e m * \sin b d b d g d a.$$

Now use:

$$\sin b d b d g d a = d J d M d K n,$$

to obtain:

$$I = e m * d J d M d K n$$

$$= e m \langle J' M' 10 | J M \rangle \langle J K | J' K' 10 \rangle.$$

We use:

$$\langle J K | J' K' 10 \rangle =$$

and,

$$\langle J' M' 10 | J M \rangle =$$

to give:

$$I = e m$$

$$= e m 8 p 2 (-i) (J' - 1 + M + J' - 1 + K)$$

$$= e m 8 p 2 (-i) (M + K)$$

The 3-J symbols vanish unless: $K' + 0 = K$ and $M' + 0 = M$.

So,

$$I = e m 8 p 2 (-i) (M + K) d M' M d K' K.$$

b. and vanish unless $J' = J + 1, J, J - 1$

$$\backslash D J = \pm 1, 0$$

The K quantum number can not change because the dipole moment lies along the molecule's C_3 axis and the light's electric field thus can exert no torque that twists the molecule about this axis. As a result, the light can not induce transitions that excite the

molecule's spinning motion about this axis.

36.

a. B atom: $1s^2 2s^2 2p^1$, 2P ground state $L = 1$, $S = \frac{1}{2}$, gives a degeneracy $((2L+1)(2S+1))$ of 6.

O atom: $1s^2 2s^2 2p^4$, 3P ground state $L = 1$, $S = 1$, gives a degeneracy $((2L+1)(2S+1))$ of 9.

The total number of states formed is then $(6)(9) = 54$.

b. We need only consider the p orbitals to find the low lying molecular states:

Which, in reality look like this:

This is the correct ordering to give a $2S^+$ ground state. The only low-lying electron configurations are $1p^3 5s^2$ or $1p^4 5s^1$. These lead to 2P and $2S^+$ states, respectively.

c. The bond orders in both states are 2.5.

d. The $2S$ is $+$ but g/u symmetry cannot be specified since this is a heteronuclear molecule.

e. Only one excited state, the 2P, is spin-allowed to radiate to the $2S^+$. Consider symmetries of transition moment operators that arise in the electric dipole contributions to the transition rate $\propto \langle S^+, x, y | P | \rangle$, the $2P \rightarrow 2S^+$ is electric dipole allowed via a perpendicular band.

f. Since ionization will remove a bonding electron, the BO^+ bond is weaker than the BO bond.

g. The ground state BO^+ is $1S^+$ corresponding to a $1p^4$ electron configuration. An electron configuration of $1p^3 5s^1$ leads to a 3P and a 1P state. The 3P will be lower in energy. A $1p^2 5s^2$ configuration will lead to higher lying states of $3S^-$, 1D, and $1S^+$.

h. There should be 3 bands corresponding to formation of BO^+ in the $1S^+$, 3P, and 1P states. Since each of these involves removing a bonding electron, the Franck-Condon integrals will be appreciable for several vibrational levels, and thus a vibrational progression should be observed.

37.

a. The bending (p) vibration is degenerate.

b. $H \cdots C \equiv N$

\hat{Y}

bending fundamental

c. $H \cdots C \equiv N$

\hat{Y}

stretching fundamental

d. CH stretch (n_3 in figure) is s, CN stretch is s, and HCN (n_2 in figure) bend is p.

e. Under z (s) light the CN stretch and the CH stretch can be excited, since $y_0 = s$, $y_1 = s$ and $z = s$ provides coupling.

f. Under x,y (p) light the HCN bend can be excited, since $y_0 = s$, $y_1 = p$ and $x, y = p$ provides coupling.

g. The bending vibration is active under (x,y) perpendicular polarized light. $\Delta J = 0, \pm 1$ are the selection rules for \wedge transitions. The CH stretching vibration is active under (z) \parallel polarized light. $\Delta J = \pm 1$ are the selection rules for \parallel transitions.

38.

$F_{fi} = \langle e_i | f_j = h | f_i + f_i$

Let the closed shell Fock potential be written as:

$V_{ij} = \epsilon_i \delta_{ij}$, and the 1e- component as:

$h_{ij} = \langle f_i | \hat{h} | f_j \rangle$, and the delta as:

$d_{ij} = \epsilon_i \delta_{ij}$, so that: $h_{ij} + V_{ij} = d_{ij} \epsilon_i$.

using: $f_i = \epsilon_i$, $f_j = \epsilon_j$, and $f_k = \epsilon_k$, and transforming from the MO to AO basis we obtain:

$$V_{ij} = C_{mi}C_{gk}C_{nj}C_{kk}$$

=

= V_{mn} where,

$V_{mn} = P_{gk}$, and $P_{gk} =$,

$h_{ij} = h_{mn}$, where

$h_{mn} = c_{m|} - \tilde{N}^2 - |c_n|$, and

$d_{ij} =$.

So, $h_{ij} + V_{ij} = d_{ij}e_j$ becomes:

$h_{mn} + V_{mn} = e_j$,

$e_j - h_{mn} - V_{mn} = 0$ for all i, j

$C_{mi}C_{nj} = 0$ for all i, j

Therefore,

$C_{nj} = 0$

This is FC = SCE in the AO basis.

39.

The Slater Condon rule for zero (spin orbital) difference with N electrons in N spin orbitals is:

$$E = +$$

$$= +$$

$$= +$$

If all orbitals are doubly occupied and we carry out the spin integration we obtain:

$$E = 2+$$

where i and j now refer to orbitals (not spin-orbitals).

40.

If the occupied orbitals obey $Ff_k = ekf_k$, then the expression for E in problem 39 can be rewritten as.

$$E = +$$

We recognize the closed shell Fock operator expression and rewrite this as:

$$E = + =$$

41.

I will use the QMIC software to do this problem. Lets just start from the beginning. Get the starting "guess" MO coefficients on disk. Using the program MOCOEFs it asks us for the first and second MO vectors. We input 1, 0 for the first mo (this means that the first MO is 1.0 times the He 1s orbital plus 0.0 times the H 1s orbital; this bonding MO is more likely to be heavily weighted on the atom having the higher nuclear charge) and 0, 1 for the second. Our beginning LCAO-MO array looks like: and is placed on disk in a file we choose to call "mocoefs.dat". We also put the AO integrals on disk using the program RW_INTS. It asks for the unique one- and two- electron integrals and places a canonical list of these on disk in a file we choose to call "ao_integrals.dat". At this point it is useful for us to step back and look at the set of equations which we wish to solve: FC = SCE. The QMIC software does not provide us with a so-called generalized eigenvalue solver (one that contains an overlap matrix; or metric), so in order to use the diagonalization program that is provided we must transform this equation (FC = SCE) to one that looks like $(F'C' = C'E)$. We do that in the following manner:

Since S is symmetric and positive definite we can find an S such that $SS^T = 1$, $SS = S$, etc.

rewrite FC = SCE by inserting unity between FC and multiplying the whole equation on the left by S . This gives:

$$SFSSC = SSCE = SCE.$$

Letting: $F' = SFS$

$C' = SC$, and inserting these expressions above give:

$$F'C' = C'E$$

Note, that to get the next iteration's MO coefficients we must calculate C from C':

$C' = SC$, so, multiplying through on the left by S gives:

$$SC' = SSC = C$$

This will be the method we will use to solve our Fock equations.

Find S by using the program FUNCT_MAT (this program generates a function of a matrix). This program will ask for the elements of the S array and write to disk a file (name of your choice ... a good name might be "shalf") containing the S array. Now we are ready to begin the iterative Fock procedure.

a. Calculate the Fock matrix, F, using program FOCK which reads in the MO coefficients from "mocoefs.dat" and the integrals from "ao_integrals.dat" and writes the resulting Fock matrix to a user specified file (a good filename to use might be something like "fock1").

b. Calculate $F' = SFS$ using the program UTMATU which reads in F and S from files on the disk and writes F' to a user specified file (a good filename to use might be something like "fock1p"). Diagonalize F' using the program DIAG. This program reads in the matrix to be diagonalized from a user specified filename and writes the resulting eigenvectors to disk using a user specified filename (a good filename to use might be something like "coef1p"). You may wish to choose the option to write the eigenvalues (Fock orbital energies) to disk in order to use them at a later time in program FENERGY. Calculate C by using, $C = SC'$. This is accomplished by using the program MATXMAT which reads in two matrices to be multiplied from user specified files and writes the product to disk using a user specified filename (a good filename to use might be something like "mocoefs.dat").

c. The QMIC program FENERGY calculates the total energy:

$$2\langle k|h|k\rangle + 2\langle k|l|kl\rangle - \langle k|l|lk\rangle + , \text{ and}$$

$$e_k + \langle k|h|k\rangle + .$$

This is the conclusion of one iteration of the Fock procedure ... you may continue by going back to part a. and proceeding onward.

d. and e. Results for the successful convergence of this system using the supplied QMIC software are as follows (this data is provided to give the student assurance that they are on the right track; alternatively one could switch to the QMIC program SCF and allow that program to iteratively converge the Fock equations):

The one-electron AO integrals:

The two-electron AO integrals:

1 1 1 1 1.054700

2 1 1 1 0.4744000

2 1 2 1 0.5664000

2 2 1 1 0.2469000

2 2 2 1 0.3504000

2 2 2 2 0.6250000

The "initial" MO-AO coefficients:

AO overlap matrix (S):

S

ITERATION 1

The charge bond order matrix:

The Fock matrix (F):

S F S

The eigenvalues of this matrix (Fock orbital energies) are:

Their corresponding eigenvectors ($C' = S * C$) are:

The "new" MO-AO coefficients ($C = S * C'$):

The one-electron MO integrals:

The two-electron MO integrals:

1 1 1 1 0.9779331

2 1 1 1 0.1924623

2 1 2 1 0.5972075

2 2 1 1 0.1170838

2 2 2 1 -0.0007945194

2 2 2 2 0.6157323

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle = -2.84219933$$

from formula:

$$e_k + \langle k|h|k\rangle = -2.80060530$$

the difference is: -0.04159403

ITERATION 2

The charge bond order matrix:

The Fock matrix:

S F S

The eigenvalues of this matrix (Fock orbital energies) are:

Their corresponding eigenvectors ($C' = S * C$) are:

The "new" MO-AO coefficients ($C = S * C'$):

The one-electron MO integrals:

The two-electron MO integrals:

1 1 1 1 0.9626070

2 1 1 1 0.1949828

2 1 2 1 0.6048143

2 2 1 1 0.1246907

2 2 2 1 0.003694540

2 2 2 2 0.6158437

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle = -2.84349298$$

from formula:

$$e_k + \langle k|h|k \rangle = -2.83573675$$

the difference is: -0.00775623

ITERATION 3

The charge bond order matrix:

The Fock matrix:

S F S

The eigenvalues of this matrix (Fock orbital energies) are:

Their corresponding eigenvectors ($C' = S * C$) are:

The "new" MO-AO coefficients ($C = S * C'$):

The one-electron MO integrals:

The two-electron MO integrals:

1 1 1 1 0.9600707

2 1 1 1 0.1953255

2 1 2 1 0.6060572

2 2 1 1 0.1259332

2 2 2 1 0.004475587

2 2 2 2 0.6158972

The closed shell Fock energy from formula:

$$2\langle k|h|k \rangle + 2\langle kl|kl \rangle - \langle kl|lk \rangle = -2.84353018$$

from formula:

$$e_k + \langle k|h|k \rangle = -2.84225941$$

the difference is: -0.00127077

ITERATION 4

The charge bond order matrix:

The Fock matrix:

S F S

The eigenvalues of this matrix (Fock orbital energies) are:

Their corresponding eigenvectors ($C' = S * C$) are:

The "new" MO-AO coefficients ($C = S * C'$):

The one-electron MO integrals:

The two-electron MO integrals:

1 1 1 1 0.9596615

2 1 1 1 0.1953781

2 1 2 1 0.6062557

2 2 1 1 0.1261321

2 2 2 1 0.004601604

2 2 2 2 0.6159065

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle = -2.84352922$$

from formula:

$$e_k + \langle k|h|k\rangle = -2.84332418$$

the difference is: -0.00020504

ITERATION 5

The charge bond order matrix:

The Fock matrix:

S F S

The eigenvalues of this matrix (Fock orbital energies) are:

Their corresponding eigenvectors ($C' = S^{-1} C$) are:

The "new" MO-AO coefficients ($C = S^{-1} C'$):

The one-electron MO integrals:

The two-electron MO integrals:

1 1 1 1 0.9595956

2 1 1 1 0.1953862

2 1 2 1 0.6062872

2 2 1 1 0.1261639

2 2 2 1 0.004621811

2 2 2 2 0.6159078

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle = -2.84352779$$

from formula:

$$e_k + \langle k|h|k\rangle = -2.84349489$$

the difference is: -0.00003290

ITERATION 6

The charge bond order matrix:

The Fock matrix:

S F S

The eigenvalues of this matrix (Fock orbital energies) are:

Their corresponding eigenvectors ($C' = S * C$) are:

The "new" MO-AO coefficients ($C = S * C'$):

The one-electron MO integrals:

The two-electron MO integrals:

1 1 1 1 0.9595859

2 1 1 1 0.1953878

2 1 2 1 0.6062925

2 2 1 1 0.1261690

2 2 2 1 0.004625196

2 2 2 2 0.6159083

The closed shell Fock energy from formula:

$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle = -2.84352827$

from formula:

$\epsilon_k + \langle k|h|k\rangle = -2.84352398$

the difference is: -0.00000429

ITERATION 7

The charge bond order matrix:

The Fock matrix:

S F S

The eigenvalues of this matrix (Fock orbital energies) are:

Their corresponding eigenvectors ($C' = S * C$) are:

The "new" MO-AO coefficients ($C = S * C'$):

The one-electron MO integrals:

The two-electron MO integrals:

1 1 1 1 0.9595849

2 1 1 1 0.1953881

2 1 2 1 0.6062936

2 2 1 1 0.1261697

2 2 2 1 0.004625696

2 2 2 2 0.6159083

The closed shell Fock energy from formula:

$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle = -2.84352922$

from formula:

$\epsilon_k + \langle k|h|k\rangle = -2.84352827$

the difference is: -0.00000095

ITERATION 8

The charge bond order matrix:

The Fock matrix:

S F S

The eigenvalues of this matrix (Fock orbital energies) are:

Their corresponding eigenvectors ($C' = S * C$) are:

The "new" MO-AO coefficients ($C = S * C'$):

The one-electron MO integrals:

The two-electron MO integrals:

1 1 1 1 0.9595841

2 1 1 1 0.1953881

2 1 2 1 0.6062934

2 2 1 1 0.1261700

2 2 2 1 0.004625901

2 2 2 2 0.6159081

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle k|l|kl\rangle - \langle k|l|lk\rangle = -2.84352827$$

from formula:

$$e_k + \langle k|h|k\rangle = -2.84352827$$

the difference is: 0.00000000

f. In looking at the energy convergence we see the following:

Iter

Formula 1

Formula 2

1

-2.84219933

-2.80060530

2

-2.84349298

-2.83573675

3

-2.84353018

-2.84225941

4

-2.84352922

-2.84332418

5

-2.84352779

-2.84349489

6

-2.84352827

-2.84352398

7

-2.84352922

-2.84352827

8

-2.84352827

-2.84352827

If you look at the energy differences (SCF at iteration n - SCF converged) and plot this data versus iteration number, and do a 5th order polynomial fit, we see the following:

In looking at the polynomial fit we see that the convergence is primarily linear since the coefficient of the linear term is much larger than those of the cubic and higher terms.

g. The converged SCF total energy calculated using the result of problem 40 is an upper bound to the ground state energy, but, during the iterative procedure it is not. Only at convergence does the expectation value of the Hamiltonian for the Hartree Fock determinant become equal to that given by the equation in problem 40.

h. Yes, the $1s^2$ configuration does dissociate properly because at $R \rightarrow \infty$ the lowest energy state is $\text{He} + \text{H}^+$, which also has a $1s^2$ orbital occupancy (i.e., $1s^2$ on He and $1s^0$ on H^+).

42.

2. At convergence the MO coefficients are:

$f_1 = f_2 =$

and the integrals in this MO basis are:

$h_{11} = -2.615842$ $h_{21} = -0.1953882$ $h_{22} = -1.315354$

$g_{1111} = 0.9595841$ $g_{2111} = 0.1953881$ $g_{2121} = 0.6062934$

$g_{2211} = 0.1261700$ $g_{2221} = 0.04625901$ $g_{2222} = 0.6159081$

a. $H =$

$=$

$=$

b. The eigenvalues are $E_1 = -4.279131$ and $E_2 = -2.007770$. The corresponding eigenvectors are:

$C_1 =$, $C_2 =$

c.

$=$

$=$

$= a - b$.

d. The third configuration $|1s2s| =$,

Adding this configuration to the previous 2×2 CI results in the following 3×3 'full' CI:

$H =$

$=$

Evaluating the new matrix elements:

$$H_{13} = H_{31} = *(-0.1953882 + 0.1953881) = 0.0$$

$$H_{23} = H_{32} = *(-0.1953882 + 0.004626) = -0.269778$$

$$H_{33} = -2.615842 - 1.315354 + 0.606293 + 0.126170$$

$$= -3.198733$$

=

e. The eigenvalues are $E_1 = -4.279345$, $E_2 = -3.256612$ and $E_3 = -1.949678$. The corresponding eigenvectors are:

$$C_1 = , C_2 = , C_3 =$$

f. We need the non-vanishing matrix elements of the dipole operator in the MO basis. These can be obtained by calculating them by hand. They are more easily obtained by using the TRANS program. Put the 1e- AO integrals on disk by running the program RW_INTS. In this case you are inserting $z_{11} = 0.0$, $z_{21} = 0.2854$, and $z_{22} = 1.4$ (insert 0.0 for all the 2e- integrals) ... call the output file "ao_dipole.ints" for example. The converged MO-AO coefficients should be in a file ("mocoefs.dat" is fine). The transformed integrals can be written to a file (name of your choice) for example "mo_dipole.ints". These matrix elements are:

$$z_{11} = 0.11652690, z_{21} = -0.54420990, z_{22} = 1.49117320$$

The excitation energies are $E_2 - E_1 = -3.256612 - -4.279345 = 1.022733$, and

$$E_3 - E_1 = -1.949678 - -4.279345 = 2.329667.$$

Using the Slater-Condon rules to obtain the matrix elements between configurations we obtain:

$$H_z =$$

=

=

Now, $\langle Y_1 | z | Y_2 \rangle = C_1 T H_z C_2$, (this can be accomplished with the program UTMATU)

$$= T$$

$$= -.757494$$

$$\text{and, } \langle Y_1 | z | Y_3 \rangle = C_1 T H_z C_3$$

$$= T$$

$$= 0.014322$$

g. Using the converged coefficients the orbital energies obtained from solving the Fock equations are $e_1 = -1.656258$ and $e_2 = -0.228938$. The resulting expression for the PT first-order wavefunction becomes:

$$|1s2\rangle(1) = -|2s2\rangle$$

$$|1s2\rangle(1) = -|2s2\rangle$$

$$|1s2\rangle(1) = -0.0441982|2s2\rangle$$

h. As you can see from part c., the matrix element $\langle 1s2 | H | 1s2s \rangle = 0$ (this is also a result of the Brillouin theorem) and hence this configuration does not enter into the first-order wavefunction.

i. $|0\rangle = |1s2\rangle - 0.0441982|2s2\rangle$. To normalize we divide by:

$$= 1.0009762$$

$$|0\rangle = 0.999025|1s2\rangle - 0.044155|2s2\rangle$$

In the 2x2 CI we obtained:

$$|0\rangle = 0.99845123|1s2\rangle - 0.05563439|2s2\rangle$$

j. The expression for the 2nd order RSPT is:

$$E(2) = - - -$$

= -0.005576 au

Comparing the 2x2 CI energy obtained to the SCF result we have:

-4.279131 - (-4.272102) = -0.007029 au

43. STO total energy: -2.8435283

STO3G total energy -2.8340561

3-21G total energy -2.8864405

The STO3G orbitals were generated as a best fit of 3 primitive Gaussians (giving 1 CGTO) to the STO. So, STO3G can at best reproduce the STO result. The 3-21G orbitals are more flexible since there are 2 CGTOs per atom. This gives 4 orbitals (more parameters to optimize) and a lower total energy.

44.

R

HeH+ Energy

H2 Energy

1.0

-2.812787056

-1.071953297

1.2

-2.870357513

-1.113775015

1.4

-2.886440516

-1.122933507

1.6

-2.886063576

-1.115567684

1.8

-2.880080938

-1.099872589

2.0

-2.872805595

-1.080269098

2.5

-2.856760263

-1.026927710

10.0

-2.835679293

-0.7361705303

Plotting total energy vs. geometry for HeH+:

Plotting total energy vs. geometry for H2:

For HeH⁺ at R = 10.0 au, the eigenvalues of the converged Fock matrix and the corresponding converged MO-AO coefficients are:

-.1003571E+01
-.4961988E+00
.5864846E+00
.1981702E+01
.4579189E+00
-.8245406E-05
.1532163E-04
.1157140E+01
.6572777E+00
-.4580946E-05
-.6822942E-05
-.1056716E+01
-.1415438E-05
.3734069E+00
.1255539E+01
-.1669342E-04
.1112778E-04
.7173244E+00
-.1096019E+01
.2031348E-04

Notice that this indicates that orbital 1 is a combination of the s functions on He only (dissociating properly to He + H⁺).

For H₂ at R = 10.0 au, the eigenvalues of the converged Fock matrix and the corresponding converged MO-AO coefficients are:

-.2458041E+00
-.1456223E+00
.1137235E+01
.1137825E+01
.1977649E+00
-.1978204E+00
.1006458E+01
-.7903225E+00
.5632566E+00
-.5628273E+00
-.8179120E+00
.6424941E+00
.1976312E+00
.1979216E+00
.7902887E+00

.1006491E+01
.5629326E+00
.5631776E+00
-.6421731E+00
-.8181460E+00

Notice that this indicates that orbital 1 is a combination of the s functions on both H atoms (dissociating improperly; equal probabilities of H₂ dissociating to two neutral atoms or to a proton plus hydride ion).

45. The H₂ CI result:

R

1Sg+
3Su+
1Su+
1Sg+
1.0
-1.074970
-0.5323429
-0.3997412
0.3841676
1.2
-1.118442
-0.6450778
-0.4898805
0.1763018
1.4
-1.129904
-0.7221781
-0.5440346
0.0151913
1.6
-1.125582
-0.7787328
-0.5784428
-0.1140074
1.8
-1.113702
-0.8221166
-0.6013855
-0.2190144

2.0

-1.098676

-0.8562555

-0.6172761

-0.3044956

2.5

-1.060052

-0.9141968

-0.6384557

-0.4530645

5.0

-0.9835886

-0.9790545

-0.5879662

-0.5802447

7.5

-0.9806238

-0.9805795

-0.5247415

-0.5246646

10.0

-0.980598

-0.9805982

-0.4914058

-0.4913532

For H₂ at R = 1.4 au, the eigenvalues of the Hamiltonian matrix and the corresponding determinant amplitudes are:

determinant

-1.129904

-0.722178

-0.544035

0.015191

|1sga1sgb|

0.99695

0.00000

0.00000

0.07802

|1sgb1sua|

0.00000

0.70711

0.70711

0.00000

|1sga1sub|

0.00000

0.70711

-0.70711

0.00000

|1sua1sub|

-0.07802

0.00000

0.00000

0.99695

This shows, as expected, the mixing of the first 1Sg+ (1sg2) and the 2nd 1Sg+ (1su2) determinants in the first and fourth states, and the

3Su+ = (),

and 1Su+= ()

states as the second and third states.

Also notice that the first 1Sg+ state has coefficients (0.99695 - 0.07802) (note specifically the + - combination) and the second 1Sg+ state has the opposite coefficients with the same signs (note specifically the + + combination). The + + combination always gives a higher energy than the + - combination.

46.

F atoms have 1s22s22p5 2P ground electronic states that are split by spin-orbit coupling into 2P3/2 and 2P1/2 states that differ by only 0.05 eV in energy.

a.

The degeneracy of a state having a given J is 2J+1, and the J=3/2 state is lower in energy because the 2p orbital shell is more than half filled (I learned this in inorganic chemistry class), so

$$q_{el} = 4 \exp(-0/kT) + 2 \exp(-0.05 \text{ eV}/kT).$$

0.05 eV is equivalent to k(500 K), so $0.05/kT = 500/T$, hence

$$q_{el} = 4 \exp(-0/kT) + 2 \exp(-500/T).$$

b.

$$Q = qN/N!$$

$$\text{so, } \ln Q = N \ln q - \ln N!$$

$$E = kT^2 \partial \ln Q / \partial T = NkT^2 \partial \ln q / \partial T = Nk \{ 1000 \exp(-500/T) / [4 + 2 \exp(-500/T)] \}$$

c. Using the fact that $kT=0.03\text{eV}$ at $T=300^\circ\text{K}$, make a (qualitative) graph of E/N vs T for T ranging from 100°K to 3000°K .

At $T = 100 \text{ K}$, E/N is small and equal to $1000k \exp(-5)/(4 + 2 \exp(-5))$.

At $T = 3000 \text{ K}$, E/N has grown to $1000k \exp(-1/6)/(4 + 2 \exp(-1/6))$ which is

approximately $1000k/6$.

47.

a.

The difference between a linear and bent transition state would arise in the vibrational and rotational partition functions. For the linear TS, one has $3N-6$ vibrations (recall that one loses one vibration as a reaction coordinate), but for the bent TS, one has $3N-7$ vibrations. For the linear TS, one has 2 rotational axes, and for the bent TS, one has 3.

So the ratio of rate constants will reduce to ratios of vibration and rotation partition functions. In particular, one will have

$$k_{\text{linear}}/k_{\text{bent}} = (q_{\text{vib}}^{3N-6} q_{\text{rot}}^2 / q_{\text{vib}}^{3N-7} q_{\text{rot}}^3) = (q_{\text{vib}}/q_{\text{rot}}).$$

b. Using

$$q_t \sim 108, q_r \sim 102, q_v \sim 1,$$

I would expect $k_{\text{linear}}/k_{\text{bent}}$ to be of the order of $1/102 = 10^{-2}$.

48.

Constructing the Slater determinant corresponding to the "state" $1s(a)1s(a)$ with the rows labeling the orbitals and the columns labeling the electron gives:

$$|1s a 1s a| =$$

$$=$$

$$= 0$$

49.

Starting with the $MS=1$ $3S$ state (which in a "box" for this $ML=0$, $MS=1$ case would contain only one product function; $|1s a 2s a\rangle$) and applying S_- gives:

$$S_- 3S(S=1, MS=1) = 3S(S=1, MS=0)$$

$$= 3S(S=1, MS=0)$$

$$= |1s a 2s a|$$

$$= S_-(1)|1s a 2s a| + S_-(2)|1s a 2s a|$$

$$= |1s b 2s a|$$

$$+ |1s a 2s b|$$

$$=$$

$$\text{So, } 3S(S=1, MS=0) =$$

$$3S(S=1, MS=0) =$$

The three triplet states are then:

$$3S(S=1, MS=1) = |1s a 2s a|,$$

$$3S(S=1, MS=0) = , \text{ and}$$

$$3S(S=1, MS=-1) = |1s b 2s b|.$$

The singlet state which must be constructed orthogonal to the three singlet states (and in particular to the $3S(S=1, MS=0)$ state) can be seen to be:

$$1S(S=0, MS=0) = .$$

Applying S^2 and S_z to each of these states gives:

$$S_z |1s a 2s a| = |1s a 2s a|$$

$$= S_z(1)|1s a 2s a| + S_z(2)|1s a 2s a|$$

$$= |1s a 2s a| + |1s a 2s a|$$

$$= |1s a 2s a|$$

$$S^2 |1s a 2s a| = (S^2 - S_+ S_- + S_z^2 + S_z) |1s a 2s a|$$

$$= S^2 |1s a 2s a| + S_z^2 |1s a 2s a| + S_z |1s a 2s a|$$

$$= 0 + 2 |1s\alpha 2s\alpha| + 2 |1s\alpha 2s\alpha|$$

$$= 22 |1s\alpha 2s\alpha|$$

$$S_z =$$

$$= |1s\beta 2s\alpha|$$

$$+ |1s\alpha 2s\beta|$$

$$= |1s\beta 2s\alpha|$$

$$+ |1s\alpha 2s\beta|$$

$$= 0$$

$$S^2 = (S - S^+ + S_z^2 + S_z)$$

$$= S - S^+$$

$$=$$

$$=$$

$$= 2$$

$$= 2$$

$$= 2 \cdot 2$$

$$S_z |1s\beta 2s\beta| = |1s\beta 2s\beta|$$

$$= S_z(1) |1s\beta 2s\beta| + S_z(2) |1s\beta 2s\beta|$$

$$= |1s\beta 2s\beta| + |1s\beta 2s\beta|$$

$$= -|1s\beta 2s\beta|$$

$$S^2 |1s\beta 2s\beta| = (S + S^- + S_z^2 - S_z) |1s\beta 2s\beta|$$

$$= S + S^- |1s\beta 2s\beta| + S_z^2 |1s\beta 2s\beta| - S_z |1s\beta 2s\beta|$$

$$= 0 + 2 |1s\beta 2s\beta| + 2 |1s\beta 2s\beta|$$

$$= 22 |1s\beta 2s\beta|$$

$$S_z =$$

$$= |1s\beta 2s\alpha|$$

$$- |1s\alpha 2s\beta|$$

$$= |1s\beta 2s\alpha|$$

$$- |1s\alpha 2s\beta|$$

$$= 0$$

$$S^2 = (S - S^+ + S_z^2 + S_z)$$

$$= S - S^+$$

$$=$$

$$=$$

$$= 0$$

$$= 0$$

$$= 0 \cdot 2$$

$$50.$$

As shown in problem 22c, for two equivalent p electrons one obtains six states:

1D (ML=2); one state (MS=0),
 1D (ML=-2); one state (MS=0),
 1S (ML=0); one state (MS=0), and
 3S (ML=0); three states (MS=1,0, and -1).

By inspecting the "box" in problem 22c, it should be fairly straightforward to write down the wavefunctions for each of these:

1D (ML=2); $|p_{1a}p_{1b}|$
 1D (ML=-2); $|p_{-1a}p_{-1b}|$
 1S (ML=0);
 3S (ML=0, MS=1); $|p_{1a}p_{-1a}|$
 3S (ML=0, MS=0);
 3S (ML=0, MS=-1); $|p_{1b}p_{-1b}|$
 51.

We can conveniently couple another s electron to the states generated from the $1s12s1$ configuration:

3S(L=0, S=1) with $3s1(L=0, S=)$ giving:
 L=0, S=, ; 4S (4 states) and 2S (2 states).
 1S(L=0, S=0) with $3s1(L=0, S=)$ giving:
 L=0, S=; 2S (2 states).

Constructing a "box" for this case would yield:

ML	MS	0
		$ 1s2s3s_a $
		$ 1s2s3s_b , 1s2s3s_c , 1s2s3s_d $

One can immediately identify the wavefunctions for two of the quartets (they are single entries):

4S(S=,MS=): $|1s2s3s_a|$
 4S(S=,MS=-): $|1s2s3s_b|$

Applying S- to 4S(S=,MS=) yields:

$S-4S(S=,MS=) = 4S(S=,MS=)$
 $= 4S(S=,MS=)$

$S-|1s2s3s_a| =$

So, $4S(S=,MS=) =$

Applying S+ to 4S(S=,MS=-) yields:

$S+4S(S=,MS=-) = 4S(S=,MS=-)$
 $= 4S(S=,MS=-)$

$S+|1s2s3s_b| =$

So, $4S(S=,MS=-) =$

It only remains to construct the doublet states which are orthogonal to these quartet states. Recall that the orthogonal combinations for systems having three equal components (for example when symmetry adapting the 3 sp² hybrids in C_{2v} or D_{3h} symmetry) give

results of $+++$, $+2--$, and $0+-$. Notice that the quartets are the $+++$ combinations and therefore the doublets can be recognized as:

$$2S(S=,MS=) =$$

$$2S(S=,MS=) =$$

$$2S(S=,MS=-) =$$

$$2S(S=,MS=-) =$$

52.

As illustrated in problem 24, a p^2 configuration (two equivalent p electrons) gives rise to the term symbols: $3P$, $1D$, and $1S$. Coupling an additional electron ($3d1$) to this p^2 configuration will give the desired $1s2s2p23d1$ term symbols:

$3P(L=1,S=1)$ with $2D(L=2,S=)$ generates;

$L=3,2,1$, and $S=$, with term symbols $4F$, $2F$, $4D$, $2D$, $4P$, and $2P$,

$1D(L=2,S=0)$ with $2D(L=2,S=)$ generates;

$L=4,3,2,1,0$, and $S=$ with term symbols $2G$, $2F$, $2D$, $2P$, and $2S$,

$1S(L=0,S=0)$ with $2D(L=2,S=)$ generates;

$L=2$ and $S=$ with term symbol $2D$.

53. The notation used for the Slater Condon rules will be as follows:

(a.) zero (spin orbital) difference;

$$= +$$

$$= +$$

(b.) one (spin orbital) difference ($f p^1 f p'$);

$$= +$$

$$= f p p' +$$

(c.) two (spin orbital) differences ($f p^1 f p'$ and $f q^1 f q'$);

$$= -$$

$$= g p q p' q' - g p q q' p'$$

(d.) three or more (spin orbital) differences;

$$= 0$$

$$\text{i. } 3P(ML=1,MS=1) = |p1ap0a|$$

$$= \langle 10 | H | 10 \rangle$$

Using the Slater Condon rule (a.) above (I will denote these SCa-SCd):

$$= f_{11} + f_{00} + g_{1010} - g_{1001}$$

$$\text{ii. } 3P(ML=0,MS=0) =$$

$$=$$

$$+ +)$$

Evaluating each matrix element gives:

$$= f_{11a1a} + f_{-1b-1b} + g_{1a-1b1a-1b} - g_{1a-1b-1b1a} \text{ (SCa)}$$

$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0$$

$$= g_{1a-1b1b-1a} - g_{1a-1b-1a1b} \text{ (SCc)}$$

$$= 0 - g_{1-1-11}$$

$$\begin{aligned}
 &= g_{1b-1a1a-1b} - g_{1b-1a-1b1a} \text{ (SCc)} \\
 &= 0 - g_{1-1-11} \\
 &= f_{1b1b} + f_{-1a-1a} + g_{1b-1a1b-1a} - g_{1b-1a-1a1b} \text{ (SCa)} \\
 &= f_{11} + f_{-1-1} + g_{1-11-1} - 0
 \end{aligned}$$

Substitution of these expressions give:

$$\begin{aligned}
 &= \\
 &+ f_{11} + f_{-1-1} + g_{1-11-1} \\
 &= f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-11}
 \end{aligned}$$

iii. $1S(ML=0, MS=0)$;

$$\begin{aligned}
 &= \\
 &- - \\
 &+ + \\
 &- + \\
 &+)
 \end{aligned}$$

Evaluating each matrix element gives:

$$\begin{aligned}
 &= f_{0a0a} + f_{0b0b} + g_{0a0b0a0b} - g_{0a0b0b0a} \text{ (SCa)} \\
 &= f_{00} + f_{00} + g_{0000} - 0 \\
 &= \\
 &= g_{0a0b1a-1b} - g_{0a0b-1b1a} \text{ (SCc)} \\
 &= g_{001-1} - 0 \\
 &= \\
 &= g_{0a0b-1a1b} - g_{0a0b1b-1a} \text{ (SCc)} \\
 &= g_{00-11} - 0 \\
 &= f_{1a1a} + f_{-1b-1b} + g_{1a-1b1a-1b} - g_{1a-1b-1b1a} \text{ (SCa)} \\
 &= f_{11} + f_{-1-1} + g_{1-11-1} - 0 \\
 &= \\
 &= g_{1a-1b-1a1b} - g_{1a-1b1b-1a} \text{ (SCc)} \\
 &= g_{1-1-11} - 0 \\
 &= f_{-1a-1a} + f_{1b1b} + g_{-1a1b-1a1b} - g_{-1a1b1b-1a} \text{ (SCa)} \\
 &= f_{-1-1} + f_{11} + g_{-11-11} - 0
 \end{aligned}$$

Substitution of these expressions give:

$$\begin{aligned}
 &= \\
 &+ g_{1-11-1} + g_{1-1-11} - g_{00-11} + g_{1-1-11} + f_{-1-1} + f_{11} + g_{-11-11} \\
 &= \\
 \text{iv. } 1D(ML=0, MS=0) &=
 \end{aligned}$$

Evaluating we note that all the Slater Condon matrix elements generated are the same as those evaluated in part iii. (the signs for the wavefunction components and the multiplicative factor of two for one of the components, however, are different).

=

$$+ f_{-1-1} + g_{1-11-1} + g_{1-1-11} + 2g_{00-11} + g_{1-1-11} + f_{-1-1} + f_{11} + g_{-11-11})$$

$$=$$

54.

i. $1D(ML=2, MS=0) = |p_{1a}p_{1b}|$

=

$$= f_{1a1a} + f_{1b1b} + g_{1a1b1a1b} - g_{1a1b1b1a} \text{ (SCa)}$$

$$= f_{11} + f_{11} + g_{1111} - 0$$

$$= 2f_{11} + g_{1111}$$

ii. $1S(ML=0, MS=0) =$

=

$$- +)$$

Evaluating each matrix element gives:

$$= f_{1a1a} + f_{1b1b} + g_{1a1b1a1b} - g_{1a1b1b1a} \text{ (SCa)}$$

$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0$$

$$= g_{1a1b1b1a} - g_{1a1b1a1b} \text{ (SCc)}$$

$$= 0 - g_{1-1-11}$$

$$= g_{1b1a1a1b} - g_{1b1a1b1a} \text{ (SCc)}$$

$$= 0 - g_{1-1-11}$$

$$= f_{1b1b} + f_{-1a-1a} + g_{1b1a1b1a} - g_{1b1a1a1b} \text{ (SCa)}$$

$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0$$

Substitution of these expressions give:

=

$$= f_{11} + f_{-1-1} + g_{1-11-1} + g_{1-1-11}$$

iii. $3S(ML=0, MS=0) =$

$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0$$

$$= g_{1a1b1b1a} - g_{1a1b1a1b} \text{ (SCc)}$$

$$= 0 - g_{1-1-11}$$

$$= g_{1b1a1a1b} - g_{1b1a1b1a} \text{ (SCc)}$$

$$= 0 - g_{1-1-11}$$

$$= f_{1b1b} + f_{-1a-1a} + g_{1b1a1b1a} - g_{1b1a1a1b} \text{ (SCa)}$$

$$= f_{11} + f_{-1-1} + g_{1-11-1} - 0$$

Substitution of these expressions give:

=

$$= f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-11}$$

55.

The order of the answers is J, I, G, K, B, D, E, A, C, H, F

56.

$$p = N/(V-Nb) - N^2 a/(kTV^2)$$

$$\text{but } p/kT = (\partial \ln Q / \partial V)_{T,N}$$

so we can integrate to obtain $\ln Q$

$$\ln Q = \int (p/kT) dV = \int [N/(V-Nb) - N^2 a/(kTV^2)] dV$$

$$= N \ln(V-Nb) + N^2 a/kT (1/V)$$

So,

$$Q = \{(V-Nb) \exp[(a/kT) (N/V)]\}^N$$

57.

a.

MD because you need to keep track of how far the molecule moves as a function of time and MC does not deal with time.

b.

MC is capable of doing this although MD is also. However, MC requires fewer computational steps, so I would prefer to use it.

c.

MC can do this, as could MD. Again, because MC needs fewer computational steps, I'd use it.

Suppose you are carrying out a Monte-Carlo simulation involving 1000 Ar atoms. Further suppose that the potentials are pairwise additive and that your computer requires approximately 50 floating point operations (FPO's) (e.g. multiply, add, divide, etc.) to compute the interaction potential between any pair of atoms

d.

For each MC move, we must compute only the change in potential energy. To do this, we need to compute only the change in the pair energies that involve the atom that was moved. This will require 999×50 FPOs (the 99 being the number of atoms other than the one that moved). So, for a million MC steps, I would need $10^6 \times 999 \times 50$ FPOs. At $10^6 \times 10^6$ FPOs per second, this will require 495 seconds, or a little over eight minutes.

e.

Because the statistical fluctuations in MC calculations are proportional to $(1/N)^{1/2}$, where N is the number of steps taken, I will have to take 4 times as many steps to cut the statistical errors in half. So, this will require 4×495 seconds or 1980 seconds.

f.

If we have one million rather than one thousand atoms, the 495 second calculation of part d would require

$$999,999/999$$

times as much time. This ratio arises because the time to compute the change in potential energy accompanying a MC move is proportional to the number of other atoms. So, the calculation would take $495 \times (999,999/999)$ seconds or about 500,000 seconds or about 140 hours.

g.

We would be taking $10^{-9} \text{ s} / (10^{-15} \text{ s per step}) = 10^6$ MD steps.

Each step requires that we compute all forces $(-\partial V / \partial R_{IJ})$ between all pairs of atoms. There are $1000 \times 999 / 2$ such pairs. So, to compute all the forces would require

$$(1000 \times 999 / 2) \times 50 \text{ FPOs} = 2.5 \times 10^7 \text{ FPOs. So, we will need}$$

$$2.5 \times 10^7 \text{ FPOs/step} \times 10^6 \text{ steps} / (10^6 \text{ FPOs per second})$$

$$= 2.5 \times 10^5 \text{ seconds or about 70 hours.}$$

h.

The graduate student is 108 times slower than the 100 Mflop computer, so it will take her/him 108 times as long, so 495×108 seconds or about 1570 years.

58.

First, Na has a 2S ground state term symbol whose degeneracy is $2S + 1 = 2$.

Na₂ has a 1S ground state whose degeneracy is 1.

The symmetry number for Na₂ is $s = 2$.

The D₀ value given is 17.3 kcal mol⁻¹.

The K_p equilibrium constant would be given in terms of partial pressures as (and then using $pV = NkT$)

$$K_p = \frac{p_{\text{Na}_2}}{p_{\text{Na}}^2} = \frac{(kT)^{-1} (q_{\text{Na}}/V)^2}{(q_{\text{Na}_2}/V)}$$

in terms of the partition functions.

a.

$$q_{\text{Na}} = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V$$

$$q_{\text{Na}_2} = \left(\frac{2\pi m' k T}{h^2} \right)^{3/2} V \left(\frac{8\pi^2 I k T}{h^2} \right)^{1/2} \left[\exp(-h\nu/2kT) (1 - \exp(-h\nu/kT))^{-1} \exp(D_0/kT) \right]$$

We can combine the D_0 and the $-h\nu/2kT$ to obtain the D_0 which is what we were given.

b. For Na (I will use cgs units in all cases):

$$q/V = \left(\frac{2\pi \cdot 23 \cdot 1.66 \times 10^{-24} \cdot 1.38 \times 10^{-16} \cdot 1000}{h^2} \right)^{3/2} \cdot 2$$

$$= (6.54 \times 10^{26}) \times 2 = 1.31 \times 10^{27}$$

For Na₂:

$$q/N = \frac{23}{2} \times (6.54 \times 10^{26}) \cdot \left(\frac{1000}{0.221} \right)^{1/2} \cdot (1 - \exp(-229/1000))^{-1} \exp(D_0/kT)$$

$$= 1.85 \times 10^{27} \cdot (2.26 \times 10^3) \cdot (4.88) \cdot (5.96 \times 10^3)$$

$$= 1.22 \times 10^{35}$$

So,

$$K_p = \frac{1.22 \times 10^{35}}{[(1.38 \times 10^{-16})(1000)(1.72 \times 10^{54})]}$$

$$= 0.50 \times 10^{-6} \text{ dynes cm}^{-2} = 0.50 \text{ atm}^{-1}.$$

59.

The differences in k_{rate} will arise from differences in the number of translational, rotational, and vibrational partition functions arising in the adsorbed and gas-phase species. Recall that

$$k_{\text{rate}} = \frac{kT}{h} \exp(-E^*/kT) \frac{[q_{\text{TS}}/V]}{[(q_{\text{NO}}/V)(q_{\text{Cl}_2}/V)]}$$

In the gas phase,

NO has 3 translations, two rotations, and one vibration

Cl₂ has 3 translations, two rotations, and one vibration

the NOCl₂ TS, which is bent, has 3 translations, three rotations, and five vibrations (recall that one vibration is missing and is the reaction coordinate)

In the adsorbed state,

NO has 2 translations, one rotation, and three vibrations

Cl₂ has 2 translations, one rotation, and three vibrations

the NOCl₂ TS, which is bent, has 2 translations, one rotation, and eight vibrations (again, one vibration is missing and is the reaction coordinate).

So, in computing the partition function ratio:

$$\frac{[q_{\text{TS}}/V]}{[(q_{\text{NO}}/V)(q_{\text{Cl}_2}/V)]}$$

for the adsorbed and gas-phase cases, one does not obtain the same number of translational, rotational, and vibrational factors. In particular, the ratio of these factors for the adsorbed and gas-phase cases gives the ratio of rate constants as follows:

$$k_{ad}/k_{gas} = (q_{trans}/V)/q_{vib}$$

which should be of the order of 108 (using the ratio of partition functions as given).

Notice that this result suggests that reaction rates can be altered by constraining the reacting species to move freely in lower dimensions even if one does not alter the energetics (e.g., activation energy or thermochemistry).

Contributions

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