

Solutions

1.

a. First determine the eigenvalues:

$$\det \begin{pmatrix} -1 - \lambda & 2 \\ 2 & 2 - \lambda \end{pmatrix} = 0$$

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

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

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

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

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

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

$$\begin{pmatrix} -1 & 2 \\ 2 & 2 \end{pmatrix} \begin{pmatrix} C_{11} \\ C_{21} \end{pmatrix} = -2 \begin{pmatrix} C_{11} \\ C_{21} \end{pmatrix}$$

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

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

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

$$C_{11}^2 + C_{21}^2 = 1 \quad (\text{from normalization})$$

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

$$4C_{21}^2 + C_{21}^2 = 1$$

$$5C_{21}^2 = 1$$

$$C_{21}^2 = 0.2$$

$$C_{21} = \sqrt{0.2}, \text{ and therefore } C_{11} = -2\sqrt{0.2}.$$

For the eigenvector associated with eigenvalue 3:

$$\begin{bmatrix} -1 & 2 \\ 2 & 2 \end{bmatrix} \begin{bmatrix} C_{12} \\ C_{22} \end{bmatrix} = 3 \begin{bmatrix} C_{12} \\ C_{22} \end{bmatrix}$$

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

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

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

$$C_{12}^2 + C_{22}^2 = 1 \text{ (from normalization)}$$

$$(0.5C_{22})^2 + C_{22}^2 = 1$$

$$0.25C_{22}^2 + C_{22}^2 = 1$$

$$1.25C_{22}^2 = 1$$

$$C_{22}^2 = 0.8$$

$$C_{22} = \sqrt{0.8} = 2\sqrt{0.2}, \text{ and therefore } C_{12} = \sqrt{0.2}.$$

Therefore the eigenvector matrix becomes:

$$\begin{bmatrix} -2\sqrt{0.2} & \sqrt{0.2} \\ \sqrt{0.2} & 2\sqrt{0.2} \end{bmatrix}$$

b. First determine the eigenvalues:

$$\det \begin{bmatrix} -2 - \lambda & 0 \\ 0 & -1 - \lambda \end{bmatrix} = 0$$

$$\det \begin{bmatrix} -2 - \lambda & 0 \\ 0 & -1 - \lambda \end{bmatrix} = 0$$

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

$$\begin{array}{ccc|ccc} -2 & 0 & 0 & C_{11} & & C_{11} \\ 0 & -1 & 2 & C_{21} & = 3 & C_{21} \\ 0 & 2 & 2 & C_{31} & & C_{31} \end{array}$$

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

$$C_{13} = 0$$

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

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

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

$$C_{13}^2 + C_{23}^2 + C_{33}^2 = 1 \text{ (from normalization)}$$

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

$$5C_{23}^2 = 1$$

$$C_{23} = \sqrt{0.2}, \text{ and therefore } C_{33} = 2\sqrt{0.2}.$$

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

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

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

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

$$C_{11}^2 + C_{21}^2 + C_{31}^2 = 1 \text{ (from normalization)}$$

$$C_{11}^2 + (-2C_{31})^2 + C_{31}^2 = 1$$

$$C_{11}^2 + 5C_{31}^2 = 1$$

$$C_{11} =$$

$$\sqrt{1 - 5C_{31}^2} \text{ (Note: There are now two equations with three unknowns.)}$$

Second, root two eigenvector two:

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

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

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

$$C_{12}^2 + C_{22}^2 + C_{32}^2 = 1 \text{ (from normalization)}$$

$$C_{12}^2 + (-2C_{32})^2 + C_{32}^2 = 1$$

$$C_{12}^2 + 5C_{32}^2 = 1$$

$$C_{12} = (1 - 5C_{32}^2)^{1/2} \text{ (Note: again, two equations in three unknowns)}$$

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

Now there are five equations with six unknowns.

$$\text{Arbitrarily choose } C_{11} = 0$$

(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).

$$C_{11} = 0 = \sqrt{1 - 5C_{31}^2}$$

$$5C_{31}^2 = 1$$

$$C_{31} = \sqrt{0.2}$$

$$C_{21} = -2\sqrt{0.2}$$

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

$$0 + -2\sqrt{0.2}(-2C_{32}) + \sqrt{0.2} C_{32} = 0$$

$$5C_{32} = 0$$

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

Therefore the eigenvector matrix becomes:

$$\begin{array}{ccc} 0 & 1 & 0 \\ -2\sqrt{0.2} & 0 & \sqrt{0.2} \\ \sqrt{0.2} & 0 & 2\sqrt{0.2} \end{array}$$

2.

a.
$$\text{K.E.} = \frac{mv^2}{2} = \frac{m}{m} \frac{mv^2}{2} = \frac{(mv)^2}{2m} = \frac{p^2}{2m}$$

$$\text{K.E.} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

$$\text{K.E.} = \frac{1}{2m} \frac{\hbar^2}{i^2 x^2} + \frac{\hbar^2}{i^2 y^2} + \frac{\hbar^2}{i^2 z^2}$$

$$\text{K.E.} = \frac{-\hbar^2}{2m} \left(\frac{2}{x^2} + \frac{2}{y^2} + \frac{2}{z^2} \right)$$

b.
$$\mathbf{p} = m\mathbf{v} = i p_x + j p_y + k p_z$$

$$\mathbf{p} = i \frac{\hbar}{i x} + j \frac{\hbar}{i y} + k \frac{\hbar}{i z}$$

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

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

$$L_y = z \frac{\hbar}{i x} - x \frac{\hbar}{i z}$$

3.

First derive the general formulas for $\frac{\partial}{\partial x}$, $\frac{\partial}{\partial y}$, $\frac{\partial}{\partial z}$ in terms of r , θ , and ϕ , and $\frac{\partial}{\partial r}$, $\frac{\partial}{\partial \theta}$,

and $\frac{\partial}{\partial \phi}$ in terms of x, y , and z . The general relationships are as follows:

$$\begin{aligned} x &= r \sin \theta \cos \phi & r^2 &= x^2 + y^2 + z^2 \\ y &= r \sin \theta \sin \phi & \sin \theta &= \frac{\sqrt{x^2 + y^2}}{\sqrt{x^2 + y^2 + z^2}} \\ z &= r \cos \theta & \cos \theta &= \frac{z}{\sqrt{x^2 + y^2 + z^2}} \\ & & \tan \theta &= \frac{y}{x} \end{aligned}$$

First $\frac{\partial}{\partial x}$, $\frac{\partial}{\partial y}$, and $\frac{\partial}{\partial z}$ from the chain rule:

$$\begin{aligned} \frac{\partial}{\partial x} &= \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi}, \\ \frac{\partial}{\partial y} &= \frac{\partial r}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y} \frac{\partial}{\partial \phi}, \\ \frac{\partial}{\partial z} &= \frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z} \frac{\partial}{\partial \phi}. \end{aligned}$$

Evaluation of the many "coefficients" gives the following:

$$\begin{aligned} \frac{\partial r}{\partial x} &= \frac{x}{r} = \sin \theta \cos \phi, \quad \frac{\partial \theta}{\partial x} = \frac{\cos \theta \cos \phi}{r}, \quad \frac{\partial \phi}{\partial x} = -\frac{\sin \phi}{r \sin \theta}, \\ \frac{\partial r}{\partial y} &= \frac{y}{r} = \sin \theta \sin \phi, \quad \frac{\partial \theta}{\partial y} = \frac{\cos \theta \sin \phi}{r}, \quad \frac{\partial \phi}{\partial y} = \frac{\cos \phi}{r \sin \theta}, \\ \frac{\partial r}{\partial z} &= \frac{z}{r} = \cos \theta, \quad \frac{\partial \theta}{\partial z} = -\frac{\sin \theta}{r}, \quad \text{and} \quad \frac{\partial \phi}{\partial z} = 0. \end{aligned}$$

Upon substitution of these "coefficients":

$$\frac{\partial x}{\partial r} = \sin \theta \cos \phi \frac{\partial \theta}{\partial r} + \frac{\cos \theta \cos \phi}{r} \frac{\partial \phi}{\partial r} - \frac{\sin \theta}{r \sin \phi} \frac{\partial \phi}{\partial r},$$

$$\frac{\partial y}{\partial r} = \sin \theta \sin \phi \frac{\partial \theta}{\partial r} + \frac{\cos \theta \sin \phi}{r} \frac{\partial \phi}{\partial r} + \frac{\cos \theta}{r \sin \phi} \frac{\partial \phi}{\partial r}, \text{ and}$$

$$\frac{\partial z}{\partial r} = \cos \theta \frac{\partial \theta}{\partial r} - \frac{\sin \theta}{r} \frac{\partial \phi}{\partial r} + 0.$$

Next $\frac{\partial x}{\partial \theta}$, $\frac{\partial y}{\partial \theta}$, and $\frac{\partial z}{\partial \theta}$ from the chain rule:

$$\frac{\partial x}{\partial \theta} = \frac{x}{r}, \quad \frac{\partial y}{\partial \theta} = \frac{y}{r}, \quad \frac{\partial z}{\partial \theta} = \frac{z}{r},$$

$$\frac{\partial x}{\partial \phi} = \frac{x}{r} \frac{\partial \theta}{\partial \phi} + \frac{y}{r} \frac{\partial \theta}{\partial \phi}, \quad \frac{\partial y}{\partial \phi} = \frac{y}{r} \frac{\partial \theta}{\partial \phi} + \frac{z}{r} \frac{\partial \theta}{\partial \phi}, \text{ and}$$

$$\frac{\partial z}{\partial \phi} = \frac{x}{r} \frac{\partial \theta}{\partial \phi} + \frac{y}{r} \frac{\partial \theta}{\partial \phi} + \frac{z}{r} \frac{\partial \theta}{\partial \phi}.$$

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

$$\frac{\partial x}{\partial r} = \frac{x}{\sqrt{x^2 + y^2 + z^2}}, \quad \frac{\partial y}{\partial r} = \frac{y}{\sqrt{x^2 + y^2 + z^2}},$$

$$\frac{\partial z}{\partial r} = \frac{z}{\sqrt{x^2 + y^2 + z^2}}, \quad \frac{\partial x}{\partial \theta} = \frac{x}{\sqrt{x^2 + y^2}}, \quad \frac{\partial y}{\partial \theta} = \frac{y}{\sqrt{x^2 + y^2}},$$

$$\frac{\partial z}{\partial \theta} = -\sqrt{x^2 + y^2}, \quad \frac{\partial x}{\partial \phi} = -y, \quad \frac{\partial y}{\partial \phi} = x, \text{ and } \frac{\partial z}{\partial \phi} = 0$$

Upon substitution of these "coefficients":

$$\begin{aligned} \frac{\partial x}{\partial r} &= \frac{x}{\sqrt{x^2 + y^2 + z^2}} \frac{\partial x}{\partial r} + \frac{y}{\sqrt{x^2 + y^2 + z^2}} \frac{\partial y}{\partial r} \\ &\quad + \frac{z}{\sqrt{x^2 + y^2 + z^2}} \frac{\partial z}{\partial r} \end{aligned}$$

$$\frac{\partial z}{\partial x} = \frac{xz}{\sqrt{x^2+y^2}} \frac{1}{x} + \frac{yz}{\sqrt{x^2+y^2}} \frac{1}{y} - \sqrt{x^2+y^2} \frac{1}{z}$$

$$\frac{\partial z}{\partial y} = -y \frac{1}{x} + x \frac{1}{y} + 0 \frac{1}{z}$$

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:

$$f(x,y,z) dx dy dz =$$

$$f(x(r, \theta, \phi), y(r, \theta, \phi), z(r, \theta, \phi)) \begin{pmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{pmatrix} dr d\theta d\phi$$

a. $\mathbf{L}_x = \frac{\hbar}{i} (y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y})$

$$\mathbf{L}_x = \frac{\hbar}{i} (r \sin \theta \sin \phi \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta} -$$

$$-\frac{\hbar}{i} r \cos \theta \sin \phi \frac{\partial}{\partial r} + \frac{\cos \theta \sin \phi}{r} \frac{\partial}{\partial \theta} + \frac{\cos \theta}{r \sin \theta} \frac{\partial}{\partial \phi})$$

$$\mathbf{L}_x = -\frac{\hbar}{i} (\sin \theta \frac{\partial}{\partial \phi} + \cot \theta \frac{\partial}{\partial \theta})$$

b. $\mathbf{L}_z = \frac{\hbar}{i} (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) = -i\hbar \frac{\partial}{\partial \phi}$

$$\mathbf{L}_z = \frac{\hbar}{i} (-y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y})$$

4.

	<u>B</u>	<u>dB/dx</u>	<u>d²B/dx²</u>
i.	$4x^4 - 12x^2 + 3$	$16x^3 - 24x$	$48x^2 - 24$
ii.	$5x^4$	$20x^3$	$60x^2$
iii.	$e^{3x} + e^{-3x}$	$3(e^{3x} - e^{-3x})$	$9(e^{3x} + e^{-3x})$
iv.	$x^2 - 4x + 2$	$2x - 4$	2
v.	$4x^3 - 3x$	$12x^2 - 3$	$24x$

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

$$(1-x^2) \frac{d^2}{dx^2} - x \frac{d}{dx} B(v.) =$$

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

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

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

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

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

$$\frac{d^2}{dx^2} B(iii.) =$$

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

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

$$x \frac{d}{dx} B(ii.) =$$

$$x (20x^3)$$

$$20x^4$$

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

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

$$\frac{d^2}{dx^2} - 2x \frac{d}{dx} B(i) =$$

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

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

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

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

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

$$x \frac{d^2}{dx^2} + (1-x) \frac{d}{dx} B(iv.) =$$

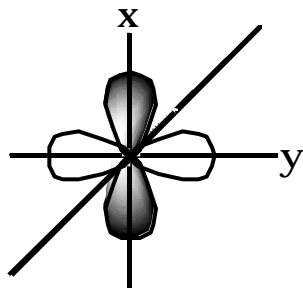
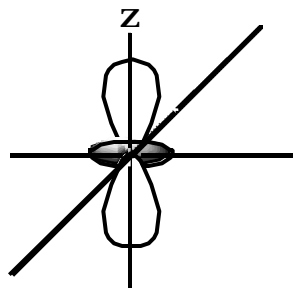
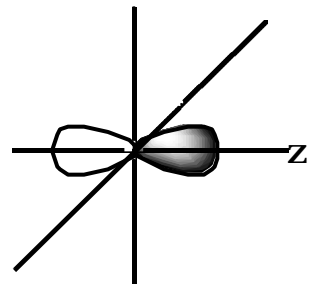
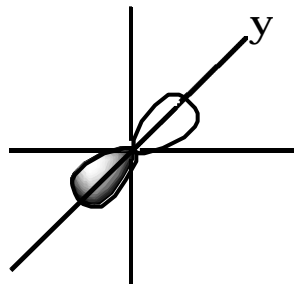
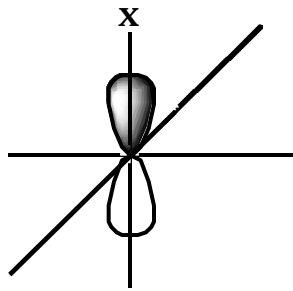
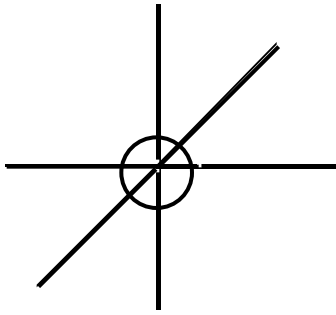
$$x (2) + (1-x) (2x - 4)$$

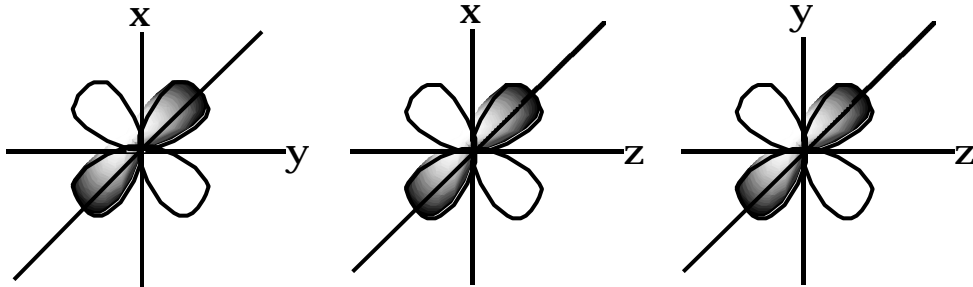
$$2x + 2x - 4 - 2x^2 + 4x$$

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

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

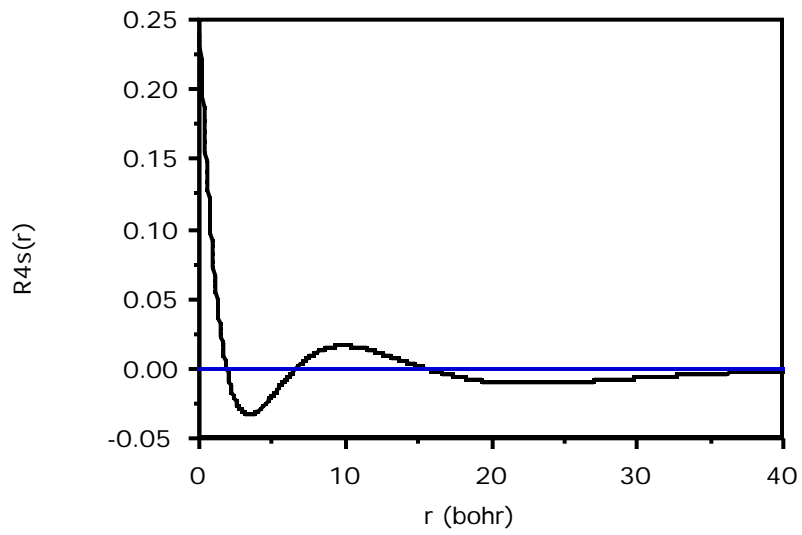
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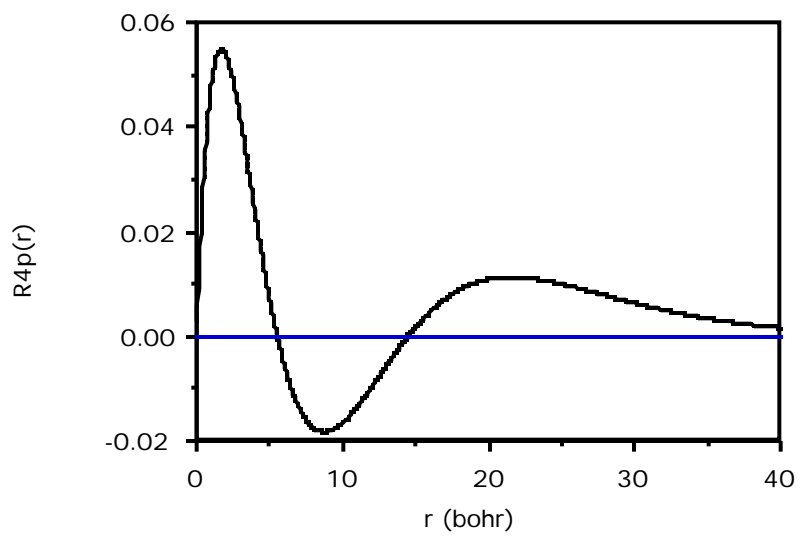


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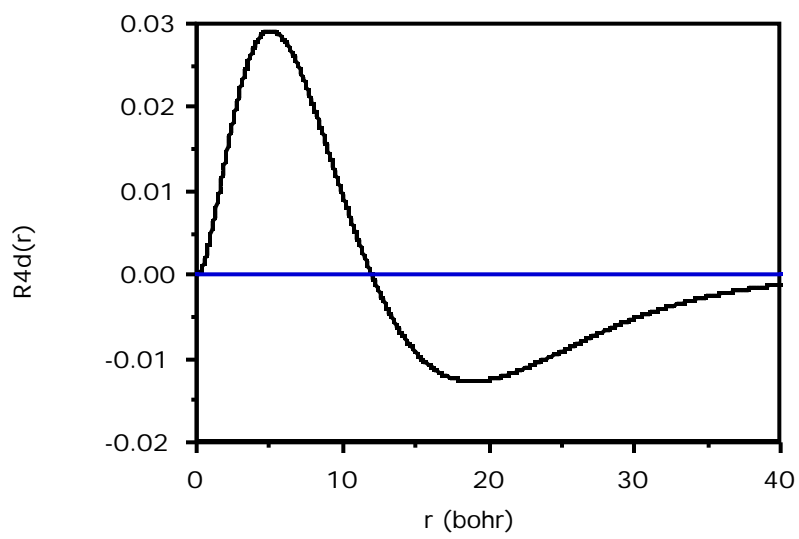
Hydrogen 4s Radial Function



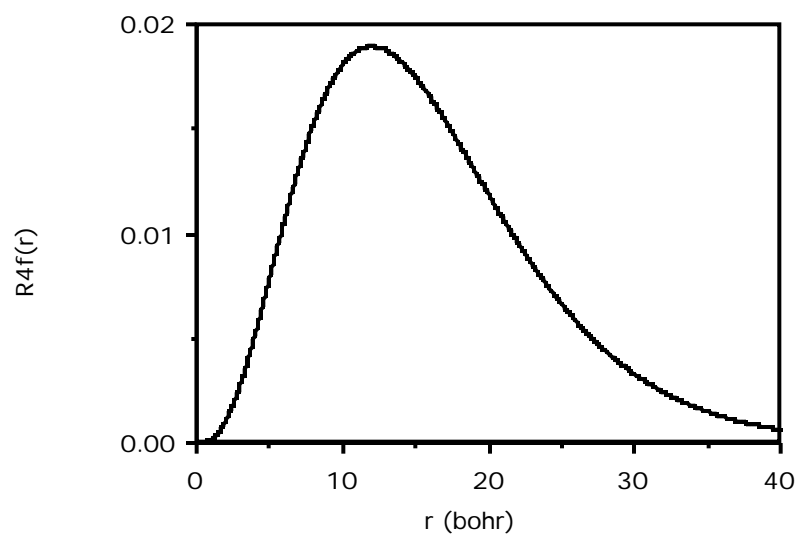
Hydrogen 4p Radial Function



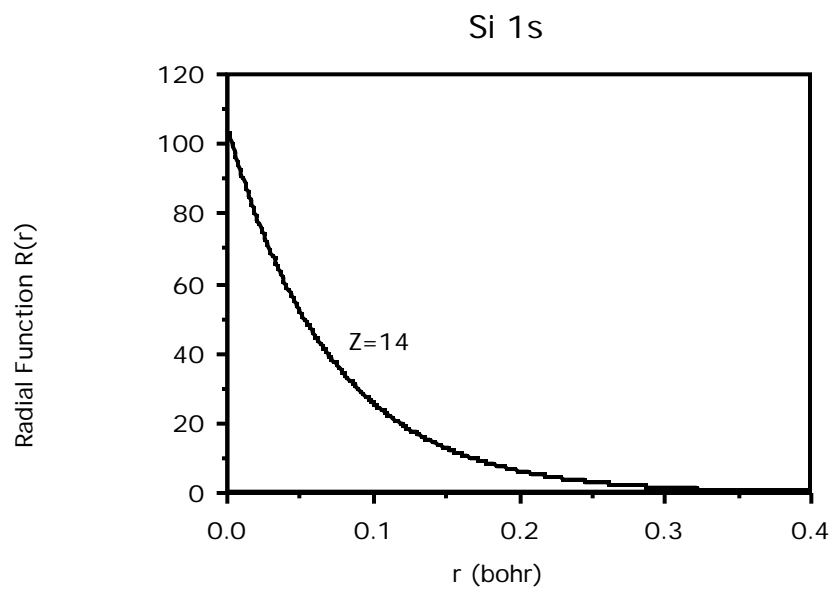
Hydrogen 4d Radial Function



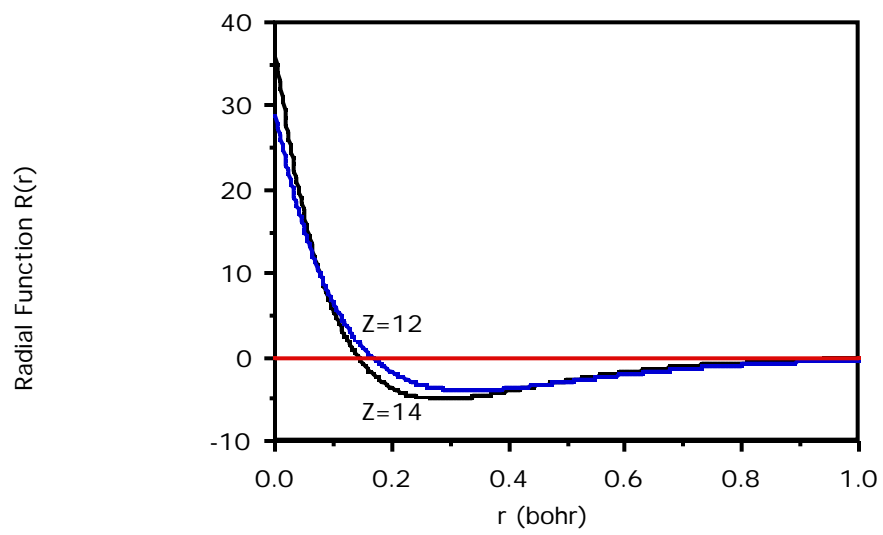
Hydrogen 4f Radial Function



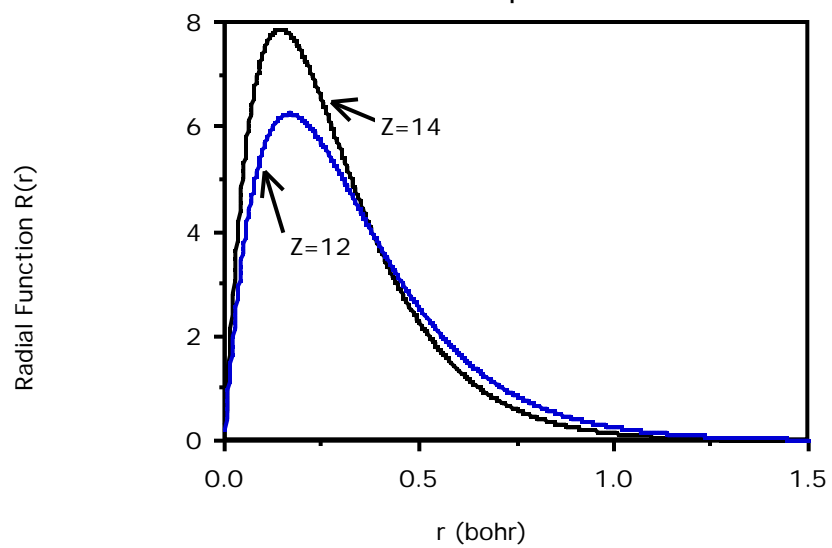
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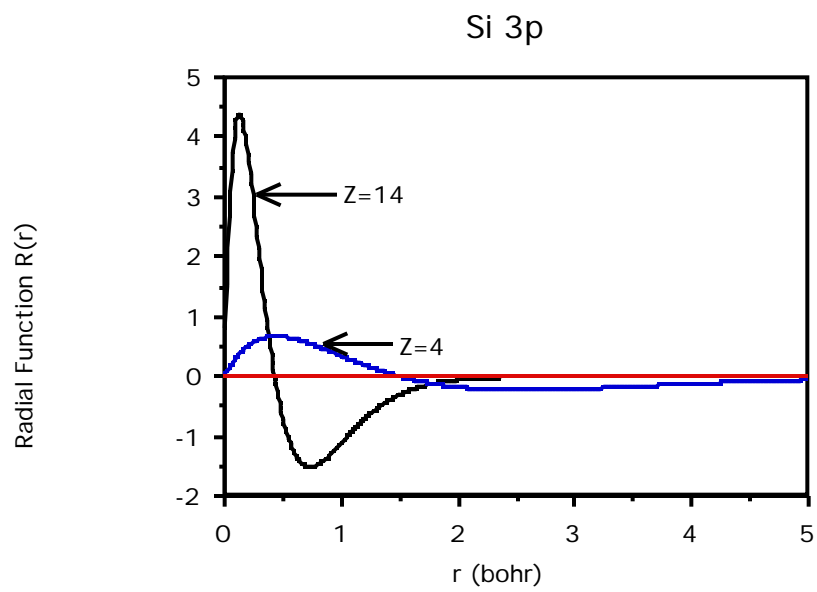
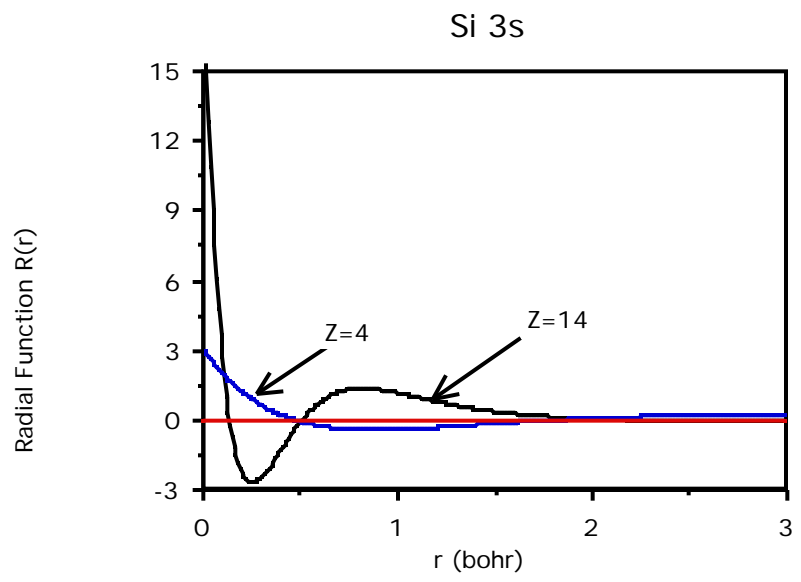


Si 2s



Si 2p





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 $2p_z = a_1$, O $2p_y$ as b_2 , and O $2p_x$ 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 $2p_x + O 2p_x = b$, O $2p_x - O 2p_x = a$, O $2p_y + O 2p_y = a$, O $2p_y - O 2p_y = b$, O $2p_z + O 2p_z = b$, O $2p_z - O 2p_z = a$, 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_h , D_{2h} , and C_{2v} point groups and the xy plane as the horizontal reflection plane in C_s symmetry.

	D_h	D_{2h}	C_{2v}	C_s
N 1s	g	a_g	a_1	a'
N 2s	g	a_g	a_1	a'
N $2p_x$	xu	b_{3u}	b_1	a'

$$\begin{array}{ccccc}
 N 2p_y & y_u & b_{2u} & b_2 & a' \\
 N 2p_z & u & b_{1u} & a_1 & a''
 \end{array}$$

9.

$$\begin{aligned}
 \text{a. } \quad P_n(x) &= \frac{2}{L} \sin^2 \frac{n x}{L} \\
 P_n(x) dx &= \left| \frac{2}{L} \sin^2 \frac{n x}{L} \right| dx
 \end{aligned}$$

The probability that the particle lies in the interval $0 \leq x \leq \frac{L}{4}$ is given by:

$$P_n = \int_0^{\frac{L}{4}} P_n(x) dx = \int_0^{\frac{L}{4}} \frac{2}{L} \sin^2 \frac{n x}{L} dx$$

This integral can be integrated to give :

$$P_n = \frac{L}{n} \int_0^{\frac{n}{4}} \frac{2}{L} \sin^2 \frac{n x}{L} d \frac{n x}{L}$$

$$P_n = \frac{L}{n} \int_0^{\frac{n}{4}} \frac{2}{L} \sin^2 d$$

$$P_n = \frac{2}{n} - \frac{1}{4} \sin 2 \frac{n}{4} + \frac{1}{2} \frac{n}{4}$$

$$= \frac{2}{n} - \frac{1}{4} \sin \frac{2n}{4} + \frac{n}{(2)(4)}$$

$$= \frac{1}{4} - \frac{1}{2n} \sin \frac{n}{2}$$

b. If n is even, $\sin \frac{n}{2} = 0$ and $P_n = \frac{1}{4}$.

If n is odd and $n = 1, 5, 9, 13, \dots$ $\sin \frac{n}{2} = 1$

$$\text{and } P_n = \frac{1}{4} - \frac{1}{2n}$$

If n is odd and $n = 3, 7, 11, 15, \dots$ $\sin \frac{n}{2} = -1$

$$\text{and } P_n = \frac{1}{4} + \frac{1}{2n}$$

The higher P_n is when $n = 3$. Then $P_n = \frac{1}{4} + \frac{1}{2 \cdot 3}$

$$P_n = \frac{1}{4} + \frac{1}{6} = 0.303$$

$$c. \quad \psi(t) = e^{\frac{-iHt}{\hbar}} [a \psi_n + b \psi_m] = a \psi_n e^{\frac{-iE_n t}{\hbar}} + b \psi_m e^{\frac{-iE_m t}{\hbar}}$$

$$H \psi = a \psi_n E_n e^{\frac{-iE_n t}{\hbar}} + b \psi_m E_m e^{\frac{-iE_m t}{\hbar}}$$

$$\langle H \rangle = |a|^2 E_n + |b|^2 E_m + a^* b e^{\frac{i(E_n - E_m)t}{\hbar}} \langle \psi_n | H | \psi_m \rangle$$

$$+ b^* a e^{\frac{-i(E_m - E_n)t}{\hbar}} \langle \psi_m | H | \psi_n \rangle$$

Since $\langle \psi_n | H | \psi_m \rangle$ and $\langle \psi_m | H | \psi_n \rangle$ are zero,

$$\langle H \rangle = |a|^2 E_n + |b|^2 E_m \quad (\text{note the time independence})$$

d. The fraction of systems observed in 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 n , it stays in n .

f. $P(E_n) = \langle n | \psi \rangle^2 = |c_n|^2$

$$c_n = \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n x}{L} \sqrt{\frac{30}{L^5}} x(L-x) dx$$

$$= \sqrt{\frac{60}{L^6}} \int_0^L x(L-x) \sin \frac{n x}{L} dx$$

$$= \sqrt{\frac{60}{L^6}} \left[\int_0^L L x \sin \frac{n x}{L} dx - \int_0^L x^2 \sin \frac{n x}{L} dx \right]$$

These integrals can be evaluated to give:

$$c_n = \sqrt{\frac{60}{L^6}} \left[L \frac{L^2}{n^2} \frac{2}{L} \sin \frac{n x}{L} - \frac{Lx}{n} \cos \frac{n x}{L} \right]_0^L$$

$$- \sqrt{\frac{60}{L^6}} \left[\frac{2xL^2}{n^2} \frac{2}{L} \sin \frac{n x}{L} - \frac{n^2 - 2x^2}{L^2} - 2 \frac{L^3}{n^3} \frac{3}{L} \cos \frac{n x}{L} \right]_0^L$$

$$c_n = \sqrt{\frac{60}{L^6}} \left\{ \frac{L^3}{n^2} \frac{2}{L} (\sin(n) - \sin(0)) \right.$$

$$\left. - \frac{L^2}{n} (L \cos(n) - 0 \cos(0)) \right.$$

$$\left. - \left(\frac{2L^2}{n^2} \frac{2}{L} (L \sin(n) - 0 \sin(0)) \right) \right.$$

$$- (n^2 - 2) \frac{L^3}{n^3} \cos(n \cdot) + \frac{n^2 - 2(0)}{L^2} - 2 \frac{L^3}{n^3} \cos(0) \Bigg\}$$

$$c_n = L^{-3} \sqrt{60} \left\{ - \frac{L^3}{n} \cos(n \cdot) + (n^2 - 2) \frac{L^3}{n^3} \cos(n \cdot) + \frac{2L^3}{n^3} \right\}$$

$$c_n = \sqrt{60} \left[- \frac{1}{n} (-1)^n + (n^2 - 2) \frac{1}{n^3} (-1)^n + \frac{2}{n^3} \right]$$

$$c_n = \sqrt{60} \left[\frac{-1}{n} + \frac{1}{n} - \frac{2}{n^3} (-1)^n + \frac{2}{n^3} \right]$$

$$c_n = \frac{2\sqrt{60}}{n^3} (-1)^n (1)$$

$$|c_n|^2 = \frac{4(60)}{n^6} (-1)^n (1)^2$$

If n is even then $c_n = 0$

$$\text{If n is odd then } c_n = \frac{(4)(60)(4)}{n^6 \cdot 6} = \frac{960}{n^6 \cdot 6}$$

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

$$E_n = \frac{n^2 \cdot 2\hbar^2}{2mL^2} \text{ is:}$$

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

$$P(E_n) = \frac{960}{n^6 \cdot 6} \text{ if n is odd}$$

$$\begin{aligned}
g. \langle |H| \rangle &= \int_0^L \frac{30}{L^5} \frac{1}{2} x(L-x) \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \frac{30}{L^5} \frac{1}{2} x(L-x) dx \\
&= \frac{30}{L^5} \frac{-\hbar^2}{2m} \int_0^L x(L-x) \frac{d^2}{dx^2} (xL-x^2) dx \\
&= \frac{-15\hbar^2}{mL^5} \int_0^L x(L-x)(-2) dx \\
&= \frac{30\hbar^2}{mL^5} \int_0^L xL-x^2 dx \\
&= \frac{30\hbar^2}{mL^5} \left[L \frac{x^2}{2} - \frac{x^3}{3} \right]_0^L \\
&= \frac{30\hbar^2}{mL^5} \left[\frac{L^3}{2} - \frac{L^3}{3} \right] \\
&= \frac{30\hbar^2}{mL^5} \frac{1}{2} \frac{1}{3} \\
&= \frac{30\hbar^2}{6mL^5} = \frac{5\hbar^2}{mL^5}
\end{aligned}$$

10.

$$\langle |H| \rangle = \sum_{ij} C_i^* e^{\frac{iE_j t}{\hbar}} \langle i|H|j\rangle e^{-\frac{iE_j t}{\hbar}} C_j$$

Since $\langle i|H|j\rangle = E_j \delta_{ij}$

$$\langle |H| \rangle = \sum_j C_j^* C_j E_j e^{\frac{i(E_j - E_j)t}{\hbar}}$$

$$\langle |H| \rangle = \sum_j C_j^* C_j E_j \quad (\text{not time dependent})$$

For other properties:

$$\langle |A| \rangle = \sum_{ij} C_i^* e^{\frac{iE_i t}{\hbar}} \langle i|A|j\rangle e^{\frac{-iE_j t}{\hbar}} C_j$$

but, $\langle i|A|j\rangle$ does not necessarily = $a_j \delta_{ij}$ because the $|j\rangle$ are not eigenfunctions of A unless $[A,H] = 0$.

$$\langle |A| \rangle = \sum_{ij} C_i^* C_j e^{\frac{i(E_i - E_j)t}{\hbar}} \langle i|A|j\rangle$$

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:

$$E_{\text{total}} = \frac{h^2}{8mL^2}(n_1^2 + n_2^2 + n_3^2) = \frac{3h^2}{8mL^2}$$

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:

$$E_{\text{total}} = \frac{h^2}{8mL^2}(n_1^2 + n_2^2 + n_3^2) = \frac{6h^2}{8mL^2}$$

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

b. distortion

$$L_1 = L_2 = L_3$$

$$L_3 \quad L_1 = L_2$$

For $L_1 = L_2 = L_3$, $V = L_1L_2L_3 = L_1^3$,

$$E_{\text{total}}(L_1) = 2 \frac{1}{L_1} + \frac{2}{L_1}$$

$$= \frac{2h^2}{8m} \frac{1^2}{L_1^2} + \frac{1^2}{L_2^2} + \frac{1^2}{L_3^2} + \frac{1h^2}{8m} \frac{1^2}{L_1^2} + \frac{1^2}{L_2^2} + \frac{2^2}{L_3^2}$$

$$= \frac{2h^2}{8m} \frac{3}{L_1^2} + \frac{1h^2}{8m} \frac{6}{L_1^2} = \frac{h^2}{8m} \frac{12}{L_1^2}$$

For $L_3 \quad L_1 = L_2$, $V = L_1L_2L_3 = L_1^2L_3$, $L_3 = V/L_1^2$

$$E_{\text{total}}(L_1) = 2 \frac{1}{L_1} + \frac{2}{L_1}$$

$$\begin{aligned}
&= \frac{2h^2}{8m} \frac{1^2}{L_1^2} + \frac{1^2}{L_2^2} + \frac{1^2}{L_3^2} + \frac{1h^2}{8m} \frac{1^2}{L_1^2} + \frac{1^2}{L_2^2} + \frac{2^2}{L_3^2} \\
&= \frac{2h^2}{8m} \frac{2}{L_1^2} + \frac{1}{L_3^2} + \frac{1h^2}{8m} \frac{2}{L_1^2} + \frac{4}{L_3^2} \\
&= \frac{2h^2}{8m} \frac{2}{L_1^2} + \frac{1}{L_3^2} + \frac{1}{L_1^2} + \frac{2}{L_3^2} \\
&= \frac{2h^2}{8m} \frac{3}{L_1^2} + \frac{3}{L_3^2} = \frac{h^2}{8m} \frac{6}{L_1^2} + \frac{6}{L_3^2}
\end{aligned}$$

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:

$$\frac{h^2}{8m} \frac{6}{L_1^2} + \frac{6}{L_3^2} < \frac{h^2}{8m} \frac{12}{L_1^2} \quad \text{as long as } L_3 > L_1.$$

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. $\frac{E_{\text{total}}}{L_1} = 0$

$$\frac{d}{dL_1} \left(\frac{h^2}{8m} \frac{6}{L_1^2} + \frac{6}{L_3^2} \right) = 0$$

But since $V = L_1 L_2 L_3 = L_1^2 L_3$, then $L_3 = V/L_1^2$. This substitution gives:

$$\frac{d}{dL_1} \left(\frac{h^2}{8m} \frac{6}{L_1^2} + \frac{6L_1^4}{V^2} \right) = 0$$

$$\frac{h^2}{8m} \frac{(-2)6}{L_1^3} + \frac{(4)6L_1^3}{V^2} = 0$$

$$-\frac{12}{L_1^3} + \frac{24L_1^3}{V^2} = 0$$

$$\frac{24L_1^3}{V^2} = \frac{12}{L_1^3}$$

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

$$L_1^6 = \frac{1}{2} V^2 = \frac{1}{2} (L_1^2 L_3)^2 = \frac{1}{2} L_1^4 L_3^2$$

$$L_1^2 = \frac{1}{2} L_3^2$$

$$L_3 = \sqrt{2} L_1$$

d. Calculate energy upon distortion:

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

$$\text{distorted: } V = L_1^2 L_3 = L_1^2 \sqrt{2} L_1 = \sqrt{2} L_1^3$$

$$L_3 = \sqrt{2} \frac{V}{\sqrt{2}}^{\frac{1}{3}} \quad L_1 = L_2 = \frac{V}{\sqrt{2}}^{\frac{1}{3}}$$

$$E = E_{\text{total}}(L_1 = L_2 = L_3) - E_{\text{total}}(L_3 \quad L_1 = L_2)$$

$$= \frac{h^2}{8m} \frac{12}{L_1^2} - \frac{h^2}{8m} \frac{6}{L_1^2} + \frac{6}{L_3^2}$$

$$= \frac{h^2}{8m} \frac{12}{V^{2/3}} - \frac{6(2)^{1/3}}{V^{2/3}} + \frac{6(2)^{1/3}}{2V^{2/3}}$$

$$= \frac{h^2}{8m} \frac{12 - 9(2)^{1/3}}{V^{2/3}}$$

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

$$E = 6.01 \times 10^{-27} \text{ erg cm}^2 \frac{12 - 9(2)^{1/3}}{4 \times 10^{-16} \text{ cm}^2}$$

$$E = 6.01 \times 10^{-27} \text{ erg cm}^2 \frac{0.66}{4 \times 10^{-16} \text{ cm}^2}$$

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

$$E = 0.99 \times 10^{-11} \text{ erg} \frac{1 \text{ eV}}{1.6 \times 10^{-12} \text{ erg}}$$

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

12.

a.
$$\mathbf{H} = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \quad (\text{Cartesian coordinates})$$

Finding $\frac{\partial}{\partial x}$ and $\frac{\partial}{\partial y}$ from the chain rule gives:

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial x} \frac{\partial}{\partial y} \frac{\partial}{\partial r} + \frac{\partial}{\partial x} \frac{\partial}{\partial y} \frac{\partial}{\partial \theta}, \quad \frac{\partial}{\partial y} = \frac{\partial}{\partial y} \frac{\partial}{\partial x} \frac{\partial}{\partial r} + \frac{\partial}{\partial y} \frac{\partial}{\partial x} \frac{\partial}{\partial \theta},$$

Evaluation of the "coefficients" gives the following:

$$\frac{\partial}{\partial x} \frac{\partial}{\partial y} = \text{Cos} \theta, \quad \frac{\partial}{\partial x} \frac{\partial}{\partial \theta} = -\frac{\text{Sin} \theta}{r},$$

$$\frac{\partial}{\partial y} \frac{\partial}{\partial x} = \text{Sin} \theta, \quad \text{and} \quad \frac{\partial}{\partial y} \frac{\partial}{\partial \theta} = \frac{\text{Cos} \theta}{r},$$

Upon substitution of these "coefficients":

$$\frac{\partial}{\partial x} = \text{Cos} \theta \frac{\partial}{\partial r} - \frac{\text{Sin} \theta}{r} \frac{\partial}{\partial \theta} = -\frac{\text{Sin} \theta}{r} \frac{\partial}{\partial \theta}; \text{ at fixed } r.$$

$$\frac{\partial}{\partial y} = \text{Sin} \theta \frac{\partial}{\partial r} + \frac{\text{Cos} \theta}{r} \frac{\partial}{\partial \theta} = \frac{\text{Cos} \theta}{r} \frac{\partial}{\partial \theta}; \text{ at fixed } r.$$

$$\begin{aligned} \frac{\partial^2}{\partial x^2} &= -\frac{\sin}{r} - \frac{\sin}{r} \\ &= \frac{\sin^2}{r^2} - \frac{2}{r^2} + \frac{\sin \cos}{r^2} \quad ; \text{ at fixed } r. \end{aligned}$$

$$\begin{aligned} \frac{\partial^2}{\partial y^2} &= \frac{\cos}{r} - \frac{\cos}{r} \\ &= \frac{\cos^2}{r^2} - \frac{2}{r^2} - \frac{\cos \sin}{r^2} \quad ; \text{ at fixed } r. \end{aligned}$$

$$\begin{aligned} \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} &= \frac{\sin^2}{r^2} - \frac{2}{r^2} + \frac{\sin \cos}{r^2} + \frac{\cos^2}{r^2} - \frac{2}{r^2} - \frac{\cos \sin}{r^2} \\ &= \frac{1}{r^2} - \frac{2}{r^2} \quad ; \text{ at fixed } r. \end{aligned}$$

$$\begin{aligned} \text{So, } \mathbf{H} &= \frac{-\hbar^2}{2mr^2} - \frac{2}{r^2} \quad (\text{cylindrical coordinates, fixed } r) \\ &= \frac{-\hbar^2}{2I} - \frac{2}{r^2} \end{aligned}$$

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

$$\mathbf{H} \psi = E \psi$$

$$\frac{-\hbar^2}{2I} \frac{\partial^2 \psi}{\partial \phi^2} = E \psi$$

$$\frac{\partial^2 \psi}{\partial \phi^2} = \frac{-2IE}{\hbar^2} \psi$$

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

$$\psi(\phi) = C_1 e^{-im\phi} + C_2 e^{im\phi}, \quad \text{where } m = \frac{2IE}{\hbar^2} \frac{1}{2}$$

Application of the cyclic boundary condition, $\psi(\phi) = \psi(\phi + 2\pi)$, results in the quantization

of the energy expression: $E = \frac{m^2 \hbar^2}{2I}$ 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 $\frac{1}{2\pi}^{\frac{1}{2}}$ for the normalization constant.

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$\frac{(\pm 4)^2 \hbar^2}{2I}$$

$$\frac{(\pm 3)^2 \hbar^2}{2I}$$

$$\frac{(\pm 2)^2 \hbar^2}{2I}$$

$$\frac{(\pm 1)^2 \hbar^2}{2I}$$

$$\frac{(0)^2 \hbar^2}{2I}$$

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

$$\frac{\hbar^2}{2mr^2} = \frac{6.06 \times 10^{-28} \text{ erg cm}^2}{(1.4 \times 10^{-8} \text{ cm})^2}$$

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

$$E = (2^2 - 1^2) 3.09 \times 10^{-12} \text{ erg} = 9.27 \times 10^{-12} \text{ erg}$$

but $E = h \nu = hc/\lambda$ So $\lambda = hc/E$

$$= \frac{(6.63 \times 10^{-27} \text{ erg sec})(3.00 \times 10^{10} \text{ cm sec}^{-1})}{9.27 \times 10^{-12} \text{ erg}}$$

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

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 π -electrons is not included in the Hamiltonian.
- iii. Benzene is not a ring.
- iv. Electrons move in three dimensions not one.

13.

$$\psi(\phi, 0) = \sqrt{\frac{4}{3}} \cos^2 \phi$$

This wavefunction needs to be expanded in terms of the eigenfunctions of the angular

momentum operator, $-\hbar^2 \nabla^2$. This is most easily accomplished by an exponential

expansion of the Cos function.

$$\begin{aligned} \psi(\phi, 0) &= \sqrt{\frac{4}{3}} \frac{e^{i\phi} + e^{-i\phi}}{2} \frac{e^{i\phi} + e^{-i\phi}}{2} \\ &= \frac{1}{4} \sqrt{\frac{4}{3}} (e^{2i\phi} + e^{-2i\phi} + 2e^{(0)i\phi}) \end{aligned}$$

The wavefunction is now written in terms of the eigenfunctions of the angular

momentum operator, $-i\hbar \frac{\partial}{\partial \phi}$, but they need to include their normalization constant, $\frac{1}{\sqrt{2}}$

$$\begin{aligned} \psi(\phi, 0) &= \frac{1}{4} \sqrt{\frac{4}{3}} \sqrt{2} \left[\frac{1}{\sqrt{2}} e^{2i\phi} + \frac{1}{\sqrt{2}} e^{-2i\phi} + 2 \frac{1}{\sqrt{2}} e^{(0)i\phi} \right] \\ &= \sqrt{\frac{1}{6}} \left[\frac{1}{\sqrt{2}} e^{2i\phi} + \frac{1}{\sqrt{2}} e^{-2i\phi} + 2 \frac{1}{\sqrt{2}} e^{(0)i\phi} \right] \end{aligned}$$

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

$$P_{2\hbar} = \left(\frac{1}{\sqrt{6}} \right)^2 = \frac{1}{6}$$

$$P_{-2\hbar} = \left(\frac{1}{\sqrt{6}} \right)^2 = \frac{1}{6}$$

$$P_{0\hbar} = \left(2 \frac{1}{\sqrt{6}} \right)^2 = \frac{4}{6}$$

14.

$$a. \frac{1}{2} mv^2 = 100 \text{ eV} \frac{1.602 \times 10^{-12} \text{ erg}}{1 \text{ eV}}$$

$$v^2 = \frac{(2)1.602 \times 10^{-10} \text{ erg}}{9.109 \times 10^{-28} \text{ g}}$$

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

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

$$v = \frac{d}{t}$$

$$t = \frac{d}{v} = \frac{2 \times 10^{-8} \text{ cm}}{0.593 \times 10^9 \text{ cm/sec}} = 3.37 \times 10^{-17} \text{ sec}$$

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

$$\psi_0 = \pi^{-1/4} e^{-x^2/2}, \quad \text{where } x = \frac{k\mu}{\hbar^2}^{1/2} \text{ and } x = r - r_e$$

Calculating constants;

$$N_2 = \frac{(2.294 \times 10^6 \text{ g sec}^{-2})(1.1624 \times 10^{-23} \text{ g})^{1/2}}{(1.0546 \times 10^{-27} \text{ erg sec})^2}$$

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

For N_2 : $\psi_0(r) = 3.53333 \text{\AA}^{-1/2} e^{-(244.83 \text{\AA}^{-2})(r-1.09769 \text{\AA})^2}$

$$N_2^+ = \frac{(2.009 \times 10^6 \text{ g sec}^{-2})(1.1624 \times 10^{-23} \text{ g})^{1/2}}{(1.0546 \times 10^{-27} \text{ erg sec})^2}$$

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

For N_2^+ : $\psi_0(r) = 3.47522 \text{\AA}^{-1/2} e^{-(229.113 \text{\AA}^{-2})(r-1.11642 \text{\AA})^2}$

$$c. P(v=0) = \langle \psi_{v=0}(N_2^+) | \psi_{v=0}(N_2) \rangle^2$$

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

$$I = \int_0^\infty (3.47522 \text{\AA}^{-1/2} e^{-(229.113 \text{\AA}^{-2})(r-1.11642 \text{\AA})^2}) \cdot$$

$$(3.53333\text{\AA}^{-\frac{1}{2}} e^{-(244.830\text{\AA}^{-2})(r-1.09769\text{\AA})^2})dr$$

$$\text{Let } C_1 = 3.47522\text{\AA}^{-\frac{1}{2}}, \quad C_2 = 3.53333\text{\AA}^{-\frac{1}{2}},$$

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

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

+

$$I = C_1 C_2 \int e^{-A_1(r-r_1)^2} e^{-A_2(r-r_2)^2} dr.$$

Focusing on the exponential:

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

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

$$\text{Let } A = A_1 + A_2,$$

$$B = 2A_1r_1 + 2A_2r_2,$$

$$C = C_1C_2, \text{ and}$$

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

+

$$I = C \int e^{-Ar^2 + Br - D} dr$$

+

$$= C \int e^{-A(r-r_0)^2 + D'} dr$$

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

$$-A(r^2 - 2rr_0 + r_0^2) + D' = -Ar^2 + Br - D$$

$$\text{such that, } 2Ar_0 = B$$

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

and, $r_0 = \frac{B}{2A}$

$$D' = Ar_0^2 - D = A \frac{B^2}{4A^2} - D = \frac{B^2}{4A} - D .$$

$$I = C \int e^{-A(r-r_0)^2 + D'} dr$$

$$= Ce^{D'} \int e^{-Ay^2} dy$$

$$= Ce^{D'} \sqrt{\frac{\pi}{A}}$$

Now back substituting all of these constants:

$$I = C_1 C_2 \sqrt{\frac{\pi}{A_1 + A_2}} \exp \left(\frac{(2A_1 r_1 + 2A_2 r_2)^2}{4(A_1 + A_2)} - A_1 r_1^2 - A_2 r_2^2 \right)$$

$$I = (3.47522)(3.53333) \sqrt{\frac{\pi}{(229.113) + (244.830)}} \\ \cdot \exp \left(\frac{(2(229.113)(1.11642) + 2(244.830)(1.09769))^2}{4((229.113) + (244.830))} \right) \\ \cdot \exp \left(- (229.113)(1.11642)^2 - (244.830)(1.09769)^2 \right)$$

$$I = 0.959$$

$P(v=0) = I^2 = 0.92$, so there is a 92% probability.

15.

$$a. \quad E = \frac{\hbar^2 k^2}{\mu} + \frac{1}{2}$$

$$E = E_{+1} - E$$

$$= \frac{\hbar^2 k^2}{\mu} + \frac{1}{2} - \left(-\frac{1}{2} \right) = \frac{\hbar^2 k^2}{\mu}$$

$$= \frac{(1.0546 \times 10^{-27} \text{ erg sec})^2 (1.87 \times 10^6 \text{ g sec}^{-2})}{6.857 \text{ g} / 6.02 \times 10^{23}} \frac{1}{2}$$

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

$$E = \frac{hc}{\lambda}$$

$$= \frac{hc}{E} = \frac{(6.626 \times 10^{-27} \text{ erg sec})(3.00 \times 10^{10} \text{ cm sec}^{-1})}{4.27 \times 10^{-13} \text{ erg}}$$

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

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

$$b. \quad \psi_0 = \frac{1}{\sqrt{\pi}} e^{-x^2/2}$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_0^* x \psi_0 dx$$

$$= \int_{-\infty}^{\infty} \frac{1}{\pi} e^{-x^2/2} x e^{-x^2/2} dx$$

$$= \frac{1}{\pi} \int_{-\infty}^{\infty} x e^{-x^2} dx$$

$$= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{1}{2} e^{-x^2/2} d(-x^2/2)$$

$$= \frac{-1}{2} e^{-x^2} + 0 = 0$$

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} \psi_{v=0}^* x^2 \psi_{v=0} dx$$

$$= \int_{-\infty}^{+\infty} \psi_{v=0}^* x^2 \psi_{v=0} dx$$

$$= \int_{-\infty}^{+\infty} \frac{1}{\sqrt{2}} e^{-x^2} x^2 dx$$

$$= 2 \int_0^{+\infty} \frac{1}{\sqrt{2}} x^2 e^{-x^2} dx$$

$$= 2 \int_0^{+\infty} \frac{1}{2^{1+1/2}} x^2 e^{-x^2} dx$$

$$= \frac{1}{2}$$

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

$$= \frac{\hbar}{2\sqrt{k\mu}}$$

$$= \frac{(1.0546 \times 10^{-27} \text{ erg sec})^2}{4(1.87 \times 10^6 \text{ g sec}^{-2})(6.857 \text{ g} / 6.02 \times 10^{23})} \frac{1}{4}$$

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

c.
$$\Delta x = \frac{\hbar}{2\sqrt{k\mu}}$$

The smaller k and μ become, the larger the uncertainty in the internuclear distance

becomes. Helium has a small μ and small attractive force between atoms. This results in

a very large x . 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.

a. $W = \int_{-\infty}^{\infty} \psi^* H \psi dx$

$$W = \int_{-\infty}^{\infty} \frac{2b}{\sqrt{2}} e^{-bx^2} \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + a|x| \right] e^{-bx^2} dx$$

$$\begin{aligned} \frac{d^2}{dx^2} e^{-bx^2} &= \frac{d}{dx} (-2bx) e^{-bx^2} \\ &= (-2bx) (-2bx) e^{-bx^2} + e^{-bx^2} (-2b) \\ &= 4b^2x^2 e^{-bx^2} - 2b e^{-bx^2} \end{aligned}$$

Making this substitution results in the following three integrals:

$$W = \frac{2b}{\sqrt{2}} \int_{-\infty}^{\infty} \frac{\hbar^2}{2m} e^{-bx^2} 4b^2x^2 e^{-bx^2} dx +$$

$$\frac{2b}{\sqrt{2}} \int_{-\infty}^{\infty} \frac{\hbar^2}{2m} e^{-bx^2} (-2b) e^{-bx^2} dx +$$

$$\begin{aligned}
& \frac{2b}{\hbar} \int_{-\infty}^{\infty} \frac{1}{2} e^{-bx^2} \left(-\frac{\hbar^2}{m} \frac{d^2}{dx^2} \right) e^{-bx^2} dx \\
&= \frac{2b}{\hbar} \int_{-\infty}^{\infty} \frac{1}{2} \left(-\frac{2b^2 \hbar^2}{m} x^2 e^{-2bx^2} \right) dx + \frac{2b}{\hbar} \int_{-\infty}^{\infty} \frac{1}{2} \frac{b \hbar^2}{m} e^{-2bx^2} dx + \\
& \frac{2b}{\hbar} \int_{-\infty}^{\infty} \frac{1}{2} a |x| e^{-2bx^2} dx \\
&= \frac{2b}{\hbar} \int_{-\infty}^{\infty} \frac{1}{2} \left(-\frac{2b^2 \hbar^2}{m} \right) \frac{1}{2} \frac{1}{2^{3/2} b} \sqrt{\frac{1}{2b}} + \frac{2b}{\hbar} \int_{-\infty}^{\infty} \frac{1}{2} \frac{b \hbar^2}{m} \frac{1}{2} \frac{1}{2} \sqrt{\frac{1}{2b}} + \\
& \frac{2b}{\hbar} \int_{-\infty}^{\infty} \frac{1}{2} a \frac{0!}{2b} \\
&= -\frac{b \hbar^2}{m} \frac{1}{2} + \frac{b \hbar^2}{m} + \frac{2b}{\hbar} \frac{1}{2} \frac{a}{2b}
\end{aligned}$$

$$W = \frac{b \hbar^2}{2m} + a \frac{1}{2b} \frac{1}{2}$$

b. Optimize b by evaluating $\frac{dW}{db} = 0$

$$\begin{aligned}
\frac{dW}{db} &= \frac{d}{db} \left(\frac{b \hbar^2}{2m} + a \frac{1}{2b} \right) \\
&= \frac{\hbar^2}{2m} - \frac{a}{2} \frac{1}{2} b^{-\frac{3}{2}}
\end{aligned}$$

$$\text{So, } \frac{a}{2} \frac{1}{2} b^{-\frac{3}{2}} = \frac{\hbar^2}{2m} \text{ or, } b^{-\frac{3}{2}} = \frac{\hbar^2}{2m} \frac{2}{a} \frac{1}{2} b^{-\frac{1}{2}} = \frac{\hbar^2}{ma} \sqrt{2} ,$$

and, $b = \frac{ma}{\sqrt{2} \hbar^2}^{\frac{2}{3}}$. Substituting this value of b into the expression for W gives:

$$\begin{aligned}
 W &= \frac{\hbar^2}{2m} \frac{ma}{\sqrt{2} \hbar^2}^{\frac{2}{3}} + a \frac{1}{2} \frac{1}{2} \frac{ma}{\sqrt{2} \hbar^2}^{-\frac{1}{3}} \\
 &= \frac{\hbar^2}{2m} \frac{ma}{\sqrt{2} \hbar^2}^{\frac{2}{3}} + a \frac{1}{2} \frac{1}{2} \frac{ma}{\sqrt{2} \hbar^2}^{-\frac{1}{3}} \\
 &= 2^{-\frac{4}{3}} \frac{1}{\hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{\frac{1}{3}}} + 2^{-\frac{1}{3}} \frac{1}{\hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{\frac{1}{3}}} \\
 &= 2^{-\frac{4}{3}} \frac{1}{\hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{\frac{1}{3}}} + 2^{-\frac{1}{3}} \frac{1}{\hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{\frac{1}{3}}} = \frac{3}{2} (2)^{-\frac{1}{3}} \frac{1}{\hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{\frac{1}{3}}} \\
 &= 0.812889106 \hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{-1/3} \text{ which is in error by only } 0.5284\% \text{ !!!!}
 \end{aligned}$$

17.

a.
$$\mathbf{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$$

$$= \sqrt{\frac{15}{16}} a^{-\frac{5}{2}} (a^2 - x^2) \quad \text{for } -a < x < a$$

$$= 0 \quad \text{for } |x| > a$$

+
***H** dx
-

$$\begin{aligned}
& +a \\
= & \sqrt{\frac{15}{16}} a^{-\frac{5}{2}} (a^2 - x^2) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right] \sqrt{\frac{15}{16}} a^{-\frac{5}{2}} (a^2 - x^2) dx \\
& -a \\
& +a \\
= & \frac{15}{16} a^{-5} (a^2 - x^2) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right] (a^2 - x^2) dx \\
& -a \\
& +a \\
= & \frac{15}{16} a^{-5} (a^2 - x^2) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} (a^2 - x^2) \right] dx \\
& -a \\
& +a \\
& + \frac{15}{16} a^{-5} (a^2 - x^2) \frac{1}{2} kx^2 (a^2 - x^2) dx \\
& -a \\
& +a \\
= & \frac{15}{16} a^{-5} (a^2 - x^2) \left[-\frac{\hbar^2}{2m} (-2) \right] dx \\
& -a \\
& +a \\
& + \frac{15}{32} a^{-5} (kx^2)(a^4 - 2a^2x^2 + x^4) dx \\
& -a \\
= & \frac{15\hbar^2}{16m} a^{-5} (a^2 - x^2) dx + \frac{15}{32} a^{-5} (a^4 kx^2 - 2a^2 kx^4 + kx^6) dx \\
& -a \qquad \qquad \qquad -a \\
= & \frac{15\hbar^2}{16m} a^{-5} a^2 x^a - \frac{1}{3} x^3 \frac{a}{-a} \\
& + \frac{15}{32} a^{-5} \frac{a^4 k}{3} x^3 \frac{a}{-a} - \frac{2a^2 k}{5} x^5 \frac{a}{-a} + \frac{k}{7} x^7 \frac{a}{-a} \\
= & \frac{15\hbar^2}{16m} a^{-5} 2a^3 - \frac{2}{3} a^3 + \frac{15}{32} a^{-5} \frac{2a^7 k}{3} - \frac{4a^7 k}{5} + \frac{2k}{7} a^7
\end{aligned}$$

$$\begin{aligned}
&= \frac{15}{16} a^{-5} \frac{4\hbar^2}{3m} a^3 + \frac{a^7 k}{3} - \frac{2a^7 k}{5} + \frac{k}{7} a^7 \\
&= \frac{15}{16} a^{-5} \frac{4\hbar^2}{3m} a^3 + \frac{k}{3} - \frac{2k}{5} + \frac{k}{7} a^7 \\
&= \frac{15}{16} a^{-5} \frac{4\hbar^2}{3m} a^3 + \frac{35k}{105} - \frac{42k}{105} + \frac{15k}{105} a^7 \\
&= \frac{15}{16} a^{-5} \frac{4\hbar^2}{3m} a^3 + \frac{8k}{105} a^7 = \frac{5\hbar^2}{4ma^2} + \frac{ka^2}{14}
\end{aligned}$$

b. Substituting $a = b \frac{\hbar^2}{km}^{\frac{1}{4}}$ into the above expression for E we obtain:

$$\begin{aligned}
E &= \frac{5\hbar^2}{4b^2m} \frac{km}{\hbar^2}^{\frac{1}{2}} + \frac{kb^2}{14} \frac{\hbar^2}{km}^{\frac{1}{2}} \\
&= \hbar^{\frac{1}{2}} k^{\frac{1}{2}} m^{-\frac{1}{2}} \frac{5}{4} b^{-2} + \frac{1}{14} b^2
\end{aligned}$$

c.
$$E = \frac{5\hbar^2}{4ma^2} + \frac{ka^2}{14}$$

$$\frac{dE}{da} = -\frac{10\hbar^2}{4ma^3} + \frac{2ka}{14} = -\frac{5\hbar^2}{2ma^3} + \frac{ka}{7} = 0$$

$$\frac{5\hbar^2}{2ma^3} = \frac{ka}{7} \text{ and } 35\hbar^2 = 2mka^4$$

$$\text{So, } a^4 = \frac{35\hbar^2}{2mk}, \text{ or } a = \frac{35\hbar^2}{2mk}^{\frac{1}{4}}$$

$$\text{Therefore } \text{best} = \sqrt[4]{\frac{15}{16} \frac{35\hbar^2}{2mk}^{-\frac{5}{8}} \frac{35\hbar^2}{2mk}^{\frac{1}{2}} - x^2},$$

$$\text{and } E_{\text{best}} = \frac{5\hbar^2}{4m} \frac{2mk}{35\hbar^2} \frac{1}{2} + \frac{k}{14} \frac{35\hbar^2}{2mk} \frac{1}{2} = \hbar^2 k^2 m^{-2} \frac{5}{14} \frac{1}{2} .$$

$$\begin{aligned} \text{d. } \frac{E_{\text{best}} - E_{\text{true}}}{E_{\text{true}}} &= \frac{\hbar^2 k^2 m^{-2} \frac{5}{14} \frac{1}{2} - 0.5}{\hbar^2 k^2 m^{-2} 0.5} \\ &= \frac{\frac{5}{14} \frac{1}{2} - 0.5}{0.5} = \frac{0.0976}{0.5} = 0.1952 = 19.52\% \end{aligned}$$

18.

$$\begin{aligned} \text{a. } \mathbf{H}_0 \quad \frac{(0)}{lm} &= \frac{\mathbf{L}^2}{2m_e r_0^2} \quad \frac{(0)}{lm} = \frac{\mathbf{L}^2}{2m_e r_0^2} Y_{1,m}(\theta, \phi) \\ &= \frac{1}{2m_e r_0^2} \hbar^2 l(l+1) Y_{1,m}(\theta, \phi) \end{aligned}$$

$$E_{lm}^{(0)} = \frac{\hbar^2}{2m_e r_0^2} l(l+1)$$

$$\text{b. } V = -e z = -e r_0 \cos \theta$$

$$\begin{aligned} E_{00}^{(1)} &= \langle Y_{00} | V | Y_{00} \rangle = \langle Y_{00} | -e r_0 \cos \theta | Y_{00} \rangle \\ &= -e r_0 \langle Y_{00} | \cos \theta | Y_{00} \rangle \end{aligned}$$

Using the given identity this becomes:

$$\begin{aligned} E_{00}^{(1)} &= -e r_0 \langle Y_{00} | Y_{10} \rangle \sqrt{\frac{(0+0+1)(0-0+1)}{(2(0)+1)(2(0)+3)}} + \\ &\quad -e r_0 \langle Y_{00} | Y_{-10} \rangle \sqrt{\frac{(0+0)(0-0)}{(2(0)+1)(2(0)-1)}} \end{aligned}$$

The spherical harmonics are orthonormal, thus $\langle Y_{00}|Y_{10}\rangle = \langle Y_{00}|Y_{-10}\rangle = 0$, and

$$E_{00}^{(1)} = 0.$$

$$E_{00}^{(2)} = \sum_{lm} \frac{\langle Y_{lm}|V|Y_{00}\rangle^2}{E_{00}^{(0)} - E_{lm}^{(0)}}$$

$$\langle Y_{lm}|V|Y_{00}\rangle = -e r_0 \langle Y_{lm}|\cos\theta|Y_{00}\rangle$$

Using the given identity this becomes:

$$\begin{aligned} \langle Y_{lm}|V|Y_{00}\rangle &= -e r_0 \langle Y_{lm}|Y_{10}\rangle \sqrt{\frac{(0+0+1)(0-0+1)}{(2(0)+1)(2(0)+3)}} + \\ &\quad -e r_0 \langle Y_{lm}|Y_{-10}\rangle \sqrt{\frac{(0+0)(0-0)}{(2(0)+1)(2(0)-1)}} \end{aligned}$$

$$\langle Y_{lm}|V|Y_{00}\rangle = -\frac{e r_0}{\sqrt{3}} \langle Y_{lm}|Y_{10}\rangle$$

This indicates that the only term contributing to the sum in the expression for $E_{00}^{(2)}$ is when $l=1$, and $m=0$, otherwise $\langle Y_{lm}|V|Y_{00}\rangle$ vanishes (from orthonormality). In quantum chemistry when using orthonormal functions it is typical to write the term $\langle Y_{lm}|Y_{10}\rangle$ 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,

$$\langle Y_{lm}|V|Y_{00}\rangle = -\frac{e r_0}{\sqrt{3}} \delta_{lm,10}, \quad \text{so}$$

$$E_{00}^{(2)} = \sum_{lm} \frac{e^2 r_0^2}{3} \frac{\delta_{lm,10}^2}{E_{00}^{(0)} - E_{lm}^{(0)}} = \frac{e^2 r_0^2}{3} \frac{1}{E_{00}^{(0)} - E_{10}^{(0)}}$$

$$E_{00}^{(0)} = \frac{\hbar^2}{2m_e r_0^2} 0(0+1) = 0 \text{ and } E_{10}^{(0)} = \frac{\hbar^2}{2m_e r_0^2} 1(1+1) = \frac{\hbar^2}{m_e r_0^2}$$

Inserting these energy expressions above yields:

$$E_{00}^{(2)} = -\frac{e^2}{3} \frac{2r_0^2}{\hbar^2} \frac{m_e r_0^2}{\hbar^2} = -\frac{m_e e^2}{3\hbar^2} 2r_0^4$$

$$c. \quad E_{00} = E_{00}^{(0)} + E_{00}^{(1)} + E_{00}^{(2)} + \dots$$

$$= 0 + 0 - \frac{m_e e^2}{3\hbar^2} 2r_0^4$$

$$= -\frac{m_e e^2}{3\hbar^2} 2r_0^4$$

$$= -\frac{2E}{2} = \frac{2}{2} \frac{m_e e^2}{3\hbar^2} 2r_0^4$$

$$= \frac{2m_e e^2 r_0^4}{3\hbar^2}$$

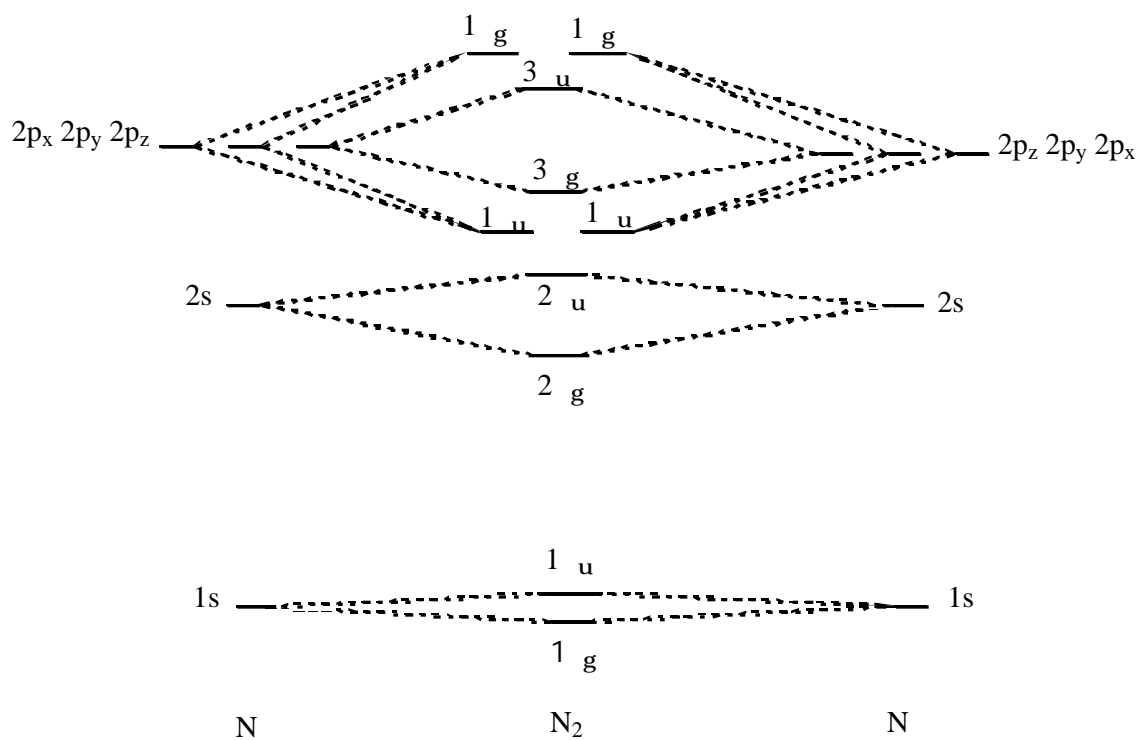
$$d. \quad = \frac{2(9.1095 \times 10^{-28} \text{g})(4.80324 \times 10^{-10} \text{g}^{\frac{1}{2}} \text{cm}^{\frac{3}{2}} \text{s}^{-1})^2 r_0^4}{3(1.05459 \times 10^{-27} \text{g cm}^2 \text{s}^{-1})^2}$$

$$= r_0^4 12598 \times 10^6 \text{cm}^{-1} = r_0^4 1.2598 \text{\AA}^{-1}$$

$$H = 0.0987 \text{\AA}^3$$

$$C_s = 57.57 \text{\AA}^3$$

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 3 g , 3 u , 1 u_x , 1 u_y , 1 g_x , and 1 g_y SALC-AOs. The Hamiltonian matrices (Fock matrices) are given. Each of these can be diagonalized to give the following MO energies:

3 g ; -15.52, -1.45, and -0.54 (hartrees)

3 u ; -15.52, -0.72, and 1.13

1 u_x ; -0.58

1 u_y ; -0.58

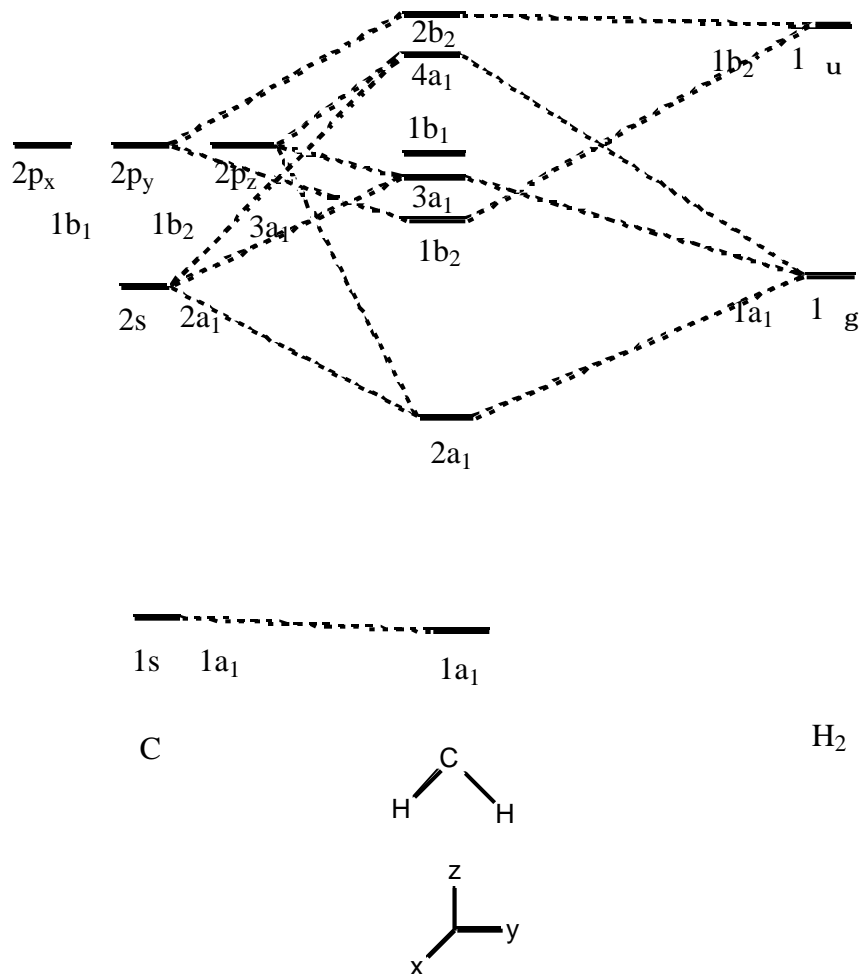
1 g_x ; 0.28

1 g_y ; 0.28

It can be seen that the 3_g orbitals are bonding, the 3_u orbitals are antibonding, the 1_{ux} and 1_{uy} orbitals are bonding, and the 1_{gx} and 1_{gy} orbitals are antibonding.

20.

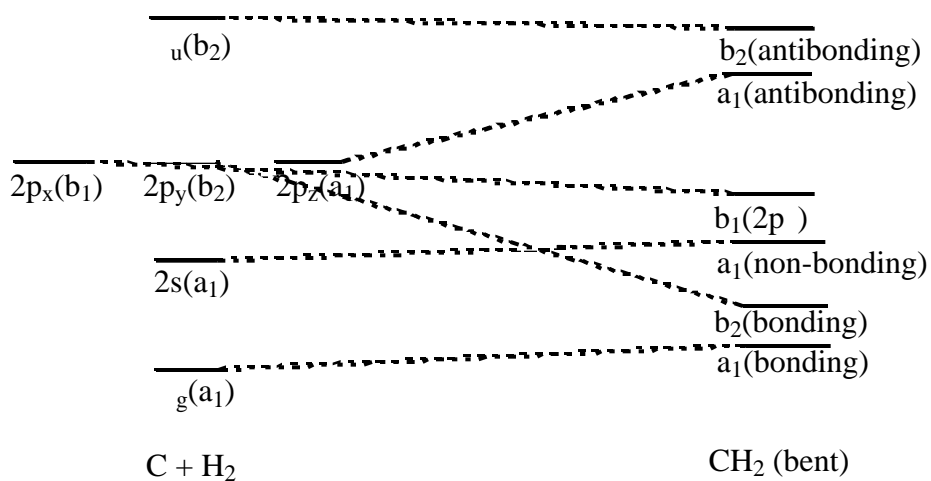
Using these approximate energies we can draw the following MO diagram:



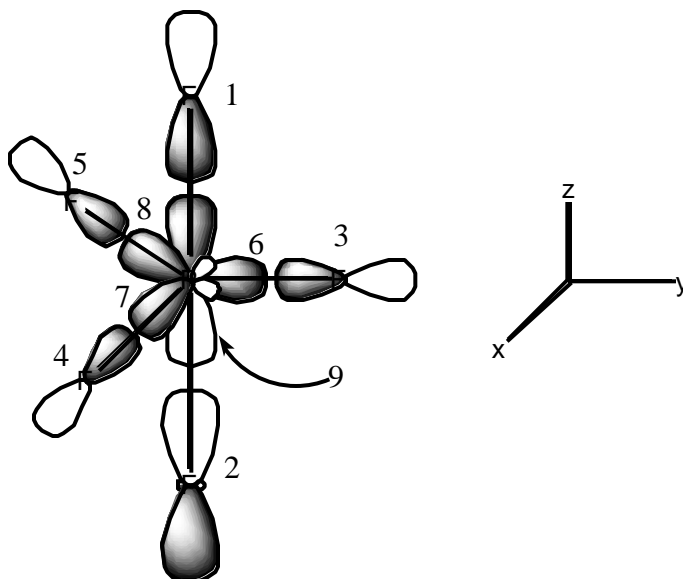
This MO diagram is not an orbital correlation diagram but can be used to help generate

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.

Orbital-correlation diagram for the reaction $C + H_2 \rightarrow CH_2$ (bent)



21.



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

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
χ	2	2	0	0	0	2

This reducible representation reduces to $1A_1'$ and $1A_2''$ irreducible representations.

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

$$a_1' = \frac{1}{\sqrt{2}}(f_1 - f_2)$$

$$a_2'' = \frac{1}{\sqrt{2}}(f_1 + f_2)$$

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

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
χ	3	0	1	3	0	1

This reducible representation reduces to $1A_1'$ 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):

$$a_1' = \frac{1}{\sqrt{3}}(f_3 + f_4 + f_5)$$

$$e' = (1/6)^{-1/2} (2 f_3 - f_4 - f_5)$$

$$e' = \frac{1}{\sqrt{2}}(f_4 - f_5) .$$

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

D _{3h}	E	2C ₃	3C ₂	h	2S ₃	3	v
sp ²	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:

$$a_1' = \frac{1}{\sqrt{3}}(f_6 + f_7 + f_8)$$

$$e' = \frac{1}{\sqrt{6}}(2f_6 - f_7 - f_8)$$

$$e' = \frac{1}{\sqrt{2}}(f_7 - f_8) .$$

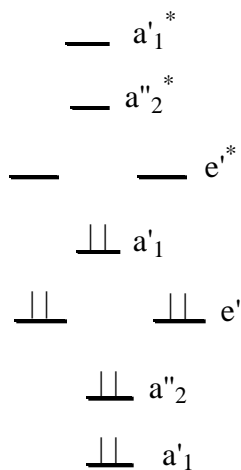
The leftover P p_z orbital generate the following irreducible representation:

D _{3h}	E	2C ₃	3C ₂	h	2S ₃	3	v
p _z	1	1	-1	-1	-1	1	

This irreducible representation is A₂'

$$a_2'' = f_9.$$

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):

$$a_1 \quad b_1 = b_1$$

Constructing a "box" in this case is unnecessary since it would only contain a single row.

Two unpaired electrons will result in a singlet ($S=0, M_S=0$), and three triplets ($S=1, M_S=1; S=1, M_S=0; S=1, M_S=-1$). The states will be: ${}^3B_1(M_S=1), {}^3B_1(M_S=0), {}^3B_1(M_S=-1)$, and ${}^1B_1(M_S=0)$.

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

($1\ u^1 2\ u^1$), we have M_L values of 1+1, 1-1, -1+1, and -1-1 (2, 0, 0, and -2). The term symbol 1D is used to denote the spatially doubly degenerate level ($M_L=\pm 2$) and there are two distinct spatially non-degenerate levels denoted by the term symbol 1D ($M_L=0$). Again, two unpaired electrons will result in a singlet ($S=0, M_S=0$), and three triplets ($S=1, M_S=1; S=1, M_S=0; S=1, M_S=-1$). The states generated are then:

- 1D ($M_L=2$); one state ($M_S=0$),
- 1D ($M_L=-2$); one state ($M_S=0$),
- 3D ($M_L=2$); three states ($M_S=1, 0$, and -1),
- 3D ($M_L=-2$); three states ($M_S=1, 0$, and -1),
- 1D ($M_L=0$); one state ($M_S=0$),
- 1D ($M_L=0$); one state ($M_S=0$),
- 3D ($M_L=0$); three states ($M_S=1, 0$, and -1), and
- 3D ($M_L=0$); three states ($M_S=1, 0$, and -1).

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

M_L	2	1	0
M_S			
1			1 -1
0	1 1		1 -1 , -1 1

From this "box" one obtains six states:

- $^1 (M_L=2)$; one state ($M_S=0$),
- $^1 (M_L=-2)$; one state ($M_S=0$),
- $^1 (M_L=0)$; one state ($M_S=0$),
- $^3 (M_L=0)$; three states ($M_S=1, 0, \text{ and } -1$).

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:

- 3G_5 (11 states),
- 3G_4 (9 states),
- 3G_3 (7 states),
- 1G_4 (9 states),
- 3F_4 (9 states),
- 3F_3 (7 states),
- 3F_2 (5 states),
- 1F_3 (7 states),
- 3D_3 (7 states),

3D_2 (5 states),
 3D_1 (3 states),
 1D_2 (5 states),
 3P_2 (5 states),
 3P_1 (3 states),
 3P_0 (1 state),
 1P_1 (3 states),
 3S_1 (3 states), and
 1S_0 (1 state).

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

M_S	1	0
4		$ d_2 d_2 $
3	$ d_2 d_1 $	$ d_2 d_1 ,$ $ d_2 d_1 $
2	$ d_2 d_0 $	$ d_2 d_0 ,$ $ d_2 d_0 ,$ $ d_1 d_1 $
1	$ d_1 d_0 ,$ $ d_2 d_{-1} $	$ d_1 d_0 ,$ $ d_1 d_0 ,$ $ d_2 d_{-1} ,$ $ d_2 d_{-1} $

$$0 \quad \left| \begin{array}{cc} |d_2 d_{-2} \rangle, & |d_1 d_{-1} \rangle \\ & |d_2 d_{-2} \rangle, & |d_2 d_{-2} \rangle, \\ & |d_1 d_{-1} \rangle, & |d_1 d_{-1} \rangle, \\ & |d_0 d_0 \rangle & \end{array} \right|$$

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:

1G_4 (9 states),

3F_4 (9 states),

3F_3 (7 states),

3F_2 (5 states),

1D_2 (5 states),

3P_2 (5 states),

3P_1 (3 states),

3P_0 (1 state), and

1S_0 (1 state).

23.

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

$$\frac{1}{\sqrt{2}}(|3a_1 \ 1b_1 \rangle - |3a_1 \ 1b_1 \rangle)$$

b. There are three states here :

$$1.) |3a_1 \ 1b_1 \ |,$$

$$2.) \frac{1}{\sqrt{2}}(|3a_1 \ 1b_1 \ | + |3a_1 \ 1b_1 \ |), \text{ and}$$

$$3.) |3a_1 \ 1b_1 \ |$$

$$c. |3a_1 \ 3a_1 \ |$$

24.

a. All the Slater determinants have in common the $|1s \ 1s \ 2s \ 2s \ |$ "core" and hence this component will not be written out explicitly for each case.

$$\begin{aligned} {}^3P(M_L=1, M_S=1) &= |p_1 \ p_0 \ | \\ &= \left| \frac{1}{\sqrt{2}}(p_x + ip_y) \ (p_z) \ | \\ &= \frac{1}{\sqrt{2}}(|p_x \ p_z \ | + i|p_y \ p_z \ |) \end{aligned}$$

$$\begin{aligned} {}^3P(M_L=0, M_S=1) &= |p_1 \ p_{-1} \ | \\ &= \left| \frac{1}{\sqrt{2}}(p_x + ip_y) \ \frac{1}{\sqrt{2}}(p_x - ip_y) \ | \\ &= \frac{1}{2}(|p_x \ p_x \ | - i|p_x \ p_y \ | + i|p_y \ p_x \ | + |p_y \ p_y \ |) \\ &= \frac{1}{2}(0 - i|p_x \ p_y \ | - i|p_x \ p_y \ | + 0) \\ &= \frac{1}{2}(-2i|p_x \ p_y \ |) \\ &= -i|p_x \ p_y \ | \end{aligned}$$

$$\begin{aligned}
{}^3P(M_L=-1, M_S=1) &= |p_{-1} p_0 \rangle \\
&= \frac{1}{\sqrt{2}}(p_x - ip_y) (p_z) \rangle \\
&= \frac{1}{\sqrt{2}}(|p_x p_z \rangle - i|p_y p_z \rangle)
\end{aligned}$$

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, $|p_x p_z \rangle$ is xz (B_1) and $|p_y p_z \rangle$ is yz (B_2) and hence the ${}^3P(M_L=1, M_S=1)$ state is a combination of B_1 and B_2 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.

$$\begin{aligned}
{}^3P(xz, M_S=1) &= |p_x p_z \rangle \\
&= \frac{1}{\sqrt{2}}({}^3P(M_L=1, M_S=1) + {}^3P(M_L=-1, M_S=1)) = {}^3B_1
\end{aligned}$$

$$\begin{aligned}
{}^3P(yx, M_S=1) &= |p_y p_x \rangle \\
&= \frac{1}{i}({}^3P(M_L=0, M_S=1)) = {}^3A_2
\end{aligned}$$

$$\begin{aligned}
{}^3P(yz, M_S=1) &= |p_y p_z \rangle \\
&= \frac{1}{i\sqrt{2}}({}^3P(M_L=1, M_S=1) - {}^3P(M_L=-1, M_S=1)) = {}^3B_2
\end{aligned}$$

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

$$\begin{aligned}
{}^1D(M_L=2, M_S=0) &= |p_1 p_1 \rangle \\
&= \frac{1}{\sqrt{2}}(p_x + ip_y) \frac{1}{\sqrt{2}}(p_x + ip_y) \rangle
\end{aligned}$$

$$= \frac{1}{2}(|p_x p_x \rangle + i|p_x p_y \rangle + i|p_y p_x \rangle - |p_y p_y \rangle)$$

$$\begin{aligned} {}^1D(M_L=-2, M_S=0) &= |p_{-1} p_{-1} \rangle \\ &= \left| \frac{1}{\sqrt{2}}(p_x - ip_y) \right. \left. \frac{1}{\sqrt{2}}(p_x - ip_y) \right| \end{aligned}$$

$$= \frac{1}{2}(|p_x p_x \rangle - i|p_x p_y \rangle - i|p_y p_x \rangle - |p_y p_y \rangle)$$

$$\begin{aligned} {}^1D(M_L=1, M_S=0) &= \frac{1}{\sqrt{2}}(|p_0 p_1 \rangle - |p_0 p_{-1} \rangle) \\ &= \frac{1}{\sqrt{2}} \left| (p_z) \right. \left. \frac{1}{\sqrt{2}}(p_x + ip_y) \right| - \left| (p_z) \right. \left. \frac{1}{\sqrt{2}}(p_x + ip_y) \right| \end{aligned}$$

$$= \frac{1}{2}(|p_z p_x \rangle + i|p_z p_y \rangle - |p_z p_x \rangle - i|p_z p_y \rangle)$$

$$\begin{aligned} {}^1D(M_L=-1, M_S=0) &= \frac{1}{\sqrt{2}}(|p_0 p_{-1} \rangle - |p_0 p_1 \rangle) \\ &= \frac{1}{\sqrt{2}} \left| (p_z) \right. \left. \frac{1}{\sqrt{2}}(p_x - ip_y) \right| - \left| (p_z) \right. \left. \frac{1}{\sqrt{2}}(p_x - ip_y) \right| \end{aligned}$$

$$= \frac{1}{2}(|p_z p_x \rangle - i|p_z p_y \rangle - |p_z p_x \rangle + i|p_z p_y \rangle)$$

$$\begin{aligned} {}^1D(M_L=0, M_S=0) &= \frac{1}{\sqrt{6}}(2|p_0 p_0 \rangle + |p_1 p_{-1} \rangle + |p_{-1} p_1 \rangle) \\ &= \frac{1}{\sqrt{6}}(2|p_z p_z \rangle + \left| \frac{1}{\sqrt{2}}(p_x + ip_y) \right. \left. \frac{1}{\sqrt{2}}(p_x - ip_y) \right| \end{aligned}$$

$$+ \left| \frac{1}{\sqrt{2}}(p_x - ip_y) \right. \left. \frac{1}{\sqrt{2}}(p_x + ip_y) \right|)$$

$$= \frac{1}{\sqrt{6}}(2|p_z p_z \rangle$$

$$\begin{aligned}
& + \frac{1}{2} (|p_x p_x\rangle - i |p_x p_y\rangle + i |p_y p_x\rangle + |p_y p_y\rangle) \\
& + \frac{1}{2} (|p_x p_x\rangle + i |p_x p_y\rangle - i |p_y p_x\rangle + |p_y p_y\rangle) \\
& = \frac{1}{\sqrt{6}} (2 |p_z p_z\rangle + |p_x p_x\rangle + |p_y p_y\rangle)
\end{aligned}$$

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:

$$\begin{aligned}
^1D(x^2-y^2, M_S=0) &= |p_x p_x\rangle - |p_y p_y\rangle \\
&= (^1D(M_L=2, M_S=0) + ^1D(M_L=-2, M_S=0)) = ^1A_1
\end{aligned}$$

$$\begin{aligned}
^1D(yx, M_S=0) &= |p_x p_y\rangle + |p_y p_x\rangle \\
&= \frac{1}{i} (^1D(M_L=2, M_S=0) - ^1D(M_L=-2, M_S=0)) = ^1A_2
\end{aligned}$$

$$\begin{aligned}
^1D(zx, M_S=0) &= |p_z p_x\rangle - |p_x p_z\rangle \\
&= (^1D(M_L=1, M_S=0) + ^1D(M_L=-1, M_S=0)) = ^1B_1
\end{aligned}$$

$$\begin{aligned}
^1D(zy, M_S=0) &= |p_z p_y\rangle - |p_y p_z\rangle \\
&= \frac{1}{i} (^1D(M_L=1, M_S=0) - ^1D(M_L=-1, M_S=0)) = ^1B_2
\end{aligned}$$

$$\begin{aligned}
^1D(2z^2-x^2-y^2, M_S=0) &= \frac{1}{\sqrt{6}} (2 |p_z p_z\rangle + |p_x p_x\rangle + |p_y p_y\rangle) \\
&= ^1D(M_L=0, M_S=0) = ^1A_1
\end{aligned}$$

The only state left is the 1S :

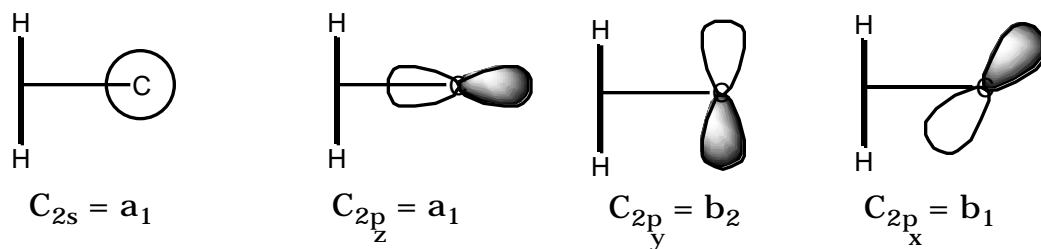
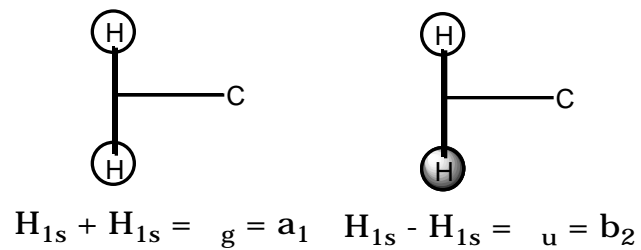
$$^1S(M_L=0, M_S=0) = \frac{1}{\sqrt{3}} (|p_0 p_0\rangle - |p_1 p_{-1}\rangle - |p_{-1} p_1\rangle)$$

$$\begin{aligned}
&= \frac{1}{\sqrt{3}} \left(|p_z \ p_z \rangle - \frac{1}{\sqrt{2}} (|p_x + ip_y \rangle - \frac{1}{\sqrt{2}} (|p_x - ip_y \rangle - \right. \\
&\quad \left. - \frac{1}{\sqrt{2}} (|p_x - ip_y \rangle - \frac{1}{\sqrt{2}} (|p_x + ip_y \rangle \right)) \\
&= \frac{1}{\sqrt{3}} \left(|p_z \ p_z \rangle - \frac{1}{2} (|p_x \ p_x \rangle - i|p_x \ p_y \rangle + i|p_y \ p_x \rangle + |p_y \ p_y \rangle) \right. \\
&\quad \left. - \frac{1}{2} (|p_x \ p_x \rangle + i|p_x \ p_y \rangle - i|p_y \ p_x \rangle + |p_y \ p_y \rangle) \right) \\
&= \frac{1}{\sqrt{3}} (|p_z \ p_z \rangle - |p_x \ p_x \rangle - |p_y \ p_y \rangle)
\end{aligned}$$

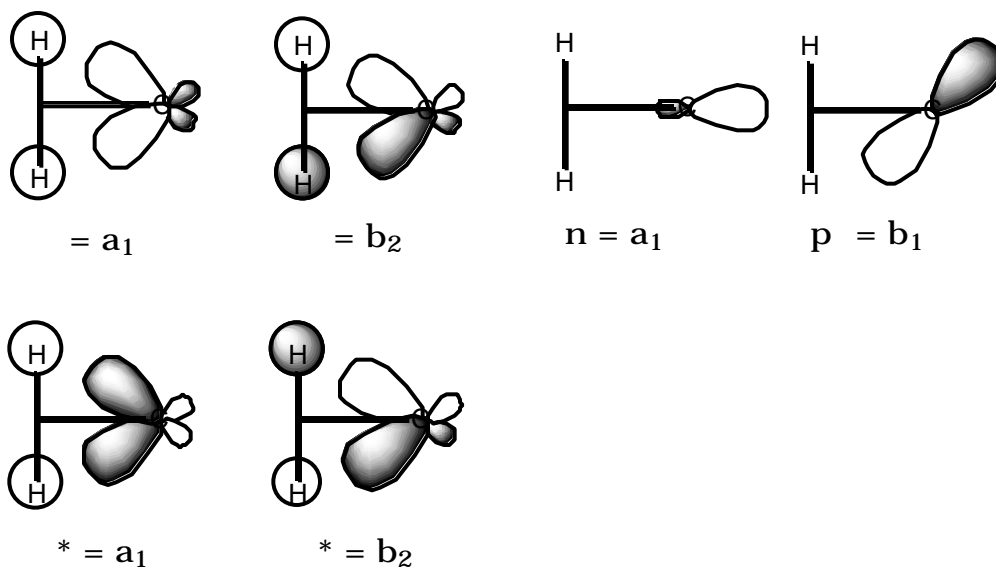
Each of the components of this state are A_1 and hence this state has

A_1 symmetry.

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

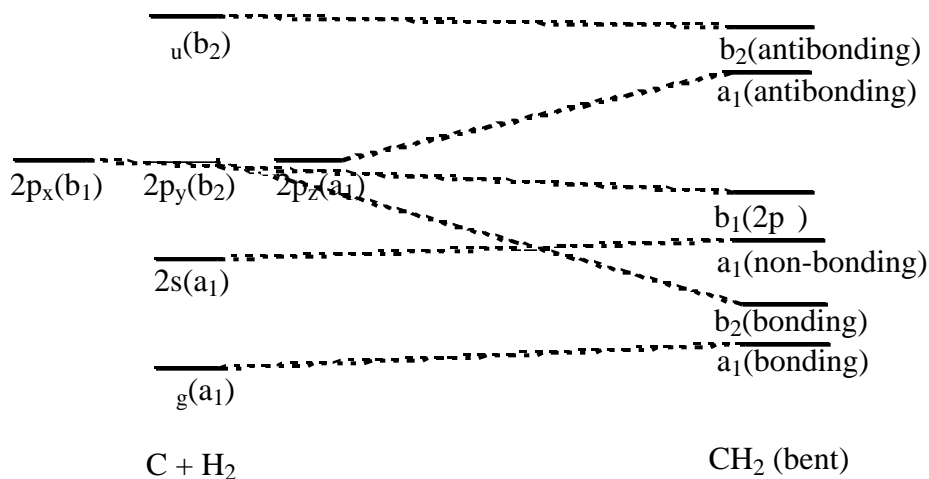


The bonding, nonbonding, and antibonding orbitals of CH_2 can be illustrated in the following manner:



c.

Orbital-correlation diagram for the reaction $C + H_2 \rightarrow CH_2$ (bent)



d. - e. It is necessary to determine how the wavefunctions found in part a.

correlate with states of the CH_2 molecule:

$${}^3P(xz, M_S=1); {}^3B_1 = g^2s^2p_xp_z \quad 2n^2p \quad *$$

$${}^3P(yx, M_S=1); {}^3A_2 = g^2s^2p_xp_y \quad 2n^2p$$

$${}^3P(yz, M_S=1); {}^3B_2 = g^2s^2p_y p_z \quad 2n^2 \quad *$$

$${}^1D(xx-yy, M_S=0); {}^1A_1 \quad 2n^2p^2 - 2n^2^2$$

$${}^1D(yx, M_S=0); {}^1A_2 \quad 2n^2 p$$

$${}^1D(zx, M_S=0); {}^1B_1 \quad 2n^2 *p$$

$${}^1D(zy, M_S=0); {}^1B_2 \quad 2n^2 *$$

$${}^1D(2zz+xx+yy, M_S=0); {}^1A_1 \quad 2 \cdot 2n^2 *^2 + 2n^2p^2 + 2n^2^2$$

Note, the $C + H_2$ state to which the lowest ${}^1A_1 (2n^2^2)$ CH_2 state decomposes would be

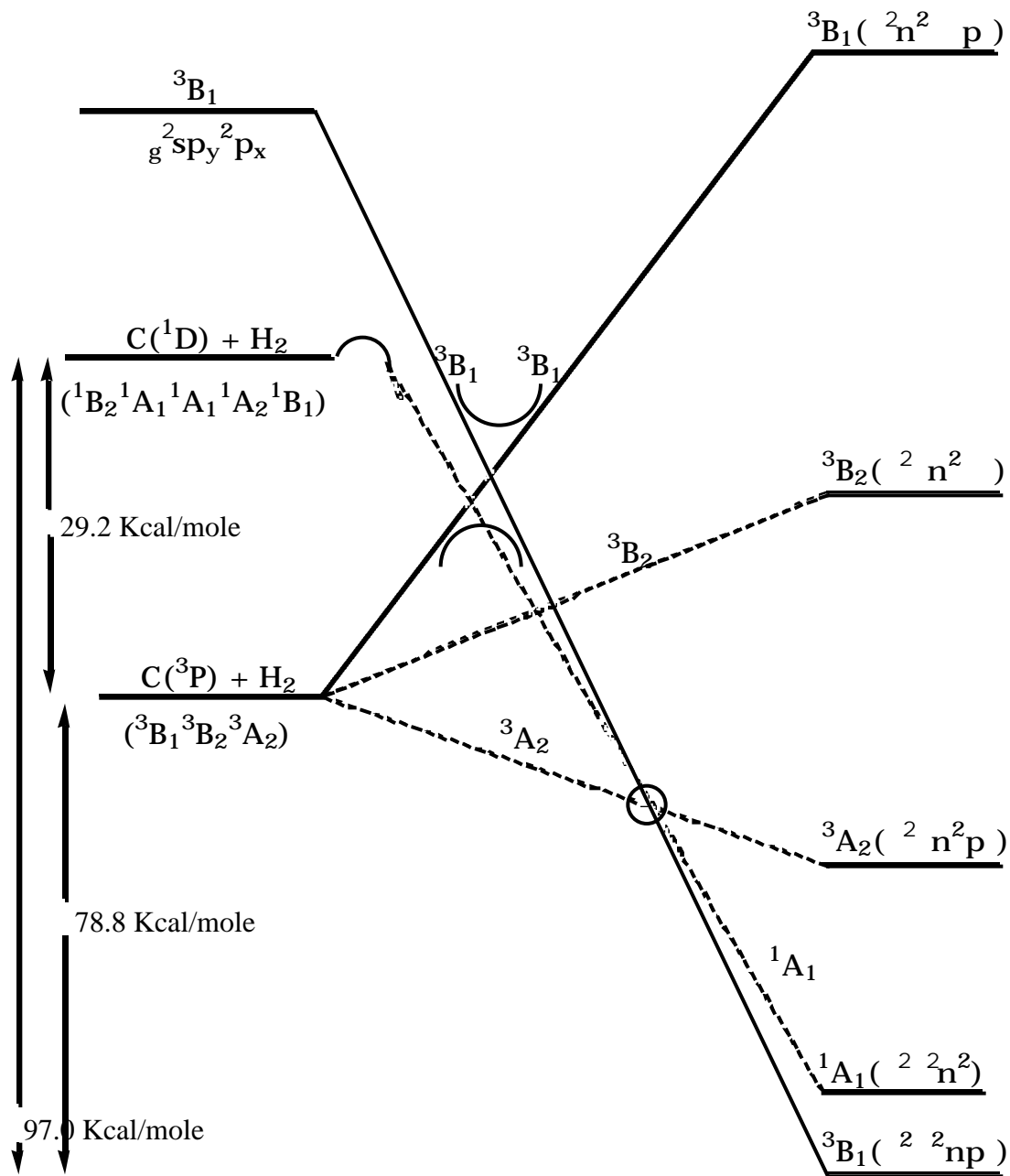
$g^2s^2p_y^2$. This state ($g^2s^2p_y^2$) cannot be obtained by a simple combination of the 1D

states. In order to obtain pure $g^2s^2p_y^2$ it is necessary to combine 1S with 1D . For

example,

$$g^2s^2p_y^2 = \frac{1}{6}(\sqrt{6} \ ^1D(0,0) - 2\sqrt{3} \ ^1S(0,0)) - \frac{1}{2}(\ ^1D(2,0) + \ ^1D(-2,0)) .$$

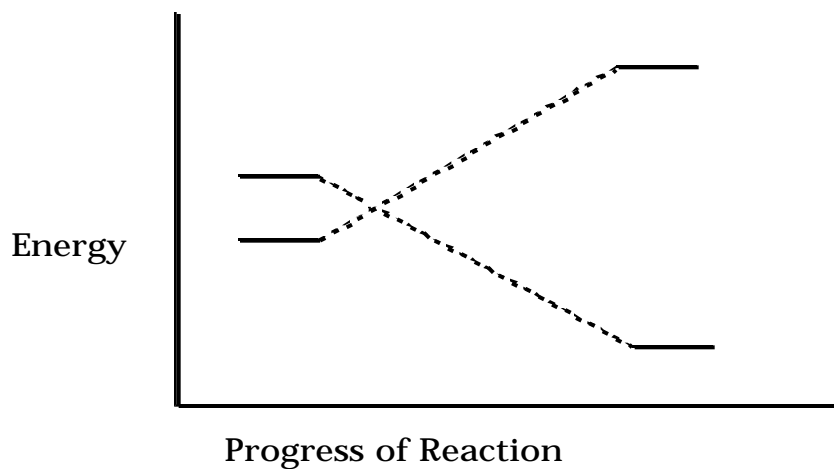
This indicates that a configuration correlation diagram must be drawn with a barrier near the 1D asymptote to represent the fact that 1A_1 CH_2 correlates with a mixture of 1D and 1S carbon plus hydrogen. The $C + H_2$ state to which the lowest 3B_1 ($^2n \ ^2p$) CH_2 state decomposes would be $g^2sp_y^2p_x$.



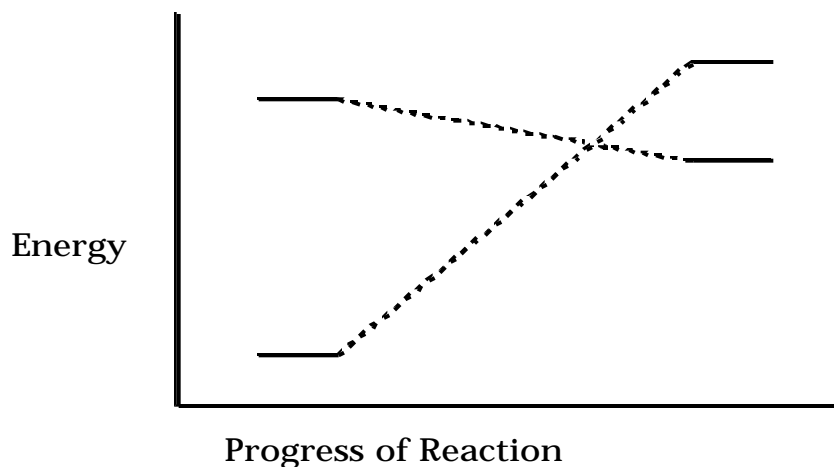
f. If you follow the 3B_1 component of the $C(^3P) + H_2$ (since it leads to the ground-state products) to $^3B_1 CH_2$ you must go over an approximately 20 Kcal/mole barrier. Of course this path produces $^3B_1 CH_2$ product. Distortions away from C_{2v} symmetry, for example to C_s symmetry, would make the a_1 and b_2 orbitals identical in

symmetry (a'). The b_1 orbitals would maintain their different symmetry going to a'' symmetry. Thus 3B_1 and 3A_2 (both ${}^3A''$ in C_s symmetry and odd under reflection through the molecular plane) can mix. The system could thus follow the 3A_2 component of the $C({}^3P) + H_2$ surface to the place (marked with a circle on the CCD) where it crosses the 3B_1 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 $C(^3P_1) + H_2 \rightarrow CH_2$ reaction of interest here has an early barrier.

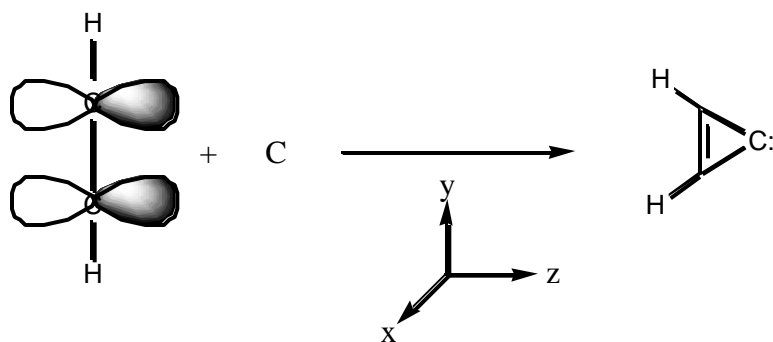
g. The reaction $C(^1D) + H_2 \rightarrow CH_2 (^1A_1)$ should have no symmetry barrier (this can be recognized by following the $^1A_1 (C(^1D) + H_2)$ reactants down to the $^1A_1 (CH_2)$ products).

25.

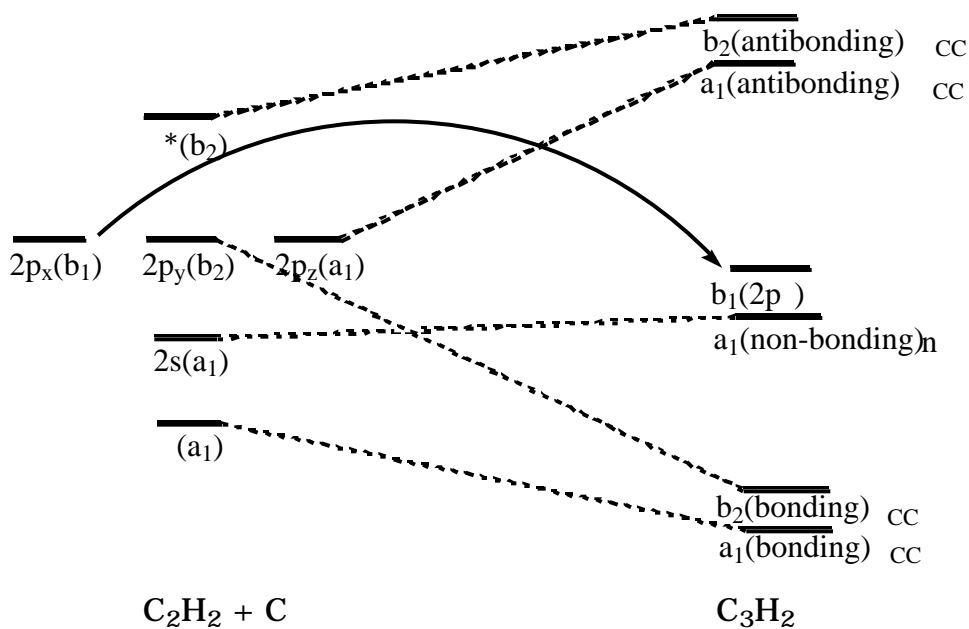
This problem in many respects is analogous to problem 24.

The 3B_1 surface certainly requires a two configuration CI wavefunction; the $^2 \ ^2np_x$ ($^2 p_y^2 sp_x$) and the $^2 n^2 p_x * (^2 s^2 p_x p_z)$. The 1A_1 surface could use the $^2 \ ^2n^2$ ($^2 s^2 p_y^2$) only but once again there is no combination of 1D determinants which gives purely this configuration ($^2 s^2 p_y^2$). Thus mixing of both 1D and 1S determinants are

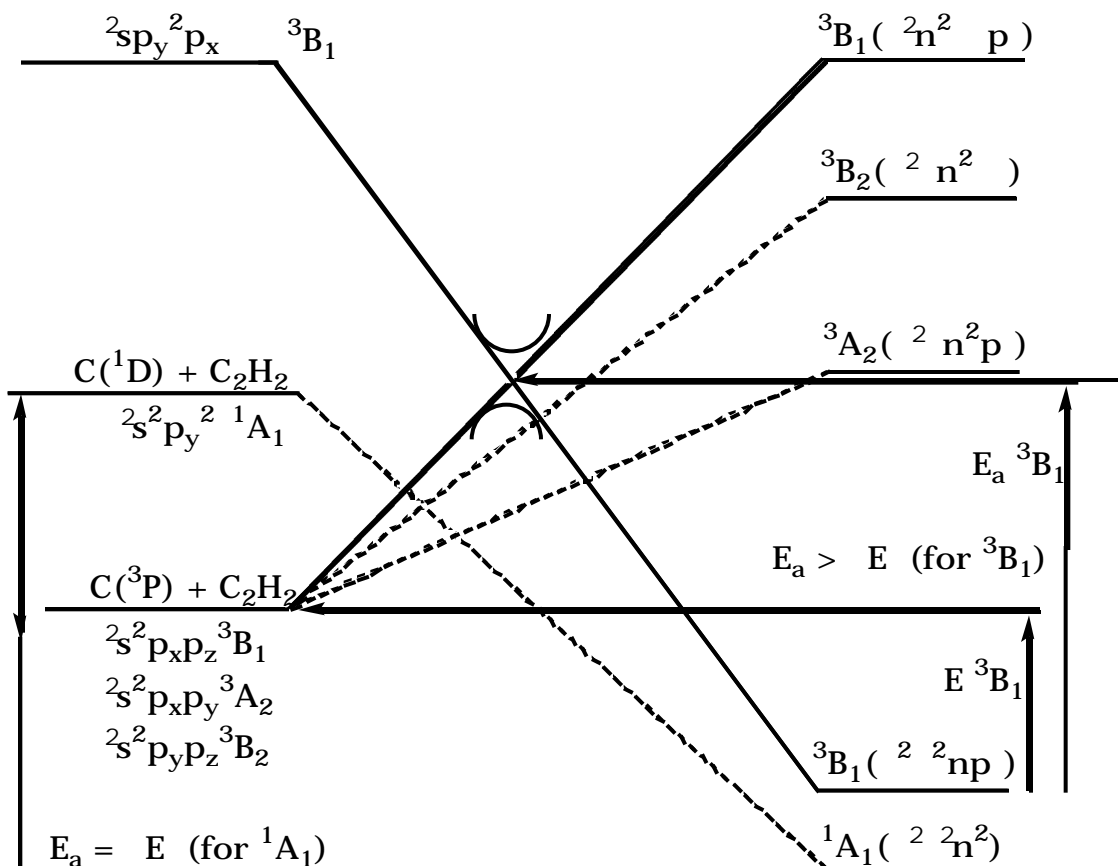
necessary to yield the required $2s^2p_y^2$ configuration. Hence even the 1A_1 surface would require a multiconfigurational wavefunction for adequate description.



Orbital-correlation diagram for the reaction $C_2H_2 + C \rightarrow C_3H_2$



Configuration correlation diagram for the reaction $C_2H_2 + C \rightarrow C_3H_2$.



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.

NH₃ 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 $J = \pm 1$, and the fact that μ_0 lies along the figure axis such that $K = 0$, to give:

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

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. $B_e = 1.78 \text{ cm}^{-1}$.

$$\text{a. } hc\bar{B}_e = \frac{\hbar^2}{2\mu R_e^2}$$

$$R_e = \frac{\hbar}{\sqrt{2\mu hc\bar{B}_e}},$$

$$\mu = \frac{m_B m_O}{m_B + m_O} = \frac{(11)(16)}{(11 + 16)} \times 1.66056 \times 10^{-27} \text{ kg}$$

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

$$hcB_e = hc(1.78 \text{ cm}^{-1}) = 3.5359 \times 10^{-23} \text{ J}$$

$$R_e = \frac{1.05459 \times 10^{-34} \text{ J sec}}{\sqrt{(2)1.0824 \times 10^{-26} \text{ kg} \cdot 3.5359 \times 10^{-23} \text{ J}}}$$

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

$$D_e = \frac{4B_e^3}{\hbar e^2}, D_e = \frac{4B_e^3}{e^2} = \frac{(4)(1.78 \text{ cm}^{-1})^3}{(1885 \text{ cm}^{-1})^2} = 6.35 \times 10^{-6} \text{ cm}^{-1}$$

$$e^{Xe} = \frac{\hbar e^2}{4D_e^0}, e^{Xe} = \frac{e^2}{4D_e^0} = \frac{(1885 \text{ cm}^{-1})^2}{(4)(66782.2 \text{ cm}^{-1})} = 13.30 \text{ cm}^{-1}.$$

$$\begin{aligned} D_0^0 &= D_e^0 - \frac{\hbar e}{2} + \frac{\hbar e^{Xe}}{4}, D_0^0 = D_e^0 - \frac{e}{2} + \frac{e^{Xe}}{4} \\ &= 66782.2 - \frac{1885}{2} + \frac{13.3}{4} \\ &= 65843.0 \text{ cm}^{-1} = 8.16 \text{ eV}. \end{aligned}$$

$$e = \frac{-6B_e^2}{\hbar e} + \frac{6\sqrt{B_e^3 \hbar e^{Xe}}}{\hbar e}$$

$$e = \frac{-6B_e^2}{e} + \frac{6\sqrt{B_e^3 e^{Xe}}}{e}$$

$$e = \frac{(-6)(1.78)^2}{(1885)} + \frac{6\sqrt{(1.78)^3(13.3)}}{(1885)} = 0.0175 \text{ cm}^{-1}.$$

$$\begin{aligned} B_0 &= B_e - e(1/2), B_0 = B_e - e(1/2) = 1.78 - 0.0175/2 \\ &= 1.77 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} B_1 &= B_e - e(3/2), B_1 = B_e - e(3/2) = 1.78 - 0.0175(1.5) \\ &= 1.75 \text{ cm}^{-1} \end{aligned}$$

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 $J = 1 \rightarrow 0$, $J = 2 \rightarrow 1$, $J = 3 \rightarrow 2$

$$E = \hbar \omega_e(v + 1/2) - \hbar \omega_e x_e(v + 1/2)^2 + B_v J(J + 1) - D_e J^2(J + 1)^2$$

$$E = \hbar \omega_e - 2\hbar \omega_e x_e - B_0 J(J + 1) + B_1 J(J - 1) - 4D_e J^3$$

$$E = \omega_e - 2 \omega_e x_e - B_0 J(J + 1) + B_1 J(J - 1) - 4D_e J^3$$

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

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

$$E(J = 1) = 1854.9 \text{ cm}^{-1}$$

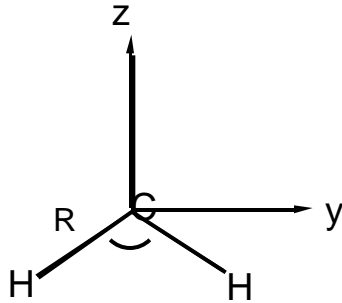
$$E(J = 2) = 1851.3 \text{ cm}^{-1}$$

$$E(J = 3) = 1847.7 \text{ cm}^{-1}$$

29.

The $C_2H_2Cl_2$ molecule has a σ_h plane of symmetry (plane of molecule), a C_2 axis (to the molecular plane), and inversion symmetry, this results in C_{2h} symmetry. Using C_{2h} symmetry, the modes can be labeled as follows: 1, 2, 3, 4, and 5 are a_g , 6 and 7 are a_u , 8 is b_g , and 9, 10, 11, and 12 are b_u .

30.



Molecule I

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

$$\text{HCH} = 104^\circ$$

$$y_H = R \sin(\theta/2) = \pm 0.8834$$

$$z_H = R \cos(\theta/2) = -0.6902$$

Molecule II

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

$$\text{HCH} = 136^\circ$$

$$y_H = \pm 0.9976$$

$$z_H = -0.4031$$

Center of Mass(COM):

clearly, $X = Y = 0$,

$$Z = \frac{12(0) - 2R \cos(\theta/2)}{14} = -0.0986$$

$$Z = -0.0576$$

$$\text{a. } I_{xx} = \sum_j m_j(y_j^2 + z_j^2) - M(Y^2 + Z^2)$$

$$I_{xy} = - \sum_j m_j x_j y_j - MXY$$

$$I_{xx} = 2(1.121)^2 - 14(-0.0986)^2$$

$$= 2.377$$

$$I_{xx} = 2(1.076)^2 - 14(-0.0576)^2$$

$$= 2.269$$

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

$$= 0.8167 \quad = 0.2786$$

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

$$= 1.561 \quad = 1.990$$

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

b. Since the moment of inertia tensor is already diagonal, the principal moments of inertia have already been determined to be

$$(I_a < I_b < I_c):$$

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

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

$$0.8167 < 1.561 < 2.377$$

$$0.2786 < 1.990 < 2.269$$

$$\text{Using the formula: } A = \frac{h}{8 \sqrt{2cI_a}} = \frac{6.626 \times 10^{-27}}{8 \sqrt{2(3 \times 10^{10})I_a}} \times \frac{6.02 \times 10^{23}}{(1 \times 10^{-8})^2}$$

$$A = \frac{16.84}{I_a} \text{ cm}^{-1}$$

$$\text{similarly, } B = \frac{16.84}{I_b} \text{ cm}^{-1}, \text{ and } C = \frac{16.84}{I_c} \text{ cm}^{-1}.$$

So,

Molecule I

Molecule II

$$y \quad A = 20.62$$

$$y \quad A = 60.45$$

$$z \quad B = 10.79$$

$$z \quad B = 8.46$$

$$x \quad C = 7.08$$

$$x \quad C = 7.42$$

c. Averaging B + C:

$$B = (B + C)/2 = 8.94$$

$$B = (B + C)/2 = 7.94$$

$$A - B = 11.68$$

$$A - B = 52.51$$

Using the prolate top formula:

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

Molecule I

$$E = 11.68K^2 + 8.94J(J + 1)$$

Molecule II

$$E = 52.51K^2 + 7.94J(J + 1)$$

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

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

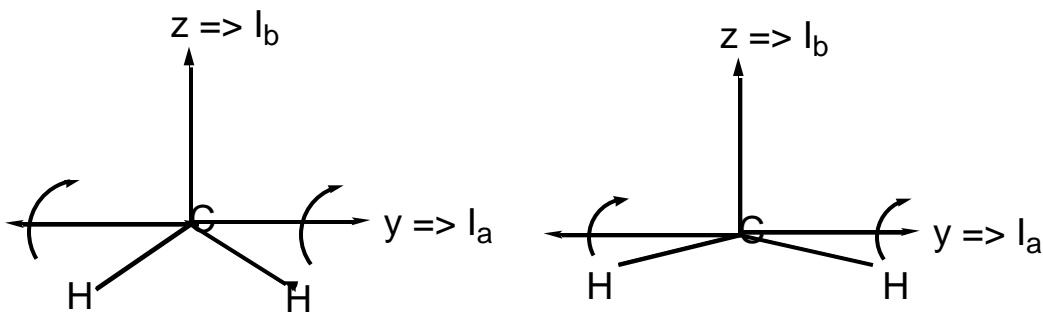
1 for $K = 0$

2 for $K \neq 0$

d.

Molecule I

Molecule II



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

$$E = E_{J_j}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-), \text{ where:}$$

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

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

$$E_R = E_{J_j}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-)$$

$$\begin{aligned}
&= 7.94(J_i + 1)(J_i + 1 + 1) - 8.94J_i(J_i + 1) \\
&= (J_i + 1)\{7.94(J_i + 1 + 1) - 8.94J_i\} \\
&= (J_i + 1)\{(7.94 - 8.94)J_i + 2(7.94)\} \\
&= (J_i + 1)\{-J_i + 15.88\}
\end{aligned}$$

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

$$\begin{aligned}
E_P &= E_{J_j}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-) \\
&= 7.94(J_i - 1)(J_i - 1 + 1) - 8.94J_i(J_i + 1) \\
&= J_i\{7.94(J_i - 1) - 8.94(J_i + 1)\} \\
&= J_i\{(7.94 - 8.94)J_i - 7.94 - 8.94\} \\
&= J_i\{-J_i - 16.88\}
\end{aligned}$$

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 $\frac{d(E_R)}{dJ} = 0$.

$$\begin{aligned}
\frac{d(E_R)}{dJ} &= \frac{d}{dJ} [(J_i + 1)\{-J_i + 15.88\}] = 0 \\
&= \frac{d}{dJ} (-J_i^2 - J_i + 15.88J_i + 15.88) = 0 \\
&= -2J_i + 14.88 = 0
\end{aligned}$$

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

At $J = 7.44$:

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

$$E_R = (7.44 + 1)\{-7.44 + 15.88\} = (8.44)(8.44) = 71.2 \text{ cm}^{-1} \text{ above}$$

the origin.

31.

a.

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2$	$3C_2$	i	$2S_3$	$2S_6$	h	3 d	3 v		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	R_x, R_y	(xz, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		

A _{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z
B _{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	
B _{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1	
E _{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x,y)
E _{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0	
C-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:

$$n_{\text{irrep}} = \frac{1}{g} \sum_{\text{R}} \text{red}(\text{R}) \cdot \text{irrep}(\text{R}),$$

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

$$\begin{aligned}
 n_{\text{A}_{1g}} &= \frac{1}{24} \sum_{\text{R}} \text{C-H}(\text{R}) \cdot \text{A}_{1g}(\text{R}) \\
 &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\
 &\quad + (3)(0)(1) + (3)(2)(1) + (1)(0)(1) + (2)(0)(1) \\
 &\quad + (2)(0)(1) + (1)(6)(1) + (3)(2)(1) + (3)(0)(1) \} \\
 &= 1 \\
 n_{\text{A}_{2g}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\
 &\quad + (3)(0)(-1) + (3)(2)(-1) + (1)(0)(1) + (2)(0)(1) \\
 &\quad + (2)(0)(1) + (1)(6)(1) + (3)(2)(-1) + (3)(0)(-1) \}
 \end{aligned}$$

$$= 0$$

$$n_{B_{1g}} = \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\ + (3)(0)(1) + (3)(2)(-1) + (1)(0)(1) + (2)(0)(-1) \\ + (2)(0)(1) + (1)(6)(-1) + (3)(2)(1) + (3)(0)(-1) \}$$

$$= 0$$

$$n_{B_{2g}} = \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\ + (3)(0)(-1) + (3)(2)(1) + (1)(0)(1) + (2)(0)(-1) \\ + (2)(0)(1) + (1)(6)(-1) + (3)(2)(-1) + (3)(0)(1) \}$$

$$= 0$$

$$n_{E_{1g}} = \frac{1}{24} \{ (1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) \\ + (3)(0)(0) + (3)(2)(0) + (1)(0)(2) + (2)(0)(1) \\ + (2)(0)(-1) + (1)(6)(-2) + (3)(2)(0) + (3)(0)(0) \}$$

$$= 0$$

$$n_{E_{2g}} = \frac{1}{24} \{ (1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) \\ + (3)(0)(0) + (3)(2)(0) + (1)(0)(2) + (2)(0)(-1) \\ + (2)(0)(-1) + (1)(6)(2) + (3)(2)(0) + (3)(0)(0) \}$$

$$= 1$$

$$n_{A_{1u}} = \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\ + (3)(0)(1) + (3)(2)(1) + (1)(0)(-1) + (2)(0)(-1) \\ + (2)(0)(-1) + (1)(6)(-1) + (3)(2)(-1) + (3)(0)(-1) \}$$

$$= 0$$

$$\begin{aligned}
n_{A_{2u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\
&\quad + (3)(0)(-1) + (3)(2)(-1) + (1)(0)(-1) + (2)(0)(-1) \\
&\quad + (2)(0)(-1) + (1)(6)(-1) + (3)(2)(1) + (3)(0)(1) \} \\
&= 0
\end{aligned}$$

$$\begin{aligned}
n_{B_{1u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\
&\quad + (3)(0)(1) + (3)(2)(-1) + (1)(0)(-1) + (2)(0)(1) \\
&\quad + (2)(0)(-1) + (1)(6)(1) + (3)(2)(-1) + (3)(0)(1) \} \\
&= 0
\end{aligned}$$

$$\begin{aligned}
n_{B_{2u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\
&\quad + (3)(0)(-1) + (3)(2)(1) + (1)(0)(-1) + (2)(0)(1) \\
&\quad + (2)(0)(-1) + (1)(6)(1) + (3)(2)(1) + (3)(0)(-1) \} \\
&= 1
\end{aligned}$$

$$\begin{aligned}
n_{E_{1u}} &= \frac{1}{24} \{ (1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) \\
&\quad + (3)(0)(0) + (3)(2)(0) + (1)(0)(-2) + (2)(0)(-1) \\
&\quad + (2)(0)(1) + (1)(6)(2) + (3)(2)(0) + (3)(0)(0) \} \\
&= 1
\end{aligned}$$

$$\begin{aligned}
n_{E_{2u}} &= \frac{1}{24} \{ (1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) \\
&\quad + (3)(0)(0) + (3)(2)(0) + (1)(0)(-2) + (2)(0)(1) \\
&\quad + (2)(0)(1) + (1)(6)(-2) + (3)(2)(0) + (3)(0)(0) \} \\
&= 0
\end{aligned}$$

We see that $c_H = A_{1g} \ E_{2g} \ B_{2u} \ E_{1u}$

c. x and y E_{1u} , z A_{2u} , so, the ground state A_{1g} level can be excited to the degenerate E_{1u} level by coupling through the x or y transition dipoles. Therefore E_{1u} is infrared active and polarized.

d. $(x^2 + y^2, z^2)$ A_{1g} , (xz, yz) E_{1g} , $(x^2 - y^2, xy)$ E_{2g} , so, the ground state A_{1g} level can be excited to the degenerate E_{2g} level by coupling through the $x^2 - y^2$ or xy transitions or be excited to the degenerate A_{1g} level by coupling through the xz or yz transitions. Therefore A_{1g} and E_{2g} are Raman active..

e. The B_{2u} mode is not IR or Raman active.

32.

a. Evaluate the z -component of μ_{fi} :

$$\mu_{fi} = \langle 2p_z | e r \cos \theta | 1s \rangle, \text{ where } 1s = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}, \text{ and } 2p_z = \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0} \right)^{5/2} r \cos \theta e^{-Zr/2a_0}.$$

$$\mu_{fi} = \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0} \right)^{5/2} \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \langle r \cos \theta e^{-Zr/2a_0} | e r \cos \theta | e^{-Zr/a_0} \rangle$$

$$= \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0} \right)^4 \langle r \cos \theta e^{-Zr/2a_0} | e r \cos \theta | e^{-Zr/a_0} \rangle$$

$$\begin{aligned}
&= \frac{e}{4\sqrt{2}} \frac{Z}{a_0}^4 \int_0^2 r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} r^2 e^{-\frac{Zr}{2a_0}} e^{-\frac{Zr}{a_0}} \cos^2 \theta d\phi \\
&= \frac{e}{4\sqrt{2}} \frac{Z}{a_0}^4 \int_0^2 r^4 e^{-\frac{3Zr}{2a_0}} dr \int_0^\pi \sin \theta \cos^2 \theta d\theta \int_0^{2\pi} d\phi \\
&= \frac{e}{4\sqrt{2}} \frac{Z}{a_0}^4 \frac{4!}{\frac{3Z}{2a_0}^5} \frac{-1}{3} \cos^3 \theta \Big|_0^\pi \\
&= \frac{e}{4\sqrt{2}} \frac{Z}{a_0}^4 \frac{2^5 a_0^5 4!}{3^5 Z^5} \frac{-1}{3} ((-1)^3 - (1)^3) \\
&= \frac{e}{\sqrt{2}} \frac{2^8 a_0}{3^5 Z} = \frac{ea_0}{Z} \frac{2^8}{\sqrt{2} 3^5} = 0.7449 \frac{ea_0}{Z}
\end{aligned}$$

b. Examine the symmetry of the integrands for $\langle 2p_z | e^x | 1s \rangle$ and $\langle 2p_z | e^y | 1s \rangle$.

Consider reflection in the xy plane:

Function	Symmetry
$2p_z$	-1
x	+1

1s	+1
y	+1

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

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

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

$$c. \quad R = \frac{3\hbar^4 c^3}{4(E_i - E_f)^3 |\mu_{fi}|^2},$$

$$E_i = E_{2p_z} = -\frac{1}{4} Z^2 \frac{e^2}{2a_0}$$

$$E_f = E_{1s} = -Z^2 \frac{e^2}{2a_0}$$

$$E_i - E_f = \frac{3}{8} \frac{e^2}{a_0} Z^2$$

Making the substitutions for $E_i - E_f$ and $|\mu_{fi}|$ in the expression for R we obtain:

$$R = \frac{3\hbar^4 c^3}{4 \left(\frac{3}{8} \frac{e^2}{a_0} Z^2 \right)^3 \left(\frac{ea_0}{Z} \frac{2^8}{\sqrt{2} 3^5} \right)^2},$$

$$= \frac{3\hbar^4 c^3}{4 \frac{3^3}{8^3} \frac{e^6}{a_0^3} Z^6 \frac{e^2 a_0^2}{Z^2} \frac{2^{16}}{(2)3^{10}}},$$

$$= \frac{\hbar^4 c^3 3^8 a_0}{e^8 Z^4 2^8},$$

Inserting $e^2 = \frac{\hbar^2}{m_e a_0}$ we obtain:

$$\begin{aligned}
 R &= \frac{\hbar^4 c^3 3^8 a_0 m_e^4 a_0^4}{\hbar^8 Z^4 2^8} = \frac{3^8 c^3 a_0^5 m_e^4}{2^8 \hbar^4 Z^4} \\
 &= 25.6289 \frac{c^3 a_0^5 m_e^4}{\hbar^4 Z^4} \\
 &= 25,6289 \frac{1}{Z^4} \times
 \end{aligned}$$

$$\begin{aligned}
 &\frac{(2.998 \times 10^{10} \text{ cm sec}^{-1})^3 (0.529177 \times 10^{-8} \text{ cm})^5 (9.109 \times 10^{-28} \text{ g})^4}{(1.0546 \times 10^{-27} \text{ g cm}^2 \text{ sec}^{-1})^4} \\
 &= 1.595 \times 10^{-9} \text{ sec} \times \frac{1}{Z^4}
 \end{aligned}$$

So, for example:

Atom	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. $H = H_0 + H'(t)$, $H'(t) = V(t)$, $H_0 |k\rangle = E_k |k\rangle$, $\omega_k = E_k/\hbar$

$$i\hbar \frac{d}{dt} = H$$

let $|\psi(t)\rangle = \sum_j c_j(t) e^{-i E_j t/\hbar}$ and insert into the Schrödinger equation:

$$i\hbar \sum_j \dot{c}_j e^{-i E_j t/\hbar} = \sum_j c_j(t) e^{-i E_j t/\hbar} (H_0 + H'(t))$$

$$\sum_j i\hbar \dot{c}_j + E_j c_j - c_j E_j - c_j H' e^{-i E_j t/\hbar} = 0$$

$$\sum_j i\hbar \dot{c}_j \langle m|j\rangle - c_j \langle m|H'|j\rangle e^{-i E_j t/\hbar} = 0$$

$$i\hbar \dot{c}_m e^{-i E_m t/\hbar} = \sum_j c_j H'_{mj} e^{-i E_j t/\hbar}$$

So,

$$c_m = \frac{1}{i\hbar} \sum_j c_j H'_{mj} e^{-i(E_j - E_m)t/\hbar}$$

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

$$\sum_j i\hbar \dot{c}_j \langle k|j\rangle - c_j \langle k|H'|j\rangle e^{-i E_j t/\hbar} = 0$$

$$i\hbar \dot{c}_k e^{-i E_k t/\hbar} = \sum_j c_j H'_{kj} e^{-i E_j t/\hbar}$$

So,

$$c_k = \frac{1}{i\hbar} \sum_j c_j H'_{kj} e^{-i(jk)t}$$

Now, let:

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

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

and substituting into above we obtain:

$$c_m^{(0)} + c_m^{(1)} + c_m^{(2)} + \dots = \frac{1}{i\hbar} \sum_j [c_j^{(0)} + c_j^{(1)} + c_j^{(2)} + \dots] H'_{mj} e^{-i(jm)t}$$

first order:

$$c_m^{(0)} = 0 \quad c_m^{(0)} = 1$$

second order:

$$c_m^{(1)} = \frac{1}{i\hbar} \sum_j c_j^{(0)} H'_{mj} e^{-i(jm)t}$$

(n+1)st order:

$$c_m^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{mj} e^{-i(jm)t}$$

Similarly:

first order:

$$c_k^{(0)} = 0 \quad c_k^{(0)} = 0$$

second order:

$$c_k^{(1)} = \frac{1}{i\hbar} \sum_j c_j^{(0)} H'_{kj} e^{-i(jk)t}$$

(n+1)st order:

$$c_k^{(n)} = \frac{1}{i\hbar} c_j^{(n-1)} H'_{kj} e^{-i(\omega_k - \omega_j)t}$$

So,

$$c_m^{(1)} = \frac{1}{i\hbar} c_m^{(0)} H'_{mm} e^{-i(\omega_m - \omega_m)t} = \frac{1}{i\hbar} H'_{mm}$$

$$c_m^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' V_{mm} = \frac{V_{mm}t}{i\hbar}$$

and similarly,

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

$$c_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' V_{km} e^{-i(\omega_k - \omega_m)t'} = \frac{V_{km}}{i\hbar(\omega_k - \omega_m)} [e^{-i(\omega_k - \omega_m)t} - 1]$$

$$c_m^{(2)} = \frac{1}{i\hbar} c_j^{(1)} H'_{mj} e^{-i(\omega_m - \omega_j)t}$$

$$c_m^{(2)} = \frac{1}{i\hbar} \int_0^t dt' \frac{V_{jm}}{i\hbar(\omega_j - \omega_m)} [e^{-i(\omega_j - \omega_m)t'} - 1] H'_{mj} e^{-i(\omega_m - \omega_j)t} + \frac{1}{i\hbar} \frac{V_{mm}t}{i\hbar} H'_{mm}$$

$$c_m^{(2)} = \frac{1}{i\hbar} \int_0^t dt' \frac{V_{jm}V_{mj}}{\hbar(\omega_j - \omega_m)} e^{-i(\omega_m - \omega_j)t} [e^{-i(\omega_j - \omega_m)t'} - 1] - \frac{V_{mm}V_{mm}}{\hbar^2} \int_0^t dt' dt'$$

$$= \frac{V_{jm}V_{mj}}{\hbar^2(\omega_j - \omega_m)} \int_0^t dt' [1 - e^{-i(\omega_j - \omega_m)t'}] - \frac{|V_{mm}|^2}{\hbar^2} \frac{t^2}{2}$$

$$\begin{aligned}
&= \sum_{j \neq m} \frac{V_{jm}V_{mj}}{i\hbar^2} t - \frac{e^{-i(jm)t} - 1}{-i(jm)} - \frac{|V_{mm}|^2 t^2}{\hbar^2} \\
&= \sum_{j \neq m} \frac{V_{jm}V_{mj}}{\hbar^2} (e^{-i(jm)t} - 1) + \sum_{j \neq m} \frac{V_{jm}V_{mj}}{i\hbar^2} t - \frac{|V_{mm}|^2 t^2}{2\hbar^2}
\end{aligned}$$

Similarly,

$$\begin{aligned}
c_k^{(2)} &= \frac{1}{i\hbar} \sum_j c_j^{(1)} H'_{kj} e^{-i(jk)t} \\
&= \sum_{j \neq m} \frac{1}{i\hbar} \frac{V_{jm}}{\hbar} [e^{-i(mj)t} - 1] H'_{kj} e^{-i(jk)t} + \\
&\qquad\qquad\qquad \frac{1}{i\hbar} \frac{V_{mm}t}{i\hbar} H'_{km} e^{-i(mk)t}
\end{aligned}$$

$$\begin{aligned}
c_k^{(2)}(t) &= \sum_{j \neq m} \frac{V_{jm}V_{kj}}{i\hbar^2} \int_0^t dt' e^{-i(jk)t'} [e^{-i(mj)t'} - 1] \\
&\qquad\qquad\qquad - \frac{V_{mm}V_{km}}{\hbar^2} \int_0^t dt' e^{-i(mk)t'} \\
&= \sum_{j \neq m} \frac{V_{jm}V_{kj}}{i\hbar^2} \frac{e^{-i(mj+jk)t} - 1}{-i(mk)} - \frac{e^{-i(jk)t} - 1}{-i(jk)} \\
&\qquad\qquad\qquad - \frac{V_{mm}V_{km}}{\hbar^2} e^{-i(mk)t} \frac{t}{-i(mk)} - \frac{1}{-(i(mk))^2} t \\
&= \sum_{j \neq m} \frac{V_{jm}V_{kj}}{\hbar^2} \frac{e^{-i(mk)t} - 1}{mk} - \frac{e^{-i(jk)t} - 1}{jk}
\end{aligned}$$

$$\begin{aligned}
& + \frac{V_{mm}V_{km}}{\hbar^2} e^{-i(\omega_m - \omega_k)t} \left[\frac{1}{i} - \frac{1}{\omega_m - \omega_k} \right] \\
= & \sum_j \frac{V_{jm}V_{kj}}{E_m - E_j} \frac{e^{-i(\omega_m - \omega_k)t} - 1}{E_m - E_k} - \frac{e^{-i(\omega_j - \omega_k)t} - 1}{E_j - E_k} \\
& + \frac{V_{mm}V_{km}}{\hbar(E_m - E_k)} e^{-i(\omega_m - \omega_k)t} \left[\frac{1}{i} - \frac{1}{\omega_m - \omega_k} \right] + \frac{1}{\omega_m - \omega_k}
\end{aligned}$$

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

$$\begin{aligned}
c_m(t) = & 1 + \frac{V_{mm}t}{i\hbar} + \sum_j \frac{V_{jm}V_{mj}}{i\hbar(E_m - E_j)} t + \\
& \sum_j \frac{V_{jm}V_{mj}}{\hbar^2(E_m - E_j)^2} (e^{-i(\omega_j - \omega_m)t} - 1) - \frac{|V_{mm}|^2 t^2}{2\hbar^2} \\
c_k(t) = & \frac{V_{km}}{(E_m - E_k)} [e^{-i(\omega_m - \omega_k)t} - 1] + \\
& \frac{V_{mm}V_{km}}{(E_m - E_k)^2} [1 - e^{-i(\omega_m - \omega_k)t}] + \frac{V_{mm}V_{km}}{(E_m - E_k)} \frac{t}{i\hbar} e^{-i(\omega_m - \omega_k)t} + \\
& \sum_j \frac{V_{jm}V_{kj}}{E_m - E_j} \frac{e^{-i(\omega_m - \omega_k)t} - 1}{E_m - E_k} - \frac{e^{-i(\omega_j - \omega_k)t} - 1}{E_j - E_k}
\end{aligned}$$

b. The perturbation equations still hold:

$$c_m^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{mj} e^{-i(\omega_j - \omega_m)t} ; c_k^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{kj} e^{-i(\omega_j - \omega_k)t}$$

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

$$c_m^{(1)} = \frac{1}{i\hbar} H'_{mm}$$

$$c_m^{(1)} = \frac{1}{i\hbar} \int_0^t V_{mm} dt' e^{-i(E_m - E_m)t'} = \frac{V_{mm} e^{-i(E_m - E_m)t}}{i\hbar}$$

$$c_k^{(1)} = \frac{1}{i\hbar} H'_{km} e^{-i(E_k - E_m)t}$$

$$c_k^{(1)} = \frac{1}{i\hbar} \int_0^t V_{km} dt' e^{-i(E_k - E_m)t'} = \frac{V_{km}}{i\hbar(-i(E_k - E_m))} [e^{-i(E_k - E_m)t} - 1]$$

$$= \frac{V_{km}}{E_m - E_k + i\hbar} [e^{-i(E_k - E_m)t} - 1]$$

$$c_m^{(2)} = \frac{1}{i\hbar} \int_0^t \frac{V_{jm}}{E_m - E_j + i\hbar} e^{-i(E_m - E_j)t'} V_{mj} e^{-i(E_m - E_m)t'} dt' + \frac{1}{i\hbar} \frac{V_{mm} e^{-i(E_m - E_m)t}}{i\hbar} V_{mm} e^{-i(E_m - E_m)t}$$

$$c_m^{(2)} = \frac{1}{i\hbar} \int_0^t \frac{V_{jm} V_{mj}}{E_m - E_j + i\hbar} e^{-i(E_m - E_j)t'} dt' - \frac{|V_{mm}|^2}{\hbar^2} \int_0^t e^{-i(E_m - E_m)t'} dt'$$

$$= \frac{V_{jm} V_{mj}}{i\hbar^2 (E_m - E_j + i\hbar)} e^{-i(E_m - E_j)t} - \frac{|V_{mm}|^2}{2\hbar^2} e^{-i(E_m - E_m)t}$$

$$c_k^{(2)} = \frac{1}{i\hbar} \int_0^t \frac{V_{jm}}{E_m - E_j + i\hbar} e^{-i(E_m - E_j)t'} H'_{kj} e^{-i(E_k - E_m)t'} dt' + \frac{1}{i\hbar} \frac{V_{mm} e^{-i(E_m - E_m)t}}{i\hbar} H'_{km} e^{-i(E_k - E_m)t}$$

$$c_k^{(2)} = \frac{1}{i\hbar} \int_0^t \frac{V_{jm} V_{kj}}{E_m - E_j + i\hbar} e^{-i(E_k - E_m)t'} dt' -$$

$$\frac{V_{mm}V_{km}}{\hbar^2} \int_0^t e^{-i(E_m - E_k + 2\hbar^{-1})t'} dt'$$

$$= \sum_j \frac{V_{jm}V_{kj} e^{-i(E_m - E_j + \hbar^{-1})t}}{(E_m - E_j + \hbar^{-1})(E_m - E_k + 2i\hbar^{-1})} - \frac{V_{mm}V_{km} e^{-i(E_m - E_k + 2i\hbar^{-1})t}}{i\hbar^{-1}(E_m - E_k + 2i\hbar^{-1})}$$

Therefore, to second order:

$$c_m(t) = 1 + \frac{V_{mm}e^{-iE_m t}}{i\hbar^{-1}} + \sum_j \frac{V_{jm}V_{mj}}{i\hbar^2(E_m - E_j + \hbar^{-1})} e^{2iE_j t}$$

$$c_k(t) = \frac{V_{km}}{i\hbar^{-1}(E_m - E_k + 2i\hbar^{-1})} [e^{-i(E_m - E_k + 2i\hbar^{-1})t}]$$

$$+ \sum_j \frac{V_{jm}V_{kj} e^{-i(E_m - E_j + \hbar^{-1})t}}{(E_m - E_j + \hbar^{-1})(E_m - E_k + 2i\hbar^{-1})}$$

c. In part a. the $c^{(2)}(t)$ grow linearly with time (for $V_{mm} = 0$) while in part b. they remain finite for $t > 0$. The result in part a. is due to the sudden turning on of the field.

$$d. |c_k(t)|^2 = \sum_j \frac{V_{jm}V_{kj} e^{-i(E_m - E_j + \hbar^{-1})t}}{(E_m - E_j + \hbar^{-1})(E_m - E_k + 2i\hbar^{-1})}^2$$

$$= \sum_{jj'} \frac{V_{kj}V_{kj'}V_{jm}V_{j'm} e^{-i(E_m - E_j + \hbar^{-1})t} e^{i(E_m - E_{j'} + \hbar^{-1})t}}{(E_m - E_j + \hbar^{-1})(E_m - E_{j'} - \hbar^{-1})(E_m - E_k + 2i\hbar^{-1})(E_m - E_k - 2i\hbar^{-1})}$$

$$= \sum_{jj'} \frac{V_{kj}V_{kj'}V_{jm}V_{j'm} e^{4iE_j t}}{[(E_m - E_j)(E_m - E_{j'}) + i\hbar^{-1}(E_j - E_{j'}) + \hbar^2] [(E_m - E_k)^2 + 4\hbar^2]}$$

$$\frac{d}{dt} |c_k(t)|^2 = \sum_{jj'} \frac{4 V_{kj}V_{kj'}V_{jm}V_{j'm}}{[(E_m - E_j)(E_m - E_{j'}) + i\hbar^{-1}(E_j - E_{j'}) + \hbar^2] [(E_m - E_k)^2 + 4\hbar^2]}$$

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

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

$$\lim_{0^+} \frac{4}{((E_m - E_k)^2 + 4\hbar^2 \gamma^2)} (E_m - E_k)$$

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

$$\frac{d}{dt} |c_k(t)|^2 = \frac{2}{\hbar} (E_m - E_k) \lim_{0^+} \sum_j \frac{V_{jm} V_{kj}}{(E_j - E_m - i\hbar \gamma)^2}$$

34.

$$a. \quad T_{nm} = \frac{|\langle n|V|m\rangle|^2}{\hbar^2 \omega_{nm}^2}$$

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:

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} e^{-\frac{Zr}{a_0}} \frac{1}{r} \frac{1}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}} r^2 dr$$

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \int_0^\infty r e^{-\frac{3Zr}{2a_0}} dr - \frac{Zr^2}{2a_0} e^{-\frac{3Zr}{2a_0}} dr$$

$$= \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \left[\frac{1}{\frac{3Z}{2a_0}} \right] - \frac{Z}{2a_0} \left[\frac{2}{\frac{3Z}{2a_0}} \right]$$

$$\langle 1s|V|2s \rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \int_0^\infty \frac{2^2 a_0^2}{3^2 Z^2} - \frac{2^3 a_0^2}{3^3 Z^2}$$

$$\langle 1s|V|2s \rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \int_0^\infty \frac{(3)2^2 a_0^2 - 2^3 a_0^2}{3^3 Z^2} = \frac{8Z}{\sqrt{2} 27 a_0}$$

Now,

$$E_n = -\frac{Z^2 e^2}{n^2 2 a_0}, E_{1s} = -\frac{Z^2 e^2}{2 a_0}, E_{2s} = -\frac{Z^2 e^2}{8 a_0}, E_{2s} - E_{1s} = \frac{3Z^2 e^2}{8 a_0}$$

So,

$$T_{nm} = \frac{\frac{8Z}{\sqrt{2} 27 a_0} \int_0^\infty r^2}{\frac{3Z^2}{8 a_0} \int_0^\infty r^2} = \frac{2^6 Z^2 2^6 a_0^2}{(2) 3^8 a_0^2 Z^4} = \frac{2^{11}}{3^8 Z^2} = 0.312 \text{ (for } Z = 1)$$

$$b. \quad m(r) = \int_0^\infty r^3 e^{-\frac{Zr}{a_0}} Y_{00}$$

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 $A_{1s,2s}$.

$$n(r) = \int_0^\infty r^3 e^{-\frac{Zr}{a_0}} \left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}}$$

Remember for $1s$ $Z = 1$ and for $2s$ $Z = 2$

$$A_{nm} = \int_0^\infty r^3 e^{-\frac{Zr}{a_0}} \frac{1}{\sqrt{2}} \frac{Z+1}{a_0} \left(1 - \frac{(Z+1)r}{2a_0}\right) e^{-\frac{(Z+1)r}{2a_0}} r^2 dr$$

$$A_{nm} = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \int_0^\infty r^3 e^{-\frac{(3Z+1)r}{2a_0}} \left(1 - \frac{(Z+1)r}{2a_0}\right) r^2 dr$$

$$A_{nm} = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \frac{Z+1}{a_0} \frac{3}{2} r^2 e^{-\frac{(3Z+1)r}{2a_0}} dr - \frac{(Z+1)r^3}{2a_0} e^{-\frac{(3Z+1)r}{2a_0}} dr$$

We obtain:

$$A_{nm} = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \frac{Z+1}{a_0} \frac{3}{2} \frac{2}{\frac{3Z+1}{2a_0}^3} - \frac{Z+1}{2a_0} \frac{(3)(2)}{\frac{3Z+1}{2a_0}^4}$$

$$A_{nm} = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \frac{Z+1}{a_0} \frac{3}{2} \frac{2^4 a_0^3}{(3Z+1)^3} - (Z+1) \frac{(3)2^4 a_0^3}{(3Z+1)^4}$$

$$A_{nm} = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \frac{Z+1}{a_0} \frac{3}{2} \frac{-2^5 a_0^3}{(3Z+1)^4}$$

$$A_{nm} = -2 \frac{[2^3 Z(Z+1)]^{\frac{3}{2}}}{(3Z+1)^4}$$

The transition probability is the square of this amplitude:

$$T_{nm} = -2 \frac{[2^3 Z(Z+1)]^{\frac{3}{2}}}{(3Z+1)^4} = \frac{2^{11} Z^3 (Z+1)^3}{(3Z+1)^8} = 0.25 \text{ (for } Z = 1\text{)}.$$

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

$$\hat{\mu} \cdot \hat{Z} = \cos \theta = \mu_{00}^{1*}(\theta)$$

So,

$$\begin{aligned} I &= \langle D_{M'K'}^J | \hat{\mu} | D_{MK}^J \rangle = D_{M'K'}^J \cdot \mu D_{MK}^J \int \sin \theta d\theta d\phi d\chi \\ &= \mu \int D_{M'K'}^J D_{00}^{1*} D_{MK}^J \sin \theta d\theta d\phi d\chi . \end{aligned}$$

Now use:

$$D_{M'n'}^{J*} D_{00}^{1*} = \sum_{jmn} \langle J'M'10|jm \rangle^* D_{mn}^{j*} \langle jn|J'K'10 \rangle^* ,$$

to obtain:

$$I = \mu \sum_{jmn} \langle J'M'10|jm \rangle^* \langle jn|J'K'10 \rangle^* D_{mn}^{j*} D_{MK}^J \int \sin \theta d\theta d\phi d\chi .$$

Now use:

$$D_{mn}^{j*} D_{MK}^J \int \sin \theta d\theta d\phi d\chi = \frac{8}{2J+1} J_j M_m n ,$$

to obtain:

$$\begin{aligned} I &= \mu \frac{8}{2J+1} \sum_{jmn} \langle J'M'10|jm \rangle^* \langle jn|J'K'10 \rangle^* J_j M_m n \\ &= \mu \frac{8}{2J+1} \langle J'M'10|JM \rangle \langle JK|J'K'10 \rangle . \end{aligned}$$

We use:

$$\langle JK|J'K'10\rangle = \sqrt{2J+1}(-i)^{(J'-1+K)} \begin{matrix} J' & 1 & J \\ K' & 0 & K \end{matrix}$$

and,

$$\langle J'M'10|JM\rangle = \sqrt{2J+1}(-i)^{(J'-1+M)} \begin{matrix} J' & 1 & J \\ M' & 0 & M \end{matrix}$$

to give:

$$\begin{aligned} I &= \mu \frac{8}{2J+1} \sqrt{2J+1}(-i)^{(J'-1+M)} \begin{matrix} J' & 1 & J \\ M' & 0 & M \end{matrix} \sqrt{2J+1}(-i)^{(J'-1+K)} \begin{matrix} J' & 1 & J \\ K' & 0 & K \end{matrix} \\ &= \mu 8 \ 2(-i)^{(J'-1+M+J'-1+K)} \begin{matrix} J' & 1 & J \\ M' & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ K' & 0 & K \end{matrix} \\ &= \mu 8 \ 2(-i)^{(M+K)} \begin{matrix} J' & 1 & J \\ M' & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ K' & 0 & K \end{matrix} \end{aligned}$$

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

So,

$$I = \mu 8 \ 2(-i)^{(M+K)} \begin{matrix} J' & 1 & J \\ M & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ K & 0 & K \end{matrix} \ M'M \ K'K.$$

b. $\begin{matrix} J' & 1 & J \\ M & 0 & M \end{matrix}$ and $\begin{matrix} J' & 1 & J \\ K & 0 & K \end{matrix}$ vanish unless $J' = J + 1, J, J - 1$

$$J = \pm 1, 0$$

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.

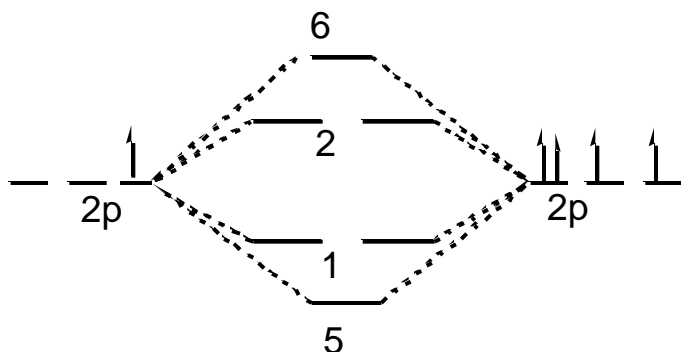
36.

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.

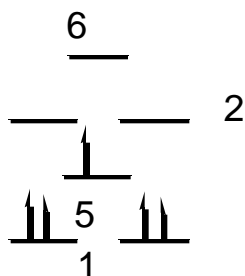
O atom: $1s^2 2s^2 2p^4$, 3P ground state $L = 1$, $S = 1$, gives a degeneracy $((2L+1)(2S+1))$ of 9.

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 $^2 +$ ground state. The only low-lying electron configurations are $1^3 5^2$ or $1^4 5^1$. These lead to $^2 -$ and $^2 +$ states, respectively.

- c. The bond orders in both states are 2.5.
- d. The 2 is + but g/u symmetry cannot be specified since this is a heteronuclear molecule.
- e. Only one excited state, the 2 , is spin-allowed to radiate to the 2 +. Consider symmetries of transition moment operators that arise in the electric dipole contributions to the transition rate $\int z^2 +, x, y$, the $^2 \rightarrow ^2$ + 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 1 + corresponding to a 1^4 electron configuration. An electron configuration of $1^3 5^1$ leads to a 3 and a 1 state. The 3 will be lower in energy. A $1^2 5^2$ configuration will lead to higher lying states of 3 -, 1 -, and 1 +.
- h. There should be 3 bands corresponding to formation of BO⁺ in the 1 +, 3 -, and 1 - 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 (δ) vibration is degenerate.
- b. H---C N

bending fundamental

c. H---C N

stretching fundamental

d. CH stretch (ν_3 in figure) is ν_3 , CN stretch is ν_4 , and HCN (ν_2 in figure) bend is ν_2 .

e. Under z (\parallel) light the CN stretch and the CH stretch can be excited, since $\nu_0 = 0$, $\nu_1 = 1$ and z = \parallel provides coupling.

f. Under x,y (\perp) light the HCN bend can be excited, since $\nu_0 = 0$, $\nu_1 = 1$ and x,y = \perp provides coupling.

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

38.

$$F_{ij} = \int \psi_i^* \psi_j = h_{ij} + \sum_k [J_k - K_k]_{ij}$$

Let the closed shell Fock potential be written as:

$$V_{ij} = \sum_k 2\langle ik|jk \rangle - \langle ik|kj \rangle, \text{ and the } 1e^- \text{ component as:}$$

$$h_{ij} = \left\langle \psi_i \left| -\frac{1}{2} \nabla^2 - \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \right| \psi_j \right\rangle, \text{ and the delta as:}$$

$$\delta_{ij} = \langle i|j \rangle, \text{ so that: } h_{ij} + V_{ij} = \delta_{ij}.$$

using: $\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}$, $\psi_j = \sum_{\nu} C_{\nu j} \phi_{\nu}$, and $\psi_k = \sum_{\lambda} C_{\lambda k} \phi_{\lambda}$, and transforming from the MO

to AO basis we obtain:

$$\begin{aligned} V_{ij} &= \sum_{k\mu} C_{\mu i} C_{\nu k} C_{\lambda j} C_{\lambda k} 2\langle \mu | \nu \lambda \rangle - \langle \mu | \lambda \nu \rangle \\ &= \sum_{k\mu} (C_{\nu k} C_{\lambda k}) (C_{\mu i} C_{\lambda j}) 2\langle \mu | \nu \lambda \rangle - \langle \mu | \lambda \nu \rangle \\ &= \sum_{\mu} (C_{\mu i} C_{\lambda j}) V_{\mu} \text{ where,} \end{aligned}$$

$$V_{\mu} = \sum_k P_{\mu k} 2\langle \mu | \nu \lambda \rangle - \langle \mu | \lambda \nu \rangle, \text{ and } P = \sum_k (C_{\nu k} C_{\lambda k}),$$

$$h_{ij} = \sum_{\mu} (C_{\mu i} C_{\lambda j}) h_{\mu}, \text{ where}$$

$$h_{\mu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 - \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \right| \right\rangle, \text{ and}$$

$$S_{ij} = \langle i | j \rangle = \sum_{\mu} (C_{\mu i} S_{\mu} C_{\mu j}).$$

So, $h_{ij} + V_{ij} = \sum_{\mu} h_{\mu} C_{\mu i} C_{\mu j}$ becomes:

$$\sum_{\mu} (C_{\mu i} C_{\mu j}) h_{\mu} + \sum_{\mu} (C_{\mu i} C_{\mu j}) V_{\mu} = \sum_{\mu} (C_{\mu i} S_{\mu} C_{\mu j}) \sum_{j} j,$$

$$\sum_{\mu} (C_{\mu i} S_{\mu} C_{\mu j}) \sum_{j} j - \sum_{\mu} (C_{\mu i} C_{\mu j}) h_{\mu} - \sum_{\mu} (C_{\mu i} C_{\mu j}) V_{\mu} = 0 \text{ for all } i, j$$

$$\sum_{\mu} C_{\mu i} [\sum_{j} j S_{\mu} - h_{\mu} - V_{\mu}] C_{\mu j} = 0 \text{ for all } i, j$$

Therefore,

$$[h_{\mu} + V_{\mu} - \sum_{j} j S_{\mu}] C_{\mu j} = 0$$

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:

$$\begin{aligned}
E = \langle H + G \rangle &= \sum_i^N \langle i | h | i \rangle + \sum_{i>j}^N \langle i j | g | i j \rangle - \sum_{i>j}^N \langle i j | g | j i \rangle \\
&= \sum_i h_{ii} + \sum_{i>j} (g_{ijij} - g_{ijji}) \\
&= \sum_i h_{ii} + \frac{1}{2} \sum_{ij} (g_{ijij} - g_{ijji})
\end{aligned}$$

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

$$E = 2 \sum_i^{\text{occ}} h_{ii} + \sum_{ij}^{\text{occ}} (2g_{ijij} - g_{ijji}),$$

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

40.

If the occupied orbitals obey $F_k = \epsilon_k k$, then the expression for E in problem 39 can be rewritten as.

$$E = \sum_i^{\text{occ}} h_{ii} + \sum_j^{\text{occ}} (2g_{ijij} - g_{ijji}) + \sum_i^{\text{occ}} h_{ii}$$

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

$$E = \sum_i^{\text{occ}} F_{ii} + \sum_i^{\text{occ}} h_{ii} = \sum_i^{\text{occ}} (\epsilon_i + h_{ii})$$

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:

$$\begin{matrix} 1.0 & 0.0 \\ 0.0 & 1.0 \end{matrix}$$

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 $S^{-\frac{1}{2}}$ such that $S^{-\frac{1}{2}} S^{-\frac{1}{2}} = 1$, $S^{-\frac{1}{2}}$

$S = S^{-\frac{1}{2}}$, etc.

rewrite $FC = SCE$ by inserting unity between FC and multiplying the whole equation on

the left by $S^{-\frac{1}{2}}$. This gives:

$$S^{-\frac{1}{2}} FS^{-\frac{1}{2}} S^{+\frac{1}{2}} C = S^{-\frac{1}{2}} SCE = S^{+\frac{1}{2}} CE.$$

Letting: $F' = S^{-\frac{1}{2}} FS^{-\frac{1}{2}}$

$C' = S^{+\frac{1}{2}} C$, 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' :

$C' = S^{+\frac{1}{2}} C$, so, multiplying through on the left by $S^{-\frac{1}{2}}$ gives:

$$S^{-\frac{1}{2}} C' = S^{-\frac{1}{2}} S^{+\frac{1}{2}} C = C$$

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

Find $S^{-\frac{1}{2}}$ 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 $S^{-\frac{1}{2}}$ 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 $F' = S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$ using the program UTMATU which reads in F and $S^{-\frac{1}{2}}$ 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 $C = S^{-\frac{1}{2}} C'$. 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:

$$2\langle k|h|k\rangle + 2\langle k|l|k\rangle - \langle k|l|k\rangle + \frac{Z_{\mu}Z}{R_{\mu}}, \quad \text{and}$$

$$\langle k + \langle k|h|k\rangle + \frac{Z_{\mu}Z}{R_{\mu}}.$$

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: -2.644200 -1.511300
 -1.511300 -1.720100

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: 1.000000 0.000000
 0.000000 1.000000

AO overlap matrix (S): 1.000000 0.578400
 0.578400 1.000000

$S^{-\frac{1}{2}}$ 1.168032 -0.3720709
 -0.3720709 1.168031

ITERATION 1

The charge bond order matrix: 1.000000 0.000000
 0.000000 0.000000

The Fock matrix (F): -1.589500 -1.036900
 -1.036900 -0.8342001

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$ -1.382781 -0.5048679
 -0.5048678 -0.4568883

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

[-1.604825 -0.2348450]

Their corresponding eigenvectors ($C' = S^{+\frac{1}{2}} * C$) are:

-0.9153809 -0.4025888
-0.4025888 0.9153810

The "new" MO-AO coefficients ($C = S^{-\frac{1}{2}} * C'$):

-0.9194022 -0.8108231
 -0.1296498 1.218985

The one-electron MO integrals:

-2.624352 -0.1644336
 -0.1644336 -1.306845

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:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.84219933$$

from formula:

$$E_k + \langle k|h|k\rangle + \frac{Z_\mu Z}{R_\mu} = -2.80060530$$

the difference is: -0.04159403

ITERATION 2

The charge bond order matrix: $\begin{matrix} 0.8453005 & 0.1192003 \\ 0.1192003 & 0.01680906 \end{matrix}$

The Fock matrix: $\begin{matrix} -1.624673 & -1.083623 \\ -1.083623 & -0.8772071 \end{matrix}$

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$ $\begin{matrix} -1.396111 & -0.5411037 \\ -0.5411037 & -0.4798213 \end{matrix}$

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

$$\begin{bmatrix} -1.646972 & -0.2289599 \end{bmatrix}$$

Their corresponding eigenvectors ($C' = S^{-\frac{1}{2}} * C$) are:

$$\begin{matrix} -0.9072427 & -0.4206074 \end{matrix}$$

$$\begin{matrix} -0.4206074 & 0.9072427 \end{matrix}$$

The "new" MO-AO coefficients ($C = S^{\frac{1}{2}} * C'$):

$$\begin{matrix} -0.9031923 & -0.8288413 \end{matrix}$$

$$\begin{matrix} -0.1537240 & 1.216184 \end{matrix}$$

The one-electron MO integrals:

$$\begin{matrix} -2.617336 & -0.1903475 \end{matrix}$$

$$\begin{matrix} -0.1903475 & -1.313861 \end{matrix}$$

The two-electron MO integrals:

$$\begin{matrix} 1 & 1 & 1 & 1 & 0.9626070 \end{matrix}$$

$$\begin{matrix} 2 & 1 & 1 & 1 & 0.1949828 \end{matrix}$$

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:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84349298$$

from formula:

$$E_k + \langle k|h|k\rangle + \frac{Z_\mu Z}{R_\mu} = -2.83573675$$

the difference is: -0.00775623

ITERATION 3

The charge bond order matrix: 0.8157563 0.1388423
 0.1388423 0.02363107

The Fock matrix:

-1.631153	-1.091825
-1.091825	-0.8853514

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$

-1.398951	-0.5470731
-0.5470730	-0.4847007

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

[-1.654745 -0.2289078]

Their corresponding eigenvectors ($C' = S^{+\frac{1}{2}} * C$) are:

-0.9058709	-0.4235546
-0.4235545	0.9058706

The "new" MO-AO coefficients ($C = S^{-\frac{1}{2}} * C'$):

-0.9004935	-0.8317733
-0.1576767	1.215678

The one-electron MO integrals:

-2.616086 -0.1945811
 -0.1945811 -1.315112

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:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84353018$$

from formula:

$$k + \langle k|h|k\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84225941$$

the difference is:

-0.00127077

ITERATION 4

The charge bond order matrix:

	0.8108885	0.1419869
	0.1419869	0.02486194

The Fock matrix:

	-1.632213	-1.093155
	-1.093155	-0.8866909

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$

	-1.399426	-0.5480287
	-0.5480287	-0.4855191

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

[-1.656015 -0.2289308]

Their corresponding eigenvectors ($C' = S^{-\frac{1}{2}} * C$) are:

-0.9056494	-0.4240271
-0.4240271	0.9056495

The "new" MO-AO coefficients ($C = S^{-\frac{1}{2}} * C'$):

-0.9000589 -0.8322428
-0.1583111 1.215595

The one-electron MO integrals:

-2.615881 -0.1952594
-0.1952594 -1.315315

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:

$$2\langle k|h|k\rangle + 2\langle k|l|k\rangle - \langle k|l|k\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84352922$$

from formula:

$$\langle k|h|k\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84332418$$

the difference is: -0.00020504

ITERATION 5

The charge bond order matrix: $\begin{matrix} 0.8101060 & 0.1424893 \\ 0.1424893 & 0.02506241 \end{matrix}$

The Fock matrix: $\begin{matrix} -1.632385 & -1.093368 \\ -1.093368 & -0.8869066 \end{matrix}$

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$ $\begin{matrix} -1.399504 & -0.5481812 \\ -0.5481813 & -0.4856516 \end{matrix}$

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

$$[-1.656219 \quad -0.2289360]$$

Their corresponding eigenvectors ($C' = S^{-\frac{1}{2}} * C$) are:

$$-0.9056138 \quad -0.4241026$$

$$-0.4241028 \quad 0.9056141$$

The "new" MO-AO coefficients ($C = S^{-\frac{1}{2}} * C'$):

$$-0.8999892 \quad -0.8323179$$

$$-0.1584127 \quad 1.215582$$

The one-electron MO integrals:

$$-2.615847 \quad -0.1953674$$

$$-0.1953674 \quad -1.315348$$

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:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84352779$$

from formula:

$$k + \langle k|h|k\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84349489$$

the difference is:

-0.00003290

ITERATION 6

The charge bond order matrix:

	0.8099805	0.1425698
	0.1425698	0.02509460

The Fock matrix:

	-1.632412	-1.093402
	-1.093402	-0.8869413

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$

	-1.399517	-0.5482056
	-0.5482056	-0.4856730

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

[-1.656253 -0.2289375]

Their corresponding eigenvectors ($C' = S^{+\frac{1}{2}} * C$) are:

-0.9056085	-0.4241144
-0.4241144	0.9056086

The "new" MO-AO coefficients ($C = S^{-\frac{1}{2}} * C'$):

-0.8999786	-0.8323296
-0.1584283	1.215580

The one-electron MO integrals:

$$\begin{array}{cc} -2.615843 & -0.1953846 \\ -0.1953846 & -1.315353 \end{array}$$

The two-electron MO integrals:

$$\begin{array}{cc} 1 & 1 & 1 & 1 & 0.9595859 \\ 2 & 1 & 1 & 1 & 0.1953878 \\ 2 & 1 & 2 & 1 & 0.6062925 \\ 2 & 2 & 1 & 1 & 0.1261690 \\ 2 & 2 & 2 & 1 & 0.004625196 \\ 2 & 2 & 2 & 2 & 0.6159083 \end{array}$$

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84352827$$

from formula:

$$E_k + \langle k|h|k\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84352398$$

the difference is: -0.00000429

ITERATION 7

The charge bond order matrix: $\begin{pmatrix} 0.8099616 & 0.1425821 \\ 0.1425821 & 0.02509952 \end{pmatrix}$

The Fock matrix: $\begin{pmatrix} -1.632416 & -1.093407 \\ -1.093407 & -0.8869464 \end{pmatrix}$

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$ $\begin{pmatrix} -1.399519 & -0.5482093 \\ -0.5482092 & -0.4856761 \end{pmatrix}$

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

[-1.656257 -0.2289374]

Their corresponding eigenvectors ($C' = S^{-\frac{1}{2}} * C$) are:

-0.9056076 -0.4241164
-0.4241164 0.9056077

The "new" MO-AO coefficients ($C = S^{-\frac{1}{2}} * C'$):

-0.8999770 -0.8323317
-0.1584310 1.215580

The one-electron MO integrals:

-2.615843 -0.1953876
-0.1953876 -1.315354

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:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84352922$$

from formula:

$$\langle k|h|k\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84352827$$

the difference is:

$$-0.00000095$$

ITERATION 8

The charge bond order matrix:

0.8099585	0.1425842
0.1425842	0.02510037

The Fock matrix:

-1.632416	-1.093408
-1.093408	-0.8869470

$$S^{-\frac{1}{2}} F S^{-\frac{1}{2}} \begin{array}{cc} -1.399518 & -0.5482103 \\ -0.5482102 & -0.4856761 \end{array}$$

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

$$[-1.656258 \quad -0.2289368]$$

Their corresponding eigenvectors ($C' = S^{+\frac{1}{2}} * C$) are:

$$\begin{array}{cc} -0.9056074 & -0.4241168 \\ -0.4241168 & 0.9056075 \end{array}$$

The "new" MO-AO coefficients ($C = S^{-\frac{1}{2}} * C'$):

$$\begin{array}{cc} -0.8999765 & -0.8323320 \\ -0.1584315 & 1.215579 \end{array}$$

The one-electron MO integrals:

$$\begin{array}{cc} -2.615842 & -0.1953882 \\ -0.1953882 & -1.315354 \end{array}$$

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:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84352827$$

from formula:

$$k + \langle k|h|k\rangle + \frac{Z_\mu Z}{R_\mu} = -2.84352827$$

the difference is:

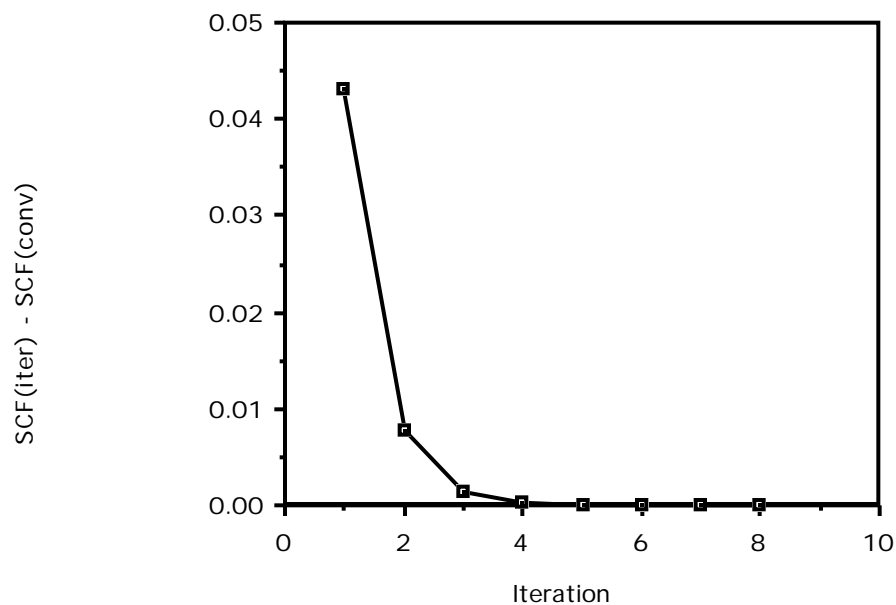
$$0.00000000$$

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:

$$y = 0.144 - 0.153x + 0.063x^2 - 0.013x^3 + 0.001x^4 \quad R = 1.00$$



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

42.

2. At convergence the MO coefficients are:

$$\begin{array}{l} \psi_1 = \begin{array}{l} -0.8999765 \\ -0.1584315 \end{array} \quad \psi_2 = \begin{array}{l} -0.8323320 \\ 1.215579 \end{array} \end{array}$$

and the integrals in this MO basis are:

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

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

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

$$\mathbf{H} = \begin{array}{cc} \langle 1 | \mathbf{H} | 1 \rangle & \langle 1 | \mathbf{H} | 2 \rangle \\ \langle 2 | \mathbf{H} | 1 \rangle & \langle 2 | \mathbf{H} | 2 \rangle \end{array} = \begin{array}{cc} 2h_{11} + g_{1111} & g_{1122} \\ g_{1122} & 2h_{22} + g_{2222} \end{array}$$

$$\begin{aligned}
 & \begin{matrix} 2*-2.615842 + 0.9595841 & 0.1261700 \\ = & 0.1261700 & 2*-1.315354 + 0.6159081 \end{matrix} \\
 & \begin{matrix} -4.272100 & 0.126170 \\ = & 0.126170 & -2.014800 \end{matrix}
 \end{aligned}$$

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

$$C_1 = \begin{pmatrix} -0.99845123 \\ 0.05563439 \end{pmatrix}, \quad C_2 = \begin{pmatrix} 0.05563438 \\ 0.99845140 \end{pmatrix}$$

c.

$$\begin{aligned}
 & \frac{1}{2} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ a & 1+b \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ 2 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ a & 1-b \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ 2 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ a & 1-b \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ 2 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ a & 1+b \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ 2 \end{pmatrix} \\
 & = \frac{1}{2\sqrt{2}} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ a & 1+b \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ 2 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ a & 1-b \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ 2 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ a & 1-b \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ 2 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ a & 1+b \end{pmatrix} \begin{pmatrix} \frac{1}{2} \\ 2 \end{pmatrix} \quad (\quad - \quad) \\
 & = \frac{1}{\sqrt{2}} (a \quad 1 \quad 1 - b \quad 2 \quad 2) \quad (\quad - \quad) \\
 & = a \begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix} - b \begin{vmatrix} 2 & 2 \\ 2 & 2 \end{vmatrix}.
 \end{aligned}$$

d. The third configuration $|1 \ 2 \rangle = \frac{1}{\sqrt{2}}[|1 \ 2 \rangle - |1 \ 2 \rangle]$,

Adding this configuration to the previous 2x2 CI results in the following 3x3 'full' CI:

$$H = \begin{matrix}
 \langle 1 \ 2 | H | 1 \ 2 \rangle & \langle 1 \ 2 | H | 2 \ 2 \rangle & \langle 1 \ 2 | H | 1 \ 2 \rangle \\
 \langle 2 \ 2 | H | 1 \ 2 \rangle & \langle 2 \ 2 | H | 2 \ 2 \rangle & \langle 2 \ 2 | H | 1 \ 2 \rangle \\
 \langle 1 \ 2 | H | 1 \ 2 \rangle & \langle 2 \ 2 | H | 1 \ 2 \rangle & \langle 1 \ 2 | H | 1 \ 2 \rangle
 \end{matrix}$$

$$\begin{aligned}
& \begin{matrix} 2h_{11} + g_{1111} & g_{1122} & \frac{1}{\sqrt{2}}[2h_{12} + 2g_{2111}] \\ g_{1122} & 2h_{22} + g_{2222} & \frac{1}{\sqrt{2}}[2h_{12} + 2g_{2221}] \\ \frac{1}{\sqrt{2}}[2h_{12} + 2g_{2111}] & \frac{1}{\sqrt{2}}[2h_{12} + 2g_{2221}] & h_{11} + h_{22} + g_{2121} + g_{2211} \end{matrix} \\
= &
\end{aligned}$$

Evaluating the new matrix elements:

$$H_{13} = H_{31} = \sqrt{2} * (-0.1953882 + 0.1953881) = 0.0$$

$$H_{23} = H_{32} = \sqrt{2} * (-0.1953882 + 0.004626) = -0.269778$$

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

$$= -3.198733$$

$$\begin{aligned}
& \begin{matrix} -4.272100 & 0.126170 & 0.0 \\ 0.126170 & -2.014800 & -0.269778 \\ 0.0 & -0.269778 & -3.198733 \end{matrix} \\
= &
\end{aligned}$$

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

$$\begin{aligned}
& \begin{matrix} -0.99825280 & -0.02605343 & -0.05302767 \\ 0.05732290 & -0.20969283 & -0.97608540 \\ 0.01431085 & -0.97742000 & 0.21082004 \end{matrix} \\
C_1 = & \quad , C_2 = \quad , C_3 =
\end{aligned}$$

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:

$$H_z = \begin{matrix} & \langle 1^2 | z | 1^2 \rangle & \langle 1^2 | z | 2^2 \rangle & \langle 1^2 | z | 1^2 2 \rangle \\ \langle 2^2 | z | 1^2 \rangle & & & \\ \langle 1^2 2 | z | 1^2 \rangle & \langle 2^2 | z | 1^2 \rangle & & \langle 1^2 2 | z | 1^2 \rangle \end{matrix}$$

$$= \begin{matrix} 2z_{11} & 0 & \frac{1}{\sqrt{2}}[2z_{12}] \\ 0 & 2z_{22} & \frac{1}{\sqrt{2}}[2z_{12}] \\ \frac{1}{\sqrt{2}}[2z_{12}] & \frac{1}{\sqrt{2}}[2z_{12}] & z_{11} + z_{22} \end{matrix}$$

$$= \begin{matrix} 0.233054 & 0 & -0.769629 \\ 0 & 2.982346 & -0.769629 \\ -0.769629 & -0.769629 & 1.607700 \end{matrix}$$

Now, $\langle 1^2 | z | 2^2 \rangle = C_1^T H_z C_2$, (this can be accomplished with the program UTMATU)

$$\begin{array}{r}
-0.99825280 \quad \mathbf{T} \quad 0.233054 \quad 0 \quad -0.769629 \quad -0.02605343 \\
= \quad 0.05732290 \quad \quad \quad 0 \quad 2.982346 \quad -0.769629 \quad -0.20969283 \\
\quad 0.01431085 \quad \quad -0.769629 \quad -0.769629 \quad 1.607700 \quad -0.97742000 \\
= -.757494
\end{array}$$

and, $\langle 1|z|3\rangle = C_1^T H_z C_3$

$$\begin{array}{r}
-0.99825280 \quad \mathbf{T} \quad 0.233054 \quad 0 \quad -0.769629 \quad -0.05302767 \\
= \quad 0.05732290 \quad \quad \quad 0 \quad 2.982346 \quad -0.769629 \quad -0.97608540 \\
\quad 0.01431085 \quad \quad -0.769629 \quad -0.769629 \quad 1.607700 \quad 0.21082004 \\
= 0.014322
\end{array}$$

g. Using the converged coefficients the orbital energies obtained from solving the Fock equations are $\epsilon_1 = -1.656258$ and $\epsilon_2 = -0.228938$. The resulting expression for the PT first-order wavefunction becomes:

$$|1^2\rangle^{(1)} = -\frac{g_{2211}}{2(\epsilon_2 - \epsilon_1)} |2^2\rangle$$

$$|1^2\rangle^{(1)} = -\frac{0.126170}{2(-0.228938 + 1.656258)} |2^2\rangle$$

$$|1^2\rangle^{(1)} = -0.0441982 |2^2\rangle$$

h. As you can see from part c., the matrix element $\langle 1^2 | H | 1^2 \rangle = 0$ (this is also a result of the Brillouin theorem) and hence this configuration does not enter into the first-order wavefunction.

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

$$\sqrt{[1 + (0.0441982)^2]} = 1.0009762$$

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

In the 2x2 CI we obtained:

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

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

$$E^{(2)} = -\frac{|g_{2211}|^2}{2(\epsilon_2 - \epsilon_1)} = -\frac{0.126170^2}{2(-0.228938 + 1.656258)}$$

$$= -0.005576 \text{ au}$$

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

$$-4.279131 - (-4.272102) = -0.007029 \text{ au}$$

43. STO total energy: -2.8435283

STO3G total energy -2.8340561

3-21G total energy -2.8864405

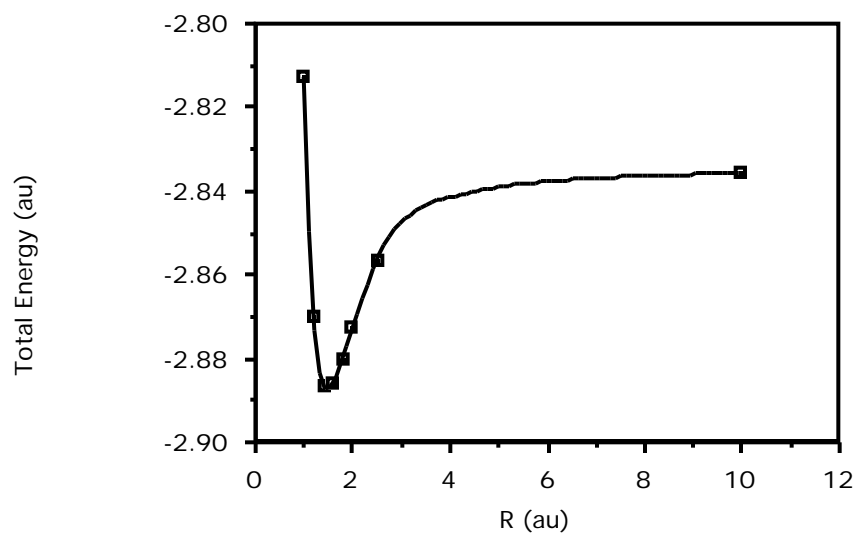
The STO3G orbitals were generated as a best fit of 3 primitive Gaussians (giving 1 CGTO) to the STO. So, STO3G can at best reproduce the STO result. The 3-21G orbitals are more flexible since there are 2 CGTOs per atom. This gives 4 orbitals (more parameters to optimize) and a lower total energy.

44.

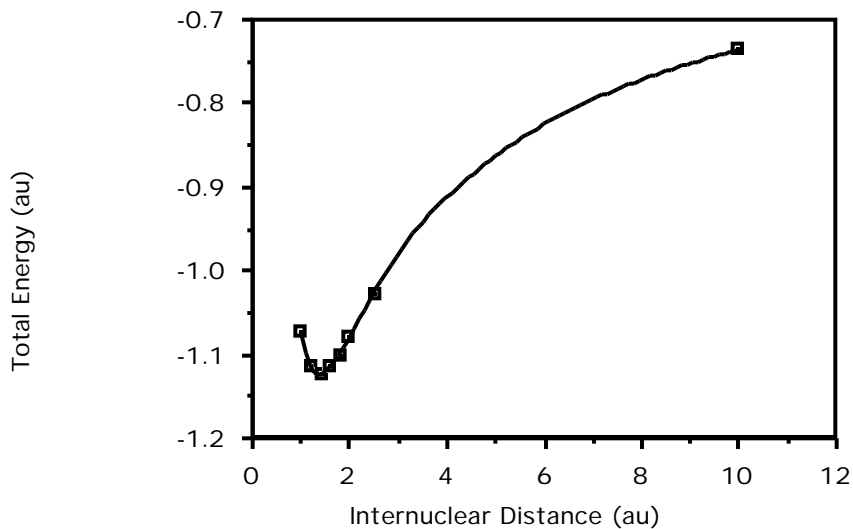
R	HeH ⁺ Energy	H ₂ Energy
1.0	-2.812787056	-1.071953297
1.2	-2.870357513	-1.113775015

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:

-1.003571E+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 $\text{He} + \text{H}^+$).

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

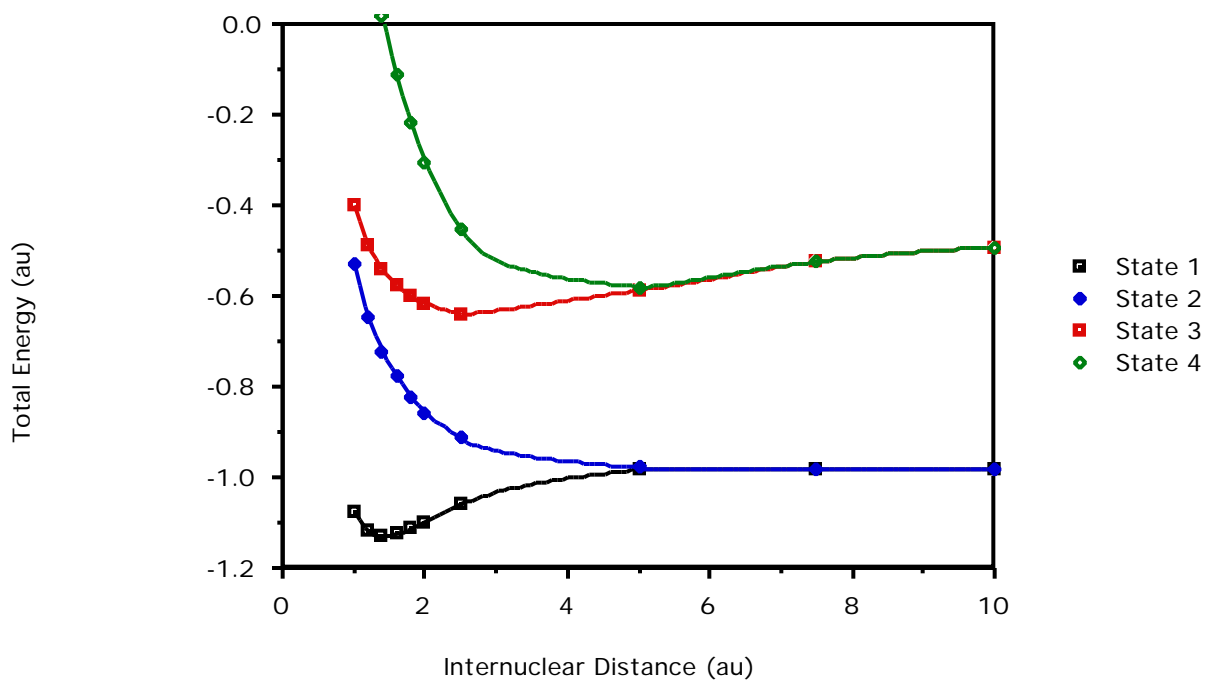
-.2458041E+00	-.1456223E+00	.1137235E+01	.1137825E+01
.1977649E+00	-.1978204E+00	.1006458E+01	-.7903225E+00
.5632566E+00	-.5628273E+00	-.8179120E+00	.6424941E+00
.1976312E+00	.1979216E+00	.7902887E+00	.1006491E+01
.5629326E+00	.5631776E+00	-.6421731E+00	-.8181460E+00

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	¹ g ⁺	³ u ⁺	¹ u ⁺	¹ g ⁺
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 H_2 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
-------------	-----------	-----------	-----------	----------

$ 1_g 1_g\rangle$	0.99695	0.00000	0.00000	0.07802
$ 1_g 1_u\rangle$	0.00000	0.70711	0.70711	0.00000
$ 1_g 1_u\rangle$	0.00000	0.70711	-0.70711	0.00000
$ 1_u 1_u\rangle$	-0.07802	0.00000	0.00000	0.99695

This shows, as expected, the mixing of the first 1_g^+ (1_g^2) and the 2nd 1_g^+ (1_u^2) determinants in the first and fourth states, and the

$$^3 u^+ = \left(\frac{1}{\sqrt{2}} (|1_g 1_u\rangle + |1_g 1_u\rangle) \right),$$

$$\text{and } ^1 u^+ = \left(\frac{1}{\sqrt{2}} (|1_g 1_u\rangle - |1_g 1_u\rangle) \right)$$

states as the second and third states.

Also notice that the first 1_g^+ state has coefficients (0.99695 - 0.07802) (note specifically the + - combination) and the second 1_g^+ 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 $1s^2 2s^2 2p^5$ 2P ground electronic states that are split by spin-orbit coupling into $^2P_{3/2}$ and $^2P_{1/2}$ 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 $k(500 \text{ K})$, so $0.05/kT = 500/T$, hence

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

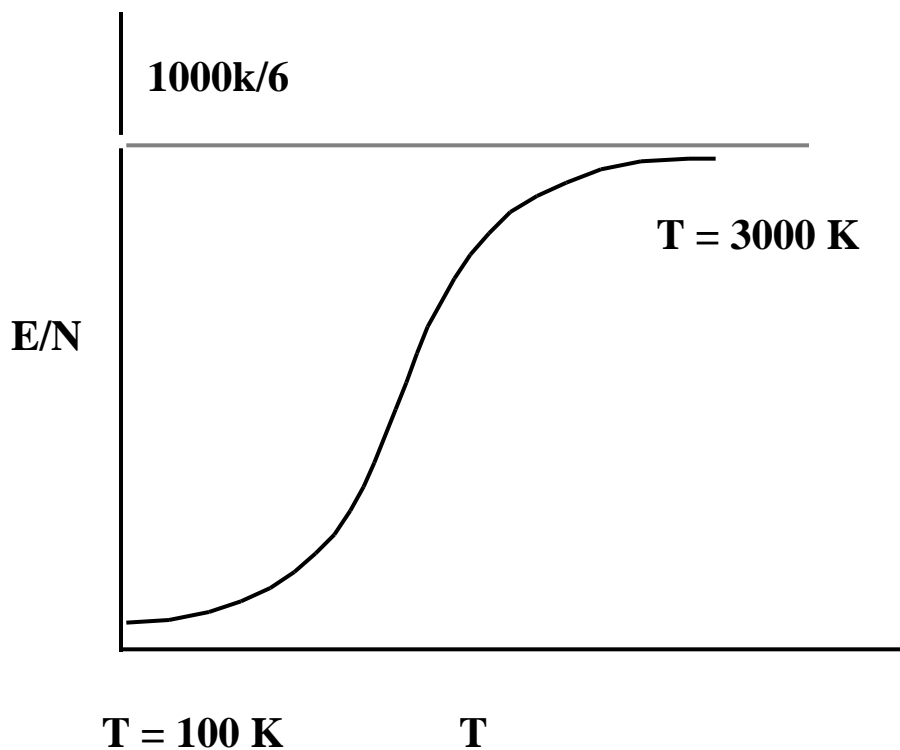
b.

$$Q = q^N/N!$$

so, $\ln Q = N \ln q - \ln N!$

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

c. Using the fact that $kT=0.03\text{eV}$ at $T=300^\circ\text{K}$, make a (qualitative) graph of \bar{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

$$q_t \sim 10^8, q_r \sim 10^2, q_v \sim 1,$$

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

48.

Constructing the Slater determinant corresponding to the "state" $1s(1)1s(2)$ with the rows labeling the orbitals and the columns labeling the electron gives:

$$\begin{aligned}
 |1s \ 1s| &= \frac{1}{\sqrt{2!}} \begin{vmatrix} 1s(1) & 1s(2) \\ 1s(1) & 1s(2) \end{vmatrix} \\
 &= \frac{1}{\sqrt{2}} (1s(1)1s(2) - 1s(1)1s(2)) \\
 &= 0
 \end{aligned}$$

49.

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

$$\begin{aligned}
 S_- \ ^3S(S=1, M_S=1) &= \sqrt{1(1+1) - 1(1-1)} \hbar \ ^3S(S=1, M_S=0) \\
 &= \hbar \sqrt{2} \ ^3S(S=1, M_S=0) \\
 &= (S_-(1) + S_-(2)) |1s \ 2s \uparrow \uparrow\rangle \\
 &= S_-(1) |1s \ 2s \uparrow \uparrow\rangle + S_-(2) |1s \ 2s \uparrow \uparrow\rangle \\
 &= \hbar \sqrt{\frac{1}{2} \frac{1}{2} + 1} \left(-\frac{1}{2} \frac{1}{2} - 1 \right) |1s \ 2s \uparrow \uparrow\rangle \\
 &\quad + \hbar \sqrt{\frac{1}{2} \frac{1}{2} + 1} \left(-\frac{1}{2} \frac{1}{2} - 1 \right) |1s \ 2s \uparrow \uparrow\rangle
 \end{aligned}$$

$$= \hbar (|1s \uparrow 2s \uparrow\rangle + |1s \uparrow 2s \downarrow\rangle)$$

So, $\hbar\sqrt{2} \ ^3S(S=1, M_S=0) = \hbar (|1s \uparrow 2s \uparrow\rangle + |1s \uparrow 2s \downarrow\rangle)$

$$^3S(S=1, M_S=0) = \frac{1}{\sqrt{2}} (|1s \uparrow 2s \uparrow\rangle + |1s \uparrow 2s \downarrow\rangle)$$

The three triplet states are then:

$$^3S(S=1, M_S=1) = |1s \uparrow 2s \uparrow\rangle,$$

$$^3S(S=1, M_S=0) = \frac{1}{\sqrt{2}} (|1s \uparrow 2s \uparrow\rangle + |1s \uparrow 2s \downarrow\rangle), \text{ and}$$

$$^3S(S=1, M_S=-1) = |1s \uparrow 2s \downarrow\rangle.$$

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

$$^1S(S=0, M_S=0) = \frac{1}{\sqrt{2}} (|1s \uparrow 2s \uparrow\rangle - |1s \uparrow 2s \downarrow\rangle).$$

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

$$\begin{aligned} S_z |1s \uparrow 2s \uparrow\rangle &= (S_z(1) + S_z(2)) |1s \uparrow 2s \uparrow\rangle \\ &= S_z(1)|1s \uparrow 2s \uparrow\rangle + S_z(2)|1s \uparrow 2s \uparrow\rangle \\ &= \hbar \frac{1}{2} |1s \uparrow 2s \uparrow\rangle + \hbar \frac{1}{2} |1s \uparrow 2s \uparrow\rangle \\ &= \hbar |1s \uparrow 2s \uparrow\rangle \end{aligned}$$

$$\begin{aligned} S^2 |1s \uparrow 2s \uparrow\rangle &= (S \cdot S + S_z^2 + \hbar S_z) |1s \uparrow 2s \uparrow\rangle \\ &= S \cdot S |1s \uparrow 2s \uparrow\rangle + S_z^2 |1s \uparrow 2s \uparrow\rangle + \hbar S_z |1s \uparrow 2s \uparrow\rangle \\ &= 0 + \hbar^2 |1s \uparrow 2s \uparrow\rangle + \hbar^2 |1s \uparrow 2s \uparrow\rangle \\ &= 2\hbar^2 |1s \uparrow 2s \uparrow\rangle \end{aligned}$$

$$\begin{aligned}
S_z \frac{1}{\sqrt{2}} (|1s \ 2s \uparrow + |1s \ 2s \downarrow\rangle) &= (S_z(1) + S_z(2)) \frac{1}{\sqrt{2}} (|1s \ 2s \uparrow + |1s \ 2s \downarrow\rangle) \\
&= \frac{1}{\sqrt{2}} (S_z(1) + S_z(2)) |1s \ 2s \uparrow \\
&\quad + \frac{1}{\sqrt{2}} (S_z(1) + S_z(2)) |1s \ 2s \downarrow \\
&= \frac{1}{\sqrt{2}} \left(\hbar \cdot \frac{1}{2} + \hbar \cdot \frac{1}{2} \right) |1s \ 2s \uparrow \\
&\quad + \frac{1}{\sqrt{2}} \left(\hbar \cdot \frac{1}{2} + \hbar \cdot \frac{1}{2} \right) |1s \ 2s \downarrow \\
&= 0 \hbar \frac{1}{\sqrt{2}} (|1s \ 2s \uparrow + |1s \ 2s \downarrow\rangle)
\end{aligned}$$

$$\begin{aligned}
S^2 \frac{1}{\sqrt{2}} (|1s \ 2s \uparrow + |1s \ 2s \downarrow\rangle) &= (S \cdot S_+ + S_z^2 + \hbar S_z) \frac{1}{\sqrt{2}} (|1s \ 2s \uparrow + |1s \ 2s \downarrow\rangle) \\
&= S \cdot S_+ \frac{1}{\sqrt{2}} (|1s \ 2s \uparrow + |1s \ 2s \downarrow\rangle) \\
&= \frac{1}{\sqrt{2}} (S \cdot (S_+(1) + S_+(2)) |1s \ 2s \uparrow + S \cdot (S_+(1) + S_+(2)) |1s \ 2s \downarrow) \\
&= \frac{1}{\sqrt{2}} (S \cdot \hbar |1s \ 2s \uparrow + S \cdot \hbar |1s \ 2s \downarrow) \\
&= 2 \hbar \frac{1}{\sqrt{2}} (S \cdot (1) + S \cdot (2)) |1s \ 2s \downarrow\rangle \\
&= 2 \hbar \frac{1}{\sqrt{2}} (\hbar |1s \ 2s \uparrow + \hbar |1s \ 2s \downarrow) \\
&= 2 \hbar^2 \frac{1}{\sqrt{2}} (|1s \ 2s \uparrow + |1s \ 2s \downarrow) \\
S_z |1s \ 2s \uparrow &= (S_z(1) + S_z(2)) |1s \ 2s \uparrow \\
&= S_z(1) |1s \ 2s \uparrow + S_z(2) |1s \ 2s \uparrow
\end{aligned}$$

$$= \hbar \frac{1}{\sqrt{2}} |1s \uparrow 2s \downarrow\rangle + \hbar \frac{1}{\sqrt{2}} |1s \downarrow 2s \uparrow\rangle$$

$$= -\hbar |1s \uparrow 2s \downarrow\rangle$$

$$S^2 |1s \uparrow 2s \downarrow\rangle = (S_+ S_- + S_z^2 - \hbar S_z) |1s \uparrow 2s \downarrow\rangle$$

$$= S_+ S_- |1s \uparrow 2s \downarrow\rangle + S_z^2 |1s \uparrow 2s \downarrow\rangle - \hbar S_z |1s \uparrow 2s \downarrow\rangle$$

$$= 0 + \hbar^2 |1s \uparrow 2s \downarrow\rangle + \hbar^2 |1s \uparrow 2s \downarrow\rangle$$

$$= 2\hbar^2 |1s \uparrow 2s \downarrow\rangle$$

$$S_z \frac{1}{\sqrt{2}} (|1s \uparrow 2s \downarrow\rangle - |1s \downarrow 2s \uparrow\rangle) = (S_z(1) + S_z(2)) \frac{1}{\sqrt{2}} (|1s \uparrow 2s \downarrow\rangle - |1s \downarrow 2s \uparrow\rangle)$$

$$= \frac{1}{\sqrt{2}} (S_z(1) + S_z(2)) |1s \uparrow 2s \downarrow\rangle$$

$$- \frac{1}{\sqrt{2}} (S_z(1) + S_z(2)) |1s \downarrow 2s \uparrow\rangle$$

$$= \frac{1}{\sqrt{2}} \left(\hbar \frac{1}{2} + \hbar \frac{1}{2} \right) |1s \uparrow 2s \downarrow\rangle$$

$$- \frac{1}{\sqrt{2}} \left(\hbar \frac{1}{2} + \hbar \frac{1}{2} \right) |1s \downarrow 2s \uparrow\rangle$$

$$= 0 \hbar \frac{1}{\sqrt{2}} (|1s \uparrow 2s \downarrow\rangle - |1s \downarrow 2s \uparrow\rangle)$$

$$S^2 \frac{1}{\sqrt{2}} (|1s \uparrow 2s \downarrow\rangle - |1s \downarrow 2s \uparrow\rangle) = (S_- S_+ + S_z^2 + \hbar S_z) \frac{1}{\sqrt{2}} (|1s \uparrow 2s \downarrow\rangle - |1s \downarrow 2s \uparrow\rangle)$$

$$= S_- S_+ \frac{1}{\sqrt{2}} (|1s \uparrow 2s \downarrow\rangle - |1s \downarrow 2s \uparrow\rangle)$$

$$= \frac{1}{\sqrt{2}} (S_- (S_+(1) + S_+(2)) |1s \uparrow 2s \downarrow\rangle - S_- (S_+(1) + S_+(2)) |1s \downarrow 2s \uparrow\rangle)$$

$$= \frac{1}{\sqrt{2}} (S_- \hbar |1s \uparrow 2s \downarrow\rangle - S_- \hbar |1s \downarrow 2s \uparrow\rangle)$$

$$\begin{aligned}
&= 0 \hbar \frac{1}{\sqrt{2}}(S_-(1) + S_-(2))|1s \ 2s \rangle \\
&= 0 \hbar \frac{1}{\sqrt{2}}(\hbar|1s \ 2s \rangle - \hbar|1s \ 2s \rangle) \\
&= 0 \hbar^2 \frac{1}{\sqrt{2}}(|1s \ 2s \rangle - |1s \ 2s \rangle)
\end{aligned}$$

50.

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

- 1 $(M_L=2)$; one state ($M_S=0$),
- 1 $(M_L=-2)$; one state ($M_S=0$),
- 1 $(M_L=0)$; one state ($M_S=0$), and
- 3 $(M_L=0)$; three states ($M_S=1, 0$, and -1).

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

- 1 $(M_L=2)$; $|1 \ 1 \ 1 \ 1 \rangle$
- 1 $(M_L=-2)$; $|1 \ -1 \ -1 \ -1 \rangle$
- 1 $(M_L=0)$; $\frac{1}{\sqrt{2}}(|1 \ 1 \ -1 \ -1 \rangle - |1 \ -1 \ 1 \ 1 \rangle)$
- 3 $(M_L=0, M_S=1)$; $|1 \ 1 \ -1 \ 1 \rangle$
- 3 $(M_L=0, M_S=0)$; $\frac{1}{\sqrt{2}}(|1 \ 1 \ -1 \ 1 \rangle + |1 \ -1 \ 1 \ 1 \rangle)$

$$^3 (M_L=0, M_S=-1); | 1 \quad -1 |$$

51.

We can conveniently couple another s electron to the states generated from the $1s^1 2s^1$ configuration:

$^3S(L=0, S=1)$ with $3s^1(L=0, S=\frac{1}{2})$ giving:

$L=0, S=\frac{3}{2}, \frac{1}{2}$; 4S (4 states) and 2S (2 states).

$^1S(L=0, S=0)$ with $3s^1(L=0, S=\frac{1}{2})$ giving:

$L=0, S=\frac{1}{2}$; 2S (2 states).

Constructing a "box" for this case would yield:

M_L	0
M_S	
$\frac{3}{2}$	$ 1s\ 2s\ 3s\rangle$
$\frac{1}{2}$	$ 1s\ 2s\ 3s\rangle, 1s\ 2s\ 3s\rangle, 1s\ 2s\ 3s\rangle$

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

$${}^4S(S=\frac{3}{2}, M_S=\frac{3}{2}): |1s\ 2s\ 3s\rangle$$

$${}^4S(S=\frac{3}{2}, M_S=-\frac{3}{2}): |1s\ 2s\ 3s\rangle$$

Applying S_- to ${}^4S(S=\frac{3}{2}, M_S=\frac{3}{2})$ yields:

$$\begin{aligned} S_- {}^4S(S=\frac{3}{2}, M_S=\frac{3}{2}) &= h \sqrt{\frac{3}{2}(\frac{3}{2}+1) - \frac{3}{2}(\frac{3}{2}-1)} {}^4S(S=\frac{3}{2}, M_S=\frac{1}{2}) \\ &= h \sqrt{3} {}^4S(S=\frac{3}{2}, M_S=\frac{1}{2}) \end{aligned}$$

$$S_- |1s\ 2s\ 3s\rangle = h (|1s\ 2s\ 3s\rangle + |1s\ 2s\ 3s\rangle + |1s\ 2s\ 3s\rangle)$$

$$\text{So, } {}^4S(S=\frac{3}{2}, M_S=\frac{1}{2}) = \frac{1}{\sqrt{3}} (|1s\ 2s\ 3s\rangle + |1s\ 2s\ 3s\rangle + |1s\ 2s\ 3s\rangle)$$

Applying S_+ to ${}^4S(S=\frac{3}{2}, M_S=-\frac{3}{2})$ yields:

$$\begin{aligned} S_+ {}^4S(S=\frac{3}{2}, M_S=-\frac{3}{2}) &= h \sqrt{\frac{3}{2}(\frac{3}{2}+1) - \frac{3}{2}(-\frac{3}{2}+1)} {}^4S(S=\frac{3}{2}, M_S=-\frac{1}{2}) \\ &= h \sqrt{3} {}^4S(S=\frac{3}{2}, M_S=-\frac{1}{2}) \end{aligned}$$

$$S_+|1s \ 2s \ 3s \rangle = h (|1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle)$$

$$\text{So, } ^4S(S=\frac{3}{2}, M_S=-\frac{1}{2}) = \frac{1}{\sqrt{3}} (|1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle)$$

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:

$$^2S(S=\frac{1}{2}, M_S=\frac{1}{2}) = \frac{1}{\sqrt{6}} (|1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle - 2|1s \ 2s \ 3s \rangle)$$

$$^2S(S=\frac{1}{2}, M_S=\frac{1}{2}) = \frac{1}{\sqrt{2}} (|1s \ 2s \ 3s \rangle - |1s \ 2s \ 3s \rangle + 0|1s \ 2s \ 3s \rangle)$$

$$^2S(S=\frac{1}{2}, M_S=-\frac{1}{2}) = \frac{1}{\sqrt{6}} (|1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle - 2|1s \ 2s \ 3s \rangle)$$

$$^2S(S=\frac{1}{2}, M_S=-\frac{1}{2}) = \frac{1}{\sqrt{3}} (|1s \ 2s \ 3s \rangle - |1s \ 2s \ 3s \rangle + 0|1s \ 2s \ 3s \rangle)$$

52.

As illustrated in problem 24, a p² configuration (two equivalent p electrons) gives rise to the term symbols: ³P, ¹D, and ¹S. Coupling an additional electron (3d¹) to this p² configuration will give the desired 1s²2s²2p²3d¹ term symbols:

³P(L=1, S=1) with ²D(L=2, S= $\frac{1}{2}$) generates;

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

$^1D(L=2, S=0)$ with $^2D(L=2, S=\frac{1}{2})$ generates;

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

$^1S(L=0, S=0)$ with $^2D(L=2, S=\frac{1}{2})$ generates;

$L=2$ and $S=\frac{1}{2}$ with term symbol 2D .

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

(a.) zero (spin orbital) difference;

$$\begin{aligned} \langle F + G | &= \sum_i \langle i | f | i \rangle + \sum_{i>j} \langle i j | g | i j \rangle - \langle i j | g | j i \rangle \\ &= \sum_i f_{ii} + \sum_{i>j} (g_{ijij} - g_{ijji}) \end{aligned}$$

(b.) one (spin orbital) difference (p p');

$$\begin{aligned} \langle F + G | &= \langle p | f | p \rangle + \sum_{j p;p'} \langle p j | g | p' j \rangle - \langle p j | g | j p' \rangle \\ &= f_{pp} + \sum_{j p;p'} (g_{pj p' j} - g_{pj p' j}) \end{aligned}$$

(c.) two (spin orbital) differences (p p' and q q');

$$\begin{aligned} \langle F + G | &= \langle p q | g | p' q' \rangle - \langle p q | g | q' p' \rangle \\ &= g_{pq p' q'} - g_{pq q' p'} \end{aligned}$$

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

$$\langle F + G | = 0$$

$$i. {}^3P(M_L=1, M_S=1) = |p_1 p_0 \uparrow|$$

$$\langle |p_1 p_0 \uparrow | H | p_1 p_0 \uparrow \rangle = \langle |10 \uparrow | H | 10 \uparrow \rangle$$

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

$$\langle |10 \uparrow | H | 10 \uparrow \rangle = f_{11} + f_{00} + g_{1010} - g_{1001}$$

$$ii. {}^3P(M_L=0, M_S=0) = \frac{1}{\sqrt{2}}(|p_1 p_{-1} \uparrow \downarrow| + |p_1 p_{-1} \downarrow \uparrow|)$$

$$\langle {}^3P(M_L=0, M_S=0) | H | {}^3P(M_L=0, M_S=0) \rangle$$

$$= \frac{1}{2} (\langle |p_1 p_{-1} \uparrow \downarrow | H | p_1 p_{-1} \uparrow \downarrow \rangle + \langle |p_1 p_{-1} \downarrow \uparrow | H | p_1 p_{-1} \downarrow \uparrow \rangle \\ + \langle |p_1 p_{-1} \uparrow \downarrow | H | p_1 p_{-1} \downarrow \uparrow \rangle + \langle |p_1 p_{-1} \downarrow \uparrow | H | p_1 p_{-1} \uparrow \downarrow \rangle)$$

Evaluating each matrix element gives:

$$\langle |p_1 p_{-1} \uparrow \downarrow | H | p_1 p_{-1} \uparrow \downarrow \rangle = f_{1 \uparrow 1 \downarrow} + f_{-1 \uparrow -1 \downarrow} + g_{1 \uparrow -1 \downarrow 1 \uparrow -1 \downarrow} - g_{1 \uparrow -1 \downarrow -1 \uparrow 1 \downarrow} \quad (\text{SCa})$$

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

$$\langle |p_1 p_{-1} \downarrow \uparrow | H | p_1 p_{-1} \downarrow \uparrow \rangle = g_{1 \downarrow -1 \uparrow 1 \downarrow -1 \uparrow} - g_{1 \downarrow -1 \uparrow -1 \downarrow 1 \uparrow} \quad (\text{SCc})$$

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

$$\langle |p_1 p_{-1} \uparrow \downarrow | H | p_1 p_{-1} \downarrow \uparrow \rangle = g_{1 \uparrow -1 \downarrow 1 \uparrow -1 \downarrow} - g_{1 \uparrow -1 \downarrow -1 \uparrow 1 \downarrow} \quad (\text{SCc})$$

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

$$\langle |p_1 p_{-1} \downarrow \uparrow | H | p_1 p_{-1} \downarrow \uparrow \rangle = f_{1 \downarrow 1 \uparrow} + f_{-1 \downarrow -1 \uparrow} + g_{1 \downarrow -1 \uparrow 1 \downarrow -1 \uparrow} - g_{1 \downarrow -1 \uparrow -1 \downarrow 1 \uparrow} \quad (\text{SCa})$$

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

Substitution of these expressions give:

$$\langle {}^3P(M_L=0, M_S=0) | H | {}^3P(M_L=0, M_S=0) \rangle$$

$$= \frac{1}{2} (f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-11} - g_{1-1-11}$$

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

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

iii. ${}^1S(M_L=0, M_S=0); \frac{1}{\sqrt{3}}(|p_0 p_0 \rangle - |p_1 p_{-1} \rangle - |p_{-1} p_1 \rangle)$

$$\langle {}^1S(M_L=0, M_S=0) | H | {}^1S(M_L=0, M_S=0) \rangle$$

$$= \frac{1}{3} (\langle p_0 p_0 | H | p_0 p_0 \rangle - \langle p_0 p_0 | H | p_1 p_{-1} \rangle$$

$$- \langle p_0 p_0 | H | p_{-1} p_1 \rangle - \langle p_1 p_{-1} | H | p_0 p_0 \rangle$$

$$+ \langle p_1 p_{-1} | H | p_1 p_{-1} \rangle + \langle p_1 p_{-1} | H | p_{-1} p_1 \rangle$$

$$- \langle p_{-1} p_1 | H | p_0 p_0 \rangle + \langle p_{-1} p_1 | H | p_1 p_{-1} \rangle$$

$$+ \langle p_{-1} p_1 | H | p_{-1} p_1 \rangle)$$

Evaluating each matrix element gives:

$$\langle p_0 p_0 | H | p_0 p_0 \rangle = f_{00} + f_{00} + g_{0000} - g_{0000} \quad (\text{SCa})$$

$$= f_{00} + f_{00} + g_{0000} - 0$$

$$\langle p_0 p_0 | H | p_1 p_{-1} \rangle = \langle p_1 p_{-1} | H | p_0 p_0 \rangle$$

$$= g_{001-1} - g_{00-11} \quad (\text{SCc})$$

$$= g_{001-1} - 0$$

$$\langle |p_0 \ p_0 \rangle |H| |p_{-1} \ p_1 \rangle = \langle |p_{-1} \ p_1 \rangle |H| |p_0 \ p_0 \rangle$$

$$= g_{0 \ 0 \ -1 \ 1} - g_{0 \ 0 \ 1 \ -1} \quad (\text{SCc})$$

$$= g_{00-11} - 0$$

$$\langle |p_1 \ p_{-1} \rangle |H| |p_1 \ p_{-1} \rangle = f_{1 \ 1} + f_{-1 \ -1} + g_{1 \ -1 \ 1 \ -1} - g_{1 \ -1 \ -1 \ 1} \quad (\text{SCa})$$

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

$$\langle |p_1 \ p_{-1} \rangle |H| |p_{-1} \ p_1 \rangle = \langle |p_{-1} \ p_1 \rangle |H| |p_1 \ p_{-1} \rangle$$

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

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

$$\langle |p_{-1} \ p_1 \rangle |H| |p_{-1} \ p_1 \rangle = f_{-1 \ -1} + f_{1 \ 1} + g_{-1 \ 1 \ -1 \ 1} - g_{-1 \ 1 \ 1 \ -1} \quad (\text{SCa})$$

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

Substitution of these expressions give:

$$\langle {}^1S(M_L=0, M_S=0) | H | {}^1S(M_L=0, M_S=0) \rangle$$

$$= \frac{1}{3} (f_{00} + f_{00} + g_{0000} - g_{001-1} - g_{00-11} - g_{001-1} + f_{11} + f_{-1-1}$$

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

$$= \frac{1}{3} (2f_{00} + 2f_{11} + 2f_{-1-1} + g_{0000} - 4g_{001-1} + 2g_{1-11-1} + 2g_{1-1-11})$$

$$\text{iv. } {}^1D(M_L=0, M_S=0) = \frac{1}{\sqrt{6}} (2|p_0 \ p_0 \rangle + |p_1 \ p_{-1} \rangle + |p_{-1} \ p_1 \rangle)$$

Evaluating $\langle {}^1D(M_L=0, M_S=0) | H | {}^1D(M_L=0, M_S=0) \rangle$ 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).

$$\begin{aligned}
 & \langle {}^1D(M_L=0, M_S=0) | H | {}^1D(M_L=0, M_S=0) \rangle \\
 &= \frac{1}{6} (4f_{00} + 4f_{00} + 4g_{0000} + 2g_{001-1} + 2g_{00-11} + 2g_{001-1} + f_{11} \\
 &\quad + f_{-1-1} + g_{1-11-1} + g_{1-1-11} + 2g_{00-11} + g_{1-1-11} + f_{-1-1} + f_{11} \\
 &\quad + g_{-11-11}) \\
 &= \frac{1}{6} (8f_{00} + 2f_{11} + 2f_{-1-1} + 4g_{0000} + 8g_{001-1} + 2g_{1-11-1} + 2g_{1-1-11})
 \end{aligned}$$

54.

i. ${}^1 (M_L=2, M_S=0) = | \begin{smallmatrix} 1 & 1 \\ 1 & 1 \end{smallmatrix} |$

$$\begin{aligned}
 & \langle {}^1 (M_L=2, M_S=0) | H | {}^1 (M_L=2, M_S=0) \rangle \\
 &= \langle | \begin{smallmatrix} 1 & 1 \\ 1 & 1 \end{smallmatrix} | H | \begin{smallmatrix} 1 & 1 \\ 1 & 1 \end{smallmatrix} | \rangle \\
 &= f_{11} + f_{11} + g_{1111} - g_{1111} \text{ (SCa)} \\
 &= f_{11} + f_{11} + g_{1111} - 0 \\
 &= 2f_{11} + g_{1111}
 \end{aligned}$$

$$\text{ii. } |^1 (M_L=0, M_S=0)\rangle = \frac{1}{\sqrt{2}}(|^1 1 \ -1 \rangle - |^1 1 \ -1 \rangle)$$

$$\begin{aligned} & \langle ^3 (M_L=0, M_S=0) | H | ^3 (M_L=0, M_S=0) \rangle \\ &= \frac{1}{2} (\langle ^1 1 \ -1 | H | ^1 1 \ -1 \rangle - \langle ^1 1 \ -1 | H | ^1 1 \ -1 \rangle \\ & \quad - \langle ^1 1 \ -1 | H | ^1 1 \ -1 \rangle + \langle ^1 1 \ -1 | H | ^1 1 \ -1 \rangle) \end{aligned}$$

Evaluating each matrix element gives:

$$\begin{aligned} \langle ^1 1 \ -1 | H | ^1 1 \ -1 \rangle &= f_{1 \ 1} + f_{-1 \ -1} + g_{1 \ -1 \ 1 \ -1} - g_{1 \ -1 \ -1 \ 1} \quad (\text{SCa}) \\ &= f_{11} + f_{-1-1} + g_{1-11-1} - 0 \end{aligned}$$

$$\begin{aligned} \langle ^1 1 \ -1 | H | ^1 1 \ -1 \rangle &= g_{1 \ -1 \ 1 \ -1} - g_{1 \ -1 \ -1 \ 1} \quad (\text{SCc}) \\ &= 0 - g_{1-1-11} \end{aligned}$$

$$\begin{aligned} \langle ^1 1 \ -1 | H | ^1 1 \ -1 \rangle &= g_{1 \ -1 \ 1 \ -1} - g_{1 \ -1 \ -1 \ 1} \quad (\text{SCc}) \\ &= 0 - g_{1-1-11} \end{aligned}$$

$$\begin{aligned} \langle ^1 1 \ -1 | H | ^1 1 \ -1 \rangle &= f_{1 \ 1} + f_{-1 \ -1} + g_{1 \ -1 \ 1 \ -1} - g_{1 \ -1 \ -1 \ 1} \quad (\text{SCa}) \\ &= f_{11} + f_{-1-1} + g_{1-11-1} - 0 \end{aligned}$$

Substitution of these expressions give:

$$\begin{aligned} & \langle ^3 (M_L=0, M_S=0) | H | ^3 (M_L=0, M_S=0) \rangle \\ &= \frac{1}{2} (f_{11} + f_{-1-1} + g_{1-11-1} + g_{1-1-11} + g_{1-1-11} + f_{11} + f_{-1-1} + g_{1-11-1}) \\ &= f_{11} + f_{-1-1} + g_{1-11-1} + g_{1-1-11} \end{aligned}$$

$$\text{iii. } |^3 (M_L=0, M_S=0)\rangle = \frac{1}{\sqrt{2}}(|^3 1 \ -1 \rangle + |^3 1 \ -1 \rangle)$$

$$\langle^3 (M_L=0, M_S=0) | H^3 | (M_L=0, M_S=0) \rangle$$

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

$$\langle | 1 \quad -1 | H | 1 \quad -1 | \rangle = g_{1 \quad -1 \quad 1 \quad -1} - g_{1 \quad -1 \quad -1 \quad 1} \quad (\text{SCc})$$

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

$$\langle | 1 \quad -1 | H | 1 \quad -1 | \rangle = g_{1 \quad -1 \quad 1 \quad -1} - g_{1 \quad -1 \quad -1 \quad 1} \quad (\text{SCc})$$

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

$$\langle | 1 \quad -1 | H | 1 \quad -1 | \rangle = f_{1 \quad 1} + f_{-1 \quad -1} + g_{1 \quad -1 \quad 1 \quad -1} - g_{1 \quad -1 \quad -1 \quad 1} \quad (\text{SCa})$$

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

Substitution of these expressions give:

$$\langle^3 (M_L=0, M_S=0) | H^3 | (M_L=0, M_S=0) \rangle$$

$$= \frac{1}{2} (f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-1-1} - g_{1-1-1-1} + f_{11} + f_{-1-1} + g_{1-11-1})$$

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

55.

The order of the answers is J, I, G, K, B, D, E, A, C, H, F

56.

$$p = N/(V-Nb) - N^2 a/(kTV^2)$$

$$\text{but } p/kT = (\ln Q / V)_{T,N}$$

so we can integrate to obtain $\ln Q$

$$\begin{aligned} \ln Q &= \int (p/kT) dV = \int [N/(V-Nb) - N^2 a/(kTV^2)] dV \\ &= N \ln(V-Nb) + N^2 a/kT (1/V) \end{aligned}$$

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 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 ($- \nabla V_{i,j}$) between all pairs of atoms. There are $1000 \times 999 / 2$ such pairs. So, to compute all the forces would require

$(1000 \times 999 / 2) \times 50$ FPOs = 2.5×10^7 FPOs. So, we will need

2.5×10^7 FPOs/step $\times 10^6$ steps/(100 FPOs per second)

= 2.5×10^5 seconds or about 70 hours.

h.

The graduate student is 10^8 times slower than the 100 Mflop computer, so it will take her/him 10^8 times as long, so 495×10^8 seconds or about 1570 years.

58.

First, Na has a 2S ground state term symbol whose degeneracy is $2S + 1 = 2$.

Na_2 has a 1 ground state whose degeneracy is 1.

The symmetry number for Na_2 is $\sigma = 2$.

The D_0 value given is $17.3 \text{ kcal mol}^{-1}$.

The K_p equilibrium constant would be given in terms of partial pressures as (and then using $pV=NkT$)

$$K_p = \frac{p_{\text{Na}}^2}{p_{\text{Na}_2}} = (kT)^{-1} \frac{(q_{\text{Na}}/V)^2}{(q_{\text{Na}_2}/V)}$$

in terms of the partition functions.

a.

$$q_{\text{Na}} = (2 m kT/h^2)^{3/2} V q_{\text{el}}$$

$$q_{\text{Na}_2} = (2 m' kT/h^2)^{3/2} V (8^2 I kT/h^2)^{1/2} [\exp(-h^2/2kT) (1 - \exp(-h^2/kT))]^{-1} \exp(D_e/kT)$$

We can combine the D_e and the $-h^2/2kT$ to obtain the D_0 which is what we were given.

b. For Na (I will use cgs units in all cases):

$$\begin{aligned} q/V &= (2 \cdot 23 \cdot 1.66 \times 10^{-24} \cdot 1.38 \times 10^{-16} \cdot 1000)^{3/2} \cdot 2 \\ &= (6.54 \times 10^{26}) \times 2 = 1.31 \times 10^{27} \end{aligned}$$

For Na_2 :

$$\begin{aligned} q/N &= 2^{3/2} \times (6.54 \times 10^{26}) (1000/0.221) (1/2) (1 - \exp(-229/1000))^{-1} \exp(D_0/kT) \\ &= 1.85 \times 10^{27} (2.26 \times 10^3) (4.88) (5.96 \times 10^3) \\ &= 1.22 \times 10^{35} \end{aligned}$$

So,

$$\begin{aligned} K_p &= [1.22 \times 10^{35}] / [(1.38 \times 10^{-16})(1000) (1.72 \times 10^{54})] \\ &= 0.50 \times 10^{-6} \text{ dynes cm}^{-2} = 0.50 \text{ atm}^{-1}. \end{aligned}$$

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

$$k_{\text{rate}} = (kT/h) \exp(-E^*/kT) [q^{\text{TS}}/V] / [(q_{\text{NO}}/V) (q_{\text{Cl}_2}/V)]$$

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:

$$[q^{\text{TS}}/V]/[(q_{\text{NO}}/V) (q_{\text{Cl}_2}/V)]$$

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:

$$k_{\text{ad}}/k_{\text{gas}} = (q_{\text{trans}}/V)/q_{\text{vib}}$$

which should be of the order of 10^8 (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).