CHEMISTRY 542

FINAL Exam
December 7, 2004

In applying the principles of Quantum Mechanics in answering each question, be sure to *state the principle you are using at each step*.

1. A system has the energy eigenfunction $\Psi = C\,x \exp(ib - ax^2)$ where C, b, a are scalar constants. The zero of potential energy is taken to be the origin, i.e., $V(x=0) = 0$.
(a) Using the Schrödinger equation, ***determine the total energy of the system and the exact form of the potential energy***.
Hint: Write V(x) as $V(x) = V_0 + V_1x + V_2x^2 + V_3x^3 + \ldots$

(b) ***Find the value of C.***

2. Apply the variational method to a particle of mass M in a box of one dimension with

$V = 0$ for $-1 \le x \le 1$ and $V = \infty$ elsewhere.

Use a trial function of the form $\Psi_{trial} = 1 + c_1x^2 + c_2x^4$.

Be sure that the trial function has the proper behavior at the edge of the box.

Show in detail how you would find the coefficients and the approximate energy E_{var}.

3. Which of the following functions, when multiplied by a normalization constant, would be acceptable one-dimensional wave functions for a bound particle and if not, why not?

(a)	$\exp[-x]$	
(b)	$\exp[-x^2]$	
(c)	$x\exp[-x^2]$	
(d)	$i\exp[-x^2]$	
(e)	$f(x) = \exp[-x^2]$ for $x<0$; $f(x) = 2\exp[-x^2]$ for $x\geq 0$;	

If A and B are two Hermitian commuting operators, and Ψ_j and Ψ_k are eigenfunctions of A with eigenvalues a_j and a_k respectively ($a_j \neq a_k$), ***prove that there are no matrix elements of B*** between states Ψ_j and Ψ_k.

The eigenfunction of a particle in a 3-dimensional box is an eigenfunction of which of these operators?

(a)	p_x	
(b)	p_x^2	
(c)	p_z^2	
(d)	x	
(e)	$\partial/\partial x$	

For the ground state of the hydrogen-like atom, ***find the average value of r, the most probable value of r***.

the average value of r	the most probable value of r

True or false, ***explain your answer***

		True/ False	Explain
(a)	The state function is always equal to a function of time multiplied by a function of coordinates		
(b)	The state function is always an eigenfunction of the Hamiltonian		
(c)	Any linear combination of eigenfunctions of the Hamiltonian is an eigenfunction of the Hamiltonian		
(d)	If the state function is not an eigenfunction of the operator A, then a measurement of the property A might give a value that is not one of the eigenvalues of A		
(e)	The probability density is independent of time for a stationary state		
(f)	If two operators do not commute, then they cannot possess any common eigenfunctions		
(g)	If two operators commute, then every eigenfunction of one must be an eigenfunction of the other		
(h)	The matrix representing a Hermitian operator is always symmetric about the diagonal		
(i)	The experimental ground state energy of the Li atom can be obtained from $E_{2s}+2E_{1s}$, where E_{2s} is the experimental energy needed to remove the 2s electron from Li and E_{1s} is the experimental energy needed to remove the 1s electron from Li		

4. For a hydrogen-like atom with Z protons in the nucleus, perturbed by a uniform applied electric field in the z direction, the perturbation Hamiltonian is

$h = e\mathcal{E}\, z = e\mathcal{E}\, r \cos\theta$, where $\mathcal{E}$ is the magnitude of the electric field.
Consider the effect of h on the n = 2 energy level, which is four-fold degenerate. Since h commutes with the angular momentum L_z, use the complex hydrogen atom orbitals 2s, $2p_0$, $2p_{+1}$ and $2p_{-1}$ which are eigenfunctions of L_z. ***Find the first order corrections to the energy and the correct zeroth order wavefunctions.***

In general, what would be the effect of $\hbar$ on any energy level (any n) of the H-like atom? Illustrate using n=3.

5. The diamagnetic shielding of the Be nucleus by the surrounding electrons can be written in the form $B_{local} = (1-\sigma)B_0$ where B_0 is the applied magnetic field, B_{local} is the field at the nucleus and σ the nuclear magnetic shielding (which gives rise to observed NMR chemical shifts). For s electrons, σ has the form

$$\sigma = \frac{e^2}{3mc^2}\langle\sum_i \frac{1}{r_i}\rangle = 17.75\times10^{-6}\ \langle\sum_i \frac{1}{r_i}\rangle$$ with r, the distance of the electron from the nucleus, in atomic units

Show how σ for Be atom can be calculated using Slater functions. Answer must be complete but final numerical answer is not required.

6. The muonic helium atom is the neutral atom system composed of a helium nucleus, an electron and a negative mu meson (or muon). A negative mu meson has the same charge as an electron (q=-e), has spin ½ and a mass 138 times that of the electron.
(i) From one point of view, the muonic helium atom is analogous to helium atom in which one electron is replaced by a negative muon. The intrinsic magnetic moment of the muon is given by $(q/2M_\mu c)g_\mu \mathrm{I}_\mu = (-e/2\cdot 138 m_e c)g_\mu \mathrm{I}_\mu$ where g_μ is the muon gyromagnetic ratio which is very similar to that for an electron (2.0023), and I_μ is the muon spin operator. In $\mathrm{He}\mu^- e^-$, the electron angular momentum operator is $\mathbf{J}$ and the electron g value in this atom is g_J.
(ii) From another viewpoint, the muonic helium atom is similar to a hydrogen atom in which the proton is replaced by the pseudonucleus $(\mathrm{He}\mu^-)^+$, since the radius of the muonic orbit in the 1s state of the muonic helium atom is small compared to that of the electron. When the He nucleus is of spin zero (^{4}He) the electron sees a *pseudonucleus with a unit positive charge and a magnetic moment equal to that of a negative muon.* Apart from the reduced mass correction, the principal difference between the electron in the muonic helium atom and the electron in the hydrogen atom is the penetration of the electron charge inside this pseudonucleus.

(a) Now consider the muonic helium atom as analogous to a hydrogen atom: $(\mathrm{He}\mu^-)^+ e^-$, that is, as if there are only the two particles, the pseudonucleus that has angular momentum $\mathbf{I}_\mu$ and the electron that has angular momentum $\mathbf{J}$.
Find the angular momentum functions, which are the eigenfunctions of $\mathbf{F}_z = (\mathbf{I}_\mu + \mathbf{J})_z$, ***for this system in its ground state.***

(b) ***Find the linear combinations of these functions that are eigenfunctions of*** $\mathbf{F}^2$.

(c) In a static magnetic field $\mathbf{B}_0$, the relevant part of the Hamiltonian for the ground state of (^{4}Heμ^-) e$^-$ is

$$a(\mathbf{I}_\mu \bullet \mathbf{J}) + - (-e/2m_ec)g_J\mathbf{J}\bullet\mathbf{B}_0 + -(-e/2\cdot 138m_ec)g_\mu\mathbf{I}_\mu \bullet\mathbf{B}_0$$

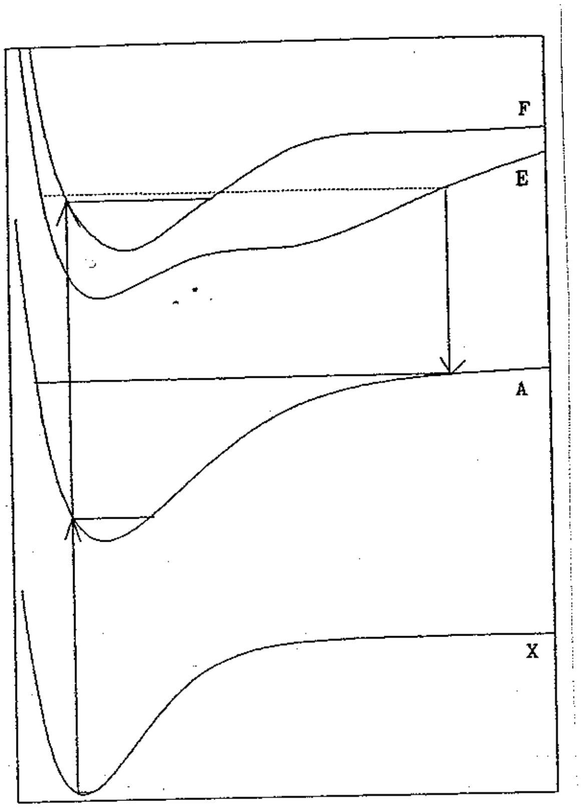
where a is the hyperfine coupling constant that is a measure of the energy of interaction between the two magnetic moments. Draw an energy level diagram, energy along the y axis and magnitude of $\mathbf{B}_0$ along the x axis, that illustrates how the energies calculated from this Hamiltonian would vary from $\mathbf{B}_0 = 0$ to higher values of magnetic field. Label the states with F, M_F, M_J, M_μ quantum numbers as appropriate.
Hint: Use perturbation theory: Think of the two limiting cases $B_0 = 0$ and B_0 very large. The z axis is along B_0. At each limit, consider which of the 3 terms in the above Hamiltonian you should assign to $\mathcal{H}^{(0)}$ and which to h, and find the zeroth order functions and $E^{(0)}$ that you will have. Draw the levels at each limit and then simply connect which levels become which.

(d) Now consider the muonic helium atom as analogous to a normal helium atom. *Assume that you have separated out the translational motion of the entire atom.* ***Write the non-relativistic, time independent Schrödinger equation for this atom. Do you have to worry about anti-symmetrization?***

To solve the problem of electron-muon repulsion, think about the fact that the radius of the muonic orbit in the 1s state of the muonic helium atom is small compared to that of the electron (the mass of the muon is 138 times that of an electron). As a consequence, the screening by the muon of the nuclear charge seen by the electron is nearly complete, whereas the muon is hardly screened by the electron. From the muon's point of view what would be the nuclear charge close to? From the electron's point of view, what would be the nuclear charge close to? On this basis, ***write down the Schrödinger equation that approximately describes the system and find its solutions.***

If we use perturbation theory, we can put back the part that was left out in the above treatment. ***What do we need to use for h***?

7. Some of the states of the Li_2 molecule are shown in the diagram below:
[from C. Linton et al., *J. Mol.. Spectrosc.* **175**, 340 (1996)]



This paper is a study of the A state of Li_2 From v=0 up to v=84 of the A state was observed, extrapolation to v=109 (the dissociation limit) was possible. X is the ground state. There are other excited states besides those shown in the figure, in particular there is a $B^1\Pi_u$, and a $G^1\Pi_g$. The A state dissociates to the atomic $(2s)^2S_{1/2}$ + $(2p)^2P_{1/2}$ states. The energy difference between the Li atom states $E[(2p)^2P_{1/2}] - E[(2s)^2S_{1/2}]$ is known accurately as 14903.296792 cm^{-1}. From the ground state v=0 to the dissociation limit of the A state is 23231.36 cm^{-1}. From the ground state v=0 to the A v=0 is 13879.087 cm^{-1}. In this work, the information from 84 vibrational levels in the A state permits a very accurate determination of the potential function which is shown in the figure.

(a) From the given data, it is possible to determine the dissociation energy, D_0, of the ground state X. ***Find it***; you may give your answer in units of cm^{-1}.

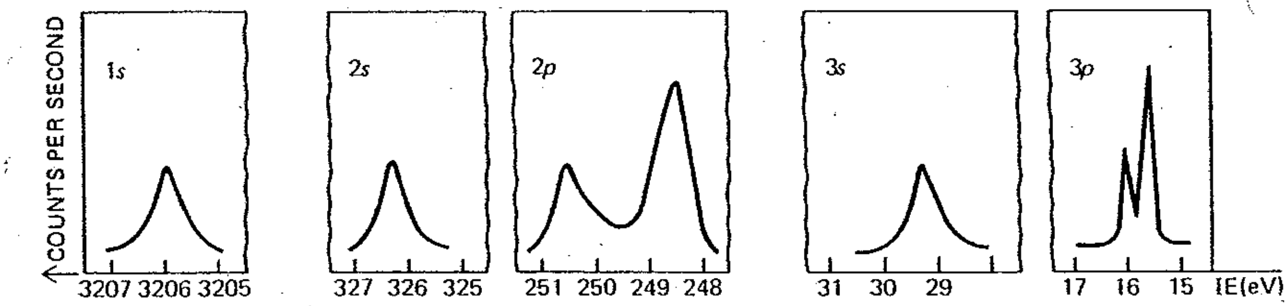
(b) From the given data, it is possible to determine the dissociation energy, D_0, of the [illegible] state A. ***Find it***; you may give your answer in units of cm^{-1}.

(c) From the electronic configuration of the atoms, use linear combinations of atomic orbitals to discover the MOs that can be formed when they overlap with + or – coefficients. Include <u>all</u> electrons. Draw the MOs (sketch contour plots or Jorgensen-Salem orbital pictures) indicating signs of the wavefunction in the various regions. Assign complete MO labels including the value of λ, symmetry with respect to ***i*** operation, bonding or antibonding.

(d) Draw the correlation diagram that connects these orbitals, from separated atoms to molecule to united atom. Label all orbitals completely

(e) From the electronic configuration and term symbols of the Li atoms into which the given A state of Li_2 molecule is known to dissociate (given), determine all the possible Li_2 molecular states that dissociate into these atomic states. (One of them is the A state)

8. (a) By photoelectron spectroscopy, XPES, or ESCA or variants thereof, a variety of ionization energies are found for the atoms of a sample. In this analytical technique, the sample is irradiated with high energy radiation and electrons are expelled. Some of the energy of the incident radiation is carried off as kinetic energy of the expelled electrons. The energy required to produce a particular ionization is equal to the energy of the incident photon ($h\nu$) less the kinetic energy of the expelled electrons (ε_{kin}). The pattern of electron kinetic energies thus yields a display (spectrum) of the various ionization energies of the atoms or molecules of a sample. Now, if we have a model of an atom, such as Slater model, in which the energy of the atom for a given electronic configuration can be written in terms of a sum over the one-electron-at-a-time (i.e., orbital) energies, then the measured ionization energies serve as measures of the orbital energies. The ionization spectrum of argon is shown below:

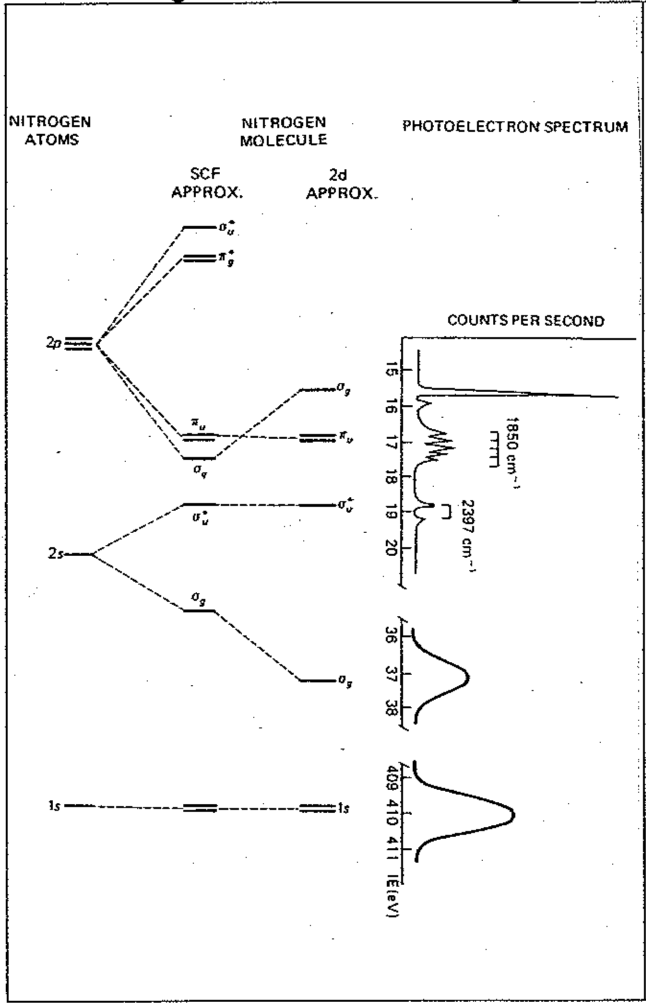


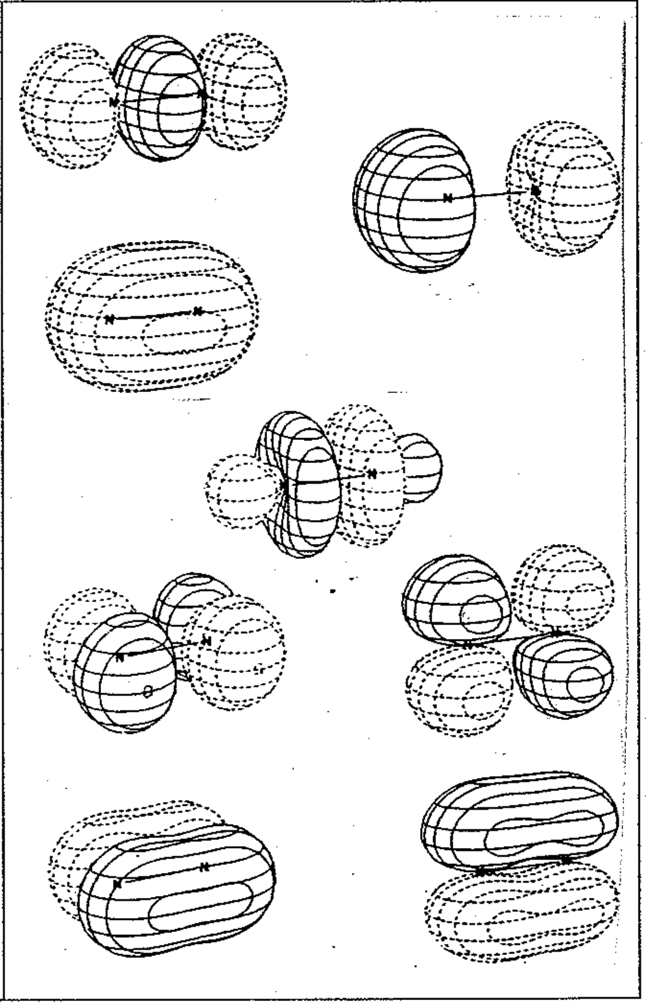
The orbital of the parent argon atom from which an electron has been expelled in each case is shown as label within the frame. For each of the 5 frames ***write under each frame the atomic term symbol*** for the Ar^+ ion formed. Write down the ***electronic configuration of the ion*** that is produced for each peak and where two peaks occur in a frame, ***provide an explanation.*** Why smaller splitting in 3p?

	Electronic configuration of Ar^+ ion	Term symbol	Why two peaks?
1s			
2s			
2p			
3s			
3p			

(b) For each of the 5 frames how would one estimate [E(Ar^+) – E(Ar)]? ***Do one example.***

(c) Below we see the molecular orbital energies of N_2 molecule can be related to its photoelectron spectrum [in which one electron is kicked off by a photon, leaving an ion; various ionization energies are found, just as in atoms. The one-electron functions (molecular orbitals) for N_2 are shown on the right, in randomized order. ***Draw a line connecting the orbitals on the right to the peaks in the spectrum on the left.***





(d) Assign an MO designation (to each orbital on the right) to provide the information about its behavior upon the ***i*** operation, its angular momentum, and the atomic orbitals that carry the largest coefficients in the linear combination that constitutes the function.

List of possibly useful integrals that will be provided with each exam

$\int \sin(ax)dx = -(1/a)\cos(ax)$
$\int \cos(ax)dx = (1/a)\sin(ax)$
$\int \sin^2(ax)dx = (½)x - (1/4a)\sin(2ax)$
$\int \sin^4(ax)dx = 3x/8 - (1/4a)\sin(2ax) + (1/32a)\sin(4ax)$
$\int \cos^2(ax)dx = (½)x + (1/4a)\sin(2ax)$
$\int \cos^4(ax)dx = 3x/8 + (1/4a)\sin(2ax) + (1/32a)\sin(4ax)$
$\int \sin(ax)\sin(bx)dx = [1/2(a-b)]\sin[(a-b)x)] - [1/2(a+b)]\sin[(a+b)x)], \quad a^2 \neq b^2$
$\int \cos(ax)\cos(bx)dx = [1/2(a-b)]\sin[(a-b)x)] + [1/2(a+b)]\sin[(a+b)x)], \quad a^2 \neq b^2$
$\int x \sin(ax)dx = (1/a^2)\sin(ax) - (x/a)\cos(ax)$
$\int x \cos(ax)dx = (1/a^2)\cos(ax) + (x/a)\sin(ax)$
$\int x^2 \cos(ax)dx = [(a^2x^2 - 2)/a^3]\sin(ax) + 2x\cos(ax)/a^2$
$\int x^2 \sin(ax)dx = -[(a^2x^2 - 2)/a^3]\cos(ax) + 2x\sin(ax)/a^2$
$\int x \sin^2(ax)dx = x^2/4 - x\sin(2ax)/4a - \cos(2ax)/8a^2$
$\int x^2 \sin^2(ax)dx = x^3/6 - [x^2/4a - 1/8a^3]\sin(2ax) - x\cos(2ax)/4a^2$
$\int x \cos^2(ax)dx = x^2/4 + x\sin(2ax)/4a + \cos(2ax)/8a^2$
$\int x^2 \cos^2(ax)dx = x^3/6 + [x^2/4a - 1/8a^3]\sin(2ax) + x\cos(2ax)/4a^2$
$\int x \exp(ax)dx = \exp(ax)\ (ax-1)/a^2$
$\int x \exp(-ax)dx = \exp(-ax)\ (-ax-1)/a^2$
$\int x^2 \exp(ax)dx = \exp(ax)\ [x^2/a - 2x/a^2 + 2/a^3]$
$\int x^m \exp(ax)dx = \exp(ax) \sum_{r=0 \text{ to } m} (-1)^r\, m!x^{m-r}/(m-r)!a^{r+1}$
$\int dx/x(a+bx) = -(1/a)\ln[(a+bx)/x]$

$\int_0^\infty x^n \exp(-ax)dx = n!/a^{n+1}$ $\quad a > 0$, n positive integer
$\int_0^\infty x^2 \exp(-ax^2)dx = (1/4a)(\pi/a)^{½}$ $\quad a > 0$
$\int_0^\infty x^{2n} \exp(-ax^2)dx = (1\cdot 3\cdot 5\cdot \ldots \cdot(2n-1)/(2^{n+1}a^n)(\pi/a)^{½}$ $\quad a > 0$
$\int_0^\infty x^{2n+1} \exp(-ax^2)dx = n!/2a^{n+1}$ $\quad a > 0$, n positive integer
$\int_0^\infty \exp(-a^2x^2)dx = (1/2a)(\pi)^{½}$ $\quad a > 0$
$\int_0^\infty \exp(-ax)\cos(bx)dx = a/(a^2+b^2)$ $\quad a > 0$
$\int_0^\infty \exp(-ax)\sin(bx)dx = b/(a^2+b^2)$ $\quad a > 0$
$\int_0^\infty x \exp(-ax)\sin(bx)dx = 2ab/(a^2+b^2)^2$ $\quad a > 0$
$\int_0^\infty x \exp(-ax)\cos(bx)dx = (a^2-b^2)/(a^2+b^2)^2$ $\quad a > 0$
$\int_0^\infty \exp(-a^2x^2)\cos(bx)dx = [(\pi)^{½}/2a]\cdot\exp[-b^2/4a^2]$ $\quad ab \neq 0$

Some useful identities:
$\sin(2x) = 2\sin x \cos x \qquad \cos(2x) = \cos^2 x - \sin^2 x = 2\cos^2 x - 1$
$e^{ix} = \cos x + i\sin x; \quad e^{-ix} = \cos x - i\sin x;$ from which, $\cos x = ½\{e^{ix} + e^{-ix}\}$

Radial factors in the hydrogenlike-atom wave functions

$$R_{1s} = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$R_{2s} = \frac{1}{\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2}\left(1-\frac{Zr}{2a}\right)e^{-Zr/2a}$$

$$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{5/2} r e^{-Zr/2a}$$

$$R_{3s} = \frac{2}{3\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2}\left(1-\frac{2Zr}{3a}+\frac{2Z^2r^2}{27a^2}\right)e^{-Zr/3a}$$

$$R_{3p} = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}-\frac{Z^2r^2}{6a^2}\right)e^{-Zr/3a}$$

$$R_{3d} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a}$$

$S_{l,m}(\theta)$

$l = 0$: $S_{0,0} = \frac{1}{2}\sqrt{2}$

$l = 1$: $S_{1,0} = \frac{1}{2}\sqrt{6}\cos\theta$

$S_{1,\pm 1} = \frac{1}{2}\sqrt{3}\sin\theta$

$l = 2$: $S_{2,0} = \frac{1}{4}\sqrt{10}\,(3\cos^2\theta - 1)$

$S_{2,\pm 1} = \frac{1}{2}\sqrt{15}\sin\theta\cos\theta$

$S_{2,\pm 2} = \frac{1}{4}\sqrt{15}\sin^2\theta$

$l = 3$: $S_{3,0} = \frac{3}{4}\sqrt{14}\,(\frac{5}{3}\cos^3\theta - \cos\theta)$

$S_{3,\pm 1} = \frac{1}{8}\sqrt{42}\sin\theta\,(5\cos^2\theta - 1)$

$S_{3,\pm 2} = \frac{1}{4}\sqrt{105}\sin^2\theta\cos\theta$

$S_{3,\pm 3} = \frac{1}{8}\sqrt{70}\sin^3\theta$

Slater's rules:

The effective charge seen by the ith electron whose quantum numbers are n ℓ in an atom whose atomic number is Z is given by

$$(Z_{eff})_i = Z - s_{n\ell}$$

Slater provides $s_{n\ell}$ as follows:

1. For i having n ℓ = 1s

   $s_{1s} = 0.30k_{same}$

   where

   k_{same} = number of other electrons in the same 1s shell

2. For i having n > 1 and $\ell = 0$ or 1

   $s_{n\ell} = 0.35k_{same} + 0.85k_{in} + 1.00k_{inner}$

   where

   k_{same} = number of other electrons in the same shell as the screened electron of interest

   k_{in} = number of electrons in the shell with principal quantum number n-1

   k_{inner} = number of electrons in the shell with principal quantum number n-2

3. For the ith electron having quantum numbers n ℓ = 3d

   $s_{3d} = 0.35k_{3d} + 1.00k_{in}$

   where

   k_{3d} = number of other electrons in the same 3d shell

   k_{in} = number of electrons with $n \le 3$ and $\ell < 2$

For the purposes of Slater's rules, the "subshells" are taken to be in the order
innermost 1s (2s,2p) (3s,3p) 3d (4s,4p) outermost

ADDITIONAL INFORMATION

$a_0 = (\hbar^2/m_e e^2)$ the "Bohr radius", 0.529177×10^{-10} m

$(e^2/2a_0) = 13.6057$ eV one rydberg, a unit of energy = (1/2) hartree

c = frequency•wavelength = 2.997924×10^{10} cm sec^{-1} the speed of light

1 eV = 8065.6 cm^{-1}

$$\mathcal{L}^2 = -\hbar^2\{(1/\sin\theta)(\partial/\partial\theta)\sin\theta\,\partial/\partial\theta \quad + (1/\sin^2\theta)\partial^2/\partial\phi^2\}$$

$$\mathcal{H} = -(\hbar^2/2M)\{(1/r)\partial^2/\partial r^2\, r\} \\ -(\hbar^2/2Mr^2)\{(1/\sin\theta)(\partial/\partial\theta)\sin\theta\,\partial/\partial\theta \quad + (1/\sin^2\theta)\partial^2/\partial\phi^2\} + V(r)$$

$$E = U_\alpha(R_e) + (v+\tfrac{1}{2})\nu_e - x_e\nu_e\,(v+\tfrac{1}{2})^2 + y_e\nu_e\,(v+\tfrac{1}{2})^3 + B_eJ(J+1) - D_e[J(J+1)]^2 - \alpha_e(v+\tfrac{1}{2})J(J+1) + Y_{00}$$

where all spectroscopic quantities are expressed in energy units (or the corresponding frequency or wavenumbers). In energy units, the following are positive quantities:

$B_e \equiv \hbar^2 / 2\mu\cdot R_e^2$ $\quad$ B_e rotational constant

$$h x_e\nu_e \equiv \tfrac{1}{4}\, B_e^2/(h\nu_e)^2 \cdot \{\, (^{10}/_{3})B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2 - U^{iv}(R_e)R_e^4 \,\}$$

$x_e\nu_e$ anharmonicity constant

$$D_e \equiv 4\, B_e^3/(h\nu_e)^2$$

D_e centrifugal distortion constant

$$\alpha_e \equiv -\,2\, B_e^2/h\nu_e \cdot \{3 + 2\, B_e[U'''(R_e)R_e^3]\,/(h\nu_e)^2\,\}$$

α_e vibrational rotational coupling constant

$$Y_{00} \equiv B_e^2/16(h\nu_e)^2 \cdot \{\, U^{iv}(R_e)R_e^4 - (^{14}/_{9})B_e[U'''(R_e)R_e^3]^2/(h\nu_e)^2\,\}$$

$h\nu_e \equiv (h/2\pi)[\,U''(R_e)/\mu\,]^{1/2}$ $\quad$ ν_e harmonic frequency

μ reduced mass $\quad 1/\mu = 1/m_A + 1/m_B$

R_e equilibrium bond length

Rotational constant for the v<u>th</u> vibrational state is B_v

$$B_v = B_e - \alpha_e\,(v+\tfrac{1}{2})$$

Y_{00} same anharmonic correction to <u>every</u> vibrational level

Since Y_{00} is a constant for the electronic state, it is usually put together with $U(R_e)$.