Chemistry 344

Exam II

Nov. 11, 2002

1. Consider particle 1 with intrinsic angular momentum (spin) such that the eigenvalues of the square of the angular momentum is $(3/2)[(3/2) + 1]\,\hbar^2$. For the purpose of this problem, call the operator for the z component of this angular momentum $S_z(1)$.
The eigenfunctions of the z component of the angular momentum of particle 1 arranged in decreasing order of the eigenvalue are $\delta(1)$ $\alpha(1)$ $\beta(1)$ and $\gamma(1)$.

(a) Write the four explicit equations that express this statement for particle 1.

The complete set of functions for particle 1 form a complete orthonormal set.

(b) Consider particle 2 with intrinsic angular momentum (spin) such that the eigenvalues of the square of the angular momentum is $(1/2)[(1/2) + 1]\,\hbar^2$. For the purpose of this problem, call the operator for the z component of this angular momentum $S_z(2)$.
The eigenfunctions of the z component of the angular momentum arranged in decreasing order of the eigenvalue are $\alpha(2)$ and $\beta(2)$.

Write the two explicit equations that express this statement for particle 2.

The complete set of functions for particle 2 also form a complete orthonormal set.

(c) Consider a new system that includes particle 1 and particle 2; the angular momenta add as vectors.
What is the operator for the total z component of the angular momentum of the system of particle 1 and 2 together ? You may call this operator $S_{z,total}$.

$S_{z,total}$ =

The complete set of functions that are eigenfunctions of the total z component of the angular momentum of the system of particle 1 and 2 together should be how many in number?

Find the possible eigenfunctions of the total z component of the angular momentum of the system of particle 1 and 2 together, $S_{z,total}$. Identify which ones are degenerate.

The eigenvalues are:	The eigenfunctions are:	The principle(s) that are the basis for the answers

Check to see that you have included them all. If you have, then you have a complete orthonormal set of functions for the 2-particle system.

From the addition of vectors and the properties of angular momentum, what are the possible eigenvalues of the square total angular momentum S^2_{total} of the system of 2 particles?

Does the square total angular momentum of the 2 particle system commute with the total z component of the angular momentum? Write the answer in the form of a mathematical statement below:

Using the properties of angular momentum, assign each of the eigenvalues found for the z component to a corresponding total angular momentum.

Eigenvalue of the total z component of angular momentum.	Eigenvalue of the square total angular momentum.		Eigenvalue of the total z component of angular momentum.	Eigenvalue of the square total angular momentum.

Recall that when degeneracy is involved, a linear combination of degenerate functions will satisfy the operator equation just as well as either one of them. Prove this for any two degenerate functions of $S_{z,total}$.

Identify all the eigenfunctions of the z component that are already <u>also</u> eigenfunctions of the <u>square total angular momentum</u>:

<u>Eigenvalue of the square total angular momentum.</u>	<u>Eigenvalue of the total z component of angular momentum.</u>	Function

2. To solve the problem of the particle on the surface of a sphere in terms of θ and ϕ, we found that: (a) We had to use separation of variables in such a way that, the quantum number that arises from insisting that the function of ϕ must be single-valued, must appear in the θ equation. (b) Another quantum number arises from insisting that to be acceptable, the function of θ must be finite. Write the relation between these quantum numbers:

The Schrödinger equation for the hydrogen-like atom becomes separable when the Cartesian coordinates of the electron and the nucleus (six coordinates altogether) are transformed into two sets of three. Identify these two sets of coordinates completely by writing them in terms of the original set:

original set of coordinates	new set of coordinates
1.	
2.	
3.	

4.	
5.	
6.	

When this separation is carried out, what are the found eigenfunctions involving the center of mass coordinates? What are the eigenvalues? Identify the symbols you use!

How does it come about that the angular momentum of the electron end up being involved in the eigenfunctions of the Hamiltonian of the hydrogen-like atom when the energy eigenvalues found in the end do not include such information?

3. (a) Write down the hamiltonian that is being used when the Slater approximation is applied to the calculation of electronic energies of the Li atom. Identify the symbols you use!

(b) Apply the Slater approximation to calculate the first ionization energy of the Be atom:

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

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

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

Some useful identities:

$\sin(2x) = 2 \sin x \cos x \qquad \cos(2x) = \cos^2 x - \sin^2 x = 2\cos^2 x - 1$

$e^{ix} = \cos x + i\sin x$; $e^{-ix} = \cos x - i\sin x$; from which, $\cos(x) = ½\{\exp[i\,x] + \exp[-i\,x]\}$

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

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

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

1. For i having n ℓ= 1s

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

   where

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

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

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

   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

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

   where

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

   k_{in} = number of electrons with $n \leq 3$ 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", $0.529177\text{x}10^{-10}$ m
$(e^2/2a_0) = 13.6057$ eV one rydberg, a unit of energy = (1/2) hartree
c = frequency•wavelength = $2.997924\text{ x}10^{10}$ cm sec^{-1} the speed of light
1 eV = 8065.6 cm^{-1}

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

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