Chemistry 344

Exam II Solutions

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.

$$S_z(1)\,\delta(1) = +\tfrac{3}{2}\hbar\,\delta(1)$$
$$S_z(1)\,\alpha(1) = +\tfrac{1}{2}\hbar\,\alpha(1)$$
$$S_z(1)\,\beta(1) = -\tfrac{1}{2}\hbar\,\beta(1)$$
$$S_z(1)\,\gamma(1) = -\tfrac{3}{2}\hbar\,\gamma(1)$$

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.

$$S_z(2)\,\alpha(2) = +\tfrac{1}{2}\hbar\,\alpha(2)$$
$$S_z(2)\,\beta(2) = -\tfrac{1}{2}\hbar\,\beta(2)$$

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 $S_{z,total}$.

$S_{z,total} = S_z(1) + S_z(2)$ When vectors add their components add.

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?

$4 \times 2 = 8$

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
	$+\frac{3}{2}\hbar + \frac{1}{2}\hbar = 2\hbar$	$\Psi(1,2) = \delta(1)\cdot\alpha(2)$	$S_{z\,total} = S_z(1) + S_z(2)$
	$-\frac{3}{2}\hbar - \frac{1}{2}\hbar = -2\hbar$	$\Psi(1,2) = \gamma(1)\cdot\beta(2)$	is separable.
degen	$+\frac{3}{2}\hbar - \frac{1}{2}\hbar = \hbar$	$\Psi(1,2) = \delta(1)\cdot\beta(2)$	$(S_z(1) + S_z(2))\Psi(1,2) =$
degen	$\frac{\hbar}{2} + \frac{\hbar}{2} = \hbar$	$\Psi(1,2) = \alpha(1)\cdot\alpha(2)$	$M_S\hbar\cdot\Psi(1,2)$ Let $\Psi(1,2) = F(1)\cdot G(2)$
degen	$-\frac{3}{2}\hbar + \frac{1}{2}\hbar = -\hbar$	$\Psi(1,2) = \gamma(1)\cdot\alpha(2)$	substitute and divide both sides by
degen	$-\frac{1}{2}\hbar - \frac{1}{2}\hbar = -\hbar$	$\Psi(1,2) = \beta(1)\cdot\beta(2)$	the product func.
degen	$+\frac{1}{2}\hbar - \frac{1}{2}\hbar = 0$	$\Psi(1,2) = \alpha(1)\cdot\beta(2)$	$\underbrace{\frac{S_z(1)F(1)}{F(1)}}_{\text{we know this}} + \underbrace{\frac{S_z(2)G(2)}{G(2)}}_{\text{we also know this}} = M_S\hbar$
degen	$-\frac{1}{2}\hbar + \frac{1}{2}\hbar = 0$	$\Psi(1,2) = \beta(1)\cdot\alpha(2)$	

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?

Since $M_S = 2\ 1\ 0\ -1\ -2$ together provide one set of z components — there must be $S(S+1)\hbar^2$ that is $2(2+1)\hbar^2$
Then $M_S = 1\ 0\ -1$ are left, which together provide another set of z components corresp. to $1(1+1)\hbar^2$ eigenvalue for S^2_{total}

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:

$[S^2_{total}, S_{z\,total}] = 0$ or $S^2_{total} S_{z\,total} - S_{z\,total} S^2_{total} = 0$

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.
$2\hbar$ $\hbar$ 0 $-\hbar$ $-2\hbar$	$2(2+1)\hbar^2$		$\hbar$ 0 $-\hbar$	$1(1+1)\hbar^2$

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 $S_{z,total}$. $\left(\frac{1}{2}\hbar+\frac{1}{2}\hbar\right)$ $\left(\frac{3}{2}\hbar-\frac{1}{2}\hbar\right)$

$$S_{z\,total}\{c_1\delta(1)\cdot\beta(2)+c_2\,\alpha(1)\cdot\alpha(2)\} = c_1(\hbar)\delta(1)\cdot\beta(2)+c_2(\hbar)\alpha(1)\cdot\alpha(2)$$
$$= \hbar\,[c_1\delta(1)\cdot\beta(2)+c_2\,\alpha(1)\cdot\alpha(2)]$$

Since c_1 and c_2 have not been specified, any values for these coeffs will work. We see that any linear combination of these degen. functions will satisfy the operator eqn and give the eigenvalue $+\hbar$

Identify all the eigenfunctions of the z component that are already also eigenfunctions of the square total angular momentum: The non-degenerate ones

Eigenvalue of the square total angular momentum.	Eigenvalue of the total z component of angular momentum.	Function
$2(2+1)\hbar^2$	$2\hbar$	$\Psi(1,2)=\delta(1)\cdot\alpha(2)$
$2(2+1)\hbar^2$	$-2\hbar$	$\Psi(1,2)=\gamma(1)\cdot\beta(2)$

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 — m number that arises from insisting that the function of ϕ must be single-valued, must appear in the θ equation. (b) Another quantum number l arises from insisting that to be acceptable, the function of θ must be finite. Write the relation between these quantum numbers:

$$m = -l, -l+1, \cdots +l$$

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. x_e	$X_{CM}\cdot M_{TOTAL} = x_e m_e + x_N m_N$
2. y_e	$Y_{CM}\cdot M_{TOTAL} = y_e m_e + y_N m_N$
3. z_e	$Z_{CM}\cdot M_{TOTAL} = z_e m_e + z_N m_N$

center of mass coords

$M_{TOTAL} = m_e + m_N$

4. x_N	$x = x_e - x_N$	relative coordinates
5. y_N	$y = y_e - y_N$	
6. z_N	$z = z_e - z_N$	

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!

$$\Psi = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi}{a}X_{CM}\right)\cdot\sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi}{b}Y_{CM}\right)\cdot\sqrt{\frac{2}{c}}\sin\left(\frac{n_z\pi}{c}Z_{CM}\right)$$

where $n_x = 1,2,3,\ldots$ $n_y = 1,2,3,\ldots$ $n_z = 1,2,3,\ldots$

eigenvalues are $E_{TRANSLATIONAL} = \frac{h^2}{8M_{TOTAL}}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)$

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?

The angular momentum arises when the ϕ and θ parts are separated from the r part, with separation constants $l(l+1)$ ~~aside~~ m^2. The θ,ϕ parts of the $\mathcal{H}$ are identical to $\frac{L^2}{2\mu r^2}$. After solving the θ part we can put $l(l+1)\hbar^2$ in place of L^2 in the $\mathcal{H}_{op}$. The energy comes from solving the r part, with quantum number n arising, and the relation $l = 0, 1, 2, \cdots n-1$

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!

$$\mathcal{H}_{Slater} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Z_{eff\,1}e^2}{r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Z_{eff\,2}e^2}{r_2} - \frac{\hbar^2}{2m}\nabla_3^2 - \frac{Z_{eff\,3}e^2}{r_3}$$

$$\nabla_1^2 = -\frac{\partial^2}{\partial x_1^2} - \frac{\partial^2}{\partial y_1^2} - \frac{\partial^2}{\partial z_1^2}$$

$$Z_{eff\,1} = Z - s_{n_1 l_1} = 3 - S_{n_1 l_1}$$

where n_1 and l_1 are the quantum numbers for the 1st electron in the electronic configuration and $S_{n_1 l_1}$ are obtained from Slater's rules

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

Be has $Z = 4$

Lowest energy config of Be atom $= 1s^2 2s^2$

Lowest energy config of Be^+ ion $= 1s^2 2s$

The difference $E(Be^+ \text{ ion}) - E(\text{Be neutral atom}) = IP_1$

$$E(\text{Be neutral atom}) = \left(-\frac{Z_{eff1}^2}{n_1^2} - \frac{Z_{eff2}^2}{n_2^2} - \frac{Z_{eff3}^2}{n_3^2} - \frac{Z_{eff4}^2}{n_4^2} \right) \frac{e^2}{2a_0}$$

$Z_{eff1} = 4 - (0.30)1, \; n_1 = 1$

$Z_{eff2} = 4 - (0.30)1, \; n_2 = 1$

$Z_{eff3} = 4 - 2(0.85) - 1(0.35), \; n_3 = 2$

$Z_{eff4} = 4 - 2(0.85) - 1(0.35), \; n_4 = 2$

$$E(Be^+ \text{ ion}) = \left(-\frac{Z_{eff1}^2}{n_1^2} - \frac{Z_{eff2}^2}{n_2^2} - \frac{Z_{eff3}^2}{n_3^2} \right) \frac{e^2}{2a_0}$$

$Z_{eff1} = 4 - (0.30)1 \quad n_1 = 1$

$Z_{eff2} = 4 - (0.30)1 \quad n_2 = 1$

$Z_{eff3} = 4 - 2(0.85) \quad n_3 = 2$

$$IP_1 = E(Be^+) - E(\text{Be neutral}) = \left\{ -\frac{[4 - 2(0.85)]^2}{2^2} + 2\frac{[4 - 2(0.85) - (0.35)]^2}{2^2} \right\} \frac{e^2}{2a_0}$$

$$= (-1.3225 + 1.90125) \frac{e^2}{2a_0}$$

$$= 0.57875 (13.6057) \text{ eV}$$