Chemical Physics Cumulative Examination
March 18, 2002

INSTRUCTIONS

- Show ALL your work. Insufficient justification will result in a loss of points.
- Electronic calculators, computers, etc. are not permitted.

1. (20 pts.) Use the standard definition of the angular momentum operator,

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}, \tag{1}$$

where $\hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z})$ and $\hat{\mathbf{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)$ are the coordinate and momentum operators,# and the commutation relationships,

$$[\hat{x}_k, \hat{x}_\ell] = 0, \quad [\hat{p}_k, \hat{p}_\ell] = 0, \quad [\hat{x}_k, \hat{p}_\ell] = \imath\hbar\delta_{k,\ell} \quad (k, \ell = 1, 2, 3), \tag{2}$$

where $\hat{x}_1 \equiv \hat{x}$, $\hat{x}_2 \equiv \hat{y}$, $\hat{x}_3 \equiv \hat{z}$, $\hat{p}_1 \equiv \hat{p}_x$, $\hat{p}_2 \equiv \hat{p}_y$, and $\hat{p}_3 \equiv \hat{p}_z$, to prove that

$$[\hat{L}_x, \hat{L}_y] = \imath\hbar\hat{L}_z. \tag{3}$$

The derivation must be purely algebraic (i.e., without any reference to a particular form of the quantum-mechanical operators in the coordinate representation).

2. (15pts.) Let $\hat{\mathbf{J}} = (\hat{J}_x, \hat{J}_y, \hat{J}_z)$ be the angular momentum operator. Use the commutation relationships,

$$[\hat{J}_x, \hat{J}_y] = \imath\hbar\hat{J}_z, \tag{4}$$

$$[\hat{J}_y, \hat{J}_z] = \imath\hbar\hat{J}_x, \tag{5}$$

$$[\hat{J}_z, \hat{J}_x] = \imath\hbar\hat{J}_y, \tag{6}$$

to prove that

$$[\hat{J}^2, \hat{J}_z] = 0, \tag{7}$$

$$[\hat{J}_+, \hat{J}_-] = 2\hbar\hat{J}_z, \tag{8}$$

where $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ and $\hat{J}_\pm = \hat{J}_x \pm \imath\hat{J}_y$.

#) Bold symbols designate vector (or tensor) quantities.

3. (15 pts.) Let $|jm\rangle$ be an eigenstate of $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ and $\hat{J}_z$, where $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ are the Cartesian components of the angular mometum operator $\hat{\mathbf{J}}$. Use the above Eqs. (4)–(6) to show that the expectation values of $\hat{J}_x$ and $\hat{J}_y$ in the state $|jm\rangle$ are zero, i.e.,

$$\langle jm|\hat{J}_x|jm\rangle = \langle jm|\hat{J}_y|jm\rangle = 0. \tag{9}$$

Hint: Use Eqs. (4)–(6) to express $\hat{J}_x$ and $\hat{J}_y$ in terms of the commutators of the components of the angular momentum operator.

4. (25 pts.) Let $\alpha(i)$ and $\beta(i)$, $i = 1, 2$, be the spin-up and spin-down spin functions of electrons 1 and 2, respectively. Let $\hat{\mathbf{S}}_1 = (\hat{S}_{1,x}, \hat{S}_{1,y}, \hat{S}_{1,z})$ and $\hat{\mathbf{S}}_2 = (\hat{S}_{2,x}, \hat{S}_{2,y}, \hat{S}_{2,z})$ be the spin angular momentum operators corresponding to electrons 1 and 2, respectively, and let $\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$ be the operator representing the total spin of a two-electron system consisting of electrons 1 and 2. Use the values of Clebsch-Gordan coefficients $\langle j_1m_1, j_2m_2|jm\rangle$ for $j_1 = j_2 = \frac{1}{2}$ provided at the end of this document to represent the eigenstates $|sm\rangle$ of $\hat{S}^2 = (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2)^2$ and $\hat{S}_z = \hat{S}_{1,z} + \hat{S}_{2,z}$ as linear combinations of the two-electron spin functions $\alpha(1)\alpha(2)$, $\alpha(1)\beta(2)$, $\beta(1)\alpha(2)$, $\beta(1)\beta(2)$. Report your results in the form of the following table:

eigenstate $\|sm\rangle$ of $\hat{S}^2$ and $\hat{S}_z$	eigenvalue of $\hat{S}^2$	eigenvalue of $\hat{S}_z$
...	...	...

Show that the $|sm\rangle$ eigenstates of $\hat{S}^2$ and $\hat{S}_z$ resulting from your calculations form an orthonormal set.

5. (25 pts.) (a) The $\hat{J}_\pm = \hat{J}_x \pm \imath\hat{J}_y$ operators are called the angular momentum raising (+) and lowering (−) operators (as usual, $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ are the Cartesian components of the angular mometum operator $\hat{\mathbf{J}}$). Show that

$$\hat{J}^2 = \tfrac{1}{2}(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+) + \hat{J}_z^2. \tag{10}$$

(b) Consider the three-electron system consisting of electrons 1, 2, and 3. Let $\alpha(i)$ and $\beta(i)$, $i = 1, 2, 3$, be the spin-up and spin-down spin functions of electrons 1, 2, and 3, respectively. Let $\hat{\mathbf{S}}_i = (\hat{S}_{i,x}, \hat{S}_{i,y}, \hat{S}_{i,z})$, $i = 1, 2, 3$, be the spin angular momentum operators corresponding to electrons 1, 2, and 3, respectively. It can be shown that

$$\hat{S}_{i,+}\alpha(i) = 0, \quad \hat{S}_{i,-}\alpha(i) = \hbar\beta(i), \quad \hat{S}_{i,+}\beta(i) = \hbar\alpha(i), \quad \hat{S}_{i,-}\beta(i) = 0, \tag{11}$$

where $\hat{S}_{i,\pm} = \hat{S}_{i,x} \pm \imath\hat{S}_{i,y}$ are the spin angular momentum raising and lowering operators ($i = 1, 2, 3$). Use Eqs. (10) and (11) to show that the following function:

$$u(1,2,3) = \frac{1}{\sqrt{6}}[2\beta(1)\alpha(2)\alpha(3) - \alpha(1)\alpha(2)\beta(3) - \alpha(1)\beta(2)\alpha(3)] \equiv \frac{1}{\sqrt{6}}[2\beta\alpha\alpha - \alpha\alpha\beta - \alpha\beta\alpha], \tag{12}$$

is an eigenstate of the total spin operator $\hat{S}^2 = (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3)^2$. What is the corresponding eigenvalue ?

The Clebsch-Gordan coefficients $\langle j_1 m_1, j_2 m_2 | j m\rangle$ for $j_1 = j_2 = \frac{1}{2}$.

		$j=1$, $m=1$	$j=1$, $m=0$	$j=0$, $m=0$	$j=1$, $m=-1$
$m_1 = \frac{1}{2}$	$m_2 = \frac{1}{2}$	1	0	0	0
$m_1 = \frac{1}{2}$	$m_2 = -\frac{1}{2}$	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0
$m_1 = -\frac{1}{2}$	$m_2 = \frac{1}{2}$	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0
$m_1 = -\frac{1}{2}$	$m_2 = -\frac{1}{2}$	0	0	0	1

Other potentially useful formulas

- $[\hat{F}_1\hat{F}_2, \hat{G}] = \hat{F}_1[\hat{F}_2, \hat{G}] + [\hat{F}_1, \hat{G}]\hat{F}_2$ ([,] is the commutator)
- $[F_1F_2, G_1G_2] = F_1G_1[F_2, G_2] + F_1[F_2, G_1]G_2 + G_1[F_1, G_2]F_2 + [F_1, G_1]G_2F_2$.