CHEM 555-75 **WORKSHEET 8** **Fall 2021**

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1. Use the matrix representations of $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ to determine the matrix representation of $\hat{S}^2$. Show that an $S = \frac{1}{2}$ wavefunction is an eigenstate of $\hat{S}^2$.

$\hat{S}^2 = (\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2) = \left(\frac{\hbar}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\right)^2 + \left(\frac{\hbar}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\right)^2 + \left(\frac{\hbar}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\right)^2$

$\hat{S}^2 = \frac{\hbar^2}{4}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} + \frac{\hbar^2}{4}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} + \frac{\hbar^2}{4}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} = \frac{3\hbar^2}{4}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$

$\hat{S}^2|\alpha\rangle = \frac{3\hbar^2}{4}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}\begin{bmatrix}1\\ 0\end{bmatrix} = \frac{3\hbar^2}{4}\begin{bmatrix}1\\ 0\end{bmatrix} = \frac{3\hbar^2}{4}|\alpha\rangle$

2. Later in the course when we discuss Roothan-Hall Hartree-Fock theory, you will encounter the density matrix **P**. We have learnt that the density is obtained from the square of the wavefunction Ψ^2 and we shall see here the density in terms of a matrix representation and how it can be used to determine the expectation value of an operator.

The expectation value of an operator $\hat{O}$ is obtained from:

$$\langle\hat{O}\rangle = \frac{\langle\Psi|\hat{O}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{1}$$

which in the case of a normalized wavefunction

$$\langle\hat{O}\rangle = \langle\Psi|\hat{O}|\Psi\rangle \tag{2}$$

Expressing a wavefunction as a linear combination of basis functions $\Psi = \sum_i c_i f_i$, we find

$$\langle\hat{O}\rangle = \langle\sum_i c_i f_i|\hat{O}|\sum_j c_j f_j\rangle \tag{3}$$

$$= \sum_{ij} c_i^* c_j \langle f_i|\hat{O}|f_j\rangle \tag{4}$$

$$= \sum_{ij} P_{ij} O_{ij} \tag{5}$$

We have now obtained an expression for the expectation value in terms of matrix representations using the basis functions f_i. The operation of summing the element-wise products of two matrices is known as "contraction". Contraction is a generalization of the trace – a property of matrices that is invariant under linear transformations (you would have met them in your course on group theory). We can rewrite the contraction as the trace by recognizing that $P_{ij} = P^T_{ji}$ such that

$$\langle \hat{O} \rangle = \sum_{ij} P_{ij} O_{ij} \tag{6}$$

$$= \sum_i \sum_j P^T_{ji} O_{ij} \tag{7}$$

$$= \sum_i (\mathbf{P}^T \mathbf{O})_{ii} \tag{8}$$

$$= \mathrm{tr}(\mathbf{P}^T \mathbf{O}) \tag{9}$$

where the density matrix has the form e.g. for a two-state system

$$\mathbf{P} = \begin{bmatrix} c_1^* c_1 & c_1^* c_2 \\ c_2^* c_1 & c_2^* c_2 \end{bmatrix} \tag{10}$$

Evaluate $\langle \hat{S}_x \rangle$, $\langle \hat{S}_y \rangle$ and $\langle \hat{S}_z \rangle$ for a system with the density matrix $\mathbf{P} = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$.

$\langle \hat{S}_x \rangle = \mathrm{tr}(\mathbf{P}^T \mathbf{S}_x) = \mathrm{tr}\left(\frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}^T \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \right) = \frac{\hbar}{4} \mathrm{tr} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \frac{2\hbar}{4} = \frac{\hbar}{2}$
$\langle \hat{S}_y \rangle = \mathrm{tr}(\mathbf{P}^T \mathbf{S}_y) = \mathrm{tr}\left(\frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}^T \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \right) = \frac{\hbar}{4} \mathrm{tr} \begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix} = \frac{0\hbar}{4} = 0$
$\langle \hat{S}_z \rangle = \mathrm{tr}(\mathbf{P}^T \mathbf{S}_x) = \mathrm{tr}\left(\frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}^T \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \right) = \frac{\hbar}{4} \mathrm{tr} \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} = \frac{0\hbar}{4} = 0$

3. Use the definitions of $\hat{J}_\pm$ to calculate the 3×3 matrix representation of the operator $\hat{J}_x$ for $j = 1$ using the basis functions $|1, 1\rangle$, $|1, 0\rangle$, $|1, -1\rangle$.

First, we write $\hat{J}_x$ as a function of $\hat{J}_+$ and $\hat{J}_-$
$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \Rightarrow \hat{J}_x = \frac{1}{2}(\hat{J}_+ + \hat{J}_-)$
The basis functions $|1, 1\rangle$, $|1, 0\rangle$, $|1, -1\rangle$ can be written as the vectors

$$|1, 1\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \qquad |1, 0\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \qquad |1, -1\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \tag{11}$$

The operators $\hat{J}_+$ and $\hat{J}_-$ have the following properties:
$\hat{J}_+ |j, m_j\rangle = \hbar\sqrt{j(j+1) - m_j(m_j+1)}|j, m_j + 1\rangle$
$\hat{J}_- |j, m_j\rangle = \hbar\sqrt{j(j+1) - m_j(m_j-1)}|j, m_j - 1\rangle$
So that there is a matrix $\mathbf{J}_+$ representing $\hat{J}_+$ whose operation transforms the basis vectors according to:

$\mathbf{J}_+ \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = 0$

$\mathbf{J}_+ \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \hbar\sqrt{2} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$

$$\mathbf{J}_+ \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \hbar\sqrt{2} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}$$

and similarly, a matrix $\mathbf{J}_-$ representing $\hat{J}_-$ whose operation transforms the basis vectors according to:

$$\mathbf{J}_- \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \hbar\sqrt{2} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}$$

$$\mathbf{J}_- \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \hbar\sqrt{2} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

$$\mathbf{J}_- \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = 0$$

The matrix that achieves these vector transformations is:

$$\mathbf{J}_+ = \begin{bmatrix} 0 & \hbar\sqrt{2} & 0 \\ 0 & 0 & \hbar\sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{J}_- = \begin{bmatrix} 0 & 0 & 0 \\ \hbar\sqrt{2} & 0 & 0 \\ 0 & \hbar\sqrt{2} & 0 \end{bmatrix}$$

Therefore:

$$\mathbf{J}_x = \tfrac{1}{2}\left(\begin{bmatrix} 0 & \hbar\sqrt{2} & 0 \\ 0 & 0 & \hbar\sqrt{2} \\ 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 \\ \hbar\sqrt{2} & 0 & 0 \\ 0 & \hbar\sqrt{2} & 0 \end{bmatrix} \right) = \tfrac{\hbar\sqrt{2}}{2} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

4. Show that the total angular momentum operator of a composite spin system defined as $\hat{j} = \hat{j}_1 - \hat{j}_2$, where $\hat{j}_1$ and $\hat{j}_2$ are total angular momentum operators of the individual spin systems, is not valid.

A valid definition of angular momentum satisfies the four spin commutation rules. Test for $[\hat{j}_x, \hat{j}_y]$:
$[\hat{j}_x, \hat{j}_y] = [\hat{j}_{1x} - \hat{j}_{2x}, \hat{j}_{1y} - \hat{j}_{2y}] = [\hat{j}_{1x}, \hat{j}_{1y}] - [\hat{j}_{2x}, \hat{j}_{1y}] - [\hat{j}_{1x}, \hat{j}_{2y}] + [\hat{j}_{2x}, \hat{j}_{2y}]$
$= i\hbar\hat{j}_{1z} - 0 - 0 + i\hbar\hat{j}_{2z} = i\hbar(\hat{j}_{1z} + \hat{j}_{2z}) = i\hbar\hat{j}_z$
So the component commutation relations are satisfied. What about the commutator $[\hat{j}^2, \hat{j}_z]$?
$[\hat{j}^2, \hat{j}_z] = [\hat{j}^2, \hat{j}_{1z} - \hat{j}_{2z}] = [\hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2, \hat{j}_{1z} - \hat{j}_{2z}]$
$= [\hat{j}_x^2, \hat{j}_{1z}] + [\hat{j}_y^2, \hat{j}_{1z}] + [\hat{j}_z^2, \hat{j}_{1z}] - [\hat{j}_x^2, \hat{j}_{2z}] - [\hat{j}_y^2, \hat{j}_{2z}] - [\hat{j}_z^2, \hat{j}_{2z}]$
From the derivation in the lecture slides we see:
$= 2i\hbar(\hat{j}_{1x}\hat{j}_{2y} - \hat{j}_{1y}\hat{j}_{2x}) + 2i\hbar(\hat{j}_{1x}\hat{j}_{2y} - \hat{j}_{1y}\hat{j}_{2x})$
$= 4i\hbar(\hat{j}_{1x}\hat{j}_{2y} - \hat{j}_{1y}\hat{j}_{2x})$
So the commutator of component angular momentum with total angular momentum squared operator (which should be zero) is not satisfied.