Química Teórica & Estrutural

Departamento de Química, Universidade de Coimbra

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Aula 8-II

1. Considere o caso em que $j = 1$:

   (a) Escreva as matrizes que representam os operadores $\hat{J}^2$, $\hat{J}_z$, $\hat{J}_\pm$, $\hat{J}_x$ e $\hat{J}_y$.
   Res.: Sabendo que $j = 1$ temos que $m_j = -1, 0, 1$, e denotando a função de onda $|j, m_j\rangle$

   A matriz $\hat{J}^2$:

$$\hat{J}^2 = \begin{bmatrix} \langle 1,1|\hat{J}^2|1,1\rangle & \langle 1,1|\hat{J}^2|1,0\rangle & \langle 1,1|\hat{J}^2|1,-1\rangle \\ \langle 1,0|\hat{J}^2|1,1\rangle & \langle 1,0|\hat{J}^2|1,0\rangle & \langle 1,0|\hat{J}^2|1,-1\rangle \\ \langle 1,-1|\hat{J}^2|1,1\rangle & \langle 1,-1|\hat{J}^2|1,0\rangle & \langle 1,-1|\hat{J}^2|1,-1\rangle \end{bmatrix}$$

   Usando agora a equação de Schrödinger para $\hat{J}^2$:

$$\hat{J}^2|j, m_j\rangle = j(j+1)\hbar^2|j, m_j\rangle$$

   Os termos vem:

$$\begin{aligned}
\langle 1,1|\hat{J}^2|1,1\rangle &= 1(1+1)\hbar^2\langle 1,1|1,1\rangle = 2\hbar^2 \\
\langle 1,1|\hat{J}^2|1,0\rangle &= 1(1+1)\hbar^2\cancel{\langle 1,1|1,0\rangle} = 0 \\
\langle 1,1|\hat{J}^2|1,-1\rangle &= 1(1+1)\hbar^2\cancel{\langle 1,1|1,-1\rangle} = 0 \\
\langle 1,0|\hat{J}^2|1,1\rangle &= 1(1+1)\hbar^2\cancel{\langle 1,0|1,1\rangle} = 0 \\
\langle 1,0|\hat{J}^2|1,0\rangle &= 1(1+1)\hbar^2\langle 1,0|1,0\rangle = 2\hbar^2 \\
\langle 1,0|\hat{J}^2|1,-1\rangle &= 1(1+1)\hbar^2\cancel{\langle 1,0|1,-1\rangle} = 0 \\
\langle 1,-1|\hat{J}^2|1,1\rangle &= 1(1+1)\hbar^2\cancel{\langle 1,-1|1,1\rangle} = 0 \\
\langle 1,-1|\hat{J}^2|1,0\rangle &= 1(1+1)\hbar^2\cancel{\langle 1,-1|1,0\rangle} = 0 \\
\langle 1,-1|\hat{J}^2|1,-1\rangle &= 1(1+1)\hbar^2\langle 1,-1|1,-1\rangle = 2\hbar^2
\end{aligned}$$

   Os termos cancelados têm origem na condição de ortogonalidade $\langle j, m_j|j', m_j'\rangle = \delta_{jj'}\delta_{m_j m_j'}$. Ou:

$$\hat{J}^2 = 2\hbar^2 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

A matriz $\hat{\boldsymbol{J}}_z$:

$$\hat{J}_z = \begin{bmatrix} \langle 1,1|\hat{J}_z|1,1\rangle & \langle 1,1|\hat{J}_z|1,0\rangle & \langle 1,1|\hat{J}_z|1,-1\rangle \\ \langle 1,0|\hat{J}_z|1,1\rangle & \langle 1,0|\hat{J}_z|1,0\rangle & \langle 1,0|\hat{J}_z|1,-1\rangle \\ \langle 1,-1|\hat{J}_z|1,1\rangle & \langle 1,-1|\hat{J}_z|1,0\rangle & \langle 1,-1|\hat{J}_z|1,-1\rangle \end{bmatrix}$$

Usando agora a equação de Schrödinger para $\hat{J}_z$:

$$\hat{J}_z|j,m_j\rangle = m_j\hbar|j,m_j\rangle$$

Os termos vem:

$$\langle 1,1|\hat{J}_z|1,1\rangle = 1\hbar\langle 1,1|1,1\rangle = \hbar$$
$$\langle 1,1|\hat{J}_z|1,0\rangle = 0\hbar\cancel{\langle 1,1|1,0\rangle} = 0$$
$$\langle 1,1|\hat{J}_z|1,-1\rangle = -1\hbar\cancel{\langle 1,1|1,-1\rangle} = 0$$
$$\langle 1,0|\hat{J}_z|1,1\rangle = 1\hbar\cancel{\langle 1,0|1,1\rangle} = 0$$
$$\langle 1,0|\hat{J}_z|1,0\rangle = 0\hbar\langle 1,0|1,0\rangle = 0$$
$$\langle 1,0|\hat{J}_z|1,-1\rangle = -1\hbar\cancel{\langle 1,0|1,-1\rangle} = 0$$
$$\langle 1,-1|\hat{J}_z|1,1\rangle = 1\hbar\cancel{\langle 1,-1|1,1\rangle} = 0$$
$$\langle 1,-1|\hat{J}_z|1,0\rangle = 0\hbar\cancel{\langle 1,-1|1,0\rangle} = 0$$
$$\langle 1,-1|\hat{J}_z|1,-1\rangle = -1\hbar\langle 1,-1|1,-1\rangle = -\hbar$$

Logo:

$$\hat{J}_z = \hbar\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

A matriz $\hat{\boldsymbol{J}}_+$:

$$\hat{J}_+ = \begin{bmatrix} \langle 1,1|\hat{J}_+|1,1\rangle & \langle 1,1|\hat{J}_+|1,0\rangle & \langle 1,1|\hat{J}_+|1,-1\rangle \\ \langle 1,0|\hat{J}_+|1,1\rangle & \langle 1,0|\hat{J}_+|1,0\rangle & \langle 1,0|\hat{J}_+|1,-1\rangle \\ \langle 1,-1|\hat{J}_+|1,1\rangle & \langle 1,-1|\hat{J}_+|1,0\rangle & \langle 1,-1|\hat{J}_+|1,-1\rangle \end{bmatrix}$$

Usando agora a equação de Schrödinger para $\hat{J}_+$:

$$\hat{J}_+|j, m_j\rangle = \hbar\sqrt{j(j+1) - m_j(m_j+1)}|j, m_j+1\rangle$$

Os termos vem:

$$\begin{aligned}
&\langle 1,1|\hat{J}_+|1,1\rangle = 0^* \\
&\langle 1,1|\hat{J}_+|1,0\rangle = \hbar\sqrt{1(1+1) - 0(0+1)}\langle 1,1|1,0+1\rangle = \sqrt{2}\hbar \\
&\langle 1,1|\hat{J}_+|1,-1\rangle = \hbar\sqrt{1(1+1) - (-1)(-1+1)}\cancel{\langle 1,1|1,-1+1\rangle} = 0 \\
&\langle 1,0|\hat{J}_+|1,1\rangle = 0^* \\
&\langle 1,0|\hat{J}_+|1,0\rangle = \hbar\sqrt{1(1+1) - 0(0+1)}\cancel{\langle 1,0|1,0+1\rangle} = 0 \\
&\langle 1,0|\hat{J}_+|1,-1\rangle = \hbar\sqrt{1(1+1) - (-1)(-1+1)}\langle 1,0|1,-1+1\rangle = \sqrt{2}\hbar \\
&\langle 1,-1|\hat{J}_+|1,1\rangle = 0^* \\
&\langle 1,-1|\hat{J}_+|1,0\rangle = \hbar\sqrt{1(1+1) - 0(0+1)}\cancel{\langle 1,-1|1,0+1\rangle} = 0 \\
&\langle 1,-1|\hat{J}_+|1,-1\rangle = \hbar\sqrt{1(1+1) - (-1)(-1+1)}\cancel{\langle 1,-1|1,-1+1\rangle} = 0
\end{aligned}$$

Os termos 0^* são devidos à acção do operador escada subida sobre $m_j = 1$ (valor máximo). Logo:

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

A matriz $\hat{J}_-$:

$$\hat{J}_- = \begin{bmatrix} \langle 1,1|\hat{J}_-|1,1\rangle & \langle 1,1|\hat{J}_-|1,0\rangle & \langle 1,1|\hat{J}_-|1,-1\rangle \\ \langle 1,0|\hat{J}_-|1,1\rangle & \langle 1,0|\hat{J}_-|1,0\rangle & \langle 1,0|\hat{J}_-|1,-1\rangle \\ \langle 1,-1|\hat{J}_-|1,1\rangle & \langle 1,-1|\hat{J}_-|1,0\rangle & \langle 1,-1|\hat{J}_-|1,-1\rangle \end{bmatrix}$$

Usando agora a equação de Schrödinger para $\hat{J}_-$:

$$\hat{J}_-|j, m_j\rangle = \hbar\sqrt{j(j+1) - m_j(m_j-1)}|j, m_j-1\rangle$$

Os termos vem:

$$
\begin{aligned}
&\langle 1,1|\hat{J}_-|1,1\rangle = \hbar\sqrt{1(1+1)-1(1-1)}\cancel{\langle 1,1|1,1-1\rangle} = 0\\
&\langle 1,1|\hat{J}_-|1,0\rangle = \hbar\sqrt{1(1+1)-0(0-1)}\cancel{\langle 1,1|1,-1\langle} = 0\\
&\langle 1,1|\hat{J}_-|1,-1\rangle = 0^*\\
&\langle 1,0|\hat{J}_-|1,1\rangle = \hbar\sqrt{1(1+1)-1(1-1)}\langle 1,0|1,1-1\rangle = \sqrt{2}\hbar\\
&\langle 1,0|\hat{J}_-|1,0\rangle = \hbar\sqrt{1(1+1)-0(0-1)}\cancel{\langle 1,0|1,0-1\rangle} = 0\\
&\langle 1,0|\hat{J}_-|1,-1\rangle = 0^*\\
&\langle 1,-1|\hat{J}_-|1,1\rangle = 0\\
&\langle 1,-1|\hat{J}_-|1,0\rangle = \hbar\sqrt{1(1+1)-0(0+1)}\langle 1,-1|1,0+1\rangle = \sqrt{2}\hbar\\
&\langle 1,-1|\hat{J}_-|1,-1\rangle = \hbar\sqrt{1(1+1)-(-1)(-1+1)}\cancel{\langle 1,-1|1,-1+1\rangle} = 0
\end{aligned}
$$

Os termos 0^* são devidos à acção do operador escada descida sobre $m_j = 1$ (valor mínimo). Logo:

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

A matriz $\hat{\boldsymbol{J}}_{\boldsymbol{x}}$:

$$
\begin{aligned}
\hat{J}_x &= \frac{1}{2}(\hat{J}_+ - \hat{J}_-)\\
\hat{J}_x &= \frac{1}{2}\left(\sqrt{2}\hbar \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} + \sqrt{2}\hbar \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}\right)\\
&= \frac{\hbar}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}
\end{aligned}
$$

A matriz $\hat{J}_y$:

$$\hat{J}_y = \frac{1}{2i}(\hat{J}_+ - \hat{J}_-) = \frac{1}{2}i(\hat{J}_- - \hat{J}_+)$$
$$\hat{J}_y = \frac{1}{2}i\left(\sqrt{2}\hbar\begin{bmatrix}0 & 0 & 0\\ 1 & 0 & 0\\ 0 & 1 & 0\end{bmatrix} - \sqrt{2}\hbar\begin{bmatrix}0 & 1 & 0\\ 0 & 0 & 1\\ 0 & 0 & 0\end{bmatrix}\right)$$
$$= \frac{\hbar}{\sqrt{2}}\begin{bmatrix}0 & -i & 0\\ i & 0 & -i\\ 0 & i & 0\end{bmatrix}$$

(b) Obtenha os vectores próprios de $\hat{J}^2$ e $\hat{J}_z$, verificando a condição de ortonormalidade e de conjunto completo.
Res: Sabendo que para uma matriz $n \times n$ diagonal, os n vectores próprios associados ao n-ésimo valor próprio são da forma:

$$|1,1\rangle = \begin{bmatrix}a\\ 0\\ 0\end{bmatrix} \qquad |1,0\rangle = \begin{bmatrix}0\\ b\\ 0\end{bmatrix} \qquad |1,-1\rangle = \begin{bmatrix}0\\ 0\\ c\end{bmatrix}$$

Para determinar as constantes usamos a condição de normalização: $\langle 1,1|1,1\rangle = 1$. Por exemplo:

$$\langle 1,1|1,1\rangle = \begin{bmatrix}a^\star & 0 & 0\end{bmatrix}\begin{bmatrix}a\\ 0\\ 0\end{bmatrix} = 1 = a^\star a = |a|^2 \Rightarrow a = 1$$

O mesmo se passa para os restantes vectores.
A demonstração que é um conjunto completo é baseada na condição:

$$\hat{I} = \sum_{m_j=-1}^{m_j=1} |1,m_j\rangle\langle 1,m_j|$$
$$= \begin{bmatrix}0\\ 0\\ 1\end{bmatrix}\begin{bmatrix}0 & 0 & 1\end{bmatrix} + \begin{bmatrix}0\\ 1\\ 0\end{bmatrix}\begin{bmatrix}0 & 1 & 0\end{bmatrix} + \begin{bmatrix}1\\ 0\\ 0\end{bmatrix}\begin{bmatrix}1 & 0 & 0\end{bmatrix} = \begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}$$

(c) Usando as matrizes de $\hat{J}_x$, $\hat{J}_y$ e $\hat{J}_z$ determine $[\hat{J}_x, \hat{J}_y]$, $[\hat{J}_y, \hat{J}_z]$ e $[\hat{J}_z, \hat{J}_x]$.
Res.: Partindo das matrizes anteriormente determinadas e $[\hat{J}_x, \hat{J}_y] =$

$\hat{J}_x\hat{J}_y - \hat{J}_y\hat{J}_x$, tem-se:

$$\hat{J}_x\hat{J}_y = \frac{\hbar^2}{2}\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{bmatrix}\begin{bmatrix}0 & -i & 0\\ i & 0 & -i\\ 0 & i & 0\end{bmatrix} = \frac{\hbar^2}{2}\begin{bmatrix}i & 0 & -i\\ 0 & 0 & 0\\ i & 0 & -i\end{bmatrix}$$

$$\hat{J}_y\hat{J}_x = \frac{\hbar^2}{2}\begin{bmatrix}0 & -i & 0\\ i & 0 & -i\\ 0 & i & 0\end{bmatrix}\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{bmatrix} = \frac{\hbar^2}{2}\begin{bmatrix}-i & 0 & -i\\ 0 & 0 & 0\\ i & 0 & i\end{bmatrix}$$

Logo:

$$\begin{aligned}[\hat{J}_x, \hat{J}_y] &= \hat{J}_x\hat{J}_y - \hat{J}_y\hat{J}_x\\ &= \frac{\hbar^2}{2}\left(\begin{bmatrix}i & 0 & -i\\ 0 & 0 & 0\\ i & 0 & -i\end{bmatrix} - \begin{bmatrix}-i & 0 & -i\\ 0 & 0 & 0\\ i & 0 & i\end{bmatrix}\right) = \frac{\hbar^2}{2}\begin{bmatrix}2i & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -2i\end{bmatrix}\\ &= i\hbar^2\begin{bmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{bmatrix} = i\hbar\hat{J}_z\end{aligned}$$

(d) Mostre que $\hat{J}_z^3 = \hbar^2\hat{J}_z$ e $\hat{J}_\pm^3 = 0$.
Res.:

$$\hat{J}_z^3 = \left(\hbar\begin{bmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{bmatrix}\right)^3 = \hbar^3\begin{bmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{bmatrix} = \hbar^2\hat{J}_z$$

$$\hat{J}_-^3 = \left(\sqrt{2}\hbar\begin{bmatrix}0 & 0 & 0\\ 1 & 0 & 0\\ 0 & 1 & 0\end{bmatrix}\right)^3 = 2\sqrt{2}\hbar^3\begin{bmatrix}0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{bmatrix} = 0$$

$$\hat{J}_+^3 = \left(\sqrt{2}\hbar\begin{bmatrix}0 & 1 & 0\\ 0 & 0 & 1\\ 0 & 0 & 0\end{bmatrix}\right)^3 = 2\sqrt{2}\hbar^3\begin{bmatrix}0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{bmatrix} = 0$$

2. Escreva a representação matricial de $\hat{S}^2$, $\hat{S}_z$, $\hat{S}_\pm$.
Res.: Assumindo $s = 1/2$ vem que $m_s = \pm\frac{1}{2}$, sendo as equações de Schrödinger

relevantes:

$$\hat{S}^2|s,m_s\rangle = s(s+1)\hbar^2|s,m_s\rangle$$
$$\hat{S}_z|s,m_s\rangle = m_s\hbar|s,m_s\rangle$$
$$\hat{S}_+|s,m_s\rangle = \hbar\sqrt{s(s+1)-m_s(m_s+1)}|s,m_s+1\rangle$$
$$\hat{S}_-|s,m_s\rangle = \hbar\sqrt{s(s+1)-m_s(m_s-1)}|s,m_s-1\rangle$$

Matriz $\hat{S}^2$:

$$\hat{S}^2 = \begin{bmatrix} \langle\frac{1}{2},\frac{1}{2}|\hat{S}^2|\frac{1}{2},\frac{1}{2}\rangle & \langle\frac{1}{2},\frac{1}{2}|\hat{S}^2|\frac{1}{2},-\frac{1}{2}\rangle \\ \langle\frac{1}{2},-\frac{1}{2}|\hat{S}^2|\frac{1}{2},\frac{1}{2}\rangle & \langle\frac{1}{2},-\frac{1}{2}|\hat{S}^2|\frac{1}{2},-\frac{1}{2}\rangle \end{bmatrix}$$

Os elementos da matriz vem dados por:

$$\langle\frac{1}{2},\frac{1}{2}|\hat{S}^2|\frac{1}{2},\frac{1}{2}\rangle = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\langle\frac{1}{2},\frac{1}{2}|\frac{1}{2},\frac{1}{2}\rangle = 3/4\hbar^2$$
$$\langle\frac{1}{2},\frac{1}{2}|\hat{S}^2|\frac{1}{2},-\frac{1}{2}\rangle = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\cancel{\langle\frac{1}{2},\frac{1}{2}|\frac{1}{2},-\frac{1}{2}\rangle} = 0$$
$$\langle\frac{1}{2},-\frac{1}{2}|\hat{S}^2|\frac{1}{2},\frac{1}{2}\rangle = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\cancel{\langle\frac{1}{2},-\frac{1}{2}|\frac{1}{2},\frac{1}{2}\rangle} = 0$$
$$\langle\frac{1}{2},-\frac{1}{2}|\hat{S}^2|\frac{1}{2},-\frac{1}{2}\rangle = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\langle\frac{1}{2},-\frac{1}{2}|\frac{1}{2},-\frac{1}{2}\rangle = 3/4\hbar^2$$

Ou seja:

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

Matriz $\hat{S}_z$:

$$\hat{S}_z = \begin{bmatrix} \langle\frac{1}{2},\frac{1}{2}|\hat{S}_z|\frac{1}{2},\frac{1}{2}\rangle & \langle\frac{1}{2},\frac{1}{2}|\hat{S}_z|\frac{1}{2},-\frac{1}{2}\rangle \\ \langle\frac{1}{2},-\frac{1}{2}|\hat{S}_z|\frac{1}{2},\frac{1}{2}\rangle & \langle\frac{1}{2},-\frac{1}{2}|\hat{S}_z|\frac{1}{2},-\frac{1}{2}\rangle \end{bmatrix}$$

Os elementos da matriz vem dados por:

$$\langle\frac{1}{2},\frac{1}{2}|\hat{S}_z|\frac{1}{2},\frac{1}{2}\rangle = \frac{1}{2}\hbar\langle\frac{1}{2},\frac{1}{2}|\frac{1}{2},\frac{1}{2}\rangle = \frac{1}{2}\hbar$$
$$\langle\frac{1}{2},\frac{1}{2}|\hat{S}_z|\frac{1}{2},-\frac{1}{2}\rangle = -\frac{1}{2}\hbar\cancel{\langle\frac{1}{2},\frac{1}{2}|\frac{1}{2},-\frac{1}{2}\rangle} = 0$$
$$\langle\frac{1}{2},-\frac{1}{2}|\hat{S}_z|\frac{1}{2},\frac{1}{2}\rangle = \frac{1}{2}\hbar\cancel{\langle\frac{1}{2},-\frac{1}{2}|\frac{1}{2},\frac{1}{2}\rangle} = 0$$
$$\langle\frac{1}{2},-\frac{1}{2}|\hat{S}_z|\frac{1}{2},-\frac{1}{2}\rangle = -\frac{1}{2}\hbar\langle\frac{1}{2},-\frac{1}{2}|\frac{1}{2},-\frac{1}{2}\rangle = -\frac{1}{2}\hbar^2$$

$$\hat{S}_z = \frac{1}{2}\hbar \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Matriz $\hat{\boldsymbol{S}}_+$:

$$\hat{S}_+ = \begin{bmatrix} \langle \frac{1}{2}, \frac{1}{2}|\hat{S}_+|\frac{1}{2}, \frac{1}{2}\rangle & \langle \frac{1}{2}, \frac{1}{2}|\hat{S}_+|\frac{1}{2}, -\frac{1}{2}\rangle \\ \langle \frac{1}{2}, -\frac{1}{2}|\hat{S}_+|\frac{1}{2}, \frac{1}{2}\rangle & \langle \frac{1}{2}, -\frac{1}{2}|\hat{S}_+|\frac{1}{2}, -\frac{1}{2}\rangle \end{bmatrix}$$

Os elementos da matriz vem dados por:

$$\langle \frac{1}{2}, \frac{1}{2}|\hat{S}_+|\frac{1}{2}, \frac{1}{2}\rangle = 0^*$$

$$\langle \frac{1}{2}, \frac{1}{2}|\hat{S}_+|\frac{1}{2}, -\frac{1}{2}\rangle = \hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - \left(-\frac{1}{2}\right)\left(-\frac{1}{2}+1\right)}\langle \frac{1}{2}, \frac{1}{2}|\frac{1}{2}, -\frac{1}{2}+1\rangle = \hbar$$

$$\langle \frac{1}{2}, -\frac{1}{2}|\hat{S}_+|\frac{1}{2}, \frac{1}{2}\rangle = 0^*$$

$$\langle \frac{1}{2}, -\frac{1}{2}|\hat{S}_+|\frac{1}{2}, -\frac{1}{2}\rangle = \hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - \left(-\frac{1}{2}\right)\left(-\frac{1}{2}+1\right)}\cancel{\langle \frac{1}{2}, -\frac{1}{2}|\frac{1}{2}, -\frac{1}{2}+1\rangle} = 0$$

Os termos 0^* são devidos à acção do operador escada subida sobre $m_s = \frac{1}{2}$ (valor máximo). Ou seja:

$$\hat{S}_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$$

Matriz $\hat{\boldsymbol{S}}_-$:

$$\hat{S}_- = \begin{bmatrix} \langle \frac{1}{2}, \frac{1}{2}|\hat{S}_-|\frac{1}{2}, \frac{1}{2}\rangle & \langle \frac{1}{2}, \frac{1}{2}|\hat{S}_-|\frac{1}{2}, -\frac{1}{2}\rangle \\ \langle \frac{1}{2}, -\frac{1}{2}|\hat{S}_-|\frac{1}{2}, \frac{1}{2}\rangle & \langle \frac{1}{2}, -\frac{1}{2}|\hat{S}_-|\frac{1}{2}, -\frac{1}{2}\rangle \end{bmatrix}$$

Os elementos da matriz vem dados por:

$$\langle \frac{1}{2}, \frac{1}{2}|\hat{S}_-|\frac{1}{2}, \frac{1}{2}\rangle = \hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - \frac{1}{2}\left(\frac{1}{2}-1\right)}\cancel{\langle \frac{1}{2}, \frac{1}{2}|\frac{1}{2}, \frac{1}{2}-1\rangle} = 0$$

$$\langle \frac{1}{2}, \frac{1}{2}|\hat{S}_-|\frac{1}{2}, -\frac{1}{2}\rangle = 0^*$$

$$\langle \frac{1}{2}, -\frac{1}{2}|\hat{S}_-|\frac{1}{2}, \frac{1}{2}\rangle = \hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - \frac{1}{2}\left(\frac{1}{2}-1\right)}\langle \frac{1}{2}, -\frac{1}{2}|\frac{1}{2}, -\frac{1}{2}-1\rangle = \hbar$$

$$\langle \frac{1}{2}, -\frac{1}{2}|\hat{S}_-|\frac{1}{2}, -\frac{1}{2}\rangle = 0^*$$

Os termos 0^* são devidos à acção do operador escada descida sobre $m_s = -\frac{1}{2}$ (valor mínimo). Logo:

$$\hat{S}_- = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

3. Obtenha os vectores próprios de $\hat{S}^2$ e $\hat{S}_z$, verificando a condição de ortonormalidade e de conjunto completo.
   Res.:
   Sabendo que para uma matriz 2×2 diagonal, os 2 vectores próprios associados ao n-ésimo valor próprio são da forma:

   $$|1/2, 1/2\rangle = \begin{bmatrix} a \\ 0 \end{bmatrix} \qquad |1/2, , -1/2\rangle = \begin{bmatrix} 0 \\ b \end{bmatrix}$$

   Para determinar as constantes usamos a condição de normalização: $\langle 1/2, 1/2 | 1/2, 1/2\rangle = 1$. Por exemplo:

   $$\langle 1/2, 1/2 | 1/2, 1/2\rangle = \begin{bmatrix} a^\star & 0 \end{bmatrix} \begin{bmatrix} a \\ 0 \end{bmatrix} = 1 = a^\star a = |a|^2 \Rightarrow a = 1$$

   O mesmo se passa para os restantes vectores.

   A demonstração que é um conjunto completo é baseada na condição:

   $$\begin{aligned} \hat{I} &= \sum_{m_j=-1/2}^{m_j=1/2} |1/2, m_j\rangle\langle 1, m_j| \\ &= \begin{bmatrix} 0 \\ 1 \end{bmatrix} \begin{bmatrix} 0 & 1 \end{bmatrix} + \begin{bmatrix} 1 \\ 0 \end{bmatrix} \begin{bmatrix} 1 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \end{aligned}$$

4. Escreva $\hat{S}_\pm$ e determine o comutador $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$.
   Res.: Dos exercícios anteriores temos:

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

$$
\begin{aligned}
\hat{S}_y &= \frac{\hbar}{2i}\left(\begin{bmatrix}0 & 1\\0 & 0\end{bmatrix} - \begin{bmatrix}0 & 0\\1 & 0\end{bmatrix}\right) = \frac{-i\hbar}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}\\
\hat{S}_x\hat{S}_y &= \frac{\hbar^2}{2^2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\begin{bmatrix}0 & -i\\i & 0\end{bmatrix} = \frac{\hbar^2}{4}\begin{bmatrix}i & 0\\0 & -i\end{bmatrix}\\
\hat{S}_y\hat{S}_x &= \frac{\hbar^2}{2^2}\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} = \frac{\hbar^2}{4}\begin{bmatrix}-i & 0\\0 & i\end{bmatrix}\\
[\hat{S}_x, \hat{S}_y] &= \frac{\hbar^2}{4}\left(\begin{bmatrix}i & 0\\0 & -i\end{bmatrix} - \begin{bmatrix}-i & 0\\0 & i\end{bmatrix}\right) = i\frac{\hbar}{2}\frac{\hbar}{2}\begin{bmatrix}2 & 0\\0 & -2\end{bmatrix}\\
&= i2\frac{\hbar}{2}\frac{\hbar}{2}\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix} = i\hbar\hat{S}_z
\end{aligned}
$$