19. Numa notação devida ao físico P.A.M. Dirac, os estados próprios normalizados do oscilador harmónico numa dimensão são designados por $|\nu\rangle$. O estado fundamental é dado por $|0\rangle = \psi_0(x)$, onde $\psi_0(x)$ é dada por

$$\psi_0(\vec{r}) \;=\; \mathcal{N}_0\, e^{-\frac{1}{2}\mu\omega r^2/\hbar} \quad , \tag{1}$$

onde $\mathcal{N}_0$ representa a constante de normalização, $\mathcal{N}_0 = \left[\frac{\mu\omega}{\pi\hbar}\right]^{1/4}$

a Mostre que é igual a $\hbar\omega/2$ o valor próprio de $|0\rangle$ sob o efeito do Hamiltoniano dado no exercício (18) e igual a $\hbar\omega\left(\nu+\frac{1}{2}\right)$ o valor próprio de $\left(a^\dagger\right)^\nu|0\rangle$ (aplicar ν vezes o operador $a^\dagger$ definido no exercício 18).

b Na notação acima definida, o valor expectável de um operador A, caso o sistema se encontre no estado excitado $|\nu\rangle = \psi_\nu(x)$, é denotado por

$$\langle A\rangle \;=\; \langle\nu\,|A|\,\nu\rangle \;=\; \int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,A\,\psi_\nu(x) \quad .$$

Determine o valor expectável do Hamiltoniano dado no exercício (18) para o estado $\left(a^\dagger\right)^\nu|0\rangle$.

c O estado $a^\dagger|\nu\rangle$ é proporcional ao estado $|\nu+1\rangle$ (porquê?). Utilizando o resultado da alínea **b**, mostre que a constante de proporcionalidade é igual a $\sqrt{\nu+1}$.

d Mostre que o valor expectável do operador x (exprimir em a e $a^\dagger$) para a transição de um estado $|\nu\rangle$ para um estado $|\nu+m\rangle$ se anula, salvo nos casos $m=\pm1$.

Solution:

a. From the discussion regarding the solution of exercise (18d), we concluded that the eigenspectrum of H is given by $\frac{1}{2}\hbar\omega$, $\frac{3}{2}\hbar\omega$, $\frac{5}{2}\hbar\omega$, ..., whereas the respective eigenstates are given by $|0\rangle$, $|1\rangle$, $|2\rangle$, ... In a more compact notation

$$H|\nu\rangle = E_\nu|\nu\rangle \quad \text{with} \quad E_\nu = \left(\tfrac{1}{2}+\nu\right)\hbar\omega \quad ,$$

b.

$$\langle H\rangle \;=\; \langle\nu\,|H|\,\nu\rangle \;=\; \int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,H\,\psi_\nu(x) =$$

$$\int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,E_\nu\,\psi_\nu(x) = E_\nu\int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,\psi_\nu(x) = E_\nu\int_{-\infty}^{+\infty} dx\;|\psi_\nu(x)|^2 = E_\nu\,1 = E_\nu \quad .$$

Hence, in the case that the system is in the eigenstate $|\nu\rangle$, E_ν is the value we expect to find when the total energy of the system, given by $\langle H\rangle$, is measured.

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c. Using the result of exercise (18d), we obtain

$$H a^\dagger|\nu\rangle = \{E_\nu + \hbar\omega\}\, a^\dagger|\nu\rangle = \left\{\left(\tfrac{1}{2}+\nu\right)\hbar\omega + \hbar\omega\right\} a^\dagger|\nu\rangle = \left\{\tfrac{1}{2}+(\nu+1)\right\}\hbar\omega a^\dagger|\nu\rangle = E_{\nu+1}a^\dagger|\nu\rangle \quad ,$$

whereas, for $|\nu+1\rangle$ we also have $H|\nu+1\rangle = E_{\nu+1}|\nu+1\rangle$.
Now, since H has only one eigenstate for $E_{\nu+1}$, we must conclude that $a^\dagger|\nu\rangle$ and $|\nu+1\rangle$ are proportional.

The proportionality constant, say $X_{\nu+1}$, can be found by determining

$$\int_{-\infty}^{+\infty} dx\, \left\{a^\dagger\psi_\nu(x)\right\}^*\, a^\dagger\psi_\nu(x) = \int_{-\infty}^{+\infty} dx\, \left\{X_{\nu+1}\psi_{\nu+1}(x)\right\}^*\, X_{\nu+1}\psi_{\nu+1}(x) =$$

$$= X^*_{\nu+1}X_{\nu+1}\int_{-\infty}^{+\infty} dx\, \psi^*_{\nu+1}(x)\,\psi_{\nu+1}(x) = |X_{\nu+1}|^2\int_{-\infty}^{+\infty} dx\, |\psi_{\nu+1}(x)|^2 = |X_{\nu+1}|^2 \quad .$$

So, we determine X_1.
We start with ($\alpha = \mu\omega/\hbar$)

$$a^\dagger\psi_0 = \sqrt{\frac{\mu\omega}{2\hbar}}\left(x - \frac{\hbar}{\mu\omega}\frac{\partial}{\partial x}\right)\mathcal{N}_0\, e^{-\frac{1}{2}\alpha x^2} =$$

$$= \mathcal{N}_0\sqrt{\frac{\mu\omega}{2\hbar}}\left(xe^{-\frac{1}{2}\alpha x^2} - \frac{1}{\alpha}\frac{\partial}{\partial x}e^{-\frac{1}{2}\alpha x^2}\right) = \mathcal{N}_0\sqrt{\frac{\mu\omega}{2\hbar}}\left(xe^{-\frac{1}{2}\alpha x^2} - \frac{1}{\alpha}\left\{-\alpha x e^{-\frac{1}{2}\alpha x^2}\right\}\right)$$

$$= \mathcal{N}_0\sqrt{\frac{\mu\omega}{2\hbar}}\left(xe^{-\frac{1}{2}\alpha x^2} + xe^{-\frac{1}{2}\alpha x^2}\right) = 2\mathcal{N}_0\sqrt{\frac{\mu\omega}{2\hbar}}xe^{-\frac{1}{2}\alpha x^2}$$

So, we must then determine

$$|X_1|^2 = \int_{-\infty}^{+\infty} dx\, \left\{a^\dagger\psi_0(x)\right\}^*\, a^\dagger\psi_0(x) = 2\,|\mathcal{N}_0|^2\,\frac{\mu\omega}{\hbar}\int_{-\infty}^{+\infty} dx\, x^2 e^{-\alpha x^2}$$

This integral may be looked up in the tables (Integral number 10 of the tables of integrals at http://www.sosmath.com/tables/integral/integ37/integ37.html maybe useful, note $\Gamma(n+1) = n\Gamma(n)$ en $\Gamma(1/2) = \sqrt{\pi}$.) We obtain then

$$|X_1|^2 = 2\left[\frac{\mu\omega}{\pi\hbar}\right]^{1/2}\frac{\mu\omega}{\hbar}\,\frac{\frac{1}{2}\sqrt{\pi}}{(\mu\omega/\hbar)^{3/2}} = 1 = \sqrt{0+1} \quad .$$

This way, one can continue, for X_2 we must determine $a^\dagger\psi_1$ and its integral, etcetera. However, there exists a faster method.
First, we can make use of the general property

$$\int_{-\infty}^{+\infty} dx\, \left\{A^\dagger\phi_1(x)\right\}^*\,\phi_2(x) = \int_{-\infty}^{+\infty} dx\, \phi_1^*(x)^*\, A\,\phi_2(x) \quad .$$

Then, we may substitute

$$aa^\dagger = aa^\dagger - a^\dagger a + a^\dagger a = \left[a\ ,\ a^\dagger\right] + a^\dagger a = 1 + \left(\frac{H}{\hbar\omega} - \tfrac{1}{2}\right) = \frac{H}{\hbar\omega} + \tfrac{1}{2} \quad ,$$

whereas, moreover

$$\left(\frac{H}{\hbar\omega} + \tfrac{1}{2}\right)\,\psi_\nu = \left(\frac{E_\nu}{\hbar\omega} + \tfrac{1}{2}\right)\,\psi_\nu = \left(\frac{\left(\frac{1}{2} + \nu\right)\hbar\omega}{\hbar\omega} + \tfrac{1}{2}\right)\,\psi_\nu = (\nu+1)\,\psi_\nu \quad .$$

This way, we obtain

$$\int_{-\infty}^{+\infty} dx\,\left\{a^\dagger\psi_\nu(x)\right\}^*\,a^\dagger\psi_\nu(x) = \int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,aa^\dagger\psi_\nu(x) = \int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,(\nu+1)\psi_\nu(x) = (\nu+1).$$

Which gives $|X_{\nu+1}|^2 = \nu + 1$.

---

d.

$$a + a^\dagger = \frac{2\mu\omega}{\hbar}\,x \quad .$$

Hence,

$$\begin{aligned}
\langle\nu\,|x|\,\nu+m\rangle &= \int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,\frac{\hbar}{2\mu\omega}\,\left(a + a^\dagger\right)\,\psi_{\nu+m}(x) = \\
&= \frac{\hbar}{2\mu\omega}\,\left\{\int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,a\,\psi_{\nu+m}(x) + \int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,a^\dagger\,\psi_{\nu+m}(x)\right\} \\
&= \frac{\hbar}{2\mu\omega}\,\left\{\int_{-\infty}^{+\infty} dx\,\left\{a^\dagger\,\psi_\nu(x)\right\}^*\,\psi_{\nu+m}(x) + \int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,a^\dagger\,\psi_{\nu+m}(x)\right\} \\
&= \frac{\hbar}{2\mu\omega}\,\left\{\int_{-\infty}^{+\infty} dx\,\left\{X_{\nu+1}\,\psi_{\nu+1}(x)\right\}^*\,\psi_{\nu+m}(x) + \int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,X_{\nu+m+1}\,\psi_{\nu+m+1}(x)\right\} \\
&= \frac{\hbar}{2\mu\omega}\,\left\{X_{\nu+1}^*\int_{-\infty}^{+\infty} dx\,\psi_{\nu+1}^*(x)\,\psi_{\nu+m}(x) + X_{\nu+m+1}\int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,\psi_{\nu+m+1}(x)\right\} \\
&= \frac{\hbar}{2\mu\omega}\,\left\{X_{\nu+1}^*\,\delta_{\nu+1,\nu+m} + X_{\nu+m+1}\,\delta_{\nu,\nu+m+1}\right\} \quad .
\end{aligned}$$

The last step follows from the orthogonality relation of the normalized eigenfunctions of H, which reads

$$\int_{-\infty}^{+\infty} dx\,\psi_\nu^*(x)\,\psi_\mu(x) = \delta_{\nu,\mu} = \begin{cases} 1 & \text{for} \quad \nu = m \\ 0 & \text{for} \quad \nu \neq m \end{cases}$$

Now, $\delta_{\nu+1,\nu+m}$ is only non-zero for $\nu + 1 = \nu + m$ and in that case equal to 1, whereas $\delta_{\nu,\nu+m+1}$ is only non-zero for $\nu = \nu + m + 1$. In the former case $m = 1$, in the latter case $m = -1$.
Electromagnetic transitions of vibrational molecular states are related to the x operator. Hence, transitions are favoured when $\Delta\nu = \pm 1$.

20. Em virtude de se estar a estudar o espectro vibracional de uma molécula polar diatómica, considere que os dois núcleos atómicos estão ligados por uma mola (frequência de mola $\omega = 2\pi\nu$) e cujos movimentos estão restritos a uma dimensão (x).

a Utilizando os resultados do exercício (19), mostre que o espectro deste oscilador é dado por

$$E_v \;=\; \hbar\omega\left(v+\frac{1}{2}\right)\,, \quad v = 0,\ 1,\ 2,\ 3,\ \ldots \quad .$$

b A probabilidade de ocorrer uma transição dipolar entre os estados $|n\rangle$ e $|n+m\rangle$ é dada pelo integral $\int_{-\infty}^{+\infty} dx\, \psi_n^*(x)\, x\, \psi_{n+m}(x)$. Utilizando os resultados do exercício (19), determine as regras de selecção para transições dipolares.

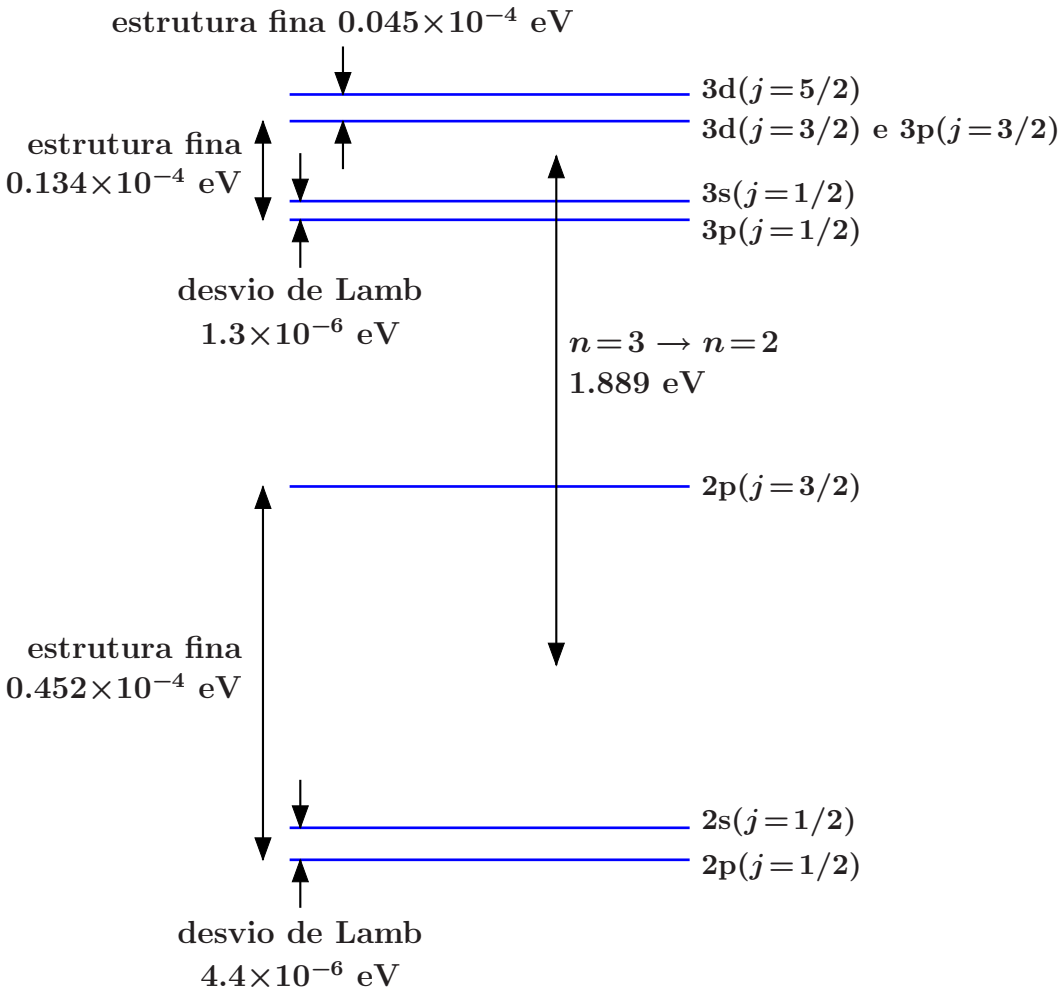
c No entanto, o potencial entre os núcleos atómicos de uma molécula polar diatómica na realidade não é dado por um oscilador harmónico. O espectro real é dado por

$$E_v \;=\; \hbar\omega\left(v+\frac{1}{2}\right)\left\{1 \;-\; a_1\left(v+\frac{1}{2}\right) \;-\; a_2\left(v+\frac{1}{2}\right)^2 \;-\; \ldots\right\}\,,$$

$$v = 0,\ 1,\ 2,\ 3,\ \ldots \quad ,$$

onde os parâmetros a_1, a_2, ... variam de molécula para molécula. Também as regras de selecção são mais flexíveis na realidade, embora as transições $\Delta v = \pm 1$ sejam mais intensas do que as transições $\Delta v = \pm 2$, etc..
Numa aproximação linear ($a_2 = a_3 = \ldots = 0$), determine $\hbar\omega$ e a_1 para a molécula $HC\ell$, caso o espectro de vibração de $HC\ell$ mostre uma linha intensa com frequência 2886 cm^{-1}, uma linha mais fraca com frequência 5668 cm^{-1} e ainda uma linha muito fraca com frequência 8347 cm^{-1}.

21. Considere a primeira linha de Balmer ($n = 3 \rightarrow n = 2$). A figura mostra os níveis energéticos dos estados com $n = 2$ e $n = 3$ do átomo de hidrogénio. Além da estrutura fina do acoplamento spin-órbita está também apresentada a estrutura dos efeitos quânticos do electromagnetismo, o desvio de Lamb (prémio Nobel de 1955).



As várias trancições electromagnéticas respeitam certas regras (as regras de selecção) devido às propriedades do campo electromagnético: O número quântico do momento angular ℓ apenas admite uma variação de uma unidade entre o estado inicial e o estado final (i.e. $\Delta\ell = \pm 1$), o número quântico do momento angular total j admite uma variação de uma unidade no máximo entre o estado inicial e o estado final (i.e. $\Delta j = 0, \pm 1$), enquanto o número quântico magnético j_z pode variar com $\Delta j_z = 0, \pm 1$ entre o estado inicial e o estado final.

a Explique os vários valores do número quântico j que aparecem na figura.

b Determine entre quais dos estados pode haver transições electromagnéticas e quantas linhas isto implica no espectro de hidrogénio.

c Caso a intensidade de uma linha depende linearmente do número de possibilidades que existam para o número quântico j_z, determine as razões das intensidades entre as várias linhas espectrais.

Solution:

We study here transitions $n = 3 \to n = 2$ for hydrogen. First, we will study how many states there are for $n = 3$ and $n = 2$ and then we will study how many dipolar transition can occur.
a. For $n = 3$ we have the possibilities $\ell < n = 3$, *i.e.* $\ell = 0$ (S), 1 (P) and 2 (D). Each combines with the two spin states $s_z = \pm 1/2$ of the electron.

For $\ell = 0$ we have one state $\ell_z = 0$. This combines to $j_z = \ell_z + s_z = 0 \pm 1/2 = \pm 1/2$. Hence, two states, which implies $j = 1/2$. Those states are collected under $3S_{\frac{1}{2}}$.

For $\ell = 1$ we have three states $\ell_z = 0, \pm 1$. Those combine to $j_z = \ell_z + s_z = 0 \pm 1/2 = \pm 1/2$, $j_z = \ell_z + s_z = -1 \pm 1/2 = -1/2$ and $-3/2$ and $j_z = \ell_z + s_z = +1 \pm 1/2 = +3/2$ and $+1/2$. Hence, six states in total, which can be grouped into two sets, one set of four states $\{j_z = -3/2,\ -1/2,\ +1/2,\ +3/2\}$, which implies $j = 3/2$, and one set of two states $\{j_z = -1/2,\ +1/2, \}$, which implies $j = 1/2$. Those states are respectively collected under $3P_{\frac{3}{2}}$ and $3P_{\frac{1}{2}}$.

For $\ell = 2$ we have five states $\ell_z = 0, \pm 1, \pm 2$. Those combine to $j_z = \ell_z + s_z = 0 \pm 1/2 = \pm 1/2$, $j_z = \ell_z + s_z = -1 \pm 1/2 = -1/2$ and $-3/2$, $j_z = \ell_z + s_z = +1 \pm 1/2 = +3/2$ and $+1/2$, $j_z = \ell_z + s_z = -2 \pm 1/2 = -3/2$ and $-5/2$ and $j_z = \ell_z + s_z = +2 \pm 1/2 = +5/2$ and $+3/2$. Hence, ten states in total, which can be grouped into two sets, one set of four states $\{j_z = -5/2,\ -3/2,\ -1/2,\ +1/2,\ +3/2,\ +5/2\}$, which implies $j = 5/2$, and one set of four states $\{j_z = -3/2,\ -1/2,\ +1/2,\ +3/2\}$, which implies $j = 3/2$. Those states are respectively collected under $3D_{\frac{5}{2}}$ and $3D_{\frac{3}{2}}$.

level	n	ℓ	j	j_z
$3D_{\frac{5}{2}}$	3	2	$\frac{5}{2}$	$-5/2,\ -3/2,\ -1/2,\ +1/2,\ +3/2,\ +5/2$
$3D_{\frac{3}{2}}$	3	2	$\frac{3}{2}$	$-3/2,\ -1/2,\ +1/2,\ +3/2$
$3P_{\frac{3}{2}}$	3	1	$\frac{3}{2}$	$-3/2,\ -1/2,\ +1/2,\ +3/2$
$3P_{\frac{1}{2}}$	3	1	$\frac{1}{2}$	$-1/2,\ +1/2$
$3S_{\frac{1}{2}}$	3	0	$\frac{1}{2}$	$-1/2,\ +1/2$

For $n = 2$ we have the possibilities $\ell < n = 2$, *i.e.* $\ell = 0$ (S) and 1 (P). Each combines with the two spin states $s_z = \pm 1/2$ of the electron.

For $\ell = 0$ we have one state $\ell_z = 0$. This combines to $j_z = \ell_z + s_z = 0 \pm 1/2 = \pm 1/2$. Hence, two states, which implies $j = 1/2$. Those states are collected under $2S_{\frac{1}{2}}$.

For $\ell = 1$ we have three states $\ell_z = 0, \pm 1$. Those combine to $j_z = \ell_z + s_z = 0 \pm 1/2 = \pm 1/2$, $j_z = \ell_z + s_z = -1 \pm 1/2 = -1/2$ and $-3/2$ and $j_z = \ell_z + s_z = +1 \pm 1/2 = +3/2$ and $+1/2$. Hence, six states in total, which can be grouped into two sets, one set of four states $\{j_z = -3/2,\ -1/2,\ +1/2,\ +3/2\}$, which implies $j = 3/2$, and one set of two states $\{j_z = -1/2,\ +1/2, \}$, which implies $j = 1/2$. Those states are respectively collected under $2P_{\frac{3}{2}}$ and $2P_{\frac{1}{2}}$.

level	n	ℓ	j	j_z
$2P_{\frac{3}{2}}$	2	1	$\frac{3}{2}$	$-3/2,\ -1/2,\ +1/2,\ +3/2$
$2P_{\frac{1}{2}}$	2	1	$\frac{1}{2}$	$-1/2,\ +1/2$
$2S_{\frac{1}{2}}$	2	0	$\frac{1}{2}$	$-1/2,\ +1/2$

b. Dipolar transitions $3 \to 2$ are limited by the selection rules $\Delta\ell = \pm 1$, $\Delta j = 0,\ \pm 1$ and $\Delta j_z = 0,\ \pm 1$. In the following table we collect the possible transitions.

		$2P_{\frac{3}{2}}$				$2P_{\frac{1}{2}}$		$2S_{\frac{1}{2}}$	
		$j_z=-\frac{3}{2}$	$j_z=-\frac{1}{2}$	$j_z=+\frac{1}{2}$	$j_z=+\frac{3}{2}$	$j_z=-\frac{1}{2}$	$j_z=+\frac{1}{2}$	$j_z=-\frac{1}{2}$	$j_z=+\frac{1}{2}$
$3D_{\frac{5}{2}}$	$j_z=-\frac{5}{2}$	X							
$3D_{\frac{5}{2}}$	$j_z=-\frac{3}{2}$	X	X						
$3D_{\frac{5}{2}}$	$j_z=-\frac{1}{2}$	X	X	X		$\Delta j = 2$		$\Delta j = 2$	
$3D_{\frac{5}{2}}$	$j_z=+\frac{1}{2}$		X	X	X			$\Delta\ell = 2$	
$3D_{\frac{5}{2}}$	$j_z=+\frac{3}{2}$			X	X				
$3D_{\frac{5}{2}}$	$j_z=+\frac{5}{2}$				X				
$3D_{\frac{3}{2}}$	$j_z=-\frac{3}{2}$	X	X			X			
$3D_{\frac{3}{2}}$	$j_z=-\frac{1}{2}$	X	X	X		X	X		
$3D_{\frac{3}{2}}$	$j_z=+\frac{1}{2}$		X	X	X	X	X	$\Delta\ell = 2$	
$3D_{\frac{3}{2}}$	$j_z=+\frac{3}{2}$			X	X		X		
$3P_{\frac{3}{2}}$	$j_z=-\frac{3}{2}$							X	
$3P_{\frac{3}{2}}$	$j_z=-\frac{1}{2}$							X	X
$3P_{\frac{3}{2}}$	$j_z=+\frac{1}{2}$		$\Delta\ell = 0$			$\Delta\ell = 0$		X	X
$3P_{\frac{3}{2}}$	$j_z=+\frac{3}{2}$								X
$3P_{\frac{1}{2}}$	$j_z=-\frac{1}{2}$							X	X
$3P_{\frac{1}{2}}$	$j_z=+\frac{1}{2}$		$\Delta\ell = 0$			$\Delta\ell = 0$		X	X
$3S_{\frac{1}{2}}$	$j_z=-\frac{1}{2}$	X	X	X		X	X		
$3S_{\frac{1}{2}}$	$j_z=+\frac{1}{2}$		X	X	X	X	X	$\Delta\ell = 0$	

From the table we observe that there are the seven possible transitions: $3D_{\frac{5}{2}} \to 2P_{\frac{3}{2}}$, $3D_{\frac{3}{2}} \to 2P_{\frac{3}{2}}$,

$3D\frac{3}{2} \rightarrow 2P\frac{1}{2}$, $3P\frac{3}{2} \rightarrow 2S\frac{1}{2}$, $3P\frac{1}{2} \rightarrow 2S\frac{1}{2}$, $3S\frac{1}{2} \rightarrow 2P\frac{3}{2}$ and $3S\frac{1}{2} \rightarrow 2P\frac{1}{2}$, represented by squares.

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c. Inside the squares are indicated, with X, the various possibilities with respect to Δj_z.

transition	number of possibilities	relative intensity
$3D\frac{5}{2} \rightarrow 2P\frac{3}{2}$	12	1.0
$3D\frac{3}{2} \rightarrow 2P\frac{3}{2}$	10	$\frac{10}{12} = 0.83$
$3D\frac{3}{2} \rightarrow 2P\frac{1}{2}$	6	$\frac{6}{12} = 0.5$
$3P\frac{3}{2} \rightarrow 2S\frac{1}{2}$	6	$\frac{6}{12} = 0.5$
$3P\frac{1}{2} \rightarrow 2S\frac{1}{2}$	4	$\frac{4}{12} = 0.33$
$3S\frac{1}{2} \rightarrow 2P\frac{3}{2}$	6	$\frac{6}{12} = 0.5$
$3S\frac{1}{2} \rightarrow 2P\frac{1}{2}$	4	$\frac{4}{12} = 0.33$