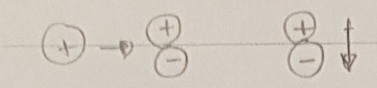
Assignment (23)

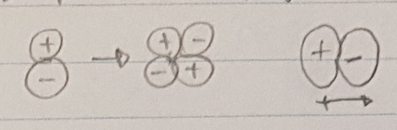
(1) a)

(2) a) 1s → 2s , no

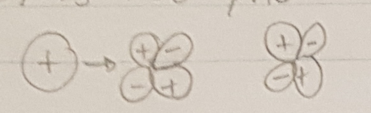
b) 1s → 2p , yes



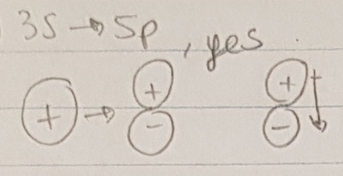
c) 2p → 3d , yes



d) 3s → 5d , no



e) 3s → 5p , yes



(3) a) $\left[-\frac{1}{2}\nabla^2 + V_{3D\text{-}box}\{x,y,z\} + V_{light}\{x,y,z,t\}\right]\Psi\{x,y,z,t\} = i\hbar\frac{\partial\Psi\{x,y,z,t\}}{\partial t}$

b) $V_{light}\{x,y,z,t\} = -2Vx\sin\{\omega t\}$.

c) $\Psi_{3D}\{x,y,z\} = \Psi_{1D}\{x\}\Psi_{1D}\{y\}\Psi_{1D}\{z\} = \sqrt{\frac{2^3}{a_x a_y a_z}}\sin\{\frac{n_x\pi x}{a_x}\}\sin\{\frac{n_y\pi y}{a_y}\}\sin\{\frac{n_z\pi z}{a_z}\}$

$\Psi_{initial}\{x,y,z\} = \Psi_{n_x,n_y,n_z}\{x,y,z\}$

$\Psi_{final}\{x,y,z\} = \Psi_{n'_x,n'_y,n'_z}\{x,y,z\}$.

$\langle\Psi_{final}|x|\Psi_{initial}\rangle = \langle\Psi_{n'_x}\Psi_{n'_y}\Psi_{n'_z}|x|\Psi_{n_x}\Psi_{n_y}\Psi_{n_z}\rangle = \langle\Psi_{n'_x}|x|\Psi_{n_x}\rangle\underbrace{\langle\Psi_{n'_y}|\Psi_{n_y}\rangle}_{\delta_{n'_y n_y}}\underbrace{\langle\Psi_{n'_z}|\Psi_{n_z}\rangle}_{\delta_{n'_z n_z}}$

$\langle\Psi_{n'_x}|x|\Psi_{n_x}\rangle = \int_0^{a_x}\frac{2}{a_x}\sin\{\frac{n'_x\pi x}{a_x}\}x\sin\{\frac{n_x\pi x}{a_x}\}dx$

$= \frac{2}{a_x}\int_0^{a_x}x\left[\frac{1}{2}\right]\left[\cos\{\frac{(n'_x-n_x)\pi x}{a_x}\} - \cos\{\frac{(n'_x+n_x)\pi x}{a_x}\}\right]dx$

$= \frac{1}{a_x}\int_0^{a_x}x\cos\{\frac{(n'_x-n_x)\pi x}{a_x}\}dx - \frac{1}{a_x}\int_0^{a_x}x\cos\{\frac{(n'_x+n_x)\pi x}{a_x}\}dx$

$u = x$; $dv = \cos\{ax\}dx$

$du = dx$; $v = \sin\{ax\}(\frac{1}{a})$

$n'_x \neq n_x$ or no transition

$= \frac{1}{a_x}\left[\frac{x a_x}{(n'_x-n_x)\pi}\sin\{\frac{(n'_x-n_x)\pi x}{a_x}\}\Big|_0^{a_x} - \frac{a_x}{(n'_x-n_x)\pi}\int_0^{a_x}\sin\{\frac{(n'_x-n_x)\pi x}{a_x}\}dx\right]$

$- \frac{1}{a_x}\left[\frac{x a_x}{(n'_x+n_x)\pi}\sin\{\frac{(n'_x+n_x)\pi x}{a_x}\}\Big|_0^{a_x} - \frac{a_x}{(n'_x+n_x)\pi}\int_0^{a_x}\sin\{\frac{(n'_x+n_x)\pi x}{a_x}\}dx\right]$ → 0

$= \frac{1}{(n'_x-n_x)\pi}\left[-\left(\frac{a_x}{(n'_x-n_x)\pi}\right)\cos\{\frac{(n'_x-n_x)\pi x}{a_x}\}\right]_0^{a_x} + \frac{1}{(n'_x+n_x)\pi}\left[-\left(\frac{a_x}{(n'_x+n_x)\pi}\right)\cos\{\frac{(n'_x+n_x)\pi x}{a_x}\}\right]_0^{a_x}$

$= \frac{-a_x}{(n'_x-n_x)^2\pi^2}\left[\cos\{(n'_x-n_x)\pi\} - \cos\{0\}\right] - \frac{a_x}{(n'_x+n_x)^2\pi^2}\left[\cos\{(n'_x+n_x)\pi\} - \cos\{0\}\right]$

* if $n'_x - n_x$ is odd:

$= \frac{-a_x}{(n'_x-n_x)^2\pi^2}[-1-1] - \frac{a_x}{(n'_x+n_x)^2\pi^2}[-1-1]$

$= \frac{2a_x}{(n'_x-n_x)^2\pi^2} + \frac{2a_x}{(n'_x+n_x)^2\pi^2}$

* if $n'_x - n_x$ is even:

$= 0$

$n'_x = n_x + 2A + 1$

odd → $n'_x - n_x = 2A+1$

$n'_x + n_x = n_x + 2A + 1 + n_x$

$= 2n_x + 2A + 1$

then $n'_x + n_x$ is also odd

$\langle\Psi_{final}|x|\Psi_{initial}\rangle = \left[\frac{8}{a_x a_y a_z}\right]\left[\frac{2a_x}{\pi^2}\right]\left[\frac{1}{(n'_x-n_x)^2} + \frac{1}{(n'_x+n_x)^2}\right]\delta_{n'_y n_y}\delta_{n'_z n_z}$

$n'_x - n_x = $ odd.

*Energy difference of allowed transitions:

$E_{n'_x n'_y n'_z} - E_{n_x n_y n_z} = \frac{h^2}{8m}\left[\frac{n'^2_x}{a_x^2} - \frac{n_x^2}{a_x^2} + \frac{n'^2_y}{a_y^2} - \frac{n_y^2}{a_y^2} + \frac{n'^2_z}{a_z^2} - \frac{n_z^2}{a_z^2}\right]$

$n'_x = n_x + 1, n_x + 3, \ldots$; $n'_y = n_y$; $n'_z = n_z$

$\Delta E = \frac{h^2}{8ma_x^2}\left[(n'_x)^2 - n_x^2\right] = \frac{h^2}{8ma_x^2}\left[(n_x+k)^2 - n_x^2\right]$; $k = 1,3,5,\ldots$

$= \frac{h^2}{8ma_x^2}\left[2kn_x + k^2\right]$; $k = 1,3,5,\ldots$; $n_x = 1,2,3,\ldots$

$\Delta E = \hbar\omega_{fi} = \frac{h}{2\pi}\omega_{fi}$

E1 → $\omega_{fi} = \frac{2\pi\Delta E}{h} = \frac{2\pi}{h}\left[\frac{h^2}{8ma_x^2}\right]\left[2kn_x + k^2\right] = \frac{\pi h}{4ma_x^2}\left[2kn_x + k^2\right]$

E2 → $\langle\Psi_{final}|xz|\Psi_{initial}\rangle = \underbrace{\langle\Psi_{n'_x}|x|\Psi_{n_x}\rangle}_{\neq 0 \text{ if } n'_x - n_x \text{ is odd}}\underbrace{\langle\Psi_{n'_y}|\Psi_{n_y}\rangle}_{\delta_{n'_y n_y}}\underbrace{\langle\Psi_{n'_z}|z|\Psi_{n_z}\rangle}_{\neq 0 \text{ if } n'_z - n_z \text{ is odd}}$

so $\Delta E = \frac{h^2}{8ma_x^2}\left[2k_x n_x + k_x^2\right] + \frac{h^2}{8ma_z^2}\left[2k_z n_z + k_z^2\right]$; $k_x, k_z = 1,3,5,\ldots$

$\omega_{fi} = \frac{2\pi\Delta E}{h} = \frac{2\pi h}{8m}\left[\frac{2k_x n_x + k_x^2}{a_x^2} + \frac{2k_z n_z + k_z^2}{a_z^2}\right]$; $n_x, n_z = 1,2,3,\ldots$

(4) a) Máx M_S and M_L is achieved when $|\ldots\phi^{\uparrow}_{3p_0}\phi^{\uparrow}_{3p_{+1}}\phi^{\uparrow}_{3p_{-1}}|$

$S = \frac{3}{2}$, $L = 0+1-1 = 0$ → ^4S

b) p^2 configuration:

	$M_L = 2$	$M_L = 1$	$M_L = 0$
$M_S = 1$		$\cancel{\lvert -p^{\uparrow}_{+1}p^{\uparrow}_{0}\rvert}$	$\cancel{\lvert -p^{\uparrow}_{+1}p^{\uparrow}_{-1}\rvert}$
$M_S = 0$	$\cancel{\lvert -p^{\uparrow}_{+1}p^{\downarrow}_{+1}\rvert}$	$\cancel{\lvert -p^{\uparrow}_{+1}p^{\downarrow}_{0}\rvert}$	$\cancel{\lvert -p^{\uparrow}_{+1}p^{\downarrow}_{-1}\rvert}$
		$\cancel{\lvert -p^{\downarrow}_{+1}p^{\uparrow}_{0}\rvert}$	$\cancel{\lvert -p^{\downarrow}_{+1}p^{\uparrow}_{-1}\rvert}$
			$\lvert -p^{\uparrow}_{0}p^{\downarrow}_{0}\rvert$

$L = 2$ → $\cancel{^1D}$, $S = 0$, 3 states

$L = 1$ → ^3P , $S = 1$, 4 states

$L = 0$ → ^1S , $S = 0$, 1 state.

* Couple with d^1 → $L = 2$, $S = \frac{1}{2}$

^1D → $^2G, ^2F, ^2D, ^2P, ^2S$

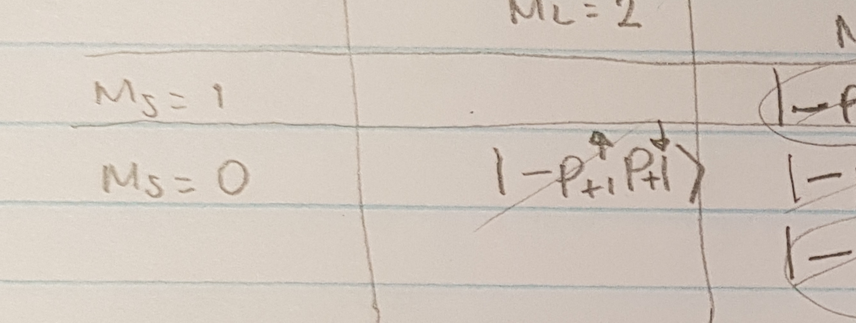
^1S → ^2D

^3P → $^2S, ^2P, ^2D, ^2F$; $^4S, ^4P, ^4D, ^4F$

$2(^2S), 2(^2P), 3(^2D), 2(^2F), ^2G, ^4S, ^4P, ^4D, ^4F$

c) $\Delta S = 0$ and $\Delta J = 1$, so E1 transition is only allowed from ^4S to ^4P.

d)



E1 allowed.

E1 forbidden.