

# SQ1

In PHYS3021, we have learned the spherical harmonics being the solutions of the angular part of a hydrogen atom, labeled as:

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

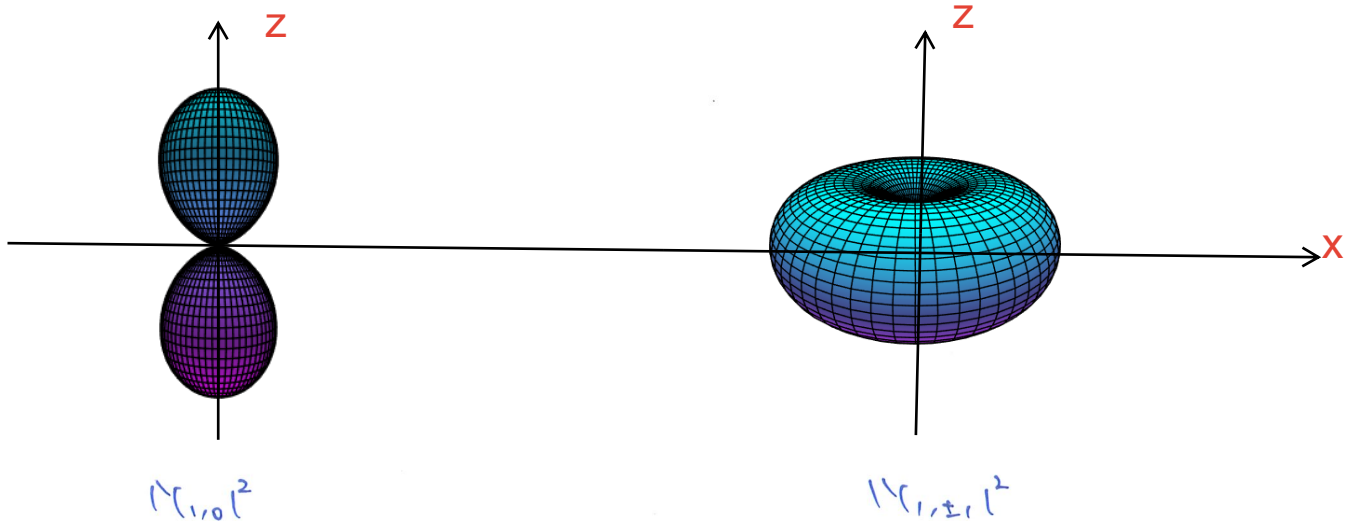
$$Y_{1,1} = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}$$

$$Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi}$$

(can be found in Note VIII-16 in 3021)

- a. While  $Y_{1,0}$  can be shown to be related to the  $P_z$  orbital, (an  $\infty$ -shaped plot pointing to  $z$ -direction), it is difficult to relate  $Y_{1,1}$  and  $Y_{1,-1}$  with  $P_x$  and  $P_y$ .

The probability density  $|Y_{1,1}|^2$  and  $|Y_{1,-1}|^2$  is  $\frac{3}{8\pi} \sin^2\theta$ , which is like a donut (no hole) shape lying on the  $x$ - $y$  plane. It is different from what we expect for  $P_x$  or  $P_y$  orbitals, which are the  $\infty$ -shaped plots pointing to  $x$  or  $y$ -axis respectively.



However, consider  $\frac{1}{\sqrt{2}} Y_{1,1} + \frac{1}{\sqrt{2}} Y_{1,-1}$ :

$$\begin{aligned} \frac{1}{\sqrt{2}} Y_{1,1} + \frac{1}{\sqrt{2}} Y_{1,-1} &= \frac{1}{\sqrt{2}} \left( \sqrt{\frac{3}{8\pi}} \right) \sin\theta (e^{i\phi} + e^{-i\phi}) \\ &= -\frac{1}{\sqrt{2}} \left( \sqrt{\frac{3}{8\pi}} \right) \sin\theta \sin\phi \\ &= -i \sqrt{\frac{3}{8\pi}} \sin\theta \sin\phi. \end{aligned}$$

(Note:  $\sin\phi = \frac{1}{2i}(e^{i\phi} - e^{-i\phi})$ )

... (1)

In spherical,  $\cos\theta = \frac{z}{r}$ .

ie,  $Y_{1,0}$  can be written as  $Y_{1,0} = \sqrt{\frac{3}{4\pi}} \frac{z}{r}$ , indicating its nature to be  $P_z$  orbital. , ie,  $\phi_{P_z} = \sqrt{\frac{3}{4\pi}} \frac{z}{r}$

Similarly, we can write down the wavefunctions of  $P_x$  and  $P_y$  directly as:

$$\phi_{P_x} = \sqrt{\frac{3}{4\pi}} \frac{x}{r}, \quad \phi_{P_y} = \sqrt{\frac{3}{4\pi}} \frac{y}{r},$$

$$\Rightarrow \begin{cases} \phi_{P_x} = \sqrt{\frac{3}{4\pi}} \frac{r \sin\theta \cos\phi}{r} = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\phi \\ \phi_{P_y} = \sqrt{\frac{3}{4\pi}} \frac{r \sin\theta \sin\phi}{r} = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\phi. \end{cases}$$

From (1), we can conclude that

$$\frac{1}{\sqrt{2}} Y_{1,1} + \frac{1}{\sqrt{2}} Y_{1,-1} = -r \phi_{P_y}$$

$$\Rightarrow \underline{\phi_{P_y} = \frac{1}{\sqrt{2}} (Y_{1,1} + Y_{1,-1})}$$

$$\text{Similarly, } \frac{1}{\sqrt{2}} Y_{1,1} - \frac{1}{\sqrt{2}} Y_{1,-1} = \frac{1}{\sqrt{2}} \left( \sqrt{\frac{3}{8\pi}} \right) (-e^{i\phi} - e^{-i\phi})$$

$$= -\sqrt{2} \left( \sqrt{\frac{3}{8\pi}} \right) \cos\phi$$

$$\left( \cos\phi = \frac{1}{2} (e^{i\phi} + e^{-i\phi}) \right)$$

$$= -\sqrt{\frac{3}{4\pi}} \cos\phi$$

$$= -\phi_{P_x}$$

$$\therefore \underline{\phi_{P_x} = -\frac{1}{\sqrt{2}} (Y_{1,1} - Y_{1,-1})}$$

b. From part a),  $\phi_{P_x} = -\frac{1}{\sqrt{2}} (Y_{1,1} - Y_{1,-1})$

$$\therefore \hat{L}^2 Y_{1,1} = 1(1+1)\hbar^2 Y_{1,1} = 2\hbar^2 Y_{1,1}$$

$$\hat{L}^2 Y_{1,-1} = 1(1+1)\hbar^2 Y_{1,-1} = 2\hbar^2 Y_{1,-1}$$

$$\therefore \hat{L}^2 \phi_{P_x} = -\frac{1}{\sqrt{2}} (\hat{L}^2 Y_{1,1} - \hat{L}^2 Y_{1,-1})$$

$$= -\frac{1}{\sqrt{2}} (2\hbar^2 Y_{1,1} - 2\hbar^2 Y_{1,-1})$$

$$= 2\hbar^2 \phi_{P_x}$$

$\therefore \phi_{P_x}$  is an eigenstate of  $\hat{L}^2$ .

b cont.

$$\therefore L_z^2 Y_{l,m} = (l) \hbar Y_{l,m} = \hbar Y_{l,m}$$

$$L_z^2 Y_{l,m-1} = (-1) \hbar Y_{l,m-1} = -\hbar Y_{l,m-1}$$

$$L_z^2 \phi_{px} = -\frac{1}{\sqrt{2}} (L_z^2 Y_{l,m} - L_z^2 Y_{l,m-1})$$

$$= -\frac{1}{\sqrt{2}} (\hbar Y_{l,m} + \hbar Y_{l,m-1})$$

$$= -\frac{\hbar}{\sqrt{2}} (Y_{l,m} + Y_{l,m-1})$$

$$= i \hbar \phi_{py}$$

$$\neq \lambda \phi_{px}, \text{ for some constant } \lambda.$$

$\therefore \phi_{px}$  is NOT an eigenstate of  $L_z^2$ .

c. From part a),  $\phi_{px} = -\frac{1}{\sqrt{2}} (Y_{l,m} - Y_{l,m-1})$

$$\phi_{py} = \frac{i}{\sqrt{2}} (Y_{l,m} + Y_{l,m-1})$$

The inner product between  $\phi_{px}$  and  $\phi_{py}$  is:

$$\int \phi_{px}^* \phi_{py} d\Omega$$

$$= -\frac{i}{2} \int (Y_{l,m}^* - Y_{l,m-1}^*) (Y_{l,m} + Y_{l,m-1}) d\Omega$$

(Note: here  $d\Omega = \sin\theta d\theta d\phi$  and the integration involves the region  $\theta \in [0, \pi]$ ,  $\phi \in [0, 2\pi]$ )

$$= -\frac{i}{2} \left[ \int Y_{l,m}^* Y_{l,m} d\Omega + \int Y_{l,m}^* Y_{l,m-1} d\Omega - \int Y_{l,m-1}^* Y_{l,m} d\Omega - \int Y_{l,m-1}^* Y_{l,m-1} d\Omega \right]$$

By the orthogonality of  $Y_{l,m}$ ,

$$= -\frac{i}{2} [ 1 + 0 - 0 - 1 ]$$

$$= 0$$

$\therefore \phi_{px}$  and  $\phi_{py}$  is ~~the~~ indeed orthogonal.

d. Similar ~~trick~~ trick can be done for  $l=2$  (d orbitals).

e.g.  $Y_{2,1} = -\sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{i\phi}$ , (Checked from Note VIII - 16 or IX - 15 of 3021)  
 $Y_{2,-1} = \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta e^{-i\phi}$

$$\begin{aligned}\frac{1}{\sqrt{2}}(Y_{2,1} + Y_{2,-1}) &= \frac{1}{\sqrt{2}} \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta (-e^{i\phi} + e^{-i\phi}) \\ &= \frac{1}{\sqrt{2}} \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta \cdot 2i \sin\phi \\ &= -i \sqrt{\frac{15}{4\pi}} \cos\theta \sin\theta \sin\phi\end{aligned}$$

$$\Rightarrow \frac{1}{\sqrt{2}}(Y_{2,1} + Y_{2,-1}) = \sqrt{\frac{15}{4\pi}} \cos\theta \sin\theta \sin\phi //$$

Similarly,  $-\frac{1}{\sqrt{2}}(Y_{2,1} - Y_{2,-1}) = -\frac{1}{\sqrt{2}} \left( \sqrt{\frac{15}{8\pi}} \right) \cos\theta \sin\theta (-e^{i\phi} - e^{-i\phi})$   
 $= \sqrt{\frac{15}{4\pi}} \cos\theta \sin\theta \cos\phi //$

$\therefore$  2 orthogonal <sup>REAL</sup> wavefunctions are created from the linear combinations of  $Y_{2,1}$  and  $Y_{2,-1}$ . In fact, the 5 d-states in chemistry come from linearly combining  $Y_{2,m_l}$  ( $m_l = 0, \pm 1, \pm 2$ ) in suitable ways.

easy to check since  $\int_0^{2\pi} \sin\phi \cos\phi d\phi = 0$ .

## SQ2

(a) In spectroscopy :  $\bar{\nu} \equiv \frac{1}{\lambda}$  ← wavelength  
↑  
Wavenumber

For transition from  $n_2 \rightarrow n_1$  (assumes  $n_2 > n_1$ )

$$E_{n_2} - E_{n_1} = \frac{me^4}{8\epsilon_0^2 h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Frequency of light emitted during the transition :

$$E_{n_2} - E_{n_1} = hf$$

$$f = \frac{me^4}{8\epsilon_0^2 h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Using the relation  $c = f\lambda$ ,

$$\lambda = \frac{c}{f} = \frac{8\epsilon_0^2 h^3 c}{me^4} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)^{-1}$$

$$\bar{\nu} = \frac{me^4}{8\epsilon_0^2 ch^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Calculating the prefactor :

$$\frac{me^4}{8\epsilon_0^2 ch^3} \approx 109737 \text{ cm}^{-1}$$

It is the limit when  $n_2 \rightarrow \infty$  and  $n_1 = 1$

(b)

NIST data of Hydrogen Atom

Configuration	Term	$J$	Level ( $\text{cm}^{-1}$ )	Ref.
1s	$^2S$	1/2	0.0000	MK00a
2p	$^2P^\circ$	1/2	82258.9191	MK00a
		3/2	82259.2850	MK00a
2s	$^2S$	1/2	82258.9544	MK00a
3p	$^2P^\circ$	1/2	97492.2112	MK00a
		3/2	97492.3196	MK00a
3s	$^2S$	1/2	97492.2217	MK00a
3d	$^2D$	3/2	97492.3195	MK00a
		5/2	97492.3556	MK00a
4p	$^2P^\circ$	1/2	102823.8486	MK00a
		3/2	102823.8943	MK00a
4s	$^2S$	1/2	102823.8530	MK00a
4d	$^2D$	3/2	102823.8942	MK00a
		5/2	102823.9095	MK00a
4f	$^2F^\circ$	5/2	102823.9095	MK00a
		7/2	102823.9171	MK00a
5p	$^2P^\circ$	1/2	105291.6287	MK00a
		3/2	105291.6521	MK00a
5s	$^2S$	1/2	105291.6309	MK00a
5d	$^2D$	3/2	105291.6520	MK00a
		5/2	105291.6599	MK00a
5f	$^2F^\circ$	5/2	105291.6598	MK00a
		7/2	105291.6637	MK00a
5g	$^2G$	7/2	105291.6637	MK00a
		9/2	105291.6661	MK00a
H	Limit		109678.7717	MK00a

} Energy levels of H atom not only depend on the quantum number  $n$

More interestingly, energies can be different even we have same  $n$  and  $l$  (e.g. 2p) It is the effect of spin-orbit coupling and you will learn it later in this course

The value is smaller than our results in part (a)

To take into account of the fact that H-atom is a two-body problem, we should replace  $m$  in Eq (2) by the reduced mass  $\mu$

$$\mu = m_{\text{proton}} m_e / (m_{\text{proton}} + m_e) = 0.999456 m_e$$

The corresponding value of

$$\frac{\mu e^4}{8 \epsilon_0^2 h^3 c} \approx 109677 \text{ cm}^{-1}$$

SQ3.

You can register to physicsworld and APS from here:

The screenshot displays two web pages. The top page is physicsworld, featuring a navigation bar with 'IOP Publishing', social media icons, and a search bar. A 'Register' button is circled in red. Below the navigation is a 'Today's headlines' section with a large image of a person jumping over a barrier labeled '2019' and '2020'. Two article teasers are visible: 'Smart contact lenses power up' under 'BIOMEDICAL DEVICES | RESEARCH UPDATE' and 'Machine learning could reveal graphene oxide's real structure' under '2D MATERIALS | RESEARCH UPDATE'. The bottom page is the APS website, with a navigation bar including 'Journals', 'Physics Magazine', 'PhysicsCentral', and 'APS News'. A 'Log in' button is circled in red. The main content area features a large article titled 'Entering a New Era of Dark Energy Cosmology' dated January 3, 2020, with a sub-headline: 'The first of a new generation of experiments aiming to shed light on the mysterious dark energy will start collecting data early this year. Read More »'. Below the article are three small image thumbnails.

Website of Nature and Science: <https://www.nature.com/>,  
<https://www.sciencemag.org/>.