SQ1

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

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

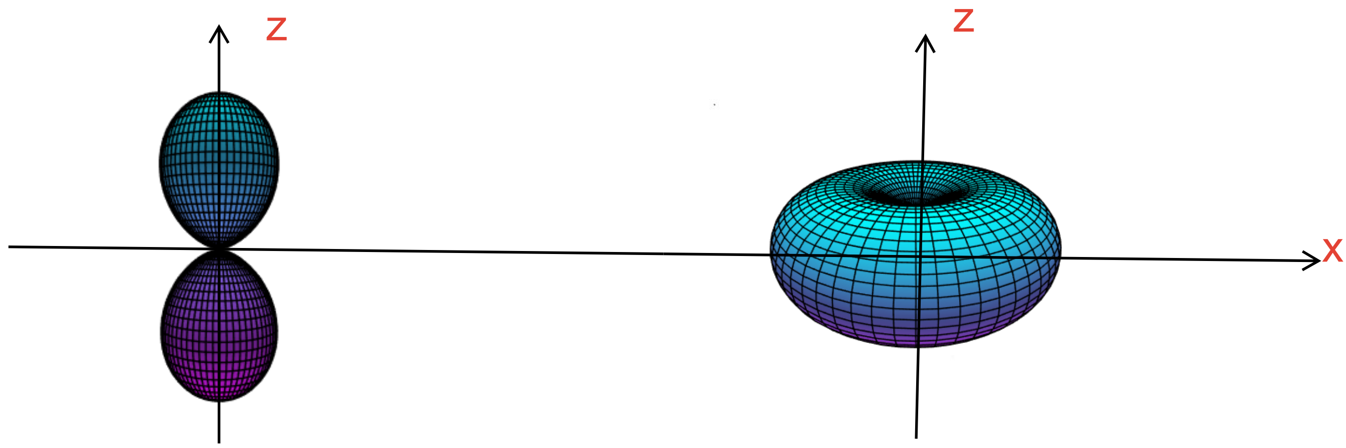
$$Y_{1,1} = -\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{i\phi}$$

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

(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 ∞-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 (but 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 ∞-shaped plots pointing to x or y-axis respectively.



$|Y_{1,0}|^2$ $\qquad$ $|Y_{1,\pm 1}|^2$

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

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

$$= -\sqrt{2}\, i \left(\sqrt{\frac{3}{8\pi}}\right)\sin\theta\sin\phi$$

$$= -i\sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi \qquad \ldots (1)$$

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

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

ie, $Y_{1,0}$ can be written ~~as~~ 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:

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

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

From (I), we can conclude that

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

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

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

$$= -\sqrt{2}\left(\sqrt{\frac{3}{8\pi}}\right)\cos\phi \qquad \left(\cos\phi = \frac{1}{2}(e^{i\phi} + e^{-i\phi})\right)$$

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

$$= -\phi_{P_x}$$

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

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

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

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

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

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

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

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

b cont.

$$\because \hat{L}_z Y_{1,1} = (1)\hbar Y_{1,1} = \hbar Y_{1,1}$$

$$\hat{L}_z Y_{1,-1} = (-1)\hbar Y_{1,-1} = -\hbar Y_{1,-1}$$

$$\hat{L}_z \phi_{p_x} = -\frac{1}{\sqrt{2}}(\hat{L}_z Y_{1,1} - \hat{L}_z Y_{1,-1})$$

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

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

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

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

$\therefore$ ϕ_{p_x} is <u>NOT</u> an eigenstate of $\hat{L}_z$.

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

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

The inner product between ϕ_{p_x} and ϕ_{p_y} is:

$$\int \phi_{p_x}^* \phi_{p_y} \, d\Omega$$

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

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

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

By the orthogonality of Y_{ℓ, m_ℓ},

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

$$= 0$$

$\therefore$ ϕ_{p_x} and ϕ_{p_y} is ~~in fact~~ indeed orthogonal.

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

e.g. $Y_{2,1} = -\sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta \, e^{i\phi}$,

$Y_{2,-1} = \sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta \, e^{-i\phi}$

(Checked from Note VIII - 16 or IX - 15 of 3021)

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

$$= i\sqrt{2}\sqrt{\frac{15}{8\pi}} \cos\theta \sin\theta \, \sin\phi$$

$$= -i\sqrt{\frac{15}{4\pi}} \cos\theta \sin\theta \sin\phi$$

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

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

$$= \sqrt{\frac{15}{4\pi}} \cos\theta \sin\theta \cos\phi \; //$$

$\therefore$ 2 orthogonal REAL 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.

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

SQ2

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

↑

wavenumber

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

$$E_{n_2} - E_{n_1} = \frac{me^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Frequency of light emitted during the transition :

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

$$f = \frac{me^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Using the relation $c = f\lambda$,

$$\lambda = \frac{c}{f} = \frac{8\varepsilon_0^2 h^3 c}{me^4}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)^{-1}$$

$$\bar{\nu} = \frac{me^4}{8\varepsilon_0^2 c h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Calculating the prefactor :

$$\frac{me^4}{8\varepsilon_0^2 c h^3} \approx 109737 \text{ cm}^{-1}$$

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

(b)

NIST data of Hydrogen Atom

Configuration	Term	J	Level (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 μ

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

The corresponding value of

$$\frac{\mu e^4}{8 \varepsilon_0^2 h^3 c} \approx 109677 \text{ cm}^{-1}$$

SQ3.

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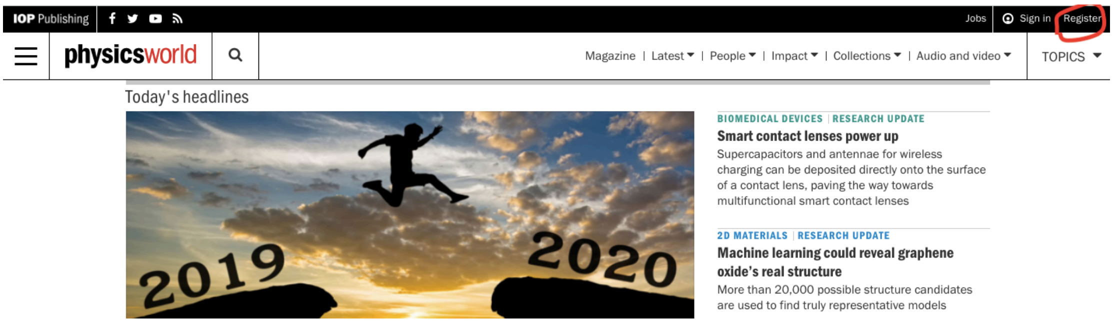

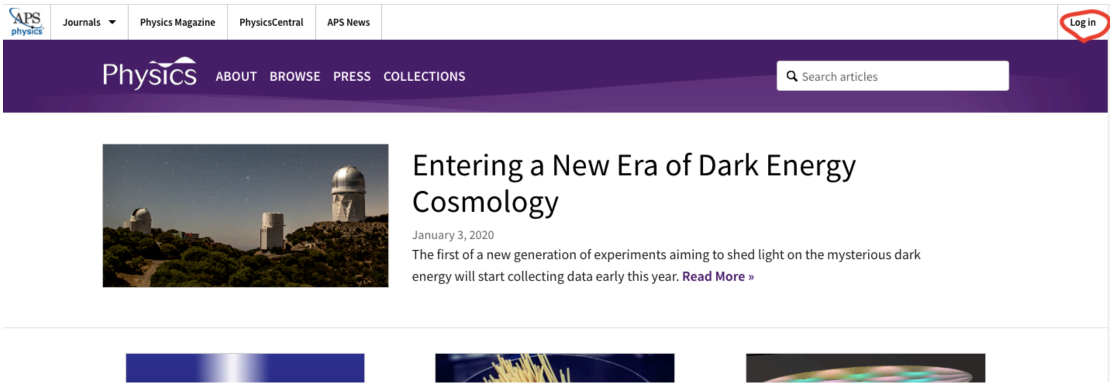

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