Physics PY4118
Physics of Semiconductor Devices

The Hydrogen Atom

The Hydrogen Atom

- We will start with the quantum mechanical description of the hydrogen atom
- This will be used to explain a great deal of how semiconductors form
- We start with the 3D Schrödinger equation

3D Schrödinger equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{2m}{\hbar^2}\left(E-\boxed{V}\right)\psi=0$$

$$\boxed{V=-\frac{e^2}{4\pi\varepsilon_0 r}}$$

Spherical coordinates

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{\boxed{r^2\sin\theta}}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$

$$+\frac{1}{\boxed{r^2\sin^2\theta}}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)\psi=0$$

H Atom: separation of variables

$$\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$

$$+\frac{\partial^2\psi}{\partial\phi^2}+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)\psi=0$$

Set: $\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$

And then divide by: $R(r)\Theta(\theta)\Phi(\phi)$

H Atom: separation of variables

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$

$$+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=\boxed{-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}}$$

The term on the right has no (r,θ) dependence

Thus, we can write the equation as:

H Atom: separation of variables

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$

$$+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=m_l^2$$

A constant

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=m_l^2$$

The second equation has a easy general solution…

H Atom: ϕ equation

$$\frac{\partial^2 \Phi}{\partial \phi^2} + m_l^2 \Phi = 0$$

$$\Phi = A e^{i m_l \phi}$$

But, we can also say that: $\Phi = A e^{i m_l \phi} = A e^{i m_l (2\pi + \phi)}$

Thus: $e^{i 2\pi m_l} = 1 \rightarrow m_l = \text{int}$

Or: $m_l = \mathbb{Z}$

Discuss symmetry of solution: $\Phi = A e^{i m_l \phi}$

H Atom: r,θ equations

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$

$$+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=m_l^2=\mathbb{Z}$$

For this equation, we divide by: $\sin\theta$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)$$ ← Only: r

$$=\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$ ← Only: θ

H Atom: r,θ equations

Both must be constant!

A solution exists, when the constant is: $l(l+1) \rightarrow l = \mathbb{Z}$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=l(l+1)$$

← Only: r

$$\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)=l(l+1)$$

← Only: θ

H Atom: r equation

First multiply by: $\dfrac{R}{r^2}$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)-\frac{l(l+1)}{r^2}\right]R=0$$

This equation can be transformed into the Laguerre equation, and this would take a few lectures

Instead, the solution will be discussed, and a link provided for the detailed calculation.

https://faculty.washington.edu/seattle/physics227/reading/reading-26-27.pdf

H Atom: r equation

Solutions available when: $E_n = -\frac{me^4}{32\pi^2\varepsilon_0\hbar^2 n^2}$ $\quad n > |l|$

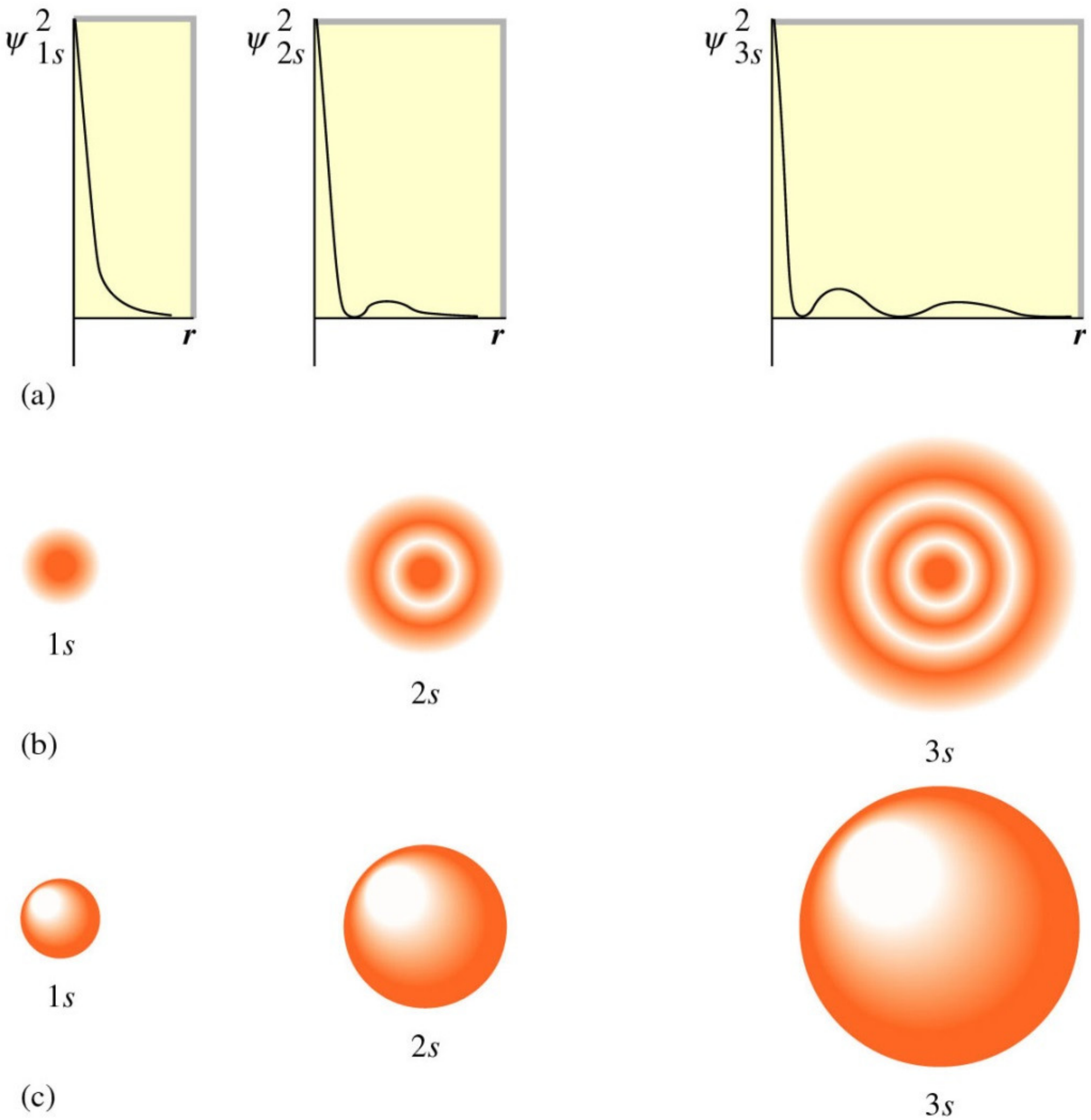
$R_{nl}(r)$ ➡

Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right)\frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}}\frac{2}{81\sqrt{3}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{6}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0^2}e^{-r/3a_0}$

H Atom: r equation

$R_{nl}(r)$



H Atom: θ equations

$$\frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) = l(l+1)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(l(l+1) - \frac{m_l^2}{\sin^2\theta}\right)\Theta = 0$$

But this equation is a function of m_l and l

Thus linking the angular equations.

We use: $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

Quantum Numbers:

Principal Quantum Number: n

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0\hbar^2 n^2}$$

Orbital angular momentum quantum number: l

$$l = \begin{bmatrix} 0 & 1 & 2 & 3 & 4 \\ s & p & d & f & g \end{bmatrix}$$ Names of orbits

Magnetic quantum number: m_l

Rules: $n > 0$

$l < n$

$m_l \leq |l|$ And all are integers

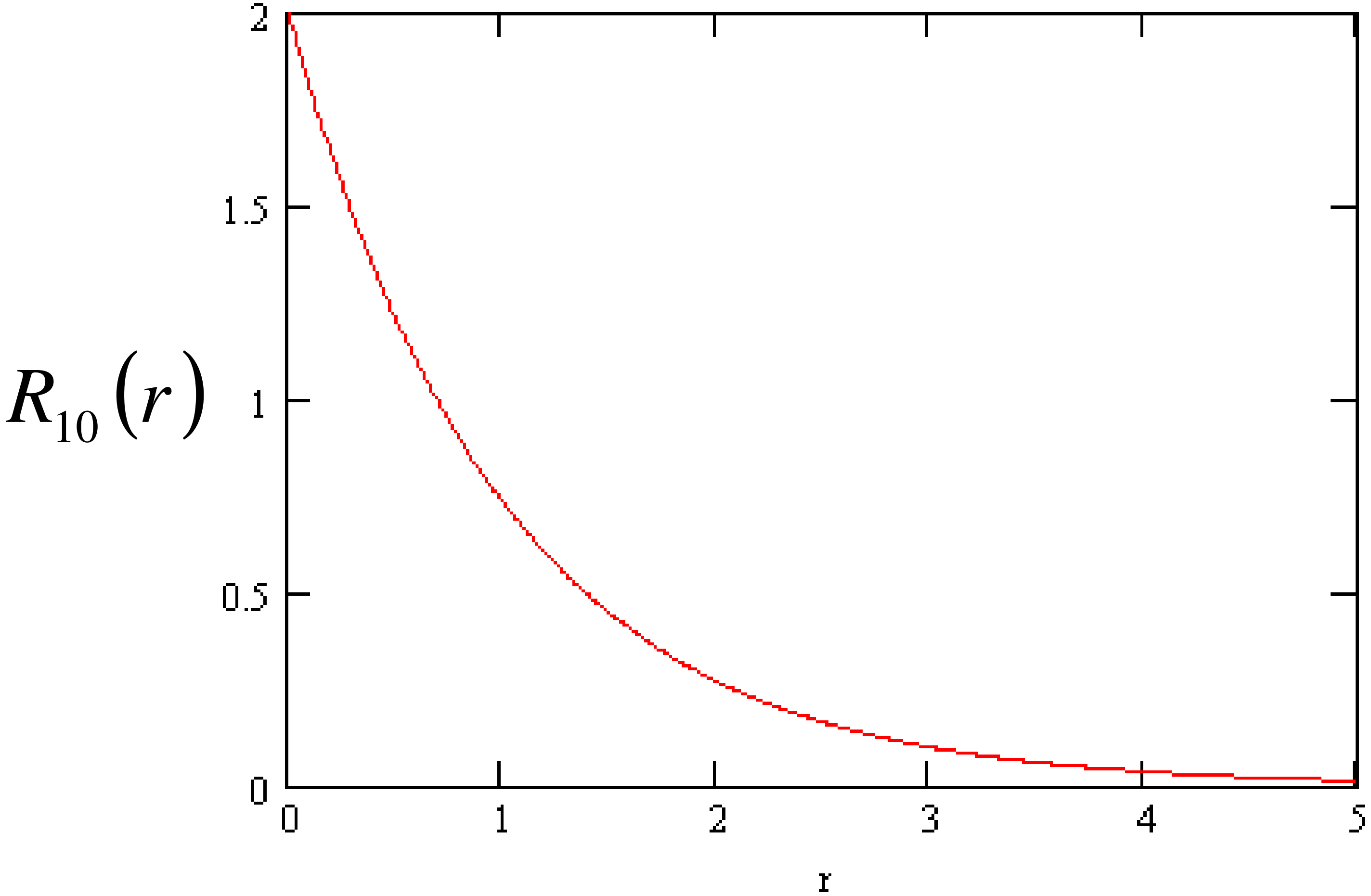
H Atom: angular equation

The angular equation can be reduced to a Legendre equation (you saw this in 2nd year E&M), with following solutions:

Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)\, e^{\pm i\phi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

Radial wavefunction



Does this mean the electron exists in the nucleus?

Probability distribution functions

The probability that the electron exits in $d\tau$ is:

$$P(r)d\tau = \psi^*\psi d\tau$$

$$= \left(R^* R\right)\left(\Theta^*\Theta\right)\left(\Phi^*\Phi\right)d\tau$$

$$= \left(R^* R r^2 dr\right)\left(\Theta^*\Theta \sin\theta d\theta\right)\left(\Phi^*\Phi d\phi\right)$$

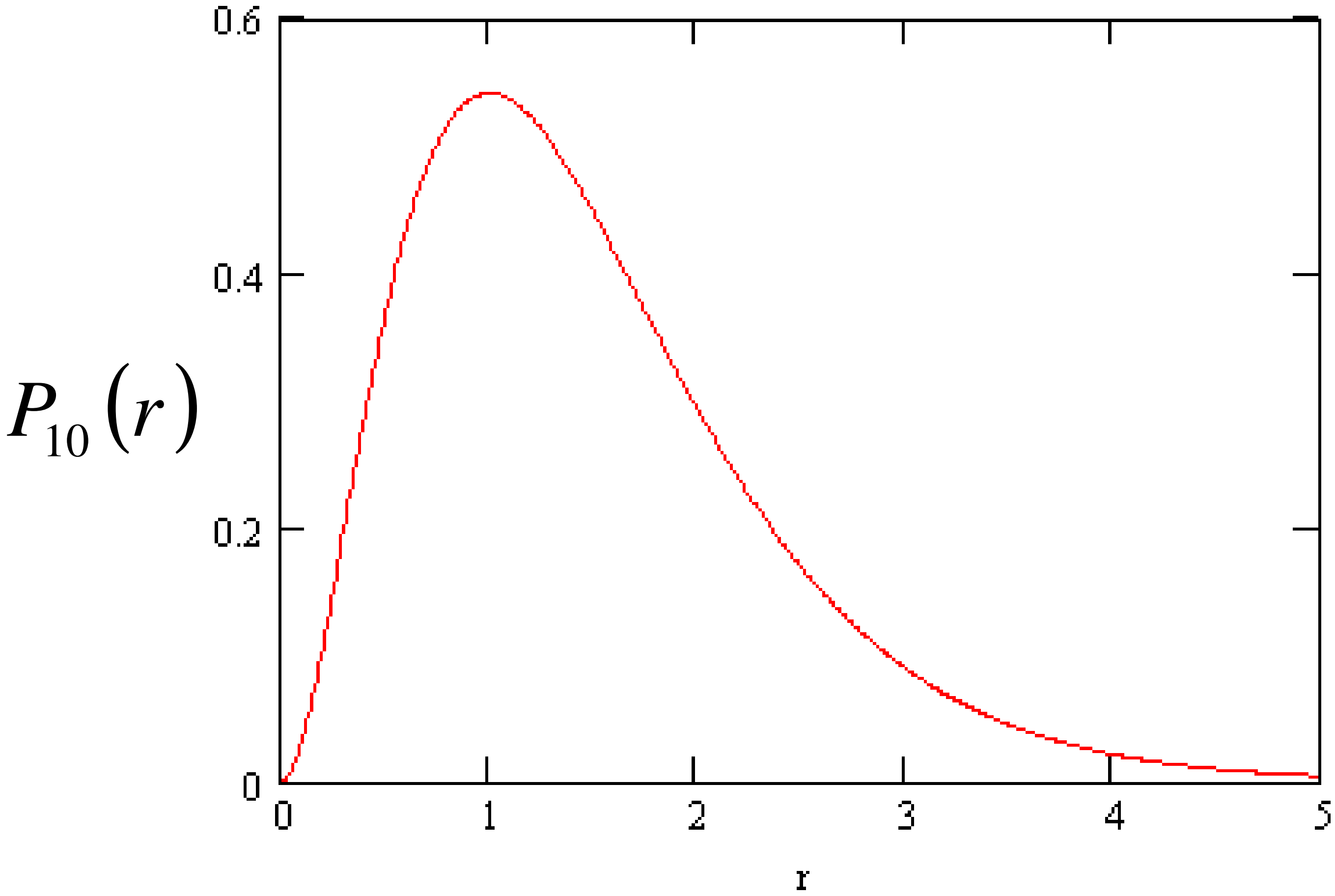
The probability that the electron exits in dr is:

$$P(r)dr = r^2 R^* R dr \int_0^{\pi} \Theta^*\Theta \sin\theta d\theta \int_0^{2\pi} \Phi^*\Phi d\phi$$

$$= r^2 R^* R dr$$

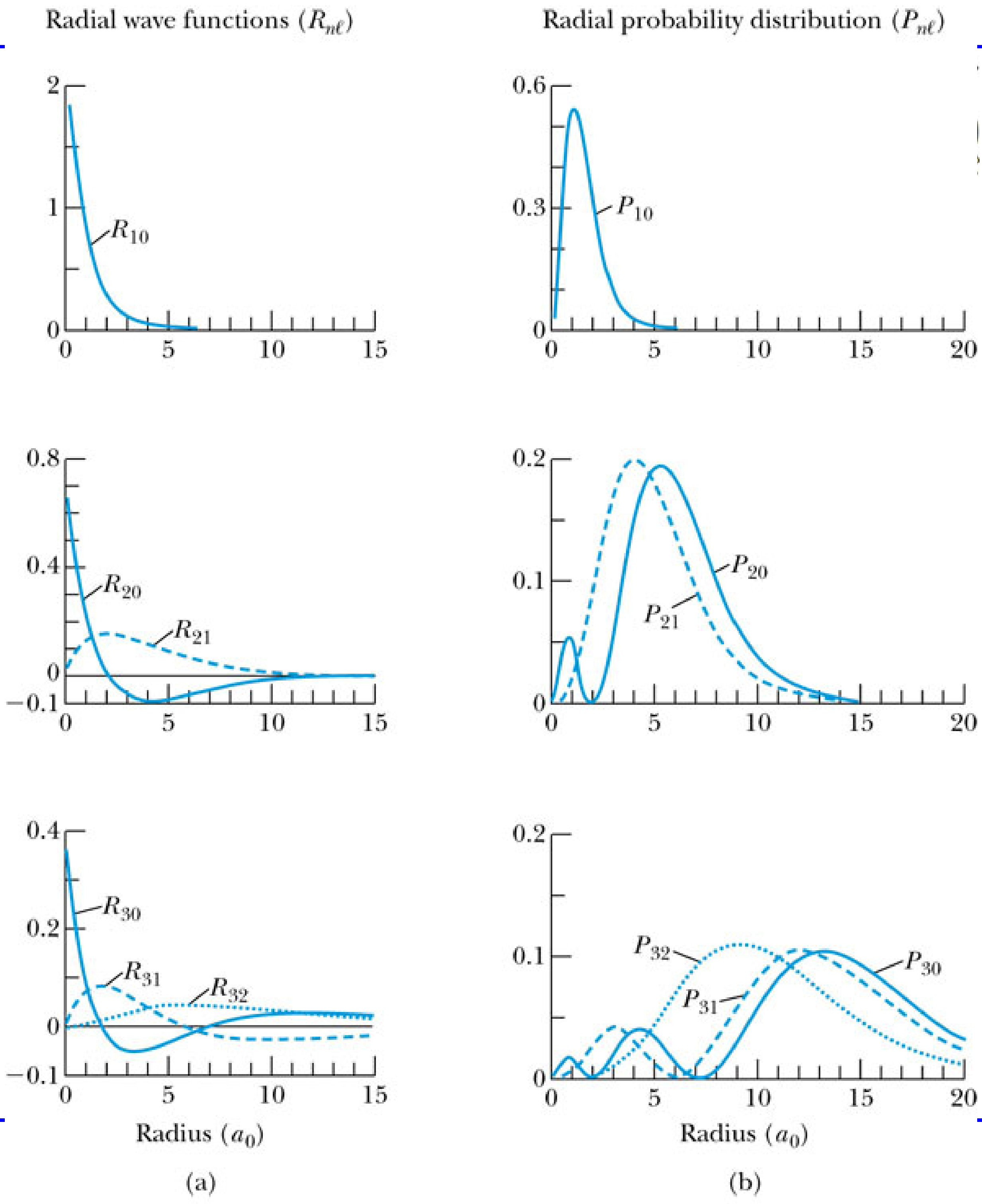
Why do the integrals cancel?

Probability distribution functions



And the electron **has** a finite probability within the nucleus

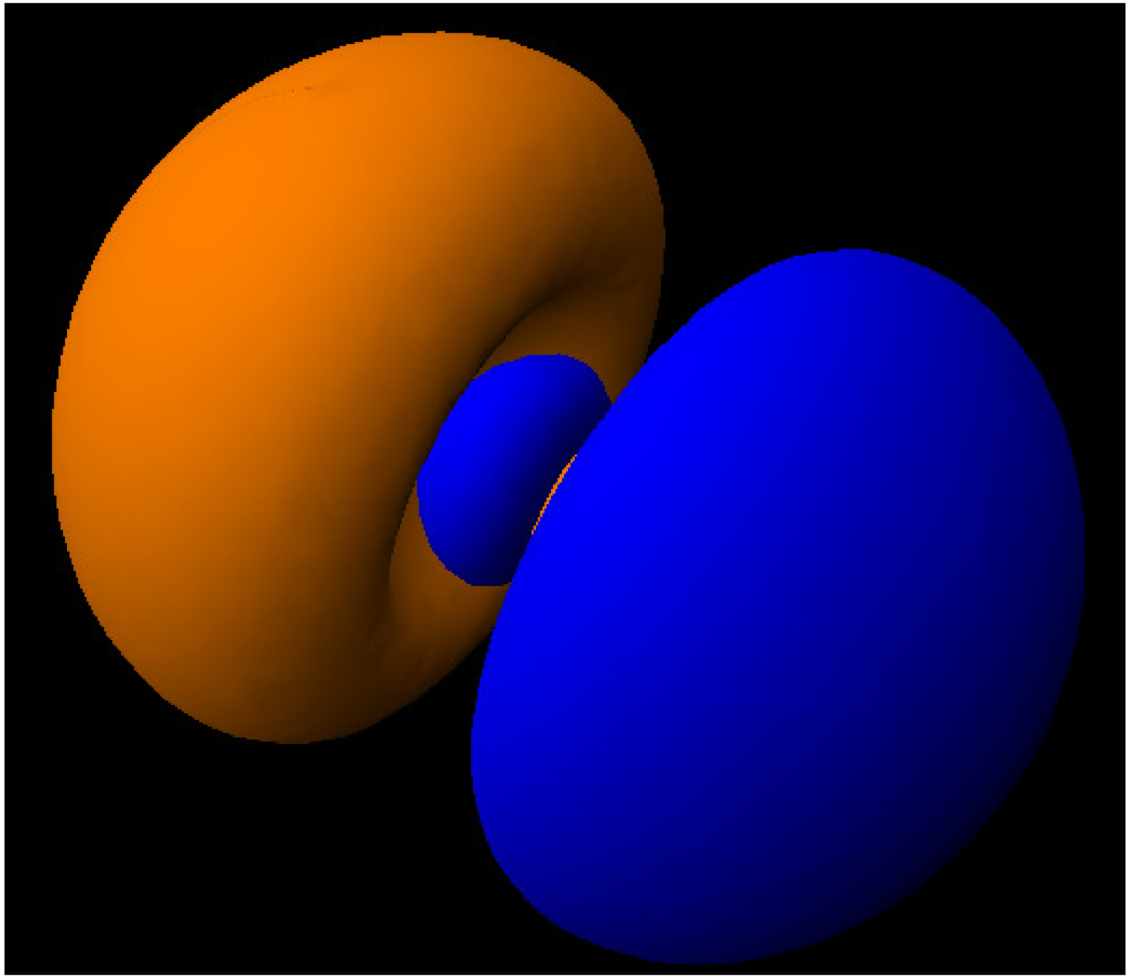
Probability



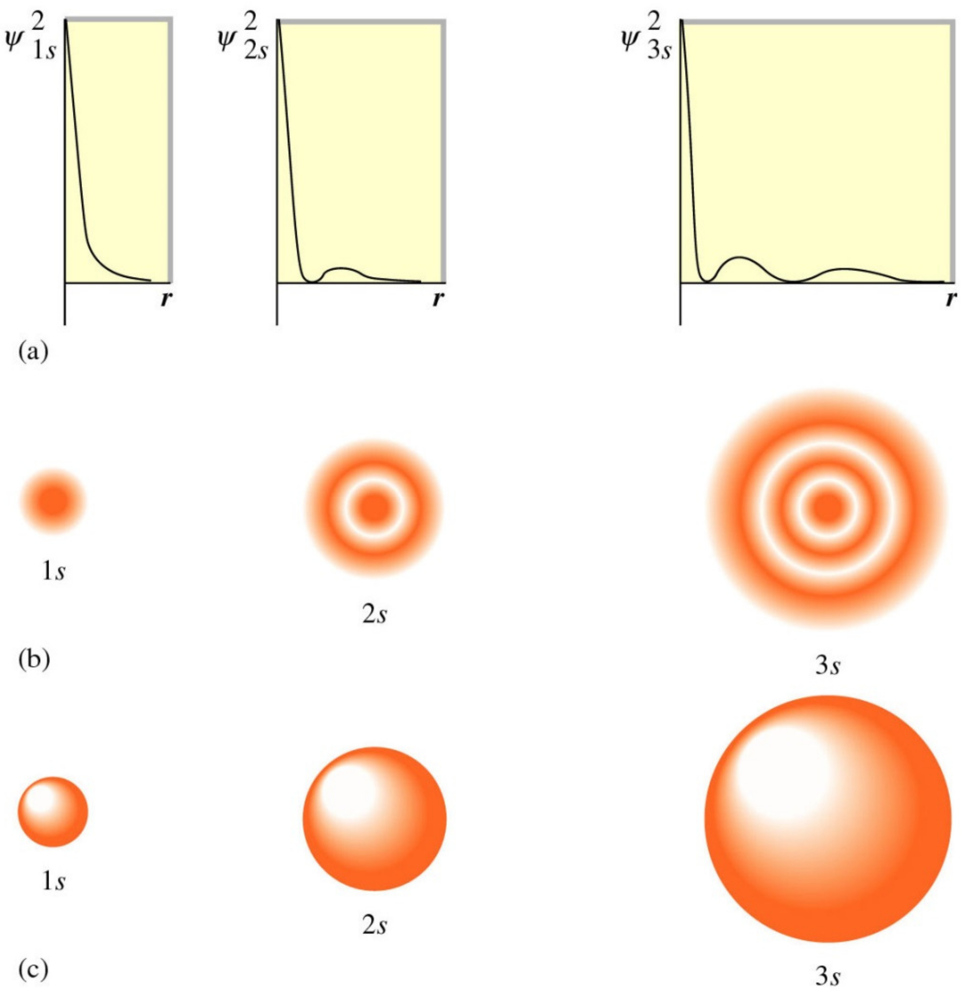
Visualise Orbitals

- The best way today is:
  - Write a program
  - Download an app.

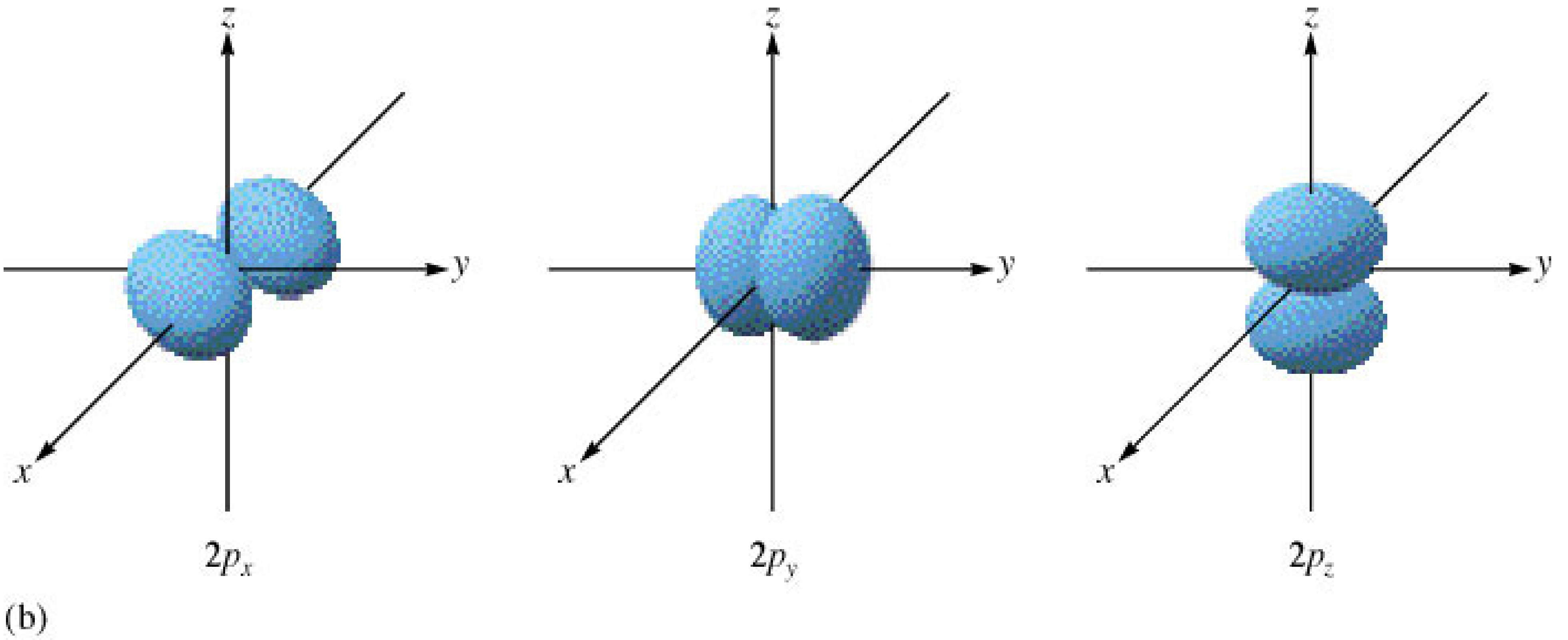
http://www.orbitals.com/orb/ov.htm



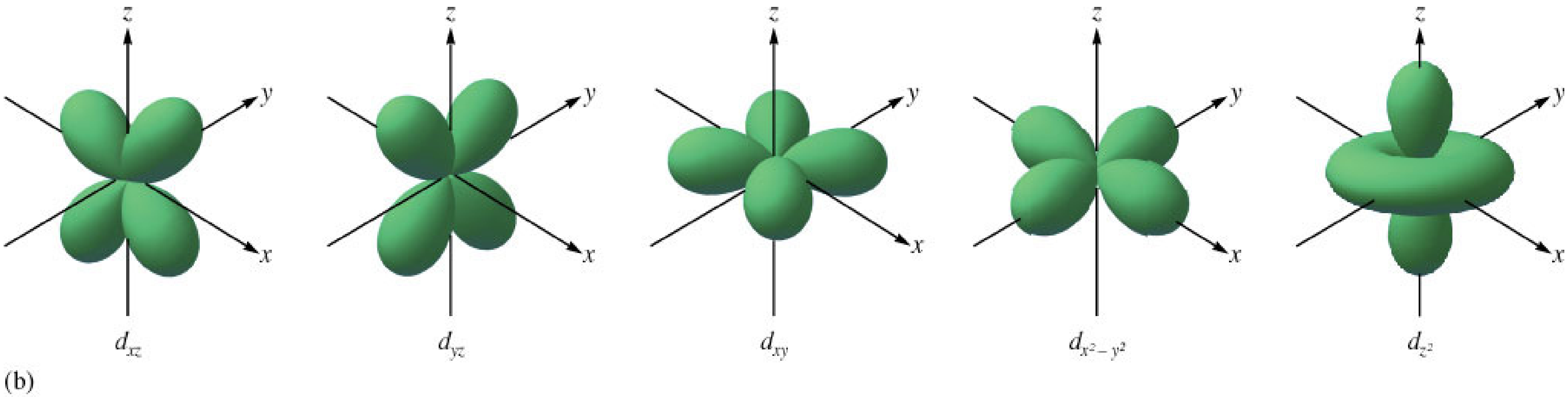
s – orbitals (l=0)



p – orbitals (l=1)

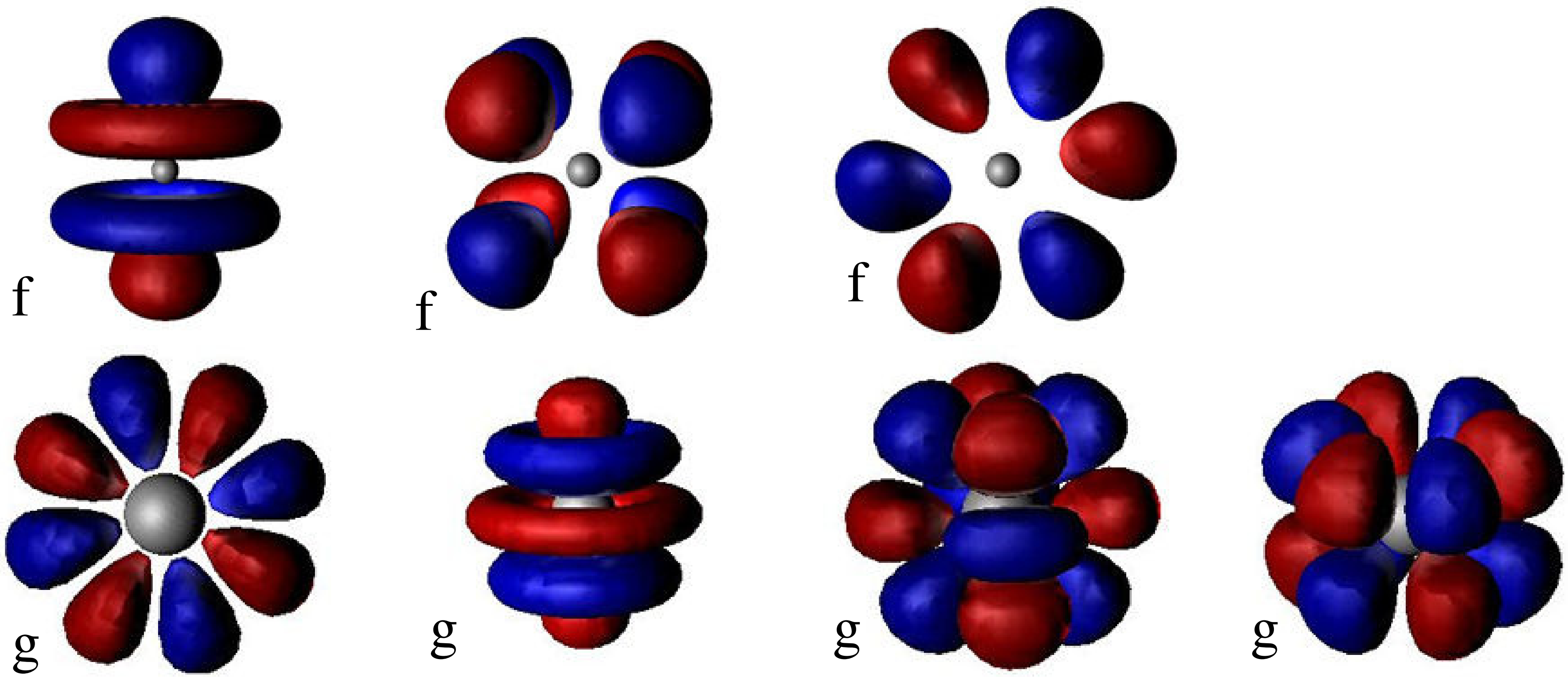


d – orbitals (l=2)



Some f and g – orbitals (l=3&4)

UCC



Question??

- If the course is on semiconductors, why are we worrying about the Hydrogen atom??
- Good question.
- We will discuss how electron orbits lead to crystal structures.
- But first…larger atoms…