Lecture 10 Atomic Orbitals

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Udom Robkob, Physics-MUSC

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Topics

1. Radial equation
2. Atomic orbitals
3. Spectroscopic notations

Radial equation

Hydrogen atom is a problem of an electron is confined within Coulomb potential well

$$U(r) = -\frac{Ke^2}{r}$$

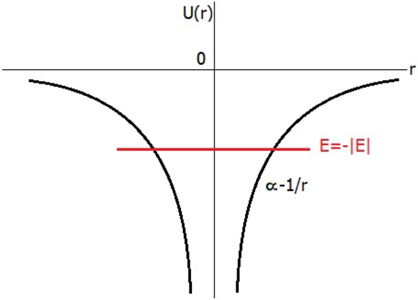
which is a kind of central potential. The Schrodinger equation will be solved in spherical system of coordinates, (r, θ, ϕ), and its angular solution will be the spherical harmonic $y_{lm}(\theta, \phi)$, with $l = 0, 1, 2, ...$ and $m = 0, \pm 1, \pm 2, ..., \pm l$. The task to be determine is the radial equation, which will appear in the form (see Equation (16) in Lecture 11)

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + \left[\frac{2m_e}{\hbar^2}\left(E + \frac{Ke^2}{r}\right) - \frac{l(l+1)}{r^2}\right]R(r) = 0 \quad (1)$$

Note: *correction may applied with replacing electron mass m_e with reduced mass between electron and proton massed.*

Rewrite (1) in the form

$$R'' + \frac{2}{r}R' + \left(\frac{2mE}{\hbar^2} + \frac{2mKe^2}{\hbar^2}\frac{1}{r} - \frac{l(l+1)}{r^2}\right)R = 0 \qquad (2)$$



For the confining problem, let us write $E = -|E|$, and then define

$$\beta = \sqrt{\frac{2m|E|}{\hbar^2}} \mapsto \rho = \beta r,\ \ \lambda = \frac{Ke^2}{\hbar}\sqrt{\frac{2m_e}{|E|}} = \alpha\sqrt{\frac{m_e c^2}{2|E|}}$$

Insertion into (2), with $R = R(\rho)$, we have

$$R'' + \frac{2}{\rho}R' + \left(-1 + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right) R = 0 \qquad (3)$$

Next we define

$$\begin{aligned} R(\rho) = \frac{U(\rho)}{\rho} \mapsto R' &= -\frac{U}{\rho^2} + \frac{U'}{\rho} \\ R'' &= 2\frac{U}{\rho^3} - 2\frac{U'}{\rho^2} + \frac{U''}{\rho} \end{aligned}$$

$$(3) \mapsto U'' + \left(-1 + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right) U = 0 \qquad (4)$$

Since $U(\rho) \xrightarrow[\rho\to\infty]{} 0$, then we write

$$\begin{aligned} U(\rho) = e^{-\rho}V(\rho) \mapsto U' &= e^{-\rho}V' - e^{-\rho}V \\ U'' &= e^{-\rho}V'' - 2e^{-\rho}V' + e^{-\rho}V \end{aligned}$$

$$(4) \mapsto V'' - 2V' + \left(\frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right) V = 0 \qquad (5)$$

To get rid the last two terms in (4), we write

$$V(\rho) = \rho^{l+1} Z(\rho) \mapsto V' = (l+1)\rho^l Z + \rho^{l+1} Z'$$

$$V'' = l(l+1)\rho^{l-1} Z + 2(l+1)\rho^l Z' + \rho^{l+1} Z''$$

$$(5) \mapsto \rho Z'' + 2(l+1-\rho)Z' + (\lambda - 2(l+1))Z = 0 \quad (6)$$

$$x = 2\rho \mapsto xZ'' + (2(l+2) - x)\, Z' + \left(\frac{\lambda}{2} - (l+1)\right) Z = 0 \quad (7)$$

with $Z = Z(x)$. Equation (7) is known in the name of *associated Laguerre equation*. Its solution exist in term of *associated Laguerre polynomial* $L^k_{n'}(x)$, with

$$k = 2l+1, \;\; n' = \frac{\lambda}{2} - (l+1) = 0, 1, 2, 3, ...$$

$$n = n' + l + 1 = 1, 2, 3, ... \mapsto l = 0, 1, 2, ..., n-1$$

n is principle quantum number, where

$$\lambda = 2n = \alpha\sqrt{\frac{m_e c^2}{2|E|}} \mapsto E = -|E| = -\frac{1}{2} m_e c^2 \alpha^2 \frac{1}{n^2} \equiv E_n$$

Back to our solution in (7)

$$\begin{aligned} Z(x) = L_{n-l-1}^{2l+1}(x) = L_{n-l-1}^{2l+1}(2\rho) = L_{n-l-1}^{2l+1}(2\beta r_n) \\ |E| = \frac{1}{2} m_e c^2 \alpha^2 \frac{1}{n^2} = \frac{1}{2} \frac{Ke^2}{a_0 n^2} \mapsto \beta = \sqrt{\frac{2m|E|}{\hbar^2}} = \frac{1}{na_0} \\ \rho = r/na_0 \ \mapsto Z(x) = L_{n-l-1}^{2l+1}(2r/na_0) \end{aligned} \tag{8}$$

Radial solution

Steps back ward, we will have

$$V(r) = (2r/na_0)^{l+1} L_{n-l-1}^{2l+1}(2r/na_0) \tag{9}$$

$$U(r) = e^{-r/na_0}(2r/na_0)^{l+1} L_{n-l-1}^{2l+1}(2r/na_0) \tag{10}$$

$$\mapsto R_{nl}(r) = C_{nl} e^{-r/na_0}(2r/na_0)^{l} L_{n-l-1}^{2l+1}(2r/na_0) \tag{11}$$

$$C_{nl} = \sqrt{\left(\frac{2}{na_0}\right)^2 \frac{(n-l-1)!}{2n[(n+2)!]^3}} \tag{12}$$

For examples:

$$R_{1,0}(r) = 2a_0^{-3/2} e^{-r/a_0}$$

$$R_{3,0}(r) = \frac{2}{\sqrt{27}} a_0^{-3/2}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$$

$$R_{2,0}(r) = \frac{1}{\sqrt{2}} a_0^{-3/2}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

$$R_{3,1}(r) = \frac{8}{27\sqrt{6}} a_0^{-3/2}\left(1 - \frac{r}{6a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$$

$$R_{2,1}(r) = \frac{1}{\sqrt{24}} a_0^{-3/2} \frac{r}{a_0} e^{-r/2a_0}$$

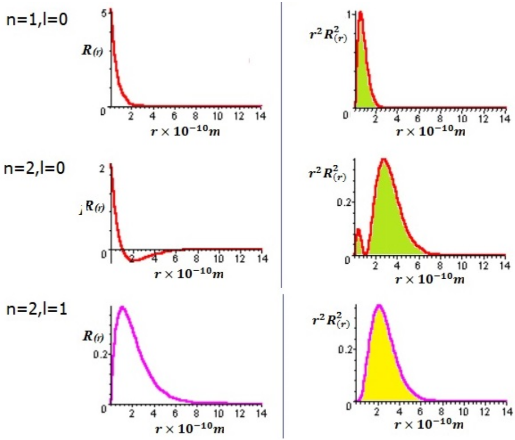
$$R_{3,2}(r) = \frac{4}{81\sqrt{30}} a_0^{-3/2} \frac{r^2}{a_0^2} e^{-r/3a_0}$$

Radial distribution function

Volume element in spherical system

$$dV = \underbrace{dxdydz}_{\text{Cartesian system}} = \underbrace{r^2 dr d\cos\theta d\phi}_{\text{Spherical system}}$$

Radial distribution function: $f_{nl}(r) = r^2 |R_{nl}(r)|^2$



Calculations of radial mean (quantum expectation) values:

$$\langle r \rangle_{10} = \int_0^\infty r f_{10}(r) dr = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr$$
$$= \frac{a_0}{4} \underbrace{\int_0^\infty y^3 e^{-y} dy}_{=6} = \frac{3}{2} a_0, \; y = 2r/a_0 \tag{13}$$

$$\langle \frac{1}{r} \rangle_{10} = \int_0^\infty \frac{1}{r} f_{10}(r) dr = \frac{4}{a_0^3} \int_0^\infty r e^{-2r/a_0} dr$$
$$= \frac{1}{a_0} \underbrace{\int_0^\infty y e^{-y} dy}_{=1} = \frac{1}{a_0}, \; y = 2r/a_0 \tag{14}$$

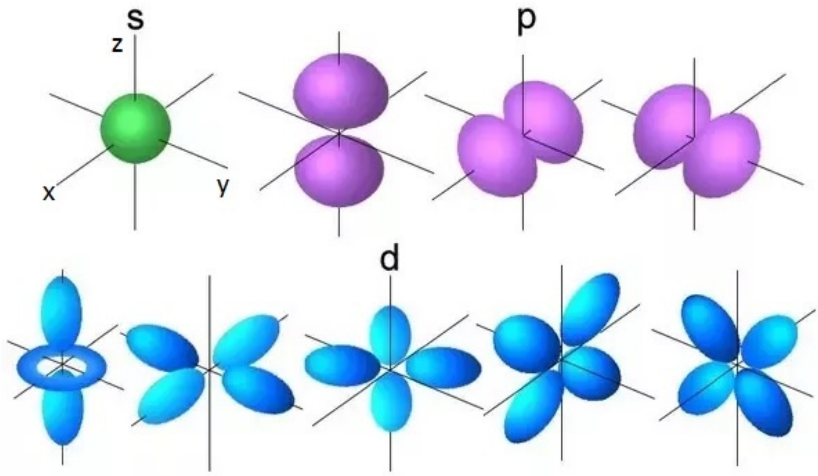
Exercise: Calculate $\langle 1/r^2 \rangle_{10}$ and $\langle 1/r^3 \rangle_{10}$

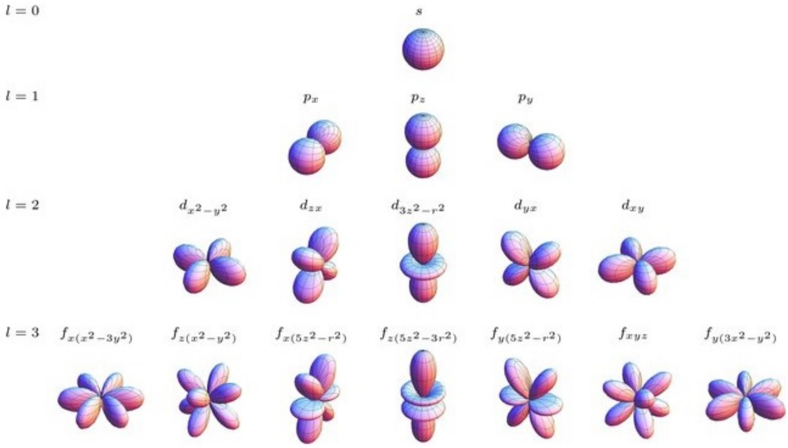
Atomic orbitals

Electron wave functions in hydrogen atom are known as *atomic orbitals*

$$\varphi_{lnm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi) \tag{15}$$

n	l	m	$\psi_{n,l,m}(r,\theta,\phi)$
1	0	0	$\frac{1}{\sqrt{\pi}a_0^{3/2}}e^{-r/a_0}$
2	0	0	$\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$
2	1	0	$\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}cos\ \theta$
2	1	±1	$\frac{1}{8\sqrt{3\pi}a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}sin\ \theta\ e^{\pm i\phi}$
3	0	0	$\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_o^2}\right)e^{-r/2a_o}$
3	1	0	$\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\ cos\ \theta$
3	1	±1	$\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\ sin\ \theta\ e^{\pm i\phi}$
3	2	0	$\frac{1}{81\sqrt{6\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ \left(3\ cos^2\ \theta-1\right)$
3	2	±1	$\frac{1}{81\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ sin\ \theta\ cos\ \theta\ e^{\pm i\phi}$
3	2	±2	$\frac{1}{162\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ sin^2\ \theta\ e^{\pm 2i\phi}$


s
z
x
y
p
d


$l = 0$
s
$l = 1$
p_x
p_z
p_y
$l = 2$
$d_{x^2-y^2}$
d_{zx}
$d_{3z^2-r^2}$
d_{yz}
d_{xy}
$l = 3$
$f_{x(x^2-3y^2)}$
$f_{z(x^2-y^2)}$
$f_{x(5z^2-r^2)}$
$f_{z(5z^2-3r^2)}$
$f_{y(5z^2-r^2)}$
f_{xyz}
$f_{y(3x^2-y^2)}$

Real orbitals, i.e., $p_z = p_0$, $p_x = (p_1 + p_{-1})/\sqrt{2}$, and $p_y = (p_1 - p_{-1})/\sqrt{2}$

s	$\frac{1}{2\sqrt{\pi}}$
p_z	$\frac{\sqrt{3}}{2\sqrt{\pi}}\cos\theta$
p_x	$\frac{\sqrt{3}}{2\sqrt{\pi}}\sin\theta\cos\phi$
p_y	$\frac{\sqrt{3}}{2\sqrt{\pi}}\sin\theta\sin\phi$
d_{z^2}	$\frac{\sqrt{5}}{4\sqrt{\pi}}(3\cos^2\theta - 1)$
d_{zx}	$\frac{\sqrt{15}}{2\sqrt{\pi}}\cos\theta\sin\theta\cos\phi$
d_{zy}	$\frac{\sqrt{15}}{2\sqrt{\pi}}\cos\theta\sin\theta\sin\phi$
$d_{x^2-y^2}$	$\frac{\sqrt{15}}{4\sqrt{\pi}}\sin^2\theta\,(2\cos^2\phi - 1)$
d_{xy}	$\frac{\sqrt{15}}{2\sqrt{\pi}}\sin^2\theta\sin\phi\cos\phi$

Spectroscopic notations

		n=1	n=2	n=3	n=4
s - - sharp	$\ell=0$	1s	2s	3s	4s
p- - principal	$\ell=1$		2p	3p	4p
d- - diffuse	$\ell=2$			3d	4d
f - - fundamental	$\ell=3$				4f

g $\ell=4$

h $\ell=5$

...

beyond this point, the notation just follows the alphabet