HYDROGEN ATOM

The hydrogen atom consists of a **proton** and an **electron**. If e symbolizes the charge on the proton ($e = +1.6\ 10^{-19}$ C), then the electron's charge is $-e$

We shall assume the electron and proton to be **point masses** whose interaction is given by **Coulomb's law**

We shall be considering **isolated systems**, ignoring interatomic and intermolecular interactions

HYDROGEN ATOM

Instead of treating the hydrogen atom, we consider a more general problem: the **hydrogenlike atom**, namely a system consisting of one electron and a nucleus of charge Ze

for $Z = 1$, we have the hydrogen atom
for $Z = 2$, the He^+ ion
for $Z = 3$, the Li^{2+} ion … and so on
Z is the atomic number

HYDROGEN ATOM

An exact solution of the Schrödinger equation for atoms with more than one electron cannot be obtained because of the **interelectronic repulsions**

If, as a first approximation, **we ignore these repulsions, then the electrons can be treated independently**. The atomic wave function will be approximated by a product of one-electron functions, which will be hydrogenlike wave functions

HYDROGEN ATOM

A one-electron wave function is called **orbital**. More precisely, **an orbital is a one-electron spatial wave function**, where the word *spatial* means that the wave function depends on the electron's coordinates x, y, and z or r, θ and ϕ

An orbital for an electron in an atom is called **atomic orbital**. We shall use atomic orbitals to construct approximate wave functions for atoms with many electrons. Orbitals are also used to construct approximate wave functions for molecules

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS (from rigid rotor treatment)

The Hamiltonian function for two particles is

$$\widehat{H} = -\frac{\hbar^2}{2M}\nabla_M^2 - \frac{\hbar^2}{2\mu}\nabla_\mu^2 + \hat{V}(x, y, z)$$

The Hamiltonian can be viewed as the sum of the Hamiltonians of two hypothetical noninteracting particles with masses M and μ, the latter being subject to the potential energy function $V(x, y, z)$. We can apply the results obtained for two noninteracting particles

REDUCTION of the TWO-PARTICLE PROBLEM to TWO ONE-PARTICLE PROBLEMS (rigid rotor treatment)

Memo $\hat{H} = -\frac{\hbar^2}{2M}\nabla_M^2 - \frac{\hbar^2}{2\mu}\nabla_\mu^2 + \hat{V}(x,y,z)$

Total energy $E = E_M + E_\mu$

Eigenfunctions $\psi = \psi_M(X,Y,Z)\,\psi_\mu(x,y,z)$

where
$$\begin{cases} -\dfrac{\hbar^2}{2M}\nabla_M^2\psi_M = E_M\psi_M \\ -\dfrac{\hbar^2}{2\mu}\nabla_\mu^2\psi_\mu + V(x,y,z)\psi_\mu = E_\mu\psi_\mu \end{cases}$$

From two-particle rigid rotor

In Cartesian coordinates, Schrödinger equation becomes

Rigid rotor
$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(x,y,z) = E\,\psi(x,y,z)$$

H atom
$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = E\,\psi(x,y,z)$$

Instead of the relative Cartesian coordinates x, y, z, it will prove more fruitful to use the relative spherical coordinates r, θ, ϕ. To go from Cartesian to spherical coordinates, we exploit the results obtained from angular momentum

Rigid rotor
$$\frac{\partial}{\partial x} = \xcancel{\left(\frac{\partial r}{\partial x}\right)_{y,z}\frac{\partial}{\partial r}} + \left(\frac{\partial \theta}{\partial x}\right)_{y,z}\frac{\partial}{\partial \theta} + \left(\frac{\partial \phi}{\partial x}\right)_{y,z}\frac{\partial}{\partial \phi}$$

H atom
$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)_{y,z}\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial x}\right)_{y,z}\frac{\partial}{\partial \theta} + \left(\frac{\partial \phi}{\partial x}\right)_{y,z}\frac{\partial}{\partial \phi}$$

HYDROGEN ATOM

The Hamiltonian is $$\widehat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + V(x,y,z)$$

In spherical coordinates $\widehat{H}$ becomes as follows

Kinetic energy operator

$$-\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2\mu r^2}\hat{L}^2$$

Potential energy operator

$$V(x,y,z) \equiv V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} = -\frac{Ze'^2}{r}$$

where $$\mu = \frac{m_p m_e}{m_p + m_e} \cong m_e \qquad e' = \frac{e}{\sqrt{4\pi\varepsilon_0}}$$

HYDROGEN ATOM

Hamiltonian $\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2\mu r^2}\hat{L}^2 - \frac{Ze'^2}{r}$

It is possible to show that $\left[\hat{H}, \hat{L}^2\right] = 0$

This allows to state $\hat{H}\psi = E\,\psi$ $\hat{L}^2\psi = c\,\psi$

The eigenfunctions of $\hat{L}^2$ are the spherical harmonics, and since $\hat{L}^2$ does not involve r, we can multiply the spherical harmonics by an arbitrary function of r and still have eigenfunctions of $\hat{L}^2$

$$\psi(r, \theta, \phi) = R(r)\, Y_l^m(\theta, \phi)$$

HYDROGEN ATOM

Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{1}{2\mu r^2}\hat{L}^2-\frac{Ze'^2}{r}\right]\psi=E\psi$$

Substituting $\psi(r,\theta,\phi)=R(r)\,Y_l^m(\theta,\phi)$ in the Schrödinger equation, we obtain an equation which is only function of r

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{l(l+1)\hbar^2}{2\mu r^2}-\frac{Ze'^2}{r}\right]R(r)=E\,R(r)$$

The solution gives $R(r)$ and the energy E

HYDROGEN ATOM

Energy:

$$E = -\frac{Z^2 \mu e'^4}{2n^2\hbar^2} \qquad n = 1, 2, 3, \ldots$$

Absorption of light:

$$\nu = \frac{E_{n_2} - E_{n_1}}{h} = \boxed{\frac{2\pi^2 Z^2 \mu e'^4}{h^3}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Rydberg constant (Z=1)

States with different values of *l* or *m*, but the same value of *n*, have the same energy; we have <u>degeneracy</u>, except for *n* = 1, where *l* and *m* must both be 0. For a given value of *n*, we can have *n* different values of *l*. For each of these values of *l*, we can have 2*l* + 1 values of *m*. **The degree of degeneracy of an H-atom bound-state level is found to equal n^2**

HYDROGEN ATOM

The radial factor in the hydrogen-atom is

$$R_{nl}(r) = r^l e^{-Zr/na} \sum_{j=0}^{n-l-1} b_j r^j \qquad l = 0, 1, \ldots, n-1$$

Bohr radius

$$b_{j+1} = \frac{2Z}{na} \frac{j + l + 1 - n}{(j + 1)(j + 2l + 2)} b_j \qquad a \equiv \hbar^2/\mu e'^2$$

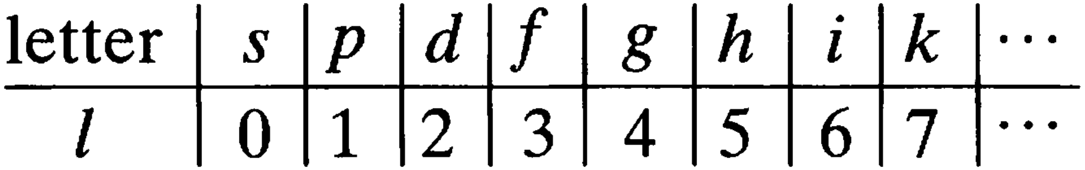
The complete hydrogenlike bound-state wave functions are

$$\psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \phi) = R_{nl}(r) S_{lm}(\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

Aside from the origin, there are $n - l - 1$ nodes in $R(r)$

HYDROGEN ATOM

We have denoted the hydrogen-atom bound-state wave functions by three subscripts that give the values of n, l, and m. In an alternative notation, the value of l is indicated by a letter:



letter	s	p	d	f	g	h	i	k	$\cdots$
l	0	1	2	3	4	5	6	7	$\cdots$

Preceding the code letter for l, we write the value of n. Thus the ground-state wave function is called ψ_{1s} or, more simply, $1s$

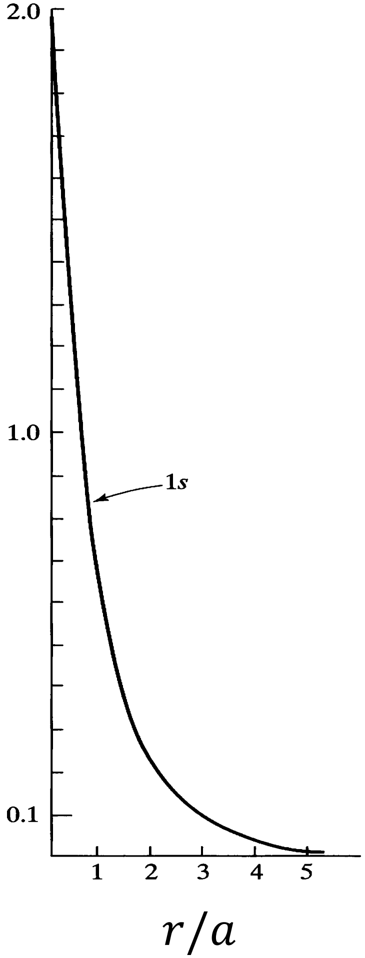
$$2s \equiv R_{20}(r)Y_0^0(\theta,\phi)$$

$$2p_{-1} \equiv R_{21}(r)Y_1^{-1}(\theta,\phi)$$

HYDROGEN ATOM (radial factors)

For the ground state of the hydrogenlike atom, we have $n = 1$, $l = 0$, and $m = 0$. The radial factor is

$$R_{10}(r) = b_0 e^{-Zr/a}$$



The constant b_0 is determined by normalization

$$|b_0|^2 \int_0^\infty e^{-2Zr/a} r^2 \, dr = 1$$

We get

$$R_{10}(r) = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

HYDROGEN ATOM

TABLE 6.1 Radial Factors in the Hydrogenlike-Atom Wave Functions

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$$R_{1s} = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$R_{2s} = \frac{1}{\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2}\left(1 - \frac{Zr}{2a}\right) e^{-Zr/2a}$$

$$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{5/2} r e^{-Zr/2a}$$

HYDROGEN ATOM (radial factors)

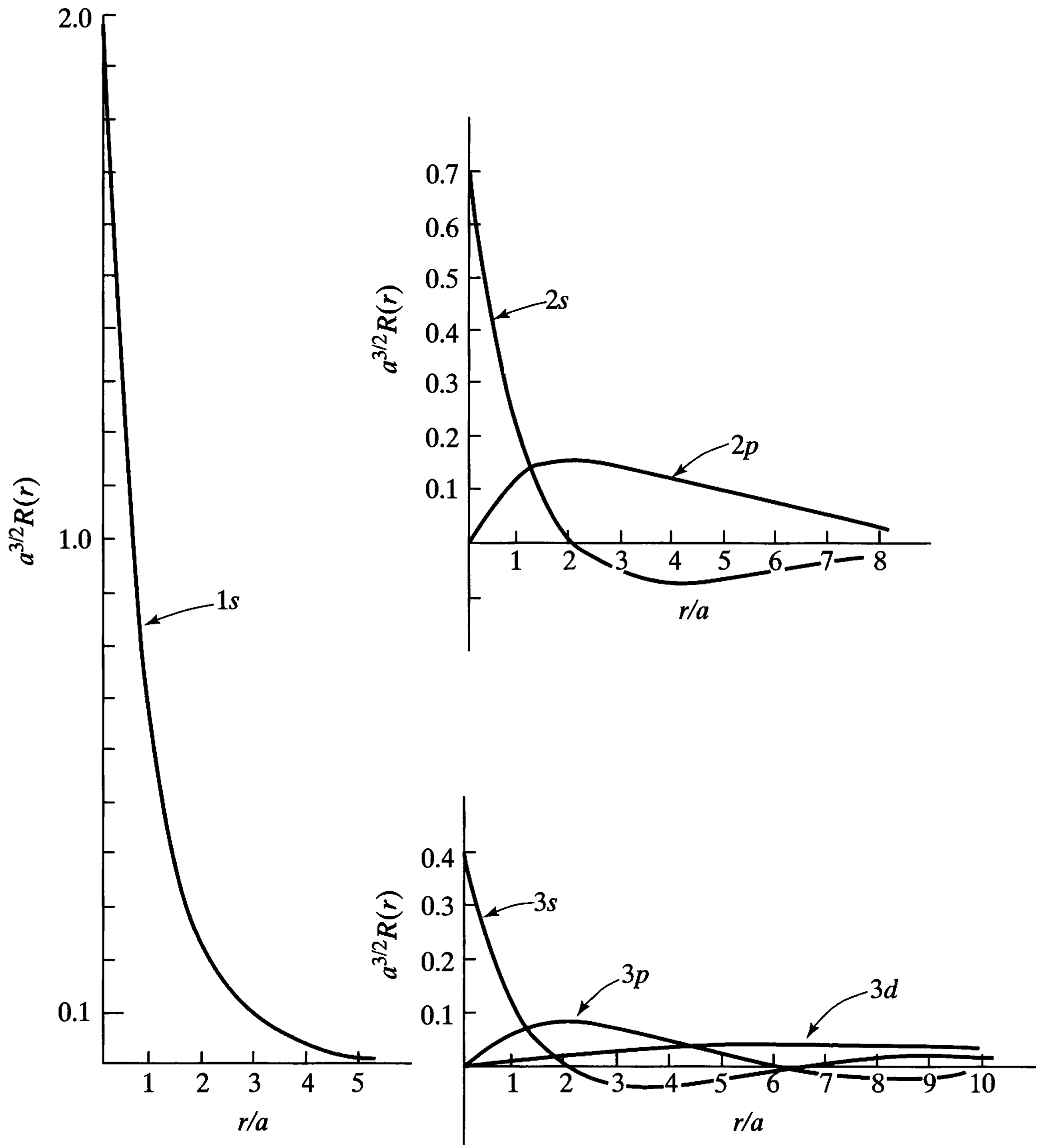


FIGURE 6.8 Graphs of the radial factor $R_{nl}(r)$ in the hydrogen-atom ($Z = 1$) wave functions. The same scale is used in all graphs. (In some texts, these functions are not properly drawn to scale.)

HYDROGEN ATOM (wave functions)

$n = 2, l = 0, m = 0$

$$2s = \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a}\right)^{3/2}\left(1 - \frac{Zr}{2a}\right)e^{-Zr/2a}$$

$n = 2, l = 1, m = -1$

$$2p_{-1} = \frac{1}{8\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a} \sin\theta \, e^{-i\phi}$$

$n = 2, l = 1, m = 0$

$$2p_0 = \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a}\right)^{5/2} re^{-Zr/2a} \cos\theta$$

$n = 2, l = 1, m = 1$

$$2p_1 = \frac{1}{8\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a} \sin\theta \, e^{i\phi}$$

HYDROGEN ATOM

EXAMPLE Find $\langle T\rangle$ for the hydrogen-atom ground state.

Equations (3.89) for $\langle T\rangle$ and (6.7) for $\nabla^2\psi$ give

$$\langle T\rangle = \int \psi^*\hat{T}\psi\,d\tau = -\frac{\hbar^2}{2\mu}\int \psi^*\nabla^2\psi\,d\tau$$

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} - \frac{1}{r^2\hbar^2}\hat{L}^2\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}$$

since $\hat{L}^2\psi = l(l+1)\hbar^2\psi$ and $l = 0$ for an s state. From (6.104) with $Z = 1$, we have $\psi = \pi^{-1/2}a^{-3/2}e^{-r/a}$, so $\partial\psi/\partial r = -\pi^{-1/2}a^{-5/2}e^{-r/a}$ and $\partial^2\psi/\partial r^2 = \pi^{-1/2}a^{-7/2}e^{-r/a}$. Using $d\tau = r^2\sin\theta\,dr\,d\theta\,d\phi$ [Eq. (5.78)], we have

$$\langle T\rangle = -\frac{\hbar^2}{2\mu}\frac{1}{\pi a^4}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\left(\frac{1}{a}e^{-2r/a} - \frac{2}{r}e^{-2r/a}\right) r^2\sin\theta\,dr\,d\theta\,d\phi$$

$$= -\frac{\hbar^2}{2\mu\pi a^4}\int_0^{2\pi} d\phi\int_0^{\pi}\sin\theta\,d\theta\int_0^{\infty}\left(\frac{r^2}{a}e^{-2r/a} - 2re^{-2r/a}\right)dr = \frac{\hbar^2}{2\mu a^2} = \frac{e'^2}{2a}$$

where Appendix integral A.7 and $a = \hbar^2/\mu e'^2$ were used. From (6.94), $e'^2/2a$ is minus the ground-state H-atom energy, and (6.108) gives $\langle T\rangle = 13.598$ eV.

HYDROGEN ATOM (radial distribution functions)

The probability of finding the electron in the region of space where its coordinates lie in the ranges r to $r + \mathrm{d}r$, θ to $\theta + \mathrm{d}\theta$, and $\phi + \mathrm{d}\phi$ is

$$|\psi|^2 \, d\tau = [R_{nl}(r)]^2 |Y_l^m(\theta, \phi)|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi$$

We now ask: what is the probability of the electron having its radial coordinate between r and $r + \mathrm{d}r$ with no restriction on the values of θ and ϕ?

$$\boxed{[R_{nl}(r)]^2 r^2} \, dr \int_0^{2\pi} \int_0^{\pi} |Y_l^m(\theta, \phi)|^2 \sin\theta \, d\theta \, d\phi = [R_{nl}(r)]^2 r^2 \, dr$$

RADIAL DISTRIBUTION FUNCTION

HYDROGEN ATOM (radial distribution functions)

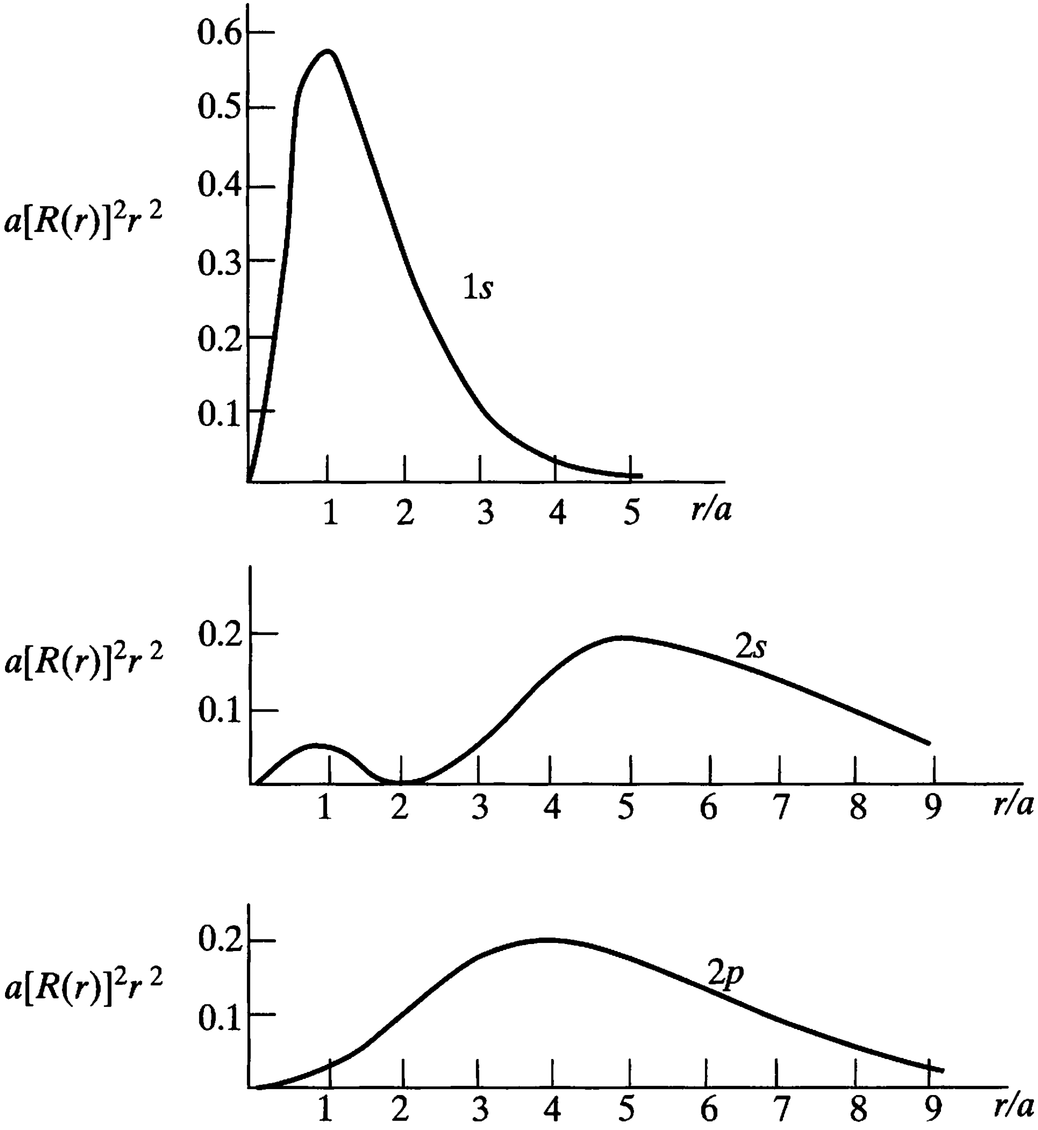


FIGURE 6.9 Plots of the radial distribution function $[R_{nl}(r)]^2r^2$ for the hydrogen atom.

HYDROGEN ATOM (real hydrogenlike functions)

The factor $\exp(im\phi)$ makes the spherical harmonics complex, except when $m = 0$. Instead of working with complex wave functions often real hydrogenlike wave functions are used. They are obtained by taking linear combinations of the complex functions. Since the energy of the hydrogen atom does not depend on m, the $2p_1$ and $2p_{-1}$ states belong to a degenerate energy level. Any linear combination of them is an eigenfunction of the Hamiltonian with the same energy eigenvalue

$$2p_x = \frac{1}{\sqrt{2}}(2p_{-1} + 2p_1) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} r\, e^{-Zr/2a} \sin\theta\cos\phi$$

Why $2px$?

$$2p_x = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} x\, e^{-Zr/2a}$$

HYDROGEN ATOM (real hydrogenlike functions)

A second way of combining the functions is

$$2p_y = \frac{1}{i\sqrt{2}}(2p_1 - 2p_{-1}) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} r\, e^{-Zr/2a}\ \sin\theta \sin\phi$$

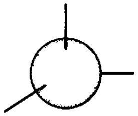
$$2p_y = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} y\, e^{-Zr/2a}$$

The function $2p_0$ is already real and is often denoted by

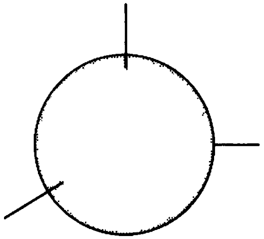
$$2p_z = 2p_0 = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a}\right)^{5/2} z\, e^{-Zr/2a}$$

HYDROGEN ATOM (atomic orbitals)

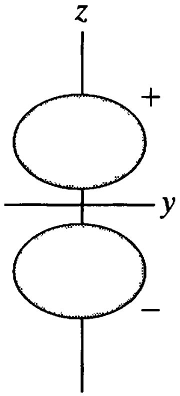
$1s$



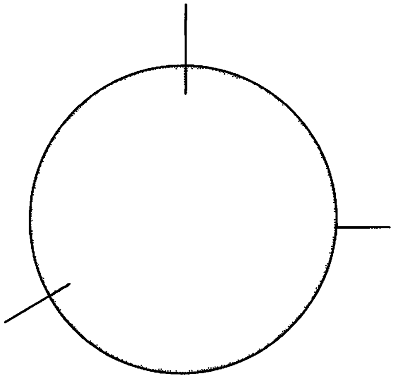
$2s$



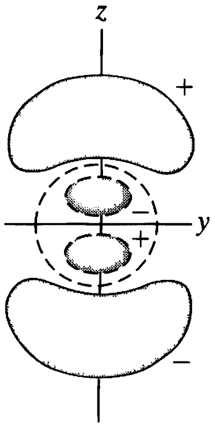
$2p_z$



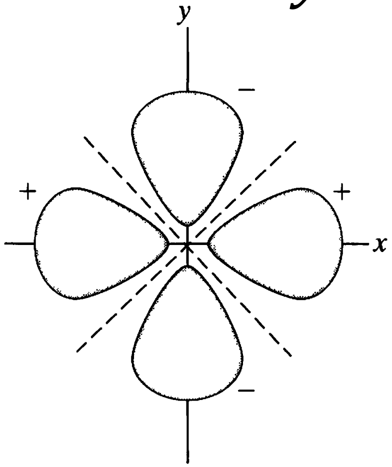
$3s$



$3p_z$



$3d_{x^2-y^2}$



$3d_{z^2}$