Ira N. Levine, Quantum Chemistry

CHAPTER 6

The hydrogen atom

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THE ONE-PARTICLE CENTRAL-FORCE PROBLEM

A single particle moving under a central force.

A central force is one derived from a potential-energy function that is spherically symmetric.

$$V = V(r)$$

$$\mathbf{F} = -\nabla V(x,y,z) = -\mathbf{i}(\partial V/\partial x) - \mathbf{j}(\partial V/\partial y) - \mathbf{k}(\partial V/\partial z)$$

$$(\partial V/\partial \theta)_{r,\phi} = 0 \qquad (\partial V/\partial \phi)_{r,\theta} = 0 \quad \Leftarrow \quad V = V(r)$$

$$\left(\frac{\partial V}{\partial x}\right)_{y,z} = \frac{dV}{dr}\left(\frac{\partial r}{\partial x}\right)_{y,z} = \frac{x}{r}\frac{dV}{dr}$$

$$r = (x^2+y^2+z^2)^{1/2}$$

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \left(\frac{1}{2}\right)(2x)(x^2+y^2+z^2)^{-1/2} = \frac{x}{r}$$

$$\left(\frac{\partial V}{\partial y}\right)_{x,z} = \frac{y}{r}\frac{dV}{dr}, \qquad \left(\frac{\partial V}{\partial z}\right)_{x,y} = \frac{z}{r}\frac{dV}{dr}$$

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THE ONE-PARTICLE CENTRAL-FORCE PROBLEM

$$\mathbf{F} = -\boldsymbol{\nabla} V(x,y,z) = -\mathbf{i}(\partial V/\partial x) - \mathbf{j}(\partial V/\partial y) - \mathbf{k}(\partial V/\partial z)$$

$$\left(\frac{\partial V}{\partial x}\right)_{y,z} = \frac{x}{r}\frac{dV}{dr}$$

$$\left(\frac{\partial V}{\partial y}\right)_{x,z} = \frac{y}{r}\frac{dV}{dr}$$

$$\left(\frac{\partial V}{\partial z}\right)_{x,y} = \frac{z}{r}\frac{dV}{dr}$$

$$\mathbf{F} = -\frac{1}{r}\frac{dV}{dr}\underbrace{(x\mathbf{i} + y\mathbf{j} + z\mathbf{k})}_{\mathbf{r}} = -\frac{dV(r)}{dr}\frac{\mathbf{r}}{r}$$

r/r is a unit vector in the radial direction

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A central-force is radially directed

THE ONE-PARTICLE CENTRAL-FORCE PROBLEM

The quantum mechanics of a single particle subject to a CF:

$$\hat{H} = \hat{T} + \hat{V} = -(\hbar^2/2m)\nabla^2 + V(r)$$

$$\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2}\operatorname{cotg}\theta\frac{\partial}{\partial \theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right)$$

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

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}\hat{L}^2 + V(r)$$

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THE ONE-PARTICLE CENTRAL-FORCE PROBLEM

- In classical mechanics: a particle subject to a central force has its angular momentum conserved.
- In quantum mechanics: whether we can have states with definite values for both the energy and angular momentum. The commutator $[\hat{H},\hat{L}^2]$ must vanish for this:

$$[\hat{H},\hat{L}^2] = [\hat{T},\hat{L}^2] + [\hat{V},\hat{L}^2]$$

$$[\hat{T},\hat{L}^2] = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}\hat{L}^2, \hat{L}^2\right]$$

$$[\hat{T},\hat{L}^2] = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}, \hat{L}^2\right] + \frac{1}{2m}\left[\frac{1}{r^2}\hat{L}^2, \hat{L}^2\right]$$

Involves only θ and φ

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THE ONE-PARTICLE CENTRAL-FORCE PROBLEM

$$[\hat{T},\hat{L}^2] = 0$$
$$[\hat{V},\hat{L}^2] = 0$$

Dos not involve r

$$[\hat{H},\hat{L}^2] = 0 \qquad \text{if } V = V(r)$$

$$[\hat{H},\hat{L}_z] = [\hat{T}+\hat{V},\hat{L}_z] \qquad \hat{L}_z = -i\hbar\partial/\partial\phi$$

$$[\hat{T},\hat{L}_z] = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}\hat{L}^2, \hat{L}_z\right]$$

$$[\hat{T},\hat{L}_z] = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}, \hat{L}_z\right] + \frac{1}{2m}\left[\frac{1}{r^2}\hat{L}^2, \hat{L}_z\right]$$

$$[\hat{V},\hat{L}_z] = 0$$

$$[\hat{H},\hat{L}_z] = 0 \qquad \text{if } V = V(r)$$

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THE ONE-PARTICLE CENTRAL-FORCE PROBLEM

$$[\hat{H}, \hat{L}^2] = 0$$
$$[\hat{H}, \hat{L}_z] = 0$$
$$[\hat{L}^2, \hat{L}_z] = 0$$

For a central force problem

Let ψ denote the common eigenfunctions:

$$\hat{H}\psi = E\psi$$
$$\hat{L}^2\psi = l(l+1)\hbar^2\psi\ , \qquad l = 0, 1, 2, \ldots$$
$$\hat{L}_z\psi = m\hbar\psi\ , \qquad m = -l, -l+1, \ldots, l$$

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THE ONE-PARTICLE CENTRAL-FORCE PROBLEM

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) + \frac{1}{2mr^2}\hat{L}^2\psi + V(r)\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) + \frac{l(l+1)\hbar^2}{2mr^2}\psi + V(r)\psi = E\psi$$

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

$$-\frac{\hbar^2}{2m}\left(R'' + \frac{2}{r}R'\right) + \frac{l(l+1)\hbar^2}{2mr^2}R + V(r)R = ER(r)$$

For any one particle problem with a spherically symmetric potential-energy function V(r), the stationary-state wave functions are $\psi = R(r)Y_l^m(\theta, \phi)$, where the radial factor R (R) satisfies the above equation

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Noniteracting particles and separation of variables

Noniteracting particles 1 and 2

(x_1, y_1, z_1) (x_2, y_2, z_2)

q_1 q_2

$$E = E_1 + E_2 = T_1 + V_1 + T_2 + V_2$$

$$H = H_1 + H_2$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2$$

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Noniteracting particles and separation of variables

The Schrödinger equation:

$$(\hat{H}_1 + \hat{H}_2)\psi(q_1, q_2) = E\psi(q_1, q_2)$$

We try a solution by separation of variables

$$\psi(q_1, q_2) = G_1(q_1)G_2(q_2)$$

$$\hat{H}_1 G_1(q_1)G_2(q_2) + \hat{H}_2 G_1(q_1)G_2(q_2) = EG_1(q_1)G_2(q_2)$$

$$G_2(q_2)\hat{H}_1 G_1(q_1) + G_1(q_1)\hat{H}_2 G_2(q_2) = EG_1(q_1)G_2(q_2)$$

$$\frac{\hat{H}_1 G_1(q_1)}{G_1(q_1)} + \frac{\hat{H}_2 G_2(q_2)}{G_2(q_2)} = E$$

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Noninteracting particles and separation of variables

$$\frac{\hat{H}_1 G_1(q_1)}{G_1(q_1)} = E_1$$

$$\frac{\hat{H}_2 G_2(q_2)}{G_2(q_2)} = E_2$$

$$E = E_1 + E_2$$

$$\hat{H}_1 G_1(q_1) = E_1 G_1(q_1), \qquad \hat{H}_2 G_2(q_2) = E_2 G_2(q_2)$$

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Noninteracting particles and separation of variables

For n particles (noninteractinh)

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \cdots + \hat{H}_n$$

$$\psi(q_1, q_2, \ldots, q_n) = G_1(q_1) G_2(q_2) \ldots G_n(q_n)$$

$$E = E_1 + E_2 + \cdots + E_n$$

$$\hat{H}_i G_i = E_i G_i, \qquad i = 1, 2, \ldots, n$$

When Hamiltonian is the sum of separate terms for each coordinate:

$$\hat{H} = \hat{H}_x(\hat{x}, \hat{p}_x) + \hat{H}_y(\hat{y}, \hat{p}_y) + \hat{H}_z(\hat{z}, \hat{p}_z)$$

$$\psi(x, y, z) = F(x) G(y) K(z)$$

$$E = E_x + E_y + E_z$$

$$\hat{H}_z K(z) = E_z K(z) \qquad \hat{H}_x F(x) = E_x F(x) \qquad \hat{H}_y G(y) = E_y G(y)$$

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Reduction of the two-particle problem to two one-particle problems

Two particles 1 and 2 with following coordinates:

(x_1, y_1, z_1) (x_2, y_2, z_2)

The potential energy is usually a function of only the relative coordiates

$x_2 - x_1$ $y_2 - y_1$ $z_2 - z_1$

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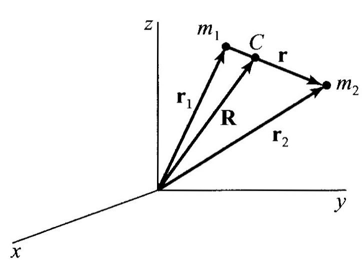
Reduction of the two-particle problem to two one-particle problems



$\mathbf{r}_1$, $\mathbf{r}_2$ Specify the positions of 1 and 2

(x_1, y_1, z_1) , (x_2, y_2, z_2) Coordinates of 1 and 2

$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ Relative or internal coordinates

$x = x_2 - x_1$, $y = y_2 - y_1$, $z = z_2 - z_1$

Components of $\mathbf{r}$

$\mathbf{R} = \mathbf{i}X + \mathbf{j}Y + \mathbf{k}Z$

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REDUCTION OF THE TWO-PARTICLE PROBLEM TO TWO ONE-PARTICLE PROBLEMS

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$
$$Y = \frac{m_1 y_1 + m_2 y_2}{m_1 + m_2}$$
$$Z = \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$$

$$\mathbf{R} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}$$

The definition of the center of mass of two-particle system

We also have:

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$$

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REDUCTION OF THE TWO-PARTICLE PROBLEM TO TWO ONE-PARTICLE PROBLEMS

$$\mathbf{R} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}$$

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$$

$$\mathbf{r}_1 = \mathbf{R} - \frac{m_2}{m_1 + m_2}\mathbf{r}$$

$$\mathbf{r}_2 = \mathbf{R} + \frac{m_1}{m_1 + m_2}\mathbf{r}$$

A transformation of coordinate

x_1, y_1, z_1 → X, Y, Z

x_2, y_2, z_2 → x, y, z

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REDUCTION OF THE TWO-PARTICLE PROBLEM TO TWO ONE-PARTICLE PROBLEMS

$$T = \tfrac{1}{2}m_1|\dot{\mathbf{r}}_1|^2 + \tfrac{1}{2}m_2|\dot{\mathbf{r}}_2|^2 \qquad \mathbf{v}_1 = d\mathbf{r}_1/dt = \dot{\mathbf{r}}_1.$$

$$T = \tfrac{1}{2}m_1\left(\dot{\mathbf{R}} - \frac{m_2}{m_1+m_2}\dot{\mathbf{r}}\right)\cdot\left(\dot{\mathbf{R}} - \frac{m_2}{m_1+m_2}\dot{\mathbf{r}}\right) + \tfrac{1}{2}m_2\left(\dot{\mathbf{R}} + \frac{m_1}{m_1+m_2}\dot{\mathbf{r}}\right)\cdot\left(\dot{\mathbf{R}} + \frac{m_1}{m_1+m_2}\dot{\mathbf{r}}\right)$$

$$|\mathbf{A}|^2 = \mathbf{A}\cdot\mathbf{A}$$

$$T = \tfrac{1}{2}(m_1+m_2)|\dot{\mathbf{R}}|^2 + \tfrac{1}{2}\frac{m_1m_2}{m_1+m_2}|\dot{\mathbf{r}}|^2$$

$$|\dot{\mathbf{r}}| = |d\mathbf{r}/dt| \neq d|\mathbf{r}|/dt$$

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REDUCTION OF THE TWO-PARTICLE PROBLEM TO TWO ONE-PARTICLE PROBLEMS

$$T = \tfrac{1}{2}(m_1+m_2)|\dot{\mathbf{R}}|^2 + \tfrac{1}{2}\frac{m_1m_2}{m_1+m_2}|\dot{\mathbf{r}}|^2$$

$$M \equiv m_1 + m_2$$

$$\mu \equiv \frac{m_1m_2}{m_1+m_2}$$

$$T = \tfrac{1}{2}M|\dot{\mathbf{R}}|^2 + \tfrac{1}{2}\mu|\dot{\mathbf{r}}|^2$$

The kinetice energy of a hypothetical particle of mass M located at the center of mass

The kinetice enrgy of internal (relative) motion of the two particles (vibration and rotation)

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$x_1, y_1, z_1, x_2, y_2, z_2 \longrightarrow p_{x_1} = m_1\dot{x}_1, \quad \ldots, \quad p_{z_2} = m_2\dot{z}_2$

$X, Y, Z, x, y, z \longrightarrow$

$$p_X \equiv M\dot{X}\ , \quad p_Y \equiv M\dot{Y}\ , \quad p_Z \equiv M\dot{Z}$$
$$p_x \equiv \mu\dot{x}\ , \quad p_y \equiv \mu\dot{y}\ , \quad p_z \equiv \mu\dot{z}$$

We define these linear momenta for the new coordinates

We define two new momentum vectors:

$$\mathbf{p}_M \equiv \mathbf{i}M\dot{X} + \mathbf{j}M\dot{Y} + \mathbf{k}M\dot{Z} \text{ and } \mathbf{p}_\mu \equiv \mathbf{i}\mu\dot{x} + \mathbf{j}\mu\dot{y} + \mathbf{k}\mu\dot{z}$$

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$$T = \tfrac{1}{2}M|\dot{\mathbf{R}}|^2 + \tfrac{1}{2}\mu|\dot{\mathbf{r}}|^2$$

$$\mathbf{p}_M \equiv \mathbf{i}M\dot{X} + \mathbf{j}M\dot{Y} + \mathbf{k}M\dot{Z} \text{ and } \mathbf{p}_\mu \equiv \mathbf{i}\mu\dot{x} + \mathbf{j}\mu\dot{y} + \mathbf{k}\mu\dot{z}$$

$$T = \frac{|\mathbf{p}_M|^2}{2M} + \frac{|\mathbf{p}_\mu|^2}{2\mu}$$

If: $V = V(x, y, z)$ V is a function only of the relative coordinates

$$H = \frac{p_M^2}{2M} + \left[\frac{p_\mu^2}{2\mu} + V(x, y, z)\right]$$

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Suppose we had a system composed of two particles:

M subject to no force

μ Subject to the potential energy function $V = V(x, y, z)$

There is no interaction between two particles

What is the Hamiltonian?

$$H = \frac{p_M^2}{2M} + \left[\frac{p_\mu^2}{2\mu} + V(x, y, z)\right]$$

$$E = E_M + E_\mu$$

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$$(\hat{p}_M^2/2M)\psi_M = E_M\psi_M$$

the Schrodinger equation for a free particle of mass M $E_M \geq 0$

$$\left[\frac{\hat{p}_\mu^2}{2\mu} + V(x, y, z)\right]\psi_\mu(x, y, z) = E_\mu\psi_\mu(x, y, z)$$

We have separated the problem to two separate one particle problems:

1) Translational motion of the entire system of mass
2) The relative or internal motion

For the hydrogen atom:

$$M = m_e + m_p \qquad \mu = m_e m_p/(m_e + m_p)$$

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THE TWO-PARTICLE RIGID ROTOR

A two particle system with the particles held at a fixed distance from each other by a rigid massless rod of length d

$$|\mathbf{r}| = d. \qquad V = 0$$

The energy of rotor is wholly kinetics and the kinetic energy of internal motion is wholly rotational

We separate off the translational motion of the system from as a whole and concern ourselves with the rotational motion

$$\hat{H} = \frac{\hat{p}_\mu^2}{2\mu} = -\frac{\hbar^2}{2\mu}\nabla^2, \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$V = V(r).$$

The coordinates of fictitious particle with mass μ is the relative coordinates of particles 1 and 2.

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THE TWO-PARTICLE RIGID ROTOR

x, y, z: relative cartizian coordinates
r, θ, φ: relative spherical coordinat

r = cte = d
Thus, the problem is equivalent to a particle of mass μ constrained to move on the surface of sphere of radius r.

$V = 0$ is a special case of $V = V(r)$.

Thus:

$$\psi = Y_J^m(\theta, \phi)$$

J rather than l is used for the rotational angular-momentum quantum number

$$H = \frac{p_M^2}{2M} + \left[\frac{p_\mu^2}{2\mu} + V(x,y,z)\right] \xrightarrow{V(r)=0} \hat{H} = (2\mu d^2)^{-1}\hat{L}^2$$

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THE TWO-PARTICLE RIGID ROTOR

$$\hat{H}\psi = E\psi$$

$$(2\mu d^2)^{-1}\hat{L}^2 Y_J^m(\theta,\phi) = EY_J^m(\theta,\phi)$$

$$(2\mu d^2)^{-1}J(J+1)\hbar^2 Y_J^m(\theta,\phi) = EY_J^m(\theta,\phi)$$

$$E = \frac{J(J+1)\hbar^2}{2\mu d^2}, \qquad J = 0, 1, 2\ldots$$

I ≡ moment of inertia

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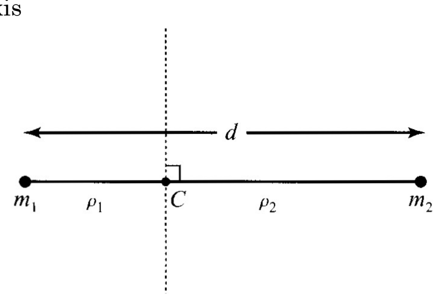
THE TWO-PARTICLE RIGID ROTOR

$$I \equiv \sum_{i=1}^{n} m_i \rho_i^2$$

m_i ≡ the mass of particle i

ρ_i ≡ the perpendicular disctance from particle i to the axis

$$I = m_1\rho_1^2 + m_2\rho_2^2$$



$$I = \mu d^2$$

$$m_1\rho_1 = m_2\rho_2$$

$$\mu \equiv m_1 m_2/(m_1 + m_2)$$

$$d \equiv \rho_1 + \rho_2$$

$$E = \frac{J(J+1)\hbar^2}{2\mu d^2}, \qquad J = 0, 1, 2\ldots$$

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THE TWO-PARTICLE RIGID ROTOR

$$E = \frac{J(J+1)\hbar^2}{2\mu d^2}$$

$$I = \mu d^2$$

$$E = \frac{J(J+1)\hbar^2}{2I}$$

$$J = 0, 1, 2, \ldots$$

The lowest level is E=0. Does this violate the uncertainty principle?

Are the energy levels degenerate for rigid rotor?

The energy depends on J when the wave function depends on J and m

$$2J + 1$$

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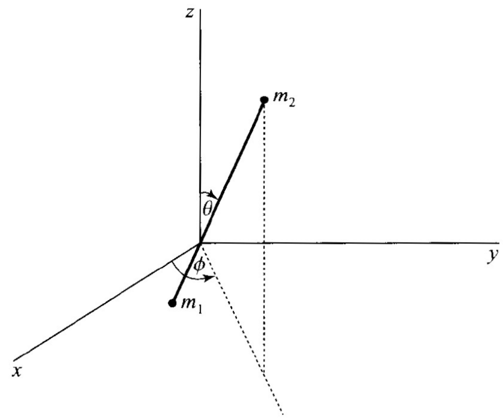
THE TWO-PARTICLE RIGID ROTOR

A Cartesian coordinate system with the origin at the rotor's center of mass

This coordinate system undergoes the same translational motion as the rotor's center of mass but does not rotate in space



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THE TWO-PARTICLE RIGID ROTOR

The rotational levels of a diatomic molecule can be well approximated by the two-particle rigid-rotor energies.

For allowed pure-rotational transitions:

1) $\Delta J = \pm 1$
2) a molecule must have a nonzero dipole moment

These transitions locate in microwave region.

$$\nu = \frac{E_{J+1} - E_J}{h} = \frac{[(J+1)(J+2) - J(J+1)]h}{8\pi^2 I} = 2(J+1)B$$

Rotational constant: $B \equiv h/8\pi^2 I\,,\qquad J = 0, 1, 2, \ldots$

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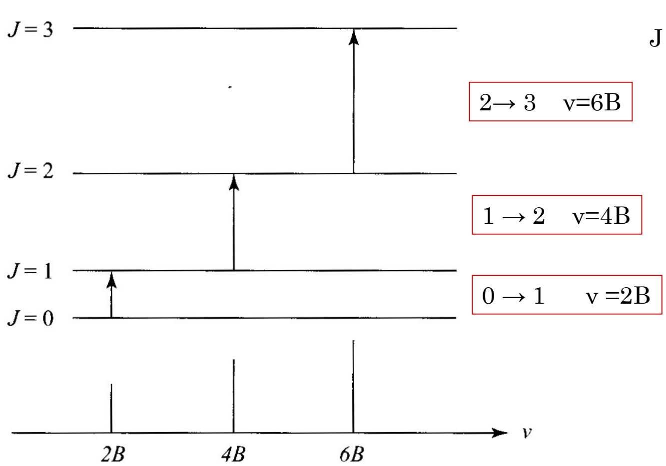
THE TWO-PARTICLE RIGID ROTOR

$\nu = 2(J+1)B$

J → J+1



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Spectrum → B → I → d

EXAMPLE:

The lowest-frequency pur-rotational absorption line of $^{12}C^{32}S$ occurs at 48991.0 MHz. Find the bond distance in $^{12}C^{32}S$

$J \to J+1 \qquad \nu = 2(J+1)B$

$$\nu = 2B$$

$$B \equiv h/8\pi^2 I = \nu/2$$

$$I = h/4\pi^2\nu$$

$$I = \mu d^2$$

$$d = (h/4\pi^2\nu\mu)^{1/2}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{12(31.97207)}{12 + 31.97207}\frac{1}{6.02214 \times 10^{23}}\text{ g} = 1.44885 \times 10^{-23}\text{ g}$$

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EXAMPLE:

$$d = \frac{1}{2\pi}\left(\frac{h}{\nu_{0\to 1}\mu}\right)^{1/2} = \frac{1}{2\pi}\left[\frac{6.62608 \times 10^{-34}\text{ J s}}{(48991.0 \times 10^6\text{ s}^{-1})(1.44885 \times 10^{-26}\text{ kg})}\right]^{1/2}$$

$$= 1.5377 \times 10^{-10}\text{ m} = 1.5377\text{ Å}$$

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THE HYDROGEN ATOM

Consists of a proton and an electron

e : proton's charge
-e : electron's charge

$e = 1.6 \times 10^{-19}$ C

Hydrogenlike atom:

A system consisting of one electron and a nucleus of charge Ze

Z = 1 hydrogen atom
Z = 2 He^{+}
Z = 3 Li^{2+}

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THE HYDROGEN ATOM

A one-electron wave function is called orbital (whether or not it is hydrogenlike)

An orbital for an electron in an atom is called an atomic orbital.

For the hydrogenlike atom let:

x, y, and z be relative coordinate of electron relative to the nucleus.
and

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$$

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The Hydrogen atom

Force on the electron:

A central force ← $\mathbf{F} = -\dfrac{Ze'^2}{r^2}\dfrac{\mathbf{r}}{r}$ → Unit vector in the **r** direction

$$\mathbf{F} = -\frac{dV(r)}{dr}\frac{\mathbf{r}}{r}$$

$$dV(r)/dr = Ze'^2/r^2$$

$$V = Ze'^2\int\frac{dr}{r^2} = -\frac{Ze'^2}{r}$$ Where V = 0 at r =∞

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The Hydrogen atom

$$V = -\frac{Ze'^2}{r}$$

↓

A two particle problem

↓

Two one particle problem

1) Translation of a particle with mass $M = m_e + m_n$
2) (internal motion) motion of a fictitious particle of mass μ at potential

$$V = -\frac{Ze'^2}{r}$$

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THE HYDROGEN ATOM

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

The Hamiltonian of internal motion

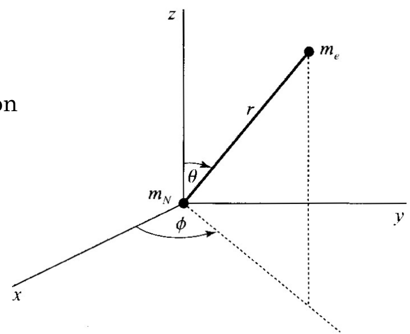
$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze'^2}{r}$$

↓

V is a function of r

↓

A one-particle central-force problem



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THE HYDROGEN ATOM

Thus:

$$\psi(r,\theta,\phi) = R(r)Y_l^m(\theta,\phi)\,, \qquad l = 0,1,2,\ldots, \qquad |m| \le l$$

Y_l^m Spherical harmonic

$R(r)$ Radial factor

$$-\frac{\hbar^2}{2\mu}\left(R'' + \frac{2}{r}R'\right) + \frac{l(l+1)\hbar^2}{2\mu r^2}R - \frac{Ze'^2}{r}R = ER(r)$$

$$a \equiv \hbar^2/\mu e'^2$$

$$R'' + \frac{2}{r}R' + \left[\frac{2E}{ae'^2} + \frac{2Z}{ar} - \frac{l(l+1)}{r^2}\right]R = 0$$

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Solution of radial equation

Power-series solution:

Tree term recursion relation

↓ A substitution

Two term recursion relation

Examining the behavior of solution for large values of r:

$$R'' + \frac{2}{r}R' + \left[\frac{2E}{ae'^2} + \frac{2Z}{ar} - \frac{l(l+1)}{r^2}\right]R = 0$$

↓ For large r

$$R'' + \frac{2E}{ae'^2}R = 0$$

Using auxiliary equation $\exp\left[\pm(-2E/ae'^2)^{1/2}r\right]$

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Solution of radial equation

$$\exp\left[\pm(-2E/ae'^2)^{1/2}r\right]$$

1) For E ≥ 0 $R(r) \sim e^{\pm i\sqrt{2\mu E}r/\hbar}$

↓

We are giving the behavior of R

R(r) remains finite for all values of r

Physically these eigenfunctions correspond to states in which the electron is not bound to the nucleus

Continuum eigenfunctions

Are not normalizable

Angular part is spherical harmonic

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Solution of radial equation

2) E < 0 (bound states)

$$\exp\left[\pm(-2E/ae'^2)^{1/2}r\right]$$

To make it finite as r goes to infinity, we prefer the minus sign

$$\exp\left[-(-2E/ae'^2)^{1/2}r\right]$$

In order to get a two-term recursion relation:

$$R(r) = e^{-Cr}K(r)$$

$$C \equiv \left(-\frac{2E}{ae'^2}\right)^{1/2}$$

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Solution of radial equation

The substitution will guarantee nothing about the behavior of wave function for large r. The differential equation will still have two linearly independent solution.

$$R(r) \doteq e^{+Cr}J(r)$$

$$J(r) = e^{-2Cr}K(r)$$

$$R'' + \frac{2}{r}R' + \left[\frac{2E}{ae'^2} + \frac{2Z}{ar} - \frac{l(l+1)}{r^2}\right]R = 0$$

$$\downarrow \quad R(r) = e^{-Cr}K(r)$$

$$r^2K'' + (2r - 2Cr^2)K' + [(2Za^{-1} - 2C)r - l(l+1)]K = 0$$

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Solution of radial equation

$$K = \sum_{k=0}^{\infty} c_k r^k$$

If we did we would find that the first few coefficients are zero

$$K = \sum_{k=s}^{\infty} c_k r^k \,, \qquad c_s \neq 0$$

The first nonzero coefficient

$$K = \sum_{j=0}^{\infty} c_{j+s} r^{j+s} = r^s \sum_{j=0}^{\infty} b_j r^j \,, \qquad b_0 \neq 0$$

$$j \equiv k - s \qquad b_j \equiv c_{j+s}$$

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Solution of radial equation

$$r^2 K'' + (2r - 2Cr^2)K' + [(2Za^{-1} - 2C)r - l(l+1)]K = 0$$

$$K(r) = r^s M(r)$$

$$M(r) = \sum_{j=0}^{\infty} b_j r^j \,, \qquad b_0 \neq 0$$

$$r^2 M'' + [(2s+2)r - 2Cr^2]M' + [s^2 + s + (2Za^{-1} - 2C - 2Cs)r - l(l+1)]M = 0$$

$$M(0) = b_0 \,, \qquad M'(0) = b_1 \,, \qquad M''(0) = 2b_2$$

$$b_0(s^2 + s - l^2 - l) = 0$$

$$s^2 + s - l^2 - l = 0 \longrightarrow s = l \,, \qquad s = -l - 1$$

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Solution of radial equation

We test the behavior of wave function

$$R(r) = e^{-Cr} r^s \sum_{j=0}^{\infty} b_j r^j$$

$$R(r) = e^{-Cr} K(r)$$

$$K(r) = r^s M(r)$$

$$M(r) = \sum_{j=0}^{\infty} b_j r^j$$

$$e^{-Cr} = 1 - Cr + \ldots$$

R(r) behaves as $b_0 r^s$ for small r

For the root l = s, R(r) behaves properly at the origin

For s = -l – 1 R(r) is proportional to $\frac{1}{r^{l+1}}$ for small r

l = 0 , 1, 2, …. Thus R(r) becomes infinite at the origin

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Solution of radial equation

That is not a good argument, since for the relativistic hydrogen atom, l = 0 eigenfunctions are infinite at r=0.

From the standpoint of quadratic integrability:

$$\int_0 |R|^2 r^2 dr \approx \int_0 \frac{1}{r^{2l}}\, dr \qquad \left.\frac{1}{r^{2l-1}}\right|_{r=0}$$

For $l = 1, 2, 3, \ldots$ is equal to infinite and s = -l -1 is not acceptable

For l = 0, it is finite and R(r) ~ r^{-1}, but why is not acceptable?

1) Further study shows that it corresponds to an energy value that the experimental hydrogen-atom spectrum shows does not exist
2) r^{-1} satisfy the Schrodinger equation everywhere in space except at the origin
3) the Hamiltonian operator is not Hermitian with respect to it

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Solution of radial equation

Taking the first root:

$$R(r) = e^{-Cr} r^s \sum_{j=0}^{\infty} b_j r^j$$

s = 1

$$R(r) = e^{-Cr} r^l M(r)$$

$$r^2 M'' + [(2s+2)r - 2Cr^2]M' + [s^2 + s + (2Za^{-1} - 2C - 2Cs)r - l(l+1)]M = 0$$

s = 1

$$rM'' + (2l + 2 - 2Cr)M' + (2Za^{-1} - 2C - 2Cl)M = 0$$

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$$M(r) = \sum_{j=0}^{\infty} b_j r^j$$

$$M' = \sum_{j=0}^{\infty} j b_j r^{j-1} = \sum_{j=1}^{\infty} j b_j r^{j-1} = \sum_{k=0}^{\infty} (k+1) b_{k+1} r^k = \sum_{j=0}^{\infty} (j+1) b_{j+1} r^j$$

$$M'' = \sum_{j=0}^{\infty} j(j-1) b_j r^{j-2} = \sum_{j=1}^{\infty} j(j-1) b_j r^{j-2} = \sum_{k=0}^{\infty} (k+1) k b_{k+1} r^{k-1}$$

$$= \sum_{j=0}^{\infty} (j+1) j b_{j+1} r^{j-1}$$

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Solution of radial equation

$$rM'' + (2l + 2 - 2Cr)M' + (2Za^{-1} - 2C - 2Cl)M = 0$$

↓

$$\sum_{j=0}^{\infty}\left[j(j+1)b_{j+1} + 2(l+1)(j+1)b_{j+1} + \left(\frac{2Z}{a} - 2C - 2Cl - 2Cj\right)b_j\right]r^j = 0$$

↓

$$b_{j+1} = \frac{(2C + 2Cl + 2Cj - 2Za^{-1})}{j(j+1) + 2(l+1)(j+1)}b_j$$

We examine the infinite series $M(r) = \sum_{j=0}^{\infty} b_j r^j$ for large r:

For large r the behaviour of the series are determined by the terms with large j

$$\frac{b_{j+1}}{b_j} \sim \frac{2Cj}{j^2} = \frac{2C}{j}$$

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Solution of radial equation

$$e^{2Cr} = 1 + 2Cr + \cdots + \frac{(2C)^j r^j}{j!} + \frac{(2C)^{j+1} r^{j+1}}{(j+1)!} + \cdots$$

$$\frac{(2C)^{j+1}}{(j+1)!}\cdot\frac{j!}{(2C)^j} = \frac{2C}{j+1} \sim \frac{2C}{j}$$

For large r, the infinite series behave like e^{2Cr}

$$R(r) = e^{-Cr} r^s \sum_{j=0}^{\infty} b_j r^j \longrightarrow R(r) \sim e^{-Cr} r^l e^{2Cr} = r^l e^{Cr}$$

$r \to \infty$ ⟹ $R(r) \to \infty$ and will not be quadratically integrable

We have to cut the series, then the e^{-Cr} factor will ensure that the wave function goes to zero as r goes to infinity

The last term: $b_k r^k$

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$$R(r) = e^{-Cr} r^s \sum_{j=0}^{\infty} b_j r^j$$

$$b_{j+1} = \frac{(2C + 2Cl + 2Cj - 2Za^{-1})}{j(j+1) + 2(l+1)(j+1)} b_j$$

= 0 for j = k

$$2C(k + l + 1) = 2Za^{-1}\,, \qquad k = 0, 1, 2, \ldots$$

k and l are integers, and we define a new integer:

$$n \equiv k + l + 1\,, \qquad n = 1, 2, 3, \ldots$$

$$l \le n - 1$$

l = 0, 1, …, n-1

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Solution of radial equation

Energy levels:

$$2C(k + l + 1) = 2Za^{-1}$$

$$n \equiv k + l + 1$$

$$Cn = Za^{-1}$$

$$C \equiv (-2E/ae'^2)^{1/2}$$

$$E = -\frac{Z^2}{n^2}\left(\frac{e'^2}{2a}\right) = -\frac{Z^2 \mu e'^4}{2n^2\hbar^2} \qquad a \equiv \hbar^2 \mu e'^2$$

Bound-state energy levels of hydrogenlike atom
They are discrete

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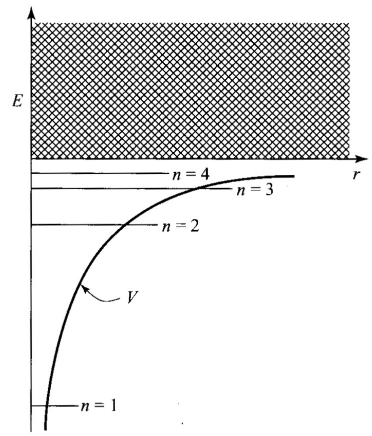
Solution of radial equation



Energy levels of the hydrogen atom and the potential energy curve

Solution of radial equation

All changes in n are allowed in light absorption and emission

H-atom spectral lines:

$$\tilde{\nu} \equiv \frac{1}{\lambda} = \frac{\nu}{c} = \frac{E_2 - E_1}{hc} = \frac{e'^2}{2ahc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \equiv R_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$R_H = 109677.6 \text{ cm}^{-1}$$

Solution of radial equation

Degeneracy:

a) For bound states: E n

Ψ n, l, m

$n = 1, 2, 3, \ldots$
$l = 0, 1, 2, \ldots, n-1$
$m = -l, -l+1, \ldots, 0, \ldots, l-1, l$

n different values for l

2l + 1 values for m

Degeneracy ≡ n^2

b) Continuum levels:

For a given level there is no restriction on the maximum value of l

Degeneracy ≡ ∞

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$$\sum_{l=0}^{n-1}(2l+1) = \sum_{l=0}^{n-1} 2l = \sum_{l=0}^{n-1} 1$$

$$\sum_{l=0}^{n-1} 2l = 2\sum_{l=0}^{n-1} l = 2\sum_{l=1}^{n-1} l$$

$$\sum_{1}^{k} l = \frac{1}{2}k(k+1)$$

$$\sum_{l=0}^{n-1}(2l+1) = 2.\frac{1}{2}(n-1) + n = n^2$$

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THE BOUND-STATE HYDROGEN-ATOM WAVE FUNCTIONS

The radial factor:

$$R(r) = e^{-Cr} r^l M(r)$$
$$M(r) = \sum_j b_j r^j$$
$$C = Z/na$$

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

$$b_{j+1} = \frac{2Z}{na} \frac{j+l+1-n}{(j+1)(j+2l+2)} b_j$$

$$a \equiv \hbar^2/\mu e'^2$$

The complete wave function:

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

How many nods do R(r) and Y(θ,φ) have?

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GROUND STATE WAVE FUNCTION AND ENERGY

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

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

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

$$R_{10}(r) = 2 \left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$
$$Y_0^0 = 1/(4\pi)^{1/2}$$

$$\psi_{100} = \frac{1}{\pi^{1/2}} \left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

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$$\mu_H = \frac{m_e m_p}{m_e + m_p} = \frac{m_e}{1 + m_e/m_p} = \frac{m_e}{1 + 0.000544617} = 0.9994557 m_e$$

$\mu \approx m_e$ → The error is about 1 part in 2000

$$a_0 \equiv \frac{\hbar^2}{m_e e'^2} = 0.52918 \text{ Å}$$

Bohr radius

$$e = 1.602177 \times 10^{-19} \text{C}$$

$$1 \text{ V·C} = 1 \text{ J} = 10^7 \text{ erg}$$

$$1 \text{ eV} = 1.602177 \times 10^{-19} \text{ J} = 1.602177 \times 10^{-12} \text{erg}$$

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EXAMPLE

Calculate the ground-state energy of the hydrogen atom using SI units and convert the result to electron volts.

$$E = -\frac{Z^2}{n^2}\left(\frac{e'^2}{2a}\right) = -\frac{Z^2 \mu e'^4}{2n^2\hbar^2}$$

$$n = 1, \; Z = 1, \quad e' = e/(4\pi\varepsilon_0)^{1/2}$$

$$E = -\mu e^4/8h^2\varepsilon_0^2$$

$$E = -\frac{0.9994557(9.10939 \times 10^{-31} \text{ kg})(1.602177 \times 10^{-19} \text{ C})^4}{8(6.62608 \times 10^{-34} \text{ J s})^2(8.8541878 \times 10^{-12} \text{ C}^2/\text{N m}^2)^2}$$

$$= -(2.17868 \times 10^{-18} \text{ J})[(1 \text{ eV})/(1.602177 \times 10^{-19} \text{ J})]$$

$$E = -13.598 \text{ eV}$$

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EXAMPLE

Find <T> for the hydrogen-atom ground state

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

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

$$\hat{L}^2\psi = l(l+1)\hbar^2\psi$$ l = 0 for an s state

$$\psi = \pi^{-1/2}a^{-3/2}e^{-r/a}$$

$$\partial\psi/\partial r = -\pi^{-1/2}a^{-5/2}e^{-r/a}$$

$$\partial^2\psi/\partial r^2 = \pi^{-1/2}a^{-7/2}e^{-r/a}$$

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$$d\tau = r^2 \sin\theta\, dr\, d\theta\, d\phi$$

EXAMPLE

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

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

$$a = \hbar^2/\mu e'^2$$

$$\langle T\rangle = 13.598 \text{ eV}$$

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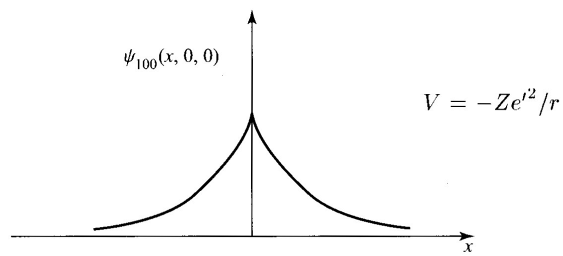
$$\langle V\rangle = \frac{2E}{n+2} \qquad \langle T\rangle = \frac{nE}{n+2}$$ n = -1

Ground state wave function

For points on the x axis

$$r = (x^2 + y^2 + z^2)^{1/2} \longrightarrow r = (x^2)^{1/2} = |x|$$

$$\psi_{100}(x,0,0) = \pi^{-1/2}(Z/a)^{3/2}e^{-Z|x|/a}$$



- ✓ ψ is continuous at the origin
- ✓ dψ/dx is discontinuous at the origin
- ✓ We say that the wave function has a cusp at the origin because the potential energy becomes infinite at the origin.

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The hydrogen-atom bound-state wave functions

The hydrogen-atom bound-state wave functions are denoted by three subscripts (n, l, m)

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

s sharp
p principle
d diffuse
f fundamental

And we go alphabetically

n l $_m$

$2p_{-1}$

n l m

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The hydrogen-atom bound-state wave functions

n=2

$$\psi_{200},\ \psi_{21-1},\ \psi_{210}\ ,\ \psi_{211}$$

$$\psi_{2s}\ ,\ \psi_{2p_{-1}},\ \psi_{2p_0},\ \psi_{2p_1}$$

The radial factors depends on n and l, but not on m

Each of three 2p wave functions has the same radial factor.

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The hydrogen-atom bound-state wave functions

Radial factors in the hydrogenlike-atom wave functions

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

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

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

$$R_{3s} = \frac{2}{3\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2}\left(1-\frac{2Zr}{3a}+\frac{2Z^2r^2}{27a^2}\right)e^{-Zr/3a}$$

$$R_{3p} = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}-\frac{Z^2r^2}{6a^2}\right)e^{-Zr/3a}$$

$$R_{3d} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}$$

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THE HYDROGEN-ATOM BOUND-STATE WAVE FUNCTIONS

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

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

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

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

$\psi^*_{2p_{+1}} = -\psi_{2p_{-1}}$ and $\psi^*_{2p_{-1}} = -\psi_{2p_{+1}}$

$$\psi^*_{2p_{+1}}\psi_{2p_{+1}} = \psi^*_{2p_{-1}}\psi_{2p_{-1}} = -\psi_{2p_{+1}}\psi_{2p_{-1}}$$

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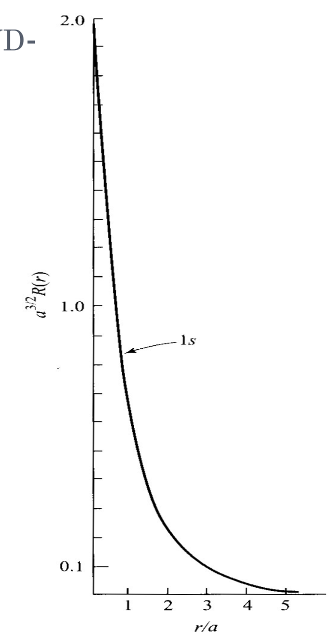
THE HYDROGEN-ATOM BOUND-STATE WAVE FUNCTIONS

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



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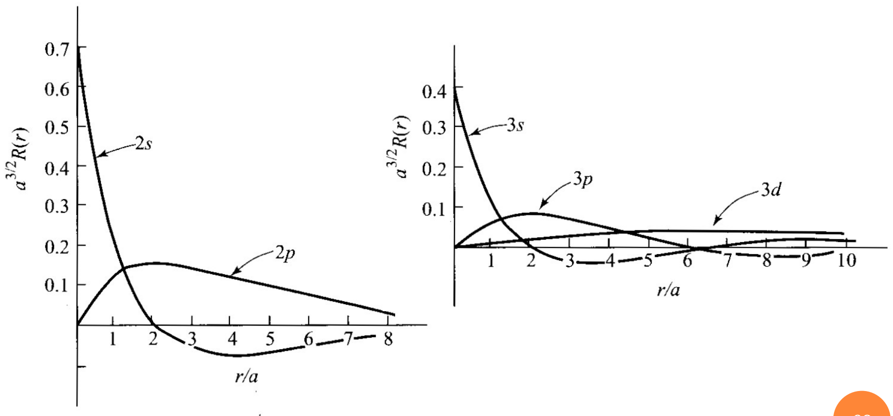
THE HYDROGEN-ATOM BOUND-STATE WAVE FUNCTIONS



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THE RADIAL DISTRIBUTION FUNCTION

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

The probability of finding the electron in the region of space where its coordinates lie in the ranges r to r + dr, θ to θ + dθ and φ to φ + dφ

What is the probability of the electron with r to r +dr with no restriction on θ and φ

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

$$\int_0^{2\pi}\int_0^{\pi} |Y_l^m(\theta, \phi)|^2 \sin\theta\, d\theta\, d\phi = 1$$

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$R^2(r)r^2$ Determines the probability of finding the electron at a distance r from the nucleus; **Radial distribution function**

$R_{1s}(r)$ is not zero at r =0, but radial distribution function for 1s is zero at r = 0

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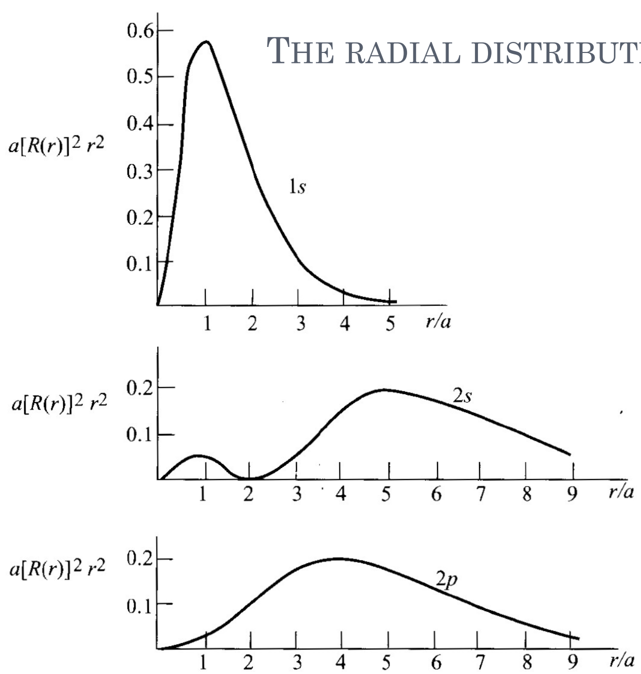
The radial distribution function



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EXAMPLE

Find the probability that the electron in the ground-state H atom is less than a distance a from the nucleus

$$\int_0^a R_{nl}^2 r^2\, dr = \frac{4}{a^3}\int_0^a e^{-2r/a} r^2\, dr = \frac{4}{a^3} e^{-2r/a}\left(-\frac{r^2 a}{2} - \frac{2ra^2}{4} - \frac{2a^3}{8}\right)\Bigg|_0^a$$

$$= 4[e^{-2}(-5/4) - (-1/4)] = 0.323$$

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REAL HYDOGENLIKE FUNCTIONS

$e^{im\varphi}$ makes the spherical harmonics complex with the exception of m = 0

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

x

$$e^{\pm i\phi} = \cos\phi \pm i\sin\phi$$

$$\int |\psi_{2p_x}|^2\, d\tau =$$

$$\frac{1}{2}\left(\int |\psi_{2p_{-1}}|^2\, d\tau + \int |\psi_{2p_1}|^2\, d\tau + \int \psi_{2p_{-1}}^*\psi_{2p_1}\, d\tau + \int \psi_{2p_1}^*\psi_{2p_{-1}}\, d\tau\right)$$

$$= \tfrac{1}{2}(1 + 1 + 0 + 0) = 1$$

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Real hydogenlike functions

ψ_{2p1} and ψ_{2p-1} are normalized and orthogonal.

$$\int_0^{2\pi} (e^{-i\phi})^* e^{i\phi}\, d\phi = \int_0^{2\pi} e^{2i\phi}\, d\phi = 0$$

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

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Real hydogenlike functions

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

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

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

ψ_{2px}, ψ_{2py}, and ψ_{2pz} are mutually orthogonal

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Real hydogenlike functions

$$\hat{H}\psi_{2p_1} = E_2\psi_{2p_1} \qquad \hat{L}^2\psi_{2p_1} = 2\hbar^2\psi_{2p_1} \qquad \hat{L}_z\psi_{2p_1} = \hbar\psi_{2p_1}$$

$$\hat{H}\psi_{2p_{-1}} = E_2\psi_{2p_{-1}} \qquad \hat{L}^2\psi_{2p_{-1}} = 2\hbar^2\psi_{2p_{-1}} \qquad \hat{L}_z\psi_{2p_{-1}} = -\hbar\psi_{2p_{-1}}$$

$$\hat{H}\psi_{2p_0} = E_2\psi_{2p_0} \qquad \hat{L}^2\psi_{2p_0} = 2\hbar^2\psi_{2p_0} \qquad \hat{L}_z\psi_{2p_0} = 0\psi_{2p_0}$$

$$\hat{H}\psi_{2p_x} = E_2\psi_{2p_x} \qquad \hat{L}^2\psi_{2p_x} = 2\hbar^2\psi_{2p_x} \qquad \hat{L}_z\psi_{2p_x} \neq cte\psi_{2p_x}$$

$$\hat{H}\psi_{2p_y} = E_2\psi_{2p_y} \qquad \hat{L}^2\psi_{2p_y} = 2\hbar^2\psi_{2p_y} \qquad \hat{L}_z\psi_{2p_y} \neq cte\psi_{2p_y}$$

$$\hat{H}\psi_{2p_z} = E_2\psi_{2p_z} \qquad \hat{L}^2\psi_{2p_z} = 2\hbar^2\psi_{2p_z} \qquad \hat{L}_z\psi_{2p_z} = 0\psi_{2p_z}$$

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Real hydogenlike functions

For n = 3:

$$\psi_{3d_{xy}} \equiv (1/i\sqrt{2})(\psi_{3d_2} - \psi_{3d_{-2}})$$

$$= \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{7/2} e^{-Zr/3a} r^2 \sin^2\theta\,(2\sin\phi\cos\phi)$$

$$= \frac{2}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{7/2} e^{-Zr/3a} xy$$

Exercise: Continue for other functions with n = 3

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$$\left.\begin{aligned}3d_{z^2} &= \\ 3d_{x^2-y^2} &= \\ 3d_{xy} &= \\ 3d_{xz} &= \\ 3d_{yz} &= \end{aligned}\right\} \frac{2}{\sqrt{2592\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{2Zr}{3a_0}\right)^2 \exp\left(\frac{-Zr}{3a_0}\right)\begin{cases}\left(1/\sqrt{3}\right)\left(3\cos^2\theta - 1\right)\\ \sin^2\theta\cos 2\phi \\ \sin^2\theta\sin 2\phi \\ \sin 2\theta\cos\phi \\ \sin 2\theta\sin\phi\end{cases}$$

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Real hydogenlike functions

Real Hydrogenlike Wave Functions

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

$$2s = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right) e^{-Zr/2a}$$

$$2p_z = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\cos\theta$$

$$2p_x = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\cos\phi$$

$$2p_y = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\sin\phi$$

$$3s = \frac{1}{81(3\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(27 - 18\frac{Zr}{a} + 2\frac{Z^2r^2}{a^2}\right) e^{-Zr/3a}$$

$$3p_z = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right) re^{-Zr/3a}\cos\theta$$

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Real hydogenlike functions

Real Hydrogenlike Wave Functions

$$3p_x = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6-\frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\cos\phi$$

$$3p_y = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6-\frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\sin\phi$$

$$3d_{z^2} = \frac{1}{81(6\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2}r^2e^{-Zr/3a}(3\cos^2\theta-1)$$

$$3d_{xz} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2}r^2e^{-Zr/3a}\sin\theta\cos\theta\cos\phi$$

$$3d_{yz} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2}r^2e^{-Zr/3a}\sin\theta\cos\theta\sin\phi$$

$$3d_{x^2-y^2} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2}r^2e^{-Zr/3a}\sin^2\theta\cos 2\phi$$

$$3d_{xy} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2}r^2e^{-Zr/3a}\sin^2\theta\sin 2\phi$$

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Hydrogenlike orbitals

The ways of depicting orbitals:
- 1) Drawing graphs of the functions
- 2) Drawing contour surfaces of constant probability density

1) Drawing graphs of the functions

To graph the variation of ψ(r, θ, φ), we need four dimensions

↓

Instead, we draw graphs of the factors in ψ

Graphing R(r) versus r, we get previous curves

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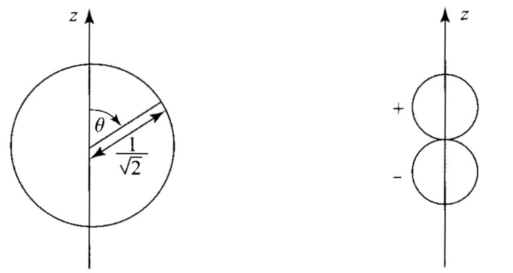
HYDROGENLIKE ORBITALS

Graphs of S(θ):



Plot of $S_{0,0}(\theta)$ Plot of $S_{1,0}(\theta)$

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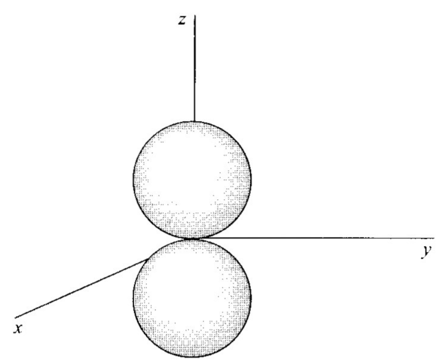
$S_{0,0} = 1/\sqrt{2}, \qquad S_{1,0} = \frac{1}{2}\sqrt{6}\cos\theta$

HYDROGENLIKE ORBITALS

We can draw a single graph that plots $|S(\theta)T(\varphi)|$ as a function of θ and φ

For an s orbital: $ST=1/(4\pi)^{1/2}$ A sphere of radius $1/(4\pi)^{1/2}$

For a p_z orbital: $ST = \frac{1}{2}(3/\pi)^{1/2}\cos\theta$



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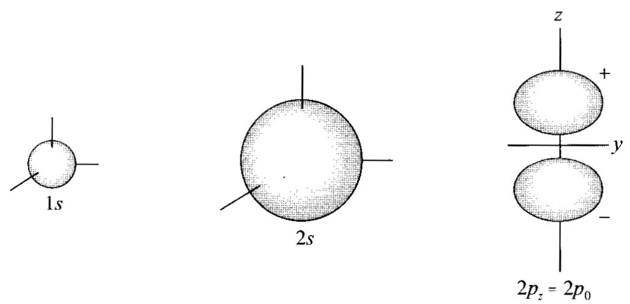
HYDROGENLIKE ORBITALS

Drawing contour surfaces of constant probability density:

We shall draw surfaces in space, on each of which the value of $|\psi|^2$ probability density, is constant.



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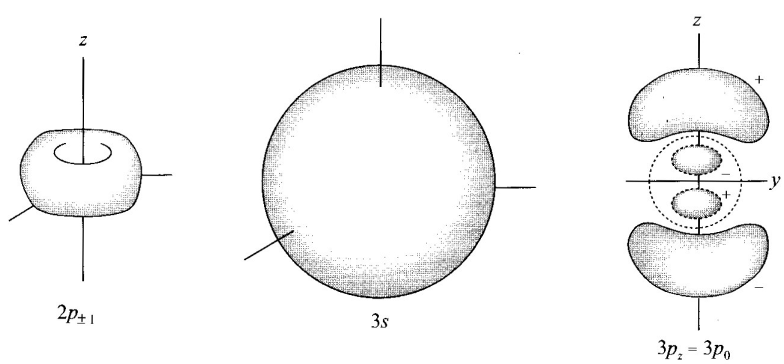
HYDROGENLIKE ORBITALS



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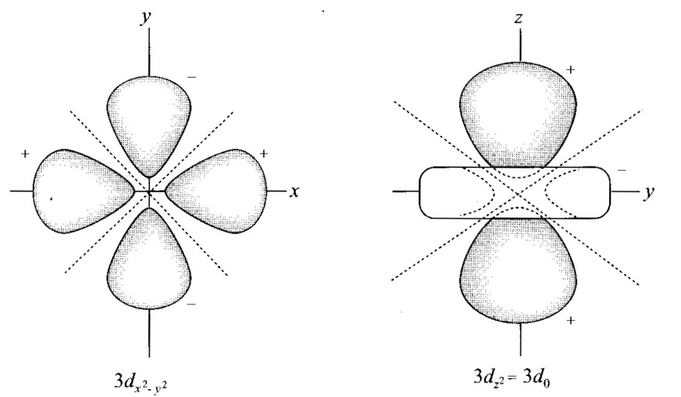
HYDROGENLIKE ORBITALS



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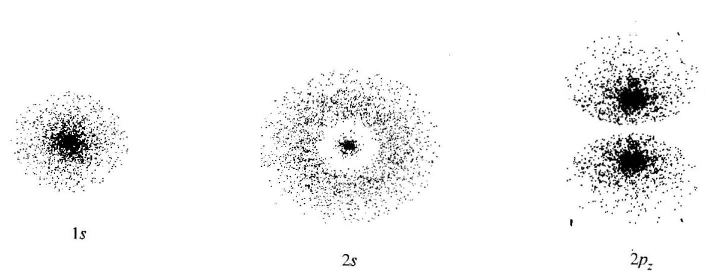
HYDROGENLIKE ORBITALS



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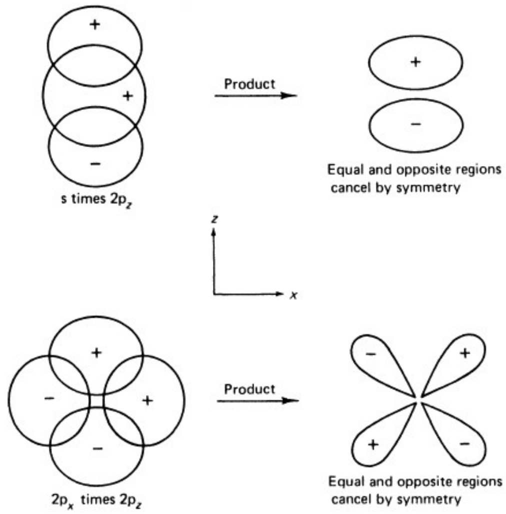
Hydrogenlike orbitals



Drawings of orbitals and their products to demonstrate orthogonality.

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The Zeeman effect

Application of an external magnetic field cause a splitting of atomic spectral lines

A charge Q with velocity **v** gives rise to a magnetic field **B** at point P in space

$$\mathbf{B} = \frac{\mu_0}{4\pi}\frac{Q\mathbf{v}\times\mathbf{r}}{r^3} \qquad \mu_0 = 4\pi \times 10^{-7}\ \ \mathrm{N\,C^{-2}\,s^2}$$

r: a vector from Q to P
μ_0: permeability of vacuum
B: magnetic induction or magnetic flux density (T)
Q is in coulomb

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Electric dipole moment: a vector from –Q to +Q with magnitude bQ

Magnetic dipole moment (**m**): a vector of magnitude IA
I ≡current, A ≡ the area of loop
m is perpendicular to the plane

The current is the charge flow per unit time. t=2πr/v

$I = Q / t = Qv/2\pi r$

$$|\mathbf{m}| = IA = (Qv/2\pi r)\pi r^2 = Qvr/2 = Qrp/2m$$

m is the mass of the charged particle
p is the linear momentum

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The Zeeman effect

r is perpendicular to **p** thus:

$$\mathbf{m}_L = \frac{Q\mathbf{r}\times\mathbf{p}}{2m} = \frac{Q}{2m}\mathbf{L}$$

$$Q = -e$$

$$\mathbf{m}_L = -\frac{e}{2m_e}\mathbf{L}$$

$$|\mathbf{m}_L| = \frac{e\hbar}{2m_e}[l(l+1)]^{1/2} = \beta_e[l(l+1)]^{1/2}$$

$$\beta_e = e\hbar/2m_e = 9.274\times 10^{-24}\ \mathrm{J/T}$$ *Bohr magneton*

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The Zeeman effect

For H atom in the presence of an external magnetic field

The interaction energy between magnetic dipole moment and external magnetic field

$$E_B = -\mathbf{m} \cdot \mathbf{B}$$

$$E_B = \frac{e}{2m_e} \mathbf{L} \cdot \mathbf{B}$$

We take the z axis along the **B**: $\mathbf{B} = B\mathbf{k}$

$$E_B = \frac{e}{2m_e} B\,(L_x\mathbf{i} + L_y\mathbf{j} + L_z\mathbf{k}) \cdot \mathbf{k} = \frac{e}{2m_e} BL_z = \frac{\beta_e}{\hbar} BL_z$$

Additional term in Hamiltonian:

$$\hat{H}_B = \beta_e B\hbar^{-1}\hat{L}_z$$

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The Zeeman effect

The Schrödinger equation for the H atom in a magnetic field

$$(\hat{H} + \hat{H}_B)\psi = E\psi$$

Ĥ is the Hamiltonian in the absence of an external field

$$(\hat{H} + \hat{H}_B)R(r)Y_l^m(\theta, \phi) = \hat{H}RY_l^m + \beta_e\hbar^{-1}B\hat{L}_zRY_l^m$$

$$= \left(-\frac{Z^2}{n^2}\frac{e'^2}{2a} + \beta_e Bm\right) RY_l^m$$

additional term

Thus, m degeneracy is removed

m is called magnetic quantum number

Spin magnetic moment of electron did not consider in this discussion

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