Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 23
Nov 1st, 2013

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Objectives

- To understand the origin of the expression of the differential volume in spherical coordinates.
- To introduce the concept of radial density distribution for hydrogenic atoms.
- To show expressions and plots of radial functions for the hydrogen atom.
- To show plots of radial probability distributions for the hydrogen atom.
- To show solved problems involving radial probability distributions.

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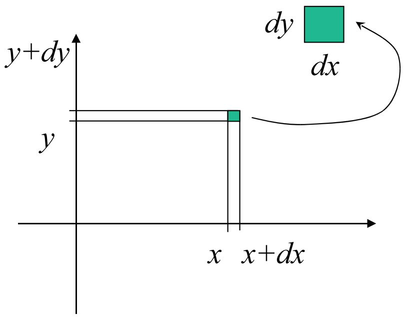
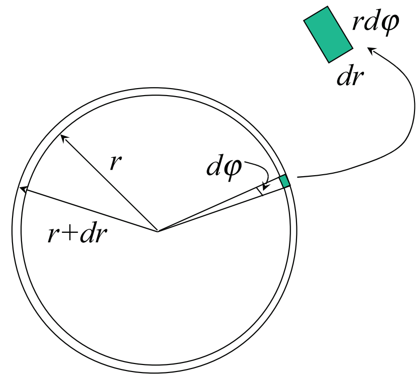
Differential area elements in Cartesian and planar polar coordinates





Area element between
x .. $x+dx$ and y .. $y+dy$

$$dS = dx\,dy$$

Area element between
r .. $r+dr$ and φ .. $\varphi+d\varphi$

$$dS = rdr\,d\varphi$$

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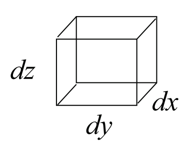
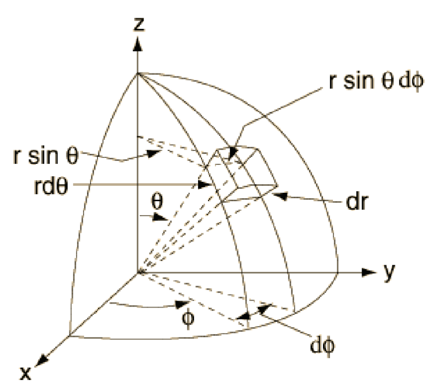
Differential volume elements in Cartesian and spherical coordinates



Volume element between
x .. $x+dx$, y .. $y+dy$, and z .. $z+dz$

$$dV = dx\,dy\,dz$$



Volume element between
r .. $r+dr$, θ .. $\theta+d\theta$, and φ .. $\varphi+d\varphi$

$$\begin{aligned} dV &= \text{length} \times \text{width} \times \text{height} \\ &= (r\,d\theta)(r\sin\theta\,d\varphi)(dr) = r^2 \sin\theta\,dr\,d\theta\,d\varphi \end{aligned}$$

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Radial density distribution in hydrogenic atoms

The probability of finding an electron in the region of space between r and $r + dr$, θ and $\theta + d\theta$, φ and $\varphi + d\varphi$ is

$$|\psi_{nlm}|^2\, dV = |\psi_{nlm}(r,\theta,\varphi)|^2 \underbrace{r^2 \sin\theta\, dr\, d\theta\, d\varphi}_{\text{differential volume element in spherical polar coordinates}}$$

The probability of finding the electron in a thin spherical shell of inner radius r and outer radius $r + dr$ (i.e., the probability of finding the electron between r and $r+dr$ at *any* angles θ and φ) is given by

$$D_{nl}(r)\, dr,$$

where $D_{nl}(r)$ is the **radial probability density** defined by

$$D_{nl}(r) \equiv \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta\, r^2 \sin\theta\, |\psi_{nlm}(r,\theta,\varphi)|^2 \qquad (1)$$

Recall that the wave functions for the hydrogen atom are of the form

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r) Y_l^m(\theta,\varphi) \qquad (2)$$

Substitution of Eq. (2) into Eq. (1) gives

$$D_{nl}(r) = r^2 [R_{nl}(r)]^2 \underbrace{\int_0^{2\pi} d\varphi \int_0^{\pi} |Y_l^m(\theta,\varphi)|^2 \sin\theta\, d\theta}_{=1 \text{ because spherical harmonics are normalized}} = r^2 R_{nl}^2(r)$$

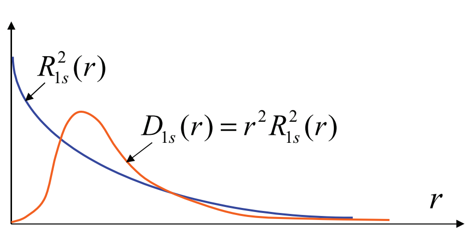
The radial distribution function

$$D_{nl}(r) = r^2 R_{nl}^2(r)$$

is the **probability density** characterizing the likelihood of finding the electron at a distance r from the nucleus.

Example:

$R_{1s}(r)$ is not zero at $r = 0$ but $D_{1s}(r)$ is zero because of the r^2 factor.



Radial functions for the hydrogen atom (Z=1)

$$R_{nl}(r) \qquad n = 1, 2, 3, \ldots$$
$$l = 0, 1, 2, \ldots, n-1$$
$$\int_0^\infty r^2 [R_{nl}(r)]^2\, dr = 1$$

$n = 1$

$$R_{10}(r) = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$n = 2$

$$R_{20}(r) = \frac{1}{2\sqrt{2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0} \qquad R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{5/2} r e^{-r/2a_0}$$

$n = 3$

$$R_{30}(r) = \frac{2}{81\sqrt{3}}\left(\frac{1}{a_0}\right)^{3/2}\left(27 - \frac{18r}{a_0} + \frac{2r^2}{a_0^2}\right)e^{-r/3a_0}$$

$$R_{31}(r) = \frac{4}{81\sqrt{6}}\left(\frac{1}{a_0}\right)^{5/2}\left(6 - \frac{r}{a_0}\right) r e^{-r/3a_0} \qquad R_{32}(r) = \frac{4}{81\sqrt{30}}\left(\frac{1}{a_0}\right)^{7/2} r^2 e^{-r/3a_0}$$

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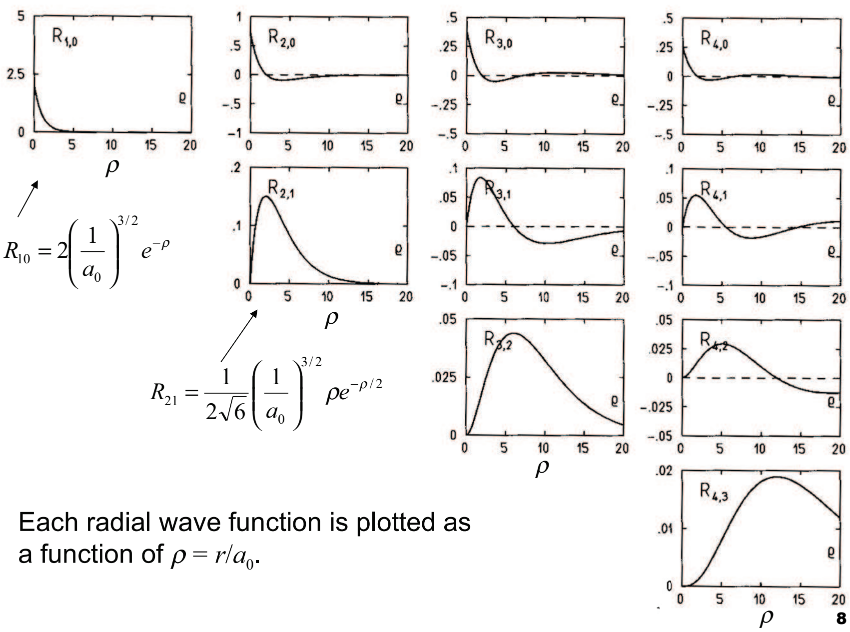
Plots of the radial functions for the hydrogen atom



$$R_{10} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-\rho}$$

$$R_{21} = \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2} \rho e^{-\rho/2}$$

Each radial wave function is plotted as a function of $\rho = r/a_0$.

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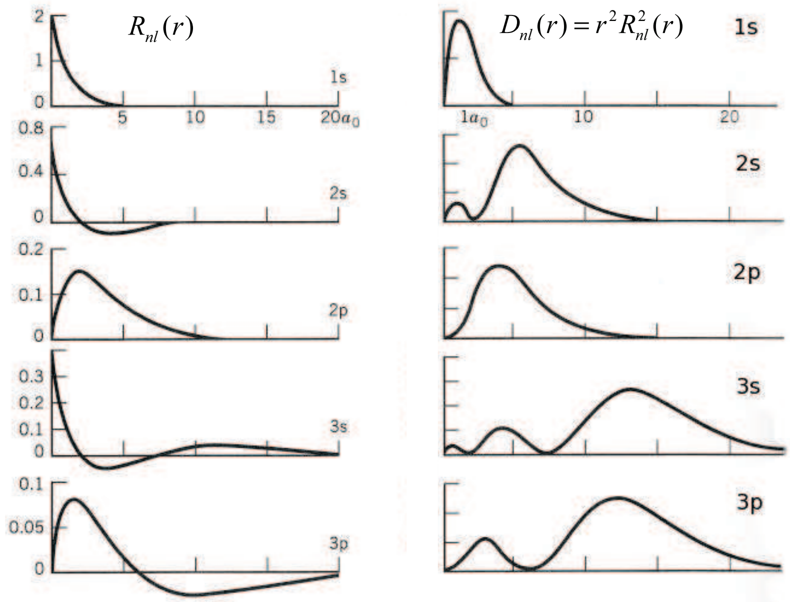
Radial functions and radial probability densities for the 1s, 2s, 2p, 3s and 3p orbitals of the H atom



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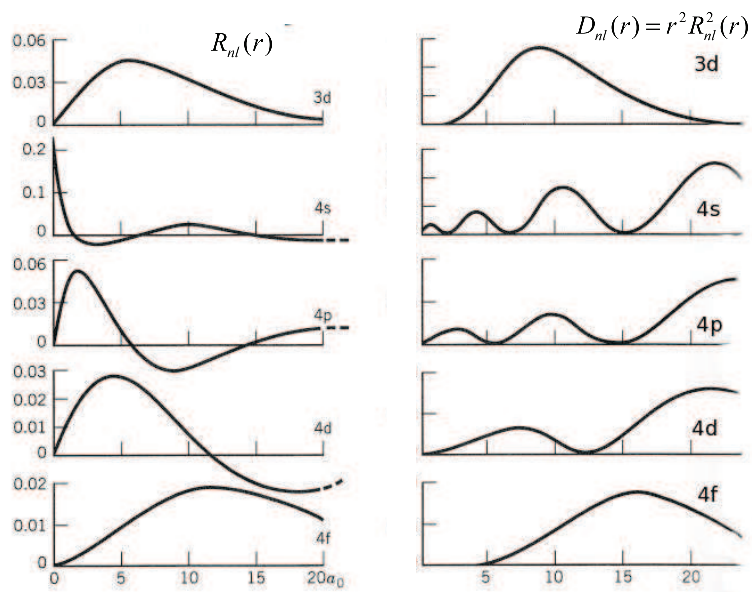
Radial functions and radial probability densities for the 3d, 4s, 4p, 3s and 4f orbitals of the H atom



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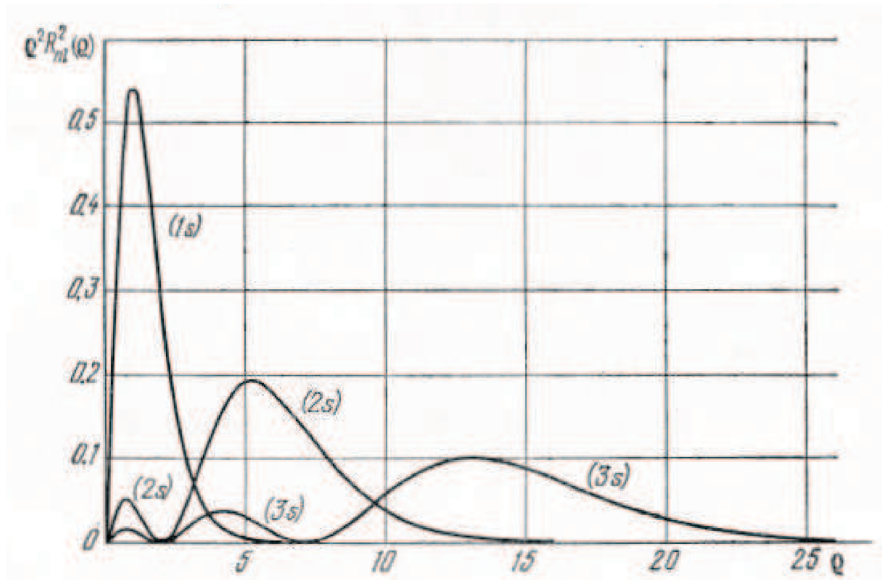
Comparison of radial probability densities for the 1s, 2s and 3s orbitals of the hydrogen atom



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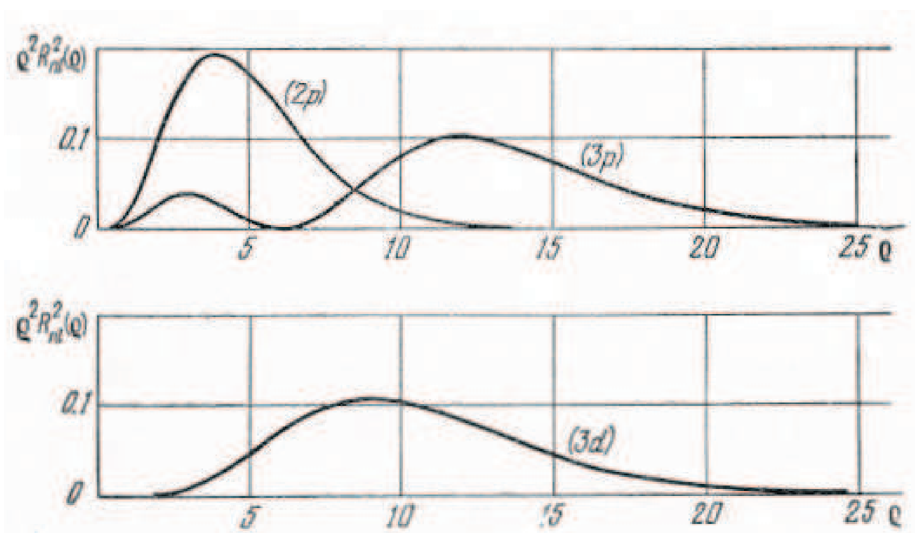
Comparison of radial probability densities for the 2d, 3p and 3d orbitals of the hydrogen atom



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More on the radial probability density

Think of the radial probability density as of a one-dimensional probability distribution function $f(r)$. There are two equivalent ways of obtaining the radial probability density:

1) From the radial function $R_{nl}(r)$ as:

$$\boxed{D_{nl}(r) = r^2 R_{nl}^2(r)}$$

2) From the total wave function (orbital) $\psi_{nlm}(r,\theta,\varphi)$ as:

$$\boxed{D_{nl}(r) = r^2 \int_0^{2\pi} d\varphi \int_0^{\pi} \left|\psi_{nlm}(r,\theta,\varphi)\right|^2 \sin\theta \; d\theta}$$

The radial probability density is normalized:

$$\int_0^{\infty} D_{nl}(r)\, dr = 1$$

which means that the probability of finding electron at any distance from the nucleus is 1.

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Some sample examples

Problem 1. Show that the 1s-electron is most likely to be found at the distance $r = a_0$ from the nucleus. The 1s-orbital is:

$$\psi_{1s}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

Solution. First we find the radial probability density for the 1s state:

$$D_{1s}(r) = \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 r^2 e^{-2r/a_0} \underbrace{\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta \, d\theta}_{=4\pi} = 4\left(\frac{1}{a_0}\right)^3 r^2 e^{-2r/a_0}$$

The condition for a maximum of $D_{1s}(r)$ is $dD_{1s}(r)/dr = 0$. Ignoring the constant prefactor, we have the equation

$$\frac{d}{dr}(r^2 e^{-2r/a_0}) = 2re^{-2r/a_0} - \frac{2}{a_0} r^2 e^{-2r/a_0} = 2r\left(1 - \frac{r}{a_0}\right)e^{-2r/a_0} = 0$$

whose solution is $r = a_0$.

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Some sample examples

Problem 2. Find the average distance between the electron and the nucleus in the 1s state. Make use of the standard integral

$$\int_0^\infty x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}}$$

Solution.

$$\langle r \rangle = \int_0^\infty r D_{1s}(r)\, dr = 4\left(\frac{1}{a_0}\right)^3 \int_0^\infty r^3 e^{-2r/a_0}\, dr = \frac{4}{a_0^3} \frac{3!}{(2/a_0)^4} = \frac{3}{2} a_0$$

Alternative solution.

$$\langle r \rangle = \int_{\text{all space}} \psi_{1s}^* r \psi_{1s}\, dV = \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta\, d\theta \int_0^\infty r |\psi_{1s}|^2 r^2 dr$$

$$= 4\pi \frac{1}{\pi a_0^3} \int_0^\infty r^3 e^{-2r/a_0}\, dr = \frac{3}{2} a_0$$

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Some sample examples

Problem 3. At which distance from the nucleus is a 1s electron more likely to be found, $r = a_0/2$ or $r = 2a_0$?

Solution. The probabilities of interest are proportional to the radial probability densities at $r = a_0/2$ or $r = 2a_0$

$$D_{1s}\left(r = \frac{a_0}{2}\right) = \frac{4}{a_0^3}\left(\frac{a_0}{2}\right)^2 e^{-2(a_0/2)/a_0} = \frac{e^{-1}}{a_0}$$

$$D_{1s}(r = 2a_0) = \frac{4}{a_0^3}(2a_0)^2 e^{-2(2a_0)/a_0} = \frac{16e^{-4}}{a_0}$$

The ratio of these probability densities is

$$\frac{D_{1s}\left(r = \frac{a_0}{2}\right)}{D_{1s}(r = 2a_0)} = \frac{e^{-1}}{16e^{-4}} = \frac{e^3}{16} \approx 1.2553 > 1$$

Thus, a 1s electron is more likely to be found at $r = a_0/2$ than at $r = 2a_0$.

Some sample examples

Problem 4. Find the probability that the electron in a ground-state H atom is at a distance less than a_0 from the nucleus.

Solution. The probability that the electron will be found between 0 and a_0:

not ∞ !

$$P(0 < r < a_0) = \int_0^{a_0} D_{1s}(r)\,dr$$

The radial distribution function for the 1s electron was found earlier:

$$D_{1s}(r) = 4\left(\frac{1}{a_0}\right)^3 r^2 e^{-2r/a_0}$$

Therefore,

$$P(0 < r < a_0) = \frac{4}{a_0^3}\int_0^{a_0} r^2 e^{-2r/a_0}\,dr$$

Using integration by parts we obtain

$$\frac{4}{a_0^3}\int_0^{a_0} r^2 e^{-2r/a_0}\,dr = -\frac{4}{a_0^3}\left(\frac{r^2 a_0}{2} + \frac{r a_0^2}{2} + \frac{a_0^3}{4}\right)e^{-2r/a_0}\Bigg|_0^{a_0} = -5e^{-2} + 1 \approx 0.3233$$

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Useful integrals

$$\int r e^{-\beta r}\,dr = -\left(\frac{r}{\beta} + \frac{1}{\beta^2}\right)e^{-\beta r}$$

$$\int r^2 e^{-\beta r}\,dr = -\left(\frac{r^2}{\beta} + \frac{2r}{\beta^2} + \frac{2}{\beta^3}\right)e^{-\beta r}$$

$$\int r^3 e^{-\beta r}\,dr = -\left(\frac{r^3}{\beta} + \frac{3r^2}{\beta^2} + \frac{6r}{\beta^3} + \frac{6}{\beta^4}\right)e^{-\beta r}$$

$$\int_0^{\infty} r^n\, e^{-\beta r}\,dr = \frac{n!}{\beta^{n+1}}$$

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