

# 3.012 Fund of Mat Sci: Bonding – Lecture 5/6

## THE HYDROGEN ATOM

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# Last Time

- Metal surfaces and STM
- Dirac notation
- Operators, commutators, some postulates

# Homework for Mon Oct 3

- Study: 18.4, 18.5, 20.1 to 20.5.
- Read – before 3.014 starts next week:  
22.6 (XPS and Auger)

# Second Postulate

- For every physical observable there is a corresponding Hermitian operator

# Hermitian Operators

1. The eigenvalues of a Hermitian operator are real
2. Two eigenfunctions corresponding to different eigenvalues are orthogonal
3. The set of eigenfunctions of a Hermitian operator is complete
4. Commuting Hermitian operators have a set of common eigenfunctions

# The set of eigenfunctions of a Hermitian operator is complete

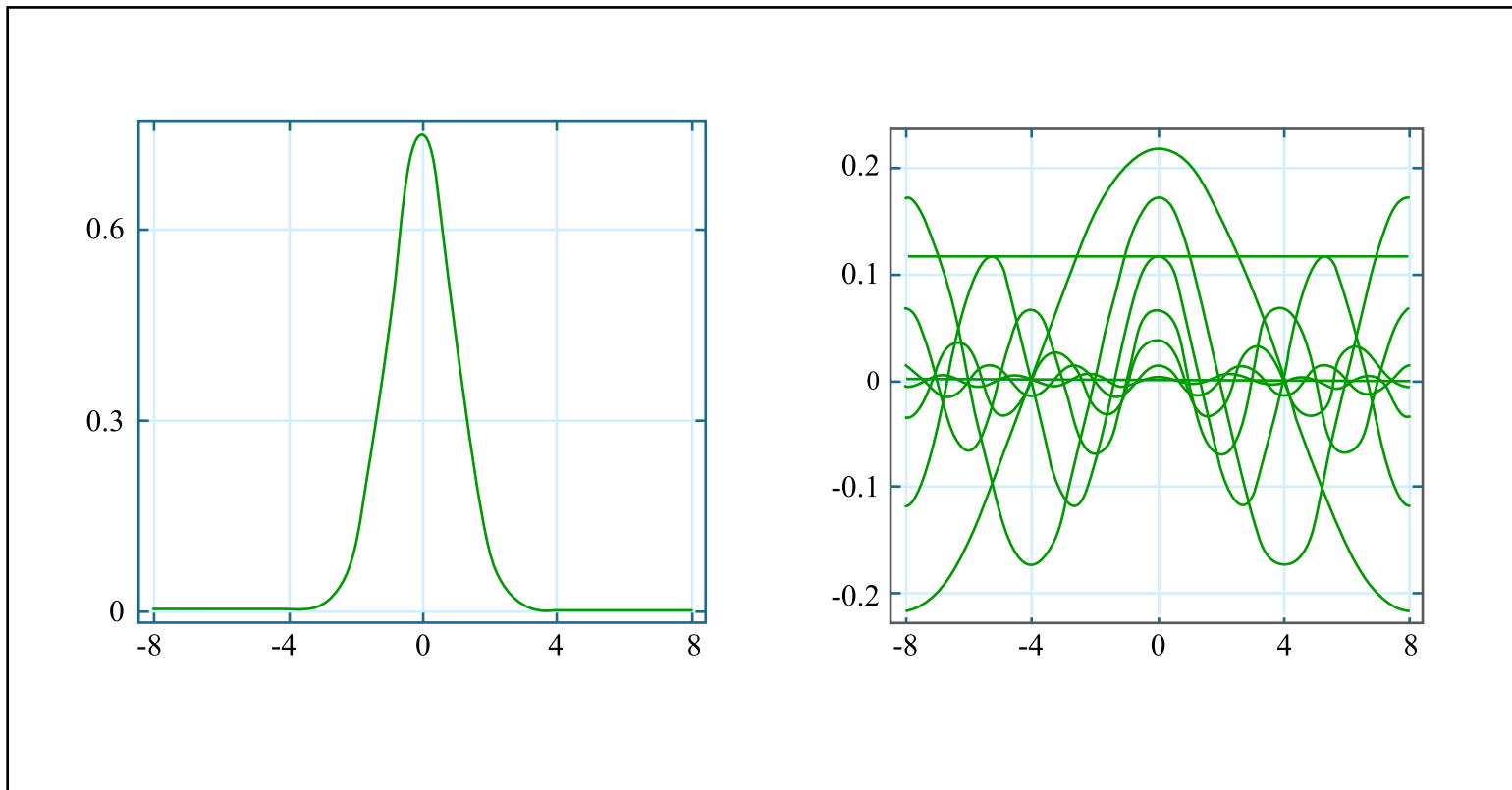


Figure by MIT OCW.

# Third Postulate

- In any single measurement of a physical quantity that corresponds to the operator  $A$ , the only values that will be measured are the eigenvalues of that operator.

# Position and probability

Graph of the probability density for positions of a particle in a one-dimensional hard box removed for copyright reasons.

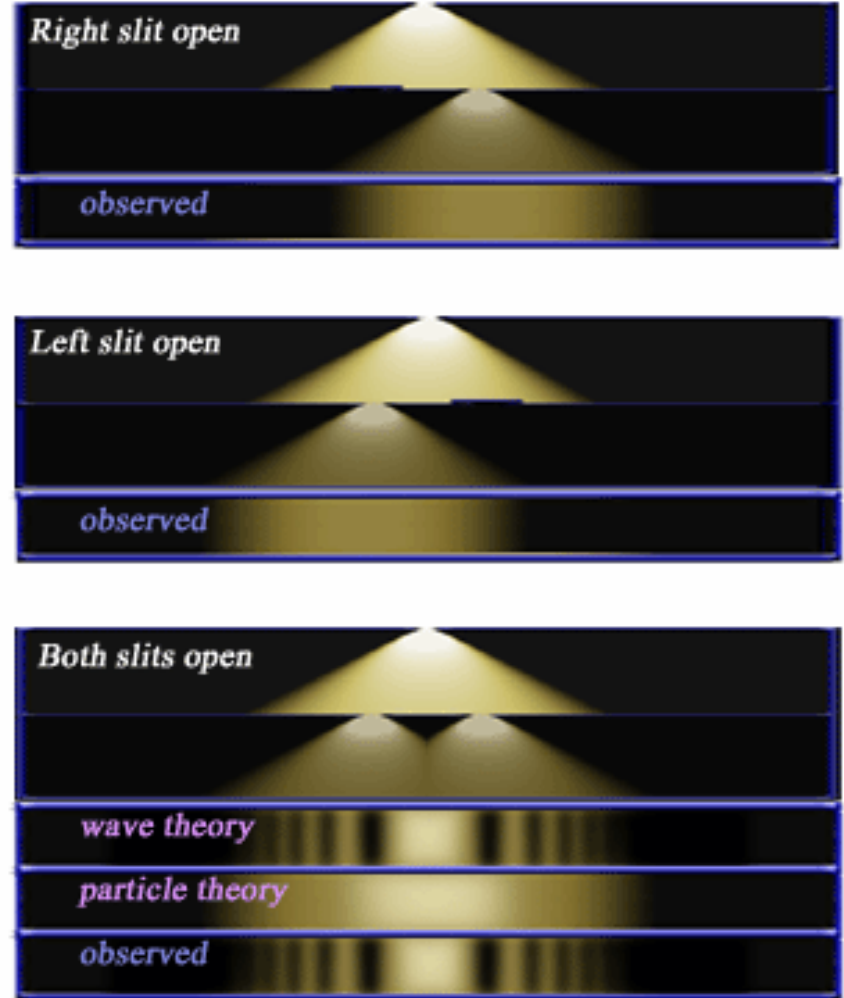
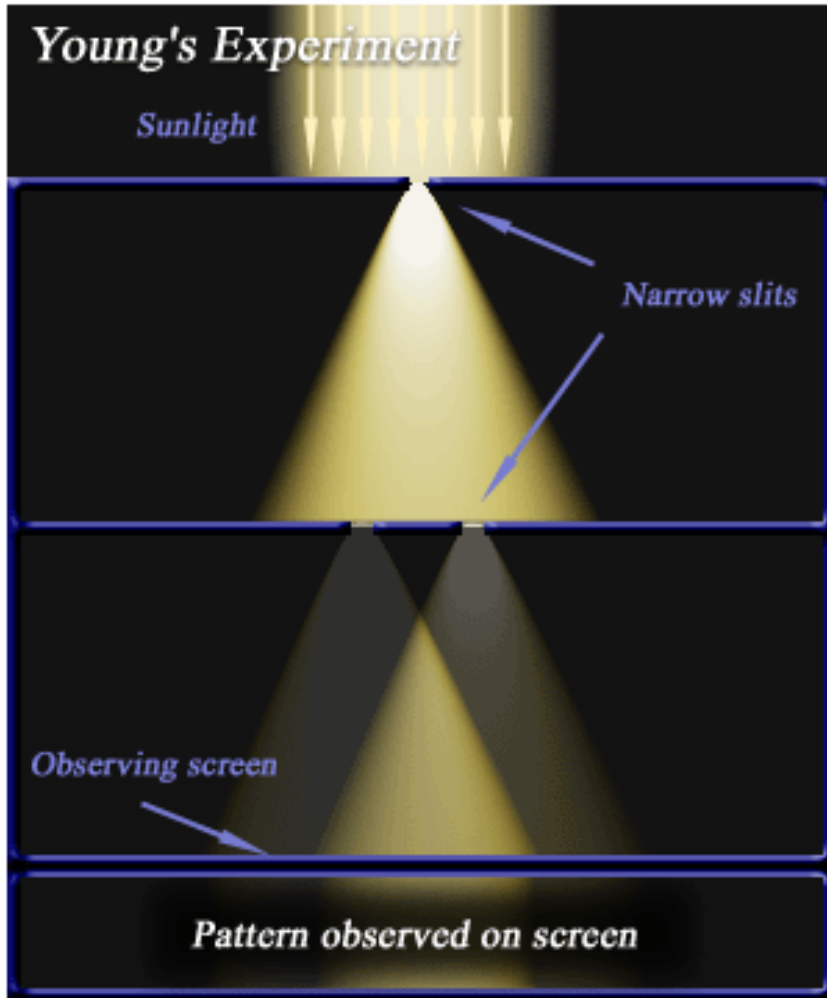
See Mortimer, R. G. *Physical Chemistry*. 2nd ed. San Diego, CA: Elsevier, 2000, p. 554, figure 15.2.

Graphs of the probability density for positions of a particle in a one-dimensional hard box according to classical mechanics removed for copyright reasons.

See Mortimer, R. G. *Physical Chemistry*. 2nd ed. San Diego, CA: Elsevier, 2000, p. 555, figure 15.3.



# Quantum double-slit



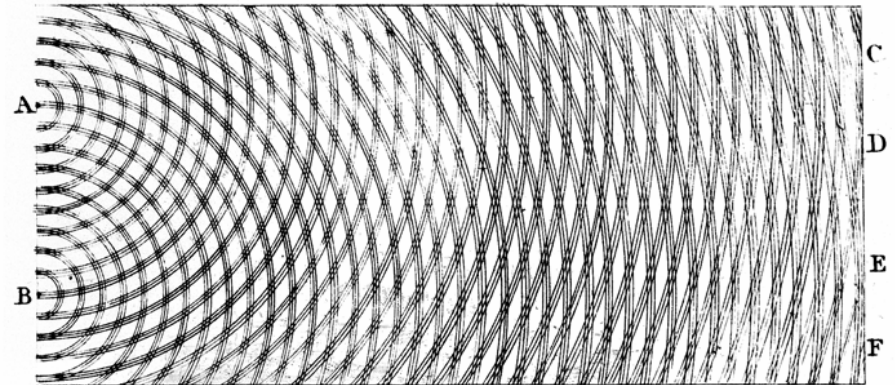
Source: Wikipedia

# Quantum double-slit

Image of the double-slit experiment removed for copyright reasons.

See the simulation at <http://www.kfunigraz.ac.at/imawww/vqm/movies.html>:

"Samples from *Visual Quantum Mechanics*": "Double-slit Experiment."



Above: Thomas Young's sketch of two-slit diffraction of light. Narrow slits at A and B act as sources, and waves interfering in various phases are shown at C, D, E, and F. Source: Wikipedia

# Fourth Postulate

- If a series of measurements is made of the dynamical variable  $A$  on an ensemble described by  $\Psi$ , the average (“expectation”) value is  $\langle A \rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

# Deterministic vs. stochastic

- Classical, macroscopic objects: we have well-defined values for all dynamical variables at every instant (position, momentum, kinetic energy...)
- Quantum objects: we have **well-defined probabilities** of measuring a certain value for a dynamical variable, when a **large number of identical, independent, identically prepared physical systems** are subject to a measurement.

# Spherical Coordinates

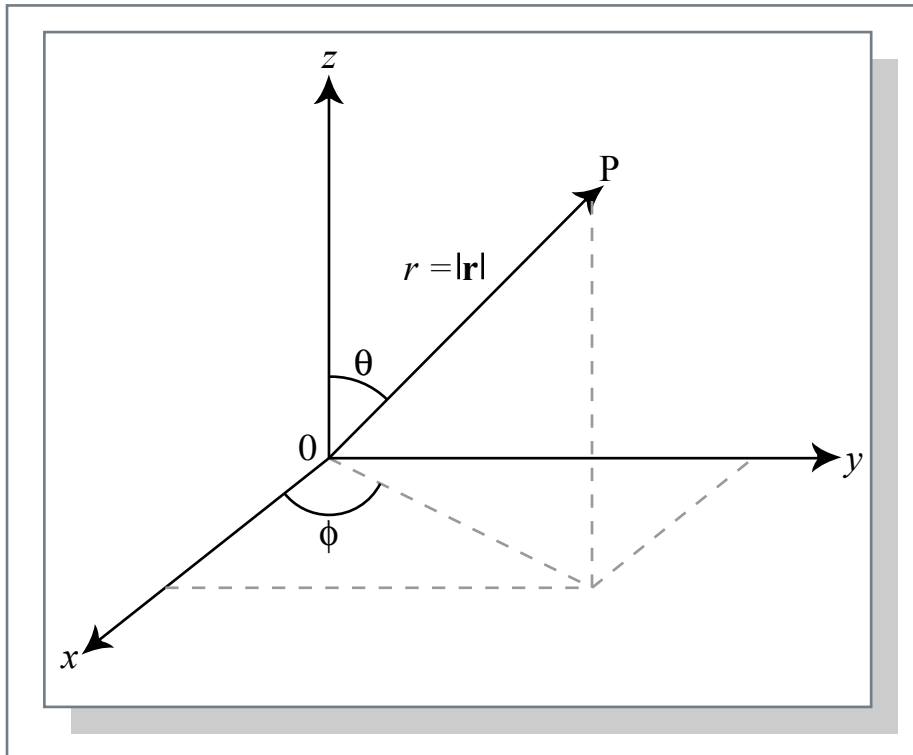


Figure by MIT OCW.

$$x = r \sin \theta \cos \varphi$$

$$y = r \sin \theta \sin \varphi$$

$$z = r \cos \theta$$

# 3-d Integration

Diagram of an infinitesimal volume element in spherical polar coordinates removed for copyright reasons.

See Mortimer, R. G. *Physical Chemistry*. 2nd ed. San Diego, CA: Elsevier, 2000, p. 1006, figure B.4.

# Angular Momentum

Classical

Quantum

$$\vec{L} = \vec{r} \times \vec{p}$$

# Commutation Relation

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$\left[ \hat{L}^2, \hat{L}_x \right] = \left[ \hat{L}^2, \hat{L}_y \right] = \left[ \hat{L}^2, \hat{L}_z \right] = 0$$

$$\left[ \hat{L}_x, \hat{L}_y \right] = i\hbar \hat{L}_z \neq 0$$



# Angular Momentum in Spherical Coordinates

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

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

# Simultaneous eigenfunctions of $L^2$ , $L_z$

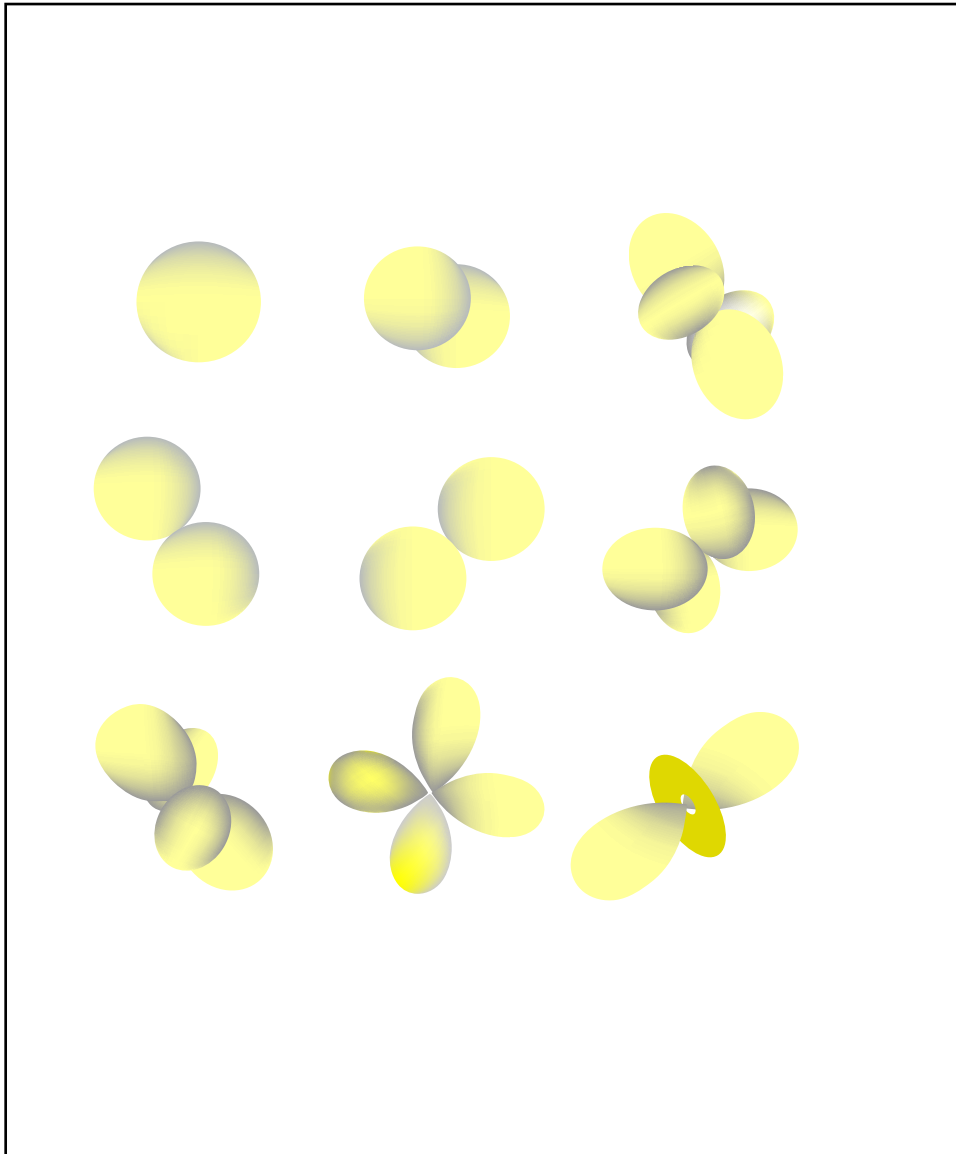
$$\hat{L}_z Y_l^m(\theta, \varphi) = m\hbar Y_l^m(\theta, \varphi)$$

$$\hat{L}^2 Y_l^m(\theta, \varphi) = \hbar^2 l(l+1) Y_l^m(\theta, \varphi)$$

$$Y_l^m(\theta, \varphi) = \Theta_l^m(\theta) \Phi_m(\varphi)$$

$$Y_0^0(\theta, \varphi) = \frac{1}{(4\pi)^{1/2}}$$
$$Y_1^0(\theta, \varphi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$
$$Y_1^{\pm 1}(\theta, \varphi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\varphi}$$
$$Y_2^0(\theta, \varphi) = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$$
$$Y_2^{\pm 1}(\theta, \varphi) = \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{\pm i\varphi}$$
$$Y_2^{\pm 2}(\theta, \varphi) = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{\pm 2i\varphi}$$

# Spherical Harmonics in Real Form



$$p_x = \frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1}) = \sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi$$

$$p_y = \frac{1}{\sqrt{2}i}(Y_1^1 - Y_1^{-1}) = \sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi$$

$$p_z = Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$d_{z^2} = Y_2^0 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$d_{xz} = \frac{1}{\sqrt{2}}(Y_2^1 + Y_2^{-1}) = \sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \cos \phi$$

$$d_{yz} = \frac{1}{\sqrt{2}i}(Y_2^1 - Y_2^{-1}) = \sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \sin \phi$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(Y_2^2 + Y_2^{-2}) = \sqrt{\frac{15}{16\pi}} \sin^2 \theta \cos 2\phi$$

$$d_{xy} = \frac{1}{\sqrt{2}i}(Y_2^2 - Y_2^{-2}) = \sqrt{\frac{15}{16\pi}} \sin^2 \theta \sin 2\phi$$

Figure by MIT OCW.

# An electron in a central potential (I)

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 + V(\vec{r}) \quad \nabla^2 \text{ needs to be in spherical coordinates}$$

$$\hat{H} = -\frac{\hbar^2}{2m_e} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right] + V(r)$$

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

# An electron in a central potential (II)

$$\hat{H} = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{\hat{L}^2}{2m_e r^2} + V(r)$$

$$\psi(\vec{r}) = R(r)Y(\mathcal{G}, \varphi)$$

# An electron in a central potential (III)

$$\left[ -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{\hbar^2}{2m_e} \frac{l(l+1)}{r^2} + V(r) \right] R_{nl}(r) = E_{nl} R_{nl}(r)$$

# What is the $V(r)$ potential ?

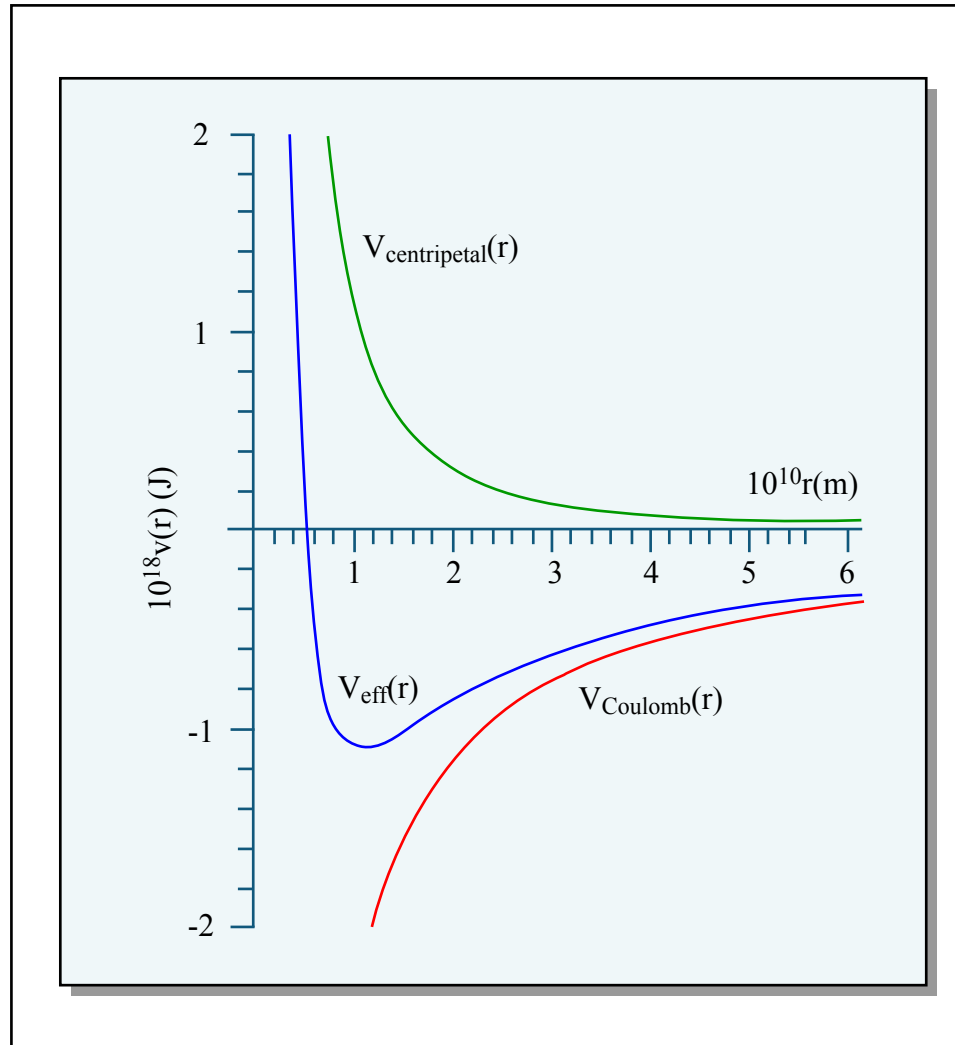


Figure by MIT OCW.

# The Radial Wavefunctions for Coulomb $V(r)$

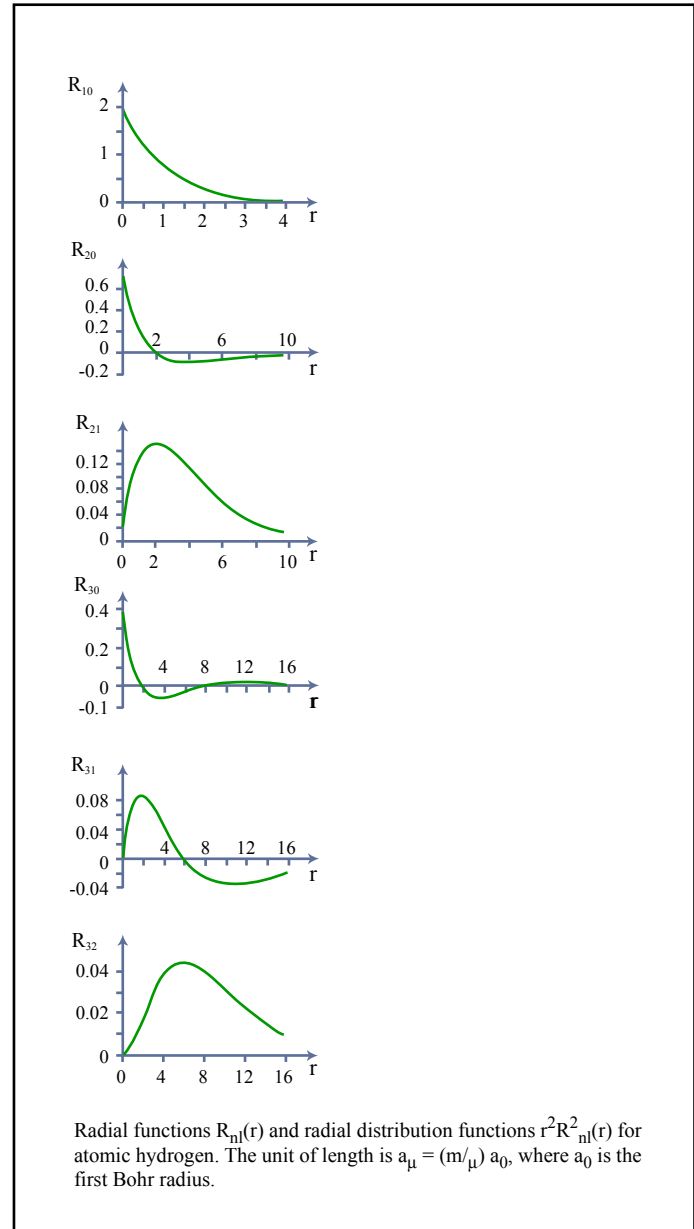


Figure by MIT OCW.



# The Radial Density

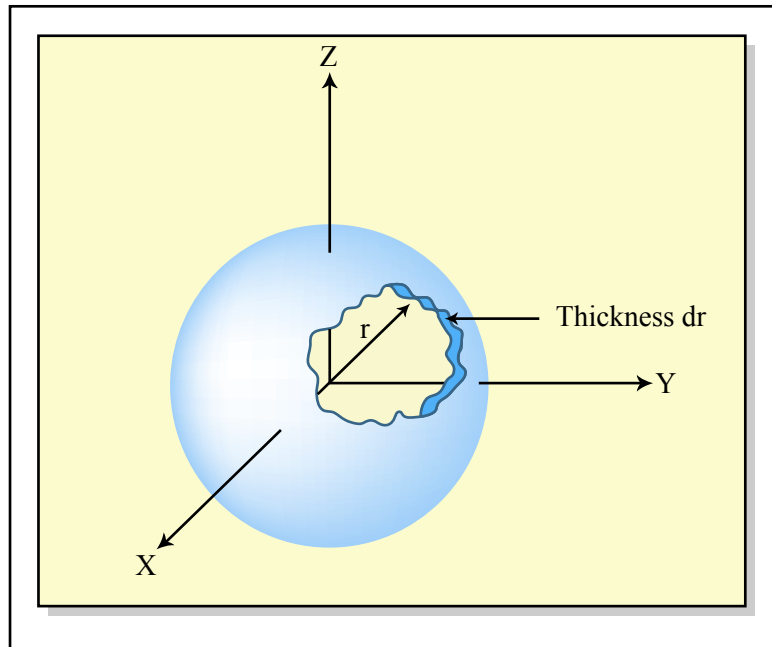


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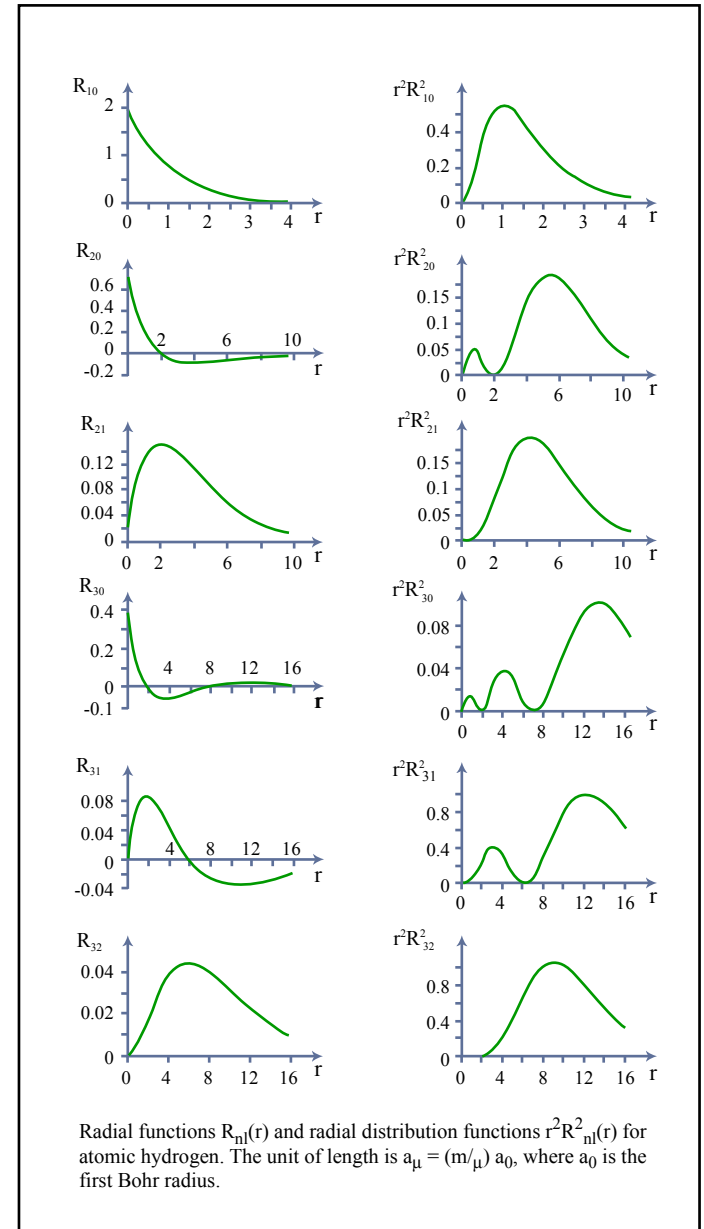


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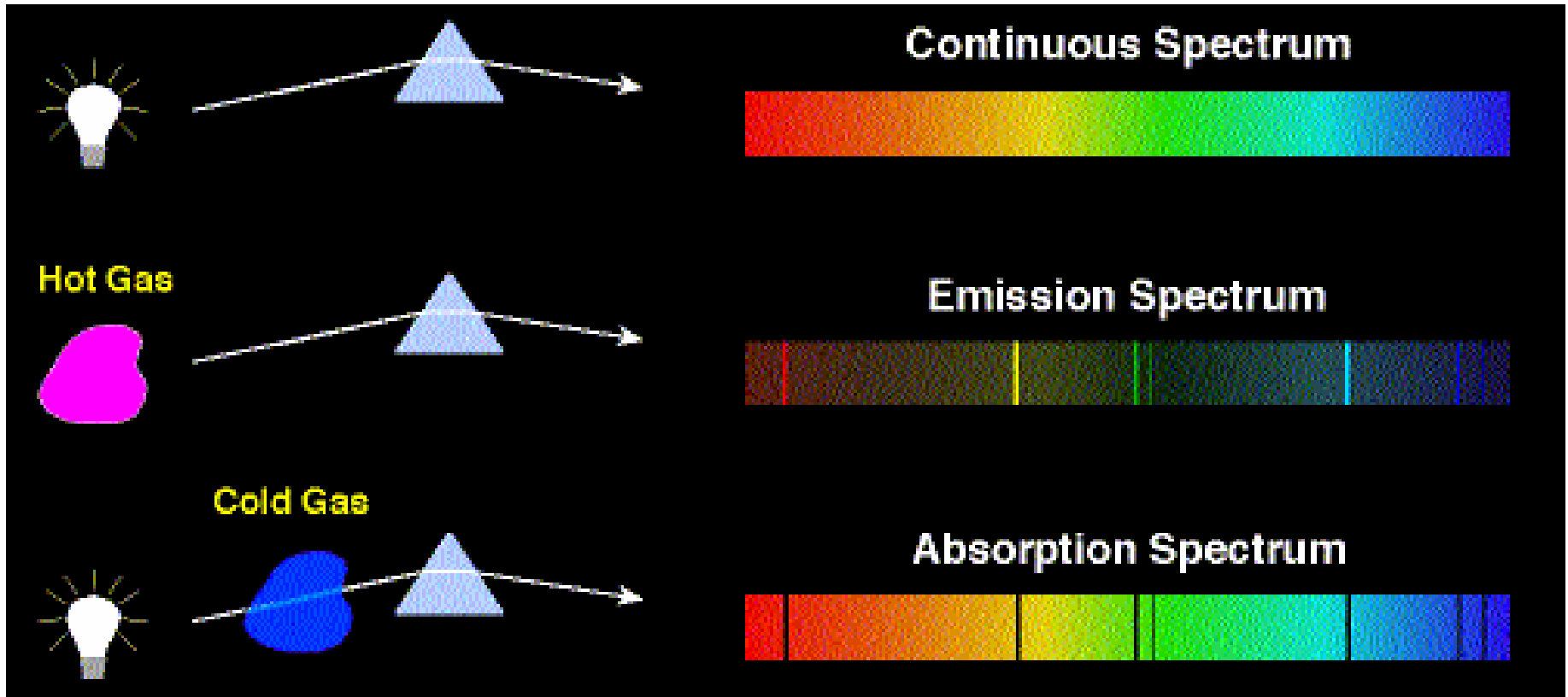
# Three Quantum Numbers

- Principal quantum number **n** (energy, accidental degeneracy)

$$E_n = -\frac{e^2}{8\pi\epsilon_0} \frac{Z^2}{a_0 n^2} = -(13.6058 \text{ eV}) \frac{Z^2}{n^2} = -(1 \text{ Ry}) \frac{Z^2}{n^2}$$

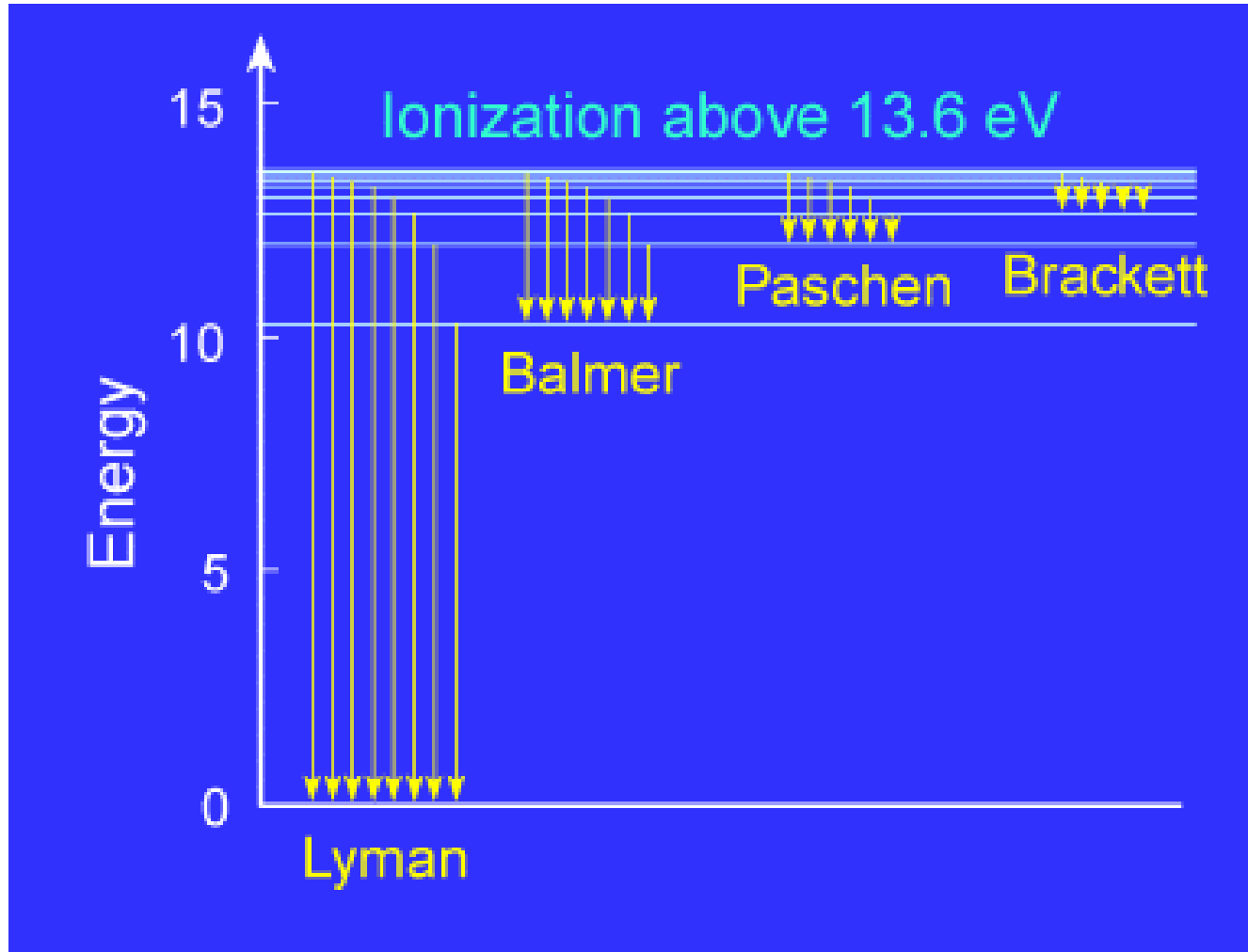
- Angular momentum quantum number **l** ( $L^2$ )  
 $l=0, 1, \dots, n-1$  (a.k.a. s, p, d... orbitals)
- Magnetic quantum number **m** ( $L_z$ )  
 $m=-l, -l+1, \dots, l-1, l$

# Emission and absorption lines



Courtesy of the Department of Physics and Astronomy at the University of Tennessee. Used with permission.

# Balmer lines in a hot star



Courtesy of the Department of Physics and Astronomy at the University of Tennessee. Used with permission.

# XPS in Condensed Matter

Diagram of Moon composition as seen in X-rays, removed for copyright reasons.

# The Grand Table

$$n = 1, l = 0, m_l = 0 \quad \psi_{100}(r) = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$

$$n = 2, l = 0, m_l = 0 \quad \psi_{200}(r) = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

$$n = 2, l = 1, m_l = 0 \quad \psi_{210}(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$$

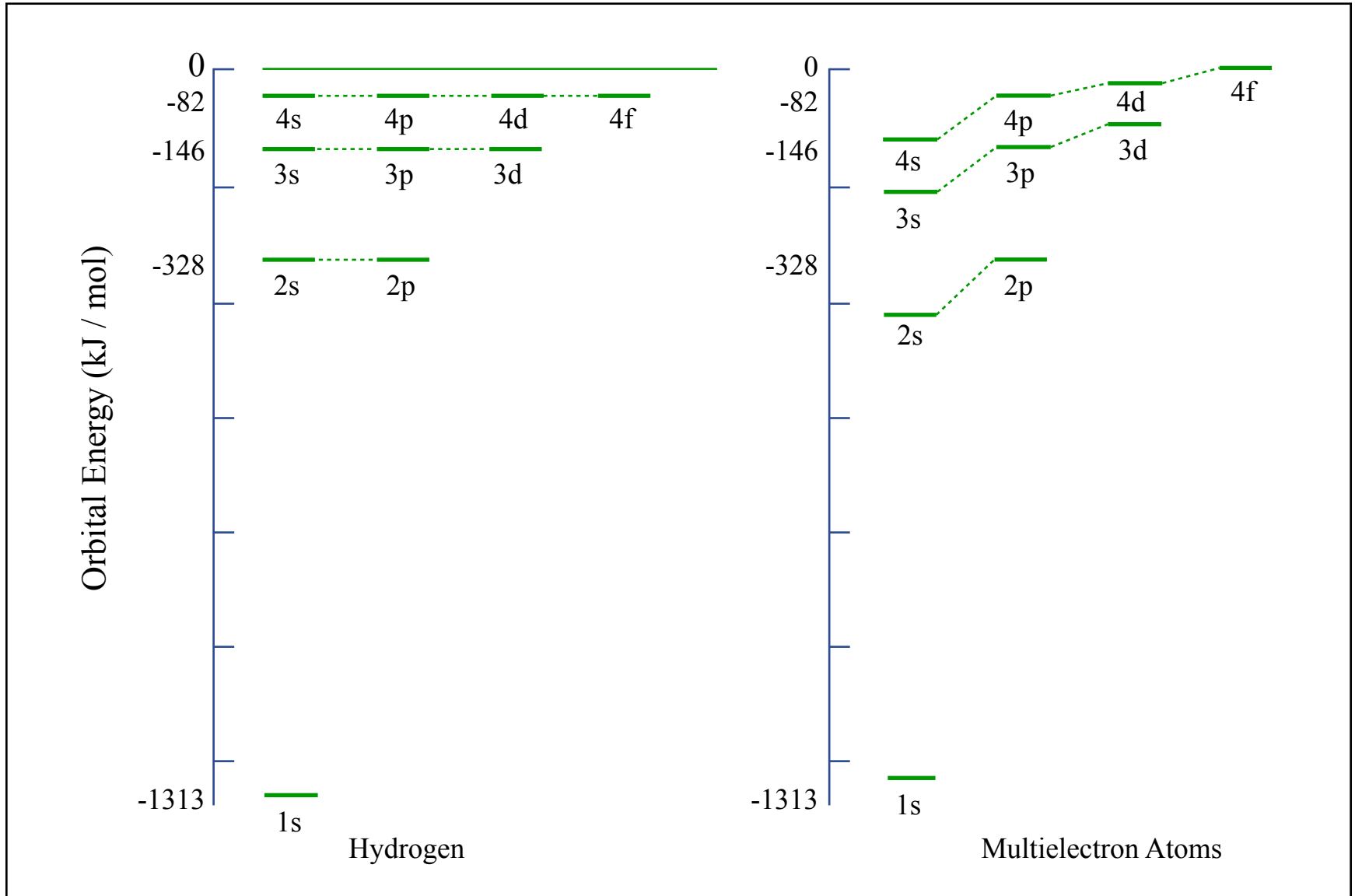
$$n = 2, l = 1, m_l = \pm 1 \quad \psi_{21\pm 1}(r, \theta, \phi) = \frac{1}{8\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$$

# Solutions in the central Coulomb Potential: the Alphabet Soup

Table of orbitals removed for copyright reasons.

See " $n$  and  $l$  versus  $m$ " at <http://www.orbitals.com/orb/orbtable.htm>.

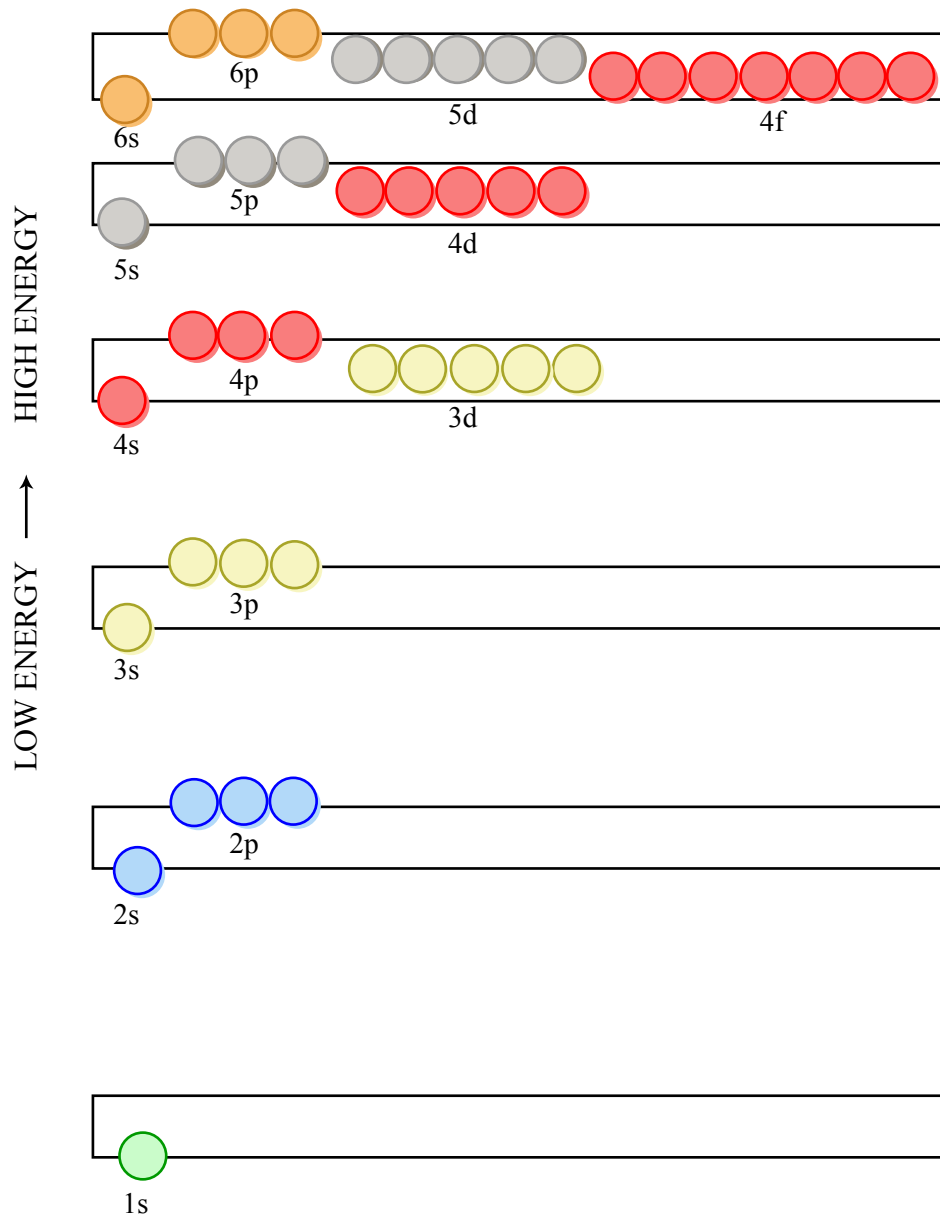
# Orbital levels in multi-electron atoms



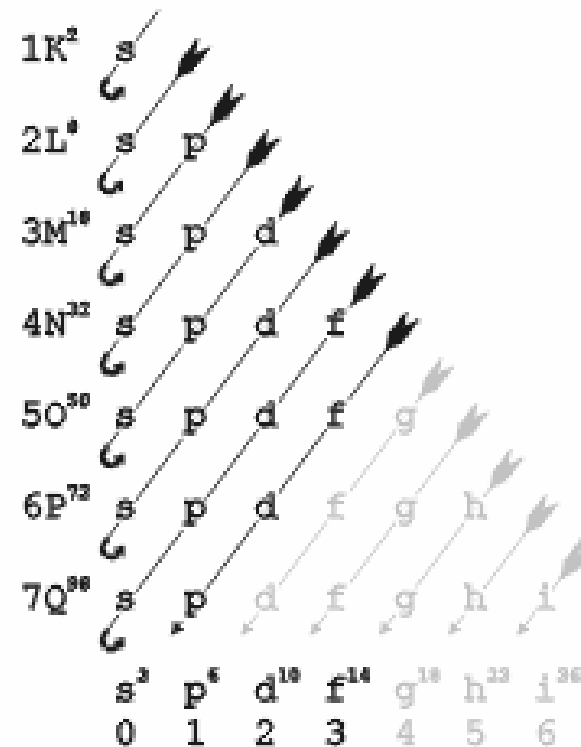


# Screening

# ENERGY LEVELS OF THE ELECTRONS ABOUT THEIR NUCLEI



# Auf-bau



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