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

$$\langle \varphi | A\psi \rangle = \langle A\varphi | \psi \rangle$$

$$\vec{p} \longmapsto -i\hbar\vec{\nabla}$$

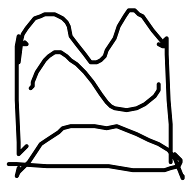
$\vec{r} \longmapsto$ MULTIPLICATIVE OPERATOR

$$V(\vec{r}) \longmapsto V(\vec{r})\,\psi(\vec{r})$$

Hermitian Operators

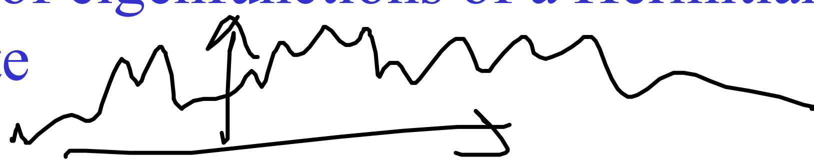
1. The eigenvalues of a Hermitian operator are real

2. Two eigenfunctions corresponding to different eigenvalues are orthogonal



$$\langle \varphi_i | \varphi_j \rangle = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases}$$

3. The set of eigenfunctions of a Hermitian operator is complete



$$f(x) = \sum_k \left(\alpha \sin kx + \beta \cos kx \right)$$

4. Commuting Hermitian operators have a set of common eigenfunctions

$$\hat{A}, \hat{B} \qquad [\hat{A}, \hat{B}] = 0 \rightarrow \hat{A}\hat{B}f - \hat{B}\hat{A}f = 0$$

The set of eigenfunctions of a Hermitian operator is complete

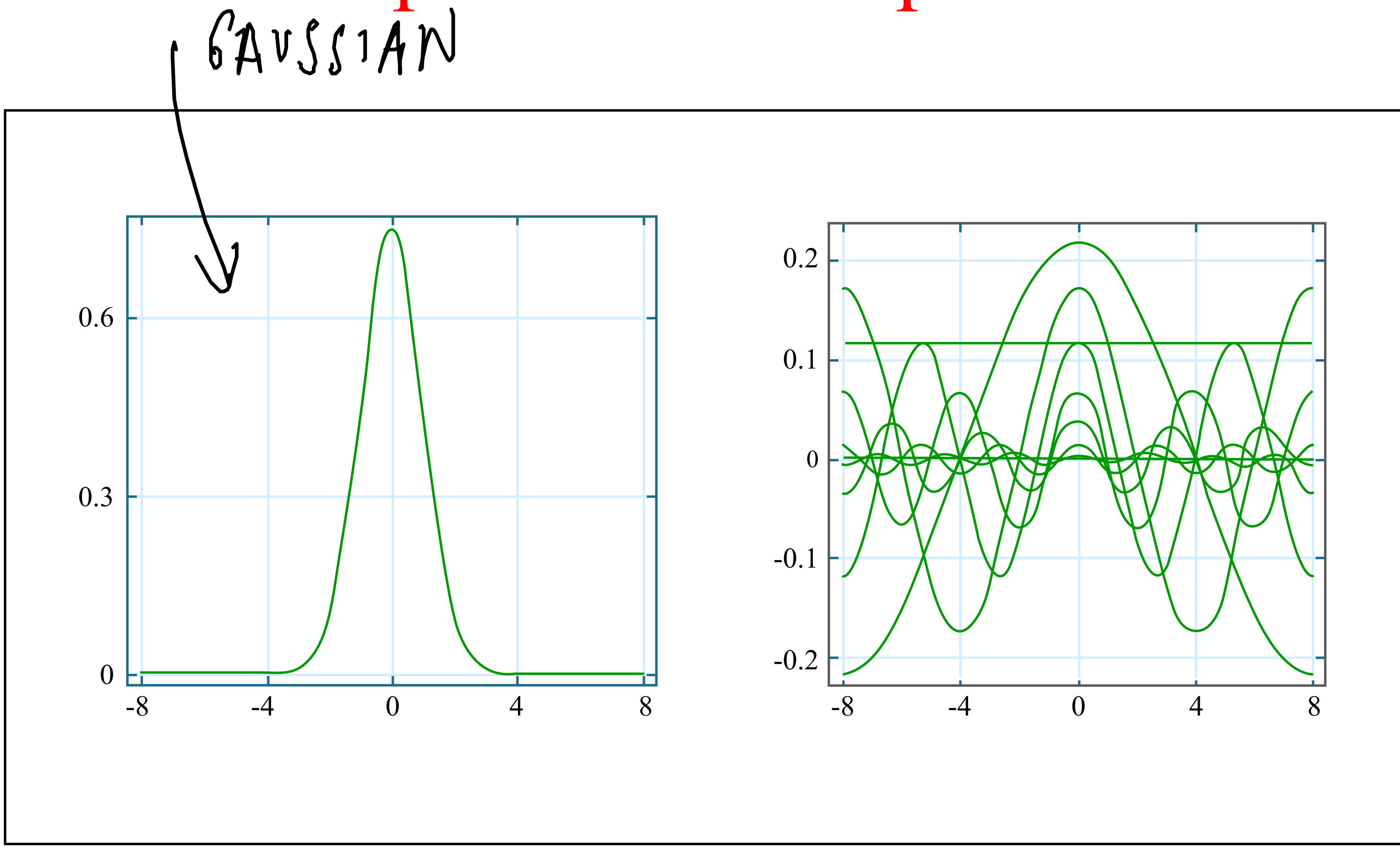
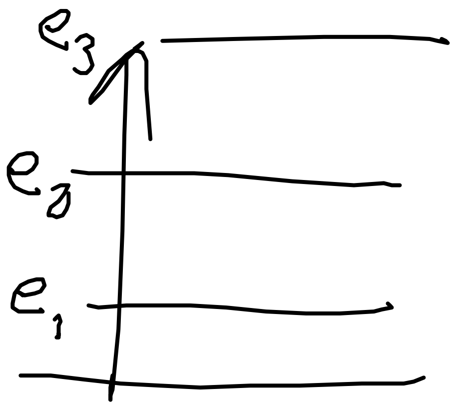


Figure by MIT OCW.

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

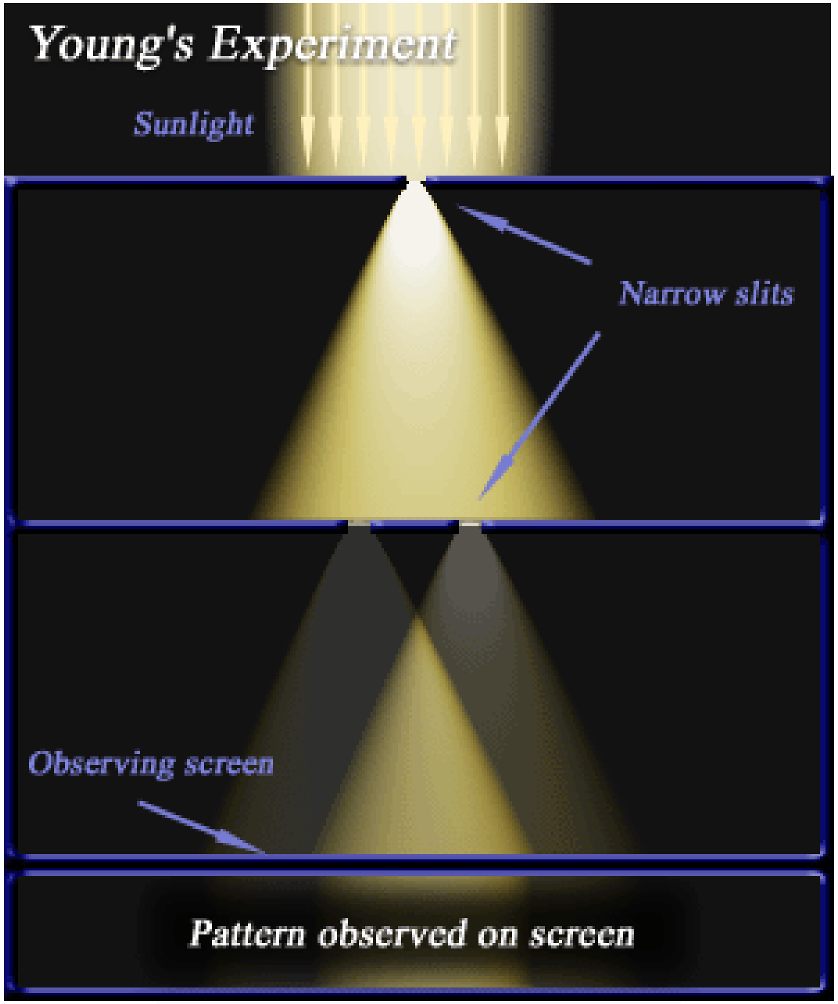
Graph of the probability density for positions of a particle in a one-dimensional hard box removed for copyright reasons.

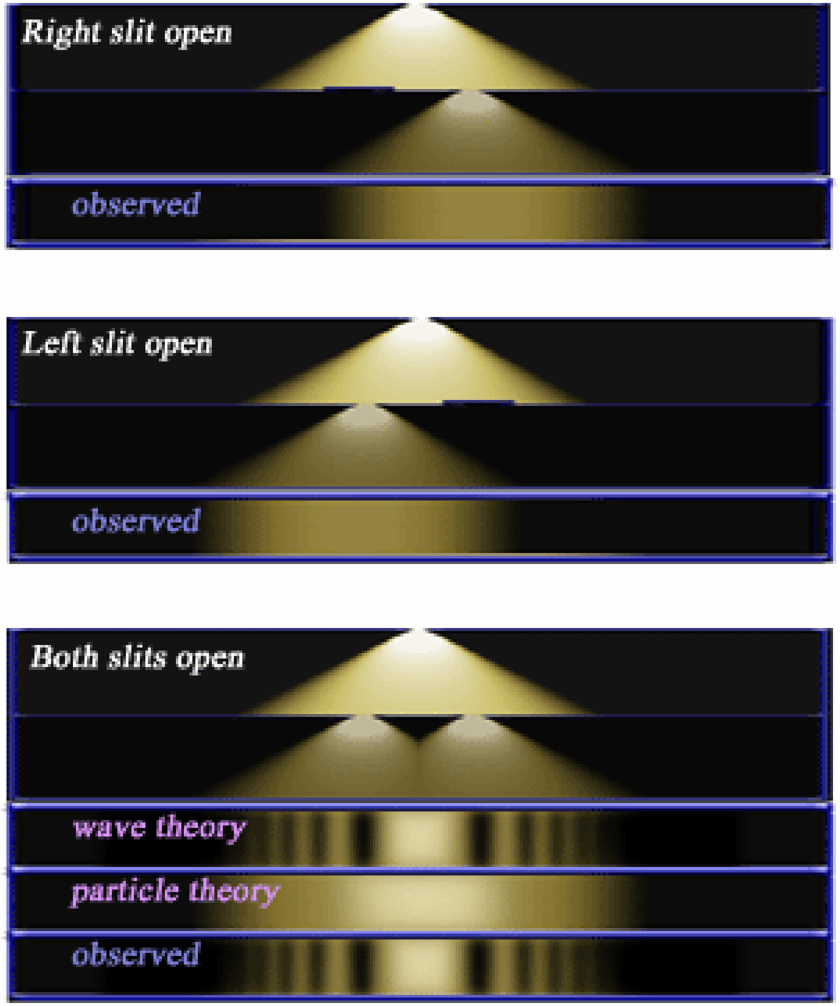
See Mortimer, R. G. *Physical Chemistry*. 2nd ed. San Diego, CA: Elsevier, 2000, p. 554, figure 15.2.

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





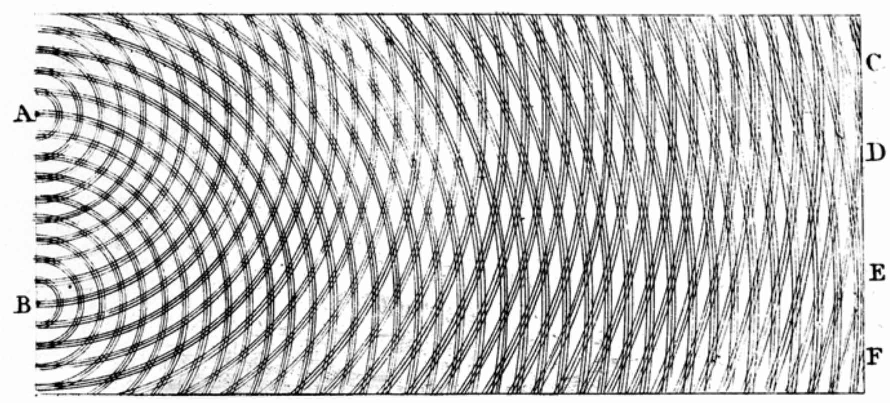
Source: Wikipedia

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 Ψ, the average ("expectation") value is $\langle A \rangle = \dfrac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

$$\int \psi^*(x) \left(\hat{H} \psi(x) \right)$$

$$\varepsilon_i \, \psi(x)$$

$$\varepsilon_i \int \psi^* \psi$$

$$1 = \int_{\text{DOMAIN}} \psi^*(x)\, \psi(x)\, dx$$

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

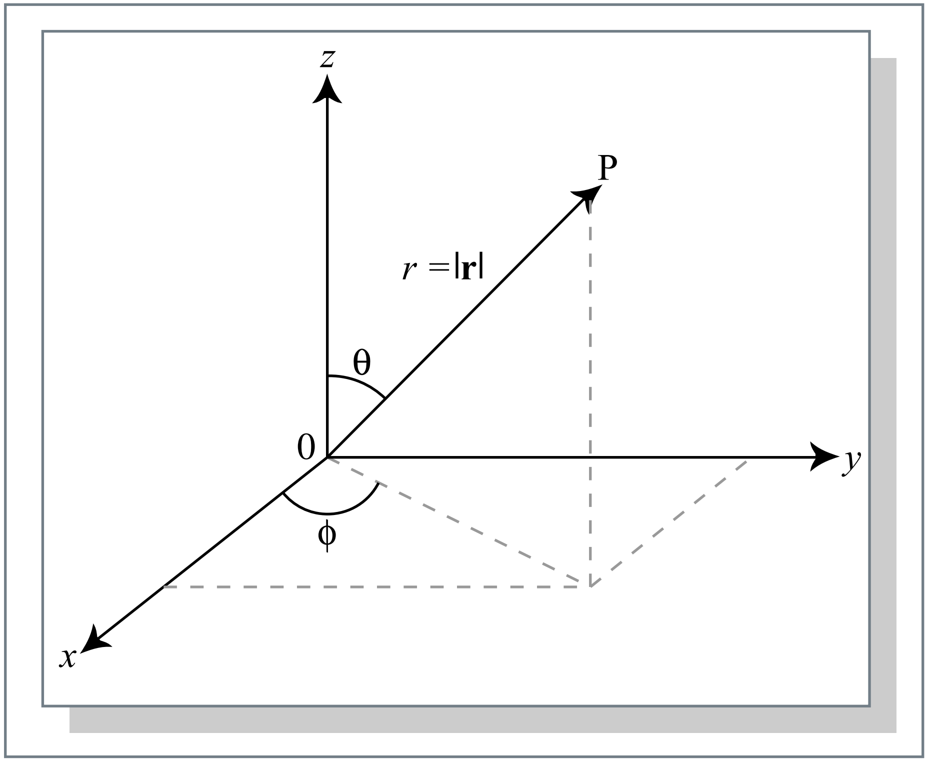


Figure by MIT OCW.

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

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

$$z = r \cos\theta$$

3-d Integration

$$f(x, y, z)$$

$$\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz$$

$$f(r, \vartheta, \varphi)$$

$$\int_0^{\infty} dr \int_0^{\pi} d\vartheta \int_0^{2\pi} d\varphi \cdot$$

$$r^2 \sin(\vartheta)\, d\varphi\, d\vartheta\, dr$$

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

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

$$L_z = x p_y - y p_x$$

Quantum

$$\hat{L}_z = \hat{x}\left(-i\hbar \frac{d}{dy}\right) - \hat{y}\left(-i\hbar \frac{\partial}{\partial x}\right)$$

Commutation Relation

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

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

CAN BE MEASURED

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

CAN'T BE MEASURED SIMULTANEOUSLY

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

m = INTEGER

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

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

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

l = INTEGER

COMMON SET OF EIGENFUNCT

$$Y_0^0(\theta,\phi) = \frac{1}{(4\pi)^{1/2}}$$

$$Y_1^0(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^{\pm1}(\theta,\phi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{\pm i\phi}$$

$$Y_2^0(\theta,\phi) = \left(\frac{5}{16\pi}\right)^{1/2} \left(3\cos^2\theta - 1\right)$$

$$Y_2^{\pm1}(\theta,\phi) = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta\, e^{\pm i\phi}$$

$$Y_2^{\pm2}(\theta,\phi) = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{\pm 2i\phi}$$

Spherical Harmonics in Real Form

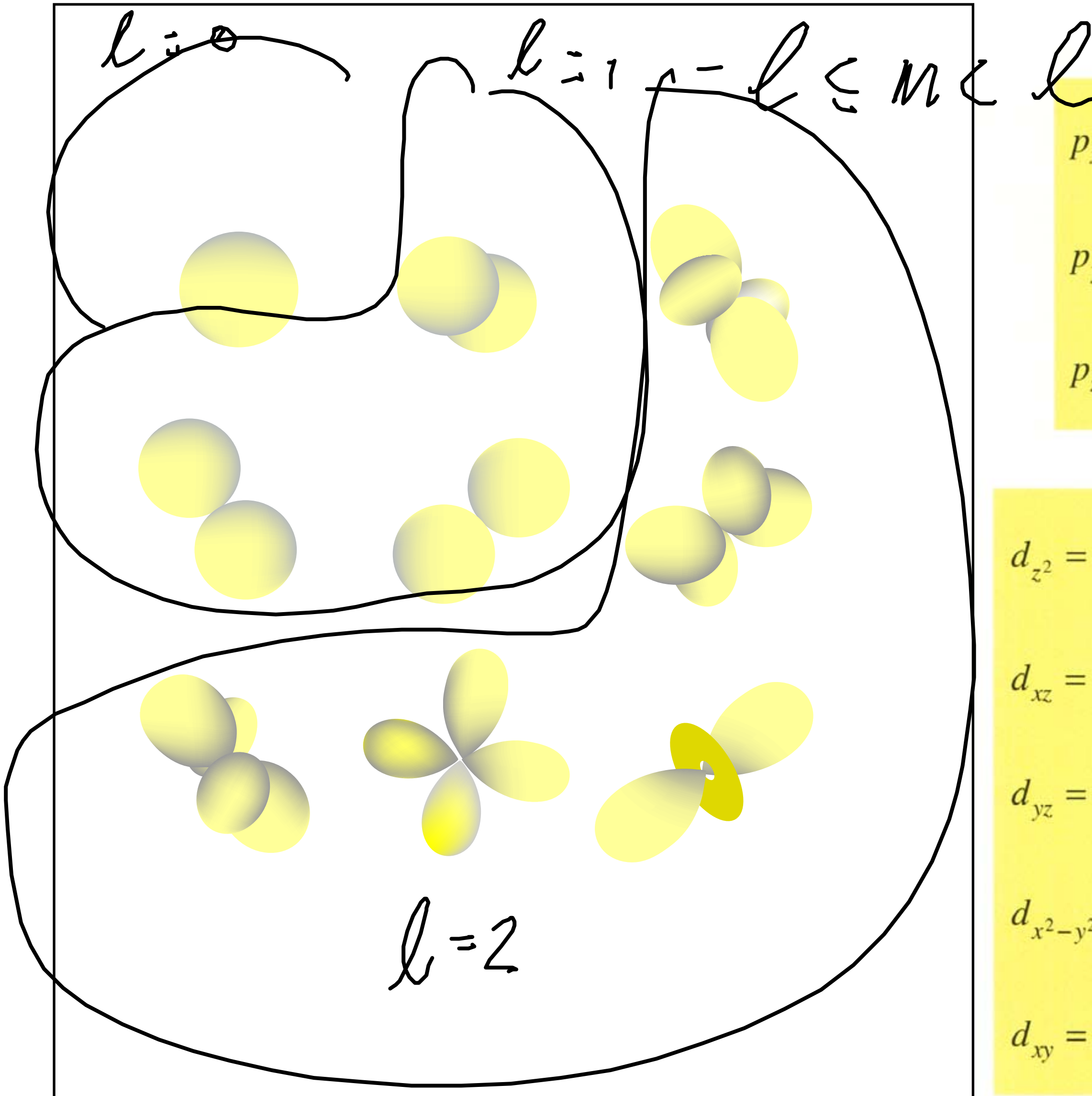


Figure by MIT OCW.

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

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

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

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

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

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

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

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

An electron in a central potential (I)

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V(r^*)$$

∇^2 needs to be in spherical coordinates

polar coordinate r

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

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

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

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

An electron in a central potential (II)

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

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

SPHERICAL HARMONIC

RADIAL FUNCTION

An electron in a central potential (III)

$$\left[\hat{T}_r + \hat{T}_L + \hat{V}(r)\right] R(r)\, Y(\vartheta,\varphi)$$

$$Y(\vartheta,\varphi)\,\hat{T}_R R(r) + R(r)\,\underbrace{\hat{T}_L Y(\vartheta,\varphi)}_{\hbar^2 l(l+1)\, Y(\vartheta,\varphi)} + V R Y$$

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

What is the V(r) potential ?

$$V(r) = \frac{(Ze)(-e)}{4\pi\varepsilon_0 r}$$

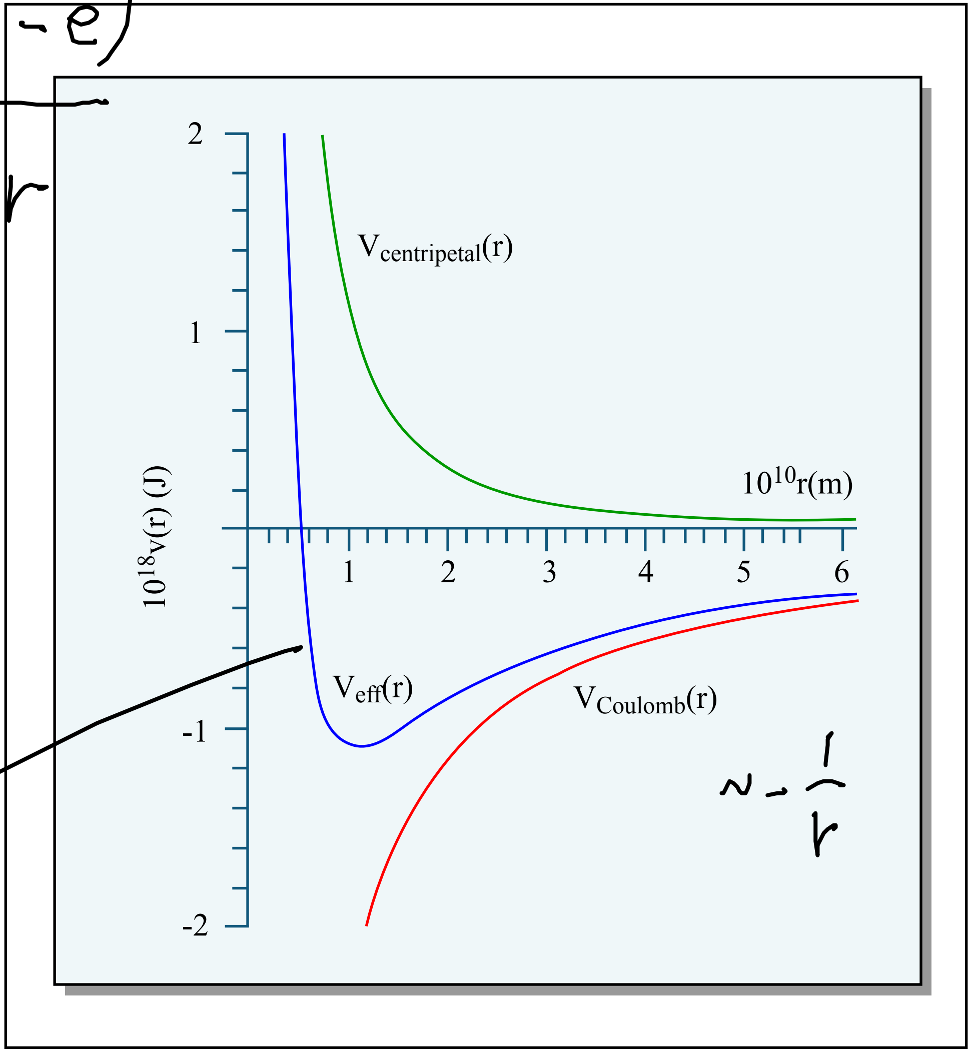


Figure by MIT OCW.

$V_{eff} = V_{coul} +$ CENTRIPETAL

The Radial Wavefunctions for Coulomb V(r)

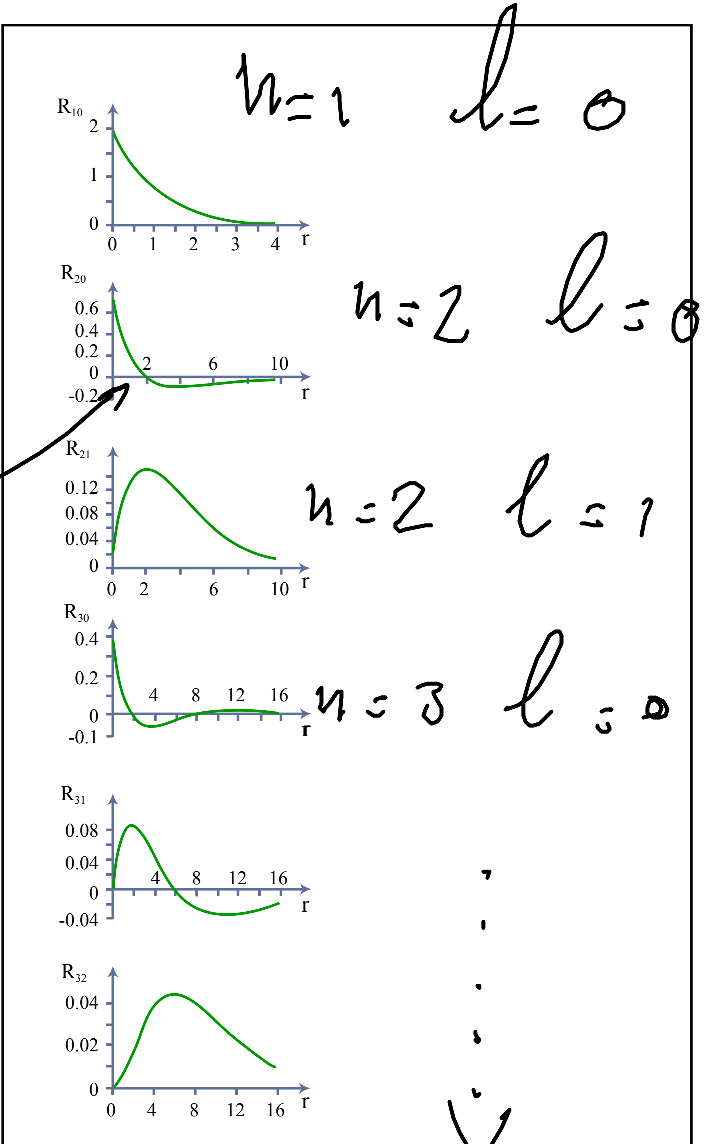
R_{nl}

PRINCIPAL NUMBER

"ANGULAR MOMENTUM"

NODE

NODAL SURF = $n - l - 1$



Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R^2_{nl}(r)$ for atomic hydrogen. The unit of length is $a_\mu = (m/_\mu)\, a_0$, where a_0 is the first Bohr radius.

Figure by MIT OCW.

The Radial Density

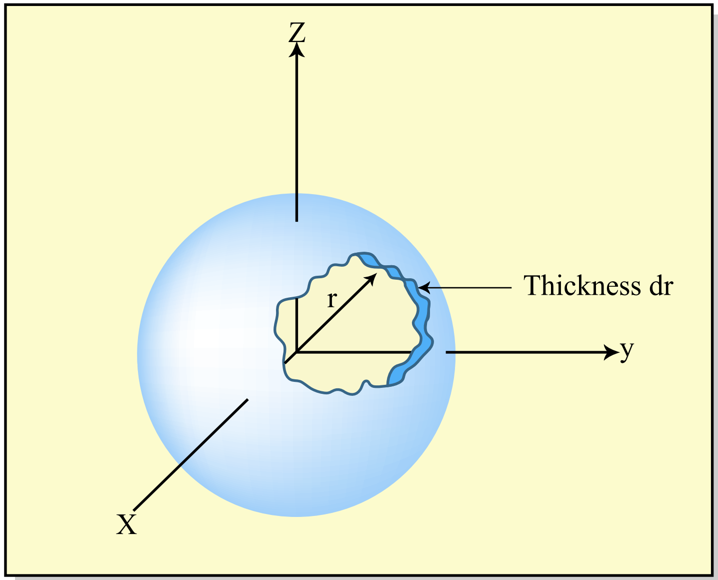


Figure by MIT OCW.

$$\| \Psi(r,\vartheta,\varphi) \|^2 \text{ in } r, \vartheta, \varphi$$

$$\| R(r) \|^2 \, \| Y(\vartheta,\varphi) \|^2$$

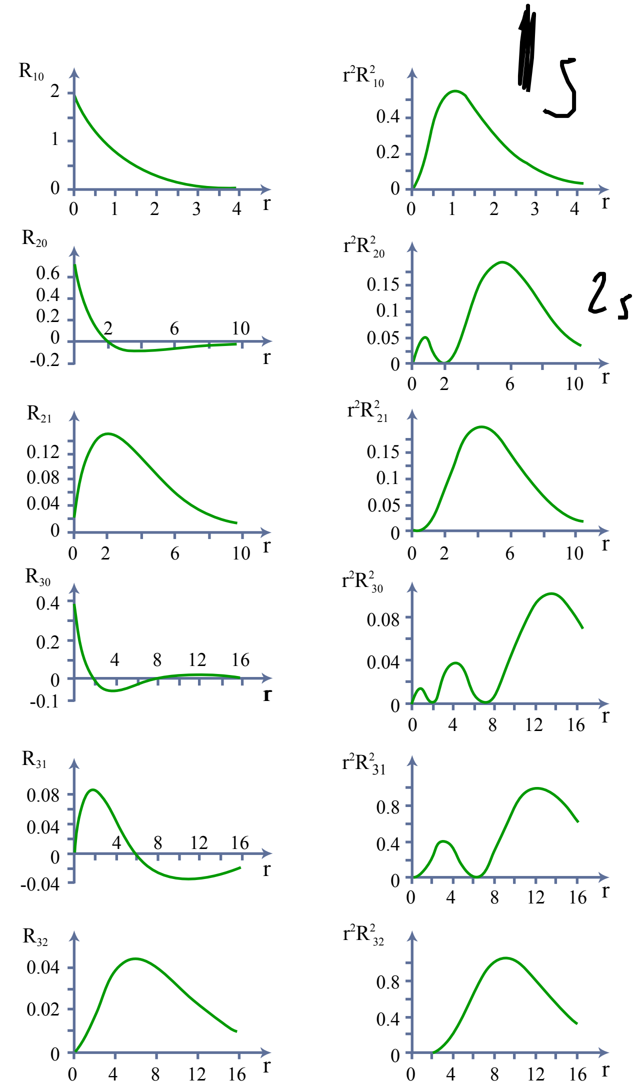


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Figure by MIT OCW.

Three Quantum Numbers

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

$$E_n = -\frac{e^2}{8\pi\varepsilon_0}\frac{Z^2}{a_0 n^2} = -(13.6058\ \text{eV})\frac{Z^2}{n^2} = -(1\ \text{Ry})\frac{Z^2}{n^2}$$

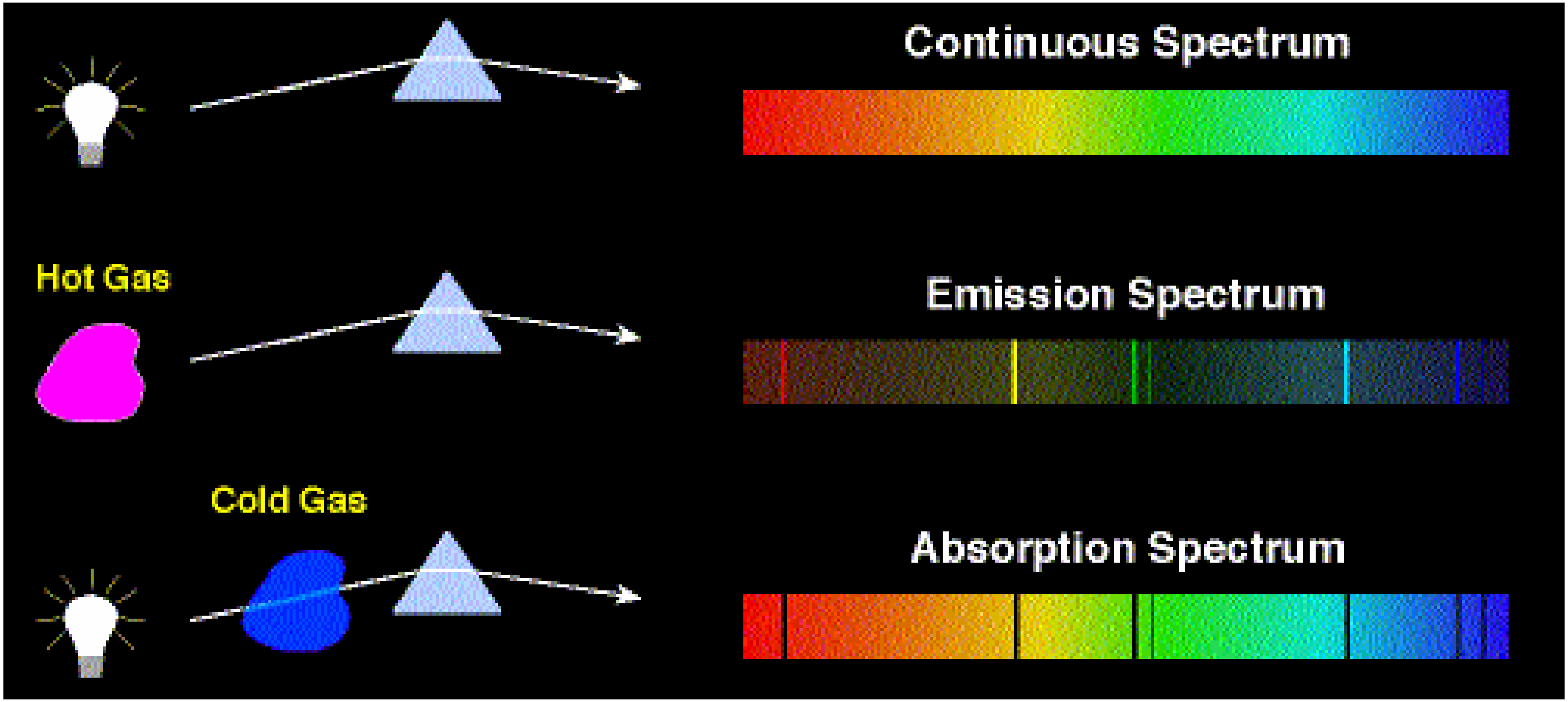
- Angular momentum quantum number **l** (L^2)

  l=0,1,…,n-1 (a.k.a. s, p, d… orbitals)

- Magnetic quantum number **m** (L_z)

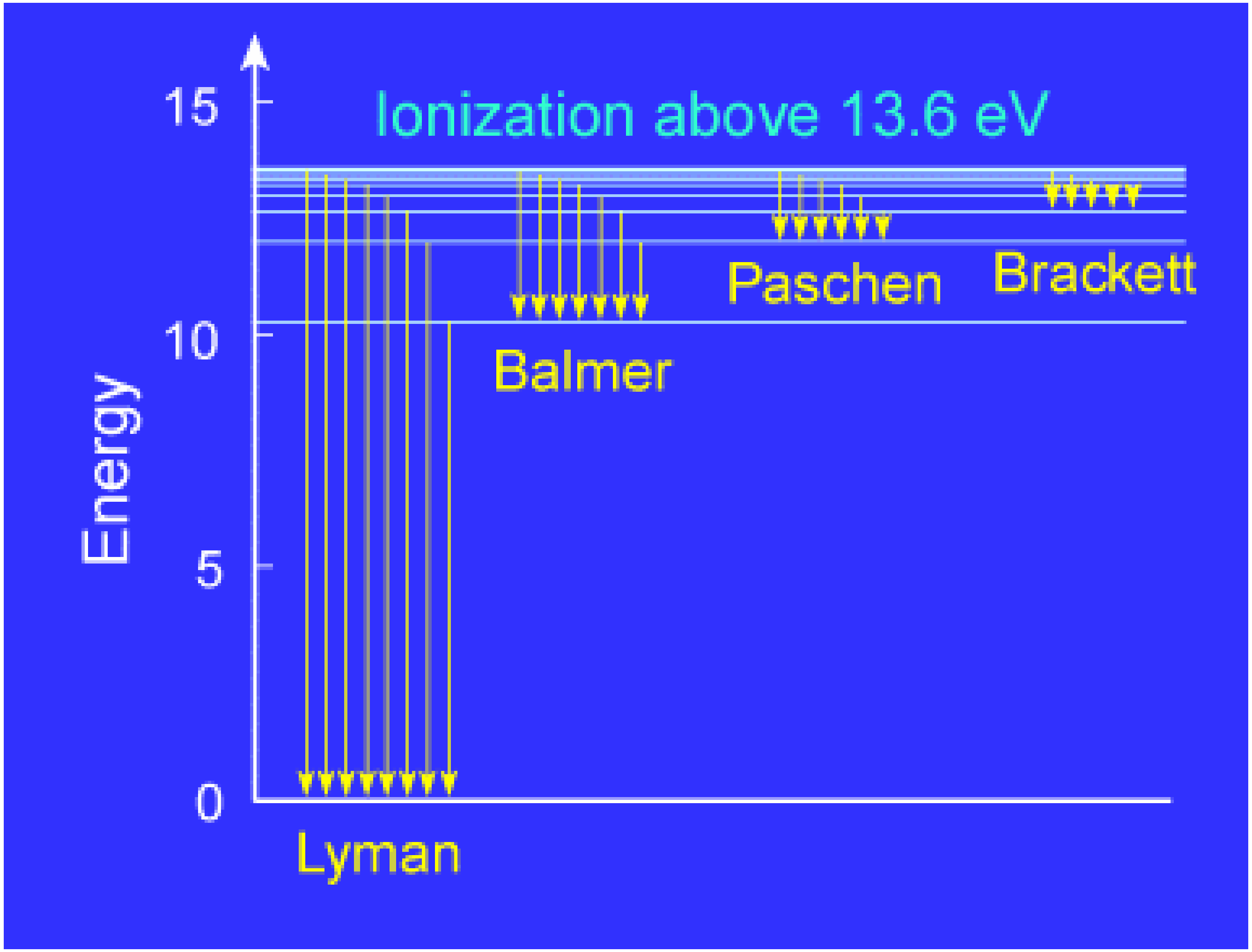
  m=-l,-l+1,…,l-1,l

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



XPS in Condensed Matter

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

The Grand Table

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

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

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

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

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

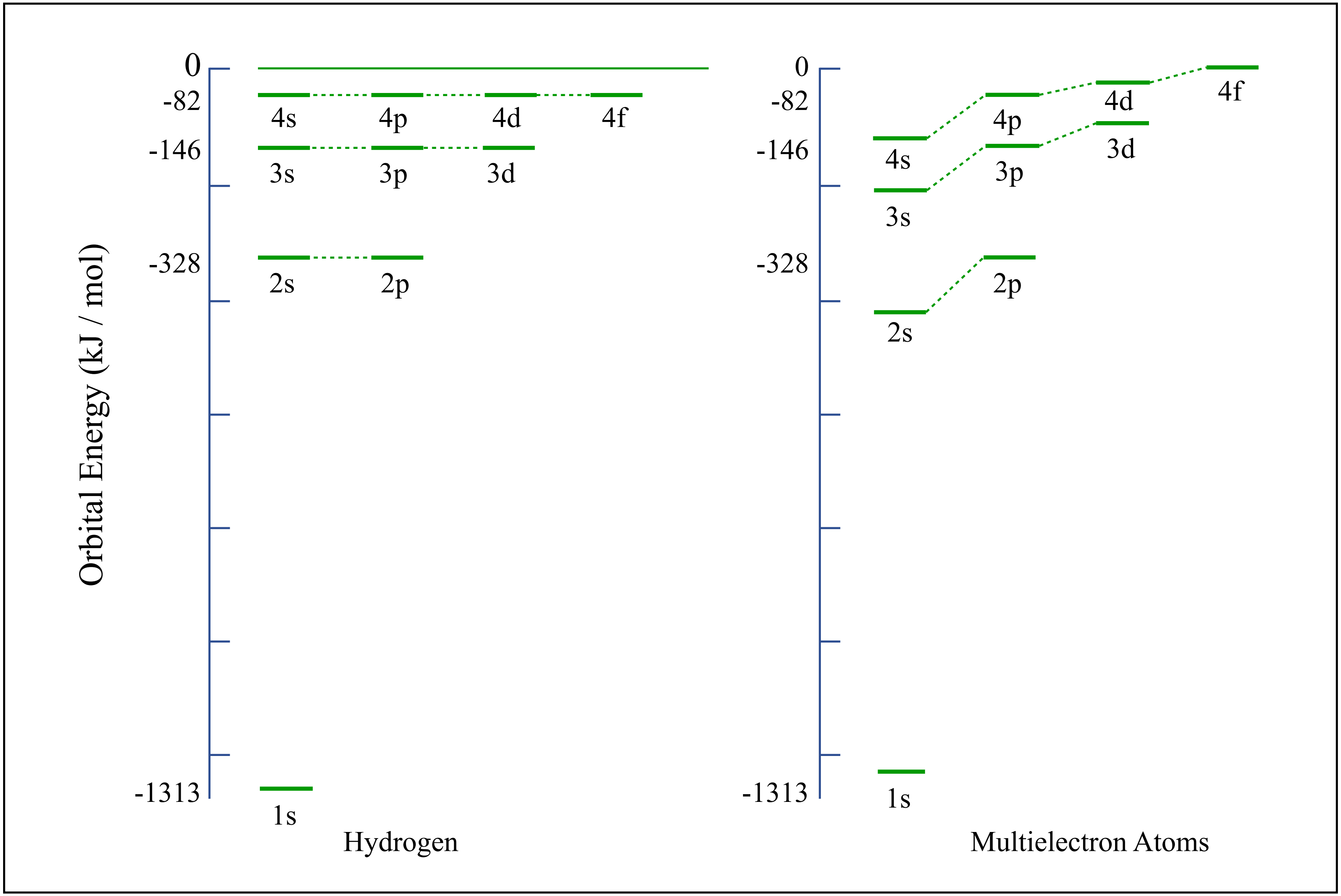
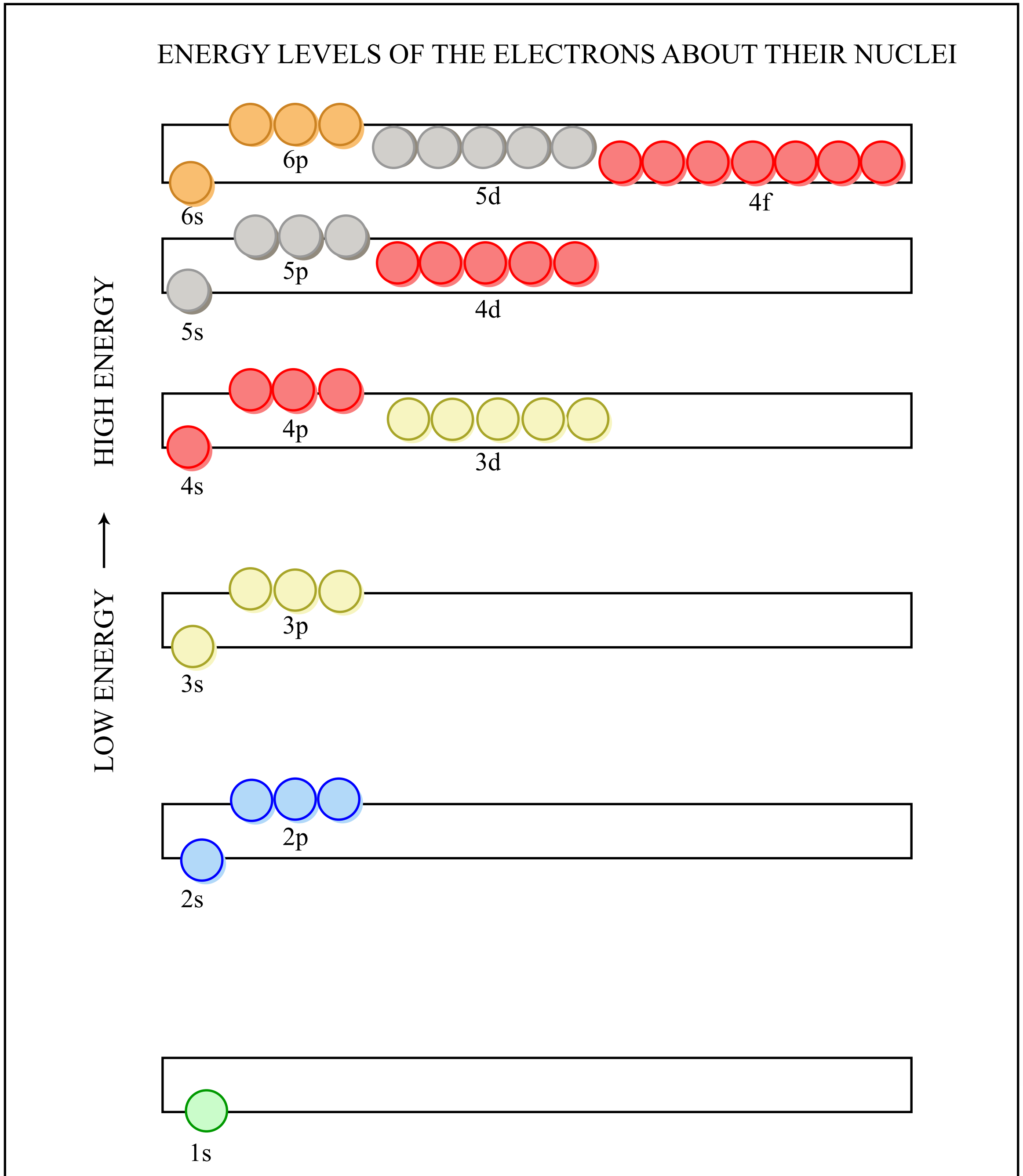


Figure by MIT OCW.

Screening

Auf-bau



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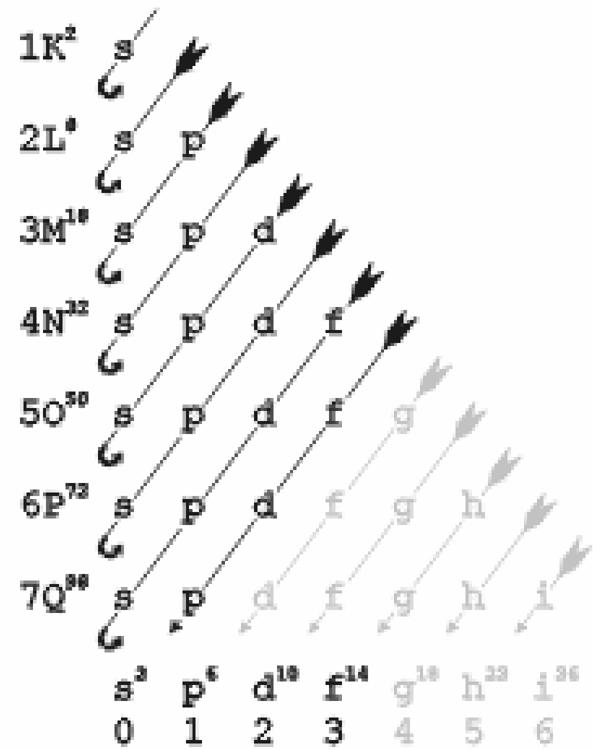

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