# Review of paradigms QM

Read McIntyre Ch. 1, 2, 3.1, 5.1-5.7, 6.1-6.5, 7, 8

# QM Postulates

① The state of a quantum mechanical system, including all the information you can know about it, is represented mathematically by a normalized ket $|\psi\rangle$.

② A physical observable is represented mathematically by a linear, Hermitian operator *A* that acts on kets.

③ The only possible result of a measurement of an observable is one of the (real) eigenvalues $a_n$ of the corresponding operator *A*.

④ The probability of obtaining the eigenvalue $a_n$ in a measurement of the observable *A* on the system in the state is

$$\wp_{a_n} = \left|\langle a_n|\psi\rangle\right|^2$$

where $|a_n\rangle$ is the normalized eigenvector of *A* corresponding to the eigenvalue $a_n$.

⑤ After a measurement of *A* that yields the result $a_n$, the quantum system is in a new state that is the normalized projection of the original system ket onto the ket (or kets) corresponding to the result of the measurement:

$$|\psi'\rangle = \frac{P_n|\psi\rangle}{\sqrt{\langle\psi|P_n|\psi\rangle}}$$

⑥ The time evolution of a quantum system is determined by the Hamiltonian or total energy operator *H*(*t*) through the Schrödinger equation

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = H(t)|\psi(t)\rangle$$

# Systems you have studied:

- Spin-1/2 and spin-1
- Infinite square well potential
- Finite square well potential
- H-atom
- Angular momentum (rigid rotor)
- Free particle

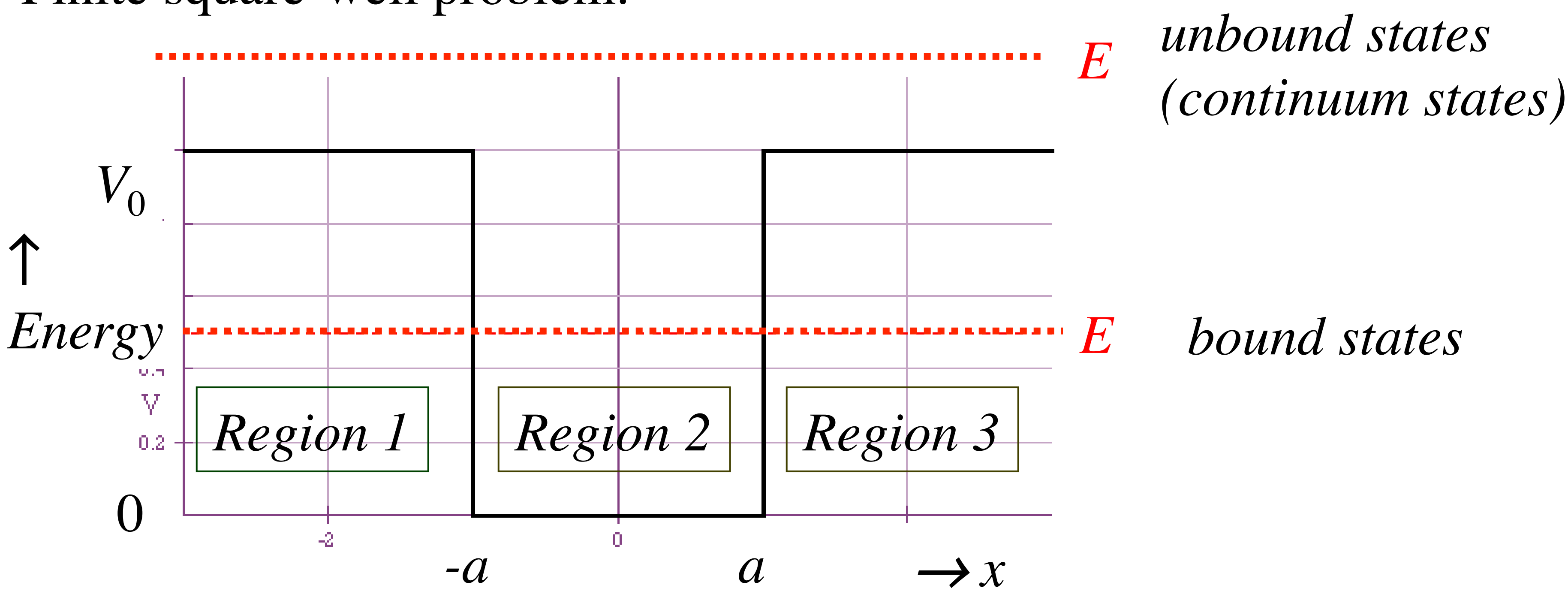
(white board or group discussions: bra-ket, wave function and matrix forms)

# Must know …

- Important operators
(abstract, matrix, position representations)
- Energy spectrum (or other spectrum), quantum numbers
- States
(ket, matrix, wave function)
- General state: coefficients, projections, probability, expectation value
- Time evolution
- Other important comments
(degeneracy, commutation, …)

- A few slides from PH424 and PH426 that capture some of the main points (not meant to be exhaustive).

Finite square-well problem:




$$V(x) = \begin{cases} V_0 & |x| > a \\ 0 & |x| < a \end{cases}$$

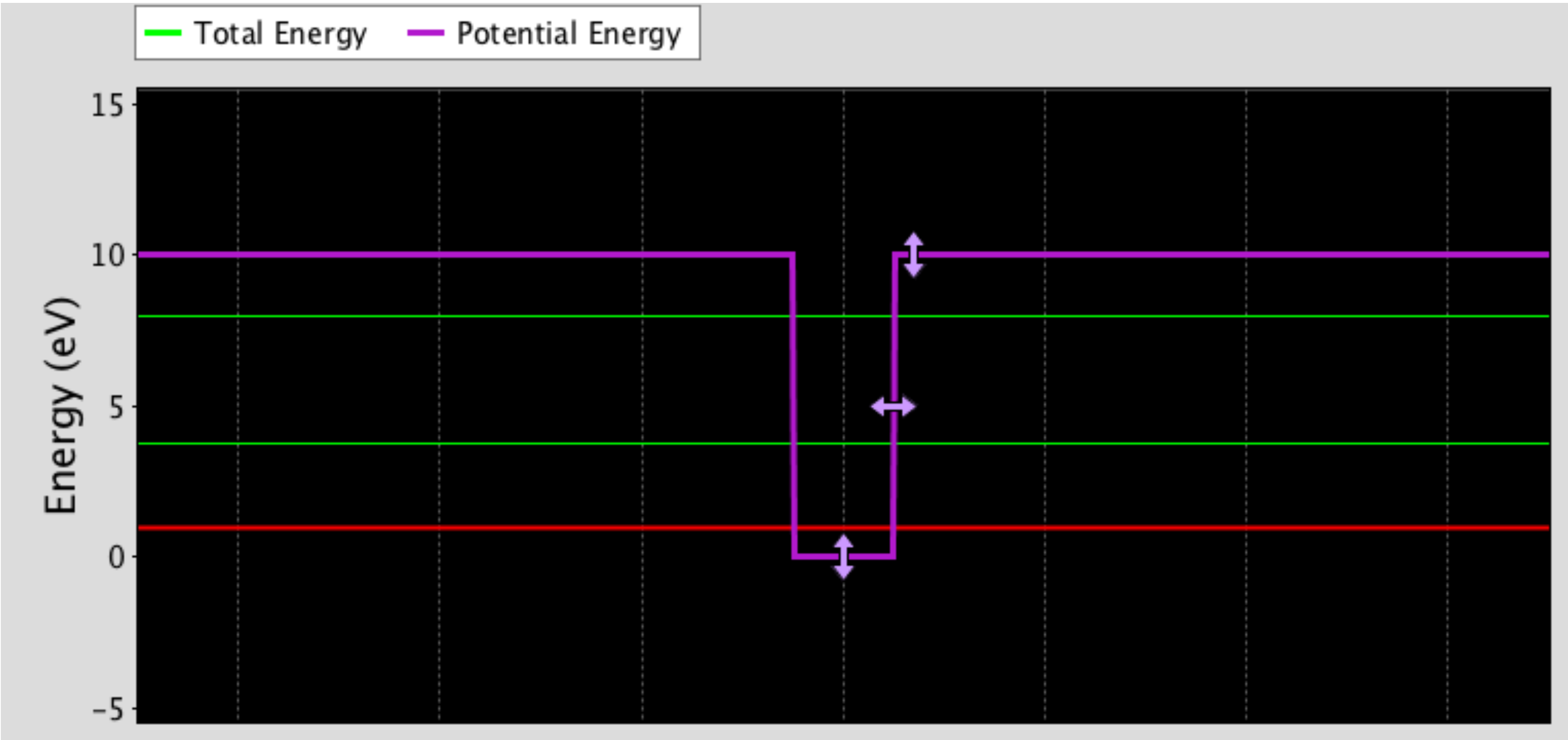
$$\varphi(x) = \begin{cases} \varphi_1 & x < -a \\ \varphi_2 & -a < x < a \\ \varphi_3 & x > a \end{cases}$$



$$H = \frac{p^2}{2m} + V; \quad H(x) = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

# Finite well: Energy spectrum (bound states only)

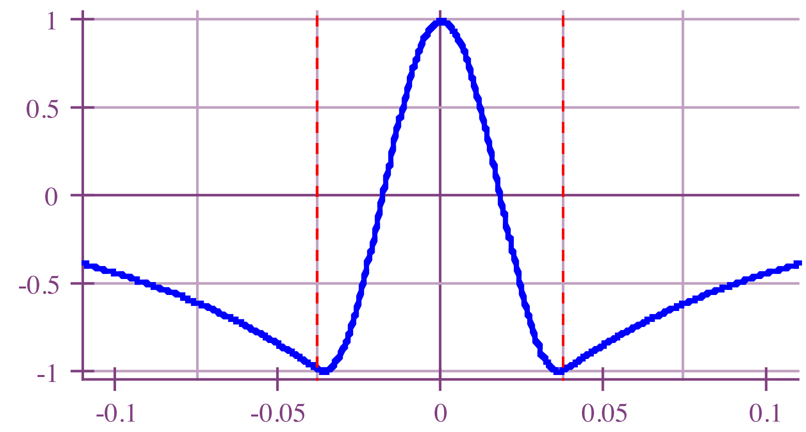
From Colorado PhET site

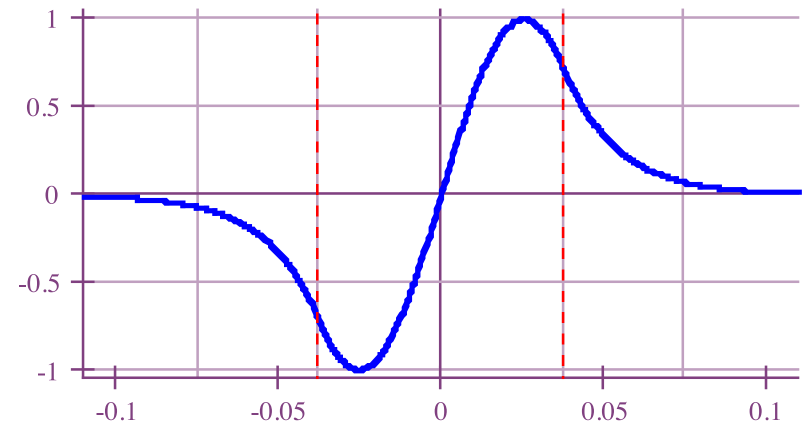



Must be at least one bound state, even for infinitely thin well.
States have alternating even and odd parity because well is symmetric.
Continuum states are not quantized.

This set of parameters gives 3 solutions (2 even and 1 odd).

Decay length increases with increasing energy. Wave function "leaks" into forbidden region - evanescent wave.



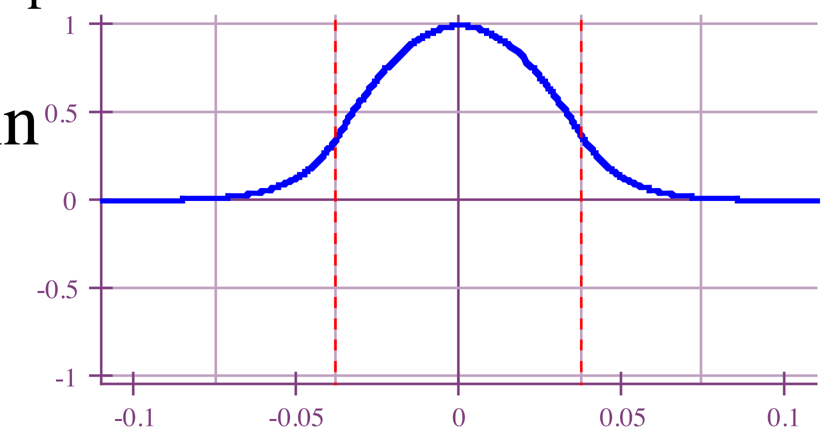




$$|\varphi_n\rangle \quad \text{for bound states, } n = 1,2,3\ldots$$

$$\varphi(x) \equiv \langle x|\varphi_n\rangle$$

complicated; basically sine or cosine joined to exponentials

$$|\varphi_E\rangle \quad \text{for continuum states, } E \text{ contin}$$

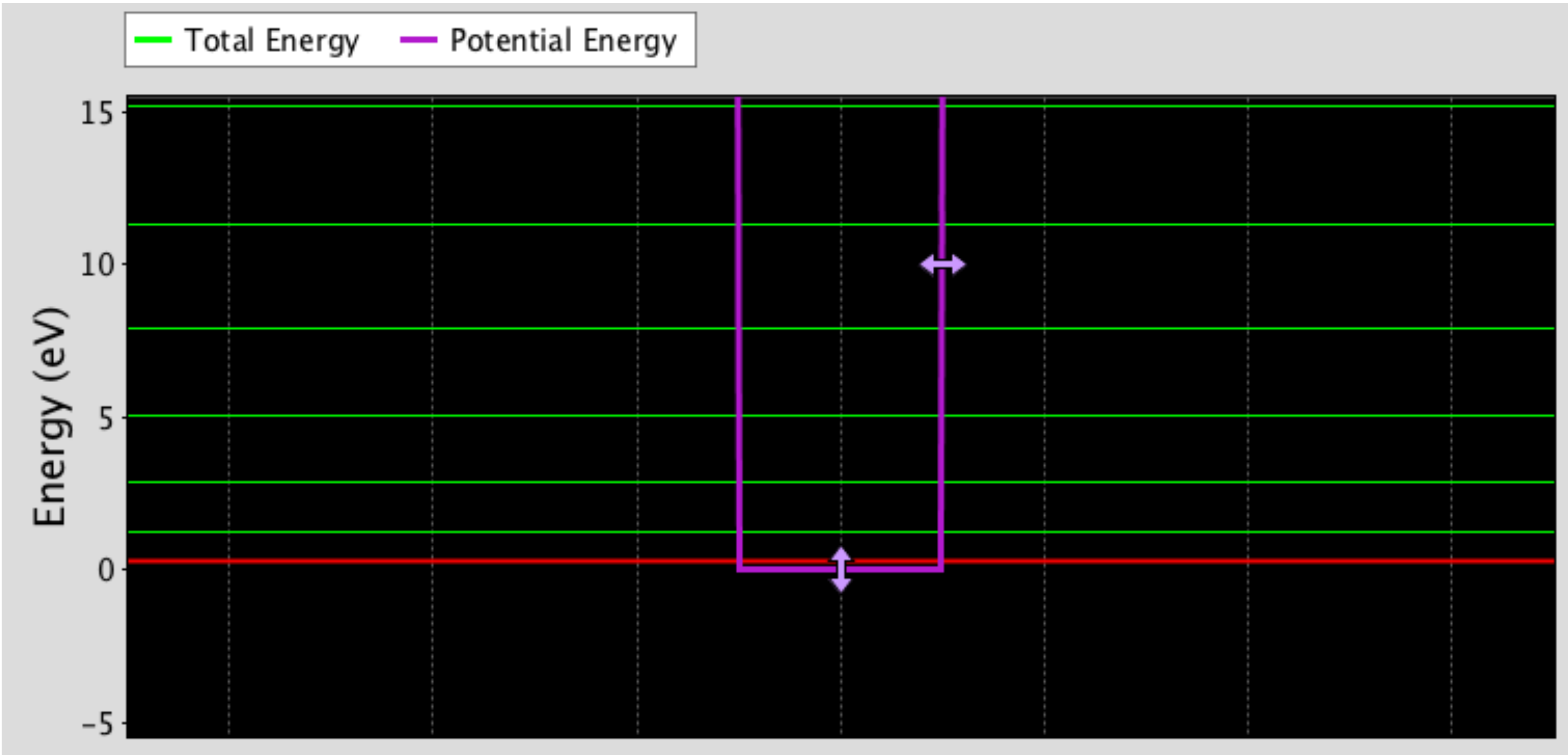



$$\varphi(x) \equiv \langle x|\varphi_E\rangle$$

complicated; basically $e^{ikx}$ modified near well

# Finite well: Energy spectrum (bound states only)

From Colorado PhET site



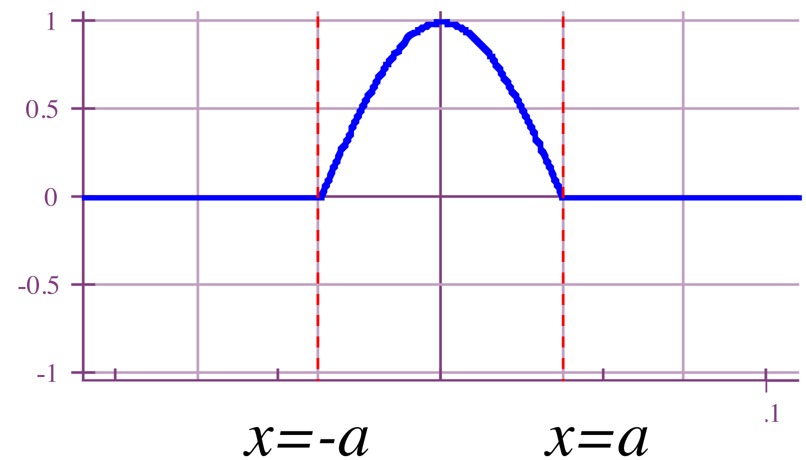
Infinite square-well problem (no continuum):

$$E_n = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}$$

$$\varphi_n(x) = 0 \quad \textit{n =1,2,3,4,5… for x<-a and x>a}$$

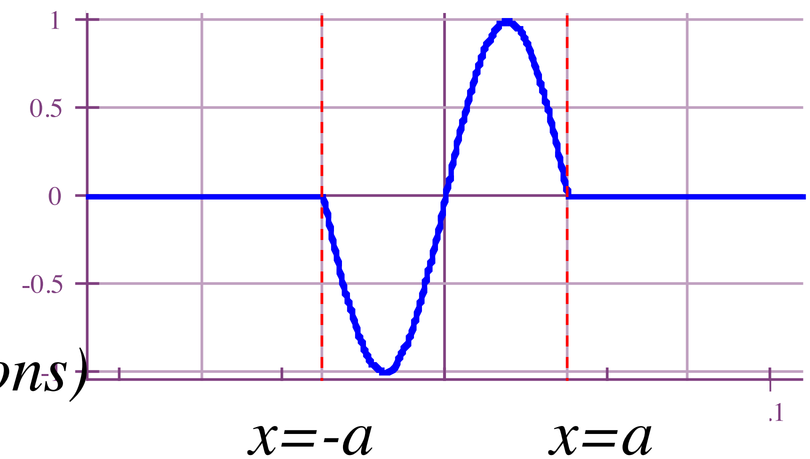
$$\varphi_n(x) = \sqrt{\frac{2}{2a}}\cos\frac{n\pi x}{2a}$$

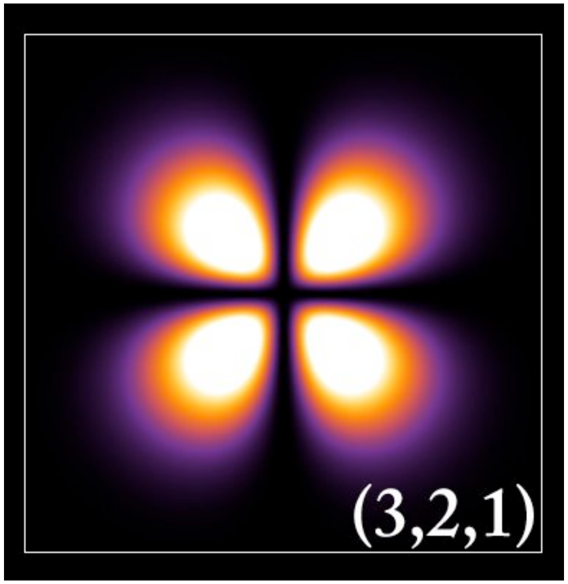
*n =1,3,5 (symmetric or even solutions)*

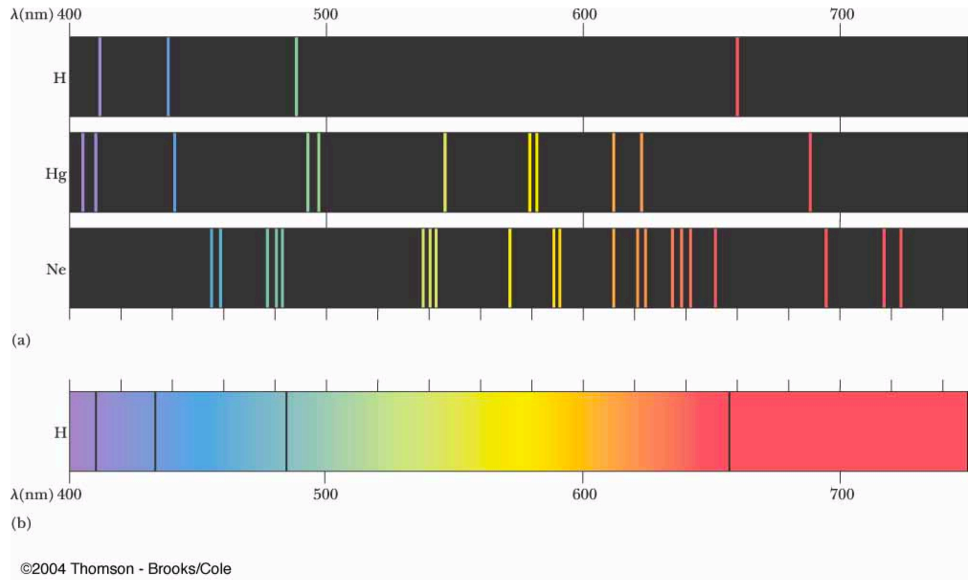



$$\varphi_n(x) = \sqrt{\frac{2}{2a}}\sin\frac{n\pi x}{2a}$$

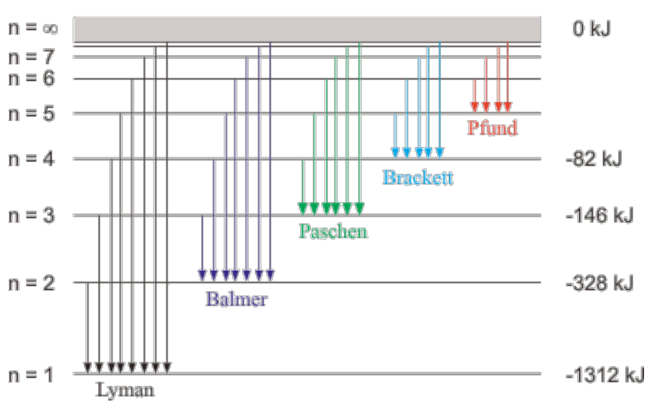
*n =2,4,6 (antisymmetric or odd solutions)*

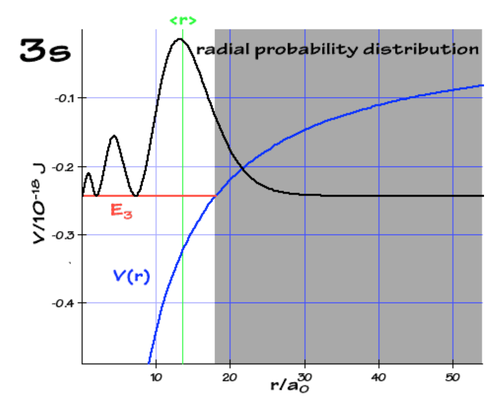


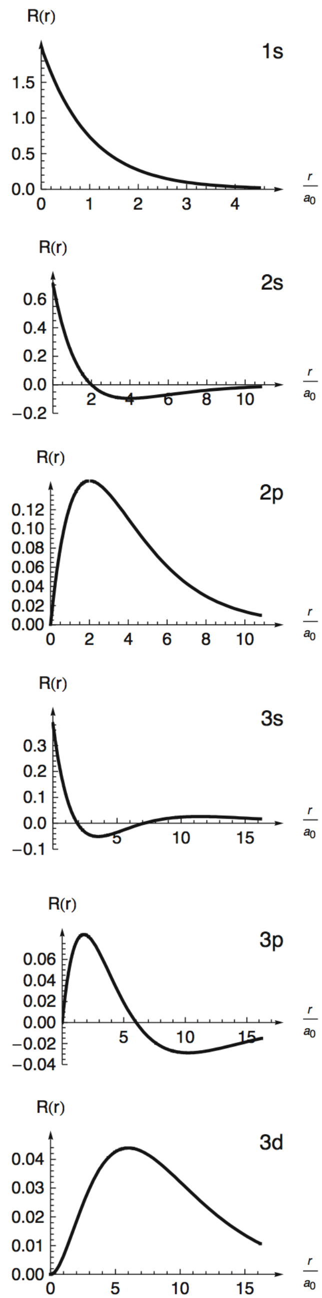



# *The Hydrogen Atom*






# Radial wave functions

- Here are more of them. Know where to look them up.
- Exponential at large r : decay length depends on energy.
- Power law at small r: non zero at origin only for s states
- Poly of order n-el-1
- Fits into the box!

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

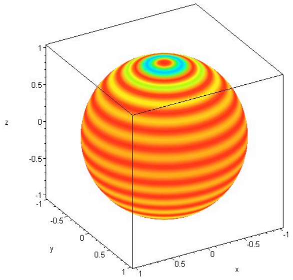
$$R_{20}(r) = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left[1-\frac{Zr}{2a_0}\right]e^{-Zr/2a_0}$$

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

$$R_{30}(r) = 2\left(\frac{Z}{3a_0}\right)^{3/2}\left[1-\frac{2Zr}{3a_0}+\frac{2}{27}\left(\frac{Zr}{a_0}\right)^2\right]e^{-Zr/3a_0}$$

$$R_{31}(r) = \frac{4\sqrt{2}}{9}\left(\frac{Z}{3a_0}\right)^{3/2}\frac{Zr}{a_0}\left(1-\frac{Zr}{6a_0}\right)e^{-Zr/3a_0}$$

$$R_{32}(r) = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$



# Spherical Harmonics

$$Y_\ell^m(\theta,\phi) = (-1)^{(m+|m|)/2}\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}P_\ell^m(\cos\theta)e^{im\phi}$$

- What is the action of these operators on the spherical harmonics?

$$L^2$$

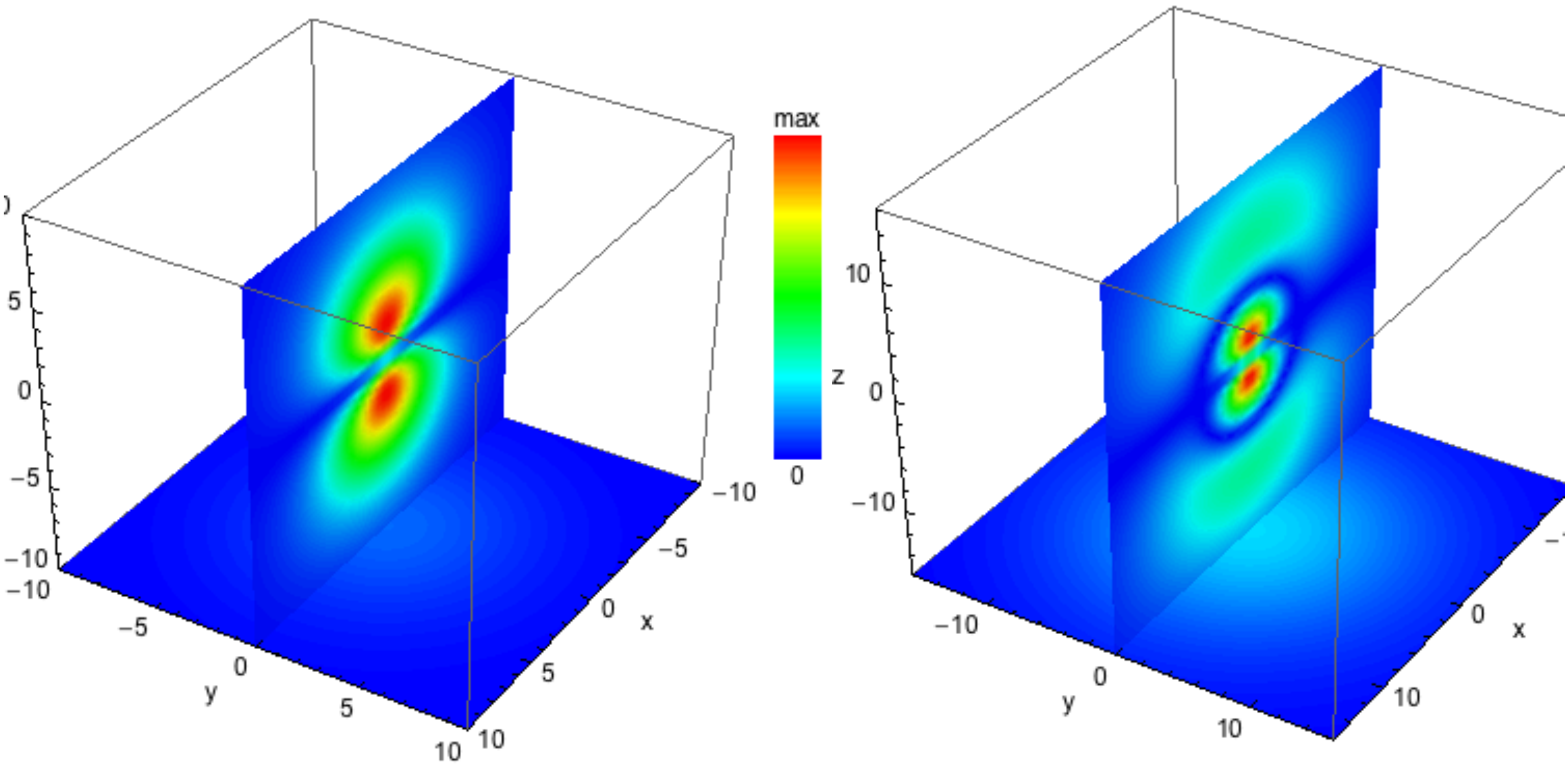
$$L_z$$

| $\ell$ | $m$ | $Y_\ell^m(\theta,\phi)$ |
|---|---|---|
| 0 | 0 | $Y_0^0 = \sqrt{\frac{1}{4\pi}}$ |
| 1 | 0 | $Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$ |
| | $\pm1$ | $Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$ |
| 2 | 0 | $Y_2^0 = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right)$ |
| | $\pm1$ | $Y_2^{\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}$ |
| | $\pm2$ | $Y_2^{\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm i2\phi}$ |
| 3 | 0 | $Y_3^0 = \sqrt{\frac{7}{16\pi}}\left(5\cos^3\theta-3\cos\theta\right)$ |
| | $\pm1$ | $Y_3^{\pm1} = \mp\sqrt{\frac{21}{64\pi}}\sin\theta\left(5\cos^2\theta-1\right)e^{\pm i\phi}$ |
| | $\pm2$ | $Y_3^{\pm2} = \sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta e^{\pm i2\phi}$ |
| | $\pm3$ | $Y_3^{\pm3} = \sqrt{\frac{35}{64\pi}}\sin^3\theta e^{\pm i3\phi}$ |

2$p$0 and 3$p$0

# $p$- states

- What additional structure does the radial wave function impose that you can't see from the Ylms?

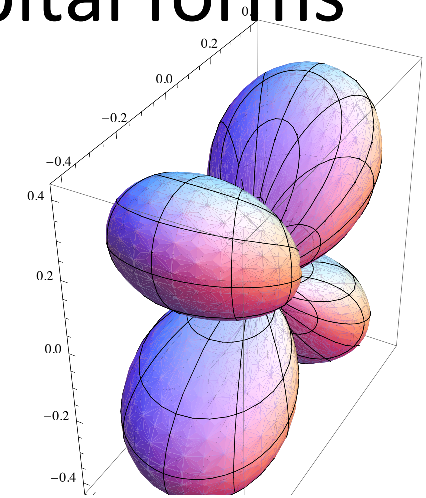


# The real (as apposed to complex) spherical harmonics

- In gravitation problems, the complex numbers in the spherical harmonics are rarely useful, so other linear combinations are used.

$$d_{yz}(\theta,\phi) \sim Y_2^1(\theta,\phi) + e^{i\delta} Y_2^{-1}(\theta,\phi)$$

- You'll recognize these as the *p, d, f* orbital forms from chemistry



# Abstract bra-ket & position state (wave function) representations

| | | |
|---|---|---|
| State superposition | $\lvert\Phi\rangle = \sum_n c_n \lvert\varphi_n\rangle$ | $\Phi(x) = \sum_n c_n \varphi_n(x)$ |
| Eigenstates & eigenvalues | $\hat{Q}\lvert\varphi_n\rangle = q_n \lvert\varphi_n\rangle$ | $\hat{Q}\varphi_n(x) = q_n \varphi_n(x)$ |
| Eigenstate orthogonality | $\langle\varphi_n\vert\varphi_m\rangle = \delta_{n,m}$ | $\int_{-\infty}^{\infty} \varphi_n^*(x)\varphi_m(x)dx = \delta_{n,m}$ |
| Normalization | $\langle\Phi\vert\Phi\rangle = 1$ | $\underbrace{\int_{-\infty}^{\infty} \underbrace{\Phi^*(x)\Phi(x)}_{\text{Probability density}} dx}_{\text{Probability}} = 1$ |
| | $\sum_n \lvert c_n\rvert^2 = 1$ | |
| Expectation value | $\langle Q\rangle = \langle\Phi\vert\hat{Q}\vert\Phi\rangle$ | $\langle Q\rangle = \int_{-\infty}^{\infty} \Phi^*(x)\hat{Q}\Phi(x)dx$ |
| | $\langle Q\rangle = \sum_n \lvert c_n\rvert^2 q_n$ | |

Projections: $c_n = \langle \varphi_n | \Phi \rangle$

$$\langle \varphi_n | \Phi \rangle = \langle \varphi_n | \sum_{m=1}^{\infty} c_m | \varphi_m \rangle = \sum_{n=1}^{\infty} c_m \langle \varphi_n | \varphi_m \rangle$$

$$= \sum_{m=1}^{\infty} c_m \delta_{n,m} = c_n$$

Coefficients: They are the projection of the general state onto the eigenstate.
Do specific example on board

Remember Fourier coefficients?

Schrödinger Wave Equation: $$\hat{H}\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}$$

More-or-less "given", just like Newton's law *F(x)* = d*p*/d*t.*
It works, and if we can show that it fails, we'll refine or discard.

You learned in *Spins* the solution to the (time-dependent) SE is, in terms of the eigenstates of the Hamiltonian:

$$\left|\psi(t)\right\rangle = \sum_n \left|\varphi_n\right\rangle e^{-iE_n t/\hbar} \quad \text{where} \quad \hat{H}\left|\varphi_n\right\rangle = E_n\left|\varphi_n\right\rangle$$

$$\psi(x,t) = \sum_n \varphi_n(x) e^{-iE_n t/\hbar} \quad \text{where} \quad \hat{H}\varphi_n(x) = E_n\varphi_n(x)$$

Notice the parallels to the rope problem we solved last week?

$|x\rangle$ is a ket that is the eigenstate of position

$$
|x_2\rangle \doteq \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix} \begin{array}{l} <- \;\; x_1 \\ <- \;\; x_2 \\ \quad\;\; \vdots \\ <- \;\; x_N \end{array}
$$

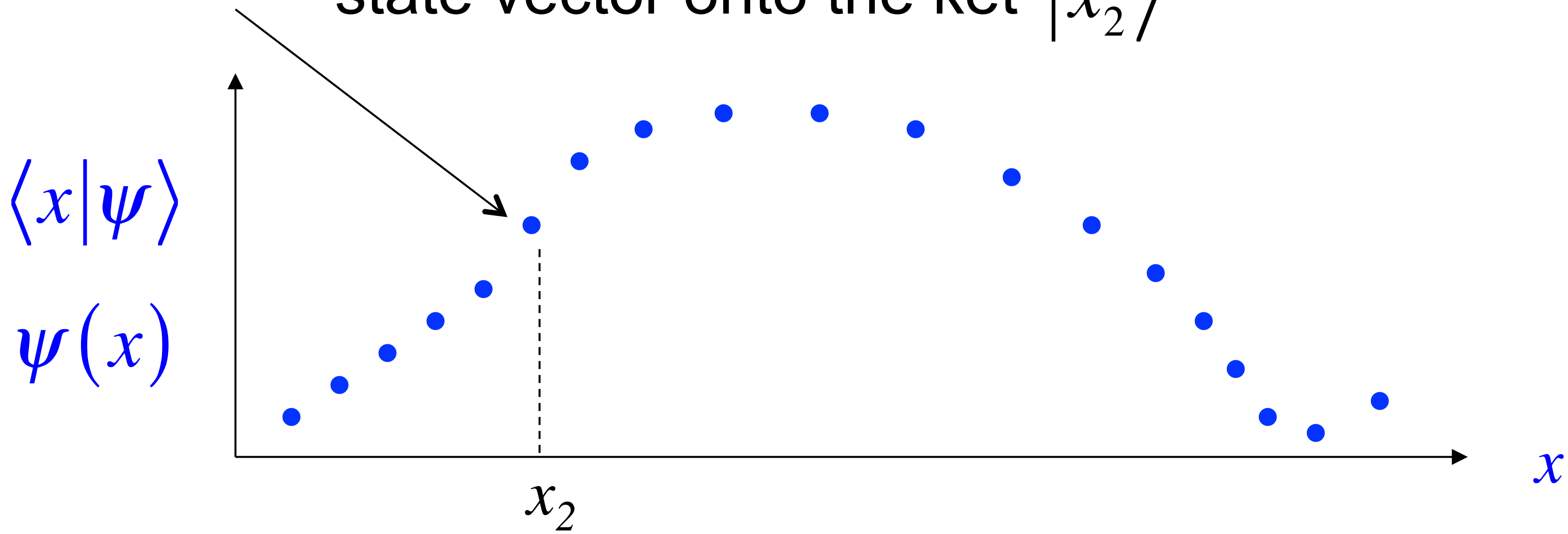
In the spins course notation, this ket represents a particle that is located precisely at position $x_2$.

Reminds you of a delta function, doesn't it?! Well, it should!

$|x\rangle$ is a **ket** that is the eigenstate of position

$\langle x_1|\psi\rangle$ is a **number** that represents the projection of the state vector onto the ket $|x_1\rangle$

$\langle x_2|\psi\rangle$ is a **number** that represents the projection of the state vector onto the ket $|x_2\rangle$




$\psi(x)$: We've represented the general state vector in a graphical form by projecting onto position eigenstates. This the "position representation". Careful, though … ψ(*x*) can be complex, so we have to plot both the real and imaginary parts for a full representation.

$$\psi(x) = \langle x | \psi \rangle$$

Then what is $\langle \psi | x \rangle$ ?

$$\langle \psi | x \rangle = \langle x | \psi \rangle^* = \psi^*(x)$$

Then we have the following identifications (not equalities)

$$|\psi\rangle \doteq \psi(x)$$

$$\langle \psi | \doteq \psi^*(x)$$

# Commutation Operator

$$\left[\hat{A},\hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

- Commutator is an OPERATOR! Must operate on something (ket, vector, wave function).
- Order matters! Only if common eigenfunctions does commutator operation yield zero.

$$\left[\hat{x},\hat{p}\right] = ?$$

$$\left[\hat{S}_x,\hat{S}_y\right] = ?$$

$$\left[\hat{H},\hat{L}^2\right] = ?$$

# Uncertainty Principle

- Uncertainty relation between observables of non-commuting operators

$$\Delta A \Delta B \geq \tfrac{1}{2} \left| \left\langle \left[ \hat{A}, \hat{B} \right] \right\rangle \right|$$

$$\Delta A \equiv \sqrt{\left\langle \hat{A}^2 \right\rangle - \left\langle \hat{A} \right\rangle^2}$$

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$