Is it possible to learn quantum mechanics without lots of math?

- Honestly, probably not very well.
- However, I think it is critical to start with quantum mechanics, because it is really the foundation of the “bottom-up” approach to biomolecular modeling.
- Also, extensive analytical derivations can obscure the big picture; it took me many years to gain a good intuitive understanding of quantum mechanics, despite lots of coursework.
- I taught a course last year (Chemistry 262) that really provides a solid foundation for using quantum mechanics as a tool. It provides lots of practical experience, but requires a fairly serious time commitment. I am willing to teach it in the future if there is sufficient demand.
- My goals for this portion of the course:
    1. Provide an intuitive feel for quantum systems using model systems.
    2. Introduce basics of electronic structure calculations, which are critical for force fields and docking calculations.
    3. Understand the key scientific ideas behind the jargon (what does 6-31G* really mean, anyways?).

In quantum mechanics, classical variables are replaced by operators

<u>Some examples in 1 dimension</u>:

Position	x	x (“multiply by x”)
Momentum	p	$-i\hbar\frac{\partial}{\partial x}$
Kinetic energy	K	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
Total energy	E/Ĥ	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+U\left(x\right)$

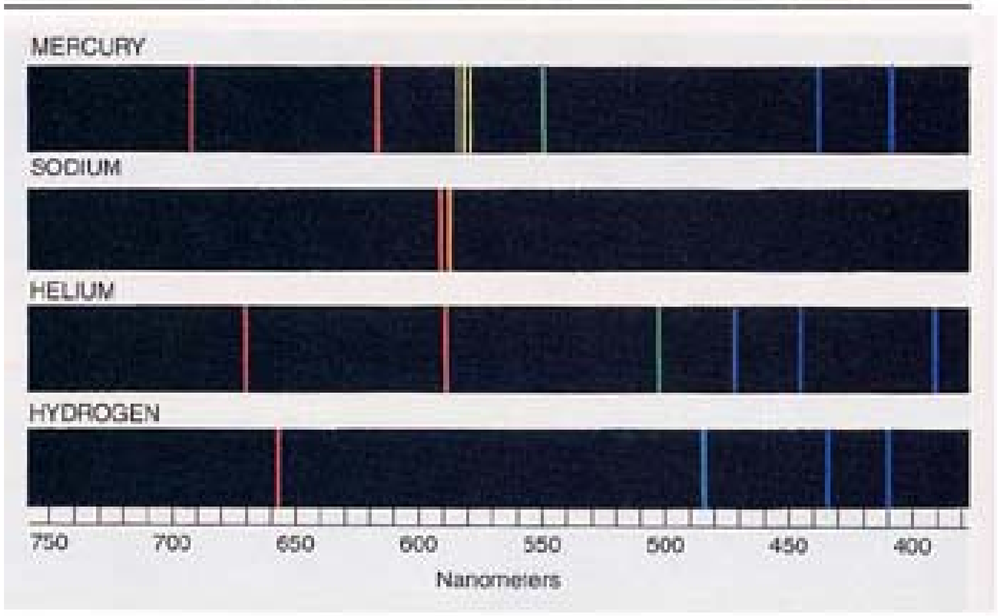
Note how Planck’s constant (ħ) shows up here. Although it’s a bit beyond the scope of our discussion, Planck’s constant provides the fundamental measure of when a system is small enough to be “quantum”. Its value is ~$1\cdot10^{-34}$ J·s.

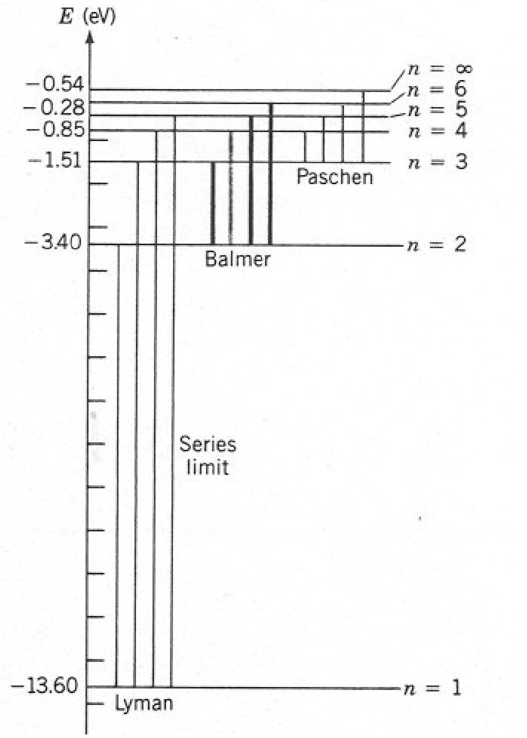
This is all a bit abstract for now, but hold tight. We’ll start looking at model systems soon ...

Quantum operators are quantized

- Quantization is one of the most fundamental concepts in QM.
- Basic definition: Measured values of observable associated with a quantum operator can only take discrete (“quantized”) values.
- In practice you solve for the quantum states by solving an eigenvalue equation by various methods (analytical, matrix methods).
- The most important operator by far is energy, the “Hamiltonian” operator.
- A simple demonstration of quantized energy is provided by atomic spectra:

Transitions between quantized states (“energy eigenstates”) leads to only discrete colors of light being absorbed/emitted.





A quantum system is completely specified by its wavefunction

$$\Psi\left(\vec{r},t\right)$$

written as a function of coordinates and time; can be complex-valued

$$\left|\Psi\left(\vec{r},t\right)\right|^2$$

the amplitude squared has a special importance: it represents probability of finding quantum system in a given state.

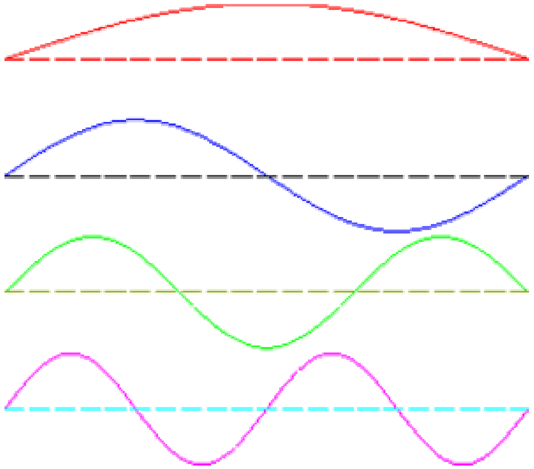
$$\hat{A}\Psi = a\Psi$$

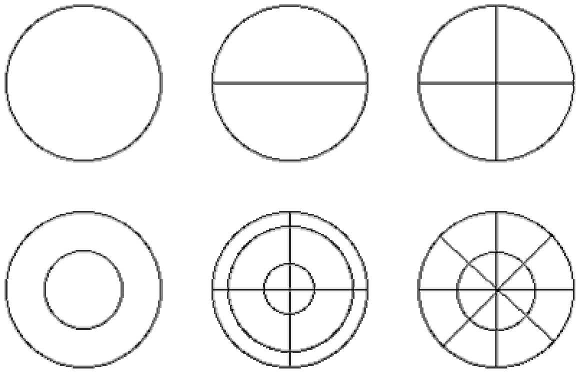
the only values of observable associated with operator A will be the eigenvalues, i.e., those that satisfy this eigenvalue equation.

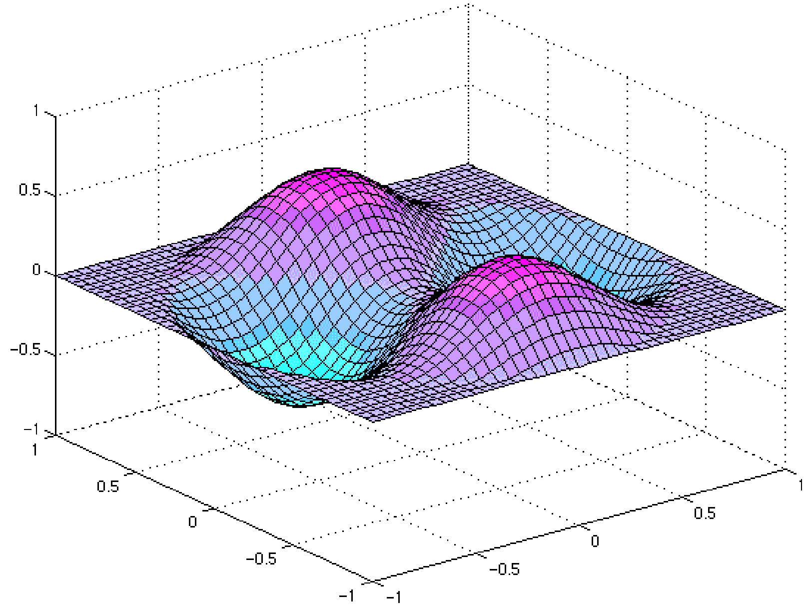
Eigenfunctions are the wavefunctions associated with the eigenvalues:

- Eigenfunctions are indexed by “quantum numbers” (integers, or half integers for spin).
- We can define eigenfunctions of any quantum operator, but by far the most important are the “energy eigenfunctions”, i.e., eigenfunctions of the Hamiltonian operator.
- All other wavefunctions can be expressed as a superposition of eigenfunctions.

Eigenfunctions are a bit like the normal modes of a string or drum







These normal modes represent the "stationary states" of the classical system, which can be in some superposition of normal modes. Similarly, eigenfunctions are stationary states of quantum systems.

One key difference: Quantum eigenstates can be imaginary.

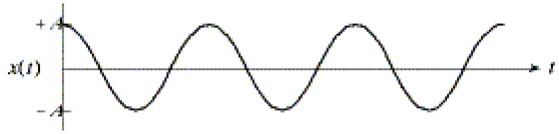
Quantum Mechanical Model Systems

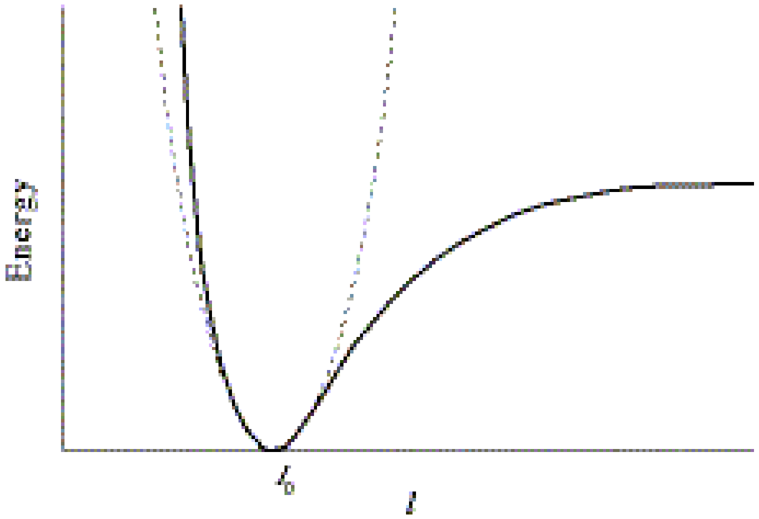
Goal: Gain intuition about quantum eigenfunctions and how they relate to classical mechanics using simple, one-dimensional systems.

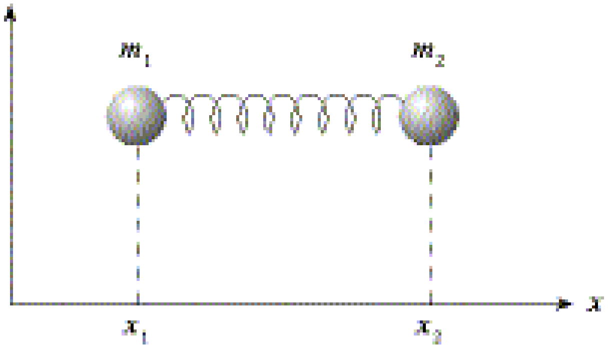
Outline:

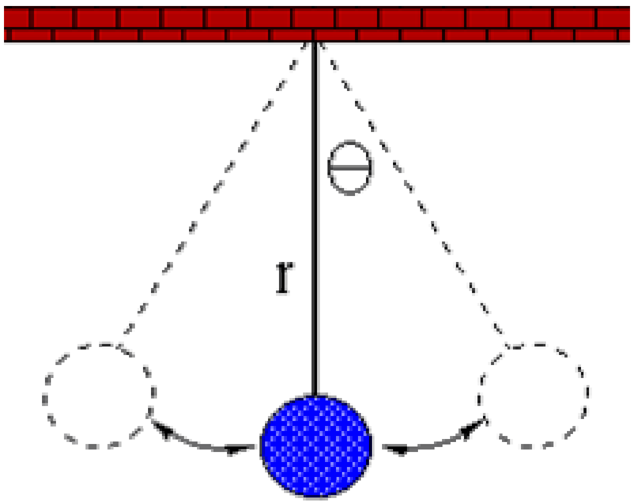
1. Harmonic oscillator
2. Anharmonic oscillator (Morse; relevant to bond stretching)
3. Pendulum (relevant to torsions/internal rotations)

Harmonic Oscillator







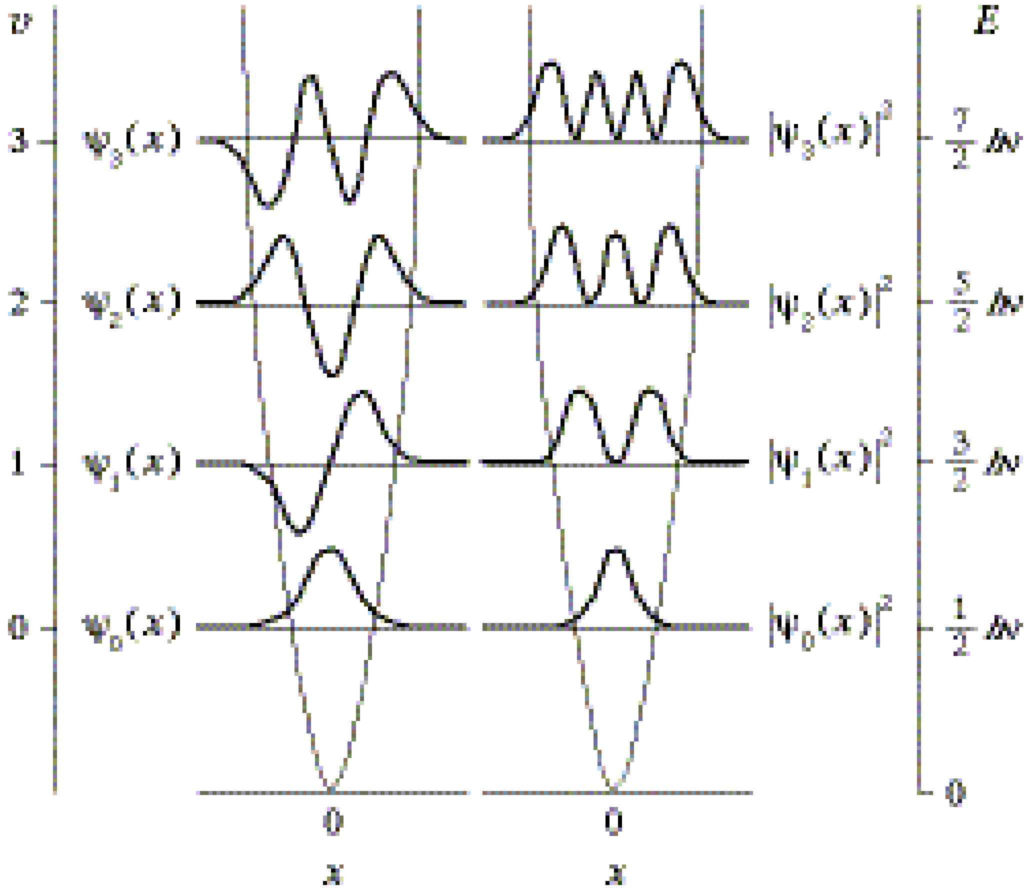


Harmonic Oscillator Eigenstates

$$E = \omega\left(v + \tfrac{1}{2}\right)$$

w is related to width of potential, e.g., spring constant. v is the quantum number. Eigenfunctions are analytical but somewhat complicated.

Amplitude Probability



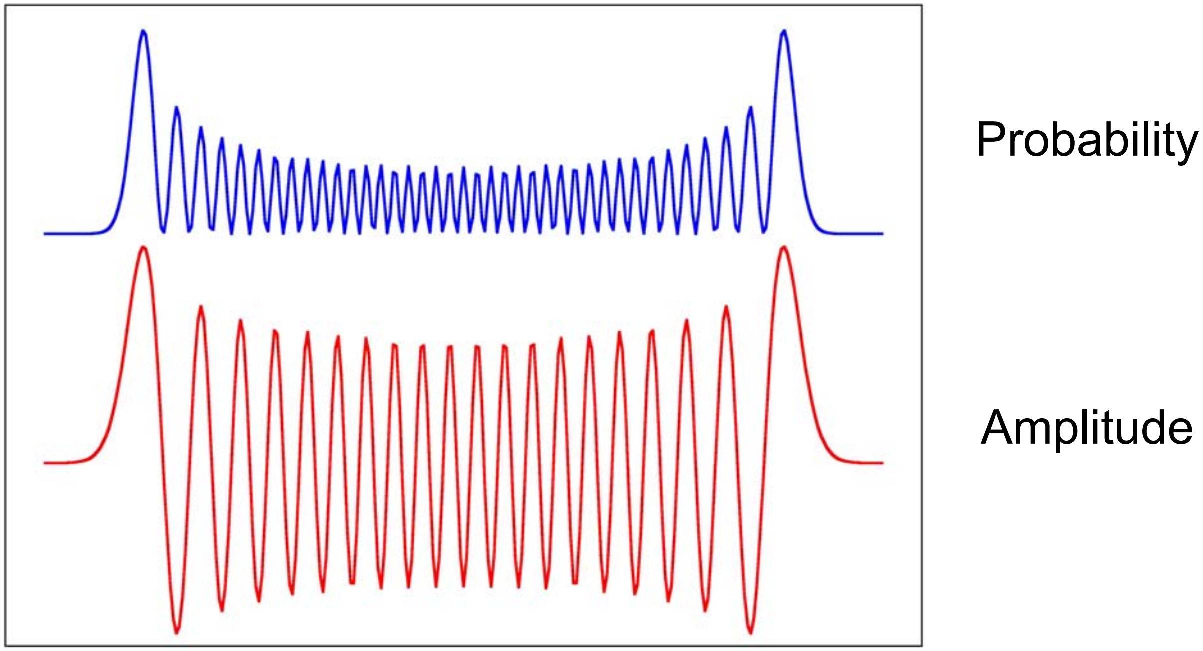
<u>Similar to classical behavior</u>:

- More probability of finding system near turning points.

<u>Purely quantum behavior</u>:

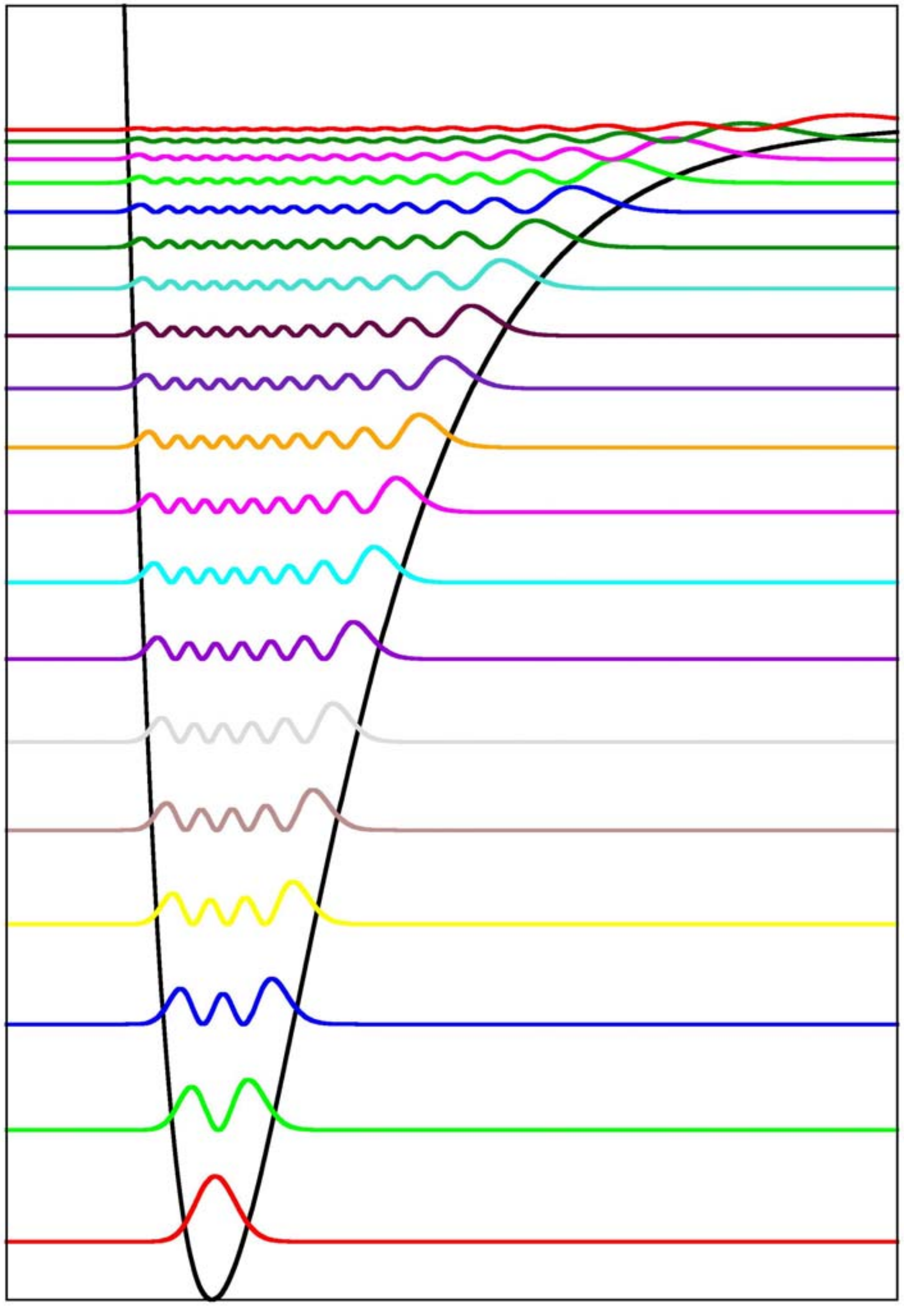
- Energy is quantized (discrete).
- Nodes (points with zero probability of finding system).
- Tunneling into classically forbidden region.
- Lowest energy state is NOT at zero energy; consequence of uncertainty principle, which we have not discussed.

40th eigenstate of the harmonic oscillator



Qualitative conclusion: As the energy increases (larger "quantum number"), the system looks increasingly classical. The relationship between quantum and classical mechanics is studied under the title "quantum-classical correspondence".

Anharmonic (Morse) Oscillator: A better approximation for vibrations of real chemical bond



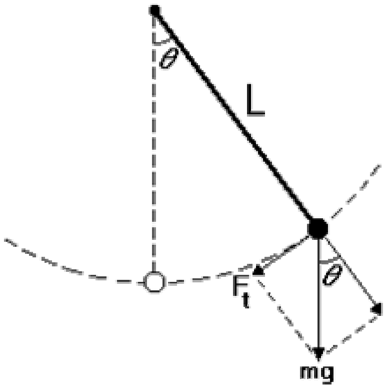
Key points:

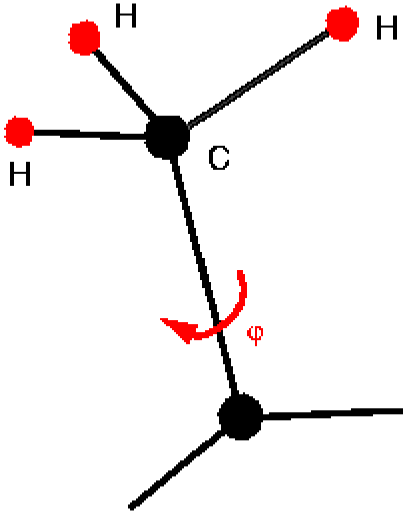
1. Energy levels more closely spaced as you approach the “dissociation limit”, i.e., as the potential become more anharmonic.
2. Probability density accumulates at outer turning point.

Both of these make sense classically.

$$E = \omega\left(v+\tfrac{1}{2}\right) - x\left(v+\tfrac{1}{2}\right)^2$$

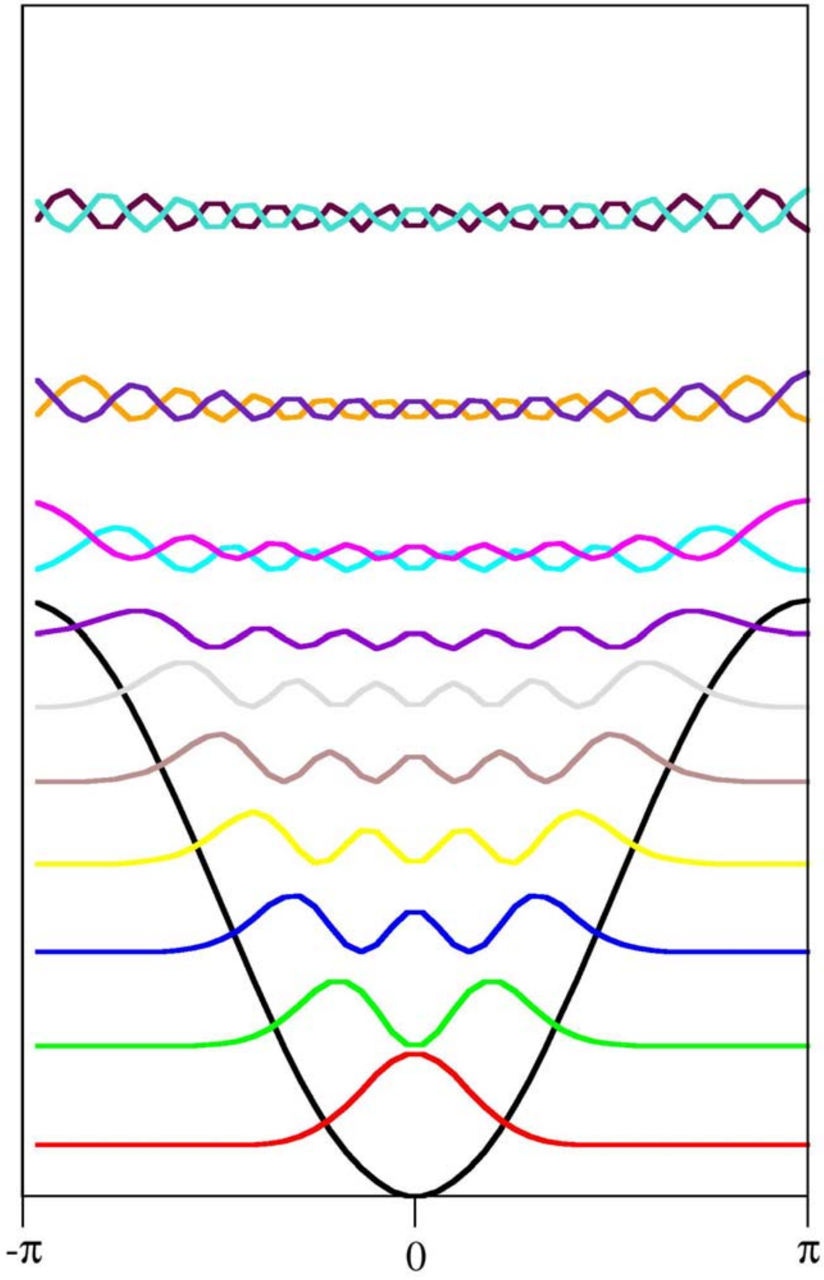
Pendulum Eigenstates





hindered internal rotation

anharmonic vibrations



Double-Well Potentials

Key points:

1. Good model systems for tunneling, e.g., .proton transfer.
2. In a symmetric potential, the eigenstates must display symmetry as well (either “odd” or “even”).
3. In symmetric double well, the splitting between pairs of states reflects tunneling.
4. Tunneling “rate” (probability) is related to the dE between the eigenstate and the top of the barrier.

Although not shown here, the eigenstates above the barrier will of course span both wells, with some increase in probability density above the barrier.