UNIVERSITY OF LUXEMBOURG
Physics and Materials Science
Research Unit (PHYMS)

12 – Schrödinger Equation

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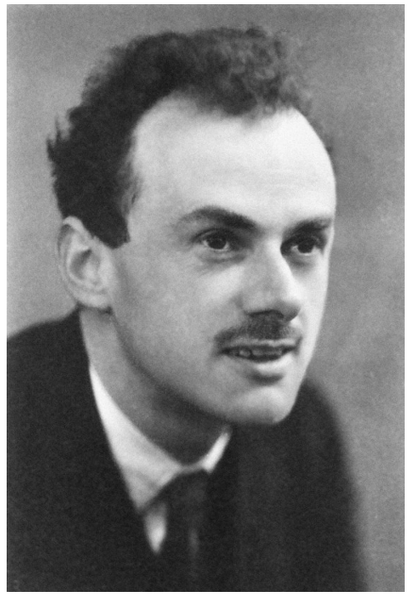
Historical Note

(1933)

Time-dependent Schrödinger equation

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H}|\psi\rangle$$

$$|\psi\rangle = |\tilde{\psi}\rangle \cdot e^{-\frac{iEt}{\hbar}}$$



(1933)

Time-independent (stationary) Schrödinger equation

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble".

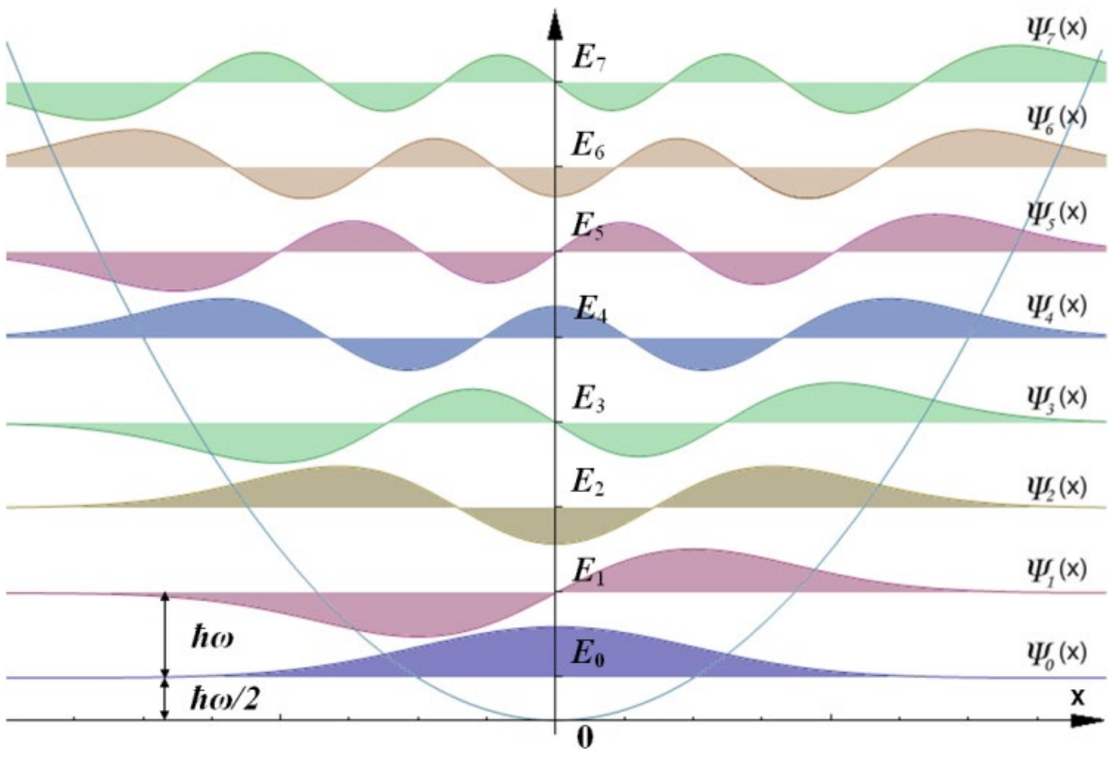
P.A.M. Dirac, 1929

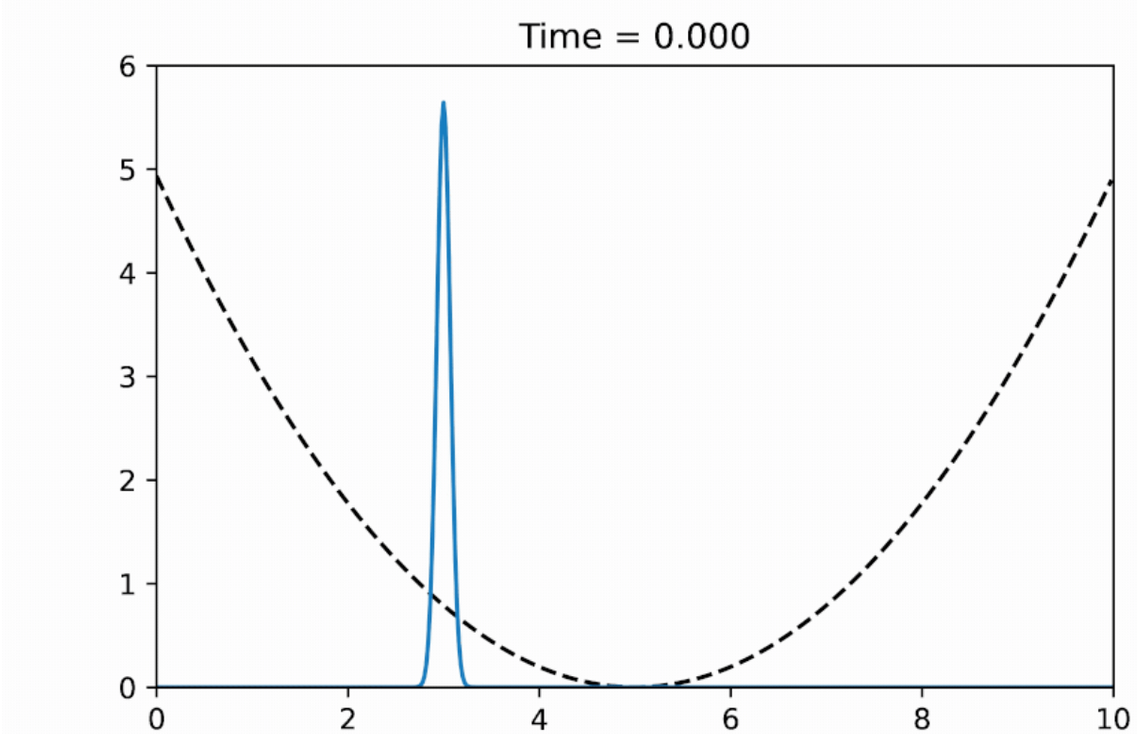
Harmonic Oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

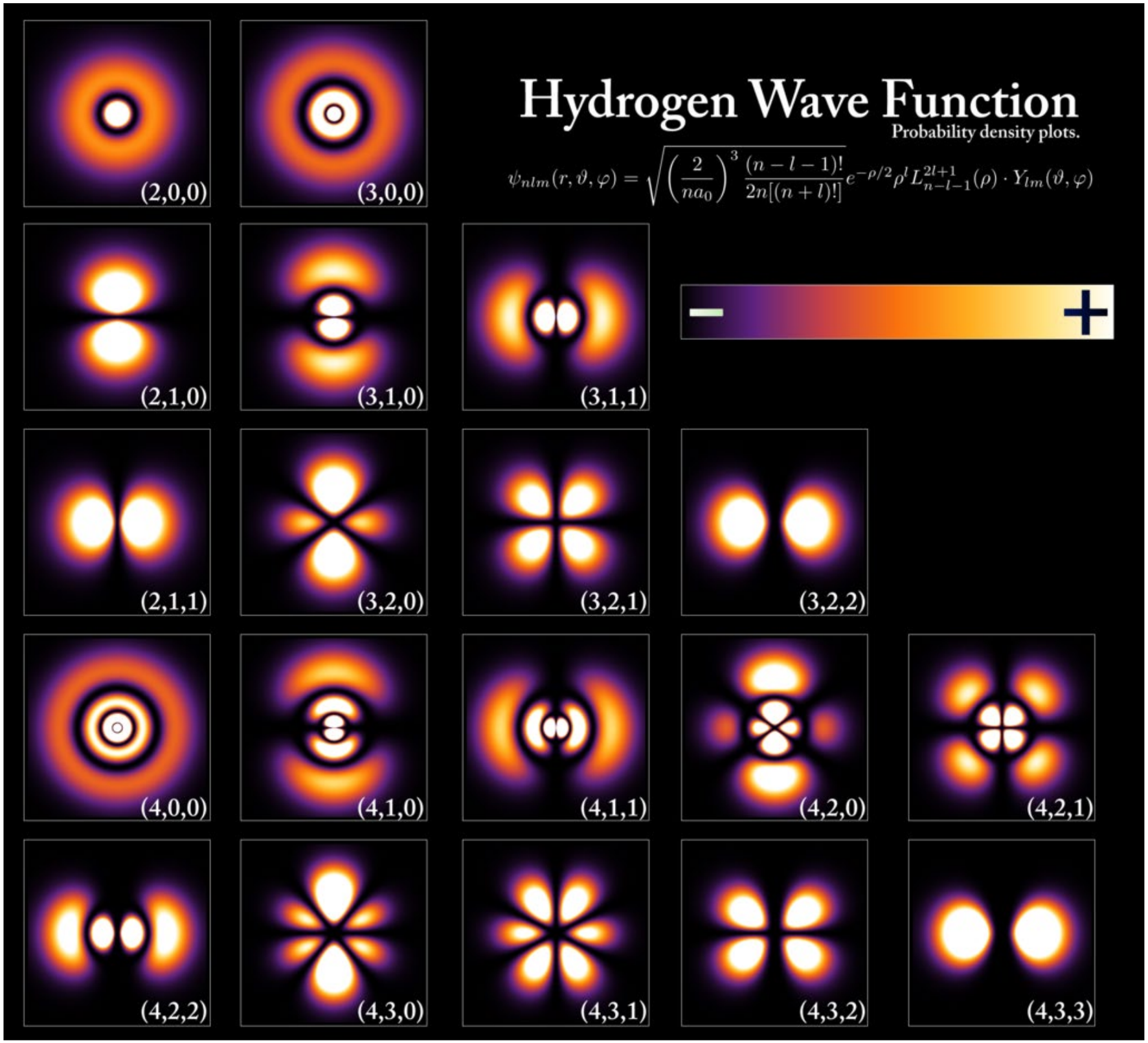
$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

$$\psi_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)$$





Hydrogen Atom



Real-Life Methods

- Coupled cluster method CCSD(T) – “golden standard” in the modern quantum chemistry; scales as $O(N^7)$; limited to ~20-30 atoms
- Quantum Monte Carlo – similar size limitations, very long calculations
- Density-Functional Theory (DFT) – the main “workhorse” in modern simulations of materials and molecules (~40k papers per year)

Exact as a theory but every implementation is approximate

Scales as $O(N^3)$

Codes:

DFT

Up to ~2k atoms

1. ψ(3N coordinates)

↓

Electronic density $\rho(\boldsymbol{r})$

2. Solve self-consistent Kohn-Sham equations (diagonalization of matrix)

3. Energy of the system E

General Properties of 1D SE

One-dimensional time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

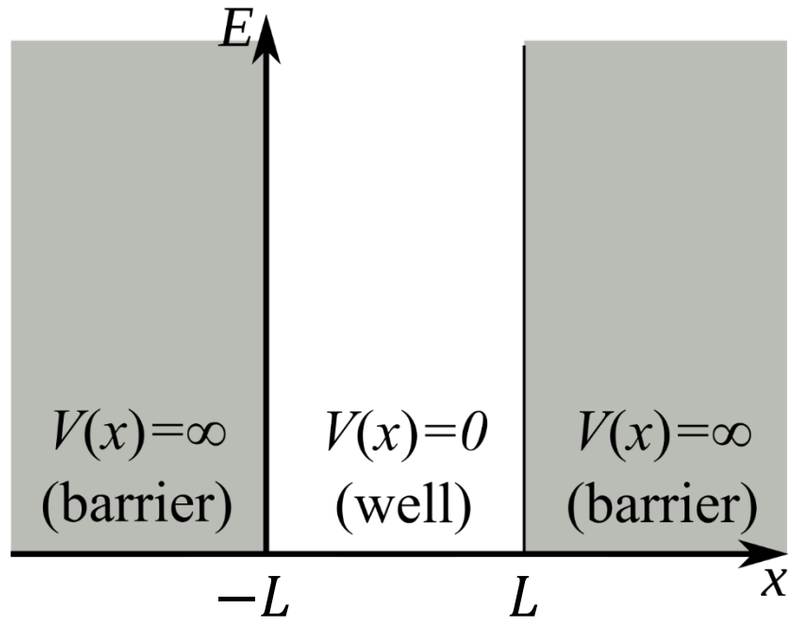
- If $\psi(x)$ is a solution, then $C \cdot \psi(x)$ is also a solution for any $C \in \mathbb{C}$
- The probability density function is given by $P(x) = \psi^*(x)\psi(x) = = |\psi(x)|^2 \longrightarrow$ should be normalized to give $\int_{-\infty}^{+\infty} |\psi(x)|^2\, dx = 1$
- If the potential $V(x)$ is symmetric (i.e. has even parity), then the solution have either even or odd parities
- If we order solutions by their energies E_n, the n^{th} solution $\psi_n(x)$ has $(n-1)$ nodes (i.e. points where $\psi_n(x) = 0$)

Particle in a Box

The simplest possible potential:

$$V(x) = \begin{cases} +\infty, & |x| > L \\ 0, & -L \le x \le L \end{cases}$$

The wave function has to vanish at $x = 0$ and $x = L$



The even solutions:

$$\psi_k(x) = A \cdot \cos(\pi k x / 2L);$$
$$k = 2n - 1; \;\; n \in \mathbb{N}$$

The odd solutions:

$$\psi_k(x) = A \cdot \sin(\pi k x / 2L);$$
$$k = 2n; \;\; n \in \mathbb{N}$$

The energy levels:

$$E_k = \frac{\hbar^2 \pi^2 k^2}{8mL^2}$$

How to Solve Numerically?

$$\psi''(x) + \frac{2mE}{\hbar^2}\psi(x) = 0$$

Looks very similar to the equation for harmonic oscillator

but…

We do not know E in advance. It should be determined consistently with $\psi(x)$ to make the wave function satisfy the boundary conditions:

$$\psi(-L) = \psi(L) = 0$$

Mathematically this is a two-point **boundary value problem**. One possible method to solve such problems is the **shooting method**.

The Shooting Method

Reduce the boundary value problem to the **initial value problem**:

$$\begin{cases} \dfrac{d}{dx}\psi(x) = \psi'(x) \\ \dfrac{d}{dx}\psi'(x) = -\dfrac{2mE}{\hbar^2}\psi(x) \end{cases}$$

Initial conditions:

$$\begin{cases} \psi(0) = \psi_0 \\ \psi'(0) = \psi'_0 \end{cases}$$

$\psi(x)$ are either even or odd, so we can restrict ourselves to the interval $[0, L]$ to reduce the amount of computations. Afterwards the solution can be continued on $[-L, L]$.

"Even" conditions:

$$\begin{cases} \psi(0) = 1 \\ \psi'(0) = 0 \end{cases}$$

"Odd" conditions:

$$\begin{cases} \psi(0) = 0 \\ \psi'(0) = 1 \end{cases}$$

The Shooting Method

The Euler-Cromer integration scheme:

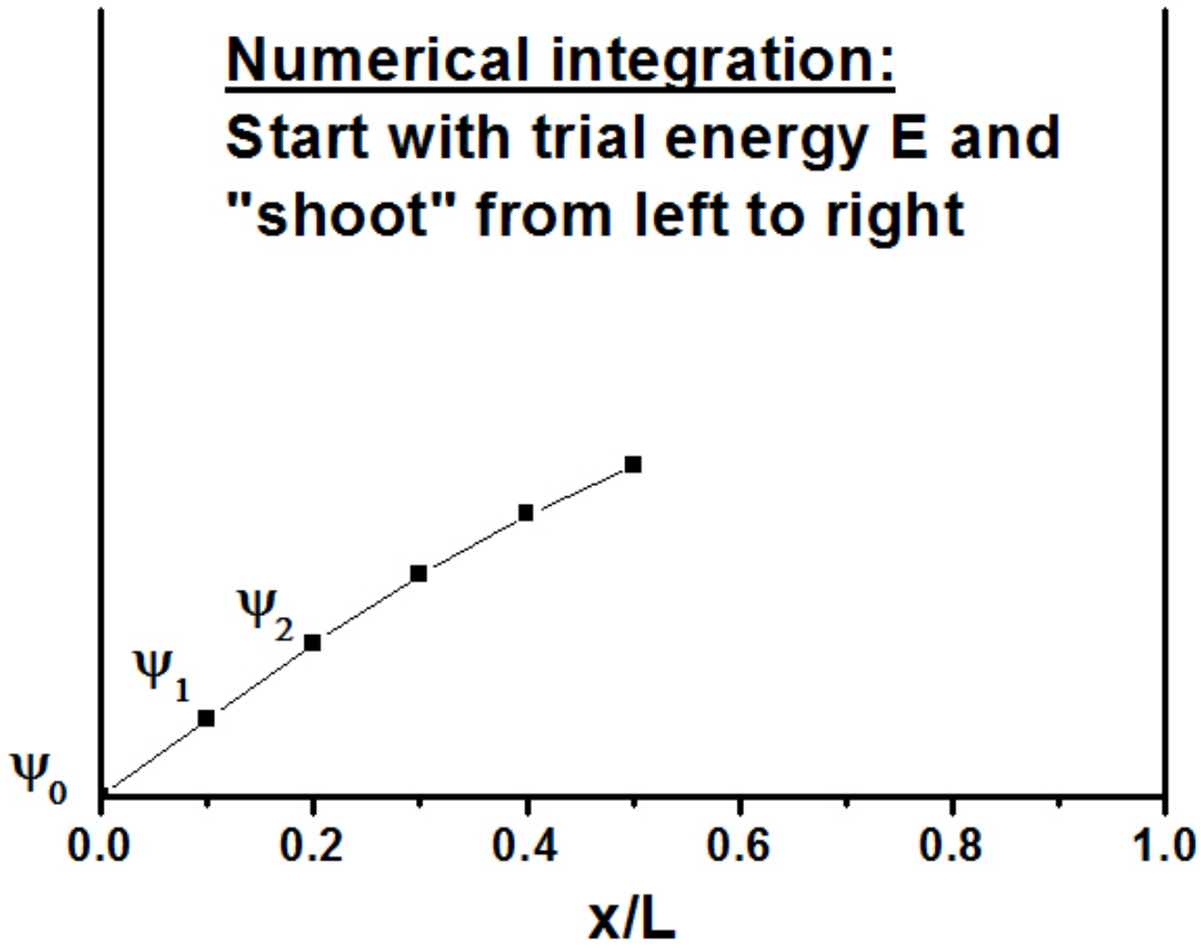
$$\begin{cases} \psi'(x+\Delta x) = \psi'(x) - \dfrac{2mE}{\hbar^2}\psi(x)\Delta x \\ \psi(x+\Delta x) = \psi(x) + \psi'(\boldsymbol{x+\Delta x})\Delta x \end{cases}$$

But we still do not know E…

Solution: fix some trial energy E and just try

Basically, we simply solve two coupled ODEs using our integration scheme.

Our goal: to have $\psi(L) = 0$



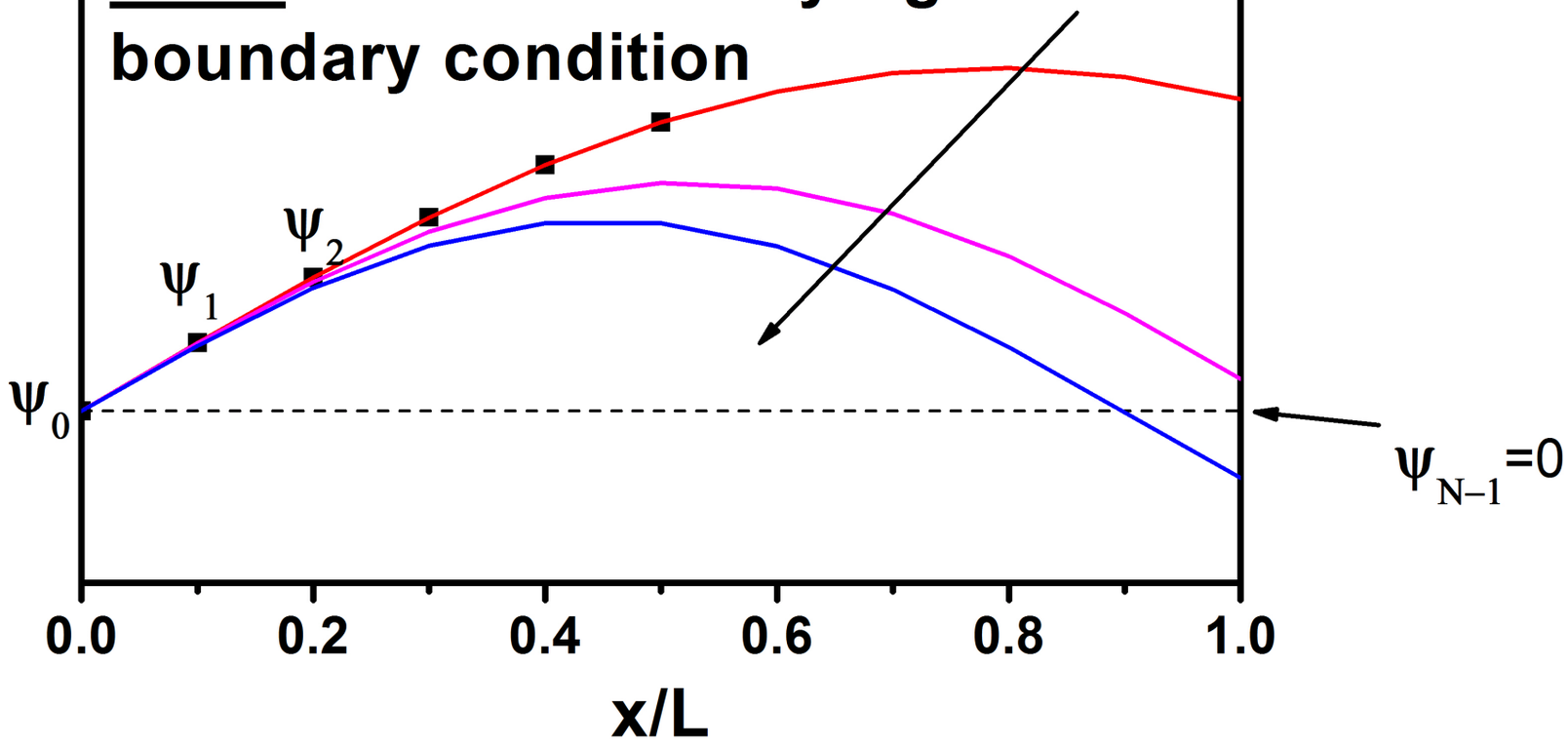
The Shooting Method

Now shoot to the right boundary. Unless your trial energy matches an eigenvalue E_k, $\psi(x)$ will not hit 0 at the right boundary. Need to increment trial energy step by step. When overshooting, need to decrease it with a smaller decrement.

Match right boundary condition:

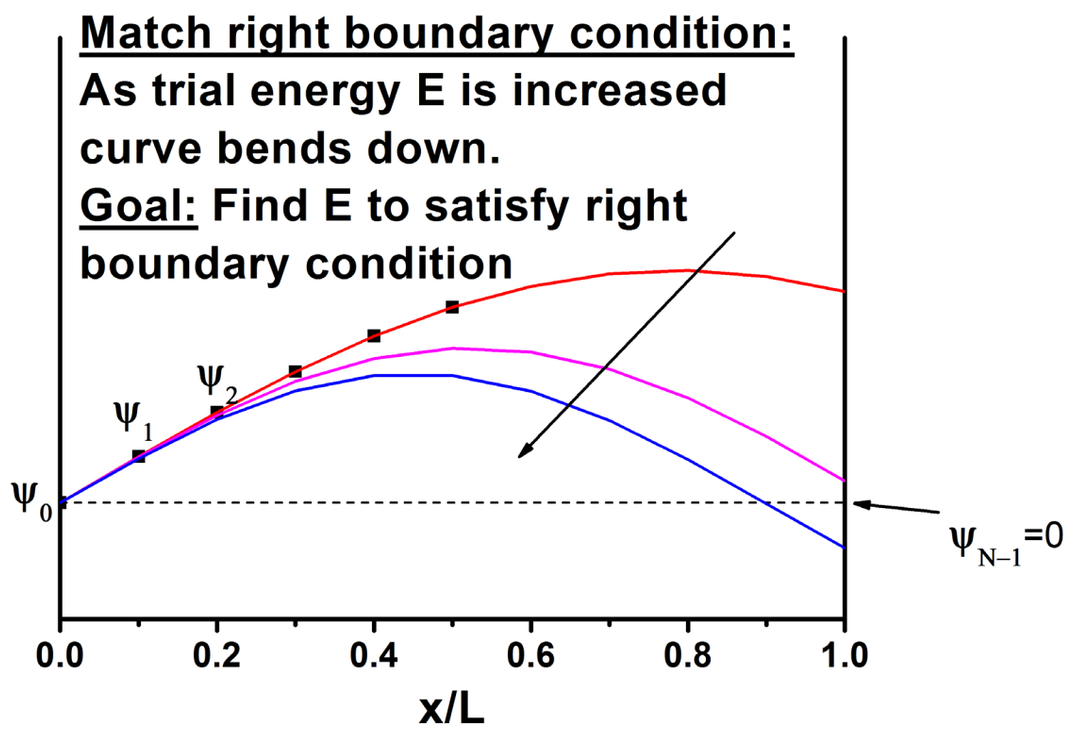
As trial energy E is increased curve bends down.

Goal: Find E to satisfy right boundary condition



The Algorithm

1. Set the trial energy E, choose the initial conditions (even or odd)
2. Make a first "shoot": evaluate $\psi(x)$ on $[0, L]$ using Euler-Cromer
3. Store the value of obtained $\psi(L)$
4. Define the energy increment dE and tolerance $\varepsilon \ll dE$
5. Update $E = E + dE$
6. "Shoot" again with a new E, obtain a new $\psi(L)$
7. If $\tilde{\psi}(L) \cdot \psi(L) < 0$, make $dE = -0.1 \cdot dE$
8. Update $\psi(L) = \tilde{\psi}(L)$
9. Repeat 5) – 8) while $dE > \varepsilon$



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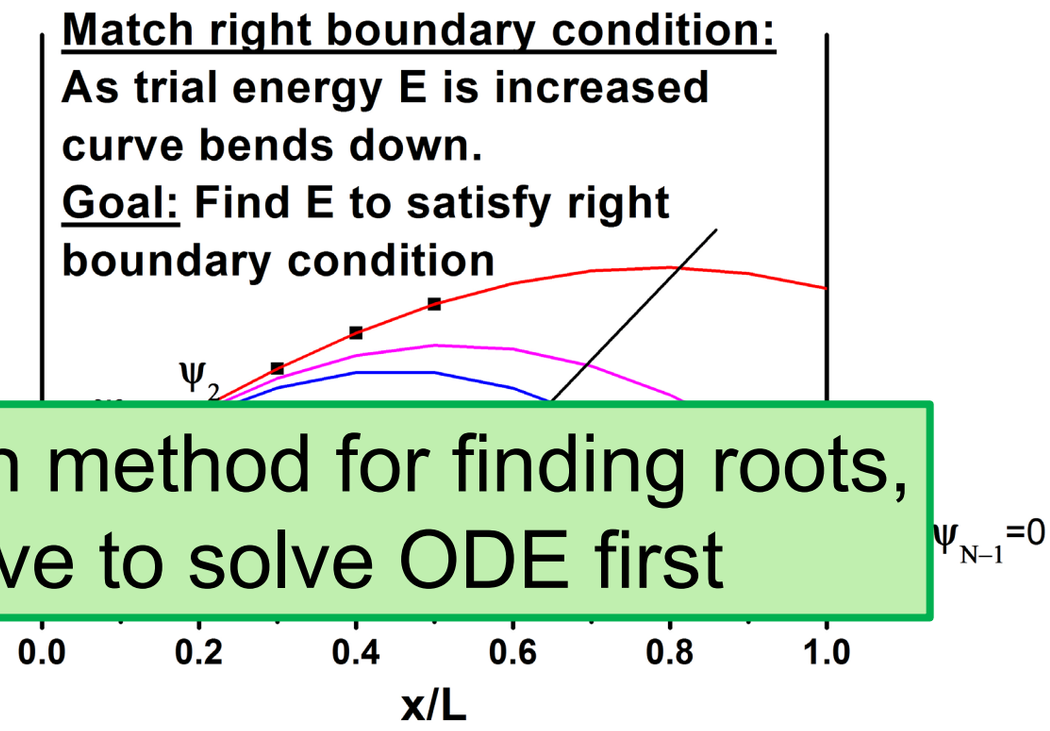

The idea is very similar to the bisection method for finding roots, but to evaluate our function we just have to solve ODE first