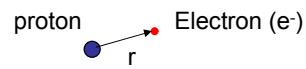


Last class



Classical mechanics

State of the system:

$$\vec{r}(t) \quad \vec{p}(t)$$

Energy:

$$V = \frac{q_i q_j}{r} = -\frac{e^2}{r}$$

$$K = \frac{p^2}{2m} = \frac{1}{2}mv^2$$

Ground state

(minimum energy):

$$r = 0$$

$$E = -\infty$$

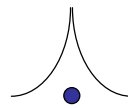
Atoms do not exist!!

Classical mechanics fails: quantum mechanics

State: wave function: $\psi(\vec{r})$

$$\text{Energy: } E = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}$$

Ground state: finite size



The Kinetic energy make atoms stable

Part 1: bonding

- Why we need Quantum Mechanics?
 - The hydrogen atom
- Basic Quantum Mechanics
 - Schrodinger equation and simple solutions
- Electronic structure of atoms
 - Hydrogen and multi-electron atoms
- Bonding in molecules
 - The simplest molecule H₂⁺
 - First row hydrides
 - Covalent, ionic and van der Waals interactions
- Bonding in crystalline solids
 - Band structure
 - Covalent vs. metallic bonding

Quantum mechanics 101: 5 postulates

1. The state of electrons is determined by their wave function

$$\Psi(r, t) \quad \begin{array}{l} \text{We will focus on equilibrium properties:} \\ \text{WF does not depend on time} \end{array} \rightarrow \Psi(r)$$

2. Physical observables \leftrightarrow linear operators

Position $\leftrightarrow \vec{r}$

$$\text{Momentum} \leftrightarrow \vec{p} = \frac{\hbar}{i} \vec{\nabla} = \frac{\hbar}{i} \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

Quantum mechanics 101: 5 postulates

3. Average results of measurements is given by

$$\langle O \rangle = \int \Psi(r) O \Psi(r) d^3 r$$

Example:

$$\langle \vec{r} \rangle = \int \Psi(\vec{r}) \vec{r} \Psi(\vec{r}) d^3 r = \int \vec{r} |\Psi(\vec{r})|^2 d^3 r$$

$$|\Psi(\vec{r})|^2 \quad \begin{array}{l} \text{Probability density of electron} \\ \text{being in volume } d^3 r \text{ around } r \end{array}$$

Quantum mechanics 101: 5 postulates

4. The equilibrium wave function can be obtained from the Schrödinger equation:

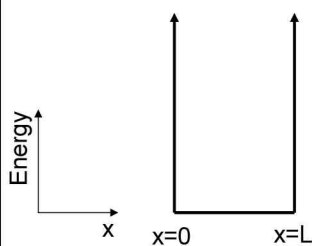
$$H\psi(\vec{r}) = E\psi(\vec{r})$$

5. Pauli's exclusion principle

- Two electrons maximum per orbital
- Electrons in one orbital must have different spin

Let's do an example: infinite potential well

"Particle in a box"



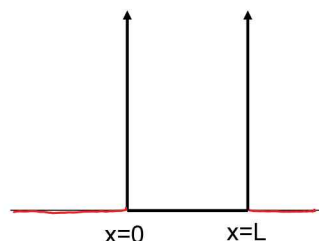
To find the possible states (WFs) of the electron solve Schrödinger Eq:

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x) = E\psi(x)$$

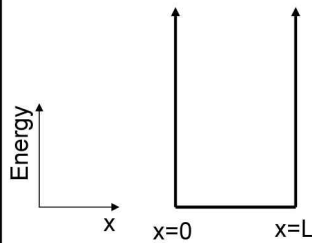
What is the probability of the electron being outside $[0:L]$?

Schrödinger Eq. inside well:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = E\psi(x)$$



Let's do an example: infinite potential well

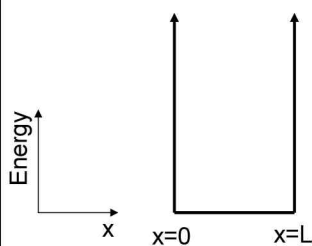


Solve the following differential equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = E \psi(x)$$

$$\psi(x=0) = 0 \quad \psi(x=L) = 0 \quad \text{Boundary condition}$$

Let's do an example: infinite potential well



We have a solution but it need to satisfy the boundary conditions

$$\psi(x) = A \sin(kx)$$

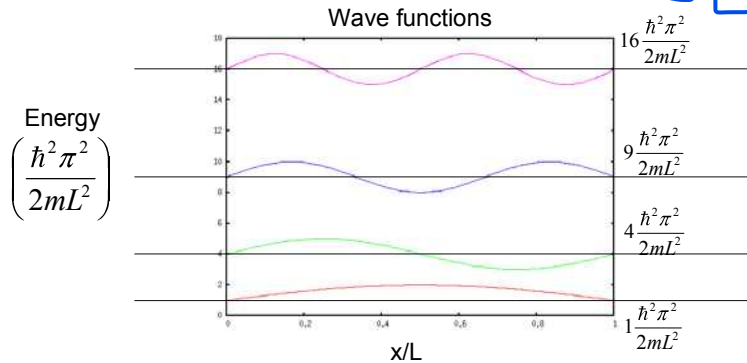
$$\psi(x=0) = 0 \quad \psi(x=L) = 0$$

Let's do an example: infinite potential well

We have a solution but it needs to satisfy the boundary conditions

$$\psi_n(x) = A \sin\left(\frac{n\pi}{L}x\right) \quad E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

node



Quick summary 1

- **5 postulates:**

- a. the state of electrons is determined by WF.
- b. Physical observables are associated with linear operators
- c. Expectation value
- d. Equilibrium WF can be obtained from the S.E.
- e. Pauli's exclusion principle
 - two electrons per orbital
 - one electron per quantum mechanical state

- **Particle in a box**

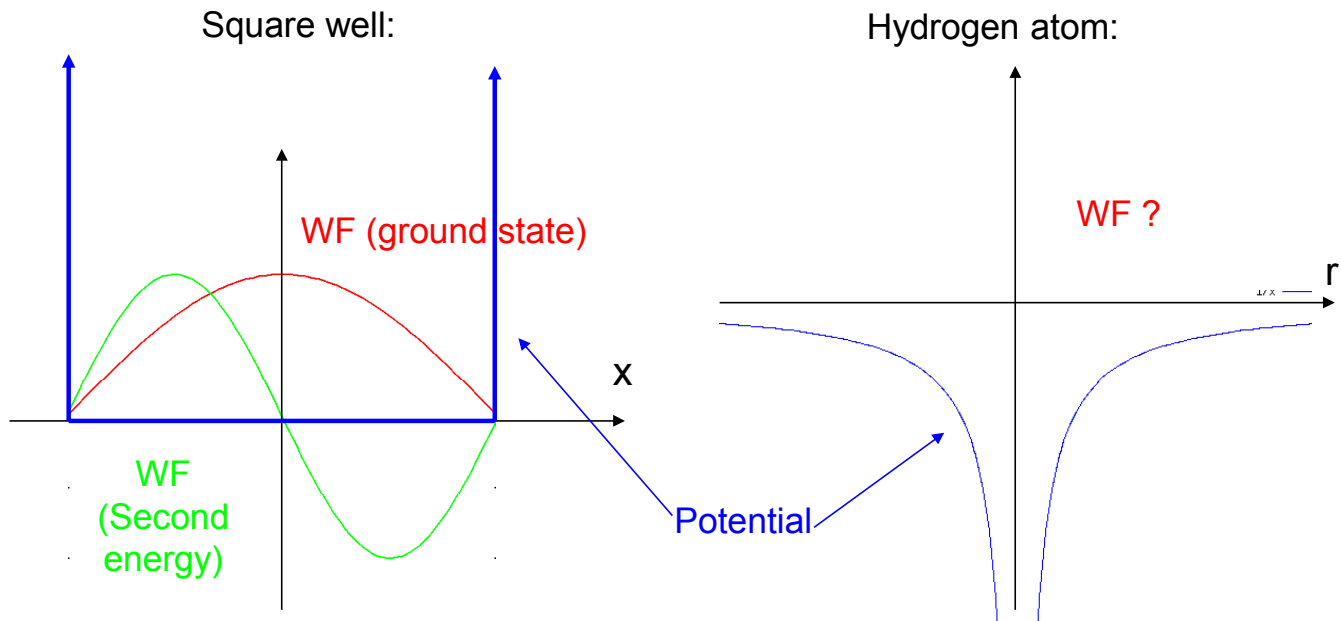
- a. Energy is quantized
- b. There are multiple function & energy pairs that satisfy S.E.
→ (Ψ_n, E_n)
- c. The more wavy WF is, the higher energy it has.

Now a slightly more difficult example: H

The Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{e^2}{|\vec{r}|} \right] \psi(\vec{r}) = E \psi(\vec{r})$$

Let's think what we should get before doing the math



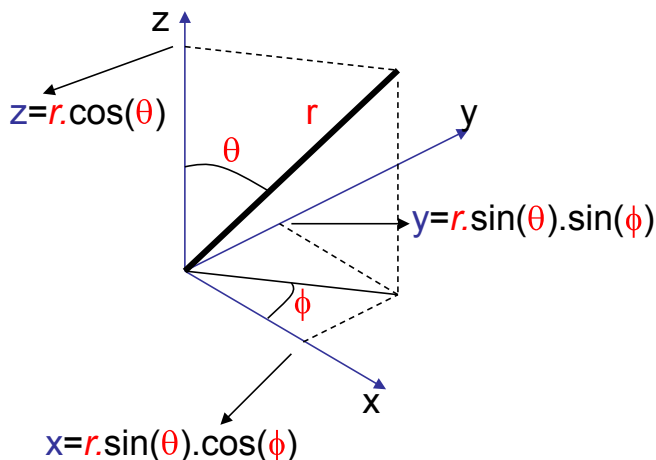
The hydrogen-like atom

Slightly more general problem:
nuclear charge Ze

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{|\vec{r}|} \right] \psi(\vec{r}) = E \psi(\vec{r})$$

The potential only depends on the magnitude of \vec{r} , that is: $r = |\vec{r}|$

So we will use **Spherical Coordinates**



A point in 3D space can be represented by:

- Three Cartesian coordinates x, y, z
- OR

- Or two angles (θ and ϕ) and r

The hydrogen-like atom

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{|\vec{r}|} \right] \psi(\vec{r}) = E \psi(\vec{r})$$

The Schrödinger Eq. in spherical coordinates, need to write the Laplacian in spherical coordinates:

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{\cos \theta}{r^2 \sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) - \frac{Ze^2}{r} \right] \psi(r, \phi, \theta) = E \psi(r, \phi, \theta)$$

We will try the following type of solution (this is called separation of variables):

$$\psi(r, \phi, \theta) = R(r) \Phi(\phi) \Theta(\theta)$$

Before finding a general solution (i.e. all the possible wave functions) we will find the ground state (GS) WF – the one with the lowest energy

We know wiggles increase kinetic energy so GS will have as little wiggles as possible → constant angular part:

$$\Phi(\phi) \Theta(\theta) = 1$$

The hydrogen atom:

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - \frac{Ze^2}{r} \right] R(r) = E R(r)$$

Trial function: $R(r) = A \exp(-r/a)$

$$\frac{\partial R(r)}{\partial r} =$$

$$\frac{\partial^2 R(r)}{\partial r^2} =$$

Now we plug the trial function into the Schrodinger Eq.:

$$= EA \exp\left(-\frac{r}{a}\right)$$

And then:

$$= E$$

Re-ordering some terms:

$$\frac{1}{r} \left(\frac{\hbar^2}{ma} - Ze^2 \right) = E + \frac{\hbar^2}{2ma^2}$$

The hydrogen atom

$$\underbrace{\frac{1}{r} \left(\frac{\hbar^2}{ma} - Ze^2 \right)}_{\text{Depends on } r} = \underbrace{E + \frac{\hbar^2}{2ma^2}}_{\text{Constant}}$$

Only possibility is the both sides are zero:

$$\frac{\hbar^2}{ma} - Ze^2 = 0 \quad \text{and} \quad 0 = E + \frac{\hbar^2}{2ma^2}$$

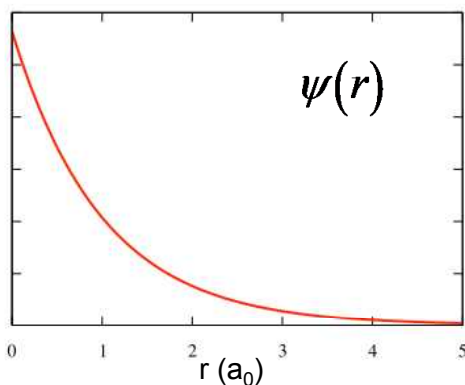
$$a = \frac{1}{Z} \frac{\hbar^2}{e^2 m} = \frac{a_0}{Z} \rightarrow \text{Bohr radius (size of the atom)}$$

$$E = -\frac{1}{2} \frac{\hbar^2}{m} \left(\frac{Ze^2 m}{\hbar^2} \right)^2 = -\frac{1}{2} Z^2 e^2 \frac{e^2 m}{\hbar^2} = -\frac{1}{2} Z^2 \frac{e^2}{a_0}$$

Ground state energy

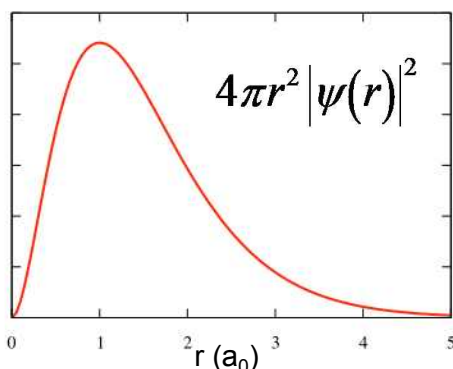
Hydrogen ground state

Ground state wave function: $\psi(r) = A \exp\left(-\frac{r}{a_0}\right)$



Bohr's radius

$$a_0 = \frac{\hbar^2}{e^2 m} = 0.52917704 \text{ \AA}$$



$$E = -\frac{1}{2} \frac{e^2}{a_0} = -13.6058 \text{ eV}$$

Hartree energy:

$$\frac{e^2}{a_0} = 27.21161 \text{ eV}$$

Excited states of Hydrogen

After separation of variables and assuming no angular dependency:

$$\psi(r, \varphi, \theta) = R(r)\Phi(\varphi)\Theta(\theta) \quad \Phi(\varphi) = \Theta(\varphi) = 1$$

We obtain a differential equation for the radial part:

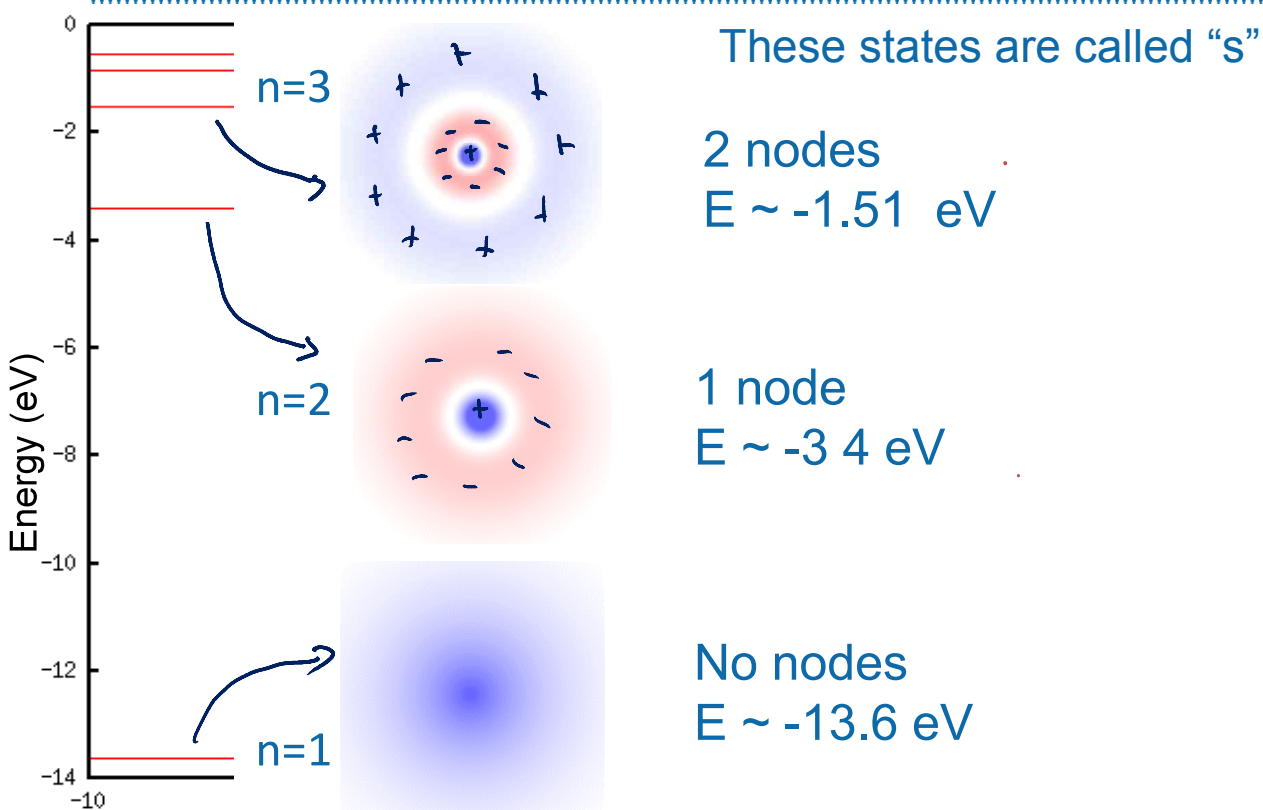
$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - \frac{Ze^2}{r} \right] R(r) = ER(r)$$

As before, there is a family of radial solutions:

$$R_n(r) \quad E_n = -\frac{13.6 \text{ eV}}{n^2} Z^2$$

n is called principal quantum number

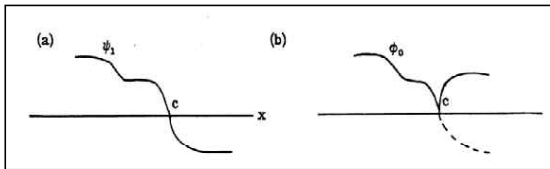
Radial solutions



n is called principal quantum number and denotes the number of nodes in the wave function – more nodes \rightarrow more wiggles \rightarrow more energy

Nodal Theorem

- Energy of φ_0



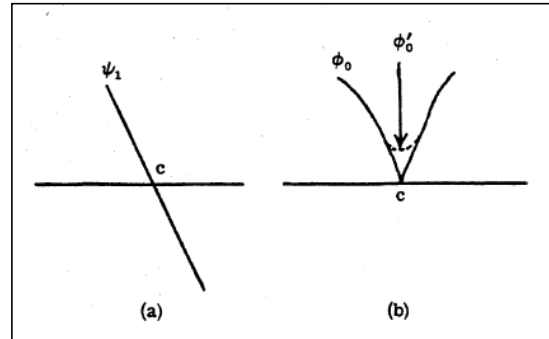
$$\psi_1 = |\varphi_0|$$

$$E_0 = \langle \varphi_0 | H | \varphi_0 \rangle = \left\langle \varphi_0 \left| -\frac{1}{2m} \frac{d^2}{dx^2} \right| \varphi_0 \right\rangle + \langle \varphi_0 | V | \varphi_0 \rangle$$

$$E_1 = \langle \psi_0 | H | \psi_0 \rangle = \left\langle \psi_0 \left| -\frac{1}{2m} \frac{d^2}{dx^2} \right| \psi_0 \right\rangle + \langle \psi_0 | V | \psi_0 \rangle$$

$$E_0 = E_1$$

$$\therefore \left| \frac{d\psi_0}{dx} \right|^2 = \left| \frac{d\varphi_0}{dx} \right|^2, |\varphi_0|^2 = |\psi_0|^2$$

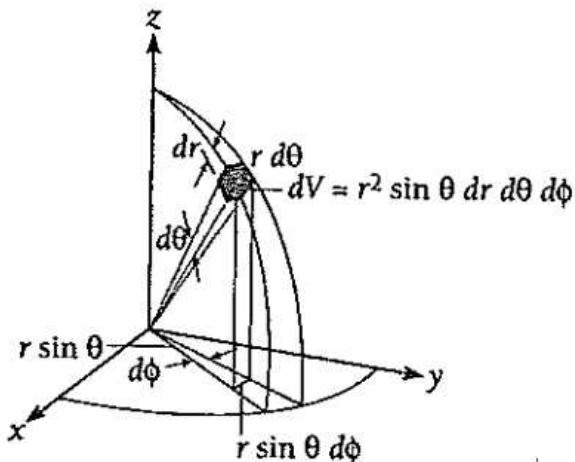


Smoothed in the region very closed to node c

- Choose φ_0' whose potential E is the same as ψ_1 (by normalization)
 φ_0' : Smaller gradient \rightarrow smaller kinetic E
 Thus, $E_1 > E_0$

Normalization of the wave function

$$\int \psi^2(r) dx dy dz = \int A^2 \exp\left(-\frac{r}{r_0}\right) \exp\left(-\frac{r}{r_0}\right) dx dy dz = 1$$



Average potential energy

$$\begin{aligned}\langle V \rangle &= \int_0^\infty 4\pi r^2 \frac{1}{\sqrt{r_0^3 \pi}} \exp\left(-\frac{r}{r_0}\right) \left(\frac{-e^2}{r}\right) \frac{1}{\sqrt{r_0^3 \pi}} \exp\left(-\frac{r}{r_0}\right) dr = \\ &= -\frac{4e^2}{r_0^3} \int_0^\infty r \exp\left(-\frac{2r}{r_0}\right) dr\end{aligned}$$

Quick summary 2

- For WF of hydrogen atom, S.E. with spherical coordinate is necessary
- Solution in spherical coordinate can be separated: product of R, Φ, Θ
- WF and energy are obtained once S.E. is solved.
- Quantified ionization energy of H is exactly same as the one experimentally measured.
- More nodes \rightarrow more wiggle \rightarrow more energy