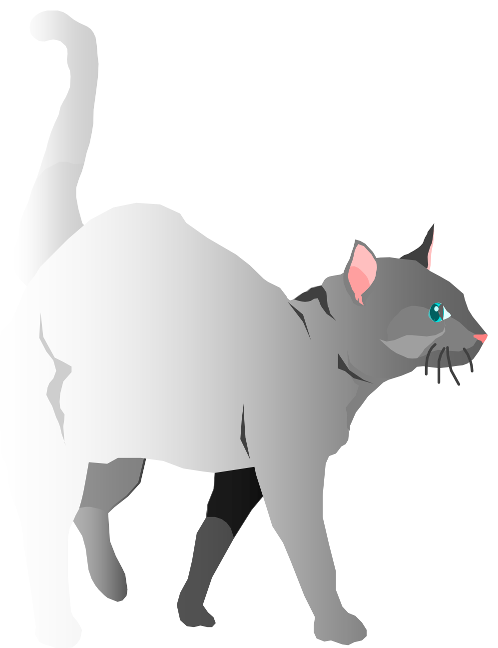
The Schrödinger Equation



Reading: OGN: (15.5 to 15.7)

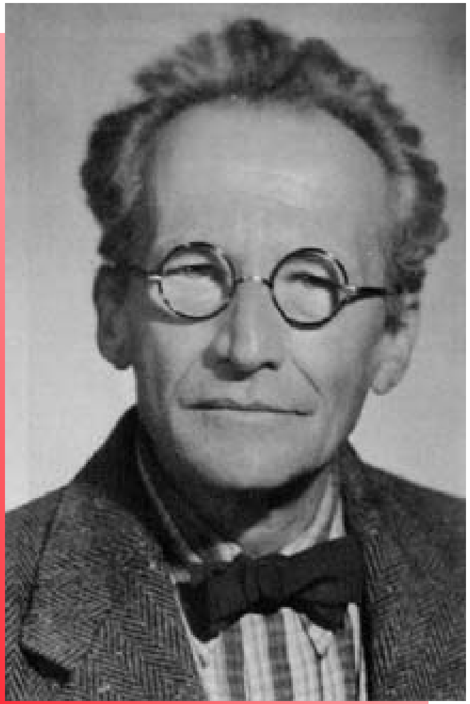
The Person Behind The Science

Erwin Schrödinger

1887-1961

Highlights

- Born and educated in Vienna
- Received Nobel Prize in Physics with Paul Dirac (1933)



Moments in a Life

- In 1927 Schrödinger moved to University of Berlin as Planck's successor
- Develops his wave equation in 1926

The Schrödinger Equation

$$H\Psi = E\Psi$$

- H is the Hamiltonian Operator; you can't "cancel" the Ψ
  - — "Cancelling" the Ψ is like "cancelling" the x in f(x) = mx. You just can't do it.

- Our goal is to <u>operate</u> on Ψ (using the H Operator) and get an energy (E) multiplied by the same Ψ.

Deriving the Schrödinger Equation

- This equation describes the energy of an electron:

Total Energy = Kinetic Energy + Potential Energy

$$E = KE + PE$$

- Start with this classical equation.
- Use classical and quantum mechanical relationships to find the Hamiltonian Operator (H).
- Find values of Ψ that fit the Schrödinger Equation:

$$H\Psi = E\Psi.$$

Describing Kinetic Energy (KE)

Classically:

$$KE = \frac{1}{2}mv^2$$

$$p = mv, \quad \text{so} \quad KE = \frac{p^2}{2m}$$

Quantum Mechanically:

$$p_x = \frac{-ih}{2\pi}\frac{\partial\Psi}{\partial x}$$

— If $f(x,y,z) = x^2+y^3+z^4$,

then $\frac{\partial f}{\partial x} = 2x$ and $\frac{\partial f}{\partial y} = 3y^2$

Combining Equations:

$$KE_x = \frac{p_x^2}{2m} = \frac{\partial^2\Psi}{\partial x^2}\frac{-h^2}{8m\pi^2}$$ (close enough for now!)

$$\text{So } KE = KE_x + KE_y + KE_z = \frac{-h^2}{8m\pi^2}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right)$$

$$= \frac{-\mathbf{h^2}}{\mathbf{8m}\pi^2}\left(\nabla^2\Psi\right)$$

(∇ is a form of mathematical shorthand notation)

Including Potential Energy (PE)

Classically, PE = $\frac{-e^2}{4\pi\varepsilon_o r}$

Quantum Mechanically, PE = $\frac{-e^2}{4\pi\varepsilon_o r}\Psi$

- We will use the quantum mechanical definition of PE.
- From the previous slide, KE $= \frac{-h^2}{8m\pi^2}\left(\nabla^2\Psi\right)$
- So our final equation is:

$$\frac{-h^2}{8m\pi^2}\left(\nabla^2\Psi\right) - \frac{e^2}{4\pi\varepsilon_o r}\Psi = E\Psi$$

- Now, we must find the special Ψ's that are solutions to this equation and also satisfy the boundary conditions.

A Solution to the Schrödinger Equation

We can prove that $\Psi(r) = Be^{-\alpha r}$ is a solution, by plugging it into Schrödinger's equation (ignoring angular derivatives):

$$\frac{-h^2}{8m\pi^2}\left(\frac{\partial^2\Psi}{\partial r^2} + \frac{2}{r}\frac{\partial\Psi}{\partial r}\right) - \frac{e^2}{4\pi\varepsilon_o r}\Psi = E\Psi = EBe^{-\alpha r}$$

- multiplying through by $\left(\frac{-h^2}{8m\pi^2}\right)^{-1}$ gives us:

$$\left(\frac{\partial^2\Psi}{\partial r^2} + \frac{2}{r}\frac{\partial\Psi}{\partial r}\right) + \frac{8m\pi^2}{h^2}\frac{e^2}{4\pi\varepsilon_o r}\Psi = \frac{-8m\pi^2}{h^2}EBe^{-\alpha r}$$

- Now we take the derivatives:

$$\frac{\partial\Psi}{\partial r} = \frac{\partial}{\partial r}Be^{-\alpha r} = -\alpha Be^{-\alpha r} \qquad \frac{\partial^2\Psi}{\partial r^2} = \frac{\partial^2}{\partial r^2}Be^{-\alpha r} = \alpha^2 Be^{-\alpha r}$$

- Plug the derivatives into Schrödinger's Equation:

$$\frac{\partial \Psi}{\partial r} = -\alpha B e^{-\alpha r} \qquad\qquad \frac{\partial^2 \Psi}{\partial r^2} = \alpha^2 B e^{-\alpha r}$$

$$\alpha^2 B e^{-\alpha r} - \frac{2}{r}\alpha B e^{-\alpha r} + \frac{8m\pi^2}{h^2}\frac{e^2}{4\pi\varepsilon_o r} B e^{-\alpha r} = \frac{-8m\pi^2}{h^2} E B e^{-\alpha r}$$

- Cancel $Be^{-\alpha r}$: $\alpha^2 - \frac{2}{r}\alpha + \frac{8m\pi^2}{h^2}\frac{e^2}{4\pi\varepsilon_o r} = \frac{-8m\pi^2}{h^2}E$

- Combining similar terms gives:

$$\left[\alpha^2 + \frac{8m\pi^2}{h^2}E\right] + \frac{1}{r}\left[\frac{2e^2 m\pi}{h^2\varepsilon_o} - 2\alpha\right] = 0$$

These sum to zero for all r only if both terms are zero

•Set both terms to zero:

$$\left[\alpha^2 + \frac{8m\pi^2}{h^2}E\right] + \frac{1}{r}\left[\frac{2e^2m\pi}{h^2\varepsilon_o} - 2\alpha\right] = 0$$

$$\alpha^2 + \frac{8m\pi^2}{h^2}E = 0$$

$$\frac{2e^2m\pi}{h^2\varepsilon_o} - 2\alpha = 0$$

$$\frac{8m\pi^2}{h^2}E = -\alpha^2$$

$$E = \frac{-h^2\alpha^2}{8m\pi^2}$$

$$\alpha = \frac{e^2m\pi}{h^2\varepsilon_o} = \frac{1}{a_0}$$

•Now set $\alpha = \frac{e^2m\pi}{h^2\varepsilon_o} = \frac{1}{a_0}$

$$E = \frac{-h^2}{8m\pi^2}\,\frac{e^4m^2\pi^2}{h^4\,\varepsilon_o^2} = \frac{-e^4m}{8h^2\,\varepsilon_o^2}$$

$$E = \frac{-e^2}{8\pi\varepsilon_o a_0}$$

So, We Find One Solution

- $\Psi(r) = Be^{-\alpha r}$ is a solution to the Schrödinger Equation:

$$\alpha = \frac{1}{a_0} \quad \text{and} \quad E = \frac{-e^2}{8\pi\varepsilon_o a_0}$$

- Because the probability of finding the e^- must be 1.0 if we look over all space:

$$B = \sqrt{\frac{1}{\pi a_0^{3}}}$$

- Other functions of the form $(Ar^2 - Br - C)e^{-\alpha r}$ also work:
- $E = \frac{1}{n^2}\frac{-e^2}{8\pi\varepsilon_o a_0}$ where the order of the polynomial is (n+1).
- Additional work is required to determine the time dependence of any given solution to the Schrödinger equation

Review

- **We can only speak of the <u>probability</u> of finding an electron somewhere**
- **A collection of such probabilities, for an electron at a given energy, is called an <u>orbital</u>**
- **Orbitals are described mathematically by <u>wavefunctions</u>, $\Psi(r,\theta,\phi,t)$**
- **<u>Square</u> Ψ to find the <u>probability</u> of observing the electron at a given point**
- **<u>Operate</u> on Ψ (Schrödinger eqn, $H\Psi=E\Psi$) to find the <u>energy</u> of the electron in that orbital**

Wavefunctions Cont'd

- **Fewer Nodes = Lower Energy**
- **n = (total # of nodes + 1)**
- **ℓ = (# of angular nodes)**
- **ℓ=0 (s); ℓ=1 (p); ℓ=2 (d); ℓ=3 (f)**
- **m, the "index," runs from -ℓ to +ℓ and tells us how many orbtials are needed to form a degenerate set in 3-dimensions**
- **Bigger n; bigger orbital; same ℓ, same shape**
- **Know how to sketch the shapes of the various orbitals**

Now We Can Understand

- Arrangement of the Periodic Table of Elements
- Trends in Atomic Size
- Trends in Ionization Energy
- Trends in Electron Affinity
- Trends in Electronegativity
- Various Types of Chemical Bonds
- Shapes of Molecules

END

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