



Chem 2430

Where is QM important in Chemistry and material science?

- All spectroscopy: electronic, vibrational, rotational, ESR, NMR, scattering, diffraction.
- Intermolecular interactions: e.g., van der Waals interactions
- Electron transfer processes
- Tunneling
- Vision

What experimental observations led to quantum mechanics?

- Black body radiation
- Photoelectric effect
- Discrete lines in spectra
- Heat capacity of solids
- Double slit experiment (book *Through Two Doors at Once*)
- Observation of tunneling

Brief history of evolution of QM

| | |
|----------------------------|--|
| Planck (1900-1901) | Blackbody radiation problem |
| Einstein (1905) | Photoelectric effect |
| Rutherford (1911) | Planetary model of atom |
| Bohr (1913) | Transitions of H atom $\Delta E = h\nu$ |
| Stern-Gerlach expt. (1922) | Demonstration of electron spin |
| de Broglie (1923) | Wave behavior of particles $\lambda = \frac{h}{p}$ |
| Heisenberg + Born (1925) | Matrix mechanics approach to QM |
| Davisson-Germer (1927) | Diffraction of electrons: wave particle duality |
| Schrödinger (1926) | Schrödinger Eq. |
| Heisenberg (1927) | Uncertainty Principle |

Blackbody radiation problem

Classical theory does not correctly predict correct current (I) vs. frequency (ν) curve of a blackbody object

Planck obtained a good fit of expt. I vs. ν curve.

Assumed that a blackbody object can be described by a set of oscillators that adsorb/emit energies $nh\nu$, where n is an integer

$$h = 6.6 \times 10^{-34} \text{ J/s} \quad (\hbar = h / 2\pi)$$

Electromagnetic waves travel at:

$$c = \nu\lambda, \text{ where } c = 2.998 \times 10^8 \text{ m/s}$$

Photoelectric Effect

Einstein: light has particle-like behavior with

$$E_{\text{photon}} = h\nu = \Phi + T,$$

$$T = \text{KE}, \Phi = \text{work function}$$

Uncertainty Princ.

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

Time dependent SE in one dimension

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right] \Psi, \quad \text{where } \Psi = \Psi(x,t) \text{ and } V = V(x,t)$$

Solution of this problem requires finding $\Psi(x,t)$ that satisfies the Eq.

Ψ is the wave function which, in general, is complex.

What is actually observable is $\Psi^* \Psi$ (associated with probability)

$$* \Rightarrow i \rightarrow -i, \text{ where } i = \sqrt{-1}$$

probabilities must be real
and positive

Note: if z is a complex number $= x + iy$

$$|z|^2 = (x - iy)(x + iy) = x^2 + y^2 \quad \text{real, positive}$$

This is equally true of functions.

$$|\Psi|^2 dx = \Psi^* \Psi dx$$

= probability at time t of particle being between x and $x+dx$

Slide 6

A2 "motivating" the SE
Author, 7/11/2019

Example from text $\Psi = ae^{-bx^2}$

x can take on any value, with $x=0$ being most probable

Question: Can we get the distribution by doing repeated measurements on the same system?

To get the distribution, we need to do many measurements of many identical systems

The text motivates the SE using results from optics

Probably more familiar to us would be a “derivation” based on a vibrating string.

A guitar string can vibrate at its fundamental frequency or at various overtones of the fundamental (Can also vibrate in a linear combination of the fundamental and various overtones).

What is responsible for this behavior?



Back to the SE

Suppose $V=V(x)$ (no time dependence)

Can we find a solution of the form $\Psi(x,t)=f(t)\psi(x)$?

If we can, we say that Ψ is **separable**

After rearrangement

$$-\frac{\hbar}{i} \frac{1}{f} \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V$$



no x dependence



no t dependence

So we can set this equal to a constant, which we choose to be E

$$-\frac{\hbar}{i} \frac{1}{f} \frac{df}{dt} = E \rightarrow \frac{df}{f} = \frac{-i}{\hbar} E dt$$

integrate

$$\ln(f) = -\frac{iE}{\hbar} t + c \rightarrow f = e^c e^{-\frac{iEt}{\hbar}} = A e^{-\frac{iEt}{\hbar}}$$

We now consider the equation in the variable x

$$\underbrace{-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2}}_{\text{"KE"}} + \underbrace{V\psi}_{\text{"PE"}} = \underbrace{E\psi}_{\text{Total E}} \quad \text{when } V \text{ is independent of } t$$

This is the time-independent SE with solution $\psi(x)$

The QM Hamiltonian operator for a one-particle, one-dimensional problem is:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V$$

So we have $H\psi = E\psi$

In general not all E 's are possible: The solution of the time-independent SE determines both E and ψ

If we combine the wave functions from the t and x equations we obtain

$$\Psi(x, t) = e^{-\frac{iEt}{\hbar}} \psi(x)$$
$$\Psi^* \Psi = \psi^*(x) \psi(x) \quad \left| \quad |\Psi(x, t)|^2 = |\psi(x)|^2\right.$$

Stationary state: probability density independent of t

Suppose: $H\psi_1 = E_1\psi_1$
 $H\psi_2 = E_2\psi_2$ } two different stationary states

Now suppose that we prepare the system in a superposition of ψ_1 and ψ_2 , i.e.

$$\psi = c_1\psi_1 + c_2\psi_2$$

$$H\psi = c_1H\psi_1 + c_2H\psi_2 = c_1E_1\psi_1 + c_2E_2\psi_2$$

$$\neq \text{constant } (c_1\psi_1 + c_2\psi_2)$$

This is not a stationary state

Do you know of any realizations of this in either the classical world or in QM?

More on Probability

We related $|\psi|^2$ to probability

If ψ is normalized

$$\int_{-\infty}^{\infty} |\psi|^2 dx = 1$$

Assuming we have normalized ψ , then the probability of finding the particle between $x = a$ and $x = b$ is

$$\int_a^b |\psi|^2 dx$$

Note that if ψ is not normalized the probability can be expressed as:

$$\int_a^b |\psi|^2 dx \bigg/ \int_{-\infty}^{\infty} |\psi|^2 dx$$

Normalization can always be done

write $\tilde{\psi} = N\psi$

$$|\tilde{\psi}|^2 = |N|^2 |\psi|^2$$

$$|N|^2 \int_{-\infty}^{\infty} |\psi|^2 dx = 1$$

$$N = \frac{1}{\sqrt{\int_{-\infty}^{\infty} |\psi|^2 dx}}$$

More On Complex Numbers

We already mentioned that we can write a complex number z as:

$$z = x + iy$$

We can also write it as:

$$z = |z|e^{i\theta} = re^{i\theta}$$

$$e^{i\theta} = \cos\theta + i\sin\theta$$

$$x = r\cos\theta, \quad y = r\sin\theta$$

