CHAPTER NUMBER 7: Quantum Theory: Introduction and Principles

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Art PowerPoints

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7.1 Energy quantization

- -Feature of classical physics
- Precisely specified motion and momenta at an instant
- Continuous vibrational, rotational, and translation modes of motion and enenrgy

classical physics doesn't hold for a small world

- -Failure of classical physics
- black body radiation & the Planck distribution
- Heat capacities
- Atomic and molecular spectra

Physical Chemistry Fundamentals: Figure 7.1



Physical Chemistry Fundamentals: Figure 7.2



One of blackbody: Nuclear Reactor



Black body radiation



Energy density $\downarrow \\ \varepsilon(T) = \int_0^\infty \rho(\lambda, T) d\lambda$ $E(T) = V\varepsilon(T)$

0 1 T

 $d\varepsilon(\lambda,T) = \rho(\lambda,T)d\lambda$ \uparrow Density of state

Classical model:
$$\rho(\lambda, T) = \frac{8\pi \kappa T}{\lambda^4}$$

Rayleigh-Jeans law

-Energy distribution of black body (experiment)



Physical Chemistry Fundamentals: Figure 7.5



Figure 7.6

-Rayleigh-Jeans law:



 $d\mathcal{E} = \rho \, d\lambda \qquad \rho = \frac{8\pi kT}{\lambda^4}$ based on classical mechanics

As $\lambda \to 0$, $\rho \to \infty$: everything in the dark will glow (UV catastrophe)

Planck distribution: Figure 7.7



Planck distribution:

$$\rho(\lambda,T) = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kt} - 1)}$$

based on quantization of energy

$$E = nhv$$
 $n = 0, 1, 2, ...$

$$As \lambda \to 0, \rho \to 0$$

2. For long
$$\lambda$$
,

$$\frac{8\pi hc}{\lambda^{5}(e^{hc/\lambda kt}-1)} \rightarrow \frac{8\pi kT}{\lambda^{4}}$$

(for large λ , $e^{hc/\lambda kt} - 1 \rightarrow \frac{hc}{\lambda kT}$)
3. Stefan-Boltzmann Law $\mathcal{E} = aT^{4}$
 $\approx \frac{8\pi hc}{\lambda^{5}(e^{hc/\lambda kt}-1)} d\lambda = aT^{4} \left(a = \frac{8\pi^{5}k^{4}}{15(hc)^{3}}\right)$

-Rayleigh-Jeans law: UV catastrophe

based on classical mechanics (all oscillators share equally in the energy)

-Planck distribution:

based on quantization of energy E=nhv(oscillators are excited only if they can acquire an energy of at least hv.)

Stefan-Boltzmann and Wien law is successfully derived from Planck distribution!!!

-heat capacities (close to 0K)

 C_v =3R (from U_m =3RT) However, this deviates as T \rightarrow 0

Einstein assumes

each atom oscillates with a single freq.

and the deviation can be successfully explained (E is confined to discrete values: E=nhv)

$$U_{\rm m} = 3N_{\rm A}kT = 3RT$$

$$U_{\rm m} = \frac{3N_{\rm A}h\nu}{e^{h\nu/kT} - 1}$$

$$C_{\rm V,m} = \left(\frac{\partial U_{\rm m}}{\partial T}\right)_{\rm V} = 3R$$

$$The Einstein temperature, \theta_{\rm E} = h\nu/k,$$

$$C_{\rm V,m} = 3Rf^2 \qquad f = \frac{\theta_{\rm E}}{T} \left(\frac{e^{\theta_{\rm E}/2T}}{e^{\theta_{\rm E}/T} - 1}\right)$$

At high T (T>> θ_E),

$$f = \frac{\theta_{\rm E}}{T} \left\{ \frac{1 + \theta_{\rm E}/2T + \cdots}{(1 + \theta_{\rm E}/T + \cdots) - 1} \right\} \approx 1 \qquad \text{san}$$

same as classical theory

At low T (T<< θ_E),

$$f \approx \frac{\theta_{\rm E}}{T} \left(\frac{{\rm e}^{\theta_{\rm E}/2T}}{{\rm e}^{\theta_{\rm E}/T}} \right) = \frac{\theta_{\rm E}}{T} {\rm e}^{-\theta_{\rm E}/2T}$$

as
$$T \rightarrow 0, \, f_E \rightarrow 0$$

Debye formula: atoms oscillate over a range of frequencies



$$C_{V,m} = 3Rf$$
 $f = 3\left(\frac{T}{\theta_{\rm D}}\right)^3 \int_0^{\theta_{\rm D}/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$



Figure 7.8

Figure 7.9

-Atomic and molecular spectra

-Atomic spectra: Radiation emitted by excited iron atom

Emission intensity 420 415 Wavelength, λ /nm -Molecular spectra: Absorbing radiation at definite frequencies due to electronic, vibrational, and rotational excitation of SO₂.



Spectroscopic transition



 $\Delta E = hv$

11.2 Wave particle duality

-Photoelectric effect: particle character of electromagnetic radiation wave-like particle (photon)

-Diffraction: wave character of particles (de Broglie wave)

-particle character of electromagnetic radiation



Photoelectric effect

- 1. No e⁻ are ejected below a threshold freq.
- -> phtoelectric effects occur only when $hv>\Phi$
- 2. E_k of ejected e⁻ increases linearly w/ freq of incident radiation
- $\rightarrow \Delta E = hv$
- 3. Even at low light intensities, e⁻ are ejected above a threshold freq.
- ->e- appears once the collision happens

Physical Chemistry Fundamentals: Figure 7.14





-De Broglie relation



 $\lambda = \frac{h}{p}$

How short? for electron, 10⁻¹² m See Ex 7.2

Figure 7.16

Physical Chemistry Fundamentals: Figure 7.17





Scanning Probe Microscopy



7.3 Shrödinger equation

For 1-d systems:
$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi = E\Psi$$

For 3-d systems:
$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = E\Psi$$

In general,
$$H\Psi = E\Psi \qquad H = -\frac{\hbar^2}{2m}\nabla^2 + V(x)$$

H : Hamiltonian operator

Time-dep Shrödinger eqn. $H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$

Table 7.1

Table 7.1 The Schrödinger equation

For one-dimensional systems

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

Where V(x) is the potential energy of the particle and E is its total energy. For three-dimensional systems

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

where *V* may depend on position and ∇^2 ('del squared') is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In systems with spherical symmetry three equivalent forms are

$$\nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \Lambda^2$$
$$= \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2$$
$$= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2$$

where

$$\Lambda^2 = \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta}$$

In the general case the Schrodinger equation is written

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

where \hat{H} is the hamiltonian operator for the system:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$$

For the evolution of a system with time, it is necessary to solve the time-dependent Schrödinger equation:

$$\hat{H}\Psi = i\hbar \frac{\partial\Psi}{\partial t}$$

Using the Schrödinger eqn to develop the de Broglie relation,





Since E-V is equal to E_k

$$k = (2mE_{\rm K}/\hbar^2)^{1/2},$$

$$E_{\rm K}=k^2\hbar^2/2m.$$

$$E_{\rm K}=p^2/2m$$





7.4 The Born interpretation of the wavefunction

-Normalization -Quantization

Born interpretation of the wave function

Probability of finding a particle between x and x+dx

$$\psi^*\psi = |\psi|^2$$



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

If the wavefunction of a particle has the value ψ at some point r, then the probability of finding the particle in an infinitesimal volume $d\tau = dx dy dz$ at that point is proportional to $|\psi|^2 d\tau$.



Figure 7.19



Figure 7.20

Normalization

$$N^{2} \int \psi^{*} \psi \, dx = 1$$
$$N = \frac{1}{\left[\int \psi^{*} \psi \, dx \right]^{1/2}}$$

For a normalized wavefunction,

$$\int \psi^* \psi \, dx = 1 \qquad \int \psi^* \psi \, dx \, dy \, dz = 1$$

(or $\int \psi^* \psi \, d\tau = 1$)





Figure 7.21

Figure 7.22

Example 11.4 Normalizing a wavefunction

Normalize the wavefunction used for the hydrogen atom in Example 11.3.

Method We need to find the factor *N* that guarantees that the integral in eqn 20 is equal to 1. Because the wavefunction is spherically symmetrical, we work in spherical polar coordinates. A useful integral for calculations on atomic wavefunctions is

$$\int_0^\infty x^n e^{-ax} \, \mathrm{d}x = \frac{n!}{a^{n+1}}$$

where n! denotes a factorial: $n! = n(n - 1)(n - 2) \cdots 1$.

Answer The integration required is

$$\int \psi^* \psi \, d\tau = N^2 \int_0^\infty r^2 e^{-2r/a_0} \, dr \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi$$

$$= N^2 \times \frac{1}{4} a_0^3 \times 2 \times 2\pi = \pi a_0^3 N^2$$

Therefore, for this integral to equal 1,

$$N = \left(\frac{1}{\pi a_0^3}\right)^{1/2}$$

and the normalized wavefunction is

$$\Psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

Quantization [1]



Since it is 2nd derivative. But, delta ftn is valid!



A particle may possess only certain energies, for otherwise its wave function would be physically unacceptable

7.5 The information in a wavefunction

- -the probability density distribution
- -Eigenvalues and eigenfunctions
- -Construction of operators
- -Hermittian operators
- -Superpositions and expectation values

The information in a wave function

When V=0,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

Solution:

$$\psi = Ae^{ikx} + Be^{-ikx}, \ E = \frac{k^2\hbar^2}{2m}$$

(a) The probability density if B=0, $\psi = Ae^{ikx}$

Then, where is the particle?

$$\left|\psi\right|^{2} = \left(Ae^{ikx}\right)^{*}\left(Ae^{ikx}\right) = \left(A^{*}e^{-ikx}\right)\left(Ae^{ikx}\right) = \left|A\right|^{2}$$

Equal probability of finding the particles



Figure 7.24 a

if A=B,
$$\psi = A\left(e^{ikx} + e^{-ikx}\right) = 2A\cos kx$$

Then, where is the particle?

$$\left|\psi\right|^{2} = \left(2A\cos kx\right)^{*} \left(2A\cos kx\right) = 4\left|A\right|^{2}\cos^{2} kx$$

Node: particles will never be found



Figure 7.24 b

The probability density

$= |wavefunction|^2 = |waveamplitude|^2$

 $=\left|\psi\right|^{2}$

(b) Operators, Eigenvalues and eigenfunctions

•operator
$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

$$H\psi = E\psi$$
 H: hamiltonian (operator)
-total E of a system
Eigenvalue

•Eigenvalue equation

(Operator)(same function)=(constant factor)X(same function)

Ex. (Energy Operator) $X\psi = (energy)X\psi$

(Operator corresponding to an observable) ψ =(constant factor) ψ

Illustration for orthogonality of eigen functions



$$f(x) = (\sin x)(\sin 2x)$$

Area = 0

(c) Construction of Operators

Observables are represented by operators,



$$V = \frac{kx^{2}}{2} \qquad \hat{V} = \frac{kx^{2}}{2} \times$$

$$E_{k} = \frac{p_{x}^{2}}{2m} \qquad E_{k} = \frac{1}{2m} \left(\frac{\hbar d}{idx}\right) \left(\frac{\hbar d}{idx}\right) = -\frac{\hbar^{2}}{2m} \frac{d^{2}}{dx^{2}}$$

$$\hat{H} = \hat{E}_{k} + \hat{V}(x) = -\frac{\hbar^{2}}{2m} \frac{d^{2}}{dx^{2}} + \hat{V}(x)$$
High curvature, high kinetic energy
$$Iow curvature, low kinetic energy$$

KE of a particle is an average contribution from the entire space.



Figure 7.26

Wave ftn of a particle in a potential decreasing towards right



Figure 7.27

Physical Chemistry Fundamentals: Figure 7.28



(d) Hermitian operators

Hermiticity

$$\int \psi_i^* \Omega \psi_j d\tau = \left(\int \psi_j^* \Omega \psi_i d\tau \right)^*$$

Orthogonality...

$$\int \psi_i^* \psi_j d\tau = 0$$

(e) Superpositions and expectation values

Ex. if $\psi = A \cos kx$

$$\frac{\hbar}{i}\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{2\hbar}{i}A\frac{\mathrm{d}\cos kx}{\mathrm{d}x} = -\frac{2k\hbar}{i}\dot{A}\sin kx$$

not an eigenfunction any more!!!

When the wavefunction of a particle is not an eigen function of an operator, the property to which the operator corresponds does not have a definite value.

	$\psi = \psi_{\rightarrow}$ Particle with linear momentum $+k\hbar$	+ ψ_{\leftarrow} Particle with linear momentum $-k\hbar$	
inear combination! $\psi = c_1 \psi_1 + c_2 \psi_2 + \dots = \sum_k c_k \psi_k$			

Weighted mean of a series of observations

$$\begin{split} \langle \Omega \rangle &= \int \psi^* \hat{\Omega} \psi \, \mathrm{d}\tau = \int \psi^* \omega \psi \, \mathrm{d}\tau = \omega \int \psi^* \psi \, \mathrm{d}\tau = \omega \\ \langle \Omega \rangle &= \int (c_1 \psi_1 + c_2 \psi_2)^* \hat{\Omega} (c_1 \psi_1 + c_2 \psi_2) \, \mathrm{d}\tau \\ &= \int (c_1 \psi_1 + c_2 \psi_2)^* (c_1 \omega_1 \psi_1 + c_2 \omega_2 \psi_2) \, \mathrm{d}\tau \\ &= c_1^* c_1 \omega_1 \int \psi_1^* \psi_1 \, \mathrm{d}\tau + c_2^* c_2 \omega_2 \int \psi_2^* \psi_2 \, \mathrm{d}\tau + c_1^* c_2 \omega_2 \int \psi_1^* \psi_2 \, \mathrm{d}\tau + c_2^* c_1 \omega_1 \int \psi_2^* \psi_1 \, \mathrm{d}\tau \\ &\langle \Omega \rangle = |c_1|^2 \omega_1 + |c_2|^2 \omega_2 \end{split}$$

Weighted mean of a series of observations

: the expectation value is the sum of the two eigencalues weighted by the probabilities that each one will be found in a series of measurements 1 When the momentum is measured, in a single observation one of the eigenvalues corresponding to the ψ_k that contribute to the superposition will be found.

2 The probability of measuring a particular eigenvalue in a series of observations is proportional to the square modulus $(|c_k|^2)$ of the corresponding coefficient in the linear combination.

3 The average value of a large number of observations is given by the expectation value, $\langle \Omega \rangle$, of the operator $\hat{\Omega}$ corresponding to the observable of interest.

Expectation value
$$\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi \, \mathrm{d} \tau$$

Ex. Mean kinetic energy

$$\langle E_k \rangle = \int \psi^* E_k \psi d\tau = -\frac{\hbar^2}{2m} \int \psi^* \frac{d^2 \psi}{dx^2} d\tau$$

1. When the momentum is measured, one of the eigenvalue will be measured

2. Measuring an eigenvalue ~ Proportional to the square of the modulus in the linear combinations

$$\langle \Omega \rangle = |c_1|^2 \omega_1 + |c_2|^2 \omega_2$$

3. Average value = Expectation value

$$\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi \, \mathrm{d} \tau$$

Summary of Operators

- position
- momentum
- •Kinetic E
- Potential E
- •Note) Expectation value

7.6 The uncertainty principle

•Heisenberg uncertainty principle

In Quantum Mechanics, Position and momentum cannot be predicted simultaneously

But, in Classical Mechanics, Position and momentum can be predicted simultaneously

Ex. Particle travelling to the right -> position is unpredictable But, the momentum is definite

 $\psi = Ae^{ikx}$

$$p_x = k\hbar$$



defined location

Position, x

An infinite number of waves is needed to construct the wavefunction of perfectly localized partile. Quantitative version of uncertainty principle

$$\Delta p \Delta q \ge \frac{1}{2}\hbar$$

$$\Delta p = \left\{ \left\langle p^2 \right\rangle - \left\langle p \right\rangle^2 \right\}^{1/2}, \ \Delta q = \left\{ \left\langle q^2 \right\rangle - \left\langle q \right\rangle^2 \right\}^{1/2}$$
Note) *p* and *q* are the same direction
Standard deviation

More general version of uncertainty principle

Complementary observables~ they do not commute $\hat{\Omega}_1(\hat{\Omega}_2\psi) \neq \hat{\Omega}_2(\hat{\Omega}_1\psi)$

commutator

$$\begin{bmatrix} \hat{\Omega}_{1}, \hat{\Omega}_{2} \end{bmatrix} = \hat{\Omega}_{1}\hat{\Omega}_{2} - \hat{\Omega}_{2}\hat{\Omega}_{1}$$
Ex. $[\hat{x}, \hat{p}_{x}] = i\hbar \longrightarrow \Delta p\Delta q \ge \frac{1}{2}\hbar$
Uncertainty principle
$$\Delta \hat{\Omega}_{1}\Delta \hat{\Omega}_{2} \ge \frac{1}{2} \left| \left\langle \left[\Delta \hat{\Omega}_{1}, \Delta \hat{\Omega}_{2} \right] \right\rangle \right|$$

•If there are a pair of complementary observables, (non-commuting)

The uncertainty principle should be applied!!!

Physical Chemistry Fundamentals: Table 7.2



* Pairs of observables that cannot be determined simultaneously with arbitrary precision are marked with a black rectangle; all others are unrestricted.

7.7 Postulates of quantum mechanics

- -wave function
- -Born interpretation
- -Acceptable wave function
- -Observables
- -Uncertainty relation







