6. Quantum Theory - Introduction

6.1 Failures of classical physics

- Black body radiation

According to the equipartition theorem all the oscillators of the field share equally the energy supplied by the heated walls ⇒ even the highest frequencies ⇒ ultraviolet catastrophe

⇒ Planck:

oscillators are excited only if they can acquire an energy of at least $h\nu$

quantization of energy: $\boxed{E = n h \nu}$

Planck's constant $6.626 08 \cdot 10^{-34}$ Js

- Heat capacities

Dulong and Petit's law (classical)

each atom can oscillate in three dimensions, the average energy of each atom is $3kT$, for N atoms: $3NkT$

$$U_m = 3 N_A k T = 3RT$$

$$C_{V,m} = \left.\frac{\partial U_m}{\partial T}\right|_V = 3R$$

fails as ~~...~~ as $T \to 0$

Einstein:

each atom oscillated about its equilibrium position with a single frequency and the energy of oscillation is confined to discrete values $n h \upsilon$

$$\Rightarrow U_m = \frac{3 N_A h \upsilon}{e^{h\upsilon/kT} - 1} \Rightarrow C_{V,m} = 3 R f^2$$

$$f = \frac{\theta_E}{T}\left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T} - 1}\right)$$

Einstein temperature

$$\theta = \frac{h\upsilon}{k}$$

for $T \gg \theta_E \Rightarrow$ classical result

for $T << \theta_E$: $f \approx \frac{\theta_E}{T}\left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T}}\right) = \frac{\theta_E}{T} e^{-\theta_E/2T}$

$$f \to 0 \text{ for } T \to 0$$

- at low temperatures only a few oscillators ~~posses~~ possess enough energy to oscillate significantly
- at higher temperatures there is enough energy available for all all oscillator to become active $\Rightarrow$ classical value

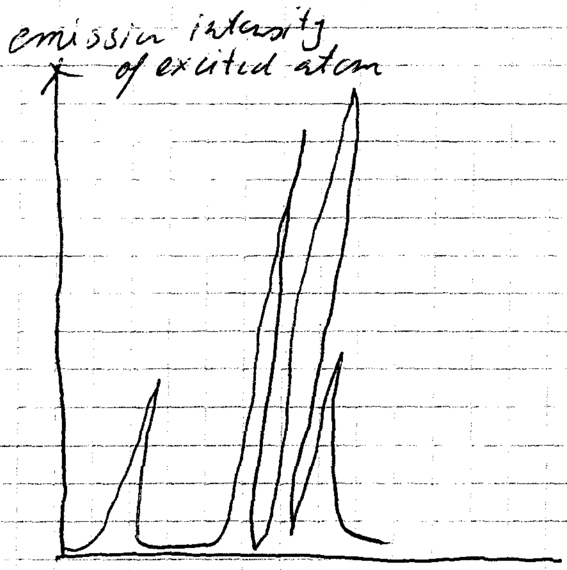
Debye: range of discrete frequencies

$$C_{V,m} = 3 R f \qquad f = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\, dx$$

$$\theta_D = \frac{h\upsilon_D}{k}$$

• Atomic and Molecular spectra

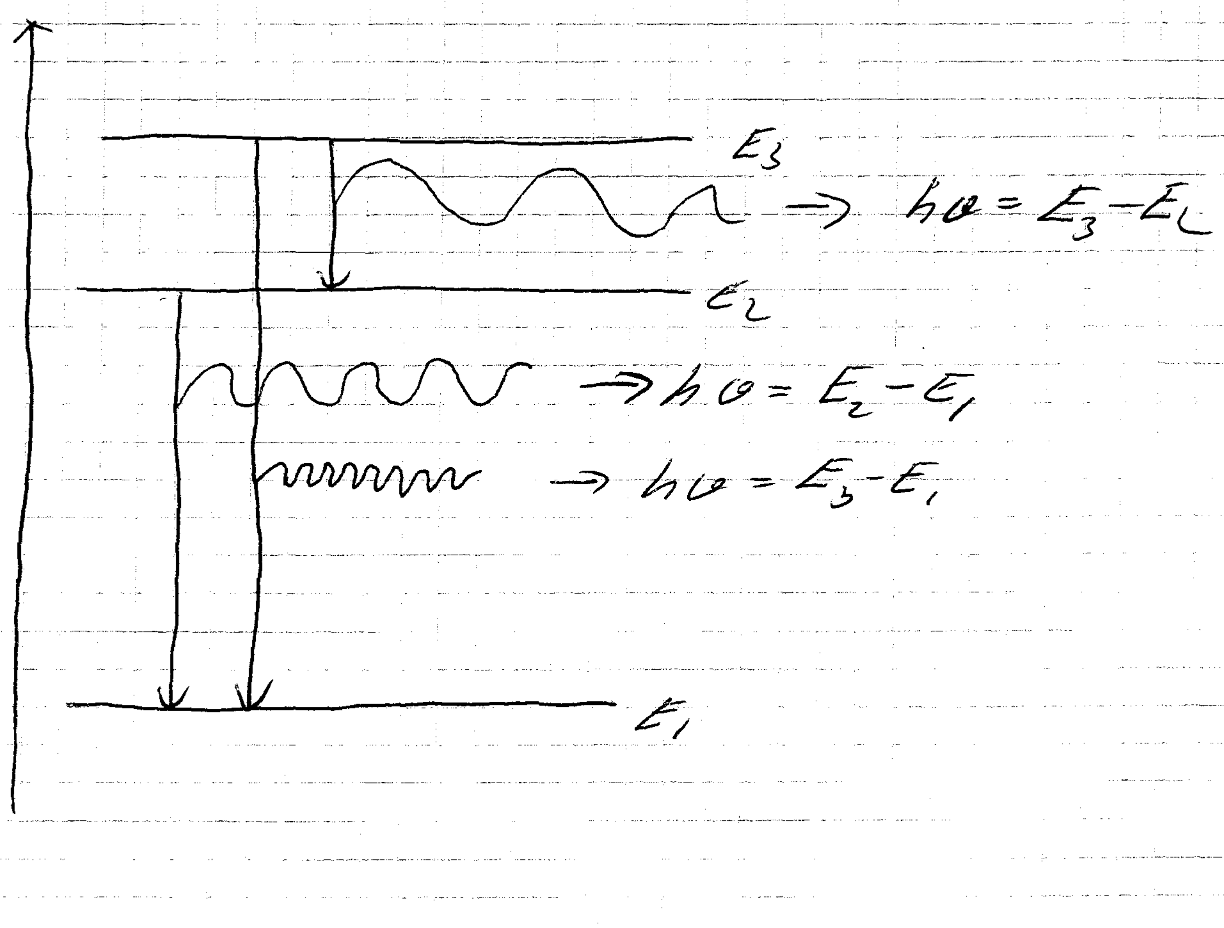
atomic spectra:



⇒ sharp lines
in absorption and emission

⇒ energy of atoms is
also confined to discrete
values

⇒ energy can be emitted or absorbed only in discrete
amounts



Bohr Radius a_B:

potentielle Energie des Elektrons hängt allein von seinem Abstand vom Kern ab

$$U(r) = -\frac{Z \cdot e^2}{(4\pi\varepsilon_0)\, r}$$

$$a_b = \frac{\hbar\, 4\pi\varepsilon_0}{m_e \cdot e^2}$$

$$R_{e^-} = n\, a_b \qquad n = 1, 2,$$

$$E_n = -\frac{e^4 m_e Z^2}{(4\pi\varepsilon_0)^2\, 2\hbar^2 n^2}$$

- Photoelectric effect

ejection of an electron when it is involved in a collision with a photon

photon

$$\frac{1}{2} m_e v^2 = h\nu - \phi$$

kinetic energy e^- — work function

- Electron diffraction

$\Rightarrow$ electron microscopy

de Broglie wave length: $\boxed{\lambda = \frac{h}{p}}$

The Schrödinger equation:

Ψ: wavefunction

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

$V(x)$: potential energy

$$\hbar = \frac{h}{2\pi}$$

3-dim $$-\frac{\hbar}{2m}\nabla^2\Psi + V\Psi = E\Psi$$

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

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

spherical

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

$$H\Psi = E\Psi$$

H: Hamiltonian operator $= -\frac{\hbar^2}{2m}\nabla^2 + V$

time-dependent:

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

e.g. $V(x) = V$

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

$$\Rightarrow \Psi = e^{ikx} \quad \text{with} \quad k = \left(\frac{2m(E-V)}{\hbar^2}\right)^{1/2}$$

$$E - V = E_{kin} \Rightarrow E_{kin} = \frac{k^2\hbar^2}{2m} = \frac{p^2}{2m}$$

$$\Rightarrow p = k\hbar = h/\lambda \quad \text{with} \quad \lambda = 2\pi/k$$

Born interpretation:

ψ probability amplitude
$|\psi^2|$ probability density

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 $|\psi|^2 d\tau$

normalization $\boxed{N^2 \int \psi^* \psi \, d\tau = 1}$

ψ: continous, continous slope, single-valued, finite, cannot be zero every where

Eigenvalues and eigenfunctions