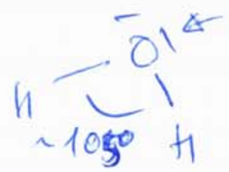
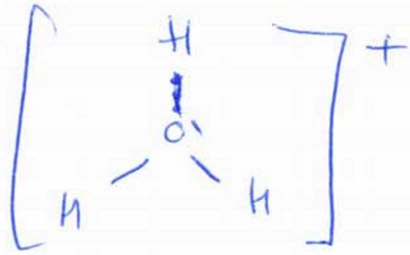
Acid - Base equilibria for the quick..

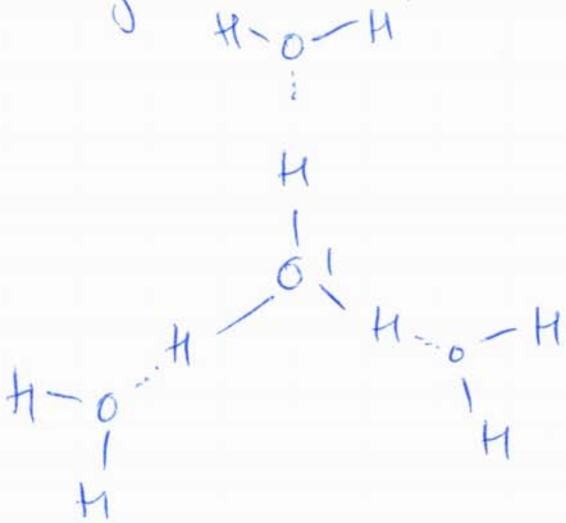
prelude Water:  lone electron pairs ~~pure water~~ :

autoprotolysis $H_2O \rightleftharpoons {}^-OH + H^+$

"Protons" 

hydronium ion

Eigen cation:

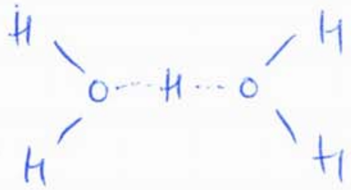


Concentration of "H^+" in pure water: $10^{-7} \frac{mol}{l}$

$\Rightarrow pH = -\lg c_{H^+} = 7$

Zundel cation:

$K_w = c_{H^+} \cdot c_{OH^-} = 10^{-14}$



cellular medium / Cytoplasm: pH ≈ 7.5
should be kept constant.
⇒ Buffers needed. What are buffers? → Keep the pH at a certain value, commonly mixtures of acids and bases. Def. acid (Brønsted): produces H^+ in water

Acid : proton donor

$$AH \rightleftharpoons A^- + H^+ \qquad K_a = \frac{c_{A^-} \cdot c_{H^+}}{c_{AH}}$$

$K_a >> 1$ (strong acid)

Base : proton acceptor

$$H^+ + B \rightleftharpoons \overset{+}{B}H \quad \text{resp.} \quad B + H_2O \rightleftharpoons {}^+BH + OH^-$$

AH, A^- : corresponding acid – base pair
(A^- can accept protons)

buffercapacity at <u>max</u>, if $c_{HA} = c_{A^-}$

$\Longrightarrow$ suitable buffer for pH (n) ?

With help of Henderson's equation (derived from $K =$ with $pK_a = -\lg K_a$

$$pH = pK_a - \lg\left(\frac{c_{A^-}}{c_{HA}}\right),$$

if $c_{A^-} = c_{AH}$ $pH = n = pK_a$ $\Rightarrow$ look for acid with $pK_a = n \pm 1$
(50% dissociated, $\alpha = 0.5$)
↑ dissociation degree
($7{,}5 \to$ <u>phosphate $K_2 = 7.2$</u>)

<u>practical</u>: get the acid and
add OH^- to obtain correct pH...

useful relations:

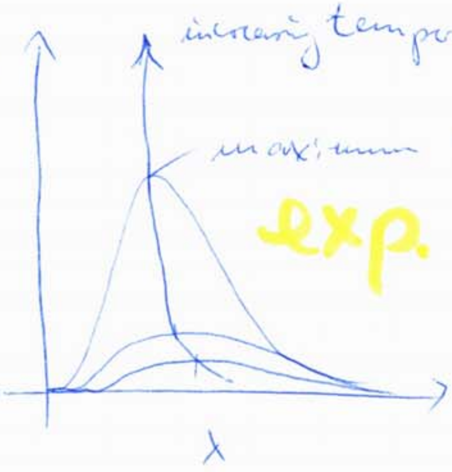
$$\alpha = \frac{K_a}{2c}\left(\sqrt{1 + \frac{4c}{K_a}} - 1\right) \qquad c = c_{A^-} + c_{HA}$$

$$\alpha = \left(10^{(pK_a - pH)} + 1\right)^{-1}$$

→ black body radiation

hot object - emits el. magn. radiation,
- high T → even visible (glowing)
more increasing → getting blue
c.f. figure

Energy distribution ρ



- ideal emitter: black body, emits and absorbs all frequencies uniformly
- approximation: pinhole in a container (empty) at constant T, radiation from the pinhole is in ~~complete~~ thermal equilibrium with the walls

⇒ Wien displacement law: $T\lambda_{max} = \frac{1}{5} c_2$, $c_2 = 1.44$ cm K (second radiation constant)

at 1000 K, $\lambda_{max} \approx 2900$ nm

Stefan - Boltzmann law:
energy density of the e-m-field inside the container increases as T is increased: $\mathcal{E} = \frac{E}{V} = a \cdot T^4$

analog expression:

M, excitance, power emitted by surface region (brightness-measure)
proportional to $\mathcal{E}$ $\quad M = \sigma T^4 \quad \sigma = 56.7$ nW m^{-2} K^{-4}
↑ Stefan-Boltzmann constant

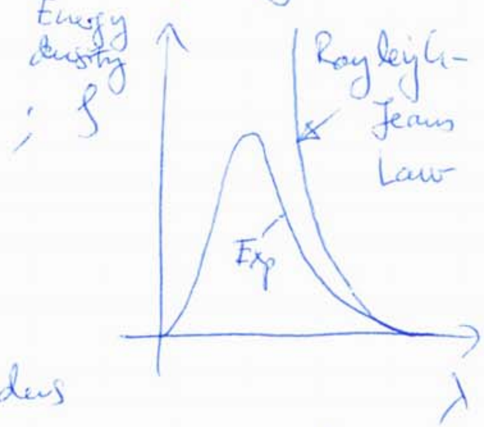
⇒ 1 cm² of a black-body surface: emit 6 W at 1000 K (over all wavelengths)

Rayleigh - Jeans law ; 4 classical derivation

equipartition theorem states that each oscillator draws an energy of kT, electromagnetic field = collection of oscillators of all possible freq.

radiation of ν signifying that the corresponding oscillator had been excited.

$dE = \rho \, d\lambda \qquad \rho = \dfrac{8\pi kT}{\lambda^4}$;



long wavelengths : well agreeing

no max. showing → short lambdas even produced at room temperature ("ultraviolet catastrophe")

classical ~~der~~

↳ ① Cool objects should "glow"

② no darkness

Planck - distribution

- Study from viewpoint of thermodynamics;
- could account for experimental data by limiting the energy of each oscillators to discrete values, quantization of energy

$E = nh\nu \quad n = 0, 1, 2, 3 \ldots$

⇒ Planck distribution derived

$dE = \rho \, d\lambda \qquad \rho = \dfrac{8\pi hc}{\lambda^5 \left(\exp(hc/\lambda kT) - 1\right)}$

h can be obtained by experimental data fit

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Translational motion

15a

Schrödinger eq.

(1) $H\psi = E\psi$ with $H = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$

general solutions:

$$\psi_k = A e^{ikx} + B e^{-ikx} \qquad E_k = \frac{k^2\hbar^2}{2m}$$

verify that functions are solutions: substitute ψ_k in left side of (1) and show that result is equal $E_k \psi_k$. Now all values of k, alle energies are permitted!! ⇒ translation of a free particle is not quantized!

- e^{ikx} wavefunction describes particle with linear momentum $p_x = +k\hbar$ to positive x

while e^{-ikx} describes particles moving in direction of negative x.

⇒ e^{ikx} eigenfunction ~~...~~ of the operator $\hat{p}_x$ with the eigenvalue $+k\hbar$, $|\psi|^2$ independent of x, position of a particle unpredictable! (uncertainty principle)

Planck $\rightarrow$ Rayleigh-Jeans at long wavelengths

-5-

$hc/\lambda k_B T \ll 1$

denominator : $\exp(hc/\lambda k_B T) - 1 = \left(1 + \frac{hc}{\lambda k_B T}\right) - 1 = \frac{hc}{\lambda k_B T}$

Planck $\rightarrow$ Stefan-Boltzmann

$$E = \int_0^\infty \rho \, d\lambda = a T^4 \qquad a = \frac{4\sigma}{c} \qquad \sigma = \frac{2\pi^5 k^4}{15 c^2 h^3}$$

Planck

Planck $\rightarrow$ Wien

looking for λ where $d\rho/d\lambda = 0$,

approx. : λ short, so $\lambda \ll \frac{hc}{kT} \Rightarrow T\lambda_{max} = \frac{hc}{5k_B}$

classical failure: all frequencies are excited

Planck: oscillators only excited if energy is at least $h\nu$

$\Rightarrow$ high frequency oscillators not unexcited

$\boxed{12}$ 12.1 Particle in a box

(1)

- confined between walls at $x=0$, $x=L$

- potential energy: zero inside the box, rises ~~..~~ abruptly to infinity at box'

- example gas molecule free to move in a 1d-container.

- basis of ~~...~~ treatment of electronic structure of metals, statistical mechanics: contribution of translational motion of molecules to thermodynamic properties.

a) solutions: between the walls, as above more convenient to write,

$$(2) \quad \psi_k(x) = C \sin kx + D \cos kx \qquad E_k = \frac{k^2 \hbar^2}{2m}$$

Boundary conditions: $\psi = 0$ at $x<0$, $x>L$ where V is infinite.

$\psi_k(0) = 0$, $\psi_k(L) = 0 \Rightarrow$ quantization

informal demonstration of quantization:

- each wave function considered as DeBroglie wave fitting in the container
  wavelengths permitted satisfy $L = n \cdot \frac{1}{2} \lambda$ $n = 1, 2, ..$
  therefore, $\lambda = \frac{2L}{n}$ with $n = 1, 2, \ldots$

according to De Broglie relation, wavelengths correspond to the momenta $p = \frac{h}{\lambda} = \frac{nh}{2L}$ (2)

Particle has only kinetic energy inside the box ($V=0$)

$\Rightarrow$ permitted energies are

(3) $E = \frac{p^2}{2m} = \frac{n^2 h^2}{8mL^2}$ with $n = 1, 2, \ldots$

– More formal, widely applicable approach considers wall at $x=0 \Rightarrow \psi(0) = D$ (see definition of 'D' (2))

$\psi(0) = 0$ (boundary cond.) $\Rightarrow D = 0$

Conclusion $\psi_k(x) = C \sin kx$, value of ψ at $x = L$ must also be zero! If $C = 0$, $\psi_k = 0$ for all x! Would conflict Born interpretation (particle must be somewhere!) $\Rightarrow$ kL must be chosen that $kL = 0$ which is satisfied by $kL = n\pi$ (4), with $n = 1, 2, \ldots$

→ $n = 0$ ruled out, because it implies $k = 0$, $\psi(x) = 0$ everywhere which is not acceptable. negative n values? $\Rightarrow$ change sign because $\sin(-x) = -\sin(x)$

wavefunctions: $\psi_n(X) = C \sin(n\pi x / L)$ $n = 1, 2, \ldots$

ψ_n instead of k — new index n

k and E_n: related in (2), k and n related in (4)

→ due to need to satisfy boundary conditions → only certain wavefunctions are acceptable, observables are restricted to discrete values

b) Normalization:

finding the normalization constant C

(2) look for C that ensures $\int \psi^2$ over all space available to the particle is 1.

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$$\int_0^L \psi\,dx = C^2 \int_0^L \sin^2 \frac{n\pi x}{L}\,dx = C^2 \cdot \frac{L}{2} = 1 \Rightarrow C = \left(\frac{2}{L}\right)^{1/2}$$

for all n. The complete solution for the problem:

$$E_n = \frac{n^2 h^2}{8mL^2} \qquad n = 1, 2, \ldots$$

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad \text{for } 0 < x < L$$

energies: labeled with quantum number 'n', integer labelling the state of a system, infinite number of acceptable solutions.

⇒ labelling it, calculate for the energy, for the explicit wavefunction

c) properties of the solutions

- wavefunctions sine functions with same amplitude, different wavelengths
- short wavelength → sharper curvature, → increased kinetic energy
- $n-1$ nodes of ψ_n, ⇒ $n\uparrow$ number nodes ↑
- linear momentum of a particle in a box:
- each wavefunction is a superposition of two momentum eigenfunctions

$$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L} = \frac{1}{2i}\left(\frac{2}{L}\right)^{1/2}\left(e^{ikx} - e^{-ikx}\right)$$

$k = n\pi/L$

conclusion: measurement of linear momentum: ④

+ $k\hbar$ and $-k\hbar$ for each ~~direction~~ half of the measurements → q.m. picture of the classical where a particle in a box spends half the time travelling right and the other time travelling left

- n can not be zero → zero point energy

$$E_1 = \frac{h^2}{8mL^2}$$

① uncertainty principle → also confined particle has kinetic energy (particle's position is not completely indefinite)

② wavefunction: zero at the walls, and not zero, smooth, continuous everywhere → curvature → kinetic energy

Separation between energy levels

$$E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2} = (2n+1)\frac{h^2}{8mL^2}$$

→ separation decreases with as the length of the container increases, free particles: not quantized

examples: $L = 1\,nm \Rightarrow E_1 = 60\,zJ = 0.37\,eV$

min excitation energy: $1.1\,eV$ ($1.8 \cdot 10^2\,zJ$)

Correspondence principle

- quantum result corresponds to classical at high quantum numbers; classical mechanics emerges from q.m. as high quantum numbers are reached!

illustration: probability density for a particle in a box:

$$\psi^2(x) = \frac{2}{L} \sin^2 \frac{n\pi x}{L}$$ (5)

varies with position!

ψ^2 becomes more uniform if n increases

d) Orthogonality / Bracket notation:

- two wave functions are orthogonal if

$$\int \psi_{n'} \psi_n^* \, d\tau = 0$$

$\uparrow$ wf 1 = $\psi_{n'}$ $\uparrow$ wf 2 = ψ_n

Integration over all space

example: wf's of a particle in a box with $n = 1$ and $n = 3$

$$\int_0^L \psi_1^* \psi_3 \, dx = \frac{2}{L} \int_0^L \sin \frac{\pi x}{L} \cdot \sin \frac{3\pi x}{L}$$ (ψ_1, ψ_3 are real)

→ Dirac bracket notation of ~~this~~ equation: $\langle n | n' \rangle = 0$ corresponds to

bra $\langle n|$ → ψ_n

ket $|n'\rangle$ → $\psi_{n'}$

Kronecker $\delta_{nn'}$:

is 1 when $n' = n$ and 0 if $n \neq n'$.

orthogonality: allows to eliminate large numbers of integrals

orthonormal: sets of functions which are normalized and mutually orthogonal ($\psi_n(x)$ for particle in a 1d box)

(4.4) Motion in two and more dimensions

e.g. 2 d ~~box~~ : Schrödinger

$$\left(\frac{\hbar^2}{2m}\right)\left(\frac{\partial^2 \psi}{\partial x^2}\right)\left(\frac{\partial^2 \psi}{\partial y^2}\right) = E\psi$$ (a partial differential equation)

Separation of variables: $\psi(x,y) = X(x)\,Y(y)$

$\Rightarrow$ separation into two ordinary DE

$$-\frac{\hbar^2}{2m}\frac{dX}{dx^2} = E_x X$$ and analogously for $Y(y)$

$E = E_x + E_y$ (E_y / E_x : energy associated with motion in the two directions

$$\Rightarrow E_{n_1,n_2} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right)\frac{h^2}{8m} \qquad 0 \le x \le L_1,\ 0 \le y \le L_2$$

independent numbers $n_1 = 1,2,\ldots$ $n_2 = 1,2,\ldots$

Dirac notation: States denoted by the ket $|n_1, n_2\rangle$

3d:

$$E_{n_1,n_2,n_3} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)\frac{h^2}{8m} \qquad 0 \le x \le L_1 \ldots$$

Degeneracy:

if $L_1 = L_2$, considering $n_1 = 1$, $n_2 = 2$
and $n_1 = 2$, $n_2 = 1$

$$\Rightarrow \quad E_{1,2} = \frac{5h^2}{8mL^2} \quad \text{and} \quad E_{2,1} = \frac{5h^2}{8mL^2}$$

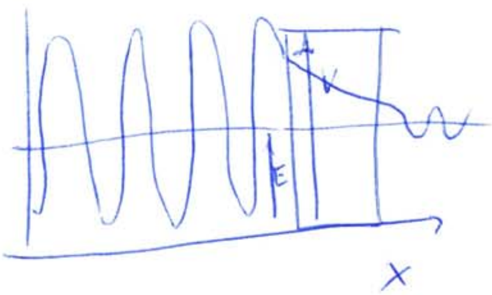
→ energy level is ~~degenerat~~ 'doubly degenerate'

or states $|2,1\rangle$ and $|1,2\rangle$ are degenerate.

→ related to symmetry of the system

Tunneling

- leakage ~~through~~ through walls, penetration through classically forbidden zones



Schrödinger:

$$\left(\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} \right) + V\psi = E\psi$$

general solution for $V-E$ is positive:

$$\psi = C e^{\kappa x} + D e^{-\kappa x} \qquad \kappa\hbar = (2m(V-E))^{1/2}$$

→ real functions

right of the barrier:

$$\psi = A' e^{(ikx)} + B' e^{-ikx} \qquad k\hbar = (2mE)^{1/2}$$

⇒ transmission probability T:

$$T = \left\{ 1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\,\varepsilon\,(1-\varepsilon)} \right\}^{-1} \quad \text{with } \varepsilon = E/V$$ 8

high, wide barriers ($\kappa L \gg 1$)

$$T \approx 16\,\varepsilon\,(1-\varepsilon)\, e^{-2\kappa L}$$

examples: – isotope-dependence of reactions → protons tunnel more readily than deuterons
- → rapid equilibration of proton-transfer; protons tunnel through barriers
- → important feature of enzyme catalyzed reactions
- – electron tunneling at electrodes, biological systems
- – Scanning tunneling microscopy

Vibrational motion

– harmonic motion $F = -kx$, $V(x) = \frac{1}{2} k x^2$ $\left(F = -\frac{dV(x)}{dx} \right)$

k: force constant

– Schrödinger equation: $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} k x^2 \psi = E\psi$

$$\Rightarrow E_v = (v + \tfrac{1}{2})\hbar\omega \qquad \omega = \left(\frac{k}{m}\right)^{1/2} \qquad v = 0, 1, 2 \ldots$$

$$E_{v+1} - E_v = \hbar\omega \qquad E_0 = \tfrac{1}{2}\hbar\omega$$

wave functions of the harmonic oscillator:

- differences to the particle in the box:

a) not abrupt increase of $V(x)$: wave function approaches zero more slowly

b) kinetic energy more complex on x dependent → curvature more complex

- general: $\Psi(x) = N \cdot (\text{polynomial in } x) \cdot (\text{bell shaped Gaussian})$
  ↑ normalization

precise: $\Psi_v(x) = N_v \cdot H_v(y)\, e^{-y^2/2}$ $\quad y = \frac{x}{\alpha}$

$$\alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

$H_v(y)$ = Hermite polynomial

$H_0(y) = 1 \quad \curvearrowright \quad \Psi_0(x) = N_0\, e^{-y^2/2} = N_0\, e^{-x^2/2\alpha^2}$

for the lowest state, $v = 0$

Rotational motion

- particle of mass m, rotating in x,y-plane with a circular path with r (radius),

total energy = kinetic energy ⇒ $E = p^2/2m$

classical: angular momentum J_z (around z-axis)

$\Rightarrow J_z = \pm pr, \Rightarrow E = J_z^2/2mr^2$ $\quad mr^2$ = moment of inertia, I

$\Rightarrow E = \frac{J_z^2}{2I}$

quantization: not all values of J_z are permitted (10)

why: Cyclic / boundary condition of wavefunctions is that the wavefunction of a rotator reproduces itself on successive circuits.

$\Rightarrow$ allowed wavelengths $\lambda = \dfrac{2\pi r}{m_l}$

q. numbers $\boxed{m_l = 0, \pm 1, \pm 2 \ldots}$

$\Rightarrow$ angular momentum:

$$J_z = \pm \frac{hr}{\lambda} = \frac{m_l h r}{2\pi r} = \frac{m_l h}{2\pi}$$

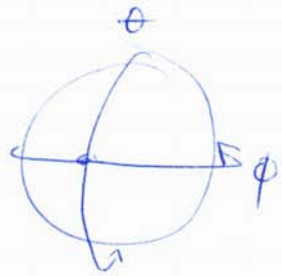
$\pm$: clockwise / counter-clockwise rotation

$$E = \frac{J_z^2}{2I} = \frac{m_l^2 \hbar^2}{2I}$$

wavefunctions:

$$\psi_{m_l}(\phi) = \frac{e^{i m_l \phi}}{(2\pi)^{1/2}}$$

Rotation in 3 dimensions



- particle on a sphere
- three dimensional Schrödinger eq
- solving with usage of Legendre functions $\Rightarrow$ spherical harmonics (wavefunctions)

$\rightarrow$ range of acceptable values of m_l is restricted by l

l = orbital angular momentum quantum number

$l = 0, 1, 2$

— given l : $2l+1$ possible values for l of the magnetic q. number m_l

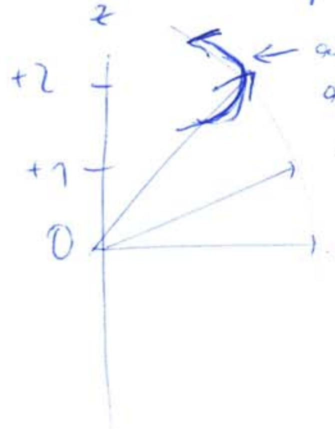
$$m_l = l, l-1 \ldots -l$$

— wavefunctions: $Y_{l,m}(\theta, \phi)$: spherical harmonics

— $E = l(l+1)\dfrac{\hbar^2}{2I}$ $\quad l = 0, 1, 2, \ldots$

— angular momentum : $(l(l+1))^{1/2}\hbar$, $l = 0, 1, 2$

z - component of angular momentum : $m_l \hbar$. $m_l = l, l-1, \ldots -l$



← azimuthal angle indeterminate

space quantization

orientation of a rotating body is quantized