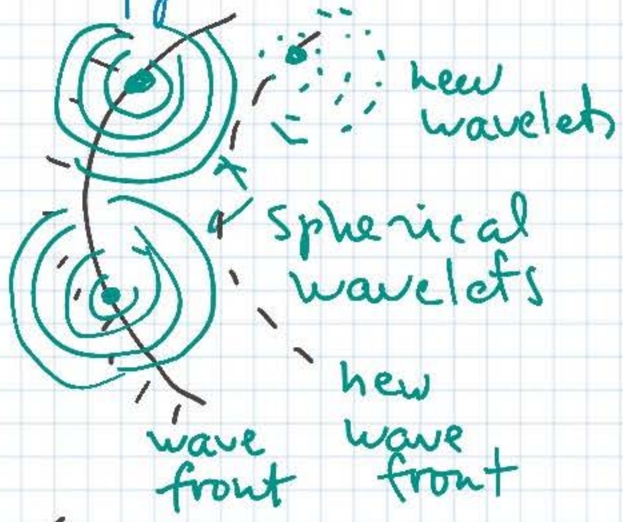
https://math.berkeley.edu/~giventh

Math 189. Math Methods of ...

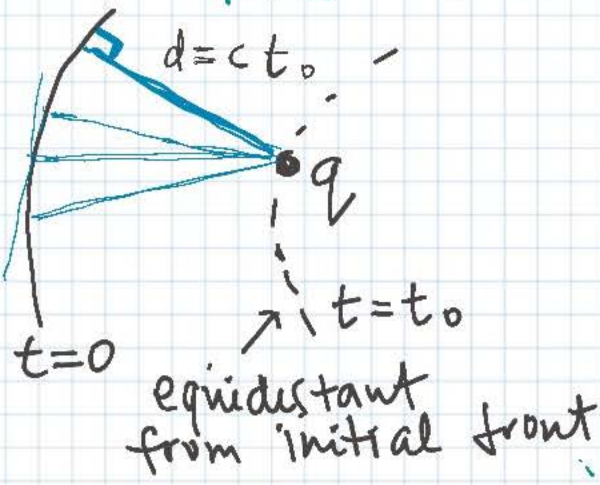
Policies / Textbook / Homework / etc.

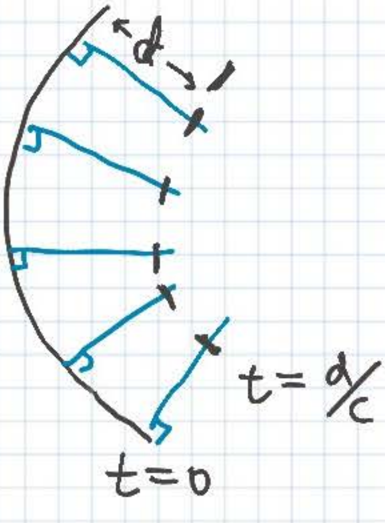
Waves or particles?

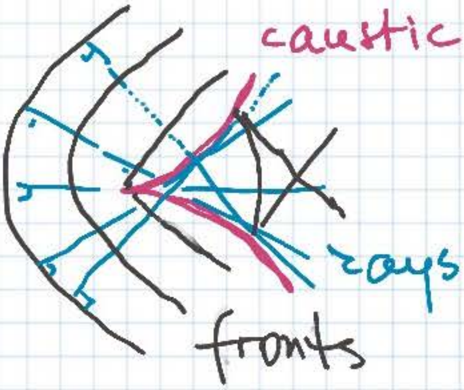
(Huygens vs. Newton)

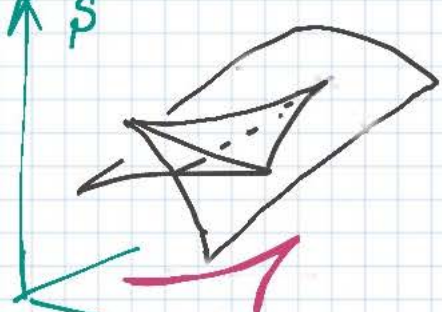


Huygens-Fresnel's Principle









optical distance function

level sets = fronts

gradient lines = rays

$$|\vec{\nabla} S| = 1$$

$$\left(\frac{\partial S}{\partial x}\right)^2 + \left(\frac{\partial S}{\partial y}\right)^2 + \left(\frac{\partial S}{\partial z}\right)^2 = 1$$

Eikonal eqn

Newton's equation "F = ma"

$$m\ddot{q} = F(q) = -\vec{\nabla} V(q)$$

$V : \mathbb{R}^n \to \mathbb{R}$ — potential energy; $\mathbb{R}^n$ — configuration space; $F = -\vec{\nabla} V$ — conservative force field

Hamilton's form of equations

$$\begin{cases} \dot{p} = -\partial H(p,q)/\partial q \\ \dot{q} = \partial H(p,q)/\partial p \end{cases}$$

$H : \mathbb{R}^{2n} \to \mathbb{R}$ — Hamilton function; $\mathbb{R}^{2n}$ — phase space

E.g.: $H = p^2/2m + V(q) = \frac{m\dot{q}^2}{2} + V(q)$

total energy = kinetic + potential

$\dot{q} = p/m \Rightarrow p = m\dot{q}$ — momentum vector

$\dot{p} = -\partial V/\partial q \Rightarrow m\ddot{q} = -\partial V/\partial q$ Newton's eqn.

Energy conservation Law:

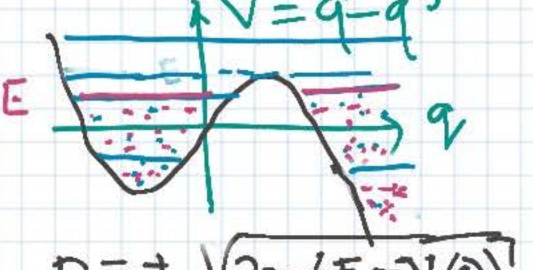
$$\frac{d}{dt} H(p(t), q(t)) = H_p \dot{p} + H_q \dot{q} = -H_p H_q + H_q H_p = 0$$

Liouville's Theorem: Phase flow of a hamiltonian vector field is volume preserving.

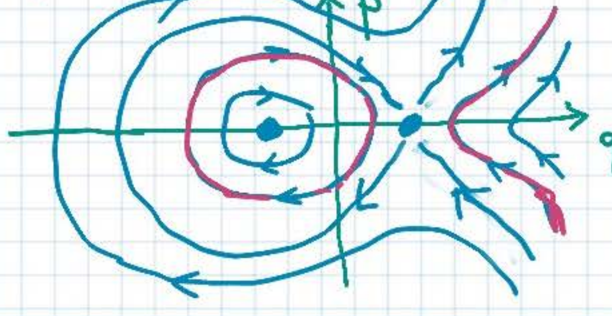
Pf. Follows from Gauss' divergence thm:

$$\text{div} = \sum_{i=1}^{n} \frac{\partial}{\partial q_i} H_{p_i} - \sum_{i=1}^{n} \frac{\partial}{\partial p_i} H_{q_i} = 0$$

Example: phase portraits for $n=1$



$p = \pm\sqrt{2m(E - V(q))}$



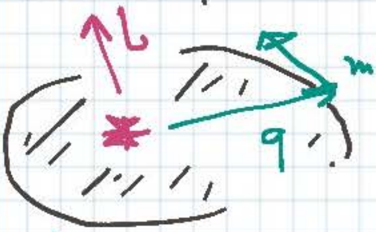
The Kepler problem

$$H = \frac{p\cdot p}{2m} - \frac{G}{(q\cdot q)^{1/2}} \qquad G = mM\gamma, \quad p, q \in \mathbb{R}^3$$

Angular momentum $L := q \times p$

is conserved in any central force field

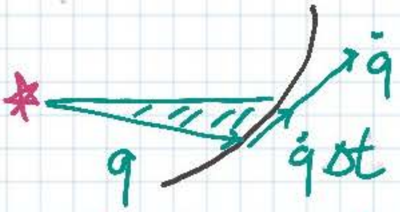
$$\dot L = \dot q \times p + q \times \dot p = \dot q \times (m\dot q) + q \times (m\ddot q) = 0 + 0$$



All trajectories are planar

$\Rightarrow$ The problem is reduced to 2D

Kepler's 2nd law



$$\frac{|L|}{m} = |q|\,|\dot q|\,|\sin\varphi|$$

sectorial velocity is constant

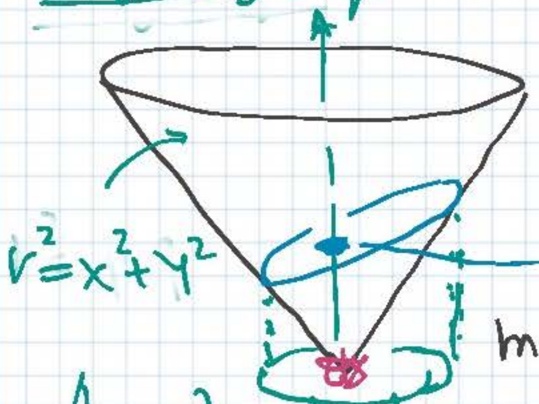
Kepler's 1st law: orbits are conic sections

Newton: $r = (q\cdot q)^{1/2} \quad \dot r = (\dot q \cdot q)/(q\cdot q)^{1/2}$

$$\ddot r = \frac{(\ddot q \cdot q)}{r} + \frac{(\dot q\cdot \dot q)(q\cdot q) - (\dot q\cdot q)(\dot q \cdot q)}{r^3}$$

$$m\ddot r = -\frac{G}{r^2} + \frac{|L|^2}{m r^3} \qquad V_{eff} = -\frac{G}{r} + \frac{|L|^2}{2mr^2}$$

Lagrange



$$m\ddot x = -\frac{Gx}{r^3(t)}$$

$$m\ddot y = -\frac{Gy}{r^3(t)}$$

$$m\left(r - \frac{|L|^2}{m^2}\right)^{\cdot\cdot} = -\frac{G\left(r - \frac{|L|^2}{m^2}\right)}{r^3(t)}$$

Any 3 solutions of a linear 2nd order ODE are lin. dependent

$$A\,x(t) + B\,y(t) + C\left(r(t) - \frac{|L|^2}{m^2}\right) = 0$$

math.berkeley.edu/~giventh/kepler_091615.pdf

Hamiltonian Mechanics

$$\begin{cases} \dot{p}_i = -H_{q_i} \\ \dot{q}_i = H_{p_i} \end{cases} \quad i = 1, \dots, n$$

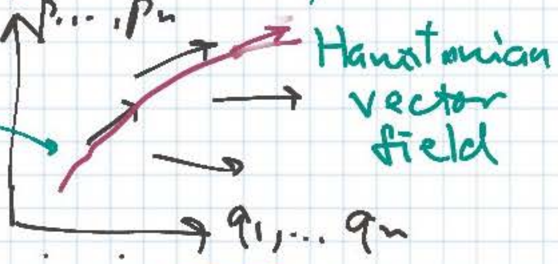
Hamilton equations

$\mathbb{R}^{2n} \xrightarrow{H} \mathbb{R}$ — phase space; H ← hamiltonian

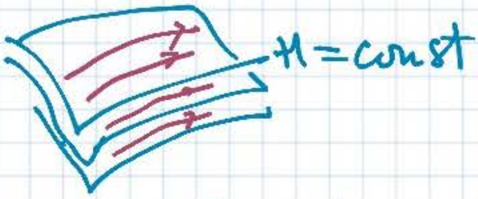
$(p, q) \longmapsto H(p, q)$ — p: (generalized) momenta, q: (generalized) positions

$t \mapsto (p(t), q(t))$ ← solutions

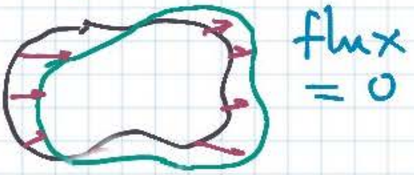
solutions generate the phase flow



Thm 1 (Conservation of Energy)
The flow preserves H.

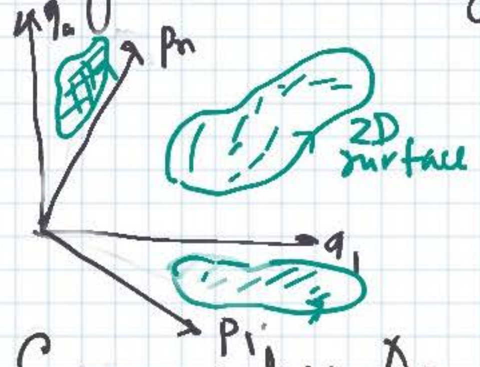


Thm 2 (Liouville)
The flow preserves phase volume



Symplectic geometry

Phase spaces of "conservative" mechanical systems carry symplectic structure — a way of assigning areas to 2-dimensional oriented surfaces

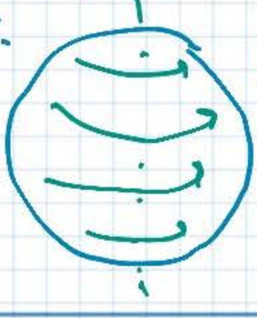


$$dp_1 \wedge dq_1 + \dots + dp_n \wedge dq_n$$

Conversely: Any space equipped with a symplectic structure can serve as a phase space of Hamiltonian mechanics

Hamiltonian flows = flows preserving the symplectic structure

Example: $x^2 + y^2 + z^2 = 1$ — phase space S^2



Rotations about any line preserve areas ⟹ are Hamiltonian flows.
Hamilton functions = $\alpha x + \beta y + \gamma z$

Poisson brackets

Observables = functions on the phase space

Example $L = q \times p$ - angular momentum in $\mathbb{R}^3$

$L_1 = q_2 p_3 - q_3 p_2, \; L_2 = q_3 p_1 - q_1 p_3, \; L_3 = q_1 p_2 - q_2 p_1$

Time derivative of an observable $\mathcal{F}$:

$$\frac{d}{dt}\mathcal{F}(p(t), q(t)) = \mathcal{F}_q \dot{q} + \mathcal{F}_p \dot{p} = \underbrace{\sum_{i=1}^{n} (H_{p_i}\mathcal{F}_{q_i} - H_{q_i}\mathcal{F}_{p_i})}_{\{H, \mathcal{F}\}}$$

$\{H, \mathcal{F}\}$ Poisson bracket

Examples $\dot{p}_i = \{H, p_i\} = -H_{q_i}$

$\dot{q}_i = \{H, q_i\} = H_{p_i}$

$\{L_1, L_2\} = -L_3, \; \{L_2, L_3\} = -L_1, \; \{L_3, L_1\} = -L_2$

×-product in $\mathbb{R}^3$!

Properties of Poisson brackets:

$\{F, G\} = -\{G, \mathcal{F}\}, \quad \{H, \mathcal{F} + G\} = \{H, \mathcal{F}\} + \{H, G\}$

$\{H, \{F, G\}\} + \{G, \{H, \mathcal{F}\}\} + \{F, \{G, H\}\} = 0$ ← Jacobi identity

→ Lie algebra! for all $\mathcal{F}, G, H$.

$\{H, \mathcal{F}G\} = \{H, \mathcal{F}\}G + \mathcal{F}\{H, G\}$

Leibniz' rule: $(FG)^{\cdot} = \dot{F}G + F\dot{G}$

Time evolution of observables: $\dot{\mathcal{F}} = \{H, \mathcal{F}\}$

$\{H, H\} = 0$ Energy conservation law

$\{F, H\} = 0 \Rightarrow \{H, \mathcal{F}\} = 0$ Noether's thm

Symmetries ⇝ Conservation laws!

$\{H, \mathcal{F}\} = 0 = \{H, G\} \Rightarrow \{H, \{\mathcal{F}, G\}\} = 0$ ← Poisson's theorem

Poisson bracket of conservation laws is a conservation law.

Example $\{H, L_1\} = 0 = \{H, L_2\} \Rightarrow \{H, L_3\} = 0$

If two components of the angular momentum are conserved, then the third one is also conserved.

Poisson manifolds $(M, \{\cdot,\cdot\})$

$C^\infty(M) \ni F, G \mapsto \{F, G\}$ ← Lie algebra structure + Leibnitz' rule

↑ smooth functions on M; M ← "geometric space" (= manifold)

$(M, \{\cdot,\cdot\})$ can serve as a phase space of Hamiltonian mechanics: given $H \in C^\infty(M)$, $\dot{F} = \{H, F\}$ determines evolution of observables

Example: $M = \mathbb{R}^3$, $\{\cdot,\cdot\}$ ⇐ "×-product"

$\{x, y\} = z$, $\{y, z\} = x$, $\{z, x\} = y$

Lemma: In $\mathbb{R}^n$, $\{F, G\} = \sum_{i,j} F_{x_i} G_{x_j} \{x_i, x_j\}$

Proof. $H = x_1$: $\{x_1, F\} = \dot{F} = \sum_i F_{x_i} \underbrace{\{x_1, x_i\}}_{\dot{x}_i}$

$H = F$: $\{F, G\} = \dot{G} = \sum_j G_{x_j} \underbrace{\{F, x_j\}}_{\dot{x}_j}$

$\{x, r^2\} = 2x\{x, x\} + 2y\{x, y\} + 2z\{x, z\} = 0$

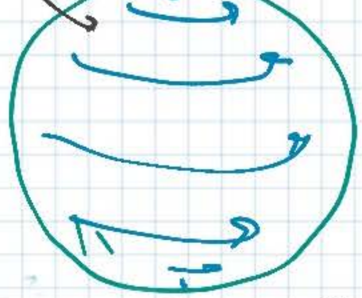
($r^2 = x^2 + y^2 + z^2$; $\{x,x\} = 0$, $\{x,y\} = z$, $\{x,z\} = -y$)

$\{H, r^2\} = H_x\{x, r^2\} + H_y\{y, r^2\} + H_z\{z, r^2\} = 0$

↖ Casimir function

$$\begin{cases} \dot{x} = \{H, x\} \\ \dot{y} = \{H, y\} \\ \dot{z} = \{H, z\} \end{cases}$$
⇐ "Hamilton equations", the flow preserves r^2.

$r^2 = \text{const}$



$H = z$
$$\begin{cases} \dot{x} = \{z, x\} = y \\ \dot{y} = \{z, y\} = -x \\ \dot{z} = \{z, z\} = 0 \end{cases}$$

flow – rotations about z-axis with angular velocity 1

$H = \alpha x + \beta y + \gamma z$ ⇝ rotations with angular velocity $\vec{\omega} = \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$

$(\mathbb{R}^3, \text{"×"})$ = the Lie algebra of Lie group SO_3.

Groups and Symmetries

$G \times G \to G$ associative multiplication

$G \to G$ inversion: $gg^{-1} = e = g^{-1}g$

$e \in G$ unit element: $ge = g = eg$

Example X – any set (e.g. $\{1, \dots, n\}$, $\mathbb{R}^3$, a phase space)

$S_X = \{$invertible functions $g: X \to X\}$ ← permutation group

$e = id$, $X \leftarrow X : g^{-1}$, $X \xrightarrow{g} X \xrightarrow{f} X$, $f \circ g$

$X \xrightarrow{h} Y \xrightarrow{g} Z \xrightarrow{f} W$

$f \circ (g \circ h) = (f \circ g) \circ h$ composition of maps is associative

Symmetries of (X + structure)

permutations on X preserving a given structure form a (sub)group (in S_X)

Examples, $X = \mathbb{R}^3$, structure = just a set

$G = \{$homeomorphism $\mathbb{R}^3 \to \mathbb{R}^3\}$ topological space

$\{$diffeomorphism $\mathbb{R}^3 \to \mathbb{R}^3\}$ smooth manifold

$\{$invertible 3×3-matrices$\}$ linear space

$\{3 \times 3$-matrices, $\det > 0\}$ oriented — " —

$SO_3 = \{$rotations in $\mathbb{R}^3\}$ Euclidean — " — — " —

Examples $X = \mathbb{R}^{2n}$ + "symplectic structure"

$\mathbb{R} \longrightarrow G = \{$symplectomorphisms of $\mathbb{R}^{2n}\}$

$t \longmapsto U(t) : \mathbb{R}^{2n} \to \mathbb{R}^{2n}$ $U(t_1 + t_2) = U(t_1)U(t_2)$

the phase flow of a hamiltonian, H. ← hamiltonian transformations

Thm (Liouville): Symplectomorphisms are volume-preserving (but not vice versa).

Thm (Noether): Symmetries ⟺ conservation laws

Homogeneity of Time, Space; Isotropy

Conservation of Energy, Momentum, Angular M

Hamilton-Jacobi equations

$$\begin{cases}\dot p = -H_q \\ \dot q = H_p\end{cases} \longleftrightarrow H(p,q) \mapsto H(\nabla_q S(q), q) = \text{const}$$

Hamilton equns — Solutions = trajectories

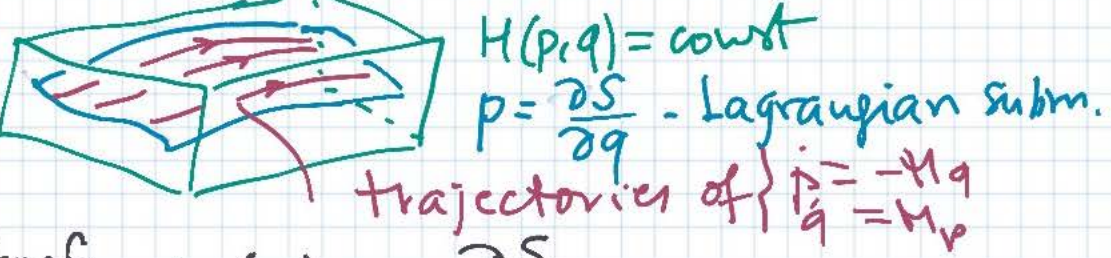
Hamilton-Jacobi eqns — solutions = "optical distance" functions, S

$$\begin{cases}\dot p = 0 \\ \dot q = p/m\end{cases} \longleftrightarrow \frac{1}{2m}\sum p_i^2 \mapsto \sum\left(\frac{\partial S}{\partial q_i}\right)^2 = \text{const}$$

free-particle trajectories — Eikonal equation

<u>Def</u>. Graphs $p = \frac{\partial S}{\partial q}$ in the phase space are called <u>Lagrangian</u> <u>submanifolds</u>.

<u>Thm</u>. If S satisfies H.-J. equ., then the Lagrangian submanifold of S consists of trajectories of the H. eqns.



<u>Proof</u>. $p_j(q) := \frac{\partial S}{\partial q_j}$

From H.-J. equation $H(p(q), q) = \text{const}$.

$$\frac{\partial}{\partial q_i}:\quad 0 = \frac{\partial H}{\partial q_i} + \sum_j \frac{\partial H}{\partial p_j}\frac{\partial^2 S}{\partial q_i \partial q_j},\quad i = 1, \dots, n$$

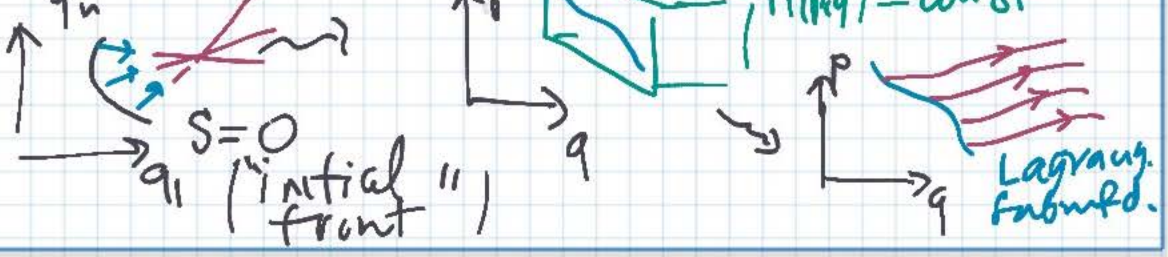
From Hamilton's eqns:

$$\frac{d}{dt}\left(-p_i + \frac{\partial S}{\partial q_i}\right) = \frac{\partial H}{\partial q_i} + \sum_j \frac{\partial^2 S}{\partial q_j \partial q_i}\frac{\partial H}{\partial p_j} = 0$$

($\frac{\partial H}{\partial q_i} = -\dot p_i$, $\frac{\partial H}{\partial p_j} = \dot q_j$)

$0 = -p_i + \frac{\partial S}{\partial q_i}$ ← Equations of the Lagrangian submfd.

The method of characteristics



Time-dependent hamiltonians

$$\begin{cases}\dot p_i = -H_{q_i}(p,q,t)\\ \dot q_i = H_{p_i}(p,q,t)\end{cases}$$

$$\frac{d}{dt}H(p,q,t) = \frac{\partial H}{\partial t} + \underbrace{\sum_i \frac{\partial H}{\partial p_i}\dot p_i + \sum_i \frac{\partial H}{\partial q_i}\dot q_i}_{=0} = \frac{\partial H}{\partial t}$$

Energy conservation ⟺ homogeneity of time

The extended phase space

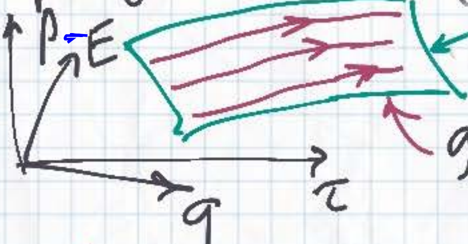
$q_1,\dots,q_n,\tau$ $\quad \mathcal{H} = H(p,q,\tau) - E$ ← new hamiltonian

$p_1,\dots,p_n,-E$ ← traditional

$$\dot p = -\mathcal{H}_q = H_q(p,q,\tau) \qquad \dot E = +\mathcal{H}_\tau = H_t(p,q,\tau)$$

$$\dot q = \mathcal{H}_p = H_p(p,q,\tau) \qquad \dot\tau = -\mathcal{H}_E = 1$$

Thm. If $t \mapsto (p(t), q(t))$ - trajectory of the time-dependent Ham. system, then $(p, E, q, \tau) = (p(t), H(p(t),q(t),t), q(t), t)$ - trajectory of the extended system. Conversely, trajectories of the latter project to trajectories of the former.



← $\mathcal{H}=0$ (i.e. $E = H(p,q,\tau)$)

← graphs of trajectories $\tau \mapsto (p(\tau), q(\tau), E(\tau))$

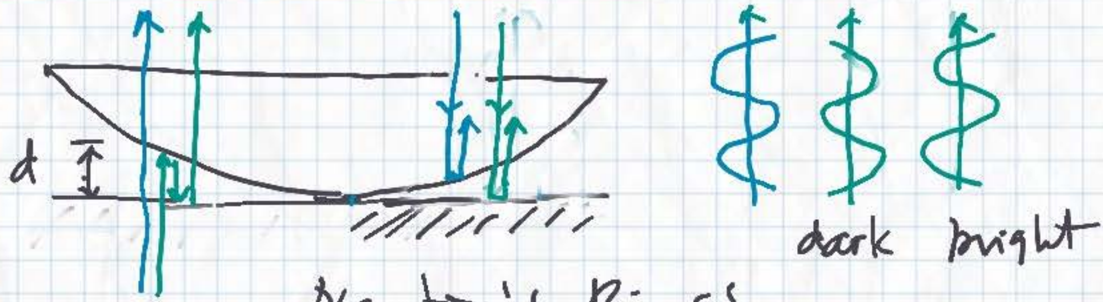
The Extended Hamilton-Jacobi Equ.

$$-\frac{\partial S(q,\tau)}{\partial \tau} = H\left(\frac{\partial S}{\partial q}, q, \not{\tau}\right)$$

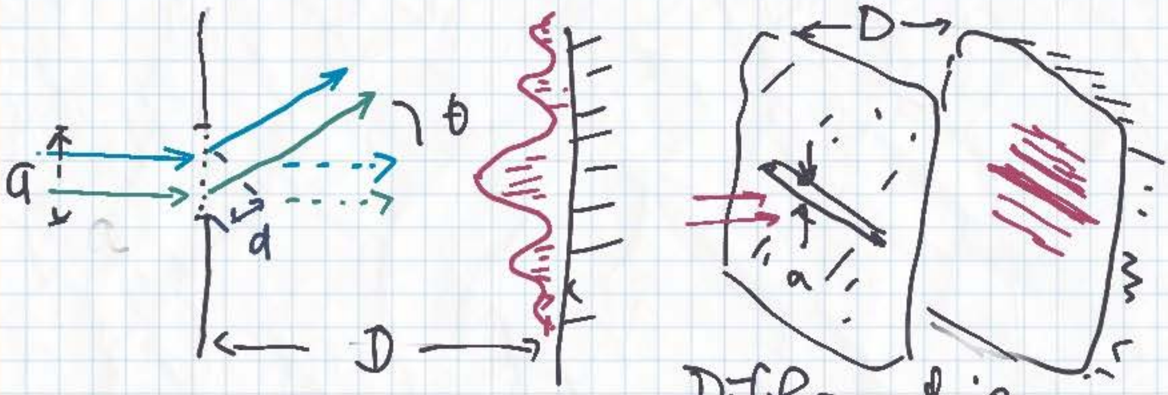
makes sense even when H is time-independent

This is the classical prototype of the quantum Schrödinger equation.

Short-wave optics



Newton's Rings

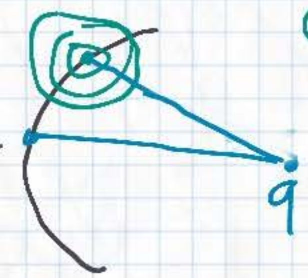


Diffraction

Wave length of visible light

$400\text{ nm} < \lambda < 780\text{ nm}$ ($< 10^{-3}$ mm)

⇒ Short-wave optics



$$\frac{A(x)\, e^{i(\omega t - 2\pi |x-q|/\lambda)}}{|x-q|}$$

amplitude → $A(x)$; ω — time frequency; λ — wave length

Energy ~ (amplitude)^2 distributed over surface of the sphere of radius $|x-q|$

$$\lambda = c\,\frac{2\pi}{\omega}$$

$$I(q) = \int a(x,q)\, e^{2\pi i f(x,q)/\lambda}\, dx$$

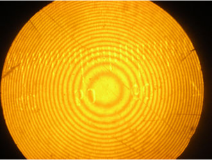
$I(q)$ — (wave field)$\cdot e^{-i\omega t}$ at q

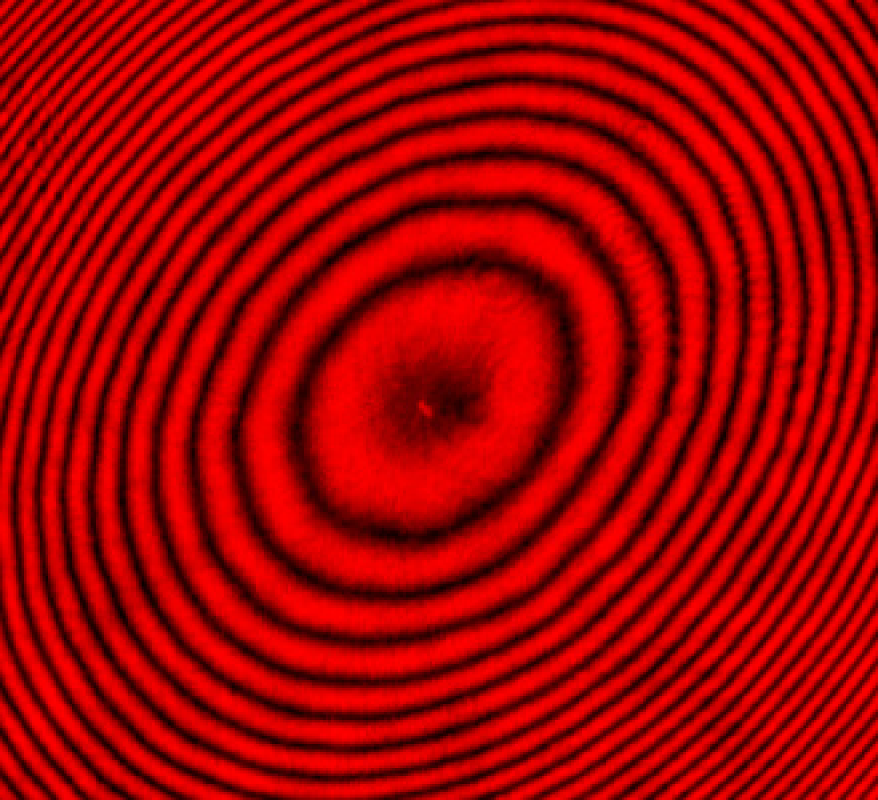
$a(x,q)$ — (generalized) amplitude

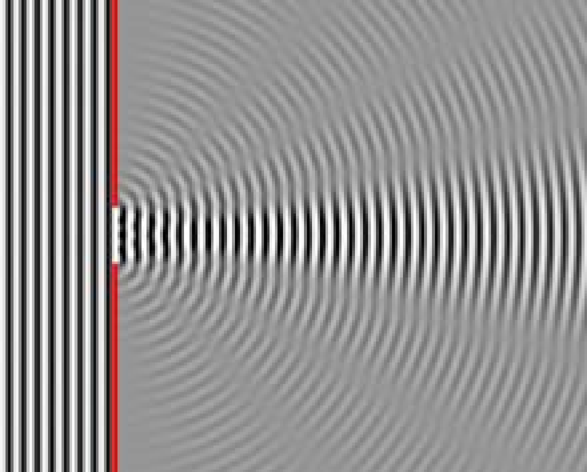
$f(x,q)$ — optical distance from x to q ("phase function")

λ — small parameter

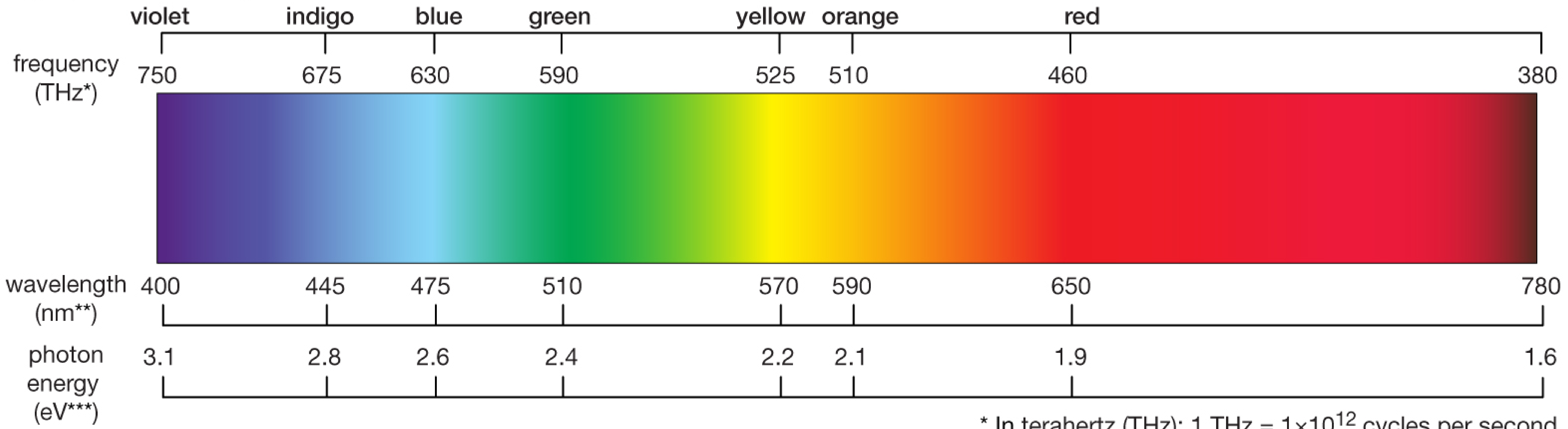
"fast-oscillating integral"







Light, the visible spectrum



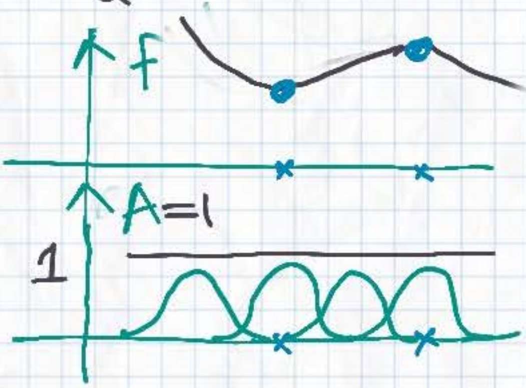
* In terahertz (THz); 1 THz = 1×10^{12} cycles per second.

** In nanometres (nm); 1nm = 1×10^{-9} metre.

*** In electron volts (eV).

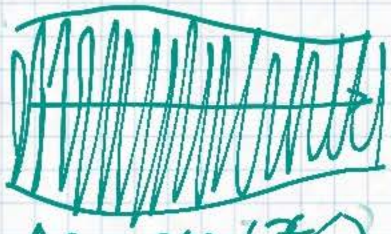
Asymptotics of oscillating integrals

$$\int_a^b A(x)\, e^{2\pi i f(x)/\lambda}\, dx \to 0 \quad \text{as } \lambda \to 0$$



– faster when the support of A does not contain critical points of f.

Intuitively speaking:



$A(x)\cos(x/\lambda)$

More precisely:

Suppose $[a,b]$ contains no critical points of f. Then

$$\int_a^b A(x)\, e^{2\pi i f(x)/\lambda} dx = \int_\alpha^\beta B(y)\, e^{iy/\lambda} dy$$

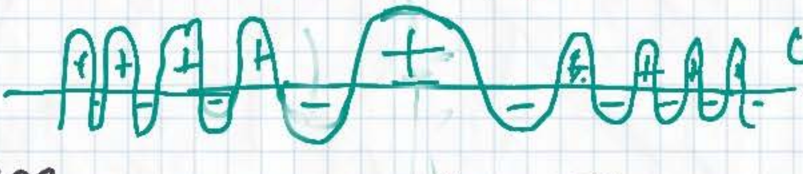
$$= i\lambda \int_\alpha^\beta B'(y)\, e^{iy/\lambda} dy = (i\lambda)^2 \int_\alpha^\beta B''(y)\, e^{iy/\lambda} dy = \dots$$

$\Rightarrow I \to 0$ as $\lambda \to 0$ faster than any power of λ.

Suppose $[a,b]$ contains one non-degenerate ($f'' \neq 0$) critical pt of f.

Intuitively speaking $f \sim y^2$

$$e^{iy^2/\lambda} = \cos y^2/\lambda + i \sin y^2/\lambda$$



$\cos(y/\sqrt{\lambda})^2$

$$\int_{-\infty}^{\infty} \cos y^2/\lambda \, dy = \sqrt{\tfrac{\pi}{2}\lambda} = \int_{-\infty}^{\infty} \sin y^2/\lambda \, dy$$

(Fresnel's integral)

More precisely: near a crit. pt $x=0$

$$\int_{-\infty}^{\infty} A(x)\, e^{2\pi i f(x)/\lambda}\, dx$$

A - compactly supported

$$= \int_{-\infty}^{\infty} (A + Bx + \ldots)\, e^{i(\alpha + \beta x^2 + \gamma x^3 + \ldots)/\lambda}\, dx$$

($A = A(0)$; α — critical value)

$$= \sqrt{\lambda}\, e^{i\alpha/\lambda} \int_{-\infty}^{\infty} (A + By\sqrt{\lambda} + \ldots)\, e^{i(\beta y^2 + \gamma y^3\sqrt{\lambda} + \ldots)}\, dy$$

$x = y\sqrt{\lambda}$

$e^{i\gamma y^3\sqrt{\lambda}} = 1 + i\gamma y^3\sqrt{\lambda} + \ldots$

$$= \sqrt{\lambda}\, e^{i\alpha/\lambda} \int_{-\infty}^{\infty} e^{i\beta y^2} \left[A + By\sqrt{\lambda} + i\gamma y^3\sqrt{\lambda} + Cy^2\lambda + iB\gamma y^4\lambda + \ldots\right] dy$$

$$= \sqrt{\lambda}\, e^{i\alpha/\lambda} \int_{-\infty}^{\infty} e^{i\beta y^2} \left[A + O(\lambda^{1/2})\right] dy$$

$$\int_{-\infty}^{\infty} e^{i\beta y^2} y^l\, dy = \begin{cases} 0 & l\text{ - odd} \\ \text{momenta of Gaussian distribution} & l\text{-even} \end{cases}$$

$$= \sqrt{i\lambda}\, \frac{e^{2\pi i f(0)/\lambda}}{\sqrt{f''(0)}} \left[A + O(\lambda)\right]$$

(critical value: $f(0)$; $O(\lambda)$ — power series in λ)

In d variables: $I = \lambda^{d/2}\left[a + O(\lambda)\right]$

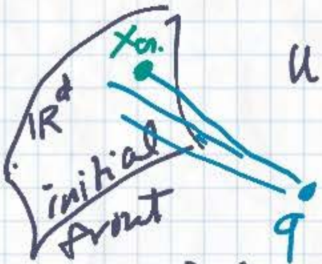
Near caustics: $f \sim x^3$, $x = y\lambda^{1/3}$

$\Rightarrow I = \lambda^{d/2 - 1/6} \leftarrow \frac{1}{3} - \frac{1}{2} = -\frac{1}{6}$

as $\lambda \to 0$, infinitely brighter than $\lambda^{d/2}$

> In short-wave approximation ($\lambda \ll 1$) the wave field picks its strength from neighborhoods of critical points of f. At $\lambda = 0$, we get geometrical optics, $f(x_{crit}, q) = S(q)$ - solution to eikonal eqn.

Asymptotics of oscillating integrals



$$u(t,q) = e^{i\omega t}\int_{\mathbb{R}^d} a(x,q)\, e^{2\pi i f(x,q)/\lambda}\, dx$$

$$= e^{i\omega t}(i\lambda)^d\, e^{2\pi i f(x_{cr}^{(q)},q)/\lambda + C_0(q) + C_1(q)\lambda + \dots}, \qquad f(x_{cr}^{(q)},q) = S(q)$$

asymptotics of the wave field as $\lambda \to 0$

The wave equation

$$\frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 u}{\partial q_1^2} + \frac{\partial^2 u}{\partial q_2^2} + \frac{\partial^2 u}{\partial q_3^2} = \Delta u$$

(The Laplace operator → Δ)

History: Faraday ⇝ Maxwell (~1865)

Theory of ElectroMagnetic Field

⇒ wave eqn., solution $u = e^{i\omega t + i\vec{k}\cdot\vec{q}}$,

$$\frac{\omega^2}{c^2} = |\vec{k}|^2 = \left(2\pi/\lambda\right)^2, \qquad \boxed{\frac{1}{c^2} = \varepsilon_0 \mu_0}$$

⇒ light = electromagnetic waves

What eqn. should S satisfy so that $u = e^{i\omega t} e^{2\pi i (S(q) + O(\lambda))/\lambda}$ would satisfy the wave eqn.?

$$\frac{\lambda^2}{c^2}\frac{\partial^2}{\partial t^2} \rightsquigarrow -\frac{\lambda^2\omega^2}{c^2} = -4\pi^2$$

$$\lambda\frac{\partial}{\partial q_k} \rightsquigarrow 2\pi i\left(\frac{\partial S}{\partial q_k} + O(\lambda)\right) e^{2\pi i (S + O(\lambda))/\lambda}$$

$$\left(\lambda\frac{\partial}{\partial q_k}\right)^2 \rightsquigarrow -4\pi^2\left[\left(\frac{\partial S}{\partial q_k}\right)^2 + O(\lambda)\right]$$

$$\boxed{\lambda\frac{\partial^2 S}{\partial q_k^2} \sim O(\lambda)}$$

Conclusion:

S must satisfy the eikonal equation

$$1 = \left(\frac{\partial S}{\partial q_1}\right)^2 + \left(\frac{\partial S}{\partial q_2}\right)^2 + \left(\frac{\partial S}{\partial q_3}\right)^2$$

The Planck constant, $\hbar$

Einstein (1905): $E\tau = 2\pi\hbar n$, $n = 1, 2, 3, \dots$

(E ← energy of light wave; τ ← period λ/c)

$2\pi\hbar \simeq 6.626 \times 10^{-34} \frac{kg \cdot m^2}{s}$ ← [action]

$E = \hbar\omega$ or $E\lambda = 2\pi\hbar c$ ← light speed

(ω ← angular frequency; λ ← wave length)

[Predecessors: Plank's theory of "black body radiation" (1901), Ehrenfest]

⋮

de Broglie (1924): At microscopic scale, matter possesses wave-like properties.

Davisson - Germer (1927): diffraction of electrons on a crystal.

Optics — Q.M. dictionary

wave field $u(t,q)$ in space-time	"psi-function" $\Psi(t,q)$ on the extended configuration space
wave-length λ	Planck's constant $2\pi\hbar$
wave equation $\frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = \Delta u$	Schrödinger eqn. ?
eikonal eqn as the limit as $\lambda \to 0$	Hamilton-Jacobi eqn. as the limit as $\hbar \to 0$
light rays	trajectories of Hamiltonian systems

(optical) illusion due to
($\lambda \approx 0$) $\hbar \approx 0$

Quantum observables

$$\Psi(t,q) = e^{i[S(t,q) + \Theta(\hbar)]/\hbar}$$

"Reverse engineering": What equation should Ψ satisfy so that in the limit $\hbar \to 0$, S would satisfy the extended Hamilton-Jacobi equ $-\frac{\partial S}{\partial t} = H\left(\frac{\partial S}{\partial q}, q\right)$?

Our experience: $E = H(p,q)$

$$i\hbar\frac{\partial}{\partial t} \rightsquigarrow -\frac{\partial S}{\partial t} \; (=E)$$

$$\frac{\hbar}{i}\frac{\partial}{\partial q_k} \rightsquigarrow \frac{\partial S}{\partial q_k} \; (=p)$$

$$q_2\frac{\hbar}{i}\frac{\partial}{\partial q_3} - q_3\frac{\hbar}{i}\frac{\partial}{\partial q_2} \rightsquigarrow q_2p_3 - p_2q_3 \; (=L_1)$$

Conclusion: Quantum observables = linear differential operators

$$\hat{p}_k = \frac{\hbar}{i}\frac{\partial}{\partial q_k}, \quad \hat{q}_k = q_k \times, \quad \hat{L}_1 = \hat{q}_2\hat{p}_3 - \hat{q}_3\hat{p}_2$$

Quantization: $H = \frac{p^2}{2m} + V(q)$

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + V(q)$$

Non-commutativity $\hat{p}_k\hat{q}_k - \hat{q}_k\hat{p}_k = \frac{\hbar}{i}$

$$\frac{\hbar}{i}\frac{\partial}{\partial q_k}q_k\psi - q_k\frac{\hbar}{i}\frac{\partial}{\partial q_k}\psi = \frac{\hbar}{i}\psi$$

$\Rightarrow$ Quantization problem: $H \rightsquigarrow \hat{H}$ is ill-posed (solution non-unique)

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\Delta\Psi + V(q)\Psi$$

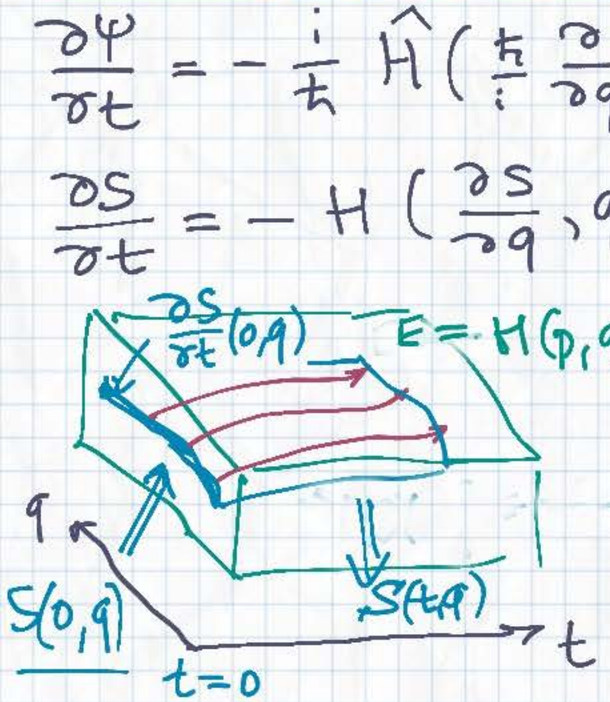
The Schrödinger equation (corresponding to Newton's mech. systems)

What does Ψ describe?

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar}\hat{H}\left(\frac{\hbar}{i}\frac{\partial}{\partial q}, q\right)\Psi$$

↑ describes evolution of quantum state: given $\Psi(0,q)$ determines $\Psi(t,q)$ in a deterministic fashion

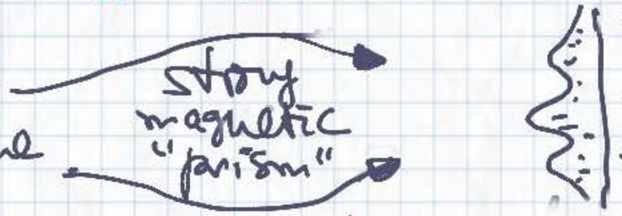
$$\frac{\partial S}{\partial t} = -H\left(\frac{\partial S}{\partial q}, q\right)$$



How to find Ψ(0,q) (or check Ψ(t,q))?

$|\Psi(q)|^2$ ~ probability density of finding the system in configuration q

Example: Hitachi's double-slit experiment



It is not possible to predict the fate of individual electrons — only the probability distribution!

What is probability?

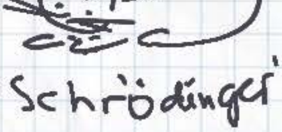
$$P = \lim_{N\to\infty}\frac{K}{N}$$

K ← # of favorable events

N ← # of all trials

Events – irreversible macroscopic detections

Particles or Waves?



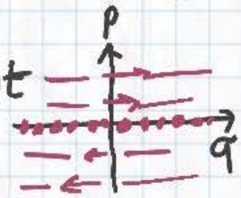
"Schrödinger's Cat"

$$\Psi(q) = |\Psi(q)|\, e^{i \arg \Psi(q)}$$

↑ probability (complex) amplitudes of probability; interference

A free particle on the line

$$H = \frac{p^2}{2m} \quad \begin{cases} \dot q = p/m \Rightarrow & q(t) = q(0) + p(0)t/m \\ \dot p = 0 & p(t) = p(0) \end{cases}$$



$$i\hbar \frac{\partial \Psi(q,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(q,t)}{\partial q^2}, \quad \Psi(q,0) = \psi(q)$$

↑ given

"Separation of varibles":

$$i\hbar \frac{\partial \Psi}{\partial t} = E\Psi = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial q^2}$$

$$\Psi = e^{Et/i\hbar}\psi(q), \quad \psi(q) = A\, e^{\pm i\sqrt{2mE}\, q/\hbar}$$

$$\Psi = A\, e^{i(kq - \omega t)}, \quad \omega = \frac{E}{\hbar}, \quad k^2 = \frac{2mE}{\hbar^2}$$

$kq - \omega t = k(q - wt)$

travelling wave with phase velocity $w = \omega/k$

$|\Psi|^2 \equiv$ const – uniform probability

In general, Ψ = superposition of travelling waves

$$\Psi(q,t) = \int_{-\infty}^{\infty} A(k)\, e^{i(kq - \omega(k)t)}\, dk \qquad \omega = \frac{k^2\hbar}{2m}$$

At $t = 0$: $\psi(q) = \int_{-\infty}^{\infty} A(k)\, e^{ikq}\, dk$

↑ Fourier transform of ψ

$$A(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \psi(q)\, e^{-ikq}\, dq$$

Remark: $(q, p) \mapsto (-p, q)$ is symplectic

$$-i\hbar\frac{\partial}{\partial q}\psi \rightsquigarrow \hbar k A \qquad \hat p = \hbar k = p$$

$$q\psi \rightsquigarrow i\frac{\partial}{\partial k} A \qquad \hat q = i\hbar\frac{\partial}{\partial p}$$

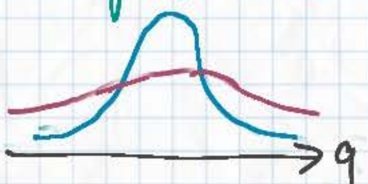
The same quantum state can be represented by $\psi(q)$ or by $A(p/\hbar)$

The Uncertainty Principle

$|\psi(q)|^2 dq$ — probability density of position

$|A(p/\hbar)|^2 dp$ — probability density of momenta

$e^{ipq/\hbar}$



Heisenberg: $\boxed{\Delta p \, \Delta q \approx \hbar}$

The Dirac delta-function

$$\delta(q-q_0) = \begin{cases} +\infty & q = q_0 \\ 0 & q \neq q_0 \end{cases} \qquad \int_{-\infty}^{\infty} \delta(q-q_0)\,\phi(q)\,dq = \phi(q_0)$$

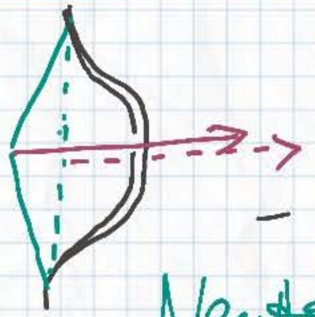
ψ''

$$A(k) := \frac{1}{2\pi} \int_{-\infty}^{\infty} \delta(q-q_0)\, e^{-ikq}\, dq = \frac{1}{2\pi} e^{-iq_0 k}$$

$|A(k)|^2 = \text{const}$ — uniform distribution

If position is certain, then the momentum is totally uncertain, and vice versa.

The arrow paradox of Zeno



The arrow is still "here" but it is already flying — a contradiction of terms!

Newton: instantaneous velocity

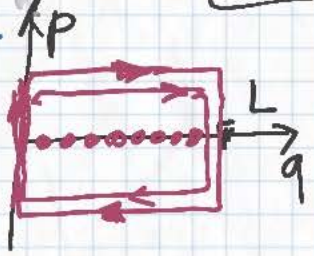
$$v = \lim_{\Delta t \to 0} \frac{\Delta q}{\Delta t}$$

Heisenberg: Zeno was right!

To measure the velocity with an error $\Delta p/m$, we must disturb the position q_0 by at least $\Delta q \geq \hbar/\Delta p$

The infinite well potential

$$H = \frac{p^2}{2m} + V(q) = \begin{cases} 0 & \text{if } 0<q<L \\ \infty & \text{otherwise} \end{cases}$$



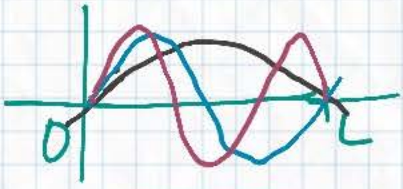
$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial q^2} + V(q)\Psi$$

$$\Psi = f(t)\psi(q), \quad f(t) = e^{-i\omega t}, \quad \omega = E/\hbar$$

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

Stationary (Time-indep.) Schrödinger eqn.

$$-\frac{\hbar^2}{2m}\psi'' = E\psi, \quad 0<q<L; \quad \psi(0)=\psi(L)=0$$



$$\psi_n(q) = A_n \sin\frac{\pi n q}{L}$$

$$E_n = \frac{\pi^2 n^2 \hbar^2}{2mL^2}, \quad n = 1, 2, 3, \dots$$

$$\Psi(q,t) = \sum_{n=1}^{\infty} e^{-iE_n t/\hbar} A_n \sin\frac{\pi n q}{L}$$

Fourier series

$$\psi(q) = \sum_{n\geq 1} A_n \sin\frac{\pi n q}{L} \qquad A_m = \frac{2}{L}\int_0^L \psi(q)\sin\frac{\pi m q}{L}\,dq$$

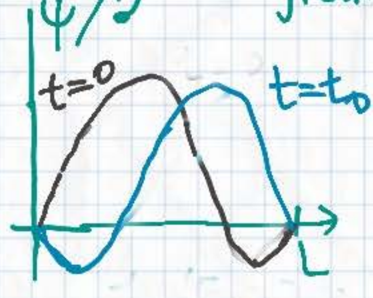
Remark: $E_1 = \frac{\pi^2\hbar^2}{2mL^2} > 0$

$$\Delta q \Delta p = L \cdot \frac{\pi\hbar}{L} \qquad \sin\frac{\pi q}{L} = \frac{e^{+i\frac{\pi}{L}q} - e^{-i\frac{\pi}{L}q}}{2i}$$

Example: $e^{-it\frac{E_1}{\hbar}}\psi_1 + e^{-it\frac{E_2}{\hbar}}\psi_2 =$

$$e^{-i\frac{E_1 t}{\hbar}}\left(\sin\frac{\pi q}{L} + e^{it\frac{(E_1-E_2)}{\hbar}}\sin\frac{2\pi q}{L}\right)$$

ground state — 1st excited state

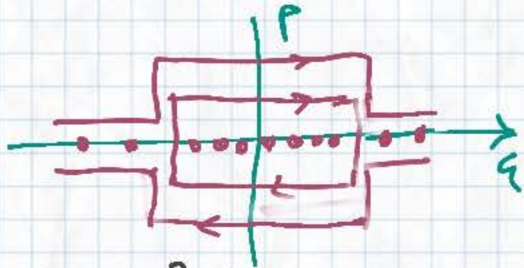


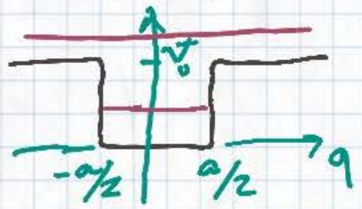
$$t = t_0 = \frac{\pi\hbar}{E_1 - E_2}$$

Ball bouncing off the walls.

Finite well potential

$V(q) = \begin{cases} 0 & |q| < a/2 \\ V_0 & |q| > a/2 \end{cases}$ 7.2





$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dq^2} + V(q)\psi = E\psi \qquad 0 < E < V_0$$

$$\psi''(q) = \begin{cases} -k^2\psi & |q| < a/2 \\ +\kappa^2\psi & |q| > a/2 \end{cases} \qquad k = \sqrt{2mE}/\hbar \qquad \kappa = \sqrt{2m(V_0 - E)}/\hbar$$

$$\psi_+(q) = \begin{cases} A\cos kq \\ Ce^{-\kappa|q|} \end{cases} \qquad \psi_-(q) = \begin{cases} B\sin kq \\ \pm De^{-\kappa|q|} \end{cases}$$

$$\underset{\text{even}}{\psi_+} + \underset{\text{odd}}{\psi_-}\,, \quad \int |\psi|^2 dq < \infty \Rightarrow \cancel{e^{+\kappa|q|}}$$

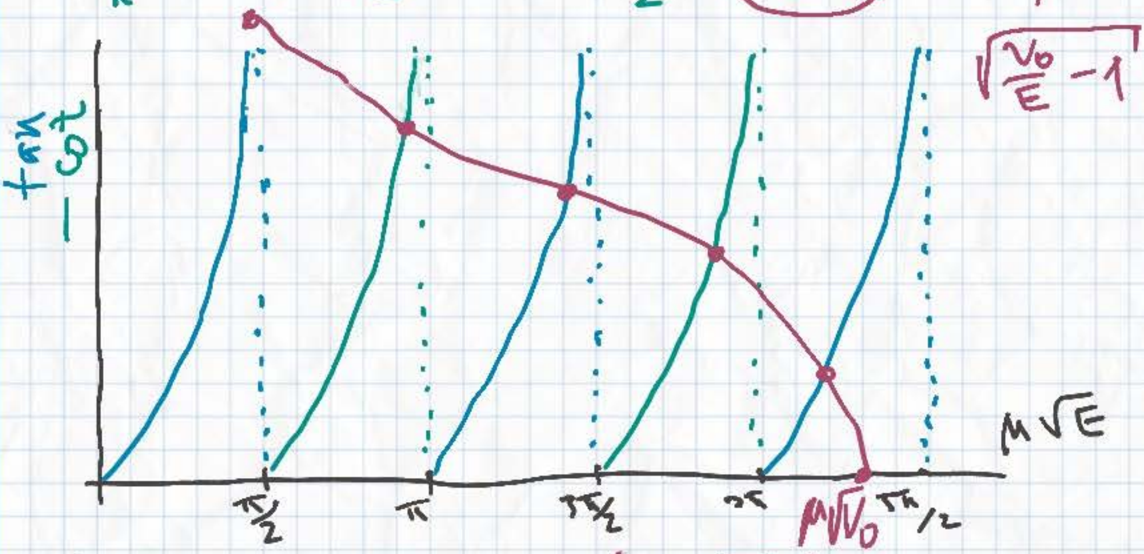
$$A\cos\frac{ka}{2} = Ce^{-\kappa a/2} \qquad B\sin\frac{ka}{2} = De^{-\kappa a/2}$$

$$Ak\sin\frac{ka}{2} = C\kappa e^{-\kappa a/2} \qquad Bk\cos\frac{ka}{2} = -De^{-\kappa a/2}$$

continuity of $\psi_\pm(\pm\frac{a}{2})$ and $\psi'_\pm(\pm\frac{a}{2})$

$$\kappa = k\tan\frac{ka}{2} \quad \leftarrow \text{ratios} \rightarrow \quad \kappa = -k\cot\frac{ka}{2}$$

$$\frac{\kappa}{k} = \sqrt{V_0/E - 1} \qquad \frac{ka}{2} = \sqrt{\frac{m}{2}}\frac{a}{\hbar}\sqrt{E} =: \mu\sqrt{E}$$

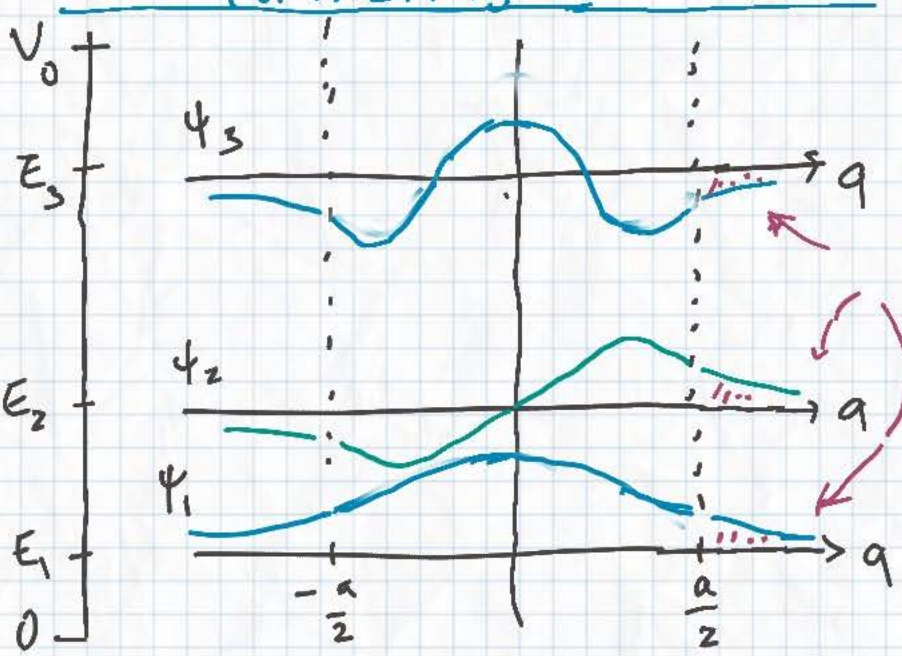


$$\#\{E_n < V_0\} = 1 + \left[\frac{2\mu\sqrt{V_0}}{\pi}\right]$$

As $V_0 \to \infty$, $E_n \to \dfrac{\pi^2 n^2}{4\mu^2} = \dfrac{\pi^2 n^2 \hbar^2}{2ma^2}$

as in the infinite well

Tunneling



The case $E > V_0$ (above the barrier)

$$\psi'' = \begin{cases} -k^2\psi & |q| < \frac{a}{2} \\ -\kappa^2\psi & |q| > \frac{a}{2} \end{cases} \qquad k = \sqrt{2mE}/\hbar, \quad \kappa = \sqrt{2m(E-V_0)}/\hbar$$

$$\psi = A\cos kq + B\sin kq \qquad |q| < \frac{a}{2}$$

$$\psi = C\cos\kappa q + D\sin\kappa q \qquad q > \frac{a}{2}$$

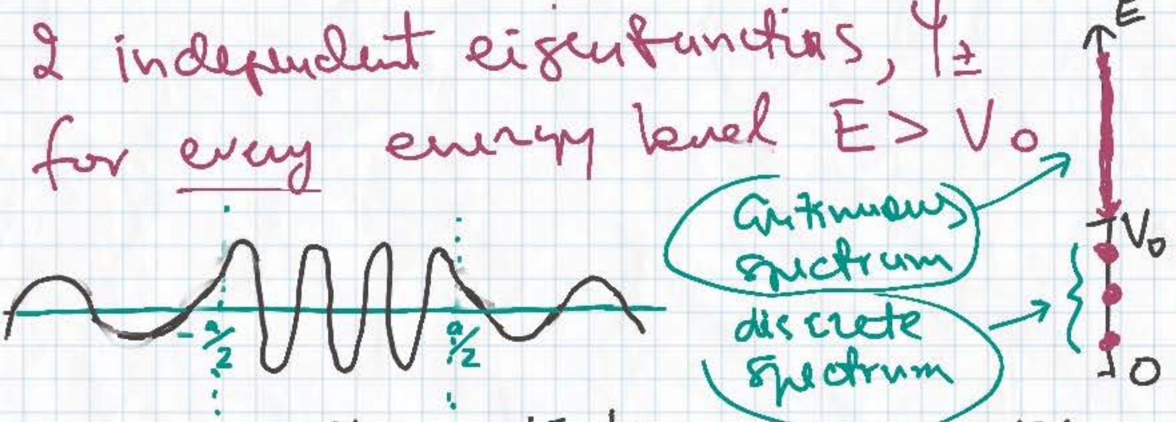
$$\psi = E\cos\kappa q + F\sin\kappa q \qquad q < -a/2$$

$$\psi\left(\tfrac{a}{2}\right)_- = \psi\left(\tfrac{a}{2}\right)_+, \quad \psi'\left(\tfrac{a}{2}\right)_- = \psi'\left(\tfrac{a}{2}\right)_+$$

$$\psi\left(-\tfrac{a}{2}\right)_- = \psi\left(-\tfrac{a}{2}\right)_+, \quad \psi'\left(-\tfrac{a}{2}\right)_- = \psi'\left(-\tfrac{a}{2}\right)_+$$

4 eqns on 6 unknowns $\Rightarrow$ 2-dim sol. space

2 independent eigenfunctions, $\psi_\pm$ for every energy level $E > V_0$



$$\Psi(q,t) = \sum_{i=1}^{N} a_n e^{-iE_n t/\hbar}\psi_n(q) + \int A(k) e^{-iE(k)t/\hbar}\psi_k(q)\,dk$$

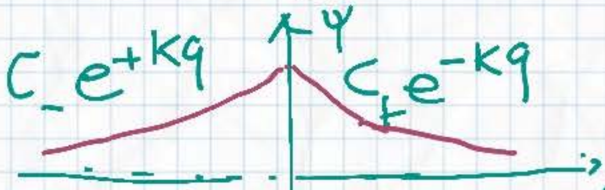
$E_n < V_0$ $\qquad$ $E(k) > V_0$

δ-function shaped well.

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dq^2} - K\,\delta(q)$$

$$\underset{[m^0]}{1} = \int \underset{[m^{-1}]}{\delta(q)}\,\underset{[m]}{dq} \Rightarrow K = \frac{\hbar^2}{2m\,\underset{[m]}{d}}$$

$$\frac{d^2\psi}{dq^2} + \frac{\delta(q)}{d}\psi = -\frac{2mE}{\hbar^2}\psi$$ Stationary Schrödinger eqn.

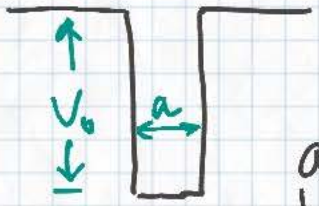


$\kappa = \sqrt{-2mE}/\hbar$

$$\psi'(0^+) - \psi'(0^-) = \int_{0^-}^{0^+} \psi''\,dq = -\int_{0^-}^{0^+} \frac{\delta\psi}{d}\,dq = -\frac{\psi(0)}{d}$$

$$\Rightarrow C_+ = C_- = \psi(0), \quad -\kappa C_+ - \kappa C_- = -\frac{\psi(0)}{d}$$

$$\Rightarrow \kappa = 1/2d \Rightarrow E_1 = -\hbar^2/8md^2$$



$$V_0 a = \frac{\hbar^2}{2md}$$

$a \to 0$

$V_0 \to \infty$

$$\mu\sqrt{V_0} = \sqrt{\frac{\hbar}{4d}} \to 0$$

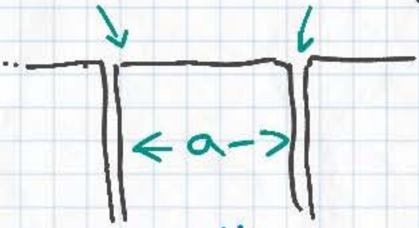
$$\Rightarrow \left[\mu\sqrt{V_0}\right] \to 1$$

Double-well and molecular bonding

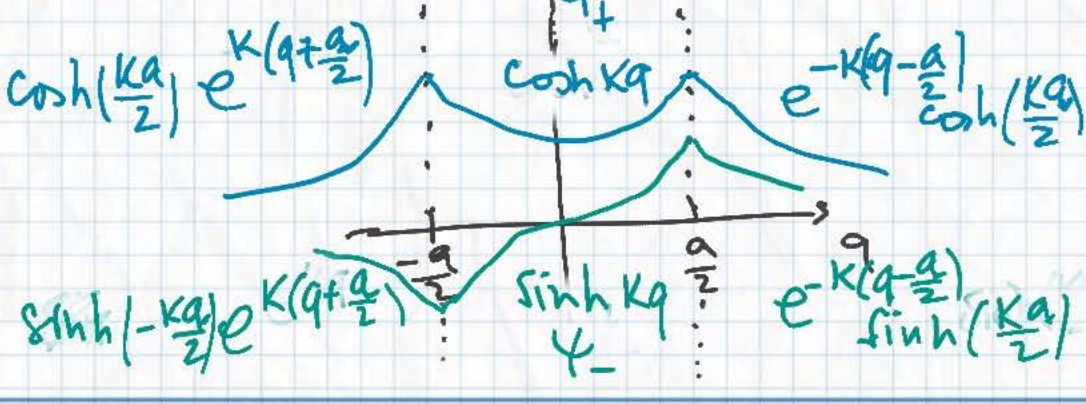
$$\frac{d^2\psi}{dq^2} + \frac{\alpha}{a}\left[\delta\left(q+\frac{a}{2}\right) + \delta\left(q-\frac{a}{2}\right)\right]\psi = -\frac{2mE}{\hbar^2}\psi$$

$$\frac{\alpha}{a} = \frac{1}{d}$$

$$[\alpha] = [m^0]$$

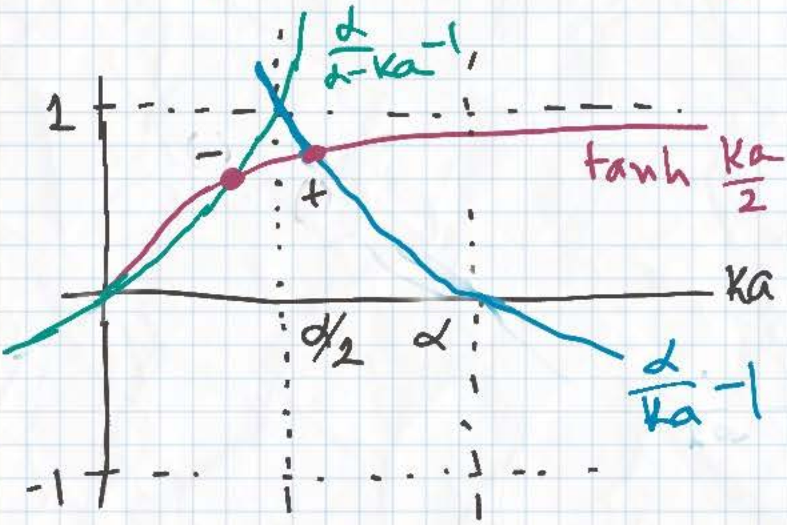


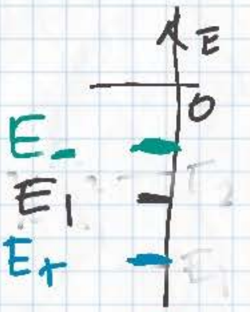
$$\kappa = \frac{\sqrt{-2mE}}{\hbar}$$



$$\psi'(\tfrac{a^+}{2}) - \psi'(\tfrac{a^-}{2}) = -\frac{\alpha}{a}\psi(\tfrac{a}{2})$$

$\Rightarrow$ $\frac{\alpha}{ka} - 1 = \tanh\frac{ka}{2}$ $\qquad$ $\frac{\alpha}{\alpha - ka} - 1 = \tanh\frac{ka}{2}$





$E = -\frac{k^2\hbar^2}{2m}$

($\alpha = a/d$)

$E_1 = -\frac{\hbar^2}{8md^2}$

- $E_+ < E_1 < E_-$

  $E_1 = E|_{ka = \frac{\alpha}{2}}$ ($\Rightarrow E_+$ saves energy comparing to E_1)

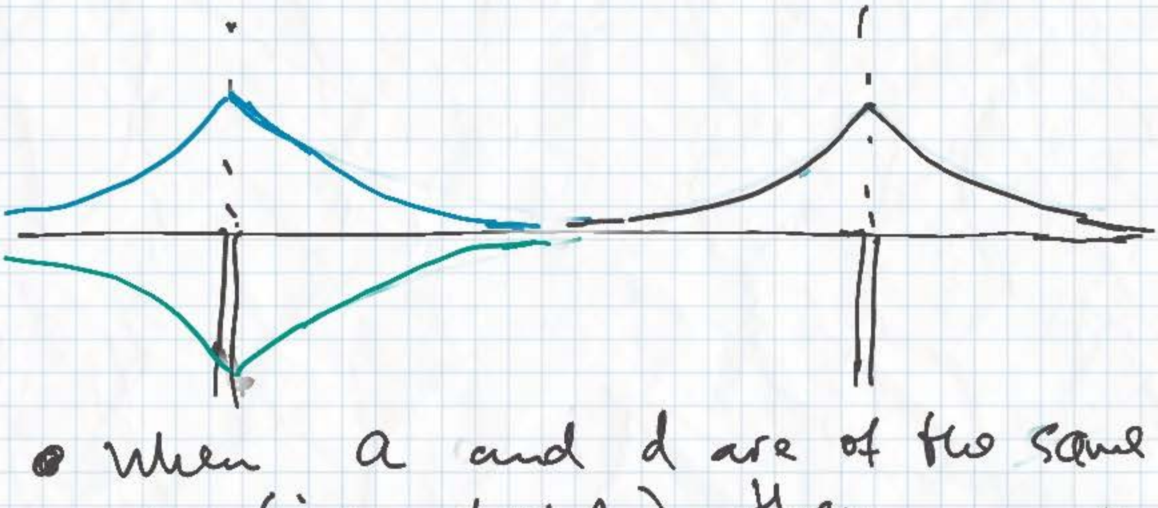
- E_- exists only when $\alpha \geq 2$

- When $a \gg d$ (but $\frac{\alpha}{a} = \frac{1}{d}$ = const)

  then $E_+ \approx E_- \approx E_1$ $\quad$ i.e. $\alpha \gg 1$

  $$\psi_\pm \approx \psi_1(q - \tfrac{a}{2}) \pm \psi_1(q + \tfrac{a}{2})$$

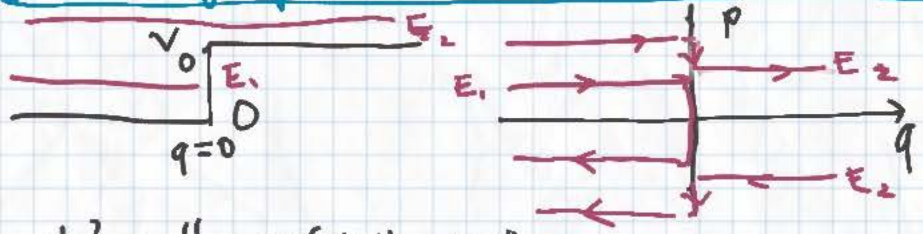
  ("degenerate" energy level)



- When a and d are of the same order (i.e. $\alpha \approx 1$) then the energy level splits ($E_+ < E_-$)

The atoms bind by the electron occupying the ground level $E_+ < E_1$

The step potential and Scattering



$$-\frac{\hbar^2}{2m}\psi'' + V(q)\psi = E\psi, \quad E > V_0$$

$$\psi(q) = \begin{cases} A_+ e^{ikq} + A_- e^{-ikq} & q<0 \quad k = \sqrt{2mE}/\hbar \\ B_+ e^{ik_0 q} + B_- e^{-ik_0 q} & q>0 \quad k_0 = \sqrt{2m(E-V_0)}/\hbar \end{cases}$$

Continuity of ψ and ψ' at $q=0$:

$$A_+ + A_- = B_+ + B_-, \quad ik(A_+ - A_-) = ik_0(B_+ - B_-)$$

Time factor: $\Psi(q,t) = e^{-itE/\hbar}\psi(q)$

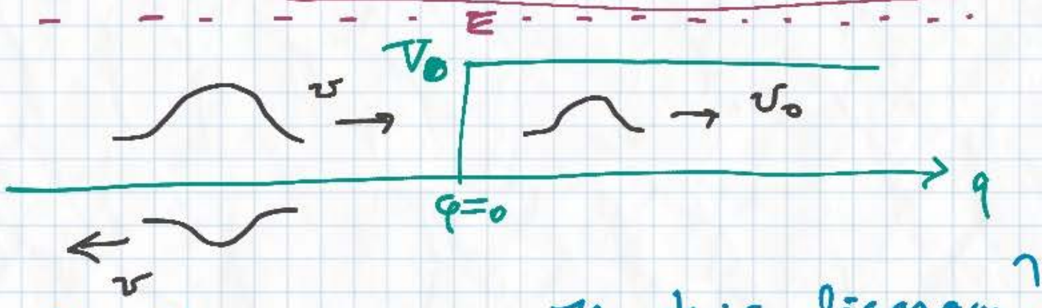
$$\Psi(t,q) = \begin{cases} q<0: \ e^{ik(q-vt)} + A_- e^{-ik(q+vt)} \\ q>0: \ B_+ e^{ik_0(q-v_0 t)} \end{cases}$$

$A_- e^{-ik(q+vt)}$ ← reflection

$B_+ e^{ik_0(q-v_0t)}$ ← transmission

$A_+ = 1$
$B_- = 0$

$$B_+ = \frac{2k}{k+k_0}, \quad A_- = \frac{k-k_0}{k+k_0}$$



What's wrong with this diagram?

Probability current

$$\Psi = e^{-iEt/\hbar}\psi, \quad \psi = \begin{cases} A_+ e^{ikq} + A_- e^{-ikq} & q<0 \\ B_+ e^{ik_0 q} + B_- e^{-ik_0 q} & q>0 \end{cases}$$

$k = \sqrt{2mE}/\hbar$, $k_0 = \sqrt{2m(E-V_0)}/\hbar$

Problem: $\int |\psi|^2 dq = \infty$

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi^*}{\partial q^2} + V(q)\Psi^*$$

complex conjugation

$$\frac{\partial}{\partial t}|\Psi|^2 = \Psi^* \dot{\Psi} + \Psi \dot{\Psi}^*$$
$$= \frac{i\hbar}{2m}\left(\Psi^* \frac{\partial^2 \Psi}{\partial q^2} - \Psi \frac{\partial^2 \Psi^*}{\partial q^2}\right)$$
$$= \frac{\partial}{\partial q}\left[\frac{i\hbar}{2m}\left(\Psi^* \frac{\partial \Psi}{\partial q} - \Psi \frac{\partial \Psi^*}{\partial q}\right)\right]$$
$$=: -j \quad \text{probability current}$$

$$\frac{d}{dt}\int_a^b |\Psi(q,t)|^2 dq = j(a,t) - j(b,t)$$

$\frac{d}{dt} P[a,b]$ — rate of influx / outflux (at a / at b)

$j(q,t)$ – rate of probability flux across q.

When Ψ, $\frac{\partial \Psi}{\partial q}$ decay at $q \to \pm\infty$

$$\frac{d}{dt}\int_{-\infty}^{\infty} |\Psi(q)|^2 dq = -j(q,t)\Big|_{-\infty}^{\infty} = 0$$

"conservation of probability"

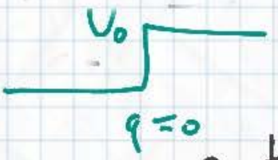
In our scattering problem:

Ψ: $A_+ e^{ikq} + A_- e^{-ikq}$ $\quad$ Ψ^*: $A_+^* e^{-ikq} + A_-^* e^{+ikq}$

$\frac{\partial \Psi^*}{\partial q}$: $ik(A_-^* e^{ikq} - A_+^* e^{-ikq})$ $\quad$ $\frac{\partial \Psi}{\partial q}$: $ik(A_+ e^{ikq} - A_- e^{-ikq})$

$$j = \frac{k\hbar}{m}\left(|A_+|^2 - |A_-|^2\right)$$

$$\psi = \begin{cases} A_+ e^{ikq} + A_- e^{-ikq} & q<0 \\ B_+ e^{ik_0 q} + B_- e^{-ik_0 q} & q>0 \end{cases}$$



$k = \sqrt{2mE}/\hbar \quad k_0 = \sqrt{2m(E-V_0)}/\hbar$

$$j = \begin{cases} \frac{\hbar k}{m}\left(|A_+|^2 - |A_-|^2\right) \\ \frac{\hbar k_0}{m}\left(|B_+|^2 - |B_-|^2\right) \end{cases}$$

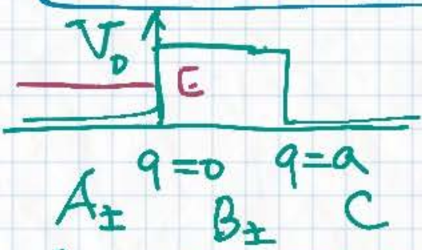
$B_- = 0, \quad \frac{A_-}{A_+} = \frac{k-k_0}{k+k_0}, \quad \frac{B_+}{A_+} = \frac{2k}{k+k_0}$

$$R = \frac{j_{ref}}{j_{inc}} := \frac{|A_-|^2}{|A_+|^2} = \frac{(k-k_0)^2}{(k+k_0)^2}$$

$$T = \frac{j_{trans}}{j_{inc}} := \frac{k_0|B_+|^2}{k|A_+|^2} = \frac{4k_0 k}{(k+k_0)^2}$$

Reflection / Transition probabilities, $R+T=1$

Rectangular barrier



$$\psi = \begin{cases} A_+ e^{ikq} + A_- e^{-ikq} & q<0 \\ B_+ e^{\kappa q} + B_- e^{-\kappa q} & 0<q<a \\ C_+ e^{ikq} & 0<q \end{cases}$$

$C_- = 0$

$k = \sqrt{2mE}/\hbar \quad \kappa = \sqrt{2m(V_0-E)}/\hbar$

$A_+ + A_- = B_+ + B_-, \quad ik(A_+ - A_-) = \kappa(B_+ - B_-)$

Continuity conditions for ψ, ψ' at $q=0,a$

$B_+ e^{\kappa a} + B_- e^{-\kappa a} = C e^{ika}, \quad \kappa(B_+ e^{\kappa a} - B_- e^{-\kappa a}) = ikCe^{ika}$

$\zeta := \kappa + ik$, eliminate $B_\pm$:

$A_+\zeta + A_-\zeta^* = 2\kappa B_+ = C\zeta e^{-a\zeta^*}$, $\quad -a\zeta^* = -\kappa a + ika$

$A_+\zeta^* + A_-\zeta = 2\kappa B_- = C\zeta^* e^{a\zeta}$, $\quad a\zeta = \kappa a + ika$

$$\frac{A_+}{C} = \frac{\zeta^2 e^{-\kappa a} - (\zeta^*)^2 e^{\kappa a}}{\zeta^2 - (\zeta^*)^2} e^{ika}$$

Tunneling.

$$T = \left|\frac{C}{A_+}\right|^2 = \frac{(\gamma^2 - (\gamma^*)^2)^2}{(\gamma^2 e^{-\kappa a} - (\gamma^*)^2 e^{\kappa a})^2} =$$

$(\alpha+\beta i)^2 = (\alpha^2-\beta^2) + 2\alpha\beta i$

$\mathrm{Re}(\alpha+\beta i)^4 = (\alpha^2-\beta^2)^2 - 4\alpha^2\beta^2 = \alpha^4+\beta^4-6\alpha^2\beta^2$

$(\alpha+\beta i)^2(\alpha-\beta i)^2 = (\alpha^2+\beta^2)^2 = \alpha^4+\beta^4+2\alpha^2\beta^2$

$$= \frac{4k^2\kappa^2}{4k^2\kappa^2 + (k^2+\kappa^2)^2 \sinh^2 \kappa a}$$

Non-zero probability to penetrate the barrier – tunneling.

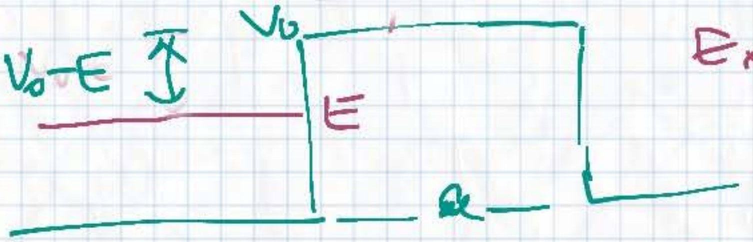
Suppose $\kappa a \gg 1$ $\quad \sinh^2 x = \dfrac{e^{2x}+e^{-2x}-2}{4}$

$$\approx \left(\frac{4k\kappa}{k^2+\kappa^2}\right)^2 e^{-2\kappa a}$$

$\kappa = \sqrt{2m(V_0-E)}/\hbar$

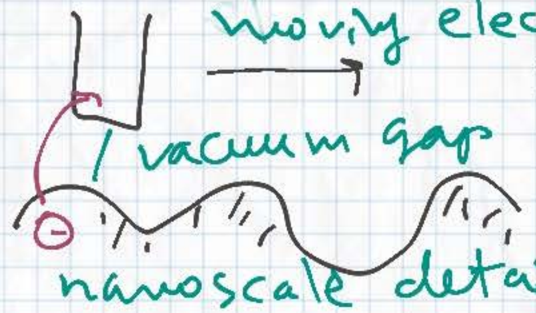
$k = \sqrt{2mE}/\hbar$

$$= 16\,\frac{E}{V_0}\left(1-\frac{E}{V_0}\right) e^{\underbrace{-2a\sqrt{2m(V_0-E)}/\hbar}_{\kappa a \gg 1}}$$



Exponential decay in V_0-E and in $\underline{a}$

Remark (from physics textbooks): This has some applications, E.g. in scanning tunneling microscopy:



Electrons tunnel into the electrod through vacuum gap, kept constant by a feedback loop.

Hermitian linear algebra

Classical observables = real-valued functions on a symplectic phase space

Quantum observables = Hermitian linear operators on a Hilbert space

$\mathcal{H}$ - a complex vectorspace equipped with an Hermitian inner product

$\langle \psi_1 | \psi_2 \rangle \in \mathbb{C}$, $\langle \psi_2 | \psi_1 \rangle = \langle \psi_1, \psi_2 \rangle^*$

$\langle \psi_3 | \psi_1 + \psi_2 \rangle = \langle \psi_3 | \psi_1 \rangle + \langle \psi_3 | \psi_2 \rangle$

$\langle \psi_2 | \lambda \psi_1 \rangle = \lambda \langle \psi_2 | \psi_1 \rangle$

$\Rightarrow \langle \lambda \psi_2 | \psi_1 \rangle = \lambda^* \langle \psi_2 | \psi_1 \rangle$

$\langle \psi | \psi \rangle =: \|\psi\|^2 > 0$ unless $\psi = 0$.

Example-exercise: Every Hermitian inner product in $\mathbb{C}^n$ in a suitable coordinate system coincide with

$\langle z | w \rangle = z_1^* w_1 + \dots + z_n^* w_n$

Hint: Gram-Schmidt orthogonalization

Def. $A: \mathcal{H} \to \mathcal{H}$ is called Hermitian if $A = A^*$, i.e. $\langle \psi_2 | A \psi_1 \rangle = \langle \psi_1 | A \psi_2 \rangle^*$ for all $\psi_1, \psi_2 \in \mathcal{H}$.

Notation: $|\psi\rangle$ - "ket" vector $\langle \psi |$ "bra" covector

$\langle \psi | A^* | \phi \rangle \underset{\text{def of "adjoint"}}{=} \langle \psi | A | \phi \rangle \underset{A^* = A}{=} \langle \psi | A | \phi \rangle$

In $\mathbb{C}^n$: $\langle z | A | w \rangle = \sum_{i,j} z_i^* a_{ij} w_j$, $a_{ij}^* = a_{ji}$

The Spectral Theorem (a.k.a. "Orthogonal diagonalization")

An Hermitian $A: \mathbb{C}^n \to \mathbb{C}^n$ has an orthonormal basis of eigenvectors: $A|\psi_i\rangle = \lambda_i |\psi_i\rangle$

$\langle \psi_i | \psi_j \rangle = \delta_{ij}$, $\lambda_i \in \mathbb{R}$, $i, j = 1, \dots, n$.

The Abstract Fourier Method

$$\langle \psi_1 | \psi_2 \rangle = \int_{-\infty}^{\infty} \psi_1^*(q)\, \psi_2(q)\, dq$$

$$\mathcal{H} = \{ \psi : \mathbb{R} \to \mathbb{C} \mid \int_{-\infty}^{\infty} |\psi(q)|^2 dq < \infty \}$$

1° $f(q)$ - real $\quad \hat{f}|\psi\rangle := f(q)\psi(q) \quad f = f^*$

"Eigenvectors" $\delta(q-q_0)$ / eigenvalues $f(q_0)$

$$\int \psi(q)\, f(q)\, \delta(q-q_0)\, dq = \int \psi(q)\, f(q_0)\, \delta(q-q_0)\, dq$$

2° $g(p)$ - real (polynomial) $\quad \hat{g}|\psi\rangle := g\left(\frac{\hbar}{i}\frac{\partial}{\partial q}\right)\psi(q)$

$$\int_{-\infty}^{\infty} \psi^*(q)\, \frac{\hbar}{i}\frac{\partial}{\partial q}\psi(q)\, dq = \left[\int_{-\infty}^{\infty} \psi^*(q)\, \frac{\hbar}{i}\frac{\partial}{\partial q}\psi(q)\, dq\right]^*$$

integration by parts

"Eigenvectors" $e^{ip_0 q/\hbar}$ / eigenvalues $g(p_0)$

$$\psi(q) = \int_{-\infty}^{\infty} \frac{A(p_0/\hbar)}{2\pi} e^{ip_0 q/\hbar}\, dp_0 \qquad \psi(q) = \int_{-\infty}^{\infty} \psi(q_0)\, \delta(q-q_0)\, dq_0$$

3° $H = \frac{p^2}{2m} + V(q) \qquad \hat{H}|\psi\rangle = E|\psi\rangle$

Assume discrete spectrum: $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

$$|\psi\rangle = \sum_{n=1}^{\infty} c_n |\psi_n\rangle \qquad \langle \psi_m | \psi \rangle = c_m$$

Fourier coefficients

$$\|\psi\|^2 = \langle \psi | \psi \rangle = \sum_{n=1}^{\infty} |c_n|^2$$ Parseval's identity

$\frac{|c_n|^2}{\|\psi\|^2}$ - probability of $H = E_n$ in the quantum state ψ.

The same for any observable $A|\psi_n\rangle = a_n|\psi_n\rangle$

Example:

$\frac{|\psi(q_0)|^2}{\|\psi\|^2} dq_0$ - probability density of the event that $\hat{q} = q_0$

The Abstract Uncertainty Principle

A, B - Hermitian $\Rightarrow$ $A+B$, λA ($\lambda \in \mathbb{R}$), $\frac{AB+BA}{2}$, $\frac{i}{\hbar}(AB-AB)$ - are Hermitian

fg $\quad \{f,g\}$ - for classical observables

$AB \overset{?}{=} (AB)^* = B^* A^* = BA$ - iff $[A,B]=0$

Lemma: $[A,B]=0 \Rightarrow$ eigenspaces of A are B-invariant

Proof. $A\,B|\psi\rangle = B A|\psi\rangle = B|a\psi\rangle = a\,B|\psi\rangle$

Corollary: Commuting Hermitian operators have a common orthonormal basis of eigenvectors: $A|\psi_n\rangle = a_n|\psi_n\rangle$, $B|\psi_n\rangle = b_n|\psi_n\rangle$

QM Interpretation: Observables A, B are simultaneously measurable.

What if $i[A,B] =: C \neq 0$?

Given a (normalized) $|\psi\rangle = \sum c_n|\psi_n\rangle$

$\langle\psi|A|\psi\rangle = \sum a_n |c_n|^2 = \bar{A}$ - expectation value of A

$A|\psi_n\rangle = a_n|\psi_n\rangle$ $\qquad$ ($|c_n|^2$ -) probabilities of $A = a_n$

Suppose $\bar{A} = 0$ $\quad (A \rightsquigarrow A - \bar{A} I)$

Then $\|A\psi\|^2 = \langle\psi|A^2|\psi\rangle = \overline{A^2} =: (\Delta A)^2$

ΔA - standard deviation

Theorem

$$\Delta A\, \Delta B \geq \frac{1}{2}|\bar{C}|, \quad \bar{C} = \langle\psi|C|\psi\rangle$$

Corollary: $i[\hat{p},\hat{q}] = \hbar$ $\Rightarrow$ $\Delta\hat{p}\cdot\Delta\hat{q} \geq \hbar/2$

Proof. Schwarz' inequality: for any $\lambda \in \mathbb{R}$

$$0 \leq \langle (A+i\lambda B)\psi | (A+i\lambda B)\psi\rangle = \langle A\psi, A\psi\rangle + \langle\psi|C|\psi\rangle\lambda + \langle B\psi|B\psi\rangle\lambda^2$$

$\Rightarrow$ the discriminant ≤ 0:

$$\langle\psi|C|\psi\rangle^2 \leq 4\|A\psi\|^2\|B\psi\|^2$$

Time evolution: $i\hbar \frac{d}{dt}|\Psi\rangle = \hat{H}|\Psi\rangle$

$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$, $|\Psi(0)\rangle = |\psi\rangle = \sum_n c_n|\psi_n\rangle$

(eigenbasis of $\hat{H}$; initial state; Fourier coefficients)

$$|\Psi(t)\rangle = \sum_n e^{tE_n/i\hbar} c_n|\psi_n\rangle = e^{t\hat{H}/i\hbar}|\psi\rangle$$

$U(t)$ – evolution operators

$t \mapsto U(t)$ – one parametric group of unitary operators

$U(t_1+t_2) = U(t_1)U(t_2)$

$\langle U\phi | U\psi\rangle = \langle\phi,\psi\rangle$ for all $\phi,\psi\in\mathcal{H}$

Example. $U(t)\psi(q) = \psi(q+t) \Rightarrow U(t) = e^{-t\hat{p}/i\hbar}$

Remark-exercise: This is Taylor's formula

Evolution of observables: $\frac{dA}{dt} = \frac{i}{\hbar}[\hat{H}, A]$

$\langle U\phi|A|U\psi\rangle = \langle\phi|U^{-1}AU|\psi\rangle$ $\quad U^{-1} = U^*$ unitarity!

$$\frac{d}{dt} e^{-t\hat{H}/i\hbar} A e^{t\hat{H}/i\hbar} = \frac{i}{\hbar}(\hat{H}A - A\hat{H})$$

(with A replaced by $e^{-t\hat{H}/i\hbar} A e^{t\hat{H}/i\hbar}$)

Corollary: $\frac{d}{dt}\bar{A} = \frac{i}{\hbar}\overline{[\hat{H}, A]}$

Example: $H = \frac{p^2}{2m} + V(q)$

$$[\hat{H}, \hat{q}] = \frac{\hbar}{im}\hat{p}, \quad [\hat{H}, \hat{p}] = -\frac{\hbar}{i}\frac{\partial V}{\partial q}$$

Corollary: Ehrenfest's Theorem:

$$\frac{d}{dt}\bar{q} = \frac{\bar{p}}{m}, \quad \frac{d}{dt}\bar{p} = -\overline{\frac{\partial V}{\partial q}} \neq \frac{\partial V}{\partial q}(\bar{q})$$

Energy-Time uncertainty: $\Delta E\,\Delta t \geq \frac{\hbar}{2}$

$$\frac{i}{\hbar}[\hat{H}, \hat{A}] = \frac{d}{dt}A \Longrightarrow \Delta E\cdot\Delta A \geq \frac{\hbar}{2}\left|\overline{\frac{dA}{dt}}\right|$$

Example: Infinite well

$$\Psi = e^{-itE_1/\hbar}\left(\sin\frac{\pi q}{L} + e^{it\frac{(E_1-E_2)}{\hbar}}\sin\frac{2\pi q}{L}\right)$$

$$\bar{E} = \frac{E_1+E_2}{2}, \quad \Delta E = \frac{E_2-E_1}{2}, \quad \frac{\Delta t(2\Delta E)}{\hbar} \approx 1$$

The Harmonic Oscillator

Motivation: Near a stable equilibrium

(kinetic, potential) ≈ (T, V) - positive quadratic forms

⟹ Orthogonal Diagonalization

$$H = \frac{1}{2}(p_1^2 + \dots + p_n^2) + \frac{1}{2}(\omega_1^2 q_1^2 + \dots + \omega_n^2 q_n^2)$$

$$\begin{cases} \ddot{q}_i = -\omega_i^2 q_i \\ i = 1, \dots, n \end{cases}$$ "ideal gas" of harmonic oscillators

$$-\frac{\hbar^2}{2}\frac{\partial^2}{\partial q^2}\psi + \omega^2 q^2 \psi = E\psi$$

$x := \sqrt{\omega/\hbar}\, q$ $\quad \left(-\frac{d^2}{dx^2} + x^2\right)\psi = \frac{E}{\hbar\omega/2}\psi$

$a_\pm := \pm\frac{d}{dx} - x \quad a_+^* = a_- \quad D = -\frac{d^2}{dx^2} + x^2$

$D = \frac{1}{2}(a_+ a_- + a_- a_+)$, $\frac{1}{2}(a_- a_+ - a_+ a_-) = 1$

Suppose: $a_- \psi_0 = 0$ **Then:** $D\psi_0 = \psi_0$

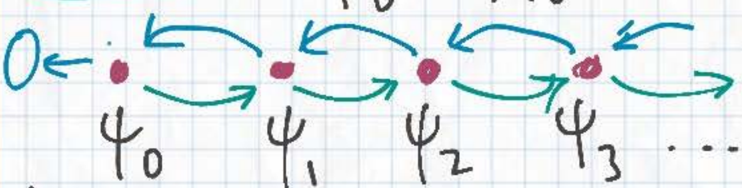
Suppose: $D\psi = \lambda\psi$ **Then** $D(a_+\psi) = (\lambda+2)(a_+\psi)$

Proof: $a_- a_+ = a_+ a_- + 2$

$$2D\,a_+ = (a_- a_+ + a_+ a_-)a_+ = a_+(a_- a_+ + 2 + a_+ a_- + 2)$$

(where $a_- a_+ + 2 + a_+ a_- + 2 = 2D + 4$)

In fact: $\psi_0 = A_0 e^{-x^2/2}$



a_- annihilation

a_+ creation

λ_n: 1 3 5 7 ... $\times \frac{\hbar\omega}{2} = E_n$

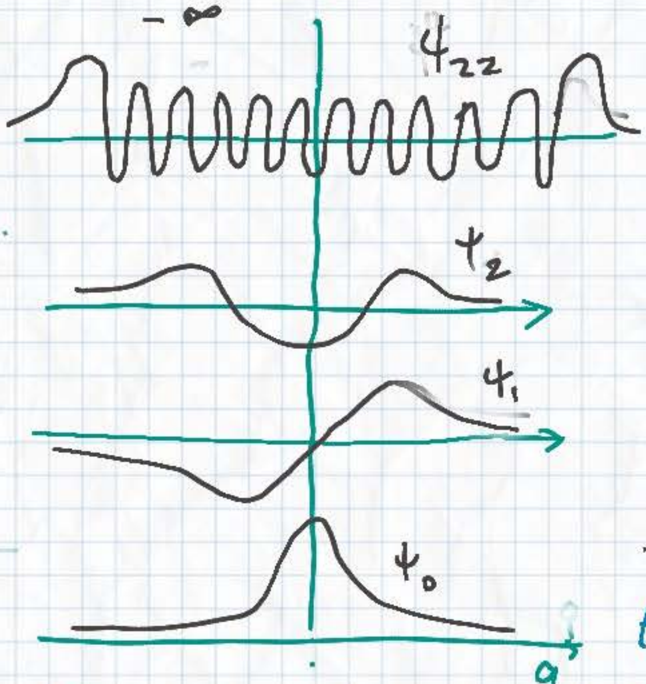
H_n: $1,\ 2x,\ 4x^2 - 2,\ 8x^3 - 12x, \dots$ Hermite polynomials

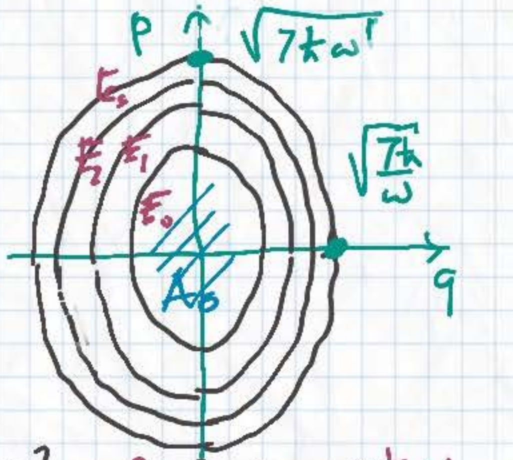
$$\psi_n = A_n\left(-\frac{d}{dx} + x\right)^n e^{-x^2/2} = A_n H_n(x) e^{-x^2/2}$$

$$H_n = (-1)^n e^{x^2}\frac{d^n}{dx^n}e^{-x^2} \qquad \left(\frac{d}{dx} - x\right) = e^{x^2/2}\frac{d}{dx}e^{-x^2/2}$$

$$\int_{-\infty}^{\infty} H_m(x) H_n(x) e^{-x^2} dx = \int_{-\infty}^{\infty} H_m(x)\left(-\frac{d}{dx}\right)^n e^{-x^2} dx = \ldots$$

$$\ldots = \int_{-\infty}^{\infty} \left(\frac{d^n}{dx^n} H_m(x)\right) e^{-x^2} dx = \begin{cases} 0 \leftarrow m<n \\ 2^n n! \sqrt{\pi} = |A_n|^2 \leftarrow m=n \end{cases}$$



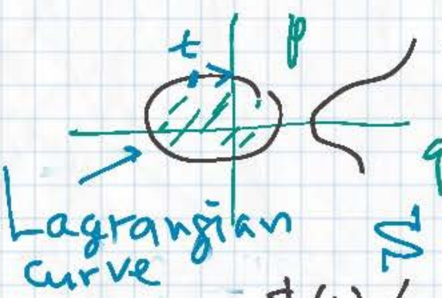


$$\frac{p^2}{2} + \omega^2 \frac{q^2}{2} = (2n+1)\frac{\hbar\omega}{2}$$

$$A_n = 2\pi\hbar\left(n + \tfrac{1}{2}\right)$$

Some universal features

- $V \to \infty$ as $|q| \to \infty \Rightarrow$ discrete spectrum $E_n \to \infty$
- In one degree of freedom: ψ_n, $n = 0, 1, 2, \ldots$ has n zeroes ($\Leftarrow$ Sturm's theory)
- "WKB - approximation"



$H = E \quad \psi \sim e^{i(S + O(\hbar))/\hbar}$ as $\hbar \to 0$

$$S = \int^t p(t)\, dq(t)$$

For $e^{iS(t)/\hbar + \ldots}$ to be single-valued

$A = \oint p(t)\, dq(t) = 2\pi\hbar n \leftarrow$ quantization condition

- For harmonic oscillator — WKB quant. cond. $A_n \equiv \pi\hbar \mod 2\pi\hbar$ is satisfied precisely for $E_n = (n + \frac{1}{2})\hbar\omega$
- Equal energy spacing $\rightsquigarrow$ Q.F.T.

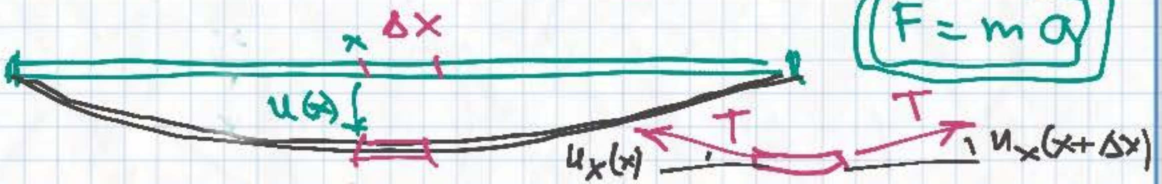
ψ_0 = vacuum, ψ_n = n particles with $E = \hbar\omega$ each

a_+ / a_- = creation / annihilation

The 1-dim wave equation

(12.1)

$$F = ma$$



$$\rho(x)\,\Delta x\, u_{tt} \approx T\,(u_x(x+\Delta x) - u_x(x))$$

mass density — acceleration — tension — force

$$\Delta x \to 0 \Rightarrow \boxed{\rho(x)\, u_{tt} = T\, u_{xx}}$$

density can vary along the string

tension must be constant ($F = \textcircled{m} a$, $m \approx 0$)

$$\boxed{u_{tt} = c^2 u_{xx} \Rightarrow c^2 = T/\rho}$$

$$\mathcal{E} = \int \rho(x) \frac{|u_t|^2}{2}\, dx + T \int \frac{|u_x|^2}{2}\, dx$$

total energy — kinetic + potential

$$\frac{\mathcal{E}}{T} = \int c_\pm^{-2} \frac{|u_t|^2}{2}\, dx + \int \frac{|u_x|^2}{2}\, dx \stackrel{?}{=} \frac{\mathcal{E}}{\rho_\pm}$$

Continuity of $u(x,t)$, $u_x(x,t)$

$$e^{ik(x-c_-t)} \qquad B\, e^{ik'(x-c_+t)}$$

$$+ A\, e^{-ik(x+c_-t)}$$

At $x=0$: $e^{-ikc_-t} + A e^{ikc_-t} \neq B e^{-ikc_+t}$

$$kc_- = \underline{\omega} = k'c_+$$

"monochromatic"

Multi-particle systems

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V_i(q_i)$$

q_i could be vectors, $p_i^2 = p_i \cdot p_i$

$$i\hbar \frac{\partial}{\partial t} \Psi(q_1, \dots, q_N, t) = \hat{H}\, \Psi(q_1, \dots, q_N, t)$$

$$\hat{H} = \sum_{i=1}^{N} \Big[\underbrace{-\frac{\hbar^2}{2m_i} \Delta_{q_i} + V_i(q_i)}_{\text{one-particle hamiltonian}} \Big]$$

Suppose: $\psi_n^{(i)}$, $E_n^{(i)}$ - eigen functions / values

Then $\psi_{\vec{n}}(q_1, \dots, q_N) := \psi_{n_1}^{(1)}(q_1) \cdots \psi_{n_N}^{(N)}(q_N)$

- eigenfunctions of $\hat{H}$ with eigenvalues $E_{\vec{n}} = E_{n_1}^{(1)} + \dots + E_{n_N}^{(N)}$

$\vec{n} = (n_1, \dots, n_N)$

Fourier Method:

$$\Psi(q_1, \dots, q_N, t) = \sum_{\vec{n}} c_{\vec{n}}\, e^{-iE_{\vec{n}} t/\hbar}\, \psi_{\vec{n}}(q_1, \dots, q_N)$$

Example: each particle in infinite well

$$\psi_{\vec{n}} = \prod_{i=1}^{N} \sqrt{\frac{2}{L_i}} \sin \frac{\pi n_i q_i}{L_i} \qquad 0 \le q_i \le L_i$$

$$E_{\vec{n}} = \sum_{i=1}^{N} \frac{\pi^2 \hbar^2 n_i^2}{2 m_i L_i^2}$$

Special case: $m_1 = \dots = m_N \Rightarrow$ a single "free" particle in an N-dim box $L_1 \times \dots \times L_N$

Special case: $m_i = m$, $V_i = V$ ($L_i = L$)

N identical but distinguishable "particles" (systems), e.g. in

E.g. $\psi_{n_1}(q_1)\psi_{n_2}(q_2)$ vs. $\psi_{n_1}(q_2)\psi_{n_2}(q_1)$, $E = E_{n_1} + E_{n_2}$

Different events: (1,2) vs. (2,1) in position (q_1, q_2)

Indistinguishable "particles" (12.3

Suppose $\psi(q_1,\dots,q_N)$ – represents a quantum state of N indisting. part.

$\sigma = \begin{pmatrix} 1, \dots, N \\ \sigma(1), \dots, \sigma(N) \end{pmatrix}$ – a permutation.

$$(\sigma\psi)(q_1,\dots,q_N) := \psi(q_{\sigma(1)},\dots,q_{\sigma(N)})$$

Indistinguishable $\Rightarrow$ $|\sigma\psi|^2 = |\psi|^2$ for all σ

$\Rightarrow \sigma\psi = \varepsilon\psi, \quad |\varepsilon| = 1$

e.g. $\psi(q_2, q_1, q_3, \dots, q_N) = \varepsilon\,\psi(q_1, q_2, q_3, \dots q_N)$

$\Rightarrow \varepsilon^2 = 1 \Rightarrow \underline{\varepsilon = \pm 1}$ $\quad = \varepsilon^2\psi(q_2, q_1, q_3, \dots q_N)$

$\Rightarrow \sigma\psi = \psi$ for all σ – **bosons**

or $\sigma\psi = \text{sign}(\sigma)\psi$ for all σ **fermions**

3 bosons, $E_1 < E_2 < \dots$, ψ_n, $n = 1, 2, \dots$

$E = 3E_1$: $\psi_{1,1,1} = \psi_1(q_1)\psi_1(q_2)\psi_1(q_3)$ ground state

$E = 2E_1 + E_2$: first excited state

$$\psi_1(q_1)\psi_1(q_2)\psi_2(q_3) + \psi_1(q_1)\psi_2(q_2)\psi_1(q_3) + \psi_2(q_1)\psi_1(q_2)\psi_1(q_3)$$

...

$E = E_\ell + E_m + E_n \quad (\ell \neq m \neq n)$

$$\psi_{\ell,m,n} \pm \psi_{m,\ell,n} + \psi_{m,n,\ell} \pm \psi_{n,m,\ell} + \psi_{n,\ell,m} \pm \psi_{\ell,n,m}$$

3 fermions

$$= \begin{vmatrix} \psi_\ell(q_1) & \psi_\ell(q_2) & \psi_\ell(q_3) \\ \psi_m(q_1) & \psi_m(q_2) & \psi_m(q_3) \\ \psi_n(q_1) & \psi_n(q_2) & \psi_n(q_3) \end{vmatrix}$$

Ground state: $(\ell, m, n) = (1, 2, 3)$

$E = E_1 + E_2 + E_3$

Pauli's Exclusion Principle:

No two identical fermions can occupy the same state!

Tensor algebra

$a \quad b \quad c \quad d$

$C = C_1 \sqcup C_2 \Rightarrow \mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2$

$\psi = (\psi_1, \psi_2)$

$\boxed{C = C_1 \times C_2}$ $\quad a, b, c, d$ $\Rightarrow \mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$

$\psi(q_1, q_2)$

Three definitions of $\mathcal{V} \otimes \mathcal{W}$

① $$\frac{\text{Span}(\vec{v} \otimes \vec{w} \mid \vec{v} \in \mathcal{V}, \vec{w} \in \mathcal{W})}{\text{Span}\begin{pmatrix} (\lambda_1 \vec{v}_1 + \lambda_2 \vec{v}_2) \otimes \vec{w} - \lambda_1(\vec{v}_1 \otimes \vec{w}) - \lambda_2(\vec{v}_2 \otimes \vec{w}) \\ \vec{v} \otimes (\lambda_1 \vec{w}_1 + \lambda_2 \vec{w}) - \lambda_1(\vec{v} \otimes \vec{w}_1) - \lambda_2(\vec{v} \otimes \vec{w}_2) \end{pmatrix}}$$ ← quotient space

② Def. $B : \mathcal{V} \times \mathcal{W} \to \mathbb{C}$ (or $\mathbb{R}$) is called bilinear if for all $\vec{v}_{(i)}, \vec{w}_{(i)}, \lambda_i$

$$B(\lambda_1 \vec{v}_1 + \lambda_2 \vec{v}_2, \vec{w}) = \lambda_1 B(\vec{v}_1, \vec{w}) + \lambda_2 B(\vec{v}_2, \vec{w})$$

$$B(\vec{v}, \lambda_1 \vec{w}_1 + \lambda_2 \vec{w}_2) = \lambda_1 B(\vec{v}, \vec{w}_1) + \lambda_2 B(\vec{v}, \vec{w}_2)$$

B_1, B_2 - bilinear $\Rightarrow \lambda_1 B_1 + \lambda_2 B_2$ - bilinear

$\mathcal{B} := ($the space of all bilinear forms $\mathcal{V} \times \mathcal{W} \to \mathbb{C}) = \mathcal{V}^* \otimes \mathcal{W}^*$

finite dim — dual!

③
$$\begin{tikzcd} \mathcal{V} \times \mathcal{W} \arrow[r, "\text{bilinear}"] \arrow[dr, "{(v,w) \mapsto v \otimes w}"', "\text{bilinear}"] & \mathcal{U} \\ & \mathcal{V} \otimes \mathcal{W} \arrow[u, "\text{linear}"'] \end{tikzcd}$$

$\mathcal{U}$ ← any vector space

$\mathcal{V} \otimes \mathcal{W}$ – universal repelling object in the category of bilinear maps

"Real life" examples

$\mathbb{C}^n = \{\text{functions } z : \{1, \dots, n\} \to \mathbb{C}\}$ $\quad (z_1, \dots, z_n)$ $(z(1), \dots, z(n))$

$\mathbb{C}^m \otimes \mathbb{C}^n = \{\text{functions } (i,j) \mapsto a(i,j) \text{ on } \{1, \dots, m\} \times \{1, \dots, n\}\}$ - $m \times n$ matrices

$e_i \otimes \tilde{e}_j$ - basis (elem. matrices) $\quad \dim = m \cdot n$

$\text{Hom}(\mathcal{V}, \mathcal{W}) = \mathcal{V}^* \otimes \mathcal{W}$ $\quad (f \otimes w)(v) = f(v) w$

linear maps $\mathcal{V} \to \mathcal{W}$ $\quad$ rank-1 linear maps

Systems of "particles" in ⊗ notation

N non-interacting particles ($\mathcal{H}_k$, $\hat{H}_k$) — $\mathcal{H}_1 \otimes \dots \otimes \mathcal{H}_N$ ← state space

$\sum_{k=1}^{N} \dots \otimes I \otimes \hat{H}_k \otimes I \otimes \dots$ (k-th position)

$\psi^{(1)}_{n_1}(q_1) \dots \psi^{(N)}_{n_N}(q_N) \rightsquigarrow \psi^{(1)}_{n_1} \otimes \dots \otimes \psi^{(N)}_{n_N}$

Basis of eigen-states, $E = E^{(1)}_{n_1} + \dots + E^{(N)}_{n_N}$

N identical distinguishable particles, ($\mathcal{H}$, $\hat{H}$) each — $\mathcal{H}^{\otimes N} := \underbrace{\mathcal{H} \otimes \dots \otimes \mathcal{H}}_{N \text{ times}}$

If N is indefinite: $\bigoplus_{N=0}^{\infty} \mathcal{H}^{\otimes N}$ – tensor algebra of $\mathcal{H}$

multiplication: $(v_1 \otimes v_2) \otimes (v_3 \otimes v_4 \otimes v_5)$

N indistinguishable bosons — $S^N(\mathcal{H})$ – totally symmetric tensors = polynomial functions on the dual space $\mathcal{H}^*$

$\psi(x) = \sum_n x_n |\psi_n\rangle$ ← coordinates on $\mathcal{H}$ = basis in $\mathcal{H}^*$

$\psi(x)^{\otimes N} = (\sum x_n \psi_n) \otimes \dots \otimes (\sum x_n \psi_n)$ N times

$\overset{N=3}{=} x_1^3 (\psi_1 \otimes \psi_1 \otimes \psi_1) + x_2^3 (\psi_2 \otimes \psi_2 \otimes \psi_2) + \dots$

$+ x_1^2 x_2 (\psi_2 \otimes \psi_1 \otimes \psi_1 + \psi_1 \otimes \psi_2 \otimes \psi_1 + \psi_1 \otimes \psi_1 \otimes \psi_2) + \dots$

$+ x_1 x_2 x_3 \left(\sum_\sigma \psi_{\sigma(1)} \otimes \psi_{\sigma(2)} \otimes \psi_{\sigma(3)}\right) + \dots$ ← all 6 permutations

$\dots$

N indistinguishable fermions — $\Lambda^N(\mathcal{H})$ – totally anti-symmetric tensors

$\psi(\xi) = \sum \xi_n \psi_n$ $\xi_m \xi_n = -\xi_n \xi_m$ ($\Rightarrow \xi_n^2 = 0$)

$\psi(\xi)^{\otimes N} = \sum_{n_1 < \dots < n_N} \xi_{n_1} \dots \xi_{n_N} \sum_{\sigma \in S_N} \text{sign}(\sigma)\, \psi_{n_{\sigma(1)}} \otimes \dots \otimes \psi_{n_{\sigma(N)}}$

Pauli → $= 0$ if $N > \dim \mathcal{H}$

$\dim \Lambda^N \mathcal{H} = \binom{\dim \mathcal{H}}{N}$

$$\begin{vmatrix} \psi_{n_1}(q_1) & \dots & \psi_{n_1}(q_N) \\ \psi_{n_N}(q_1) & \dots & \psi_{n_N}(q_N) \end{vmatrix}$$

Indefinite number of bosons

$$S(\mathcal{H}) := \bigoplus_{N=0}^{\infty} S^N(\mathcal{H}) = \mathbb{C} \oplus \mathcal{H} \oplus S^2(\mathcal{H}) \oplus \dots$$

↑ dual to $\mathbb{C}[x_1, x_2, \dots]$ = polynomial functions on $\mathcal{H}^*$

$$\mathcal{H} = \bigoplus_n |\psi_n\rangle \Rightarrow \mathbb{C}[x_1, x_2 \dots] = \mathbb{C}[x_1] \otimes \mathbb{C}[x_2] \otimes \dots$$

$x_1^{k_1} \otimes x_2^{k_2} \otimes \dots$

$$S(\mathcal{H}) = \bigotimes_{n=1}^{\infty} \mathcal{H}_n$$

($\mathcal{H}_n$:) space of states of a harmonic oscillator.

Namely: If $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ then $\omega_n = E_n/\hbar$

$$\mathcal{H}_n = \bigoplus_{k=0}^{\infty} |\psi_n^{\otimes k}\rangle \quad E = k E_n, \ k = 0, 1, 2, \dots$$

Energy level E_n is occupied by k identical bosons
$\Leftrightarrow$ k ficticious particles of sort n are present

Indefinite number of fermions

$$\Lambda(\mathcal{H}) = \bigoplus_{N=0}^{\infty} \Lambda^N(\mathcal{H}) = \mathbb{C} \oplus \mathcal{H} \oplus \Lambda^2(\mathcal{H}) \oplus \dots$$

↑ dual to Grassmann algebra $\mathbb{C}[\xi_1, \xi_2 \dots]$

$$\mathbb{C}[\xi_1, \xi_2, \dots] = \mathbb{C}[\xi_1] \otimes \mathbb{C}[\xi_2] \otimes \dots$$

$$\mathbb{C}[\xi] = \{a + b\xi \mid a, b \in \mathbb{C}\} \quad \xi^2 = 0$$

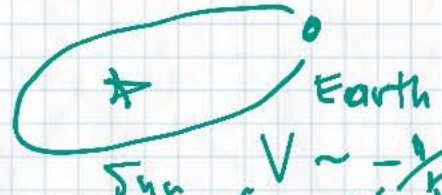
$$\mathcal{H} = \bigoplus_n |\psi_n\rangle \Rightarrow \mathcal{H}_n = \mathbb{C}[\xi]^* = \mathrm{Span}(\psi_n^{\otimes 0}, \psi_n^{\otimes 1})$$

"qubit"

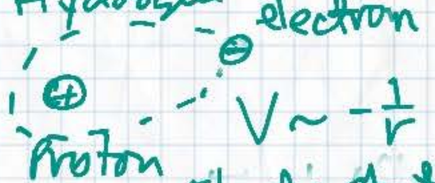
Level E_n is occupied (or not) by a fermion
$\Leftrightarrow$ ficticious fermion of sort n is present (or not)

Conclusion: Indefinite # of bosons / fermions
$\Leftrightarrow$ ideal gas of (distinguishable) harmonic oscillators / qubits (of sort E_n, $n = 1, 2, \dots$)

Classical & Quantum Kepler Problems



$V \sim -\frac{1}{r}$ Gravitation

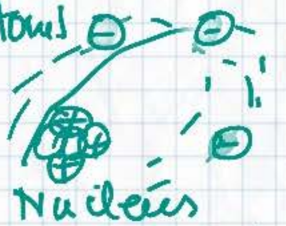


$V \sim -\frac{1}{r}$? Electrostatics

Solar system

$m_{planet} \ll m_{sun}$

Atoms



$m_e \ll m_p$

Periodic System of Elements

Central Force Field (Rotational Symmetry)

$$-\frac{\hbar^2}{2m_e}\Delta\psi + V(r)\psi = E\psi \qquad \Delta = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$\mp e$ - charge of electron/proton
Z = # protons in nucleus
ε_0 - "dielectric constant"

$r = \sqrt{x^2+y^2+z^2}$ $\quad 4\pi$ = area of unit sphere

(Orbital) Angular momentum

$\vec{L} = \vec{q} \times \vec{p}$ $\quad L_x, L_y, L_z = x p_y - y p_x$

$\hat{L} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$ $\quad \hat{L}_z = i\hbar(y\partial_x - x\partial_y)$

$i\hbar\frac{\partial\psi}{\partial t} = \hat{L}_z\psi$ rotations about z-axis $\quad \dot{x} = y \quad \dot{y} = -x$

$$\psi(t,x,y,z) = \psi(0, x\cos t + y\sin t, x\sin t - y\cos t, z)$$

$\Rightarrow \hat{L}_x, \hat{L}_y, \hat{L}_z$ commute with $\hat{H} = -\frac{\hbar^2}{2m}\Delta + V(r)$

Commuting observables have a common eigenbasis

$\hat{L}_z\psi = \lambda_z\psi$ In cylindrical coord: $-i\hbar\frac{d\psi}{d\theta} = \lambda_z\psi$

$\psi(\theta) = \psi_0 e^{i\lambda_z\theta/\hbar} \Rightarrow \lambda_z = k\hbar,\ k = 0, \pm1, \pm2, \ldots$

Example: $\psi_{a,b,c} = (x+iy)^a(x-iy)^b z^c = w^a \bar{w}^b z^c$

$= |w|^{a+b} e^{i(a-b)\theta} z^c \Rightarrow \hat{L}_z\psi_{a,b,c} = \hbar(a-b)\psi_{a,b,c}$

Total orbital angular momentum

Proposition: $\hat{L}^2 := \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

$$= -\hbar^2 \left[r^2 \Delta - (\vec{r}\cdot\nabla)^2 - (\vec{r}\cdot\nabla) \right]$$

Classically $|L|^2 = |q \times p|^2 = (q\cdot q)(p\cdot p) - (q\cdot p)^2$

$$-\frac{1}{\hbar^2}\hat{L}_z^2 = (y\partial_x - x\partial_y)^2 = y^2\partial_x^2 + x^2\partial_y^2 - 2xy\partial_x\partial_y - x\partial_x - y\partial_y$$

Same for $L_x^2, L_y^2, \ldots$

$\partial_x x\psi = 1\cdot\psi + x\partial_x\psi$

$(x^2 + y^2 + z^2)\partial_x^2 - x^2\partial_x^2$

same for $\partial_y^2, \partial_z^2$

$$(\vec{r}\cdot\nabla)^2 := (x\partial_x + y\partial_y + z\partial_z)^2$$

$$= x\partial_x + x^2\partial_x^2 + \ldots + 2xy\partial_x\partial_y + \ldots$$

$$-\frac{1}{\hbar^2}|L|^2 + (\vec{r}\cdot\nabla)^2 - \vec{r}\cdot\nabla + 2(\vec{r}\cdot\nabla) = r^2\Delta^2$$

Euler's identity for homogeneous functions

Def. f is homogeneous, degree d, if

$$f(tx, ty, tz) = t^d f(x, y, z)$$

Exercise: $(\vec{r}\cdot\nabla) f = d\cdot f$

Homogeneous function = eigenfunctions of the Euler operator $\vec{r}\cdot\nabla := x\partial_x + y\partial_y + z\partial_z$

Separation of variables: $[\hat{H}, \hat{L}^2] = 0$

$\hat{L}^2\psi = \hbar^2\mu\psi$ $\quad [\hat{L}^2, \vec{r}\cdot\nabla] = 0 \Rightarrow \psi = \sum f_k(r)\,\phi_k$

$\hat{H}\psi = E\psi$ $\quad [\hat{L}^2, r^2] = 0$ $\quad (\vec{r}\cdot\nabla)\phi_k = 0$ degree 0

$\hat{H}_{eff} f_k = E f_k$ for each k $\quad \hat{L}^2\phi_k = \hbar^2\mu\phi_k$

$$-\Delta = \frac{1}{r^2}\left[\underbrace{\frac{\hat{L}^2}{\hbar^2}}_{=\mu} - \underbrace{(\vec{r}\cdot\nabla)^2 - (\vec{r}\cdot\nabla)}_{\text{radial derivatives}}\right]$$

The Effective Potential

$\psi = \frac{u(r)}{r}\phi$, $\hat{L}^2\phi = \hbar^2\mu\phi$, $(\vec{r}\cdot\nabla)\phi = 0$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{\mu\hbar^2}{2mr^2} + V(r)\right]u = Eu$$

centrifugal term

$[(\vec{r}\cdot\nabla)^2 + (r\cdot\nabla r)]\frac{u(r)}{r} = ru''$ $\quad \hat{L}^2\psi = \hbar^2\mu\psi$

This is quantization of the classical Kepler problem in polar coordinates at a fixed value of sectorial velocity.

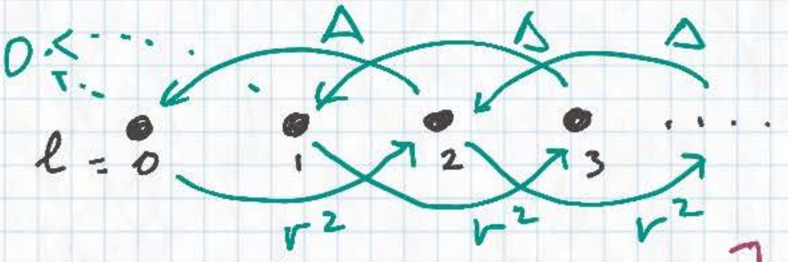
Spherical Harmonics, $\phi : S^2 \to \mathbb{C}$

More general problem: $\mathcal{P} = \mathbb{C}[x,y,z]$
decompose into (invariant subspaces of SO_3)
eigenspaces of $\hat{L}^2$.

$\mathcal{P} = \mathcal{P}_0 \oplus \mathcal{P}_1 \oplus \mathcal{P}_2 \oplus \dots$ (by degrees of polynomials)

$\mathcal{P}_0 = \mathbb{C}$, $\mathcal{P}_1 = \langle x,y,z\rangle$, $\mathcal{P}_2 = \langle x^2, y^2, z^2, xy, yz, zx\rangle$

$\dim \mathcal{P}_l = \binom{l+2}{2}$, $\hat{L}^2\mathcal{P}_l \subset \mathcal{P}_l$



$[\hat{L}^2, \Delta] = 0$

$[\hat{L}^2, r^2] = 0$

$\mathcal{H}_l := \{p \in \mathcal{P}_l \mid \Delta p = 0\}$ harmonic polynomials of degree l

$\mathcal{H}_0 = \mathbb{C}$, $\mathcal{H}_1 = \langle x,y,z\rangle$, $\mathcal{H}_2 = \langle x^2-y^2, y^2-z^2, xy, yz, zx\rangle$

dim = 1, 3, 5

Theorem. $\mathcal{P}_l = r^2\mathcal{P}_{l-2} \oplus \mathcal{H}_l$

Corollary. $\dim \mathcal{H}_l = \binom{l+2}{2} - \binom{l}{2} = 2l+1$

Corollary. $\mathcal{P}_l = \mathcal{H}_l \oplus r^2\mathcal{H}_{l-2} \oplus r^4\mathcal{H}_{l-4} \oplus \dots$

$\hat{L}^2 = \hbar^2(\vec{r}\cdot\nabla)^2 + \hbar^2(\vec{r}\cdot\nabla) - \hbar^2 r^2\Delta \,\big|_{\mathcal{H}_l} = \hbar^2 l(l+1)$

Corollary. $\mathcal{H} = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_2 \oplus \dots$ ← spherical polynomials

$p|_{S^2} = p_0 + p_1 + p_2 + \dots + p_N$, $p_l \in \mathcal{H}_l$

Spherical harmonics

$\mathcal{H} = \bigoplus_{l=0}^{\infty} \mathcal{H}_l$ ← Null-space of $\Delta : \mathcal{P}_l \to \mathcal{P}_{l-2}$

↑ degree l polynomials

$\mathbb{C}[x,y,z] \,|\, S^2 = \{x^2+y^2+z^2=1\}$

Theorem: $\mathcal{P}_l = \mathcal{H}_l \oplus r^2 \mathcal{P}_{l-2} = \ldots = \bigoplus_{k=0}^{[l/2]} r^{2k} \mathcal{H}_{l-2k}$

Remark (on representation theory)

SO_3 acts on $\mathcal{H}$, and on $\mathcal{P} := \mathbb{C}[x,y,z]$

Problem 1° Decompose a given SO_3-module into a sum of indecomposable invariant subspaces.

2° Classify indecomposable SO_3-modules.

Answer to 2°: The indecomposables are $\mathcal{H}_l$.

[All indecomposables are irreducible (have no nontrivial invariant subspaces)

Proof: Averagate an Hermitian form over SO_3 to make it invariant, and use orthogonal complements.]

Theorem ⟸ Lemma: $\mathcal{P}_l = \mathcal{H}_l \oplus r^2 \mathcal{P}_{l-2}$

i.e. null space of Δ is complementary to the range of r^2.

Proof: Introduce on $\mathcal{P}$ (Hermitian or not) symmetric inner product such that Δ and r^2 are ~~transposed~~ adjoint operators.

$$\langle f | g \rangle := f^*(\partial_x, \partial_y, \partial_z)\, g(x,y,z) \Big|_{(x,y,z)=(0,0,0)}$$

$$\langle x^a y^b z^c | x^\alpha y^\beta z^\gamma \rangle = \begin{cases} 0 & \text{if } (\alpha,\beta,\gamma) \neq (a,b,c) \\ \alpha!\,\beta!\,\gamma! & \text{if } (\alpha,\beta,\gamma) = (a,b,c) \end{cases}$$

⟹ symmetric, non-degenerate

Obviously: $\langle r^2 f | g \rangle = \langle f | \Delta g \rangle$

$\mathcal{P}_l \ni f, \ \Delta f = 0 \iff \langle \Delta f | g \rangle = 0$ for all $g \in \mathcal{P}_{l-2}$

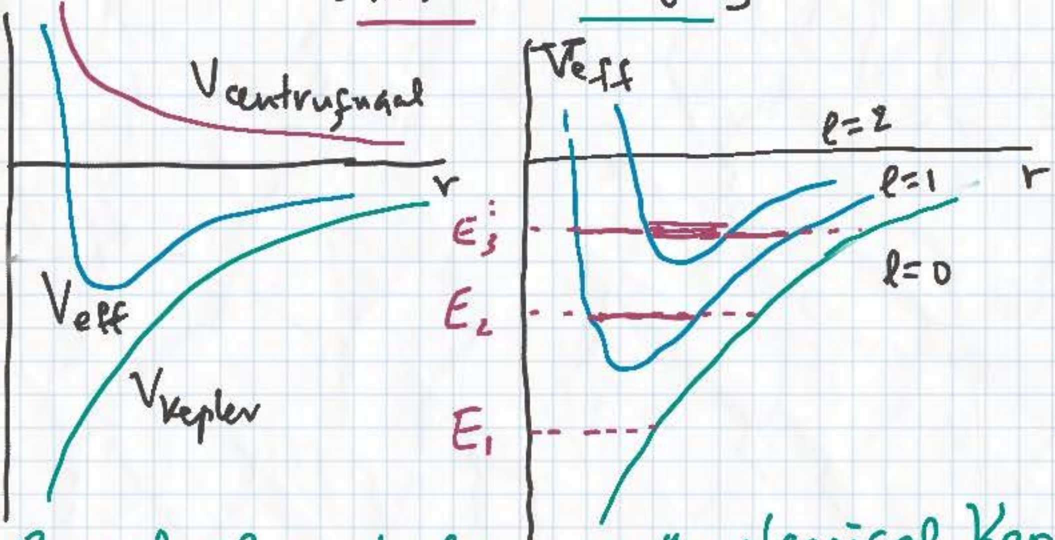
$\iff \langle f | r^2 g \rangle = 0$ for all $g \in \mathcal{P}_{l-2}$ $\iff f \perp r^2 \mathcal{P}_{l-2}$

The Quantum Kepler Problem

$$\psi = \frac{u(r)}{r}\phi, \quad \deg \phi = 0, \quad \hat{L}^2 \phi = \hbar^2 \ell(\ell+1)\phi$$

("orbital quantum #" ↑ ℓ)

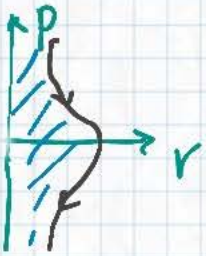
$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]u = Eu$$



Period of revolution in the classical Kepler problem depends only on energy level E.

Bohr - Sommerfeld prediction

Take $\ell = 0$ $\quad \frac{p^2}{2m} - \frac{Q}{r} = E < 0 \quad Q = \frac{Ze^2}{4\pi\varepsilon_0}$



$$\int_{-\infty}^{\infty} r(p)\,dp = 2\pi\hbar n, \quad n = 1, 2, 3, \ldots$$

$$r = \frac{Q}{-E + p^2/2m} \qquad \frac{Q}{-E}\int_{-\infty}^{\infty}\frac{dp}{1 + p^2/{-2mE}} = \pi Q\sqrt{\frac{2m}{-E}}$$

$$4\hbar^2 n^2 = \frac{Q^2\, 2m}{-E_n} \qquad E_n = -\frac{mQ^2}{2n^2\hbar^2} = -\frac{mZ^2e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2}$$

$$\min(\mu x^2 - Qx) =$$

$$= -\mu\frac{Q^2}{4\mu^2} = -\frac{Q^2 m}{2\ell(\ell+1)\hbar^2} < E_n \iff \ell < n$$

$$\hat{H}\psi = E_n\psi : \quad \mathcal{H}_0 \oplus \ldots \oplus \mathcal{H}_\ell \oplus \ldots \oplus \mathcal{H}_{n-1}$$

principal quantum number (n)

$$\dim = 1 + 3 + \ldots + 2n - 1 = n^2$$

$$\psi \in \mathcal{H}_\ell \iff \hat{L}^2\psi = \ell(\ell+1)\hbar^2\psi$$

Solving $-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \underbrace{\left[\frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{Q}{r}\right]}u = Eu$

Suppose $E<0$ and $V_{eff} \equiv 0$. Then $u(r) = v\, e^{-\lambda r}$, $\lambda = \sqrt{-2mE}/\hbar$

Look for $u(r) = v(r)\, e^{-\lambda r}$, $E = -\lambda^2\hbar^2/2m$:

(*) $$v'' - 2\lambda v' + \left[\frac{2mQ}{\hbar^2 r} - \frac{\ell(\ell+1)}{r^2}\right] v = 0$$

Assume $v(r) = \sum v_\alpha r^\alpha$ (finite sum):

$$\alpha(\alpha-1) r^{\alpha-2} - 2\lambda\alpha r^{\alpha-1} + \frac{2mQ}{\hbar^2} r^{\alpha-1} - \ell(\ell+1) r^{\alpha-2}$$

(1) α - highest exponent: $\lambda\alpha = \frac{mQ}{\hbar^2}$

(2) α - lowest exponent: $\alpha = \ell+1$ or $\alpha = -\ell$.

Recall $\psi = \phi \frac{v}{r} e^{-\lambda r}$, $\iiint |\psi|^2 dx\,dy\,dz < \infty$

$\Rightarrow \int_0^\varepsilon \frac{|v|^2}{r^2} r^2 dr < \infty \Rightarrow \alpha > -1/2$

$\Rightarrow \alpha = \ell+1$ for $\ell \geq 0$

But $\alpha = -\ell = 0$ leaves $\frac{2mQ}{r}$ uncanceled!

Now (*) serves as recursion for

$$v(r) = r^{\ell+1} + v_{\ell+2} r^{\ell+2} + \dots + v_n r^{(n)}$$ ← highest exponent

where $\lambda n = mQ/\hbar^2$.

This is possible only for one value of E:

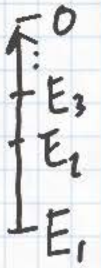
$$E_n = -\frac{\lambda^2\hbar^2}{2m} = -\frac{mQ^2}{2\hbar^2 n^2} = -\frac{mZ^2e^2}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2}$$

$$\psi = \phi\, \frac{v_{n,\ell}(r)}{r} e^{-\lambda r} = \left(\sum_{k=0}^{n-\ell-1} v_{k+\ell+1} r^k\right) e^{-\lambda r} h(x,y,z)$$

- ψ ← class C^ℓ
- ϕ ← $\frac{h(x,y,z)}{r^\ell}$
- $v_{n,\ell}(r)$ ← "Laguerre polynomials"
- $e^{-\lambda r}$ ← $\lambda = \frac{mQ\hbar^2}{n}$
- $h(x,y,z)$ ← harmonic degree-ℓ polynomial

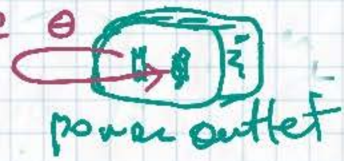
Quantum Kepler: Summary

$$E_n = -\frac{m_e e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\frac{Z^2}{n^2}, \quad n = 1, 2, 3, \dots$$



$Z = 1$ (hydrogen), $E_1 \approx -13.7$ eV

$8 \times E_1 \approx -110$ eV



$$E_n \leftrightarrow \mathcal{H}_0 \oplus \dots \oplus \mathcal{H}_\ell \oplus \dots \oplus \mathcal{H}_{n-1}$$

$$\dim = 1 + 3 + \dots + 2\ell+1 + \dots + 2n-1 = n^2$$

$$L^2/\hbar^2 = 0, 2, \dots \ell(\ell+1), \dots, (2n-1)2n$$

Hydrogen Spectral Lines

Visible range – Johann Balmer's (1885) empirical formula $\lambda = \textcircled{B}\left(\frac{n^2}{n^2-4}\right)$

$B \sim 364.5$ nm

Johannes Rydberg's

$$\frac{1}{\lambda} = \textcircled{R}\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \quad \frac{1}{R} = \frac{B}{4} \approx 91.13 \text{ nm}$$

$$\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right) Z^2$$

$m = 1$: Theodore Layman's series (1906–14)

$m = 3$: Friederik Paschen's (Bohr's) 1908

$m = 4$: Frederick Brackett's 1922

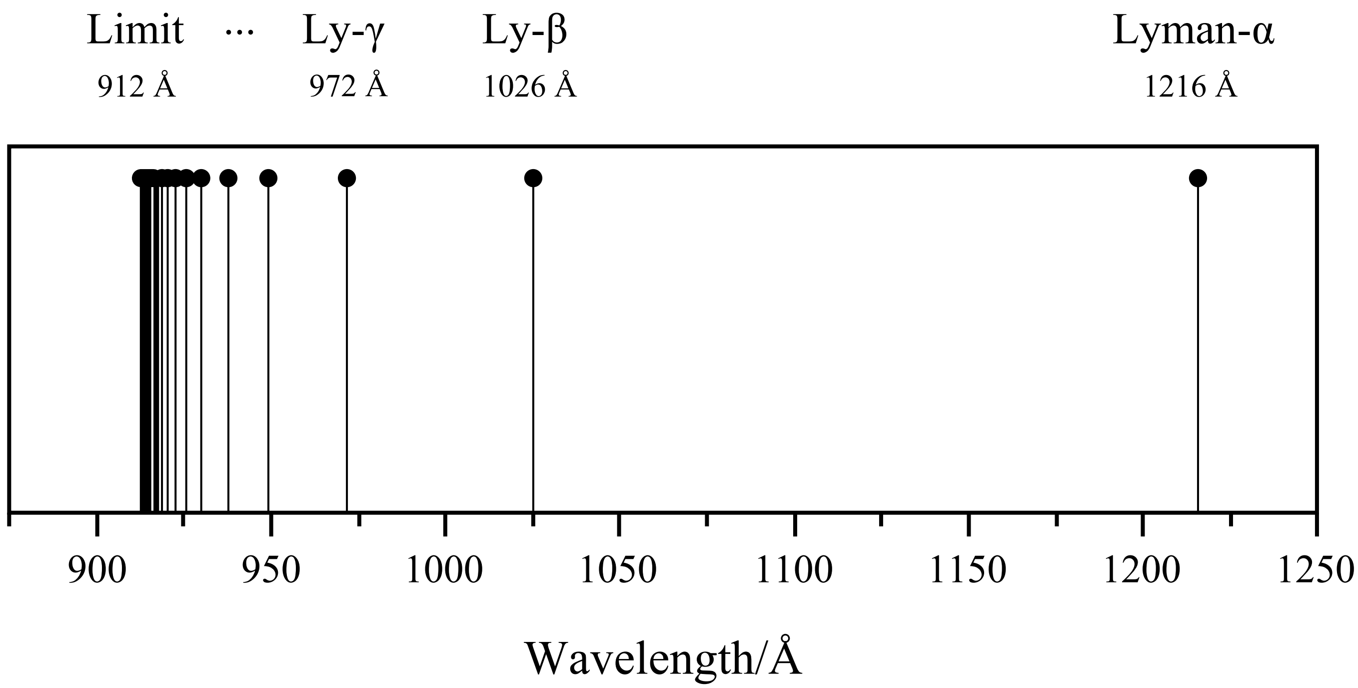
$m = 5$: August Pfund's 1924

$$2\pi\hbar\frac{c}{\lambda} = E_n - E_m = \frac{me^4}{(4\pi\varepsilon_0)^2 2\hbar^2} Z^2\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

(energy of photon)

Bohr's model (1913), Schrodinger (1925–26)

Difficulties: At a finer resolution each lines splits into several lines ⇐ relativistic effect: $E \mid \mathcal{H}_\ell$ depends on ℓ.


Limit
912 Å
···
Ly-γ
972 Å
Ly-β
1026 Å
Lyman-α
1216 Å
900
950
1000
1050
1100
1150
1200
1250
Wavelength/Å

	1	2	3†		4	5	6	7	8	9	10	11	12‡	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	58-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	90-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
					58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
					90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Metals: Alkali, Alkaline earth, Transition, Lanthanide, Actinide, Post-transition

Metalloids

Nonmetals: Reactive, Noble gas

† (a) Whether group 3 is composed of -La-Ac or -Lu-Lr is under review by the IUPAC. (b) The last two members of the group are also known as transition metals.
‡ Some authors treat Zn, Cd and Hg as transition metals.

Properties not yet determined

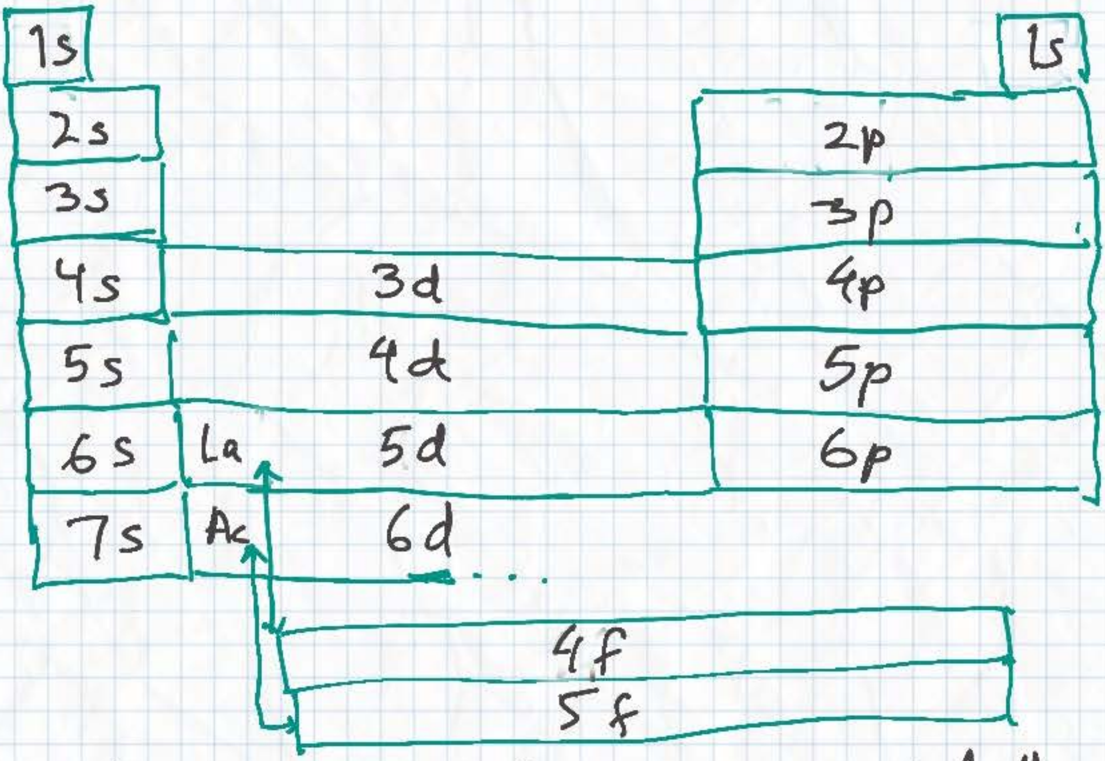
The Periodic Table

Periods' lengths: 2, 8, 8, 18, 18, 32, 32, ??

2× (1, 4, 4, 9, 9, 16, 16, ?, ?...)

E_1	1s				1
E_2	2s	2p			$1 \oplus 3$
E_3	3s	3p	3d		$1 \oplus 3 \oplus 5$
E_4	4s	4p	4d	4f	$1 \oplus 3 \oplus 5 \oplus 7$
E_5	5s	5p	5d	5f	$1 \oplus 3 \oplus 5 \oplus 7$
E_6	6s	6p	6d	...	$1 \oplus 3 \oplus 5 \ldots$
E_7	7s				

$\mathcal{H}_0 \quad \mathcal{H}_1 \quad \mathcal{H}_2 \quad \mathcal{H}_3$



- The order of filling the (orb) shells is, very roughly, due to shielding:

"s-orbitals ($\ell = 0$) are larger than p, d, f"

- Why two electrons per state?
- If bosons, why don't all sink 1s?
- All particles have intrinsic "spin" states invisible classically:

s	0	½	1	3/2	...
dim	1	2	3	4	...

bosons   fermions

$s_e = s_p = s_n = \frac{1}{2}$

$s_{photon} = 1$

Mystery!

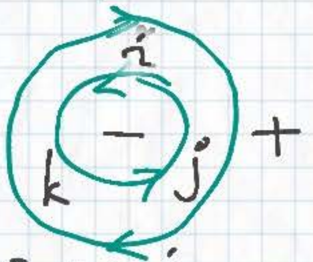
Broome bridge in Dublin, Ireland
16.3

$$\boxed{i^2 = j^2 = k^2 = ijk = -1}$$

W. Hamilton, October 16, 1843

$$\mathbb{H} \ni q = a + bi + cj + dk$$

$$ij = k = -ji$$



$$\mathbb{H} = \mathbb{C}^2 \ni q = (a+bi) + (c+di)j = z + wj$$

$$q^* := a - bi - cj - dk = z^* - wj$$

$$qq^* = zz^* - wjwj + wjz^* - zwj = zz^* + ww^*$$

$$jw = w^* j$$

$$\Rightarrow qq^* = a^2 + b^2 + c^2 + d^2 = q^* q \Rightarrow q^{-1} = \frac{q^*}{\sqrt{qq^*}}$$

$\mathbb{H}$ is an associative division algebra.

Operator description

$$(x + yj)(z + wj) = (xz - yw^*) + (xw + yz^*)j$$

$$\begin{bmatrix} x \\ y \end{bmatrix} \mapsto \begin{bmatrix} z & -w^* \\ w & z^* \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

matrix product $\Leftrightarrow \mathbb{H}^{\text{opposite}}$

$$a \underbrace{\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}}_{I} + bi \underbrace{\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}}_{\sigma_z} - ci \underbrace{\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}}_{\sigma_y} + di \underbrace{\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}}_{\sigma_x}$$

Pauli basis in 2×2-Hermitian matrices

$$Sp_1 := \{ q \in \mathbb{H} \mid \|q\| = 1 \} \simeq S^3 \subset \mathbb{R}^4$$

$$\det \begin{bmatrix} z & -w^* \\ w & z^* \end{bmatrix} = zz^* + ww^* = 1$$

Therefore: $Sp_1 = SU_2$ — unitary 2×2-matrices with det = 1.

Theorem: $SO_3 = SU_2 / (\pm I)$

Quaternions $\mathbb{H}$, Sp_1, SU_2, SO_3

$\mathbb{H} = \mathbb{R}^4 = \mathbb{C}^2 = \{ z + wj \mid z, w \in \mathbb{C},\ i^2 = -1,\ ij = -ji \}$

$(x + yj) \mapsto (x+yj)(z+wj)$ $\quad \begin{bmatrix} x \\ y \end{bmatrix} \mapsto \underbrace{\begin{bmatrix} z & -w^* \\ w & z^* \end{bmatrix}}_{q} \begin{bmatrix} x \\ y \end{bmatrix}$

$\det \begin{bmatrix} z & -w^* \\ w & z^* \end{bmatrix} = zz^* + ww^* = \|q\|^2$

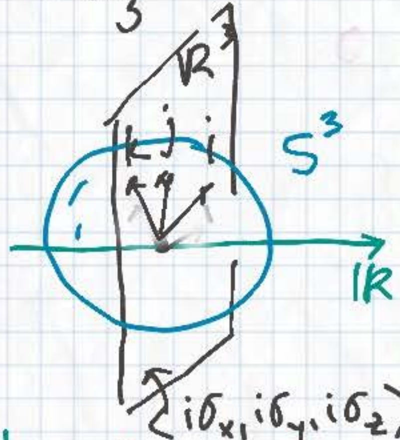
$Sp_1 = \{ q \in \mathbb{H} \mid \|q\| = 1 \}$ $\quad U_1 = \{ z \in \mathbb{C} \mid |z| = 1 \} \subset \mathbb{C}$

(compact) symplectic gr. $\quad O_1 = \{ x \in \mathbb{R} \mid |x| = 1 \} \subset \mathbb{R}$

$Sp_1 = SU_2$ special unitary 2×2, $\det = 1$

$\downarrow$ $\quad R_q : x \mapsto q x q^{-1}$

SO_3 $\quad x^* = -x \quad q q^* = 1$



traceless anti-Hermitian 2×2

- $(q x q^{-1})^* = q^{-1*} x^* q^* = -q x q^{-1}$ $\Rightarrow R_q : \mathbb{R}^3 \to \mathbb{R}^3$
- $\|q x q^{-1}\| = \|x\|$ $\Rightarrow R_q \in O_3$

Cosine thm $\Leftrightarrow$ SSS-test

$x \cdot y = \frac{1}{2}\left(\|x+y\|^2 - \|x\|^2 - \|y\|^2 \right)$

- S^3 is connected $\Rightarrow \det R_q = 1$ $(\neq -1)$
  $\Rightarrow R_q \in SO_3$
- $R_{q_1} R_{q_2} = R_{q_1 q_2}$ $\quad q_1 (q_2 x q_2^{-1}) q_1^{-1}$
- $R_{q_1} = R_{q_2} \Rightarrow [q_1 q_2^{-1}, \begin{smallmatrix} i \\ j \\ k \end{smallmatrix}] = 0 \Rightarrow q_1 q_2^{-1} \in \mathbb{R}$
  $\Rightarrow q_1 = \pm q_2 \Rightarrow Sp_1 \to Sp_1/(\pm 1) \subset SO_3$
- $\dim S^3/\pm 1 = \dim SO_3$ $\Longrightarrow$ "onto"
  $\uparrow$ connected!

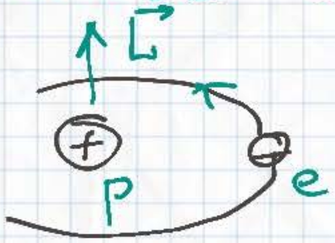
$\operatorname{rk}(d_R) = 3$ $\Rightarrow$ range is closed (compactness) and open (Inverse Fun. Th.)

somewhere $\Rightarrow$ everywhere $\quad \Rightarrow$ the whole conn. comp.

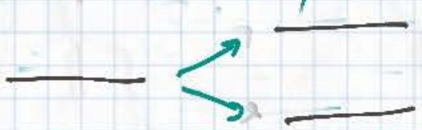
Discovery (invention?) of spin.

<u>1925</u> Samuel Goudsmit - quantum spectra
George Uhlenbeck - classical physics
(+ Paul Ehrenfest - prof. at Leiden)

- Components $\bigoplus_{\ell=0}^{n-1} \mathcal{H}_\ell$ of E_n-eigenspace and even different states in each $\mathcal{H}_\ell$ can be "resolved" by magnetic field

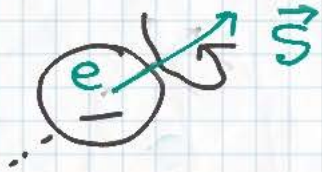


- Spectroscopy shows <u>doublets</u>



Goudsmit published some "numerological" formulas in 1925

- When he told Uhlenbeck about it, the latter suggested that "electron spins"



Google up Goudsmit's 1971 lecture "The discovery of the electron spin".

[• It turned out that a year earlier Pauli ridiculed a similar idea of Ralph Kronig.]

What have they really discovered?

Space is isotropic $\Rightarrow$
Space of states of any quantum system carries an action of SO_3.

$\Rightarrow$ $\mathcal{H}$ carries a unitary action of G s.t. $G/U_1 = SO_3$, where $U_1 = \{e^{i\varphi}\}$

1° $G = U_1 \times SO_3$

2° $G = U_2 \supset U_1 = \left\{\begin{bmatrix} e^{i\phi} & 0 \\ 0 & e^{i\phi}\end{bmatrix}\right\} \xrightarrow{\det} U_1$, $\mapsto e^{2i\phi}$

$U_1 \ni 1 \xleftarrow{\det} SU_2 > (\pm I)$

$\Rightarrow U_2/U_1 = SU_2/(\pm I) = SO_3$

1° ∪ 2°: $\mathcal{H}$ is an SU_2-module

$\mathcal{H} = \mathcal{H}_+ \oplus \mathcal{H}_-$ (eigenspaces of $-I$)

Superspaces: $\mathcal{V} = \mathcal{V}^0 \oplus \mathcal{V}^1$

Coordinates super-commute: $ab = (-1)^{\bar{a}\bar{b}} ba$

$P(v) = (-1)^{\bar{v}} v : \mathcal{V} \to \mathcal{V}$ parity operator

"Symmetric" functors: $S(\mathcal{V}^0)$ $\Lambda(\mathcal{V}^1)$

The Spin-Statistics "theorem": $P = -I \in SU_2$.

i.e. bosons have $-I$ acting as $+1$ and fermions have $-I$ acting as -1

Example: $\mathcal{H}' \otimes \mathcal{H}''$ – boson (hydrogen atom)
fermion (proton), fermion (electron)

Hilbert space in the hydrogen atom model

$\mathcal{H} \otimes \mathbb{C}^2 \ni \psi$ - "quaternion-valued functions"

$SO_3 \times SU_2$

SO_3: rotation invariance of V

$\hat{H}$ - commutes with SU_2

$\Rightarrow$ eigenvalues E_n the same

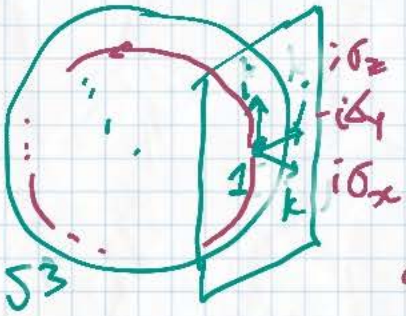
eigenspaces $\bigoplus_{l=0}^{n-1} \mathcal{H}_l \otimes \mathbb{C}^2$

(i) enables Pauli's principle (ii) explains "2 electrons per state", (iii) spectral doublets (magnetic properties) $\Leftarrow$ representations of SU_2.

Irreducible representations of SU_2

$$V_{d/2} = \{a_0 x^d y^0 + a_1 x^{d-1} y^1 + \dots + a_d x^0 y^d\} \simeq \mathbb{C}^{d+1}$$

$$SU_2: \begin{bmatrix} x \\ y \end{bmatrix} \mapsto \begin{bmatrix} z & -w^* \\ w & z^* \end{bmatrix}, \quad |z|^2 + |w|^2 = 1$$



$$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$\frac{\hbar}{2}\sigma_x \qquad \frac{\hbar}{2}\sigma_y \qquad \frac{\hbar}{2}\sigma_z$

Spin $\hat{S} := (S_x, S_y, S_z)$

$$[S_x, S_y] = i\hbar S_z, \dots \Leftarrow ij - ji = 2k, \dots$$

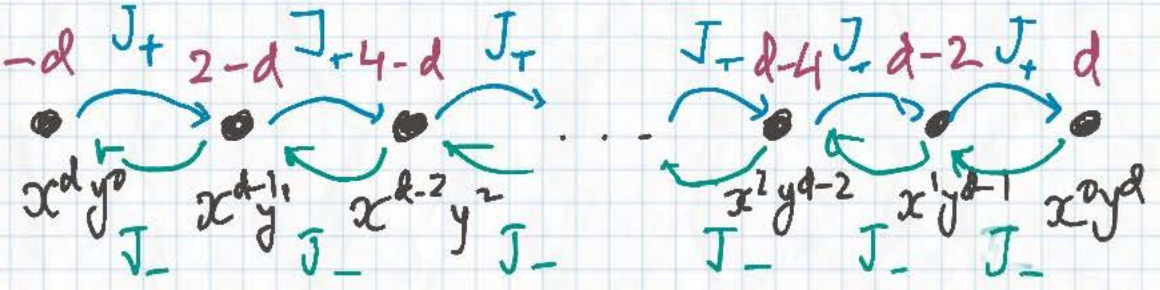
$$i\hbar \frac{d}{dt}\Psi = S_z \Psi \Rightarrow \Psi(t) = U_z(t)\,\Psi(0)$$

$$U_z(t) = e^{-i S_z/\hbar} = \begin{bmatrix} e^{-it/2} & 0 \\ 0 & e^{it/2} \end{bmatrix}$$

$$\Longrightarrow S_z = i\hbar \frac{d}{dt}\Big|_{t=0} U_z(t)$$

$$V_d \ni p \mapsto S_z p = i\hbar \frac{d}{dt}\Big|_{t=0} p\left(e^{+it/2} x, e^{-it/2} y\right)$$

$$= \frac{\hbar}{2}\left(y\frac{\partial}{\partial y} - x\frac{\partial}{\partial x}\right) p \qquad \boxed{p(g_1 g_2 x) = (g_2(g_1 p))(x)}$$



$$J_\pm := S_x \pm i S_y, \quad J_+ = \begin{bmatrix} 0 & \hbar \\ 0 & 0 \end{bmatrix}, \quad J_- = \begin{bmatrix} 0 & 0 \\ \hbar & 0 \end{bmatrix}$$

$$e^{-iJ_+ t/\hbar} = \begin{bmatrix} 1 & -it \\ 0 & 1 \end{bmatrix} \qquad \text{Ladder operators}$$

$$i\hbar \frac{d}{dt}\Big|_{t=0} p(x + ity, y) = -\hbar y \frac{\partial}{\partial x} p, \quad \dots \quad -\hbar x \frac{\partial}{\partial y}$$

Ladder commutation relations

$$[S_z, J_\pm] = [S_z, S_x \pm i S_y] = i\hbar(S_y \mp i S_x)$$
$$= \pm\hbar(S_x \pm i S_y) = \pm\hbar J_\pm$$

$S_z v = \frac{\lambda\hbar}{2} v \Rightarrow S_z(J_\pm v) = J_\pm S_z v \pm \hbar J_\pm v = \frac{\hbar}{2}(\lambda \pm 2) J_\pm v$

V - any (finite dim) repr. of SU_2 (may assume unitary)

$\Downarrow$

v_0 $\quad S_z v_0 = \frac{\lambda_0\hbar}{2} v_0$ ← greatest eigenvalue of S_z

Put $v_k = (J_-)^k v_0$. Then $S_z v_k = \frac{\hbar}{2}(\lambda_0 - 2k) v_k$

$$[J_+, J_-] = [S_x + iS_y, S_x - iS_y] = 2\hbar S_z$$

$\Rightarrow \quad J_+ v_{k+1} = \hbar^2 (k+1)(\lambda_0 - k) v_k$

$J_+ J_- v_k = 2\hbar S_z v_k + J_- J_+ v_k$ (induction hypothesis)

$\quad \hbar^2(\lambda_0 - 2k) v_k \quad\quad \hbar^2 k(\lambda_0 - k + 1) v_k$

$\dim V < \infty \Rightarrow \lambda_0 = d$ for some $d \geq 0$.

$\Rightarrow V \supset W = \mathrm{span}(v_0, v_1, \dots, v_d) \underset{SU_2}{\simeq} V_{d/2}$

V - irreducible $\Rightarrow V = W$ (Q.E.D.)

Def. A "particle" has spin ℓ if its Hilbert space is $V_\ell \otimes \mathcal{H}$ as an SU_2-module

$\mathcal{H}$ ← some other Hilbert space.

$\mathcal{H} = \widehat{\bigoplus}_{\alpha=1,2,\dots} L_\alpha \; (\simeq \mathbb{C}) \Rightarrow V_\ell \otimes \mathcal{H} = \widehat{\bigoplus}_{\alpha=1,2,\dots} V_\ell \otimes L_\alpha$

In general, a Hilbert space with an SU_2-action

$\widehat{\bigoplus}_{\ell=0,\frac{1}{2},1,\frac{3}{2}} V_\ell \otimes \mathcal{H}_\ell$ ← "multiplicity space"

isotypical component

Examples

$\ell = 0$: $V_0 \simeq \mathbb{C}$ – trivial representation

$\ell = 1/2$: $V_{1/2} = (\mathbb{C}^2)^* \simeq \mathbb{C}^2$ (irreducible, dim $= 2$)

$A: V \xrightarrow{\sim} V^* \iff B(u,v) := A(u)(v)$

What is the SU_2-inv. non-deg. bilinear form on $\mathbb{C}^2$?

det $= 1$ $\Rightarrow$ $\det \begin{bmatrix} x & x' \\ y & y' \end{bmatrix}$ is invariant ($u = \begin{pmatrix} x \\ y \end{pmatrix}$, $v = \begin{pmatrix} x' \\ y' \end{pmatrix}$)

$\ell = 1$: V_1 – irreducible 3-dim reps. of SO_3.

$\Rightarrow V_1 \simeq (\mathbb{R}^3)^{\mathbb{C}} \simeq V_1^*$ $\quad B(u,v) = u_1v_1 + u_2v_2 + u_3v_3$

↑ complexification

Exercise: B is symmetric on vector V_ℓ ($-I$ acts as $+1$) and anti-symmetric on spinor V_ℓ ($-I$ acts as -1)

Question The space of all bilinear forms on $\mathbb{C}^2$,

$\mathcal{B} = \left\{ B\left(\begin{bmatrix} x \\ y \end{bmatrix}, \begin{bmatrix} x' \\ y' \end{bmatrix}\right) = \alpha x x' + \beta x y' + \gamma y x' + \delta y y' \right\}$

↑ 4-dim SU_2-module, $(g B)(u,v) := B(g^{-1}u, g^{-1}v)$.

How does it fit the classification?

$\mathcal{B} \underset{SU_2}{\simeq} \underset{\text{vector}}{V_{1/2} \otimes V_{1/2}} \not\simeq \underset{\text{spinor}}{V_{3/2}}$

An idea: Examine the spectrum of S_z.

$S_z = i\hbar \frac{d}{dt}\Big|_{t=0} U_z(t)$ (in any representation)

$\Rightarrow S_z(u \otimes v) = i\hbar \frac{d}{dt}\Big|_{t=0} (U_z(t)u) \otimes (U_z(t)v)$

$= (S_z u) \otimes v + u \otimes (S_z v) = (S_z \otimes I + I \otimes S_z)\, u \otimes v$

Spectrum of S_z on $V_{1/2}$: $(-\frac{\hbar}{2}, \frac{\hbar}{2})$

—— " —— on $V_{1/2} \otimes V_{1/2}$: $(-\hbar, 0, 0, \hbar)$

—— " —— on $V_{d/2}$: $(-\frac{d\hbar}{2}, -\frac{d\hbar}{2} + \hbar, \dots, \frac{d\hbar}{2} - \hbar, \frac{d\hbar}{2})$

$(-\hbar, 0, 0, \hbar) = (-\hbar, 0, \hbar) \sqcup (0) \Rightarrow V_{1/2} \otimes V_{1/2} \simeq V_0 \oplus V_1$

Tensor product of representations

Example: $(V_{\frac12}\otimes \mathcal{H})\otimes(V_{1/2}\otimes\mathcal{H}') = (V_0\oplus V_1)\otimes(\mathcal{H}\otimes\mathcal{H}')$ — spin $\frac12, \frac12$: 0 or 1

$$G \hookrightarrow G\times G \quad g\mapsto(g,g)$$

$$\begin{matrix} G \longrightarrow GL(V) \\ \times \qquad\quad \times \\ G \longrightarrow GL(W)\end{matrix} \longrightarrow GL(V\otimes W)$$

$(g_1,g_2)(v\otimes w)=(g_1v)\otimes(g_2w)$

$\mathcal{R} := \{\sum_\ell m_\ell V_\ell \mid m_\ell\in\mathbb{Z}\}$ $\otimes$ - ring structure

finite formal sums, $\Sigma=\oplus$, V_ℓ - irreducibles

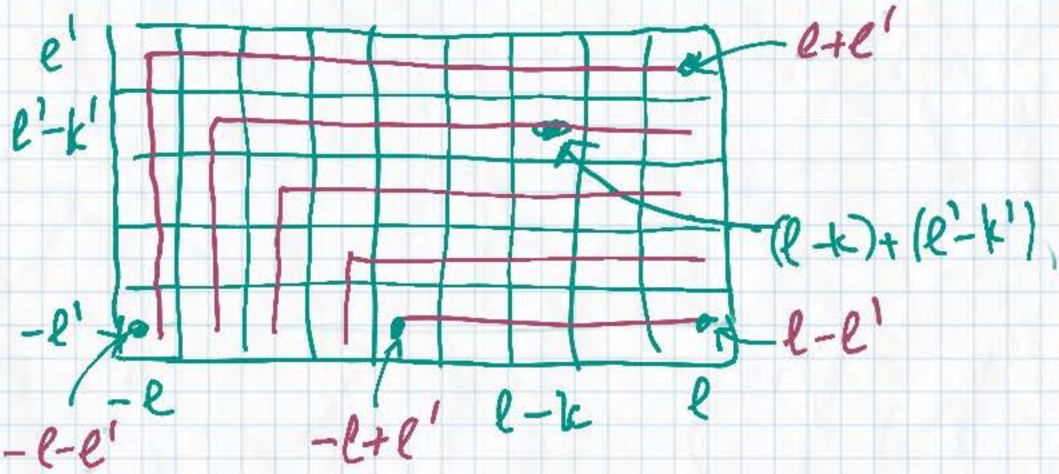
$V_\ell\otimes V_{\ell'} = \sum c^{\ell''}_{\ell\ell'} V_{\ell''}$ — $c^{\ell''}_{\ell\ell'}$: Clebsch-Gordan coefficients

$G=SU_2$: Clebsch-Gordan formula

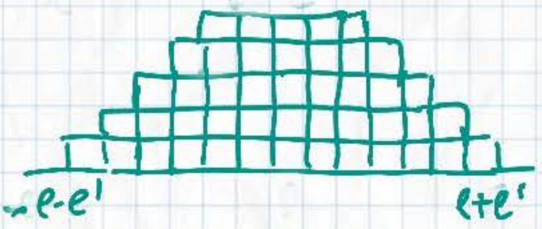
Spectrum of S_z on V_ℓ, $\ell=0,\frac12,1,\frac32,\dots$

$\hbar(-\ell,-\ell+1,-\ell+2,\dots,\ell-2,\ell-1,\ell)$

Spectrum of $\frac1\hbar[S_z\otimes I + I\otimes S_z]$ on $V_\ell\otimes V_{\ell'}$



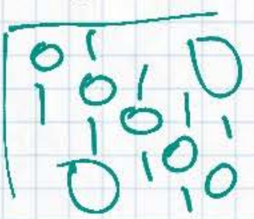
$$V_\ell\otimes V_{\ell'} \underset{\ell\geq\ell'}{=} V_{\ell-\ell'}\oplus V_{\ell-\ell'+1}\oplus\dots\oplus V_{\ell+\ell'-1}\oplus V_{\ell+\ell'}$$



$$V_\ell^{\otimes 2} = V_0\oplus V_1\oplus\dots\oplus V_{2\ell}$$

$$V_{\frac12}\otimes V_\ell = V_{\ell-\frac12}\oplus V_{\ell+\frac12}$$

$V_{\frac12}\otimes =$



$\mathcal{R} = \mathbb{Z}[V_{\frac12}] \ni 1 = V_0\otimes V_\ell = V_\ell$

The Total Spin Operator

$$\hat{S}^2 := S_x^2 + S_y^2 + S_z^2, \quad [S_{x,y,z}, \hat{S}^2] = 0$$

$\Rightarrow$ $\hat{S}^2$ commutes with SU_2 action

$\Rightarrow$ (Schur's lemma) $\hat{S}^2$ is scalar on V_ℓ.

$$J_- J_+ = (S_x - iS_y)(S_x + iS_y)$$

$$= S_x^2 + S_y^2 + i[S_x, S_y] = S_x^2 + S_y^2 - \hbar \hat{S}_z$$

$$\hat{S}^2 = J_- J_+ + \hat{S}_z^2 + \hbar \hat{S}_z \quad \text{(apply to } v_0\text{)}$$

Thm. $\hat{S}^2$ acts on $V_{d/2}$ by $\hbar^2 \frac{d}{2}\left(\frac{d}{2}+1\right)$

Corollary. Isotypical components of an SU_2-module $\mathcal{H} = \bigoplus_\ell \underline{V_\ell \otimes \mathcal{H}_\ell}$ are eigenspaces of $\hat{S}^2$ with different eigenvalues.

Revisiting spherical harmonics

$$\mathbb{C}[x,y,z]\Big|_{\{x^2+y^2+z^2=1\}} = \bigoplus_{\ell=0}^{\infty} \mathcal{H}_\ell$$

$$\mathcal{H}_\ell = \{p \in \mathcal{P}_\ell \mid \Delta p = 0\}, \quad \hat{L}^2 p = \underline{\hbar^2 \ell(\ell+1)} p$$

$SU_2/\pm I = SO_3$ acts on $V_{d/2}$, $d = 0, 2, 4, \ldots$; $\ell = d/2 = 0, 1, 2, \ldots$

$\Rightarrow$ $\hat{S}^2$ acts on V_ℓ by $\hbar^2 \ell(\ell+1)$

[on V_1 by $2\hbar^2$ – the same as $\hat{L}^2$ on $\mathcal{H}_1$]

$\Rightarrow$ $\hat{S}^2 = \hat{L}^2$ (the same normaliz. on V_1 and hence on all V_ℓ)

$\Rightarrow$ $\mathcal{H}_\ell \simeq V_\ell$ as an SO_3-module because $\dim \mathcal{H}_\ell = 2\ell+1$, $\hat{L}^2|_{\mathcal{H}_\ell} = \hbar^2 \ell(\ell+1)$

The classical limit

$$\frac{\hat{A}\hat{B}+\hat{B}\hat{A}}{2} \xrightarrow[\hbar\to 0]{} AB, \quad \frac{i}{\hbar}[\hat{A},\hat{B}] \xrightarrow[\hbar\to 0]{} \{A,B\}$$

The universal enveloping algebra $\mathcal{U}$ of SU_2

generators: X, Y, Z (a.k.a. S_x, S_y, S_z)

relations: $XY - YX = i\hbar Z$, etc.

1° $\mathcal{U}$ independent of $\hbar \neq 0$: $\frac{X}{\hbar}\frac{Y}{\hbar} - \frac{Y}{\hbar}\frac{X}{\hbar} = i\frac{Z}{\hbar}$

2° At $\hbar = 0$, $\mathcal{U}$ turns into $\mathbb{C}[X,Y,Z]$.

3° $\mathcal{U}$ acts in all V_ℓ, $\ell = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$
by $X = S_x$, $Y = S_y$, $Z = S_z$ ($\hbar \neq 0$)

4° $\mathcal{U}^{(n)} := \mathrm{Span}(X^a Y^b Z^c, \; a+b+c \leq n)$
↑
~~subalgebras~~, $\mathcal{U}^{(m)} \cdot \mathcal{U}^{(n)} \subset \mathcal{U}^{(m+n)}$

$$\mathcal{U}^{(0)} \subset \mathcal{U}^{(1)} \subset \mathcal{U}^{(2)} \subset \ldots \subset \mathcal{U}^{(k)} \subset \ldots \; \mathcal{U}$$

$\langle 1 \rangle = \mathcal{U}^{(0)}$, $\langle 1, X, Y, Z \rangle = \mathcal{U}^{(1)}$, $\langle X^2, Y^2, Z^2, XY, YZ, XZ, 1, X, Y, Z \rangle = \mathcal{U}^{(2)}$. ~

5° $A \in \mathcal{U}^{(m)}$, $B \in \mathcal{U}^{(n)} \Rightarrow \frac{i}{\hbar}(AB - BA) \in \mathcal{U}^{(m+n-1)}$

$$X^a Y^b \underline{Z}^c \; \underline{X}^\alpha Y^\beta Z^\gamma = X^{a+\alpha} Y^{b+\beta} Z^{c+\gamma} +$$
$a \leq b \leq c \qquad \alpha' \leq \beta' \leq \gamma'$

$$i\hbar\left[\; c\alpha \, X^{a+\alpha-1} Y^{b+\beta+1} Z^{c+\gamma-1} + \ldots\right] + o(\hbar)$$

6° $\mathbb{C}[X,Y,Z] = \bigoplus_{n=0}^{\infty} \mathcal{U}^{(n)}/\mathcal{U}^{(n-1)}$

$\{Z,X\} = -Y$ etc.

$$\frac{i}{\hbar}[A,B] \;\underset{\text{mod } \mathcal{U}^{(m+n-2)}}{=\!=}\; \{A, B\} \quad \text{mod } \mathcal{U}^{(m-1)}, \mathcal{U}^{(n-1)}$$

$$= \left(\frac{\partial A}{\partial Z}\frac{\partial B}{\partial X} - \frac{\partial B}{\partial Z}\frac{\partial A}{\partial X}\right)\{Z,X\} + \text{etc.}$$

Representation theory (of SU_2) = quantization of Poisson structures (on $\mathbb{R}^3$). (Kirillov-Kostant-Souriaux, ~1960)

Special Relativity (Classical)

A Newtonian free particle of mass m:

$$E = \frac{p \cdot p}{2m}$$

p, q, E, τ - extended phase space

Galilean group of symmetries:

- translations in space
- translations in time
- rotations/reflections
- "Galilean transformations"

$$p \mapsto p + m v_0 \quad (q \mapsto q + v_0 \tau)$$

$$E \mapsto E + p \cdot v_0 + m \frac{v_0 \cdot v_0}{2}$$

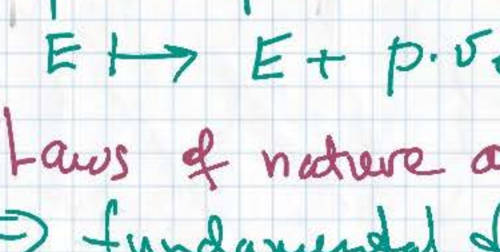
"Laws of nature are Galilean-invariant"

$\Rightarrow$ fundamental forces don't depend on $\dot{q}$

(Magnetic force $= Q(\dot{q} \times \vec{B})$ — charge & magnetic field.)

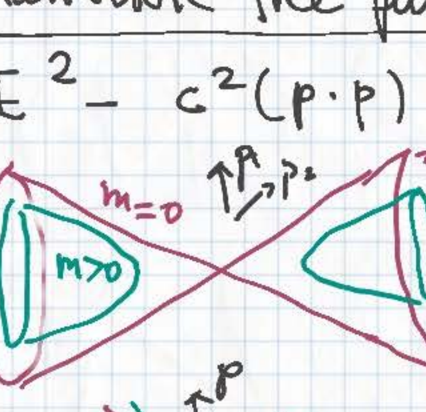
Relativistic free particle of rest mass m:

$$E^2 - c^2(p \cdot p) = m^2 c^4$$



Poincaré group:

- translations in space-time
- rotations in "space"
- Lorentz boosts



$$\begin{bmatrix} E \\ p \end{bmatrix} = \frac{1}{\sqrt{1 - v_0^2/c^2}} \begin{bmatrix} 1 & v_0 \\ v_0/c^2 & 1 \end{bmatrix} \begin{bmatrix} E \\ p \end{bmatrix}$$

$$E = \sqrt{m^2 c^4 - c^2 (p \cdot p)} = mc^2 \sqrt{1 + \frac{p \cdot p}{m^2 c^2}}$$

$$= mc^2 + \frac{p \cdot p}{2m} + O\left(\frac{1}{c^2}\right)$$

Einstein's "rest energy" (mc^2); non-relativistic energy ($\frac{p \cdot p}{2m}$)

Quantization: Klein-Gordon eqn.

$$\left(i\hbar \frac{\partial}{\partial t}\right)^2 \Psi + c^2\hbar^2 \Delta \Psi = m^2c^4\Psi$$

Solutions = Fourier integral

"harmonic waves" $A(k)e^{i(k\cdot q-\omega t)}$

$$\hbar^2\omega^2 = m^2c^4 + c^2\hbar^2(k\cdot k)$$

$$\hbar\omega = E = \sqrt{m^2c^4 + c^2(p\cdot p)}, \quad p = \hbar k$$

$m=0$ $\quad \frac{\partial^2\Psi}{\partial t^2} = c^2\Delta\Psi$ wave equation

$E = \hbar\omega$, $\vec{p} = \hbar\vec{k}$, $\omega^2 = \vec{k}\cdot\vec{k}\cdot c^2$

- massless spin-0 "particle" (unknown!)

Massless, spin-1: Maxwell eqn.

$E = E_x i + E_y j + E_z k$, $B = B_x i + B_y j + B_z k$ — not quaternions!

$\nabla\cdot E = 0$, $\frac{1}{c}\frac{\partial E}{\partial t} = \nabla\times B$

$\nabla\cdot B = 0$, $\frac{1}{c}\frac{\partial B}{\partial t} = -\nabla\times E$

divergence $\quad \nabla = i\partial_x + j\partial_y + k\partial_z \quad$ curl

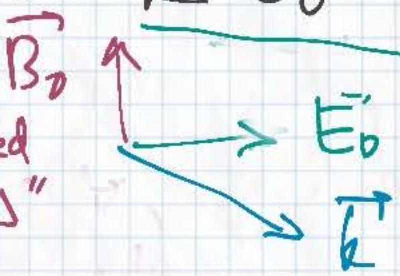
$$\text{grad}(\text{div}\, V) - \text{curl}(\text{curl}\, V) = \Delta V$$

$$\frac{\partial^2}{\partial t^2}E = c\nabla\times\frac{\partial B}{\partial t} = -c^2\nabla\times(\nabla\times E) = c^2\Delta E$$

Photon: $E = \vec{E}_0 e^{\sqrt{-1}(\vec{k}\cdot q-\omega t)}$, $B = \vec{B}_0 e^{\sqrt{-1}(\vec{k}\cdot q-\omega t)}$

$q = (x,y,z)$ $\quad \vec{k}\cdot\vec{E}_0 = 0$, $\vec{k}\cdot\vec{B}_0 = 0$

$\frac{\omega}{c}\vec{B}_0 = \vec{k}\times\vec{E}_0 \quad \frac{\omega}{c}\vec{E}_0 = \vec{B}_0\times\vec{k}$



polarized "photons"

$\Rightarrow$ wave equ. $\quad (\omega = c|k|)$

$$|\vec{E}_0| = |\vec{B}_0|$$

Dirac equ (massive, spin 1/2)

Find 1-st order ODE system implying Klein-Gordon (like Maxwell implies wave equ)

$$(i\partial_x + j\partial_y + k\partial_z)^2 \overset{?}{=} -(\partial_x^2 + \partial_y^2 + \partial_z^2)$$

$$= i^2\partial_x^2 + j^2\partial_y^2 + k^2\partial_z^2 + (ij + ji)\partial_x\partial_y + \dots$$

$$\Leftarrow \; i^2 = j^2 = k^2 = ijk = -1$$

$$\not\nabla := \sigma_x \frac{\partial}{\partial x} + \sigma_y \frac{\partial}{\partial y} + \sigma_z \frac{\partial}{\partial z}$$ Pauli matrices

$$\not\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \Delta$$

to be applied to $\mathbb{C}^2$-valued functions

$$\frac{i\hbar}{c}\frac{\partial \Psi_+}{\partial t} = mc\Psi_+ - i\hbar\not\nabla\Psi_-$$

$$\frac{i\hbar}{c}\frac{\partial \Psi_-}{\partial t} = -mc\Psi_- - i\hbar\not\nabla\Psi_+$$

$$\Rightarrow \left(i\hbar\frac{\partial}{\partial t} \pm mc^2\right)\underbrace{\left(i\hbar\frac{\partial}{\partial t} \mp mc^2\right)\Psi_\pm}_{-i\hbar c\not\nabla\Psi_\pm}$$

$$= (-i\hbar c)^2\not\nabla^2\Psi_\pm = -\hbar^2c^2\Delta\Psi_\pm$$

Components of $\Psi_\pm$ satisfy Klein-Gordon

Remark # components = 6 (spin 1) and 4 (spin 1/2) instead of 3 and 2 is due to Lorentz' SO(3,1) rather than SO_3-symmetry.

Hint: $SO_4 = SU_2 \times SU_2 / \pm(1,1)$

Revisiting the hydrogen model

Stationary Dirac eqn. with Kepler's potential:

$$mc^2\psi_+ - i\hbar c\not\nabla\psi_- - \frac{Z\alpha\hbar c}{r}\psi_+ = E\psi_+$$

$$-mc^2\psi_- - i\hbar c\not\nabla\psi_+ - \frac{Z\alpha\hbar c}{r}\psi_- = E\psi_-$$

$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137}$ - fine structure constant

Limit $E = mc^2 + E'$, $|E'| \ll mc^2$

$$\psi_- = \frac{-i\hbar c\not\nabla\psi_+}{2mc^2 + E' + Z\alpha\hbar c/r}$$

$$\left(E' + \frac{Z\alpha\hbar c}{r}\right)\psi_+ = -\frac{\hbar^2c^2}{2mc^2}\not\nabla\left(\frac{\not\nabla\psi_+}{1 + \frac{E'}{2mc^2} + \frac{Z\alpha\hbar c}{2mc^2 r}}\right)$$

$\approx -\frac{\hbar^2}{2m}\Delta\psi_+$ if $|E'|, Z\alpha\frac{\hbar c}{r} \ll mc^2$

The non-relativistic limit - the quantum Kepler equation on a spinor-valued ψ_+

It is $SO_3 \times SU_2$ - invariant.

ψ_- is determined from ψ_+.

Before limit - not invariant.

$$\hbar^2\left(\not\nabla\frac{r^2}{2}\right)\not\nabla\psi_+$$

$$= \hbar^2(x\sigma_x + y\sigma_y + z\sigma_z)(\sigma_x\partial_x + \sigma_y\partial_y + \sigma_z\partial_z)\psi_+$$

$$= \hbar^2(x\partial_x + y\partial_y + z\partial_z)\psi_+$$

$$+ \hbar^2\sigma_z(x\partial_y - y\partial_x)\psi_+ + \ldots$$

$$= \hbar^2\vec{r}\cdot\nabla\psi_+ + 2(\hat{S}\cdot\hat{L})\psi_+$$

($\hat{S}\cdot\hat{L}$) does not act componentwise on ψ_+

Total angular momentum

$\hat{L}\otimes I + I\otimes\hat{S}$ acting in $V_\ell \otimes V_{\frac{1}{2}}$

(SO_3 rotates $\vec{r}$; SU_2 acts in $\mathbb{C}^2$)

eigenvalue

$\hbar^2 j(j+1)$, $j = \ell \pm \frac{1}{2}$ on $V_{\ell+\frac{1}{2}} \oplus V_{\ell-\frac{1}{2}}$

j · total angular momentum quantum number

$n=$	1	2	3	4
	V_0	$V_0\oplus V_1$	$V_0\oplus V_1\oplus V_2$	$V_0\oplus V_1\oplus V_2\oplus V_3$
$V_{\frac{1}{2}}\otimes$ / j	$V_{\frac{1}{2}}$	$2V_{\frac{1}{2}}\oplus V_{\frac{3}{2}}$	$2V_{\frac{1}{2}}\oplus 2V_{\frac{3}{2}}\oplus V_{\frac{5}{2}}$	$2V_{\frac{1}{2}}\oplus 2V_{\frac{3}{2}}\oplus 2V_{5/2}\oplus V_{7/2}$
dim $=2j+1$	2	4 + 4	4 + 8 + 6	4 + 8 + 12 + 8

$$E_{n,j} = mc^2\left[1+\left(\frac{Z\alpha}{n-j-\frac{1}{2}+\sqrt{(j+\frac{1}{2})^2-(Z\alpha)^2}}\right)^2\right]^{-\frac{1}{2}}$$

($(Z\alpha)^2 \approx 0$)

$$= mc^2\left[1-\frac{(Z\alpha)^2}{2n^2}+\frac{(Z\alpha)^4}{n^4}\left[\frac{3}{8}-\frac{n}{2j+1}\right]+O(\alpha^6)\right]$$

non-relativ. E_n — fine splitting

- Fine splitting of energy levels agrees with observable splitting of spectral lines — Dirac's success!!
- Critique: We could take $E = -mc^2 + E'$ express ψ_+ via ψ_-, and solve eqns for ψ_-
  $\Rightarrow$ reversal of energy spectrum, $-E_{n,j}$

Dirac's response: All energy levels $\sim -mc^2$ are occupied, and if vacated, behave as "holes", mass $= m_e$, charge $= +e$

- Positrons! - discovered by Anderson in 1932

"Second Quantization"

photon → electron + positron → photon

creation — annihilation

⇒ # of electrons/positrons, etc. Not conserved

New interpretation: (Schrodinger)

Klein-Gordon, Maxwell, Dirac eqns describe classical fields

"particles" - excitations of the fields yet to be quantized.

Quantum field theory:

Free field near vacuum $(\psi(x,y,z)=0)$

$$\frac{d^2}{dt^2}\psi = \left[c^2\Delta - \frac{m^2c^4}{\hbar^2}\right]\psi$$ ideal gas of harmonic oscillators

Fourier modes $\overset{*}{A}(k)e^{i(k\cdot q \mp \omega(k)t)}$ ← for each $\vec{k}$

⇒ $\hat{A}(k)$, $\hat{A}^*(k)$ - creation/annihilation

Quantization of $\frac{1}{2}(p^2+\omega(k)^2q^2)$

Energy levels $\hbar\omega(k)(n+\frac{1}{2})$

- n "particles" with energy $\hbar\omega(k)$ with the momentum $p=\hbar\vec{k}$

Q.E.D. - "Second quantization" of Dirac.

⇒ pin down the value of $\frac{1}{\alpha}$ up to 10^{-8}

Revisiting Einstein's quantum hypothesis

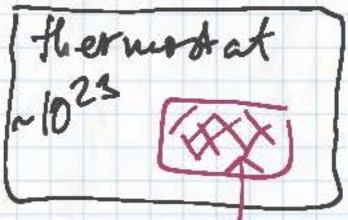
Photons - excitations of Maxwell (no $\hbar$)

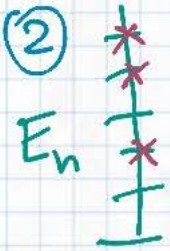
but "second quantization" of Maxwell requires $\Delta E = \hbar\omega$ (one photon energy)

why $\hbar \simeq 1.05.. \times 10^{-34}$ kg·m²/s ??

A system in a thermostat

"Our" small system put in a random energy exchange with a large energy reservoir ("thermostat")

① 

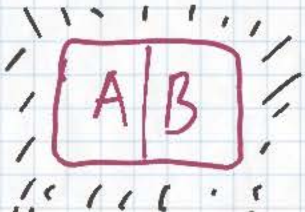
② 

atoms with energy levels occupied with electrons and exchanging photons with the environment

- energy (or even # of particles) is not conserved ($\Leftarrow$ exchange the thermostat)
- yet properties of the system (e.g. E_n) are not affected by the interaction

The canonical (Gibbs) ensemble

The thermostat does not discriminate between states with the same energy



$$P(\psi_a) = \rho(E_a)\, P(\psi_0)$$

$$P(\phi_b) = \rho(E_b)\, P(\phi_0)$$

probabilities; ρ depends only on the state of thermostat; ψ_0, ϕ_0 — reference states

$$P(\psi_a)P(\phi_b) = P(\psi_a \otimes \phi_b) = \rho(E_a + E_b)\, P(\psi_0 \otimes \phi_0)$$

probability is multiplicative; energy is additive

$$\Rightarrow \quad \rho(E_a + E_b) = \rho(E_a)\,\rho(E_b)$$

$$\Rightarrow \quad \boxed{\rho = e^{-\beta E}}$$

β - characterizes thermostat

$$\{\psi_a, E_a\} \quad P(\psi_a) = e^{-\beta E_a} / Z$$

$$Z = \sum_a e^{-\beta E_a}$$

Gibbs distribution (canonical ensemble)

Temperature

(Quasi)classical harmonic oscillator:

$E_n = \hbar\omega n$, $\hbar \to 0$

$$\mathcal{Z} = \int_0^\infty e^{-\beta E} dE = 1/\beta \Rightarrow P(E) = \beta e^{-\beta E}$$

$$\bar{E} = \beta \int_0^\infty E e^{-\beta E} dE = -E e^{-\beta E}\Big|_0^\infty + \int_0^\infty e^{-\beta E} dE$$

expectation

$$-0+0+1/\beta$$

$\frac{1}{\beta}$ = average energy per degree of freedom (for an "ideal gas" of harmonic oscillators in equilibrium with thermostat)

$= k_B T$ — T: temperature in kelvins, K; $k_B \approx 1.38 \cdot 10^{-23}$ J/K — Boltzmann constant; joule $= kg \cdot m^2/s^2$

($kT/2$ - kinetic energy per degree of freedom)

The grand ensemble & chemical potentials

Number N of distinguishable "particles" can vary due to exchange with a large "reservoir"

$$\Rightarrow \rho(N+N', E+E') = \rho(N,E)\,\rho(N',E')$$

$$\Rightarrow \rho = e^{\beta(\mu N - E)}$$

$$P(\psi_{a,N_a}) = e^{(\mu N_a - E_a)/kT} \Big/ \mathcal{Z}_{grand}$$

$$\mathcal{Z}_{grand}(\mu, \beta) = \sum_a e^{(\mu N_a - E_a)/kT}$$

μ: chemical potential (willingness to supply particles of a given species)

$\mathcal{Z}_{grand}$: statistical sum (= partition function)

$$\bar{E} = -\frac{\partial \log \mathcal{Z}}{\partial \beta}, \quad \bar{N} = kT \frac{\partial \log \mathcal{Z}_{grand}}{\partial \mu}$$

The Maxwell-Boltzmann statistics

= identical distinguishable particles, each with states ψ_n, energy E_n.

$$\frac{\overline{N(\psi_n)}}{N} = \frac{e^{-E_n/kT}}{Z}, \quad Z = \sum_n e^{-E_n/kT}$$

expected fraction of particles in state ψ_n ; probability of finding a given particle in state ψ_n

- **Canonical ensemble**: $\mathcal{H}^{\otimes N} \ni \{\psi_{m_1} \otimes \dots \otimes \psi_{m_N}\}$, $E_{m_1} + \dots + E_{m_N}$

$$\mathcal{Z}(\beta, E_1, E_2 \dots)^N = \sum_{m_1,\dots,m_N} e^{-\beta(\sum_n N_n(m_1 \dots m_N) E_n)}$$

N_n: $\# m_i = n$

$$\overline{N(\psi_n)} = -\frac{1}{\beta} \frac{\partial}{\partial E_n} \log Z^N = \sum_{m_1 \dots m_N} N_n(m_1 \dots m_N) \mathbb{P}(\psi_{m_1} \otimes \dots \otimes \psi_{m_N})$$

$$= -\frac{N}{\beta} \frac{\partial}{\partial E_n} \log Z = N e^{-\beta E_n} / Z$$

- **Grand canonical ensemble**

$$T(\mathcal{H}) = \bigoplus_{N=0}^{\infty} \mathcal{H}^{\otimes N}$$

$$Z_{grand} = \sum_{N=0}^{\infty} e^{\beta \mu N} Z^N = \frac{1}{1 - e^{\beta\mu} Z}$$

$$e^{\beta\mu N} Z^N = \sum_{m_1 \dots m_N} e^{\beta(\mu N - E_{m_1} - \dots - E_{m_N})}$$

$$\overline{N} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_{grand} = \frac{e^{\beta\mu} Z - 1 + 1}{1 - e^{\beta\mu} Z} = Z_{grand} - 1$$

$$\overline{N(\psi_n)} = -\frac{1}{\beta} \frac{\partial}{\partial E_n} \log Z_{grand} = e^{\beta(\mu - E_n)} Z_{grand}$$

$$\frac{\overline{N(\psi)}}{\overline{N} + 1} = \frac{1}{e^{(E(\psi) - \mu)/kT}}$$

Bose-Einstein statistics

Indefinite number of identical bosons

$\{\psi_n, E_n\}$, $S(\mathcal{H}) = \bigoplus_{N=0}^{\infty} S^N(\mathcal{H})$

$\Leftrightarrow$ ideal gas of quantum harmonic oscillators, $\{\psi_n^{\otimes L}, L E_n\}$, $n = 1, 2, \ldots$

$$Z_n = \sum_{L=0}^{\infty} e^{L(\mu - E_n)/kT} = \frac{1}{1 - e^{(\mu - E_n)/kT}}$$

L = # of bosons in state ψ_n. ($=$ holds for $E_n > \mu$)

Z_n = "Z grand" for a system with one state, ψ_n

$$Z_{total} = \prod_{n=1,2,\ldots} Z_n$$

$$\overline{N(\psi_n)} = kT \frac{\partial}{\partial \mu} \log Z_n = \frac{1}{e^{(E_n - \mu)/kT} - 1}$$

Fermi-Dirac statistics

Indefinite # of identical fermions

$$\Lambda(\mathcal{H}) = \bigoplus_{N=0}^{\infty} \Lambda^N \mathcal{H} = \bigotimes_n \Lambda(\mathbb{C}\psi_n)$$

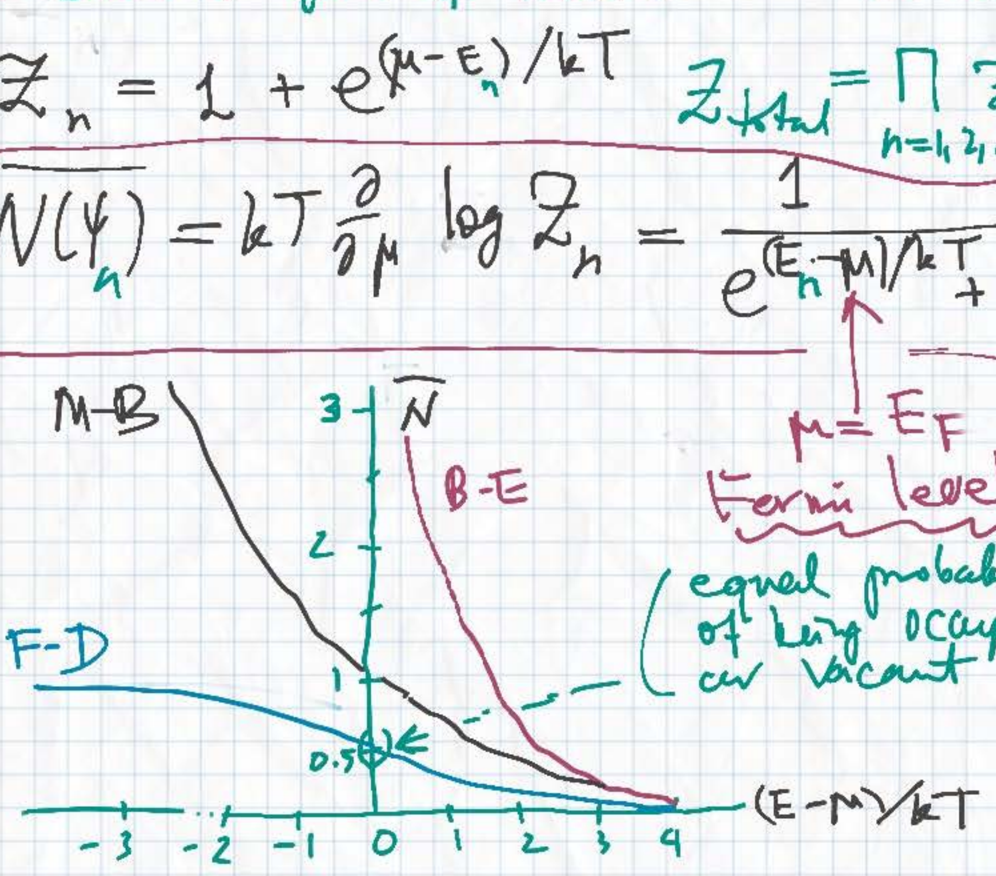
$\Leftrightarrow$ Ideal gas of "qubits" $\{\psi_n^{\otimes 0} + \psi_n^{\otimes 1}\}_n$

$$Z_n = 1 + e^{(\mu - E_n)/kT} \qquad Z_{total} = \prod_{n=1,2,\ldots} Z_n$$

$$\overline{N(\psi_n)} = kT \frac{\partial}{\partial \mu} \log Z_n = \frac{1}{e^{(E_n - \mu)/kT} + 1}$$

$\mu = E_F$ Fermi level

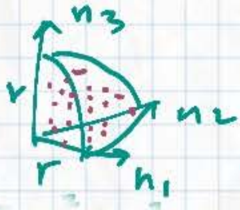
(equal probability of being occupied or vacant)



Free-electron model

$\prod_{i=1}^{3} \sin \frac{\pi n_i x_i}{L}$ electrons in a crystal as free particles in a box.

$$E_{n_1,n_2,n_3} = (n_1^2+n_2^2+n_3^2)\frac{\hbar^2\pi^2}{2mL^2}, \quad n_i = 1,2,3\ldots$$



$$D(E)dE = 2 \times \frac{\pi\, dr^3}{6} \qquad \sum n_i^2 \le r^2$$

electron density (under $D(E)$); spin $=1/2$ (under the 2); $\frac{4}{3}\pi r^3/8$ (under $\frac{\pi\, dr^3}{6}$)

$$= \frac{\pi}{3} d\left(\frac{2mL^2}{\hbar^2\pi^2}E\right)^{3/2} = \frac{(2m)^{3/2} V}{2\hbar^2\pi^2}\sqrt{E}\,dE$$

$T \simeq 0 \Rightarrow$ # electrons N = # states with $E \le E_F$

$$N = \int_0^{E_F} D(E)dE = \frac{(2m)^{3/2} V}{3\hbar^3\pi^2} E_F^{3/2} \qquad E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$E_{total} = \int_0^{E_F} E\, D(E)dE = \frac{(2m)^{3/2} V}{5\hbar^3\pi^2} E_F^{5/2} = \frac{3}{5} N E_F$$

Electron degeneracy pressure:

$dE_{total} = -P\,dV$ (V decreases $\Rightarrow E_{total}$ increases)

$$P = -\frac{dE_{total}}{dV} = (3\pi^2)^{2/3}\frac{\hbar^2}{5m}\left(\frac{N}{V}\right)^{5/3}$$

some calculation (at the $=$); particle density (under $\frac{N}{V}$)

$T > 0$: Relations between N, E_F & E_{total}:

$$\frac{N}{E_{total}} = \int_0^{\infty} \frac{1}{e^{(E-E_F)/kT}+1} \frac{(2m)^{3/2} V}{2\hbar^3\pi^2} E^{\cancel{1/2}\ 3/2} dE$$

- Electron degeneracy pressure accounts for metal's resistance to compression.
- Relativistic version (Chandrasekhar) predicts the Sun's fate to turn into a white Dwarf.

Bose-Einstein condensation

23.3

Phase transition (predicted ~1925, observed ~1995)

Diluted gas ⟶ condensate with most atoms in the lowest energy

$T \simeq 0$

Heuristics: $N = N_0 + N_1$, $E_0 < E_1$,

$$N_0 = \frac{1}{e^{(E_0-\mu)/kT} - 1} \xrightarrow[T\to 0]{} N \Rightarrow \mu \to E_0 .$$

$$N_1 \approx \frac{1}{e^{(E_1-E_0)/kT} - 1} = \text{const}(N) \text{ at } T \simeq 0$$

Remark: In B-M: $N_1/N_0 = e^{-(E_1-E_0)/kT} = \text{const}$

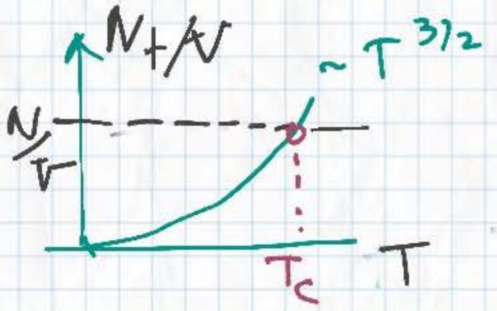
Computing $T_{critical}$ (L×L×L-box model)

$$\underset{N-N_0}{\overset{\shortparallel}{N_+}} \simeq \int_{E_0 \simeq E_1}^{\infty} \frac{1}{e^{(E-E_0)/kT} - 1} \, \frac{(2m)^{3/2} V}{4\hbar^3 \pi^2} \sqrt{E-E_0} \, dE$$

($E_0 \simeq \mu$; Spin 0)

$$= \frac{(2mkT)^{3/2} V}{4\hbar^3 \pi^2} \int_0^\infty \frac{\sqrt{x}\, dx}{e^x - 1} \quad (*) = \text{const} = \frac{\sqrt{\pi}}{2} \zeta(3/2)$$

Define $T_{critical}$ from $N_+ = N$



$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

$$T < T_c = \frac{2\pi\hbar^2}{mk} \left(\frac{N/V}{\zeta(3/2)}\right)^{2/3}$$

(*) $$\int_0^\infty \frac{\sqrt{x}\, dx}{e^x - 1} = \sum_{n=1}^{\infty} \int_0^\infty e^{-nx} \sqrt{x}\, dx$$

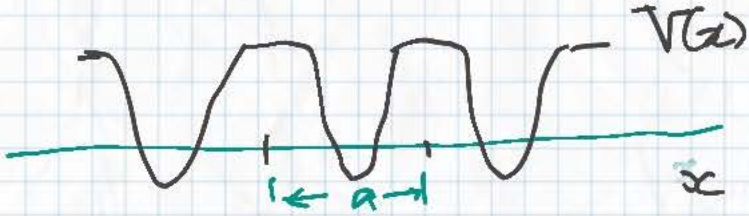
$$= \left(\sum_{n=1}^{\infty} \frac{1}{n^{3/2}}\right) \int_0^\infty e^{-y} \sqrt{y}\, dy = \zeta(3/2) \frac{\sqrt{\pi}}{2}$$

$$= \frac{1}{2} \int_0^\infty e^{-y} \frac{dy}{\sqrt{y}} = \int_0^\infty e^{-z^2} dz = \frac{\sqrt{\pi}}{2}$$

Solid State Physics

Electrons in crystals (conductors/insulators)

1 electron in 1D periodic potential



$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi, \quad V(x+a) \equiv V(x)$$

$$V \equiv 0 \Rightarrow \psi = e^{ikx}, \quad k = \pm\sqrt{2mE}/\hbar \quad (E > 0)$$

Problem: Study bounded eigenfunctions

Dynamical Interpretation: x – "time".

$$H(p,q,x) = \frac{p^2}{2} + \frac{2m}{\hbar^2}(E - V(x))\frac{q^2}{2}$$

linear "time"-dependent hamiltonian system

Solutions: vector space $\mathbb{R}^2$, $\begin{bmatrix}\psi(0)\\ \psi'(0)\end{bmatrix}$

$\psi_1 : \begin{bmatrix}1\\0\end{bmatrix}$, $\psi_2 : \begin{bmatrix}0\\1\end{bmatrix}$, $\psi = \lambda_1\psi_1 + \lambda_2\psi_2$ ← general solution

$x \mapsto x+a \Rightarrow M : \mathbb{R}^2 \to \mathbb{R}^2$ – monodromy transf.

$$M = \begin{bmatrix} a & b \\ c & d\end{bmatrix} := \begin{bmatrix}\psi_1(a) & \psi_2(a) \\ \psi_1'(a) & \psi_2'(a)\end{bmatrix}$$

$$\begin{bmatrix}\psi(na)\\ \psi'(na)\end{bmatrix} = \begin{bmatrix} a & b \\ c & d\end{bmatrix}^n \begin{bmatrix}\psi(0)\\ \psi'(0)\end{bmatrix}, \quad n = 0, \pm1, \pm2, \ldots$$

$\det M = 1$ (symplectic transf.) $M \in SL_2(\mathbb{R})$

$$\frac{d}{dx}\begin{vmatrix}\psi_1(x) & \psi_2(x) \\ \psi_1'(x) & \psi_2'(x)\end{vmatrix} = \begin{vmatrix}\psi_1' & \psi_2' \\ \psi_1' & \psi_2'\end{vmatrix} + \begin{vmatrix}\psi_1 & \psi_2 \\ \psi_1'' & \psi_2''\end{vmatrix} = 0 + 0$$

"Wronskian" $\qquad \psi_i'' = 2m\hbar^{-2}(V-E)\psi_i$

Monodromy matrices $M \in SL_2(\mathbb{R})$

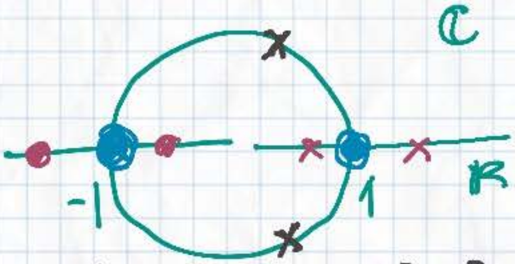
$\det(\lambda I - M) = \lambda^2 - (\operatorname{tr} M)\lambda + 1, \quad \lambda_+\lambda_- = 1$

(i) $\lambda_\pm = e^{\pm i\theta}$ $\qquad -2 < \operatorname{tr} M < 2$

(ii) $\lambda_+ > 1 > \lambda_- = 1/\lambda_+ > 0 \qquad \operatorname{tr} > 2$

or $0 > \lambda_+ > -1 > \lambda_- = 1/\lambda_+ \qquad \operatorname{tr} < -2$

(iii) $\lambda_{\pm 1} = 1$ or -1



(i) $M \sim \begin{bmatrix} e^{i\theta} & 0 \\ 0 & e^{-i\theta} \end{bmatrix}$

(ii) $M \sim \begin{bmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{bmatrix}$

(iii) $M \sim \pm\begin{bmatrix} 1 & 1 \\ 0 & 1 \end{bmatrix}$ or $\pm\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$

(i) $\psi_\pm(x+na) = e^{\pm in\theta}\psi_\pm(x)$ – bounded eigenfunct.

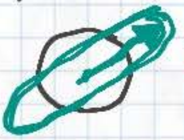
(ii) $\psi_\pm(x+na) = \lambda_\pm^n \psi_\pm(x)$ all linear combin. are unbounded

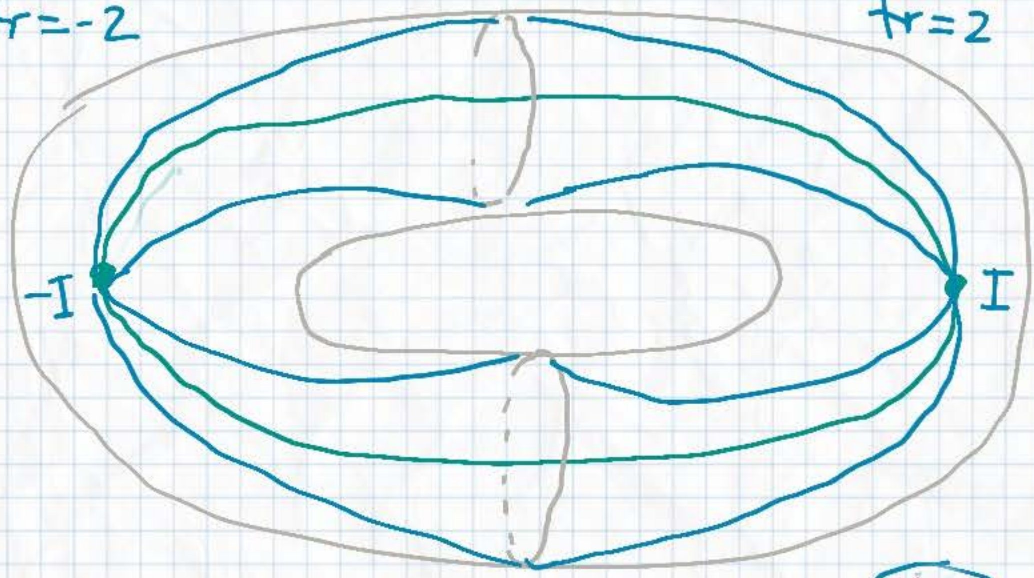
(iii) $M^n \sim (-1)^n \begin{bmatrix} 1 & n \\ 0 & 1 \end{bmatrix}$ $\qquad M^n = (\pm I)^n$ – 2 dim eigenspa.

1 eigenstate: $\psi(x+a) = \pm\psi(x)$

a-periodic or a-anti-periodic

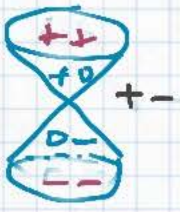
$SL_2(\mathbb{R}) \approx S^1 \times D^2$





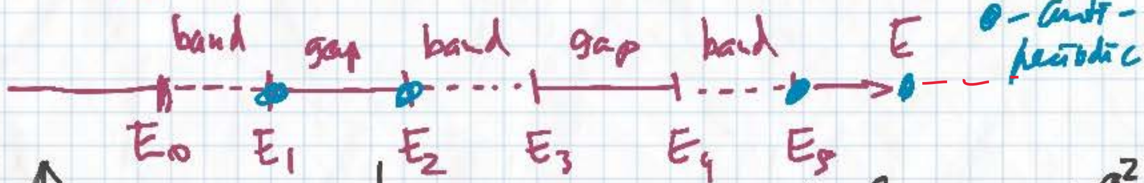
$M = \pm I e^{\Lambda}$

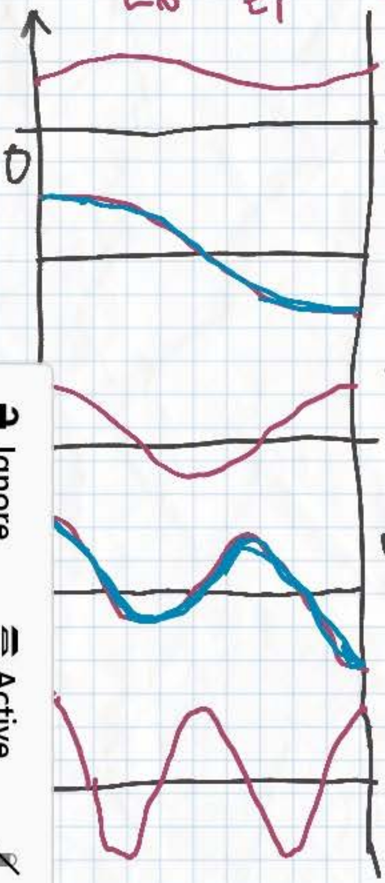
$\Lambda \leftrightarrow \frac{1}{2}(\underline{a}p^2 + 2\underline{b}pq + \underline{c}q^2)$



The band structure of the spectrum

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





$\psi_0 = 1$

$a = \pi$

$\psi_1 = \cos x$

$\psi_2 = \sin x$

$\psi_3 = \cos 2x$

$\psi_4 = \sin 2x$

$\psi_5 = \cos 3x$

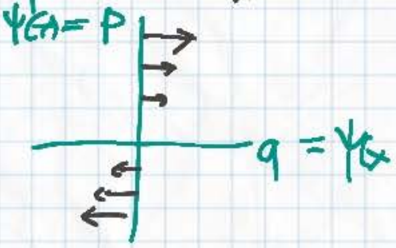
$\psi_6 = \sin 3x$

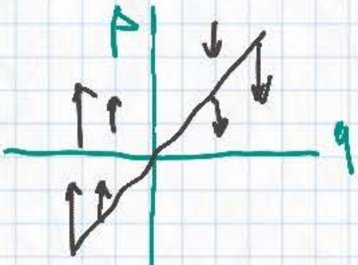
$\psi_7 = \cos 4x$

$\psi_8 = \sin 4x$

$$H = \frac{p^2}{2} + \frac{2m}{\hbar^2}(E - V(x))\frac{q^2}{2}$$

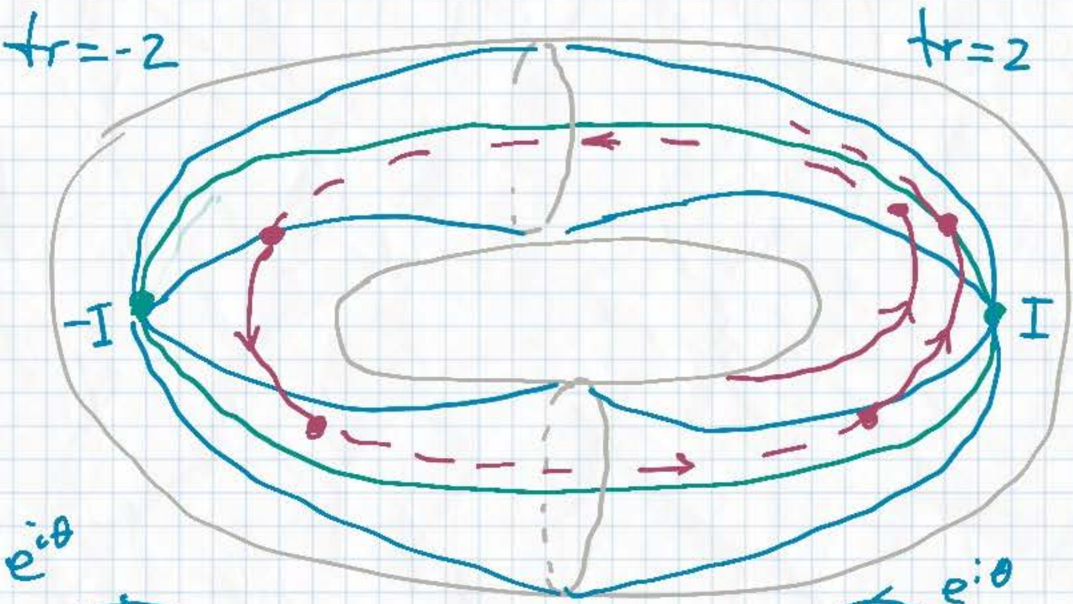
$$q' = p, \quad p' = \frac{2m}{\hbar^2}(V - E)q$$

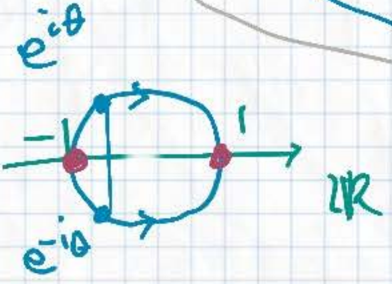




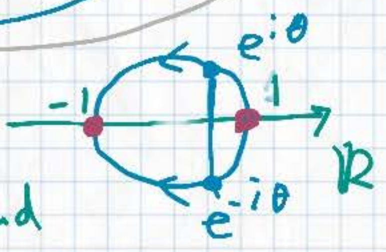
$$\Delta H = \frac{m}{\hbar^2}\Delta E\, q^2$$

$SL_2(\mathbb{R}) \approx S^1 \times D^2$





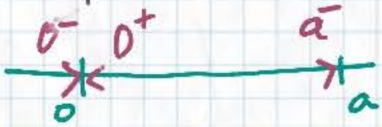
evolution of $\lambda_\pm$ inside a band



The Kronig–Penney model

$$V(x) = \frac{\hbar^2 \alpha}{2ma}\left(\sum_{n=-\infty}^{\infty} \delta(x - na)\right)$$

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



$$0 = \int_{na^-}^{na^+}\left[\psi''(x) - \frac{2m}{\hbar^2}V(x)\psi(x)\right]dx = \psi'(x)\Big|_{na^-}^{na^+} - \frac{\alpha}{a}\psi(na)$$

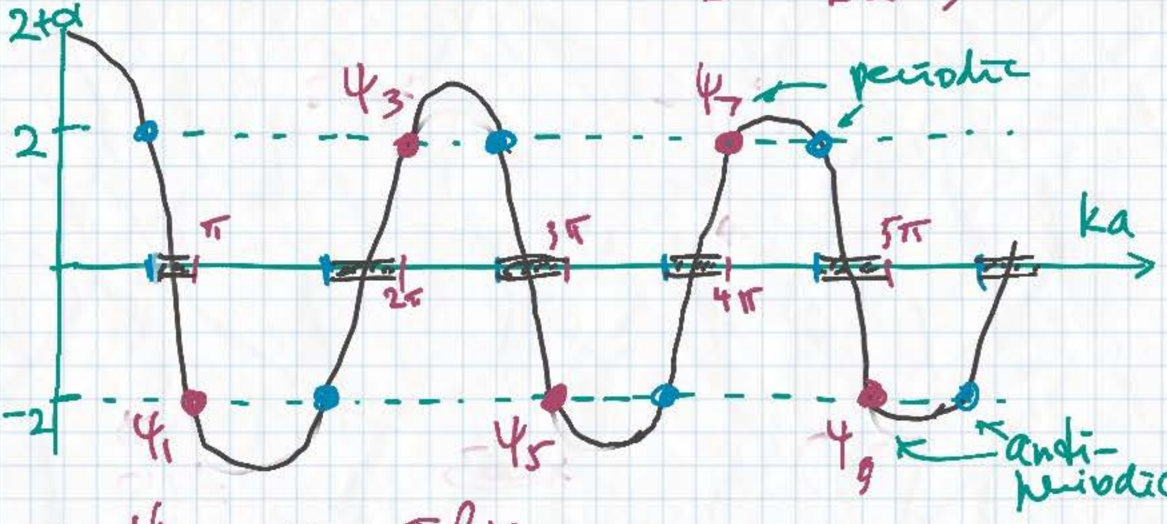
$$\begin{bmatrix}\psi_1 & \psi_2\\ \psi_1' & \psi_2'\end{bmatrix}(0^-) = \begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} \Rightarrow \begin{bmatrix}\psi_1 & \psi_2\\ \psi_1' & \psi_2'\end{bmatrix}(0^+) = \begin{bmatrix}1 & 0\\ \frac{\alpha}{a} & 1\end{bmatrix}$$

$$\begin{bmatrix}\psi_1 & \psi_2\\ \psi_1' & \psi_2'\end{bmatrix}(0^+) = \begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} \Rightarrow \begin{bmatrix}\psi_1 & \psi_2\\ \psi_1' & \psi_2'\end{bmatrix} = \begin{bmatrix}\cos kx & \frac{1}{k}\sin kx\\ -k\sin kx & \cos kx\end{bmatrix}$$

$0 < x < a$ $\quad k = \sqrt{2mE}/\hbar$

$$M = \begin{bmatrix}\cos ka & \frac{1}{k}\sin ka\\ -k\sin ka & \cos ka\end{bmatrix}\begin{bmatrix}1 & 0\\ \frac{\alpha}{a} & 1\end{bmatrix}$$

$$\operatorname{tr} M = 2\left(\cos ka + \frac{\alpha}{2}\frac{\sin ka}{ka}\right)$$



- $\psi_{2l-1} = \sin \frac{\pi l x}{a}$

l zeros per period

- ψ_{2l} (ψ_{2l}' breaks at $x = na$)

ψ_0:

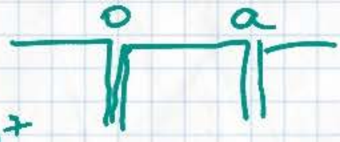
- Continuous spectrum

In a real (finite) crystal – assume circular

$\psi(x + Na) = \psi(x)$, $\quad \lambda_\pm = e^{2\pi i\, l/N} = e^{i\theta}$ $\quad N \div 10^7$ per cm

The 2nd Kronig-Penney model [25.1]

$$V(x) = -\frac{\hbar^2 \alpha}{2ma}\left(\sum_{n=-\infty}^{\infty} \delta(x-na)\right)$$

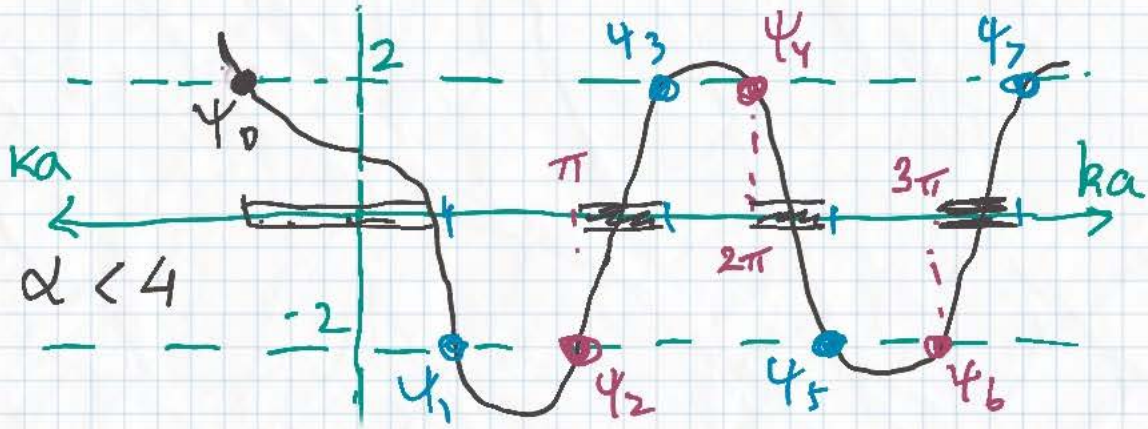


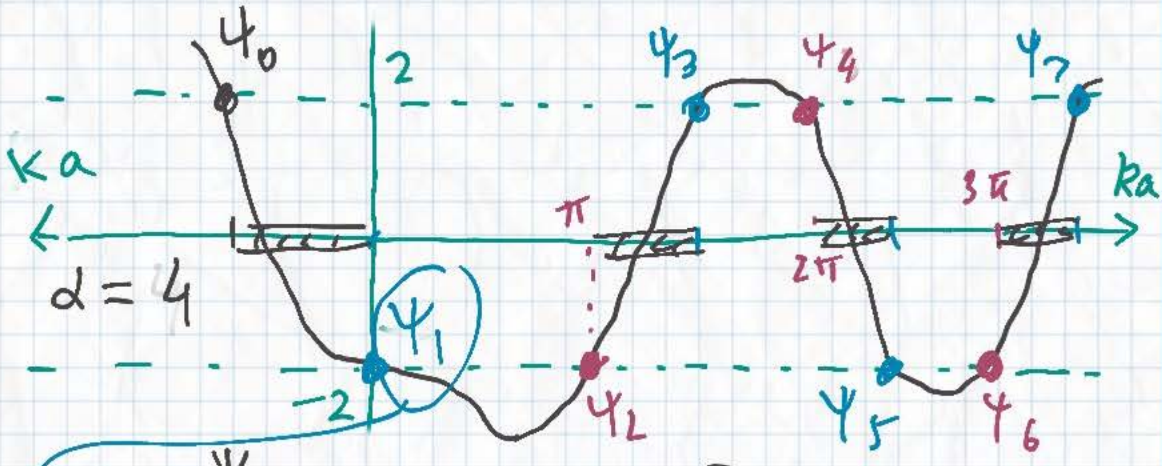
$$-\frac{\hbar^2}{2m}\psi'' + V(x)\psi = E\psi, \quad \psi'(x)\Big|_{na^-}^{na^+} = -\frac{\alpha}{a}\psi(na)$$

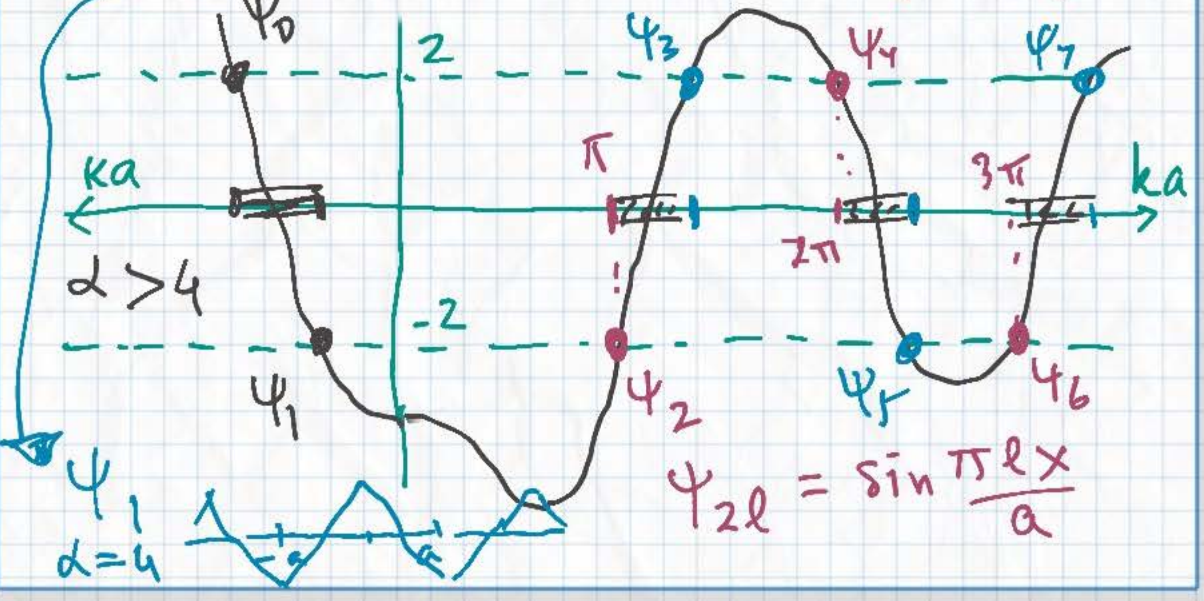
$$\mathrm{tr}\, M = 2\left(\cos ka - \frac{\alpha}{2}\frac{\sin ka}{ka}\right), \quad k = \sqrt{2mE}/\hbar$$

$$E<0: \quad \underline{M} = \begin{bmatrix} \cosh \kappa a & \frac{1}{\kappa}\sinh \kappa a \\ \kappa \sinh \kappa a & \cosh \kappa a \end{bmatrix}\begin{bmatrix} 1 & 0 \\ -\frac{\alpha}{a} & 1 \end{bmatrix}$$

$$\mathrm{tr}\, \underline{M} = 2\left(\cosh \kappa a - \frac{\alpha}{2}\frac{\sinh \kappa a}{\kappa a}\right), \quad \kappa = \frac{\sqrt{-2mE}}{\hbar}$$







$$\psi_{2l} = \sin\frac{\pi l x}{a}$$

"Bloch's theorem"

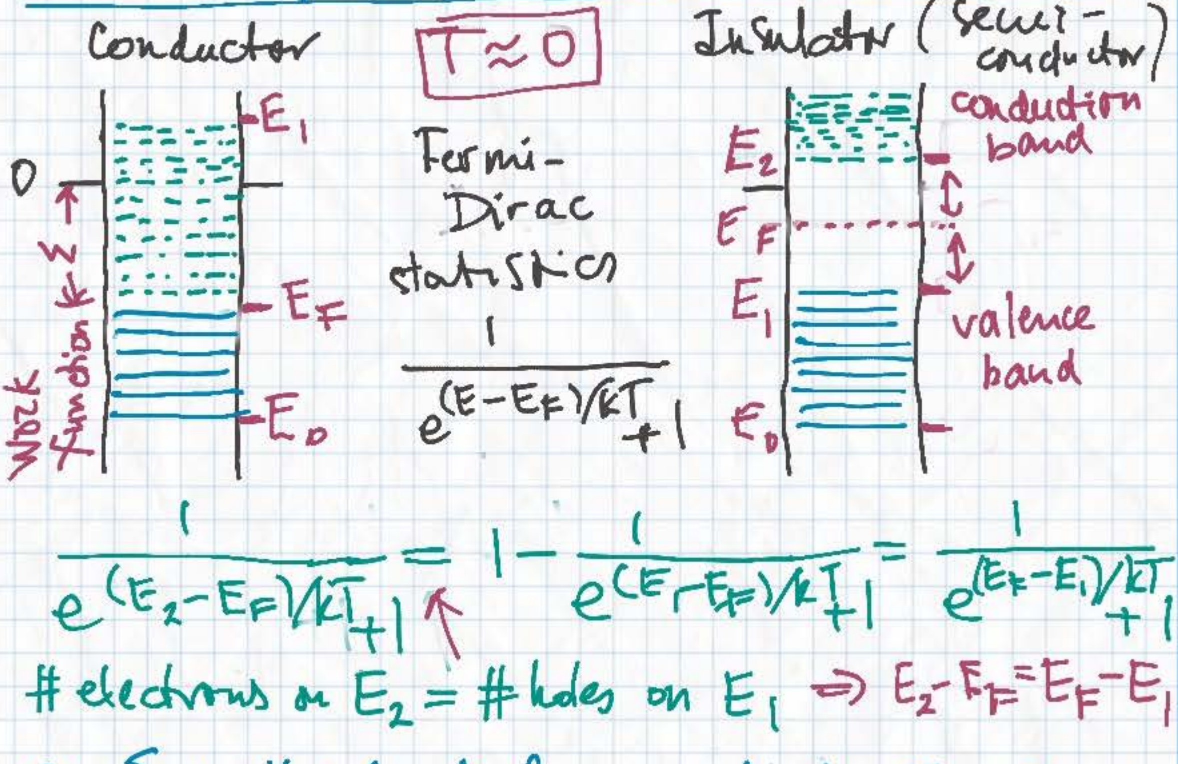
Eigen-functions in 3D lattice-periodic potentials are quasi-periodic:

$$\psi(q) = e^{ik\cdot q}\, u(q)\,,\quad u(q+a) = u(q),\ a \in \underline{\Lambda}$$

$$\psi(q+a) = e^{i\theta}\,\psi(q)\,,\quad \theta = k\cdot a \quad (k \in \mathbb{R}^3/\underline{\Lambda}^*)$$

[Band structure also holds in 3D-theory]

Conductors, semi-conductors and insulators



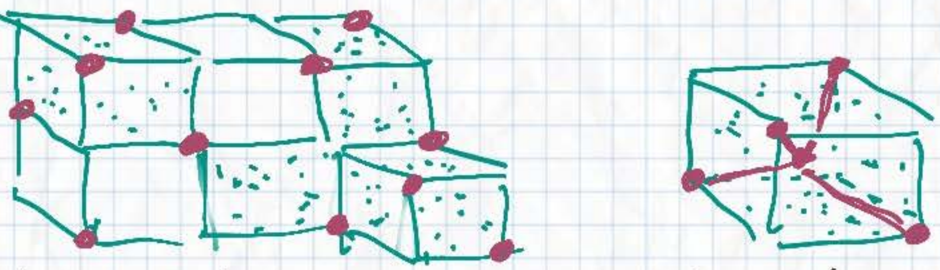
$$\frac{1}{e^{(E_2-E_F)/kT}+1} = 1 - \frac{1}{e^{(E_1-E_F)/kT}+1} = \frac{1}{e^{(E_F-E_1)/kT}+1}$$

electrons on E_2 = # holes on E_1 $\Rightarrow E_2 - E_F = E_F - E_1$

- δ-well potential – one level $E < 0$
- In gas state – level E is $\approx 10^{23}$-fold degenerate (as in two δ-well model)
- Crystallization = covalent bonding: "sharing" electrons (of outer subshells) saves energy (inner shells remain degenerate) ~~Degeneration~~ (Valence) band is formed
- Voltage $\Rightarrow$ mixed state (of $\sim 10^{23}$ electrons) $\Longrightarrow$ Probability current in voltage's direction
- Semiconductors = insulators at $T \approx 0$, "conductors" at $T > 0$ (gap $E_2 - E_1$ is small)

Tetrahedral Crystal (Si)

$1s^2 2s^2 2p^6 3s^2 3p^2$

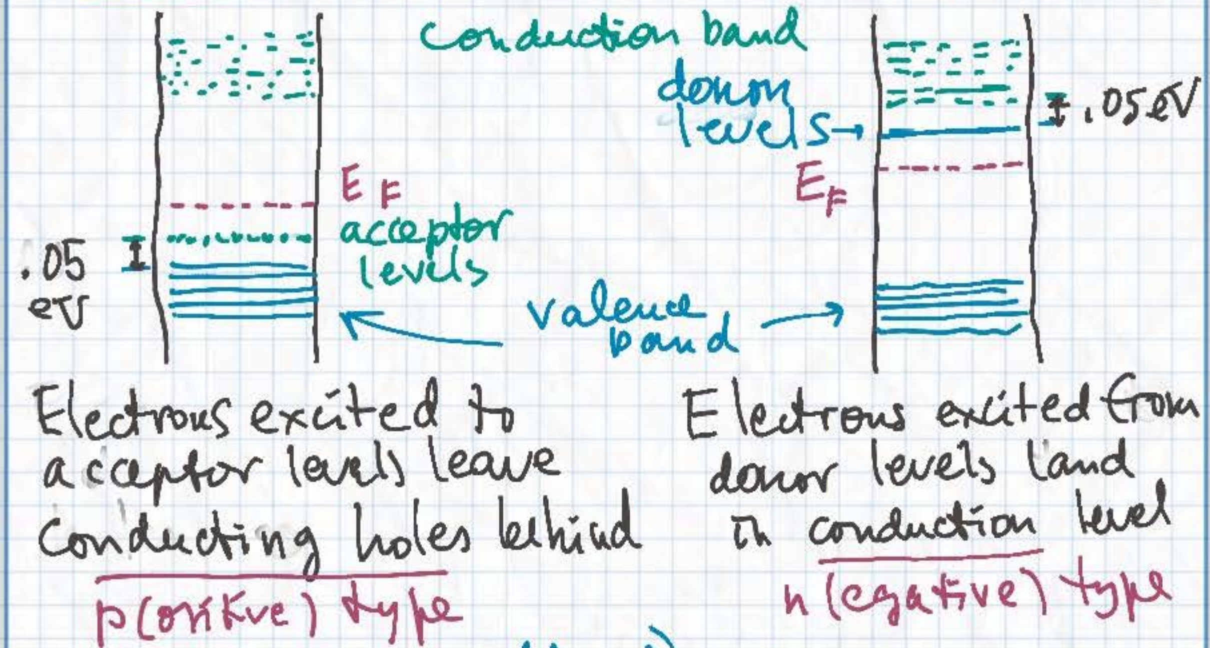


Classically : Valence shells filled to capacity

Quantum-mechanically : Valence band filled up

Gap to conduction band: 1.1 eV (semiconductor)

p-doping (Boron) & n-doping (As)



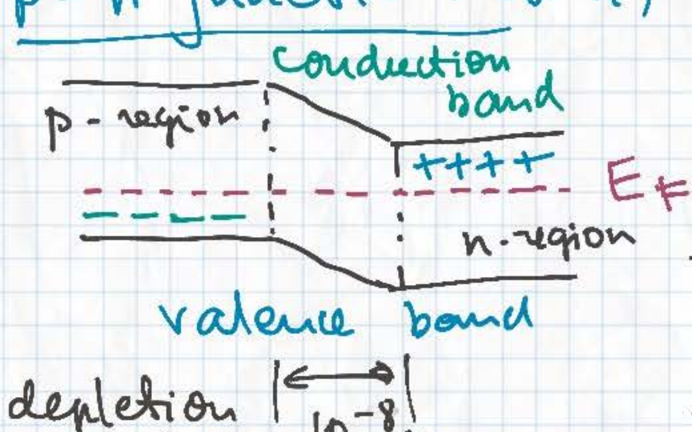
Electrons excited to acceptor levels leave conducting holes behind

p(ositive) type

Electrons excited from donor levels land in conduction level

n(egative) type

p-n junction (diod)



Thermal current I_0 ← caused by migration of electrons p → n

Recombination current → caused by electrons scaling the depletion barrier

Voltage ~ 10^8 V/m

$$I = I_0\left(e^{q\phi/kT} - 1\right)$$

- I: current p → n
- I_0: thermal current
- q: electron's charge
- ϕ: applied Voltage

Korteweg - de Vries eqn., 1895

$$u_t + 6uu_x + u_{xxx} = 0$$

John Scott Russell (Aug. 1834, Edinburgh)

Solitary running wave

$u_t + uu_x = 0$ Boussinesq eqn.

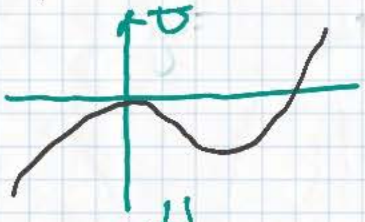
$$\Delta u = u(x - u\Delta t) - u(x) \approx -uu_x \Delta t$$

u_{xxx} - "viscosity" (?)

Solitons: $u(x,t) = \phi(x - vt)$ $v > 0$

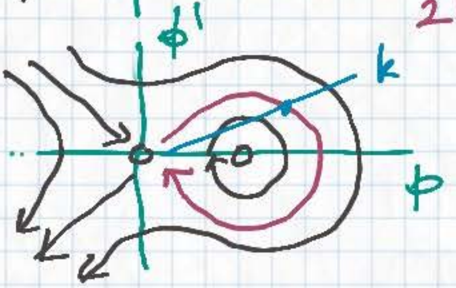
$$-v\phi' + 6\phi\phi' + \phi''' = 0 \qquad \phi \to 0,\ x \to \pm\infty$$

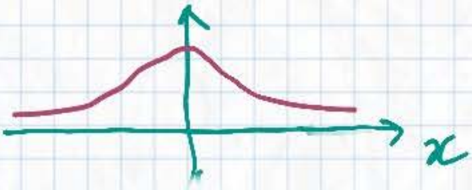
$$\phi'' = v\phi - 3\phi^2 + \alpha$$



$$U(\phi) = \phi^3 - v\frac{\phi^2}{2} - \alpha\phi \text{ (crossed out: } \alpha\phi)$$

$$\frac{1}{2}\left(\frac{d\phi}{dx}\right)^2 + \phi^3 - v\frac{\phi^2}{2} = 0$$





$$\int dx = \int \frac{d\phi}{y(\phi)} \qquad y^2 = v\phi^2 - 2\phi^3$$

$$y = k\phi \Rightarrow k^2 \phi^2 = (v - 2\phi)\phi^2$$

$$= \int \frac{d\,\frac{v-k^2}{2}}{k\left(\frac{v-k^2}{2}\right)} = -\int \frac{2\,dk}{v-k^2} = \frac{1}{\sqrt{v}} \log \frac{\sqrt{v}-k}{\sqrt{v}+k}$$

$$e^{\sqrt{v}x} = \frac{\sqrt{v}-k}{\sqrt{v}+k} \qquad k\left(1 + e^{\sqrt{v}x}\right) = \sqrt{v}\left(1 - e^{\sqrt{v}x}\right)$$

$$k = -\sqrt{v}\tanh\frac{\sqrt{v}x}{2} \qquad \phi = \frac{v - k^2}{2}$$

$$= \frac{v}{2}\left(1 - \tanh^2\frac{\sqrt{v}x}{2}\right) = \frac{v/2}{\cosh^2 \sqrt{v}x/2}$$

Lax Pairs

Kruskal – Zabusky (1965) – Soliton interaction

$L := -\frac{d^2}{dx^2} - u(x)$ – Schrodinger operator

$\hbar = 1$, $m = 1/2$ ↗ ; ↑ potential energy

$A := 4\frac{d^3}{dx^3} + 3\left(u\frac{d}{dx} + \frac{d}{dx}u\right)$ $L^* = L$, $A^* = -A$

Theorem: $\dot{L} = [L, A] \Leftrightarrow$ KdV

Proof: $\dot{L} = -u_t$

$(-\partial^2 - u)(4\partial^3 + 3u\partial + 3\partial u) + (4\partial^3 + 3u\partial + 3\partial u)(\partial^2 + u)$

$= -4\partial^5 - 4u\partial^3 - 3\partial^2 u\partial - 3u^2\partial - 3\partial^3 u - 3u\partial u$

$+ 4\partial^5 + 4\partial^3 u + 3u\partial^3 + 3u\partial u + 3\partial u\partial^2 + 3\partial u^2$

$= \partial^3 u - u\partial^3 - 3\partial u_x\partial + 3(u^2)_x$

$\partial^3 u\varphi = u_{xxx}\varphi + 3\partial u_x\partial\varphi + u\partial^3\varphi$

$= u_{xxx} + 6uu_x$ Q.E.D.

Proposition: $\frac{dU}{dt} = U(t)A(t)$, $U(0) = I$.
If $A^* = -A$, then $U(t)$ – unitary ($\neq e^{tA}$)

Proof: $\frac{dU^*}{dt} = A^*(t)U^*(t)$

$\frac{d}{dt}(UU^*) = \dot{U}U^* + U\dot{U}^* = UAU^* + UA^*U^* = 0$

$\Rightarrow U(t)U^*(t) = U(0)U^*(0) = I$

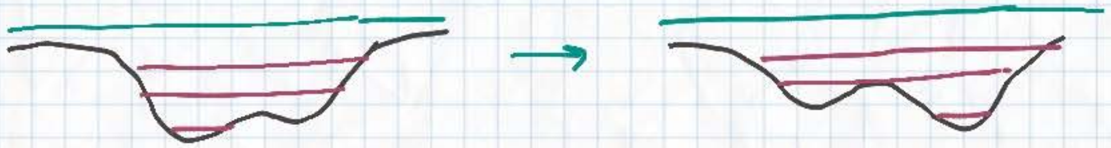
Exc. $U^*(t)U(t) = I$ (Is it automatic?)

Proposition: $L(t) := U^*(t)L(0)U(t)$ satisfies Lax's equation $\dot{L} = [L, A]$

Proof: $\dot{L} = \dot{U}^*L(0)U + U^*L(0)\dot{U}$
$= -AU^*L(0)U + U^*L(0)UA = [L, A]$

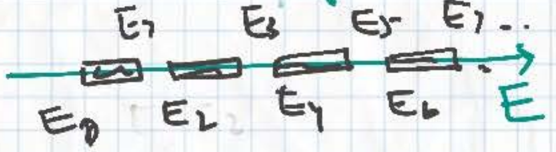
Conservation Laws

Corollary. When u evolves in time according to KdV, the spectrum of the Schrödinger operator $L = -\partial^2 - u$ remains unchanged.



1976. Dubrovin, Matveev, Novikov

KdV for periodic functions: $u(x+a) = u(x)$



$\{E_0 < E_1 < \dots\}$ – conservation laws

KdV – completely integrable Hamiltonian system (1971 – Zakharov, Faddeev)

Def. A Hamiltonian system with n degrees of freedom is completely integrable if it has n indep. Poisson-commuting conservation laws: $H = H_1, H_2, \dots, H_n$, $\{H_i, H_j\} = 0$.

Phase space M = functions $u(x)$ (e.g.: fast-decaying; e.g. a-periodic).

$$H = \int_{-\infty}^{\infty} \left(\frac{u_x^2}{2} - u^3\right) dx \quad = \oint (\dots)\, dx$$

Calculus of Variations: $\frac{\delta H}{\delta u} = -u_{xx} - 3u^2$

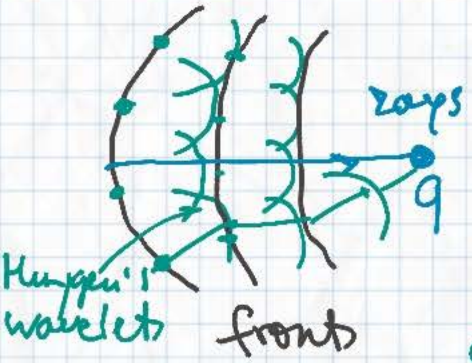
$$\dot{\mathcal{F}} = \{H, \mathcal{F}\} := \int \frac{\delta \mathcal{F}}{\delta u} \frac{d}{dx} \frac{\delta H}{\delta u}\, dx$$

(↑ Poisson structure)

$\mathcal{F}_\varphi := \int \varphi u\, dx$, $\frac{\delta \mathcal{F}}{\delta u} = \varphi$,

$$\dot{\mathcal{F}}_\varphi = \int \varphi \underbrace{\dot{u}}_{u_t}\, dx = \int \varphi \underbrace{\frac{d}{dx}(-u_{xx} - 3u^2)}_{-u_{xxx} - 6uu_x}\, dx$$

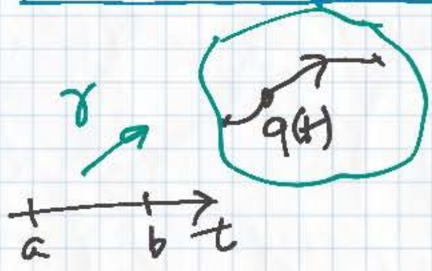
Fermat's Least Time Principle



Fermat: light chooses paths of least time

- Least of all paths
- Is there an extremist approach to classical mechanics?

Calculus of Variations



$$\gamma \mapsto \mathcal{F}(\gamma) = \int_a^b L\left(q(t), \frac{dq}{dt}(t)\right) dt$$

Lagrangian, $L(q, \dot{q})$ — q: position, $\dot{q}$: tangent vector

Critical points of $\mathcal{F}$:

$$\frac{d}{d\varepsilon}\Big|_{\varepsilon=0} \mathcal{F}(\gamma_\varepsilon) = 0 \quad \text{for all}$$

$$\gamma_\varepsilon : t \mapsto q(t) + \varepsilon\,\delta(t)$$

$$\frac{d}{d\varepsilon}\Big|_{\varepsilon=0} \int_a^b L\left(q + \varepsilon\delta, \frac{dq}{dt} + \varepsilon\frac{d\delta}{dt}\right) dt =$$

$$\int_a^b \left[\frac{\partial L}{\partial q}\left(q, \frac{dq}{dt}\right)\cdot\delta + \frac{\partial L}{\partial \dot{q}}\left(q, \frac{dq}{dt}\right)\cdot\frac{d\delta}{dt}\right] dt =$$

$$\frac{\partial L}{\partial \dot{q}}\left(q, \frac{dq}{dt}\right)\cdot\delta\Big|_a^b - \int_a^b \left[\frac{d}{dt}\frac{\partial L}{\partial \dot{q}}\left(q, \frac{dq}{dt}\right) - \frac{\partial L}{\partial q}\left(q, \frac{dq}{dt}\right)\right]\cdot\delta\, dt$$

$\gamma_0 : t \to q(t)$ - a critical point of $\mathcal{F}$

$$\overset{?}{\Longleftrightarrow} \quad \frac{d}{dt}\frac{\partial L}{\partial \dot{q}}\left(q, \frac{dq}{dt}\right) = \frac{\partial L}{\partial q}\left(q, \frac{dq}{dt}\right)$$

Euler-Lagrange eqn.

Example: $L = m\dfrac{\dot{q}\cdot\dot{q}}{2} - V(q) \Rightarrow m\ddot{q} = -\dfrac{\partial V}{\partial q}$

Newton's eqn.

Lagrangian vs. Hamiltonian mechanics

Lagrangian mechanics = Calculus of Variations

$\frac{d}{dt} L_{\dot q} = L_q \qquad \sum_j \frac{\partial^2 L}{\partial \dot q_i \partial \dot q_j} \ddot q_j + \sum_j \frac{\partial^2 L}{\partial \dot q_i \partial q_j} \dot q_j = \frac{\partial L}{\partial q_i}, \; i=1,\dots,n$

Non-degeneracy condition: $\det \left[\frac{\partial^2 L}{\partial \dot q_i \partial \dot q_j} \right] \neq 0$

Legendre transform (in $\dot q$)

$$H(p,q) := \text{crit}_{\dot q} \left[p \cdot \dot q - L(q, \dot q) \right]$$

$$p = \frac{\partial L}{\partial \dot q}(q, \dot q) \Rightarrow \dot q = \dot Q(p,q)$$

↑ generalized momenta ← new function

$\sum p_i \dot q_i = (dL)(\dot q) \qquad H(p,q) = p \cdot \dot Q(p,q) - L(q, \dot Q(p,q))$

Example: $L = m \frac{\dot q \cdot \dot q}{2} - V(q) \qquad p = m \dot q, \; \dot Q = \frac{p}{m}$

$$H = p \cdot \frac{p}{m} - \frac{m}{2} \frac{p}{m} \cdot \frac{p}{m} + V(q) = \frac{p \cdot p}{2m} + V(q)$$

Hamilton equns:

$$\frac{\partial H}{\partial p} = \dot q + (p - L_{\dot q}) \cdot \frac{\partial \dot Q}{\partial p} = \dot q$$

$$\frac{\partial H}{\partial q} = (p - L_{\dot q}) \cdot \frac{\partial \dot Q}{\partial q} - \frac{\partial L}{\partial q} \overset{\text{E.-L.}}{=} -\frac{d}{dt} L_{\dot q} = -\dot p$$

(with $L_{\dot q} = p$)

Inverse Legendre Transform

$$H(p) = \max_{\dot q} \, p \cdot \dot q - L(\dot q), \qquad L(\dot q) = \max_p \, p \cdot \dot q - H(p)$$

convex up ↑ convex up ↑

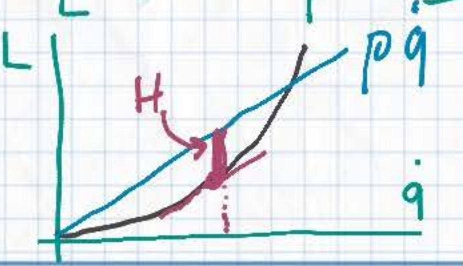
$$H(p) + L(\dot q) - p \cdot \dot q \geq 0 \quad \text{"Young inequality"}$$

$\min_{\dot q} \Rightarrow p = L_{\dot q} \Rightarrow \; = 0 \quad \Rightarrow \left[p = L_{\dot q} \Rightarrow \min_p \right]$

Example: $L = \frac{\dot q^\alpha}{\alpha}$

$\Rightarrow H = \frac{p^\beta}{\beta}, \quad \frac{1}{\alpha} + \frac{1}{\beta} = 1$

$p \dot q \leq \dot q^\alpha / \alpha + p^\beta / \beta$



Least Action Principle

$$\mathcal{F}(\gamma) := \int_a^b \left[p(t) \cdot \frac{d}{dt} q(t) - H(p(t), q(t)) \right] dt = \int p\,dq - H\,dt$$

Lagrangian interpretation: $\gamma : t \mapsto q(t)$

$p(t) = L_{\dot q}\left(q(t), \frac{d}{dt} q(t)\right)$, $p\,dq - H\,dt = L\left(q, \frac{dq}{dt}\right) dt$

Hamiltonian interpretation: $\gamma : t \mapsto p(t), q(t)$

$$\mathcal{L} = p \cdot \dot q - H(p, q) \qquad \dot q = H_p, \quad \dot p = -H_q$$

"Euler-Lagrange": $0 = \mathcal{L}_p$, $\frac{d}{dt} \mathcal{L}_{\dot q} = \mathcal{L}_q$

Hamiltonian trajectories are critical points of the action functional $\int p\,dq - H\,dt$

Feynman's Summation over Histories

$$\text{Quantum amplitudes} = \int e^{i \mathcal{F}(\gamma)/\hbar} \, d\gamma$$

(suitable space of paths) — all paths contribute!

- universal quantization proposal
- classical limit as $\hbar \to 0$ (oscillating integrals are concentrated near critical pts = classical trajectories)
- path integrals are ill-defined.

Making sense of path integrals

$$\mathcal{F}(\gamma) = \mathcal{F}(\gamma_0) + \frac{1}{2} d^2_{\gamma_0} \mathcal{F} + \langle \text{higher order terms} \rangle$$

(γ_0: critical pt)

$$\int e^{i \mathcal{F}/\hbar} d\gamma \sim e^{i \mathcal{F}(\gamma_0)/\hbar} \int e^{\frac{i}{2} d^2_{\gamma_0} \mathcal{F}/\hbar} e^{\langle \downarrow \rangle} d\gamma$$

asymptotical expansion; "Gaussian integral"

Wick's Theorem ⇒ power series in $\hbar$

Asymptotics of oscillating integrals

$$\psi = \int e^{i\left[\mathcal{F}(x) + \frac{1}{2}\langle x|A|x\rangle + \sum t_a \frac{x^a}{a!}\right]/\hbar} \, dx$$

parameters! (t_a)

$$\frac{x^a}{a!} := \frac{x_1^{a_1}}{a_1!}\frac{x_2^{a_2}}{a_2!}\cdots \quad A = [a_{ij}],\ a_{ij} = a_{ji} \quad dx = dx_1 dx_2 \ldots$$

$$\psi \sim \hbar^{D/2} e^{i\mathcal{F}(x_{crit})/\hbar}(A + B\hbar + C\hbar^2 + \ldots),\ A \neq 0$$

$$\log\psi = \text{Const} + \frac{i}{\hbar}\mathcal{F}(x_{crit}) + \alpha + \beta\hbar + \gamma\hbar^2 + \ldots$$

$$\partial \log\psi/\partial t_a = \partial\psi/\partial t_a \,/\psi \rightsquigarrow \text{expectation values}$$

$$\int e^{\frac{i}{\hbar}\left[\frac{1}{2}\langle x|A|x\rangle + \sum t_a \frac{x^a}{a!}\right]} dx =$$

$$\sqrt{\det \frac{A}{2\pi i\hbar}}\left[e^{\frac{i\hbar}{2}\langle \frac{\partial}{\partial x}|A^{-1}|\frac{\partial}{\partial x}\rangle} e^{\frac{i}{\hbar}\sum t_a \frac{x^a}{a!}}\right]_{x=0}$$

$$\hat{f}(p) = \int_{\mathbb{R}^D} e^{-i(p\cdot x)/\hbar} f(x)\,dx, \quad f(x) = \frac{1}{(2\pi\hbar)^D}\int_{\mathbb{R}^D} e^{i(p\cdot x)/\hbar}\hat{f}(p)\,dp$$

$$\int e^{-i(p\cdot x)/\hbar} e^{-\frac{i}{2\hbar}\langle \frac{\hbar}{i}\frac{\partial}{\partial x}|B|\frac{\hbar}{i}\frac{\partial}{\partial x}\rangle} f(x)\,dx = e^{-\frac{i}{2\hbar}\langle p|B|p\rangle}\hat{f}(p)$$

$$f(0) = \frac{1}{(2\pi\hbar)^D}\int \hat{f}(p)\,dp \implies$$

$$\left[e^{\frac{i\hbar}{2}\langle \frac{\partial}{\partial x}|B|\frac{\partial}{\partial x}\rangle} f\right]_{x=0} = \frac{1}{(2\pi\hbar)^D}\iint e^{-\frac{i}{2\hbar}\langle p|B|p\rangle - i(p\cdot x)/\hbar} f(x)\,dx\,dp$$

$$\underset{p}{\text{crit}}\left(p\cdot x + \tfrac{1}{2}\langle p|B|p\rangle\right) = -\tfrac{1}{2}\langle x|B^{-1}|x\rangle$$

$x + Bp = 0$

$$= \frac{1}{(2\pi\hbar)^D}\underbrace{\int e^{-\frac{i}{2\hbar}\langle p|B|p\rangle} dp}_{(-2\pi i\hbar)^{D/2}/\sqrt{\det B}} \int e^{\frac{i}{2\hbar}\langle x|B^{-1}|x\rangle} f(x)\,dx$$

Take $B^{-1} = A$, $f(x) = e^{\frac{i}{\hbar}\sum_a t_a x^a/a!}$

Wick's Formula

$$\log\left[\sqrt{\det\frac{A}{2\pi i\hbar}}\int e^{\frac{i}{\hbar}\left[\frac{\langle x|A|x\rangle}{2}+\sum t_a x^a/a!\right]}dx\right]$$

$$\sim \sum_{\text{connected graphs }\Gamma}\frac{(i\hbar)^{|E(\Gamma)|}\left(\frac{i}{\hbar}\right)^{|V(\Gamma)|}}{|\mathrm{Sym}(\Gamma)|}\sum_{\text{decorations }\Delta\text{ of }\Gamma} W(\Gamma,\Delta)$$

$V(\Gamma)$ = vertices, $E(\Gamma)$ = edges

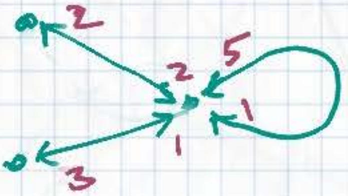
$\mathrm{Sym}(\Gamma)$ = group of symmetries of Γ

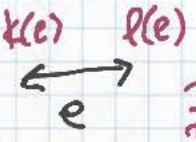
Γ

$\mathrm{Sym}(\Gamma) = \mathbb{Z}_2,\quad S_2\times S_3,\quad D_5\times\mathbb{Z}_2^5$

$|\mathrm{Sym}(\Gamma)| = 2,\quad 2\times 3!,\quad 5\times 2\times 2^5$

Δ decoration





$\frac{\partial}{\partial x_k}$ $\quad$ $\frac{\partial}{\partial x_l}$

$B = A^{-1}$

$$W(\Gamma,\Delta) := \prod_{e\in E(\Gamma)} b_{k(e)l(e)}\prod_{v\in V(\Gamma)} t_{a(v)}\quad \frac{x^a}{a!}$$

Feynman's weight

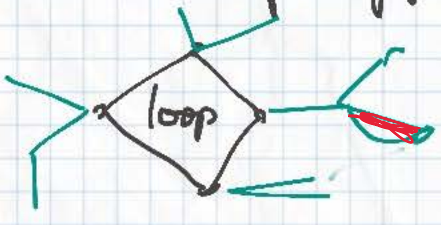
$$W = b_{22}\,b_{13}\,b_{15}\,t_{(010\ldots)}\,t_{(0010\ldots)}\,t_{(210010\ldots)}$$

(x_2, x_3, $\frac{x_1^2}{2}x_2x_5$)

Remarks

- $\hbar^{E(\Gamma)-V(\Gamma)} = \hbar^{-\chi(\Gamma)}$ Euler characteristic, $\chi(\text{connected graph})\le 1$
- $\frac{i}{\hbar}F(x_{crit}) = \sum_{\text{trees}}$ tree-level approximation

  $\frac{1}{2}\langle x|A|x\rangle + t_0 + \sum t_{(\ldots 010\ldots)_k}\, x_k^1$
- $\hbar^{\le 0}$ – "one-loop approximation"



Proof of Wick's Formula

- $e^{\log[\cdots]}$ = sum over all graphs (not necessarily connected)

$$\exp(X+Y+Z+\ldots) = \sum \frac{X^a}{a!}\frac{Y^b}{b!}\frac{Z^c}{c!}$$

"connected" objects — "disconnected"/symmetries

$\frac{XXXYYZ}{3!\,2!\,1!}$

- $$[\ldots] = \left[e^{\frac{i\hbar}{2}\langle \frac{\partial}{\partial x}|B|\frac{\partial}{\partial x}\rangle} e^{\frac{i}{\hbar}\sum t_a x^a/a!} \right]_{x=0}$$

sum over all graphs ?

$$\sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{i\hbar}{2}\sum_{kl} b_{kl}\frac{\partial^2}{\partial x_k \partial x_l}\right)^N$$

$k \leftrightarrow l$ decorated edge

decorated vertex; $a!$ - symm. of decoration

$$\begin{bmatrix}\text{All collections} \\ \text{of decorated} \\ \text{edges}\end{bmatrix} \begin{bmatrix}\text{All collections} \\ \text{of decorated} \\ \text{vertices}\end{bmatrix}\Bigg|_{x=0}$$

gluing together so that decorations match

- Resum by undecorated graphs Γ

$\frac{1}{|\mathrm{Sym}(\Gamma)|}$ guarantees that each gluing is counted exactly once.

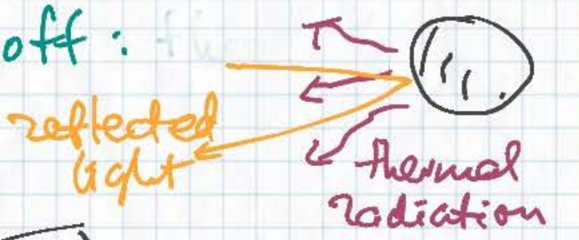
Quantum Field Theory

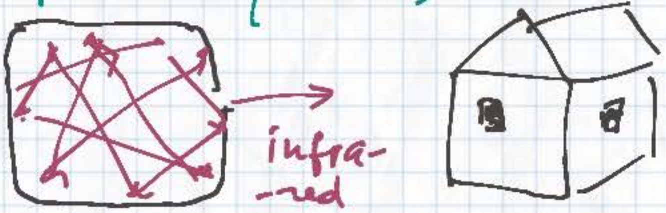
- "Free field": ideal gas of harmonic oscillators = Fourier modes of a classical field near "vacuum" state.
- Lagrangian action functional, $\frac{1}{2}\langle x|A|x\rangle$ in infinitely many variables.
- Interactions $\rightsquigarrow$ $t_a x^a$
- Wick's formula $\rightsquigarrow$ computation correlators, $\frac{\partial}{\partial t_a}\log\Psi$, via graph summation
- Individual graphs aquire physical meaning $\rightsquigarrow$ "Feynman diagrams"
+ long heroic effort $\rightsquigarrow$ Q.E.D.

Black-body radiation

1860 Gustav Kirchoff:

Thermal radiation depends only on ν, T.

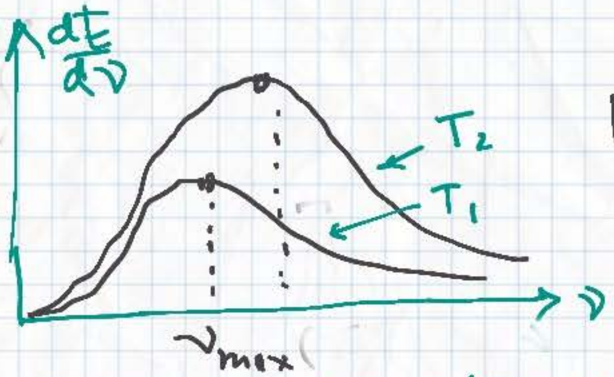




Rayleigh - Jeans law

$$dE = k_B T \times 2 \times d\, \tfrac{4}{3}\pi\left(\frac{L\nu}{c}\right)^3 = k_B T\, \frac{8\pi V}{c^3}\nu^2 d\nu \qquad (V = L^3)$$

$$e^{2\pi i\left(\frac{k\cdot q}{L} - \nu t\right)} \qquad k \in \mathbb{Z}^3, \quad \frac{k^2}{L^2} = \frac{\nu^2}{c^2}$$



1893 Wien's displacement law:

$$\nu_{max} \sim T$$

1900 Max Planck's hypothesis:

harmonic oscillator energies $\varepsilon_0, 2\varepsilon_0, \dots, n\varepsilon_0, \dots$

$$Z = \sum_{n=0}^{\infty} e^{-\beta n \varepsilon_0} = \frac{1}{1 - e^{\beta\varepsilon_0}} \qquad \text{Maxwell-Boltzmann}$$

$$\bar{\varepsilon} = -\frac{d}{d\beta}\log Z = \frac{\varepsilon_0}{e^{\varepsilon_0/k_B T} - 1} \to k_B T \quad (\varepsilon_0 \to 0)$$

$\varepsilon_0 = h\nu \,(= \hbar\omega)$ from Wien's law

$$dE = \frac{8\pi V}{c^3}\nu^2 \frac{h\nu}{e^{h\nu/k_B T} - 1} = (k_B T)^4 \frac{8\pi V}{h^3 c^3}\frac{x^3 dx}{e^x - 1} \qquad (h\nu/k_B T = x)$$

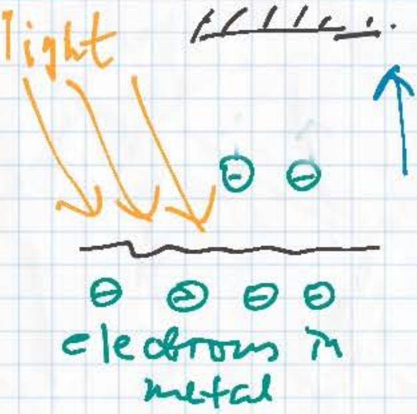
Total Energy $/V$

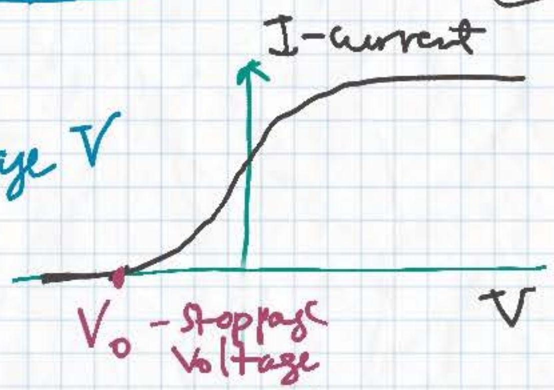
$$= \frac{8\pi^5 k_B^4}{15 c^3 h^3} T^4$$

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \zeta(4)\,3! = \frac{\pi^4}{15}\cdot 6$$

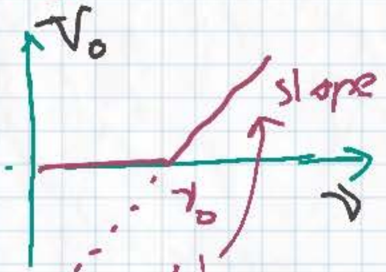
Stephan-Boltzmann Law

Photoelectric Effect





Einstein's Theory, 1905



$$K_{max} = h\nu - W$$

kinetic energy — photon's energy — "work function" $= h\nu_0$

$\Rightarrow V_0 = h(\nu - \nu_0)$

Millikan's experiments (1914)

$\Rightarrow$ Einstein's Nobel Prize (1921)

Compton's Scattering (1923)

$$E^2 = m^2c^4 + c^2|p_e|^2 \qquad |p_e|^2 = \left(\frac{E-mc^2}{c}\right)\left(\frac{E+mc^2}{c}\right)$$

↑ energy of scattered electron

Energy conservation: $E - mc^2 = c(|p| - |\tilde{p}|)$

Cosine theorem: $|p_e|^2 = |p|^2 + |\tilde{p}|^2 - 2|p||\tilde{p}|\cos\theta$

$$= (|p| - |\tilde{p}|)(|p| - |\tilde{p}| + 2mc)$$

$$\Rightarrow -2|p||\tilde{p}|\cos\theta = -2|p||\tilde{p}| + 2mc(|p| - |\tilde{p}|)$$

$$\Rightarrow 1 - \cos\theta = \frac{mc}{|\tilde{p}|} - \frac{mc}{|p|} = \frac{mc}{2\pi\hbar}(\tilde{\lambda} - \lambda)$$

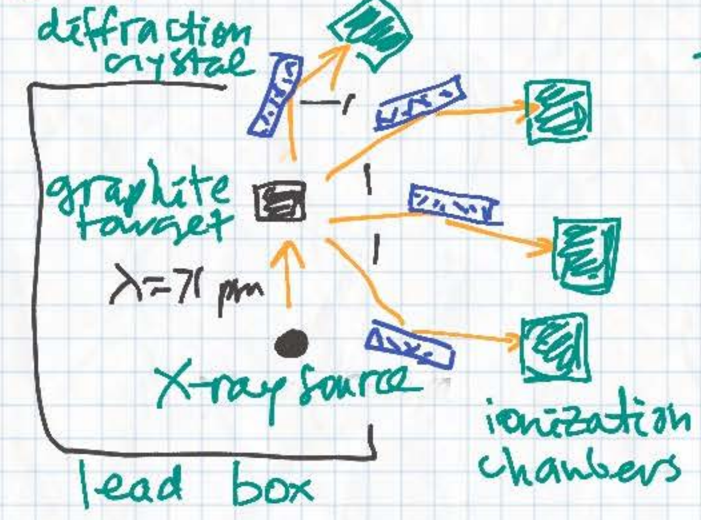
$$= \frac{\tilde{\lambda} - \lambda}{\lambda_0}$$

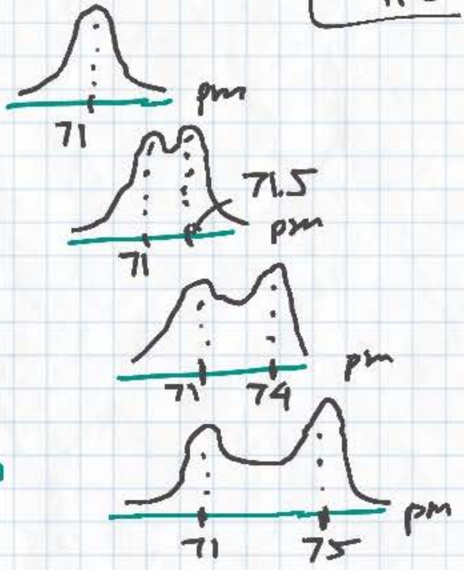
λ_0 — Compton's wavelength of mass m

$\hbar\omega = 2\pi\hbar c/\lambda_0 := mc^2$

$$\Delta\lambda = \lambda_0(1 - \cos\theta) \qquad \lambda_0 = 0.0024\ \text{nm} = 2.4\ \text{pm}$$

Compton's experiment



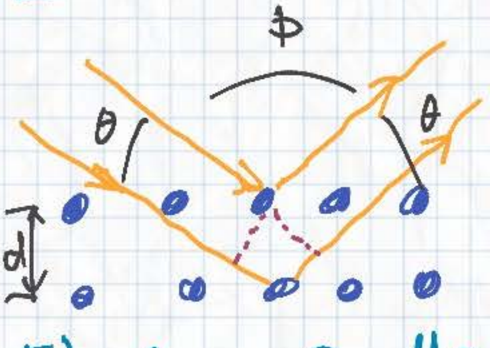


Thompson's classical scattering theory

radiation excites electrons and the re-emitted in all directions with the same wavelength
– explains the fixed maximum at 71 pm

the 2nd maximum is due to $\lambda|p| = 2\pi\hbar$

Bragg's condition (1912)



$2d \sin\theta = n\lambda$
additive (constructive) interference

Electron scattering

de Broglie (1924): $p\lambda = 2\pi\hbar$ not only for photons

$\lambda := 2\pi\hbar / p = 2\pi\hbar / \sqrt{2mE}$ – de Broglie wavelength

1921–1925 Davisson & Germer

Scattered electrons (accelerated to 54 eV) on a nickel plate (mono-crystal by accident) and observed a diffraction pattern.

Bragg's condition, $n=1$, $d = 91$ pm (X-ray scattering)
$\phi = 50°$, $\theta = 65°$ $\Rightarrow$ $\lambda \approx 165$ pm
de Broglie $\lambda \approx 167$ pm (at $E = 54$ eV) $\Big\} \Rightarrow$ 1929 N.P. for de Broglie

Emergence of the hydrogen model

Rutherford (1909)

gold foil experiment

⇒ nuclei (+), cloud of electrons (−)

Bohr (1913)

$|L| = n\hbar$, $n = 1, 2, \dots$

$$E_n = -\frac{m e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} \qquad \frac{1}{\lambda} = \frac{E_n - E_m}{2\pi\hbar c} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

Sommerfeld

: Action $= n\hbar$, $l = 0, 1, \dots, n-1$

⇒ spectral line splitting in a weak magnetic field

Classical particle in a magnetic field

$$m\ddot{q} = Q(\dot{q} \times B) - \nabla V(q) \qquad \text{Newton}$$

$$L(q,\dot{q}) = m\frac{\dot{q}\cdot\dot{q}}{2} + Q(A\cdot\dot{q}) - V \qquad \text{Lagrange}$$

$A = (B \times q)/2$ - vector potential $\quad B = \nabla \times A \ (\nabla\cdot B = 0)$

Exc. $(A\cdot\dot{q})_q - \frac{d}{dt}A = \dot{q} \times (\nabla \times A)$

$$p = m\dot{q} + QA \Rightarrow \dot{q} = (p - QA)/m$$

$$H(p,q) = \frac{p\cdot(p-QA)}{m} - Q\frac{A\cdot(p-QA)}{m} - \frac{m}{2}\frac{(p-QA)}{m}\cdot\frac{(p-QA)}{m} + V$$

$$= \frac{(p-QA)\cdot(p-QA)}{2m} + V(q)$$

$$\approx \frac{p\cdot p}{2m} - \frac{Q}{2m} B\cdot L + V$$

↑ small constant B

$$B\cdot(q\times p) = p\cdot(B\times q) \quad (B\times q) \to 2A$$

Quantization:

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + V(q) - \frac{Q}{2m} B\cdot\hat{L}$$

Normal Zeeman Effect

$$\hat{H}_{Zeeman} = \hat{H}_{Kepler} + \frac{e|B|}{2m_e}\hat{L}_z \qquad Q = -e$$

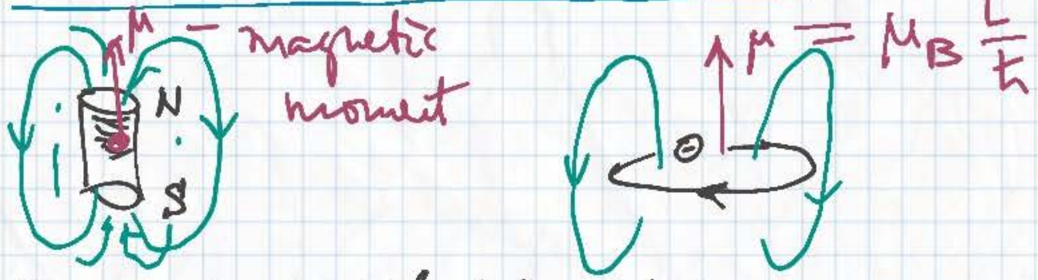
$E_n : \bigoplus_{l=0}^{n-1} V_l \qquad V_l :$

$E_n + \mu_B |B| k \,, \quad k = 0, \pm 1, \dots, \pm l$

Bohr magneton, $\frac{e\hbar}{2m_e} \approx 5.8 \times 10^{-5} \frac{eV}{Tesla}$

$E_1 \approx -13.6\, eV$, 1 Tesla = 1000 × (fridge magnet)

Semi-classical explanation



$B \cdot \mu$ = energy of interaction between exterior magnetic field and dipole μ.

⇒ Splitting of spectral lines, proportional to $|B|$.
(predicted by Lorentz & observed by Zeeman, 1896)

Anomalous Zeeman Effect (Preston, 1897)

Splitting into even # of lines ($\dim V_l = 2l+1$)

Spin $\quad V_l \otimes V_{1/2} = V_{l+\frac{1}{2}} \oplus V_{l-\frac{1}{2}}$

$$\hat{H}_z = \hat{H}_K + B \cdot \frac{\mu_B}{\hbar}\left(\hat{L}\otimes 1 + 2 \otimes \hat{S}\right)$$

orbital magnetic moment; spin magnetic moment; relativistic effect

Goudsmit – Uhlenbeck discovery of Spin was preceeded by Goudsmit's numerological invention of 1/2-integer quantum numbers.

Splits spectral lines into "doublets".

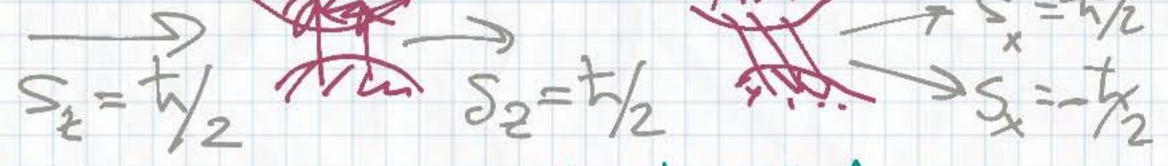
Stern – Gerlach's Experiment (1922)

beam of silver atoms → N / S strongly inhomogeneous magnetic field → (screen)

$Ag\ \underbrace{1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4d^{10} 4p^6 4d^{10}}_{Kr} 5s^1$

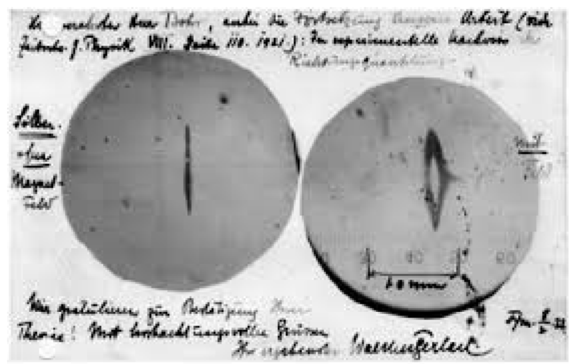
- Spin-unpaired state has $\ell = 0$ $(k=0)$
  Stern & Gerlach thought $\ell = 1$ $(k = 0, \pm 1)$
- Atom is neutral ⇒ no deflection in homogeneous magnetic field.
- In inhomogeneous magnetic field
  μ ↑ ⊙ = N/S magnet: interact differently with exterior magnetic field
- magneton $= \frac{e\hbar}{2m_{proton}} \ll \mu_B$ nucleus can be neglected
- Classical expectations → screen
  random orientation of μ relative to ∇B
- Stern – Gerlach's expectation → screen
  3 deflected beams corresponding to $k = -1, 0, 1$.
- Observed results – two deflected beams corresponding to $S_z = \pm \hbar/2$

Iterated Stern-Gerlach Experiments



$[S_z, S_x] \neq 0$ In the 2nd run the value $S_z = \hbar/2$ is forgotten

measurement causes "collapse of wave function"



Hochverehrter Herr Bohr, anbei die Fortsetzung unserer Arbeit (vergl. Zeitschr. f. Physik VIII. Seite 110. 1921): den experimentellen Nachweis der Richtungsquantelung.
Silber. ohne Magnet-Feld
mit Feld
10 mm
Wir gratulieren zur Bestätigung Ihrer Theorie! Mit hochachtungsvollen Grüssen
Ihr ergebener Walther Gerlach
Ffm. 8/2 22