Quantum Mechanics
and
Quantum Chemistry

Part 2: Classical and quantum mechanics

by Alexey V. Akimov

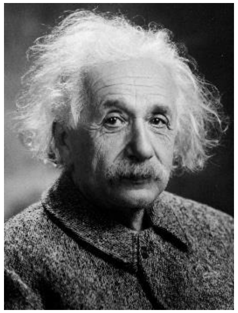
Domains of dynamics

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

but

$$H = \left(c\alpha \cdot p + \beta mc^2\right) + V$$

$$F = ma$$

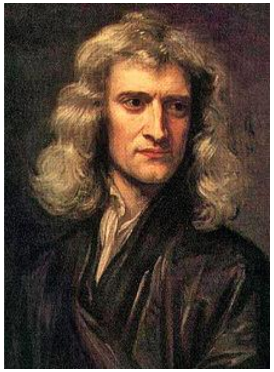


but

$$m = \frac{m_0}{\sqrt{1 - v^2 / c^2}}$$

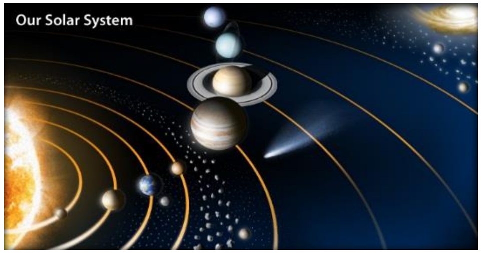
$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi$$

$$F = ma$$



Basic terminology: of classical mechanics

Material point = neglect size



Coordinate system ⇨ $f\left(\vec{r},\dot{\vec{r}},\ddot{\vec{r}}\right)=0$ Equations of motion (EOM)

Trajectory $\vec{r}(t)=\begin{pmatrix} x(t) \\ y(t) \\ z(t) \end{pmatrix}$ …for all particles

Newton's (vector) Mechanics

1. $\vec{F} = 0 \Rightarrow \vec{v} = const$ Existence of **inertial system of coordinates**

mass: inertia measure

2. $\vec{F} = m\vec{a}$ This is NOT how to compute force

force: measure of action of one object on another

3. $\vec{F}_{ij} = -\vec{F}_{ji}$ Action - reaction

Forces: They just exist

Keeps the nucleus together

Neutron to proton (beta-decay)

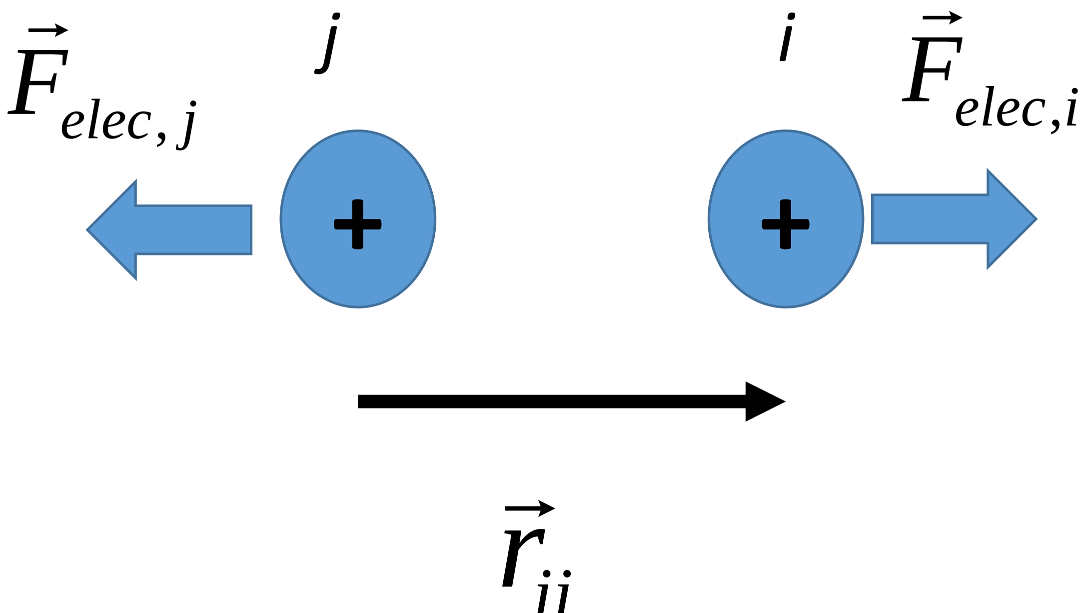
		Range	Strength
Strong interactions:	Quarks	$<10^{-15}$	100
Weak interaction:	Quarks, Leptons		0.001
Electromagnetic:	Charged particles	∞	1
Gravitational:	Mass particles		10^{-40}

$$\vec{F}_{elec} = -C\frac{q_i q_j}{r_{ij}^2}\frac{\vec{r}_{ij}}{r_{ij}} \qquad \vec{F}_{grav} = C\frac{m_i m_j}{r_{ij}^2}\frac{\vec{r}_{ij}}{r_{ij}}$$

Closer look

$$\vec{F}_{elec,i} = C\frac{q_i q_j}{r_{ij}^2}\frac{\vec{r}_{ij}}{r_{ij}}$$

In atomic units: C = 1



Conservation laws and Integrals (invariants) of motion

1. $$\vec{P} = \sum_i \vec{p}_i$$

Total momentum (if no total forces) prove

2. $$\vec{L} = \sum_i \vec{l}_i = \sum_i \vec{r}_i \times \vec{p}_i$$

Total angular momentum (if no total torques) prove

$$\dot{\vec{L}} = \sum_i \dot{\vec{r}}_i \times \vec{p}_i + \sum_i \vec{r}_i \times \dot{\vec{p}}_i = \sum_i \frac{1}{m_i} \vec{p}_i \times \vec{p}_i + \sum_i \vec{r}_i \times \vec{F}_i$$

$$\sum_i \vec{r}_i \times \vec{F}_i = \sum_i \vec{r}_i \times \left(\vec{F}_i^{ext} + \vec{F}_i^{\text{int}}\right) = T_{ext} + \sum_i \vec{r}_i \times \vec{F}_i^{\text{int}}$$

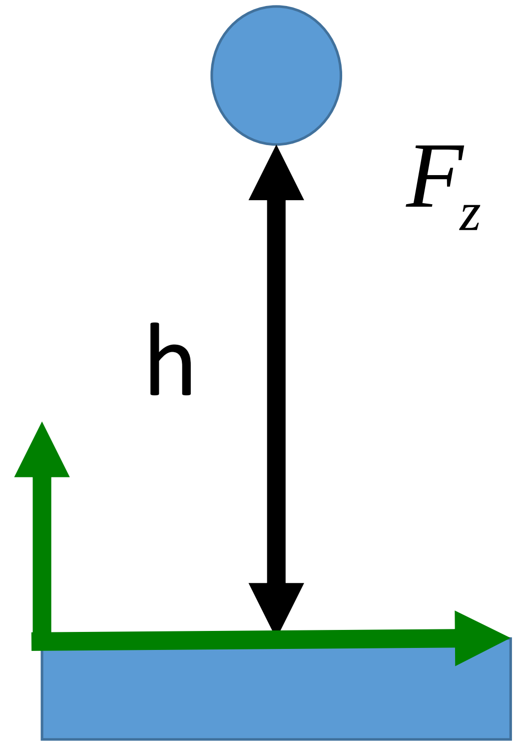
$$\sum_i \vec{r}_i \times \vec{F}_i^{\text{int}} = \sum_i \vec{r}_i \times \sum_j \vec{F}_{ij} = \sum_{\substack{i,j \\ i<j}} \left(\vec{r}_i - \vec{r}_j\right) \times \vec{F}_{ij} = 0$$

Work and internal energy

$$A = -\int_0^r \vec{F} \cdot d\vec{r}$$

Sign: the matter of convention

Example:



$$F_z = -mg$$

$$A = -\int_0^h \vec{F} \cdot d\vec{r} = -\int_0^h F_z \cdot dz = -F_z h = mgh$$

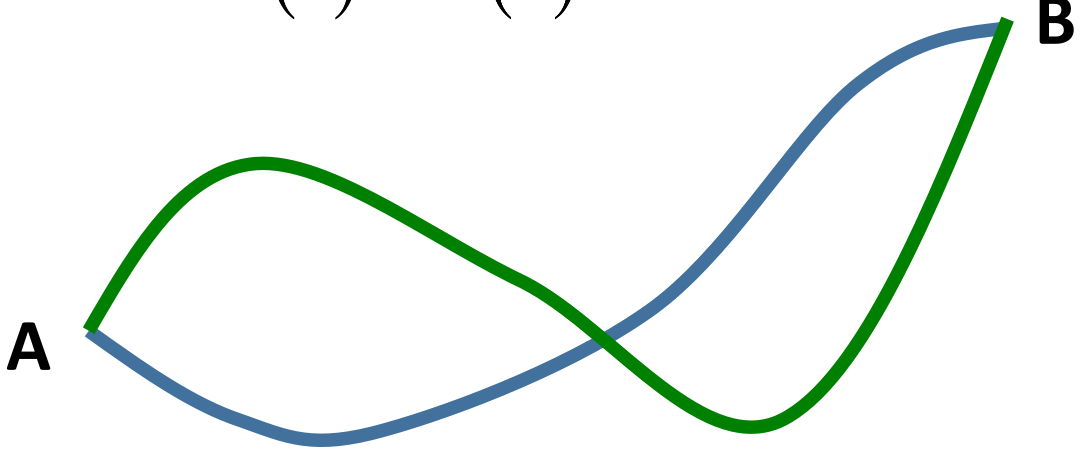
Potential forces

If: $$U : dU = -\vec{F} \cdot d\vec{r}$$

potential

potential forces

$$A = -\int_0^r \vec{F} \cdot d\vec{r} = \int_0^r dU = U(r) - U(0)$$



U - function of state

Forces

$$\boxed{\vec{F} = -\frac{\partial U}{\partial \vec{r}}} \Leftrightarrow \begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix} = \begin{pmatrix} -\dfrac{\partial U}{\partial x} \\ -\dfrac{\partial U}{\partial y} \\ -\dfrac{\partial U}{\partial z} \end{pmatrix}$$

Where to get U? Quantum Mechanics

Analysis of the dynamics

Derivative = negative
Force = positive
Result = acceleration in positive x

Derivative = positive
Force = negative
Result = deceleration in positive x

Lagrangian (analytic) mechanics

$$m\vec{a} = m\ddot{\vec{r}} = \frac{d}{dt}m\dot{\vec{r}} = \frac{d}{dt}\frac{\partial}{\partial\dot{\vec{r}}}\left(\frac{1}{2}m\dot{\vec{r}}^{2}\right) = \frac{d}{dt}\frac{\partial T}{\partial\dot{\vec{r}}} = \vec{F} = -\frac{\partial U}{\partial\vec{r}}$$

$$T \equiv \frac{1}{2}m\dot{\vec{r}}^{2}$$

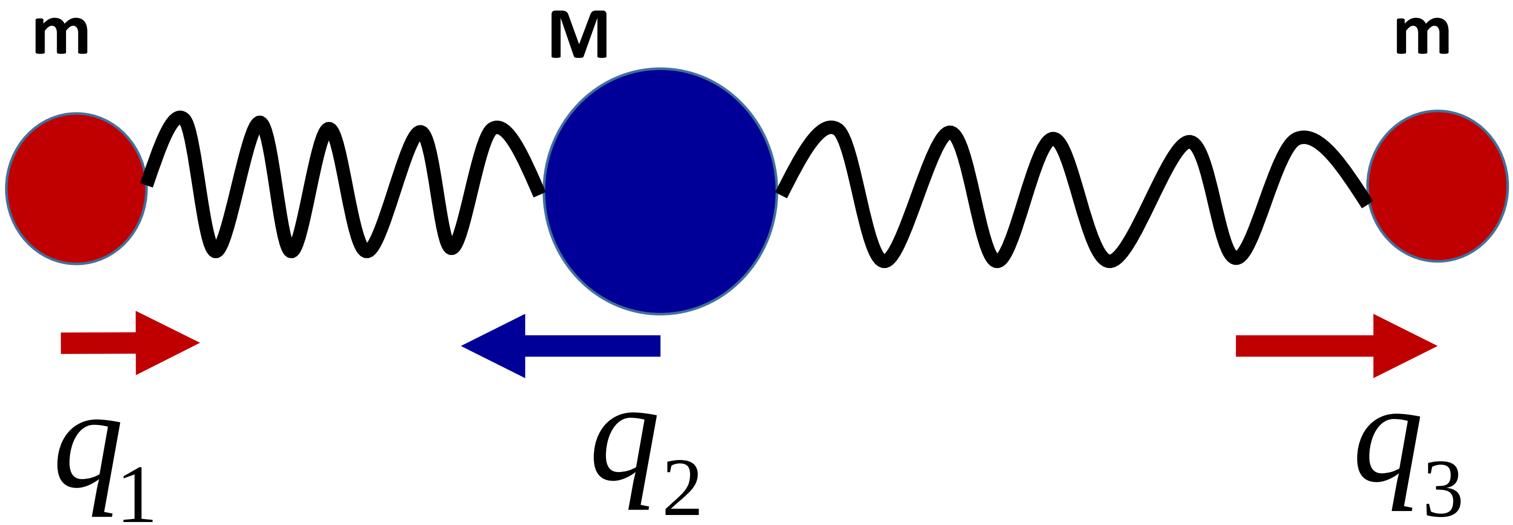
Note that: $U = U(r) \Rightarrow \frac{\partial U}{\partial\dot{\vec{r}}} = 0$ $\quad T = T(\dot{\vec{r}}) \Rightarrow \frac{\partial T}{\partial\vec{r}} = 0$

Define: $L(\vec{r},\dot{\vec{r}}) \equiv T - U$ Lagrange function

$$\frac{d}{dt}\frac{\partial L}{\partial\dot{\vec{r}}} = \frac{\partial L}{\partial\vec{r}} \Rightarrow$$

$$\boxed{\frac{d}{dt}\frac{\partial L}{\partial\dot{\vec{r}}} - \frac{\partial L}{\partial\vec{r}} = 0}$$

Example: Normal modes



$$T = \frac{1}{2} m\left(\dot{q}_1^2 + \dot{q}_3^2\right) + \frac{1}{2} M\dot{q}_2^2$$

$$V = \frac{1}{2} k\left(q_1 - q_2\right)^2 + \frac{1}{2} k\left(q_3 - q_2\right)^2$$

$$
\begin{aligned}
m\ddot{q}_1 &= k\left(q_2 - q_1\right) \\
M\ddot{q}_2 &= k\left(q_1 - q_2\right) + k\left(q_3 - q_2\right) \\
m\ddot{q}_3 &= k\left(q_2 - q_3\right)
\end{aligned}
$$

Search in the form: $$q_i = A_i e^{i\omega t + \delta_i}$$

$$
\begin{aligned}
-m\omega^2 q_1 &= k\left(q_2 - q_1\right) \\
-M\omega^2 q_2 &= k\left(q_1 - q_2\right) + k\left(q_3 - q_2\right) \\
-m\omega^2 q_3 &= k\left(q_2 - q_3\right)
\end{aligned}
\quad \Rightarrow \quad
\begin{aligned}
\left(-m\omega^2 + k\right)q_1 - kq_2 &= 0 \\
-kq_1 + \left(-M\omega^2 + 2k\right)q_2 - kq_3 &= 0 \\
-kq_2 + \left(-m\omega^2 + k\right)q_3 &= 0
\end{aligned}
$$

$$\begin{aligned}
&\left(-m\omega^2+k\right)q_1-kq_2=0\\
&-kq_1+\left(-M\omega^2+2k\right)q_2-kq_3=0\\
&-kq_2+\left(-m\omega^2+k\right)q_3=0
\end{aligned}
\quad\Longrightarrow\quad
\begin{aligned}
&\left(m\omega^2-k\right)q_1+kq_2=0\\
&kq_1+\left(M\omega^2-2k\right)q_2+kq_3=0\\
&kq_2+\left(m\omega^2-k\right)q_3=0
\end{aligned}$$

$$\begin{pmatrix} m\omega^2-k & k & 0 \\ k & M\omega^2-2k & k \\ 0 & k & m\omega^2-k \end{pmatrix}\begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

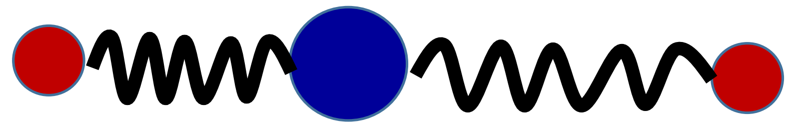
$$\det\begin{pmatrix} m\omega^2-k & k & 0 \\ k & M\omega^2-2k & k \\ 0 & k & m\omega^2-k \end{pmatrix}=$$

$$=\left(m\omega^2-k\right)\left[\left(M\omega^2-2k\right)\left(m\omega^2-k\right)-k^2\right]-k\left[k\left(m\omega^2-k\right)\right]=$$

$$=\left(m\omega^2-k\right)\left[\left(M\omega^2-2k\right)\left(m\omega^2-k\right)-2k^2\right]=0$$

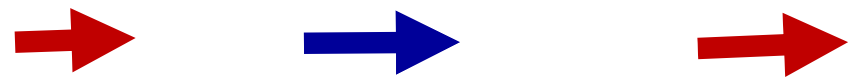
$$\left(M\omega^2 - 2k\right)\left(m\omega^2 - k\right) - 2k^2 = Mm\omega^4 - 2km\omega^2 - kM\omega^2 =$$
$$= \omega^2\left[Mm\omega^2 - k\left(2m + M\right)\right]$$

Normal modes



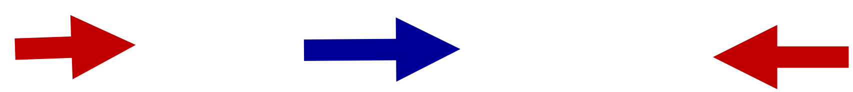
$$\omega_1 = 0$$

(translation)



$$\left(m\omega^2 - k\right) = 0 \Rightarrow \omega_2 = \sqrt{\frac{k}{m}}$$

$$Mm\omega^2 - k\left(2m + M\right) = 0 \Rightarrow$$
$$\omega_3 = \sqrt{\frac{k\left(2m + M\right)}{Mm}}$$



Importance

All is derived from a scalar function

Can be formulated in any variables

Can incorporate constraints

Can generalize forces

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11
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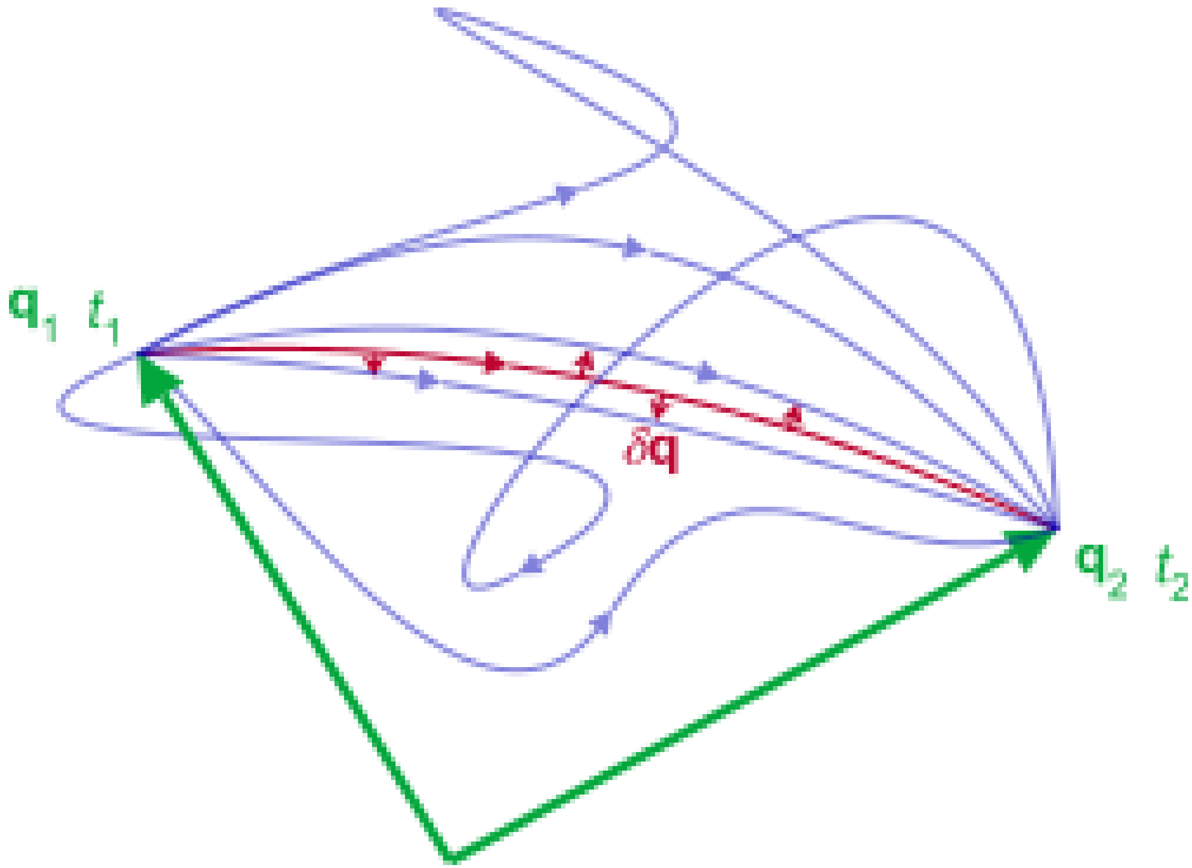
Hamilton's principle
Least action principle

$$S = \int_{t_0}^{t_1} L\left(\vec{r}, \dot{\vec{r}}\right) dt$$

action



$$\delta S = \int_{t_0}^{t_1} \delta L(\vec{r}, \dot{\vec{r}}) dt = \int_{t_0}^{t_1} \left[\frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \vec{r}} \delta \vec{r} + \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} \delta \dot{\vec{r}} \right] dt$$

$$\int_{t_0}^{t_1} \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} \delta \dot{\vec{r}} dt = \int_{t_0}^{t_1} \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} d\delta \vec{r} = \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} \delta \vec{r} \Big|_{t_0}^{t_1} - \int_{t_0}^{t_1} \delta \vec{r} \frac{d}{dt} \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} dt = -\int_{t_0}^{t_1} \delta \vec{r} \frac{d}{dt} \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} dt$$

Because: $\delta \vec{r}(t_0) = \delta \vec{r}(t_1) = 0$

$$\delta S = \int_{t_0}^{t_1} \delta \vec{r} \left[\frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \vec{r}} - \frac{d}{dt} \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} \right] dt = 0 \Rightarrow \boxed{\frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \vec{r}} - \frac{d}{dt} \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} = 0}$$

Hamiltonian mechanics

$$H(q,p) = \dot{q}p - L(q,\dot{q})$$

Legendre transform

Hamilton's function (Hamiltonian)

also note: generalized coordinates

$$H(q,p) = \sum_i \dot{q}_i p_i - L(q,\dot{q})$$

$$p = \frac{\partial L}{\partial \dot{q}}$$

Example

$$L(x, y, \dot{x}, \dot{y}) = \frac{m\dot{x}^2 + m\dot{y}^2}{2} - \frac{1}{2}kx^2 - \frac{1}{2}ky^2$$

$$p_x = \frac{\partial L}{\partial \dot{x}} = m\dot{x} \Rightarrow \dot{x} = \frac{p_x}{m}$$

$$p_y = \frac{\partial L}{\partial \dot{y}} = m\dot{y} \Rightarrow \dot{y} = \frac{p_y}{m}$$

$$H(q, p) = \dot{x}p_x + \dot{y}p_y - L(x, y, \dot{x}, \dot{y}) = \frac{p_x^2}{m} + \frac{p_y^2}{m} - \frac{m\left(\frac{p_x}{m}\right)^2 + m\left(\frac{p_y}{m}\right)^2}{2} + \frac{1}{2}kx^2 + \frac{1}{2}ky^2 =$$

$$= \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{1}{2}kx^2 + \frac{1}{2}ky^2$$

Hamiltonian

$$H(q,p)=\frac{p_x^2}{2m}+\frac{p_y^2}{2m}+\frac{1}{2}kx^2+\frac{1}{2}ky^2$$

$$H(q,p)=T+U=\sum_i \frac{\vec{p}_i^{\,2}}{2m_i}+U(\{q\})$$

$$\frac{\partial H}{\partial p_i}=\frac{p_i}{m_i}=v_i=\dot{q}_i$$

$$-\frac{\partial H}{\partial q_i}=-\frac{\partial U}{\partial q_i}=F_i=ma_i=\frac{d}{dt}(mv_i)=\frac{d}{dt}p_i=\dot{p}_i$$

Hamiltonian equations of motion (EOM)

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$

Momenta conjugate to coordinate

Hamiltonian equations of motion (EOM)

$$\begin{pmatrix} \dot{q}_i \\ \dot{p}_i \end{pmatrix} = \begin{pmatrix} \dfrac{\partial H}{\partial p_i} \\ -\dfrac{\partial H}{\partial q_i} \end{pmatrix} \qquad z_i = \begin{pmatrix} q_i \\ p_i \end{pmatrix}$$

then

$$\dot{z}_i = iL \cdot z_i$$

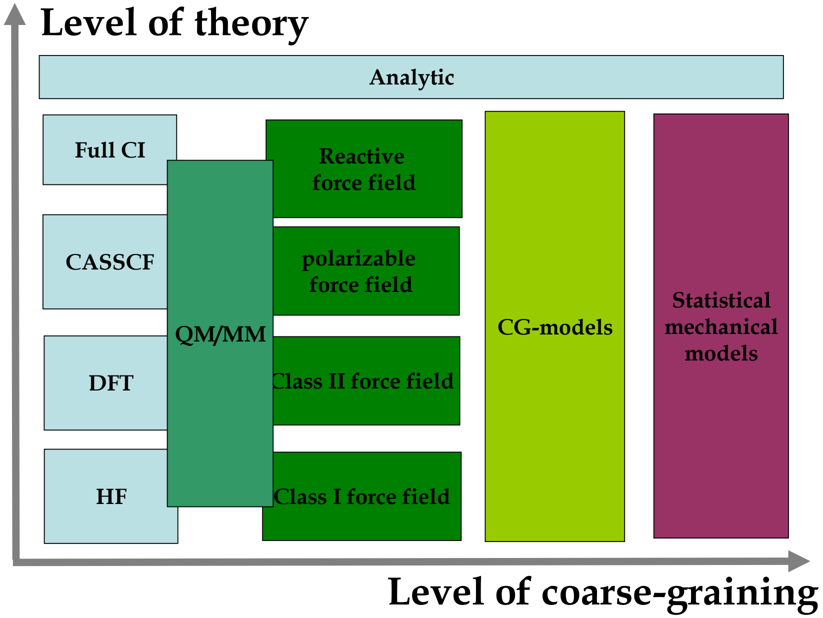
$$iL = \dot{q}_i \frac{\partial}{\partial q_i} + \dot{p}_i \frac{\partial}{\partial p_i} = \frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i}$$

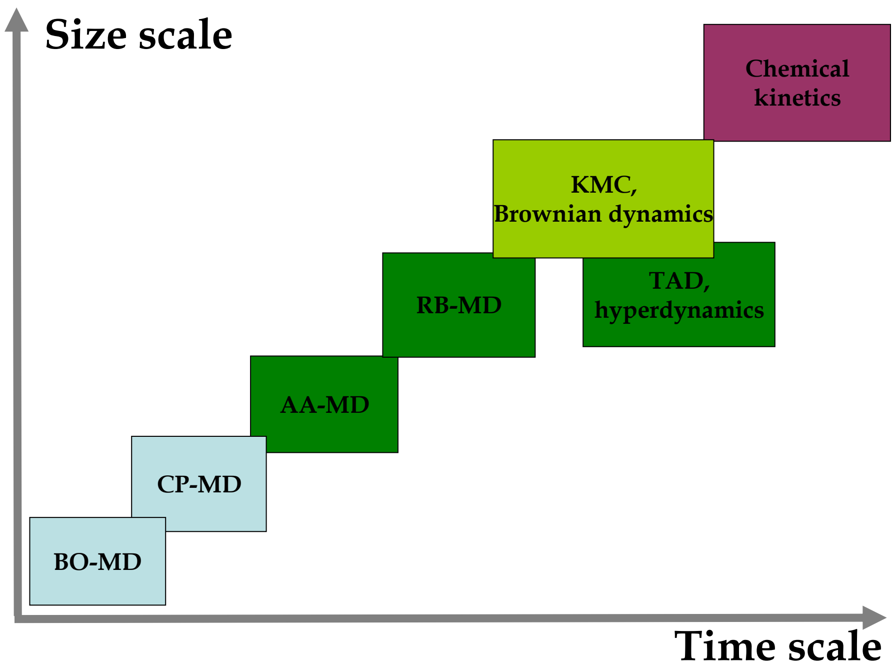
$$\dot{z}_i = \{H, z_i\}$$

$$iL \cdot q_i = \left(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i} \right) q_i = \frac{\partial H}{\partial p_i} = \dot{q}_i$$

$$iL \cdot p_i = \left(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i} \right) p_i = -\frac{\partial H}{\partial q_i} = \dot{p}_i$$

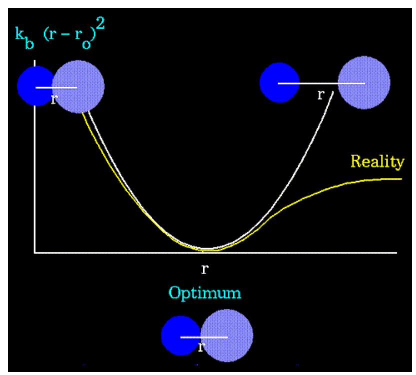
Classical **Poisson bracket**

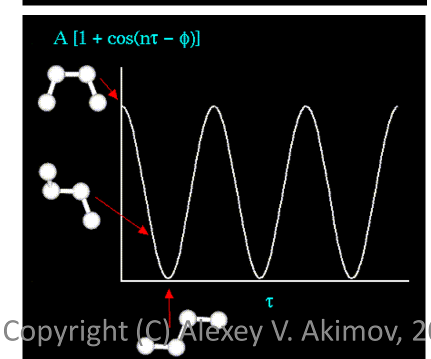

Level of theory
Analytic
Full CI
CASSCF
DFT
HF
QM/MM
Reactive
force field
polarizable
force field
Class II force field
Class I force field
CG-models
Statistical
mechanical
models
Level of coarse-graining


Size scale
Chemical
kinetics
KMC,
Brownian dynamics
TAD,
hyperdynamics
RB-MD
AA-MD
CP-MD
BO-MD
Time scale

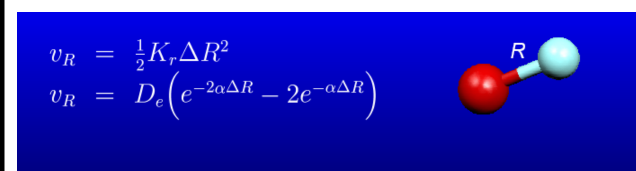
$$E_{tot} = E_{bonded} + E_{non-bonded}$$

$$E_{bonded} = E_{bonds} + E_{angles} + E_{dihedrals} + E_{oop}$$

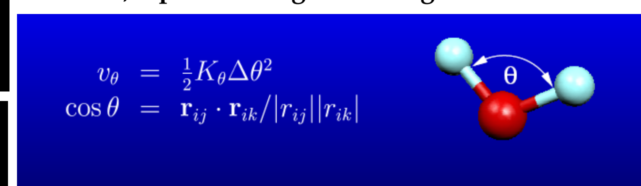




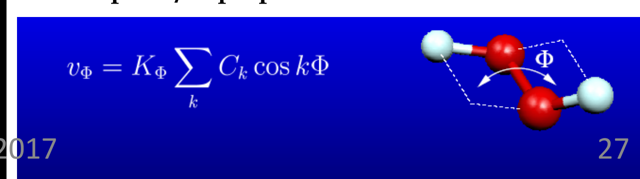
bonded, 2-particle: bond stretching



bonded, 3-particle: angle bending

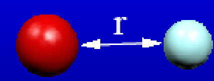


bonded, 4-particle: torsion/dihedral,
out-of-plane/improper dihedrals

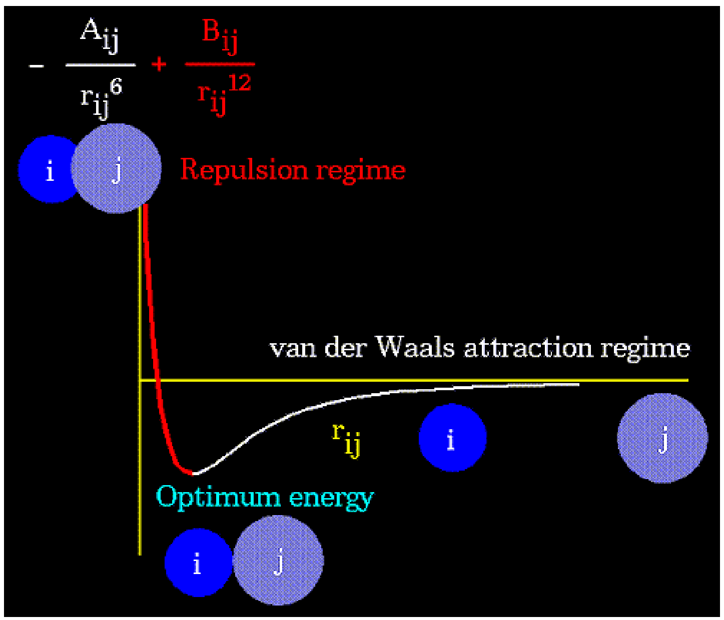


$$E_{non-bonded} = E_{vdW} + E_{el}$$

$$\begin{aligned} v_{disp}(r_i, r_j) &= -\frac{C_6}{|\mathbf{r}_i - \mathbf{r}_j|^6} \\ v_{el}(r_i, r_j) &= \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|} \end{aligned}$$



non-bonded
2-particle
vdw and Coulomb
interactions



Performing MD simulations: Intra-molecular potential

$$E_{phys,bonded} = \sum_{i \in bonds} k_i \left(r_i - r_{0,i}\right)^2 + \sum_{j \in angles} \frac{k_j}{4\sin^2\theta_{0,j}} \left[\left(2\cos^2\theta_{0,j} + 1\right) - 4\cos\theta_{0,j}\cos\theta_j + \cos 2\theta_j\right]$$

$$E_{phys,nonbonded} = \sum_{\substack{i>j,\\ i,j \in molecule}} D_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - 2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

All parameters are taken from the UFF force field

$$\boxed{E_{torsion} = \sum_{k \in torsions} \frac{1}{2} V_\phi \left[1 - \cos n\phi_{0,k} \cos n\phi\right]}$$

Used only in last Parameter sets

$$E_{phys,elec} = \sum_{\substack{i>j,\\ i,j \in molecule}} \frac{q_i q_j e^2}{r_{ij}}$$

Charges are calculated using charge equilibration method of Rappe et. al.

Performing MD simulations: Surface-molecule potential

Physisorption: All atoms, except S

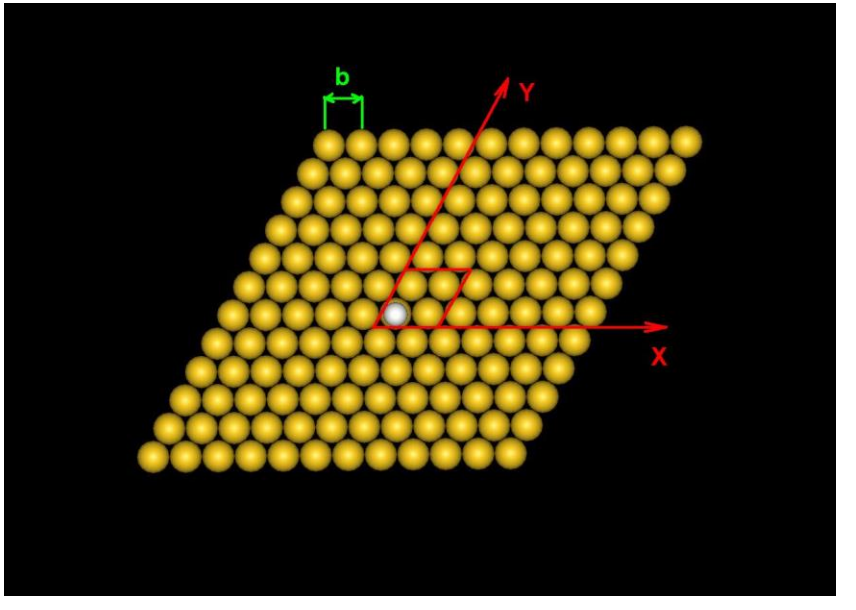
$$E_{phys,nonbonded} = \sum_{\substack{i,j \\ i \in molecule \\ j \in surface}} D_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] SW(r_{ij})$$

Chemisorption: S atom

$$E_{chem} = \sum_{\substack{i,j \\ i \in molecule \\ j \in surface}} D_{ij} \left[\left(e^{-\alpha \left(r_{ij} - r_{ij}^0 \right)} - 1 \right)^2 - 1 \right] SW(r_{ij})$$

Special care about discontinuities

$$SW(R, R_{on}, R_{off}) = \begin{cases} 1, R < R_{on} \\ \left(\frac{R_{off} - R}{R_{off} - R_{on}} \right)^3 \left[1 + 3 \left(\frac{R - R_{on}}{R_{off} - R_{on}} \right) + 6 \left(\frac{R - R_{on}}{R_{off} - R_{on}} \right)^2 \right], R_{on} \le R \le R_{off} \\ 0. R > R_{off} \end{cases}$$



b=2.878 Å

$$R_{on} = 2\sqrt{3}b$$

$$R_{off} = 5b$$

$$E(\vec{x}) = E(\vec{0}) + \sum_{i=1}^{N} \frac{\partial E}{\partial x_i} x_i + \frac{1}{2} \sum_{i,j=1}^{N} \frac{\partial^2 E}{\partial x_i \partial x_j} x_i x_j + \dots$$

Class I (diagonal), Class II (+ cross-terms)

$$E = \sum_{(i,j)} a_{ij} bo_{ij} + \sum_{\substack{(i_1,j_1),\\(i_2,j_2)}} a_{i_1 j_1} a_{i_2 j_2} bo_{i_1 j_1} bo_{i_2 j_2} + \dots + \sum_{\substack{(i_1,j_1),\\ \dots \\ (i_n,j_n)}} a_{i_1 j_1} \dots a_{i_n j_n} bo_{i_1 j_1} \dots bo_{i_n j_n}$$

$$bo_{ij} = Ae^{-\alpha r_{ij}}$$

$$E = \sum_{(i,j)} D_{ij} \left[bo_{ij}^2 - 2bo_{ij} \right] \quad a)$$

$$\sum_{(i,j)} bo_{ij} = 1 \quad b)$$

$$\frac{d\vec{q}}{dt} = J\,\frac{dH(\vec{q})}{d\vec{q}}$$

$$J = \begin{pmatrix} 0 & I_d \\ -I_d & 0 \end{pmatrix}$$

Canonical structure matrix

$$H = T + V(\{\vec{r}\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m_i} + V(\{\vec{r}\})$$

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}$$

$$\dot{\vec{p}}_i = -\frac{\partial V}{\partial \vec{r}_i} \equiv \vec{f}_i$$

$$\vec{r}_i(t+dt) = \vec{r}_i(t) + dt \cdot \frac{\vec{p}_i(t)}{m_i} + \frac{dt^2}{2!}\frac{\vec{f}_i(t)}{m_i} + O(dt^3) + O(dt^4)$$

$$\vec{r}_i(t-dt) = \vec{r}_i(t) - dt \cdot \frac{\vec{p}_i(t)}{m_i} + \frac{dt^2}{2!}\frac{\vec{f}_i(t)}{m_i} - O(dt^3) + O(dt^4)$$

$$\Rightarrow \vec{r}_i(t+dt) = 2 \cdot \vec{r}_i(t) - \vec{r}_i(t-dt) + dt^2 \frac{\vec{f}_i(t)}{m_i} + O(dt^4)$$

Verlet algorithm

$$\vec{p}_i \equiv \frac{\vec{r}_i(t+dt) - \vec{r}_i(t-dt)}{2 \cdot dt}$$

$$\forall i \quad \vec{p}_i(dt) = \vec{p}_i(0) + \frac{dt}{2}\left[\vec{f}_i(0) + \vec{f}_i(dt)\right]$$

Velocity Verlet

$$\forall i \quad \vec{r}_i(t) = \vec{r}_i(0) + dt\vec{p}_i(0) + \frac{dt^2}{2}\vec{f}_i(0)$$

Molecular Dynamics (MD)

Dynamical equations

$$\dot{\vec{r}}_i = \vec{p}_i / m_i \qquad \dot{\vec{p}}_i = \vec{F}_i$$

$$\dot{\vec{l}}_i^{(e)} = \vec{\tau}_i^{(e)} + \vec{l}_i^{(e)} \times I^{-1} \vec{l}_i^{(e)}$$

Algorithm:

Initialization:

$$t = t_0$$

$$\vec{V}(t_0) \Leftarrow Temperature$$

$$\vec{R}(t_0) \Leftarrow Geometry$$

Get forces:

$$\vec{F}(t) = -\frac{dU(\vec{R}(t))}{dR}$$

Move atoms and update velocity:

$$\vec{R}(t+dt) = \vec{R}(t) + \vec{V}(t)dt + \frac{1}{2m}\vec{F}(t)dt^2$$

$$\vec{V}(t+dt) = \vec{V}(t) + \frac{\vec{F}(t) + \vec{F}(t+dt)}{2m}dt$$

$$t = t + dt$$

Experimental foundations of QM

Energy levels (quantization)

- Atomic spectra
- Black body radiation

Wave-particle duality

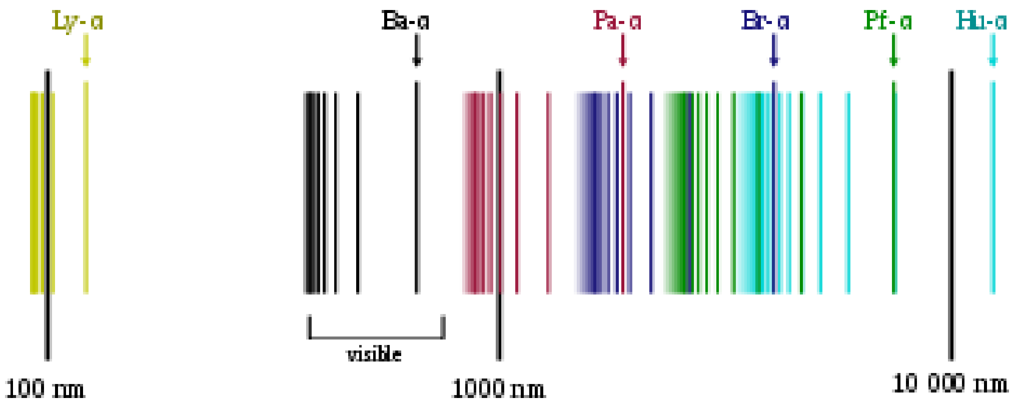
- Interference
- Photoeffect

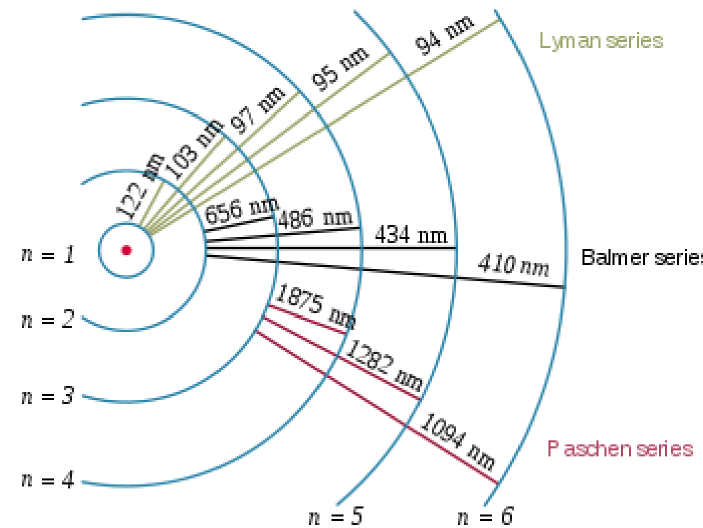
Spectral lines of H atom

1885, Balmer $$\lambda = B\frac{n^2}{n^2-4}, n = 3,4,5,\ldots$$

Rydberg $$\frac{1}{\lambda} = \frac{4}{B}\left(\frac{1}{4}-\frac{1}{n^2}\right) \Leftrightarrow \nu = R\left(\frac{1}{2^2}-\frac{1}{n^2}\right)$$

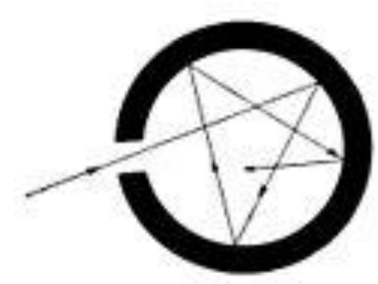
Lyman, Balmer, Paschen (Ritz), Bracket, Pfund, Hampfrey

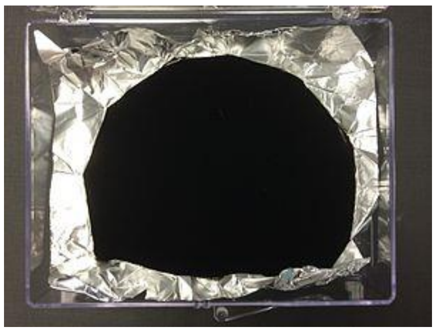




Black body (BB)

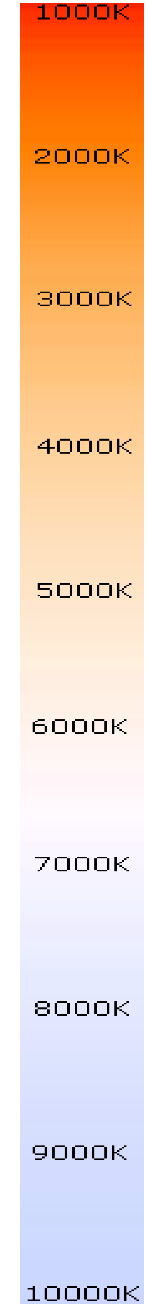
Absorbs everything (at all wavelengths)





Vantablack = vertically aligned nanotube arrays
Absorbs: 99.965% of the incident light

… but can radiate (so has a color). This is determined only by T



Energy density of BB radiation

$$u = \nu^3 f\left(\frac{\nu}{T}\right)$$

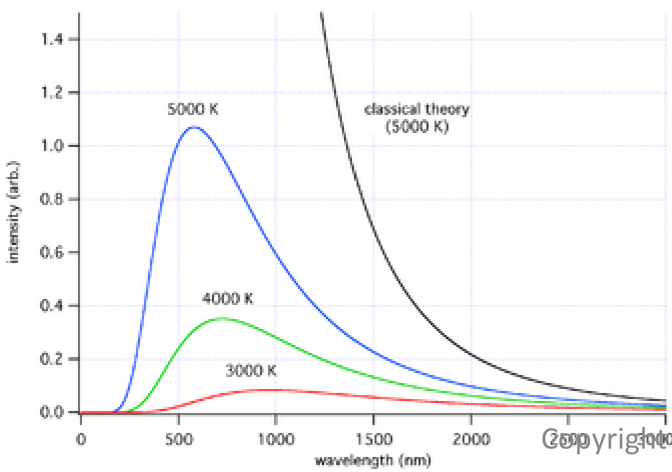
First Wien's law - general

$$u = C_1 \nu^3 \exp\left(-C_2 \frac{\nu}{T}\right)$$

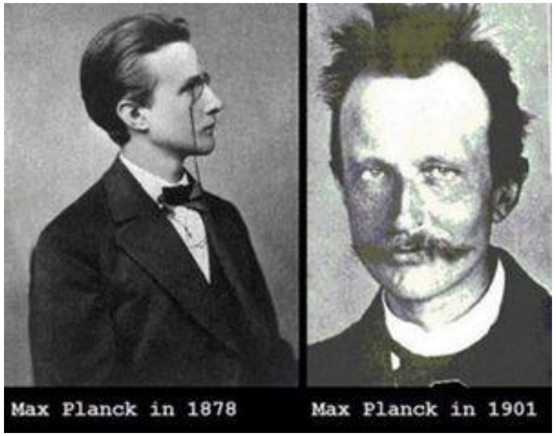
Second Wien's law (high frequency)

$$u = k_B T \frac{4\nu^2}{c^3}$$

Rayleigh-Jeans (low frequency)



Ultraviolet catastrophe



$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

Planck, 1900

$$Z = \sum_n \exp\left(-E_n / k_B T\right) = \sum_n \exp\left(-\hbar\omega / 2k_B T\right)\exp\left(-n\hbar\omega / k_B T\right)$$

$$1 + x + x^2 + \ldots = \frac{1}{1-x}$$

so:

$$Z = \frac{\exp\left(-\hbar\omega / 2k_B T\right)}{1 - \exp\left(-\hbar\omega / k_B T\right)}$$

Average energy of the (equilibrium!) EM radiation:

Probability: $P_n = \frac{1}{Z}\exp\left(-E_n / k_B T\right)$

$$\overline{E} = \sum_n E_n P_n = k_B T^2\left(\frac{\partial \ln Z}{\partial T}\right) = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp\left(-\frac{\hbar\omega}{k_B T}\right) - 1}$$

$$u(v, T) = \frac{\omega^2}{\pi^2 c^3}\frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} = \frac{4v^2}{c^3}\frac{hv}{\exp\left(\frac{hv}{k_B T}\right) - 1}$$

Predicted:
Boltzmann const. and Avogadro #

Bohr's (planetary) model

Problem: continuous radiation and atom instability

$$E_m - E_n = \hbar\omega$$

Postulated: Stationary states

$$l = n\hbar, n \in N$$

Postulated: Angular momentum is quantized

$$\vec{l} = \vec{r} \times \vec{p} \qquad l = mvr \qquad mvr = n\hbar$$

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \Rightarrow v = \sqrt{\frac{Ze^2}{mr}}$$

centripetal force

Coulombic force

$$mr_n\sqrt{\frac{Ze^2}{mr_n}} = \sqrt{Ze^2 mr_n} = n\hbar \Rightarrow r_n = \frac{\hbar^2}{Zme^2}n^2$$

"orbital" radius

$$E = \frac{mv^2}{2} - \frac{Ze^2}{r} = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r}$$

Total energy

$$E_n = -\frac{Ze^2}{2}\left(\frac{\hbar^2}{Zme^2}n^2\right)^{-1} = -\frac{Ze^2}{2\hbar^2}Zme^2\frac{1}{n^2} = -\frac{me^4}{2\hbar^2}\frac{1}{n^2} = -R\frac{Z^2}{n^2}$$

$$R = \frac{me^4}{2\hbar^2} = 0.5\,\mathrm{a.u.}\,(\mathrm{Ha}) \approx 13.6\,\mathrm{eV}$$

Rydberg constant

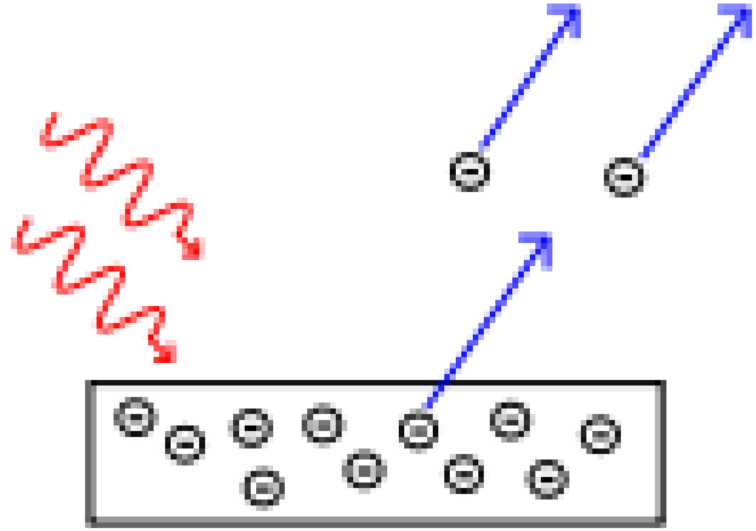
$$-\frac{1}{2}\frac{1}{1^2} = -0.5\,\mathrm{a.u.}\,(\mathrm{Ha}) = -\frac{1}{1^2}\,\mathrm{Ry}$$

Energy of H atom in the ground state

$$\oint p_r dq_r = nh$$

Bohr –Zommerfeld (action-angle)

Photoeffect



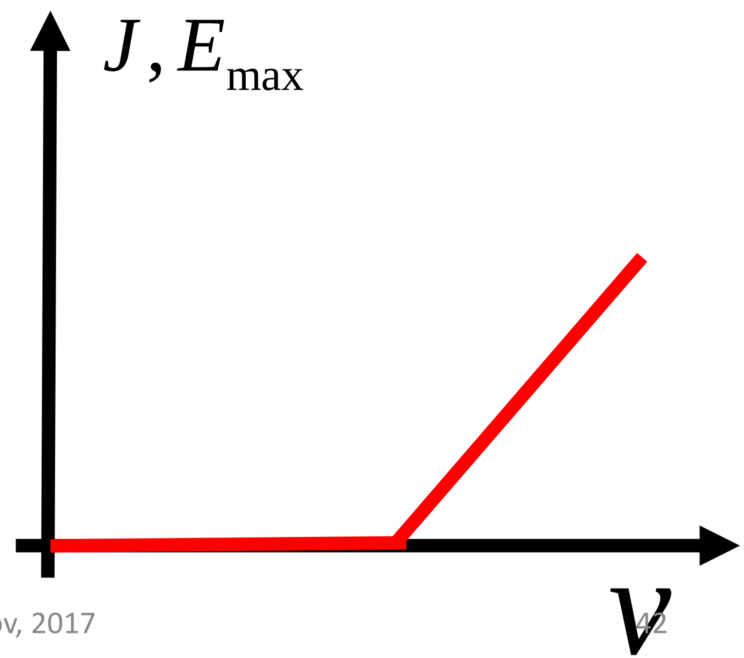
Stoletov laws

1-st law : $J \sim I$

2-nd law : $E_{\max} \sim \nu$

$$\frac{\partial E_{\max}}{\partial I} = 0$$

3-rd law : $\exists \nu_{crit} : \forall \nu < \nu_{crit} , J = 0$



Photoeffect

1905 **Einstein**

Nobel Prize

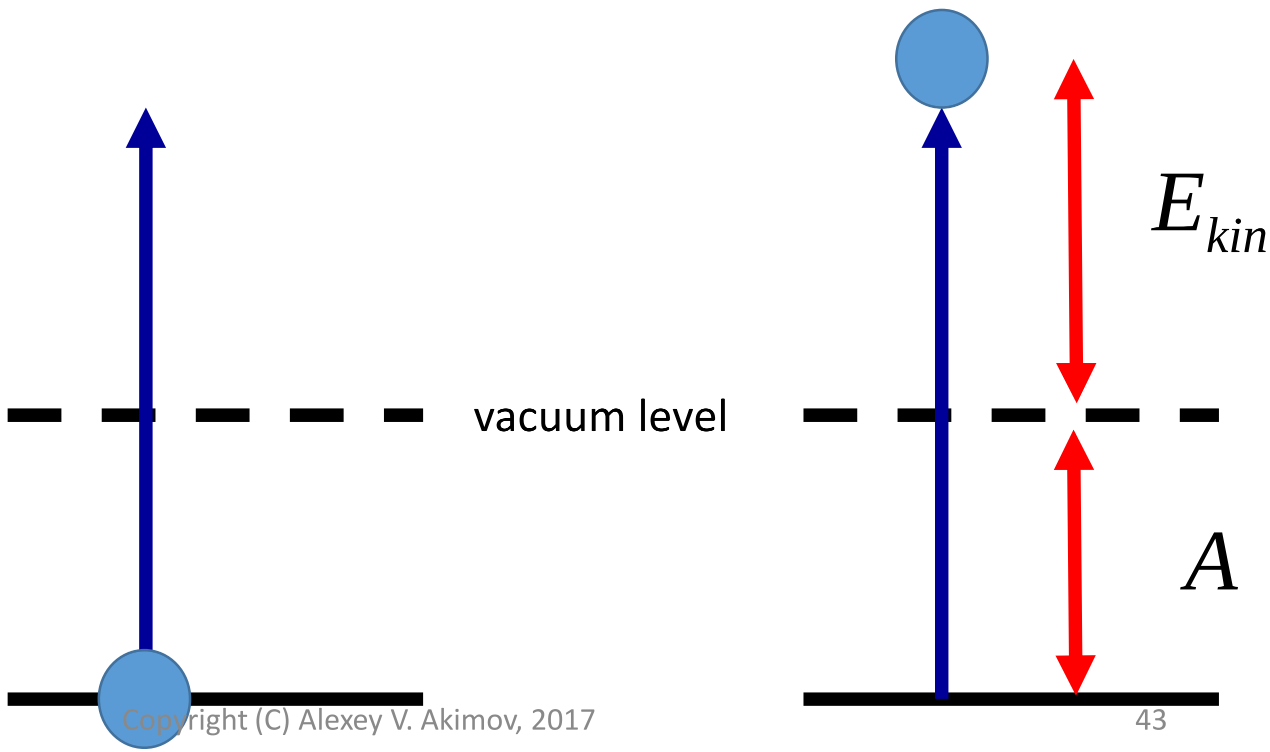
Light is composed of “particles” that concentrate energy

$$h\nu = A + E_{kin}$$

“particles” = photons

A – the **workfunction**

Modern explanation



De Broglie's waves

1924 **De Broglie**

Louis-Victor-Pierre-Raymond, 7ème duc de Broglie,
Louis de Broglie

Wave-particle dualism established for photons is

true for all other particles (Nobel Prize)

so, same equations hold:

$$E = h\nu \qquad c = \lambda\nu \qquad \text{so} \qquad E = \frac{hc}{\lambda} = pc$$

so $$\frac{h}{\lambda_B} = p \Leftrightarrow \boxed{\lambda_B = \frac{h}{p}}$$

Large m, v ➔ small wavelength
(wave-like properties can not be observed)

1927 – **Davisson & Thompson** – electron diffraction on crystals – found the interference pattern, so electrons have wavelike properties. (also got a Nobel Prize)

Wave-particle duality

All "particles" **propagate as waves** but **interacts as a particles**

Thesis + Anti-thesis = Synthesis

Need a theory that combines both

$$\psi(x,t) \sim \exp(i(xk-\omega t)) = \exp\left(i\frac{(xp_x - Et)}{\hbar}\right)$$

Ger Manches rechnet Erwin schon

Mit Seiner Wellenfunction

Nur Wissen Mocht’man wohl

Was man sich dabei vorstell’n soll?

Erwin with his psi can do
Calculations quite a few.
But one thing has not been seen:
Just what does psi really mean?

Erwin Rudolf Josef Alexander Schrödinger

“Derivation” of the Schrodinger’s equation

$$\psi = \exp(i(xk - \omega t)) = \exp\left(i\frac{(xp_x - Et)}{\hbar}\right)$$

$$\frac{\partial\psi}{\partial t} = -i\frac{E}{\hbar}\psi \quad \Rightarrow \quad i\hbar\frac{\partial\psi}{\partial t} = E\psi$$

$$\frac{\partial\psi}{\partial x} = i\frac{p_x}{\hbar}\psi$$

$$\frac{\partial^2\psi}{\partial x^2} = -\left(\frac{p_x}{\hbar}\right)^2\psi = -\frac{2m}{\hbar^2}\frac{p_x^2}{2m}\psi \quad \Rightarrow \quad -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = T\psi$$

Free particle: $E = T$ $\Rightarrow$ $i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$

Generalize the SE

$$i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}\Leftrightarrow i\hbar\frac{\partial\psi}{\partial t}=\hat{H}\psi$$

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}=\frac{\hat{p}_x^2}{2m}$$

Hamiltonian

$$\hat{H}=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)=\left(\frac{\hat{p}_x^2}{2m}+\frac{\hat{p}_y^2}{2m}+\frac{\hat{p}_z^2}{2m}\right)=-\frac{\hbar^2}{2m}\nabla^2$$

$$\hat{H}=\sum_i-\frac{\hbar^2}{2m_i}\nabla_i^2$$

$$\hat{H}=\sum_i-\frac{\hbar^2}{2m_i}\nabla_i^2+V\left(\{\vec{r}\}\right)$$

Postulates of QM

1. Existence of wavefunction

$$\exists \psi = \psi(x,t)$$

defines a state

2. Superposition principle

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

3. Expectation values, operators, observables

$$A = \langle \hat{A} \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\hat{A}\psi(x,t)dx$$

4. TD-SE

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

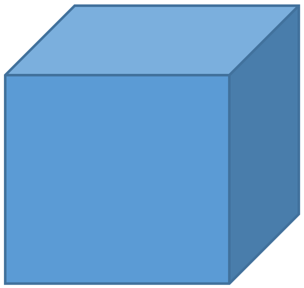
Postulate #1: Wavefunction

$$\psi(x,t)$$

- Contains all information about the system
- Doesn't have physical meaning on its own

$$dP = |\psi(x,t)|^2 dV$$

Probability to find in dV at time t



$$\int_{-\infty}^{\infty} dP = \int_{-\infty}^{\infty} |\psi(x,t)|^2 dV = 1$$

Probability to find anywhere at any time t

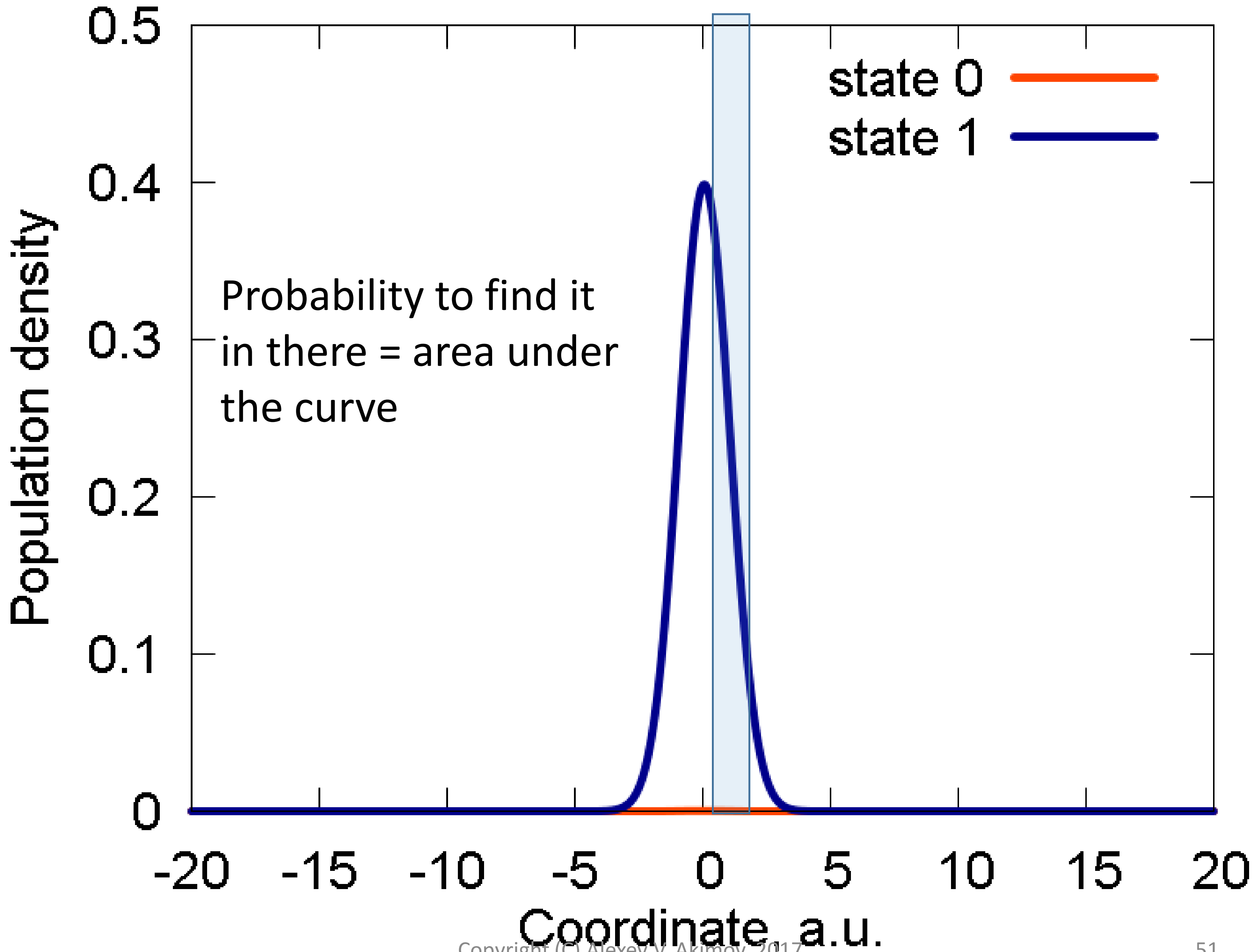
Normalization

$$|\psi(x,t)|^2$$

Probability density

Requirement of the form of WFC:

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dV < \infty \Leftrightarrow \psi \in L^2(-\infty,+\infty)$$


0.5
0.4
0.3
0.2
0.1
0
Population density
state 0
state 1
Probability to find it
in there = area under
the curve
-20
-15
-10
-5
0
5
10
15
20
Coordinate, a.u.

Dirac bra-ket notation for states

$|i\rangle$ Abstract state i (whatever it is) **KET**

$|\psi\rangle$ Misleading

$|\psi_i\rangle$ Better = OK

$\langle r|i\rangle = \psi_i(r)$ This is what you really mean (coordinate/**position representation**)

$\Big\downarrow$ FT

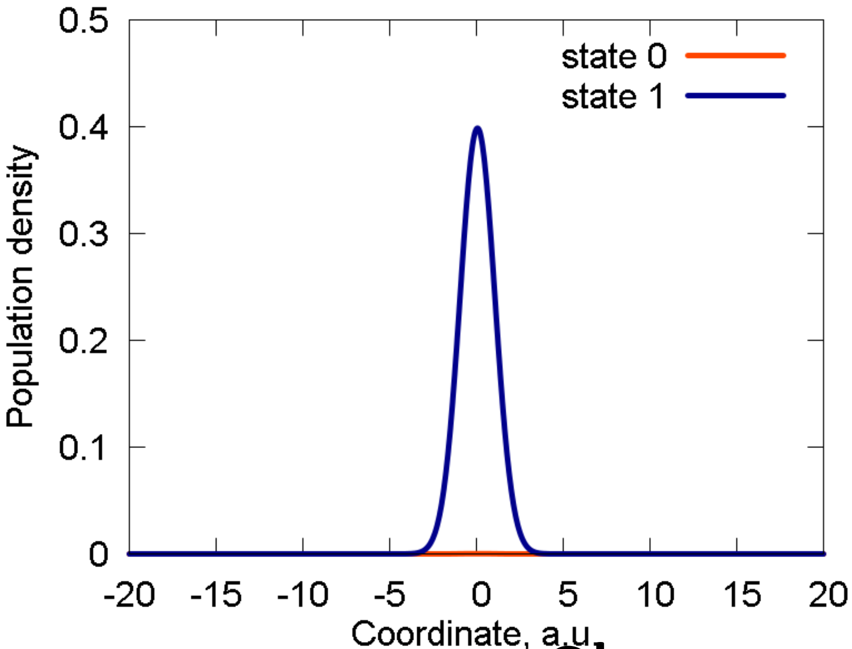
$\langle k|i\rangle = \tilde{\psi}_i(k)$ **Momentum representation**

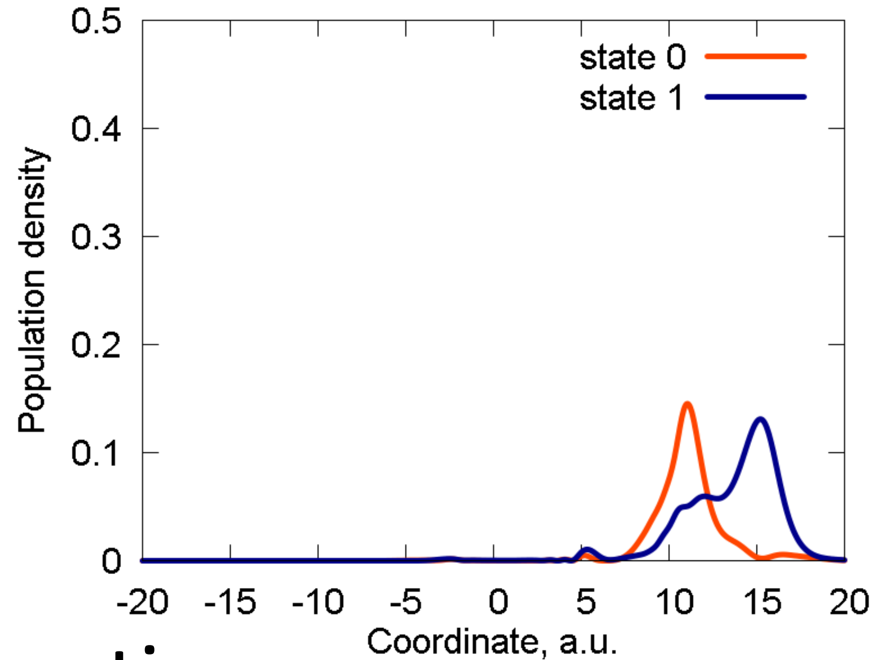
Dirac bra-ket notation for states

$\langle i |$ Abstract state i (whatever it is) **BRA**

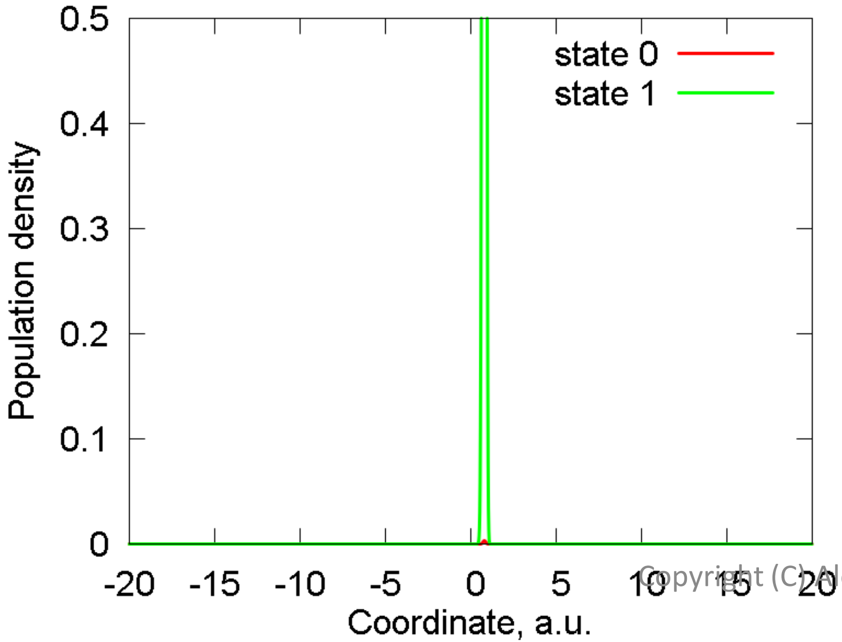
Overlap = scalar product

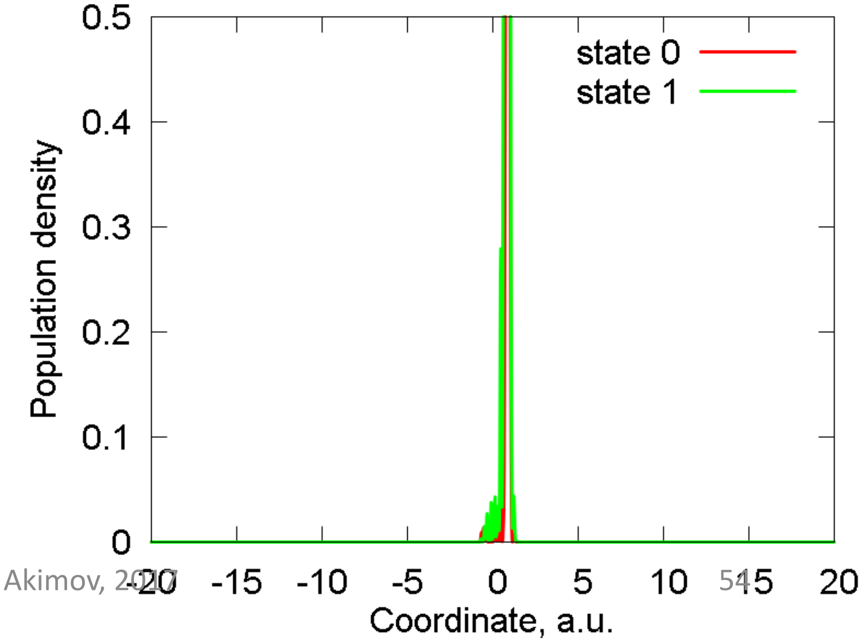
$$\langle i | j \rangle = (\psi_i, \psi_j) = \int_{-\infty}^{+\infty} \psi_i^*(\vec{r}) \psi_j(\vec{r}) d\vec{r}$$





Show animation





Dirac Delta-function and representations

$$\langle x | x' \rangle = \delta(x - x')$$

"grid states"

(Dirac) Delta-function
Is a functional!

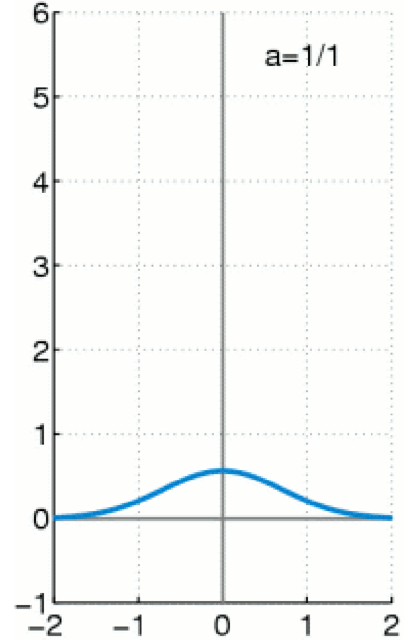
$$\delta(x) = \begin{cases} +\infty, x = 0 \\ 0, x \neq 0 \end{cases}$$

$$\int_{-\infty}^{+\infty} \delta(x) dx = 1$$

Representations of the delta-function

$$\delta_a(x) = \frac{1}{a\sqrt{\pi}} e^{-x^2/a^2}$$

$$\delta(x) = \lim_{a \to 0} \delta_a(x)$$



As a Fourier transform

$$\delta(x-a) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i(x-a)y}\,dy$$

$$\hat{I} = \int |y\rangle\langle y|\,dy$$

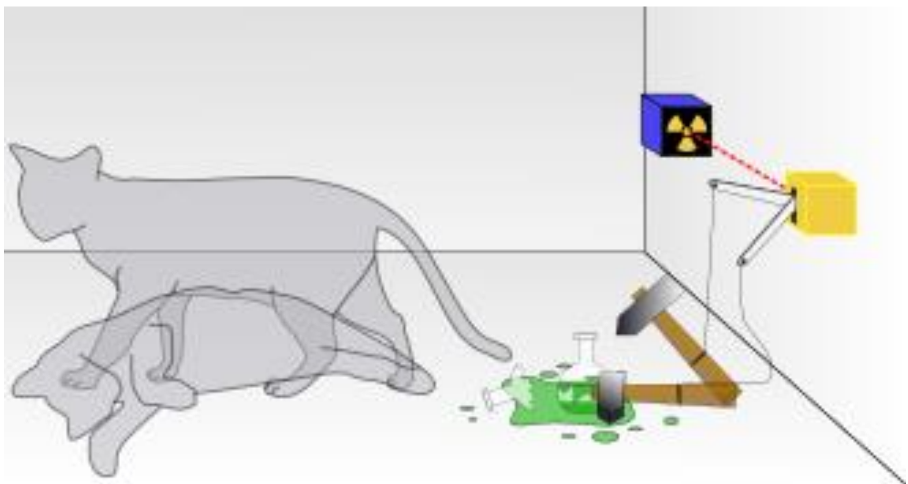
$$f(x) = \int_{-\infty}^{+\infty} \delta(x-a) f(a)\,da$$

$$\psi(x) = \langle x|\psi\rangle$$

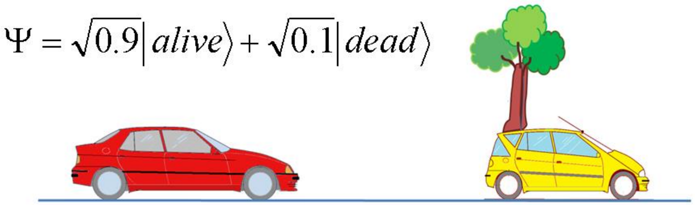
functional operator

$$\langle x|x'\rangle = \int \langle x|x''\rangle\langle x''|x'\rangle dx'' = \int \delta(x-x'')\delta(x''-x')dx'' = \delta(x-x') = \hat{I}$$

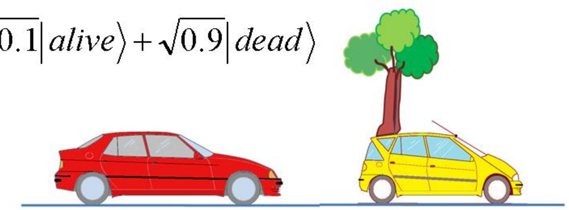
2 Superposition principle



$$\Psi = \sqrt{0.9}\,|alive\rangle + \sqrt{0.1}\,|dead\rangle$$

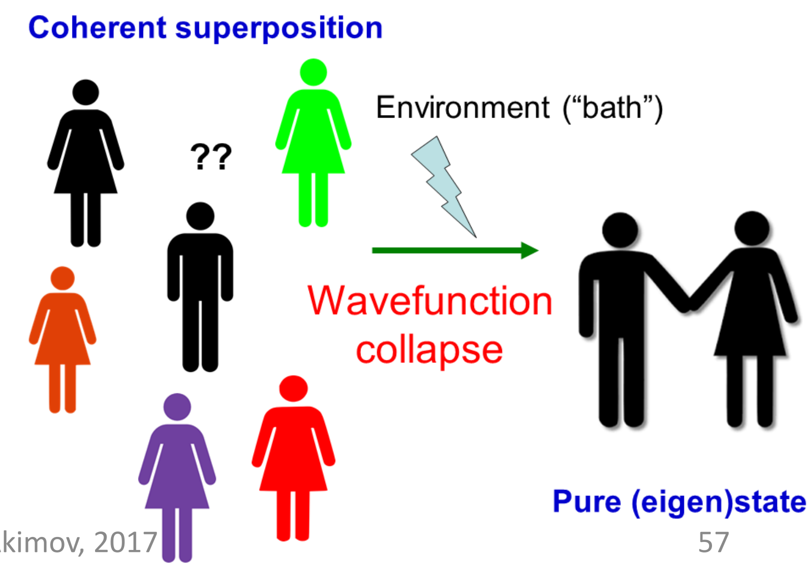


$$\Psi = \sqrt{0.1}\,|alive\rangle + \sqrt{0.9}\,|dead\rangle$$

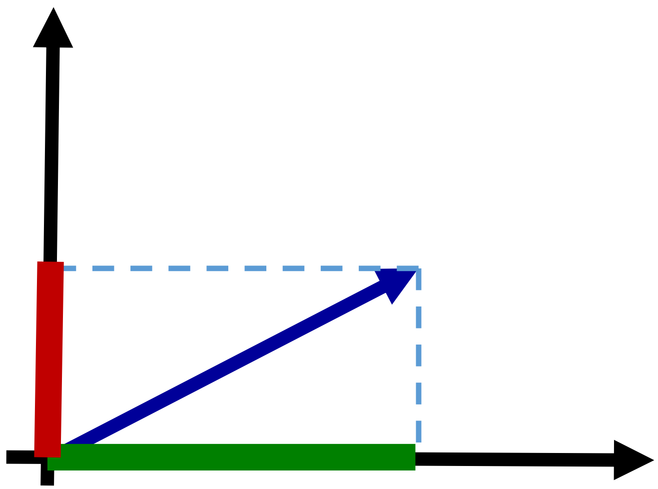


Pure

Mixed
(coherent superposition)



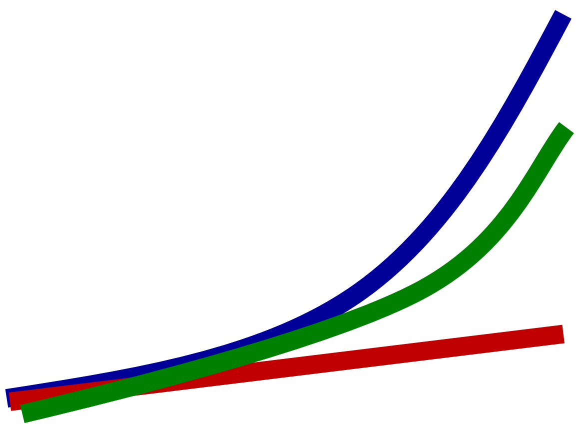
Projections (wfc **collapse**)



$$\vec{r} = \begin{pmatrix} 2 \\ 1 \end{pmatrix} = \boxed{2 \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix}} + \boxed{1 \cdot \begin{pmatrix} 0 \\ 1 \end{pmatrix}}$$

$$\langle \vec{e}_1 | \vec{r} \rangle = (\vec{e}_1, \vec{r}) = 2$$

$$\langle \vec{e}_2 | \vec{r} \rangle = (\vec{e}_2, \vec{r}) = 1$$



$$f(x) = \boxed{1 \cdot x^2} + \boxed{2 \cdot x}$$

$$\langle x^2 | f \rangle = (x^2, f(x)) = 1$$

$$\langle x | f \rangle = (x, f(x)) = 2$$

3 Operators

$$x \rightarrow \hat{x} \equiv x \qquad p_x \rightarrow \hat{p}_x \equiv -i\hbar \frac{\partial}{\partial x}$$

In **position** representation

that is: $\langle x | \psi \rangle = \psi(x)$ $\quad \hat{x}\psi(x) = x\psi(x)$ $\quad \hat{p}_x \psi(x) = -i\hbar\psi'(x)$

$$x \rightarrow \hat{x} \equiv i\hbar \frac{\partial}{\partial p_x} \qquad p_x \rightarrow \hat{p}_x \equiv p_x$$

In **momentum** representation

that is: $\langle p_x | \psi \rangle = \psi(p_x)$ $\quad \hat{x}\psi(p_x) = i\hbar\psi'(p_x)$ $\quad \hat{p}_x \psi(p_x) = p_x \psi(p_x)$

3 Operators

Overlap = scalar product

$$\langle i | j \rangle = \left(\psi_i , \psi_j \right) = \int_{-\infty}^{+\infty} \psi_i^* (\vec{r}) \psi_j (\vec{r}) d\vec{r}$$

Matrix element = "dress" the operator

$$A_{ij} = \langle i | \hat{A} | j \rangle = \left\langle i \middle| \hat{A} j \right\rangle = \left(\psi_i , \hat{A} \psi_j \right) = \int_{-\infty}^{+\infty} \psi_i^* (\vec{r}) \hat{A} \psi_j (\vec{r}) d\vec{r}$$

Practical way

Operators acting backwards

Original = acts forward

$$A_{ij} = \langle i | \hat{A} | j \rangle = \langle i \,|\, \hat{A} j \rangle = \left(\psi_i , \hat{A} \psi_j \right) = \int_{-\infty}^{+\infty} \psi_i^*(\vec{r}) \hat{A} \psi_j(\vec{r}) d\vec{r}$$

Adjoint = acts backward

$$A_{ij}^{+} = \langle i | \hat{A}^{+} | j \rangle = \left(\hat{A} \psi_i , \psi_j \right) = \int_{-\infty}^{+\infty} \left(\hat{A} \psi_i (\vec{r}) \right)^* \psi_j(\vec{r}) d\vec{r}$$

Hermitian = acts both ways the same $\quad \hat{A}^{+} = \hat{A}$

Outer product of state vectors

$$|i\rangle\langle j|$$

What is this?

Lets “act by it” on $|k\rangle$ from the left

$$\left(|i\rangle\langle j|\right)|k\rangle = |i\rangle\langle j|k\rangle = |i\rangle a_{jk} = a_{jk}|i\rangle$$

So this is an operator!!!

$$\left(|i\rangle\langle i|\right)|k\rangle = a_{ik}|i\rangle = \delta_{ik}|i\rangle = \begin{cases} |i\rangle, k = i \\ 0, k \neq i \end{cases}$$

Projector

Resolution of identity and Hamiltonian

If $\langle i | j \rangle = \delta_{ij}$ then $\sum_i |i\rangle\langle i| = \hat{1}$

$$\langle a | \left(\sum_i |i\rangle\langle i| \right) | b \rangle = \sum_i \langle a | i \rangle \langle i | b \rangle = \sum_i \delta_{ia}\delta_{ib} = \delta_{ab}$$

corresponds to
the identity matrix

$$\hat{H} = \hat{I}\hat{H}\hat{I} = \sum_{i,i} |i\rangle\langle i|\hat{H}| j\rangle\langle j|$$

Compute the matrix element

Why p is Hermitian?

$$\langle i|\hat{p}|j\rangle = -i\hbar\int \psi_i^* d\psi_j = -i\hbar\left[\psi_i^*\psi_j\Big|_{-\infty}^{+\infty} - \int \psi_j d\psi_i^*\right] =$$

$$= i\hbar\int \psi_j d\psi_i^* = \left(-i\hbar\int \psi_j^* d\psi_i\right)^* = \left(\langle j|\hat{p}|i\rangle\right)^*$$

Eigenvalues and eigenfunctions

functional form

$$\hat{A}|i\rangle = a_i|i\rangle$$

eigenstate

eigenvalue

matrix representation

$$\langle i|\hat{A}|j\rangle = \langle i|a_j|j\rangle = a_j\langle i|j\rangle \Leftrightarrow A_{ij} = a_j S_{ij}$$

Example:

$$A_{00} = a_0 S_{00}$$
$$A_{01} = a_1 S_{01}$$
$$A_{10} = a_0 S_{10}$$
$$A_{11} = a_1 S_{11}$$

$$\Leftrightarrow \begin{pmatrix} A_{00} & A_{01} \\ A_{10} & A_{11} \end{pmatrix} = \begin{pmatrix} S_{00} & S_{01} \\ S_{10} & S_{11} \end{pmatrix} \begin{pmatrix} a_0 & 0 \\ 0 & a_1 \end{pmatrix}$$

Finding the Eigenvalues and Eigenfunctions

$$\begin{pmatrix} A_{00} & A_{01} \\ A_{10} & A_{11} \end{pmatrix} = \begin{pmatrix} S_{00} & S_{01} \\ S_{10} & S_{11} \end{pmatrix} \begin{pmatrix} a_0 & 0 \\ 0 & a_1 \end{pmatrix}$$

if orthogonal basis $$\begin{pmatrix} A_{00} & A_{01} \\ A_{10} & A_{11} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} a_0 & 0 \\ 0 & a_1 \end{pmatrix} = \begin{pmatrix} a_0 & 0 \\ 0 & a_1 \end{pmatrix}$$

secular equation $$\det \begin{pmatrix} A_{00} - a & A_{01} \\ A_{10} & A_{11} - a \end{pmatrix} = 0$$

Thinking of quantum mechanics…

Theorems about Hermitian operators

1. Eigenvalues of Hermitian op are **real**

2. Non-degenerate eigenstates of Hermitian op
that correspond to different eigenvalues are **orthogonal**

Proof

Eigenvalues of Hermitian op are **real**

$$H\left| j \right\rangle = E_j \left| j \right\rangle$$

$$\left\langle i \middle| H \middle| j \right\rangle = E_j \left\langle i \middle| j \right\rangle$$

$$\left\langle i \middle| H \middle| j \right\rangle = \left\langle i \middle| H^+ \middle| j \right\rangle = \left\langle j \middle| H \middle| i \right\rangle^* = E_i^* \left\langle j \middle| i \right\rangle^* = E_i^* \left\langle i \middle| j \right\rangle$$

$$\left(E_j - E_i^*\right)\left\langle i \middle| j \right\rangle = 0$$

$$i = j \qquad \left(E_i - E_i^*\right)\left\langle i \middle| i \right\rangle = 0 \Rightarrow E_i = E_i^* \Rightarrow E_i \in R$$

$$i \neq j \qquad \left(E_i - E_j\right)\left\langle i \middle| j \right\rangle = 0 \Rightarrow \left\langle i \middle| j \right\rangle = 0 \Rightarrow i \perp j$$

$$E_i \neq E_j$$

Theorems about commuting operators

1. If two operators commute with each other, they have a common set of eigenvectors

2. If two operators have a common set of eigenvectors, they commute with each other

Proof

$$A\left|i\right\rangle = a_i\left|i\right\rangle, \forall i \qquad\qquad B\left|i\right\rangle = b_i\left|i\right\rangle, \forall i$$

$$\left\{\left|i\right\rangle\right\} - complete \Rightarrow \left|\psi\right\rangle = \sum_i c_i\left|i\right\rangle, \forall\,\psi$$

then

$$\hat{A}\hat{B}\left|\psi\right\rangle = \hat{A}\hat{B}\left(\sum_i c_i\left|i\right\rangle\right) = \hat{A}\left(\sum_i c_i\hat{B}\left|i\right\rangle\right) = \hat{A}\left(\sum_i c_i b_i\left|i\right\rangle\right) = \sum_i c_i b_i\hat{A}\left|i\right\rangle = \sum_i c_i b_i a_i\left|i\right\rangle$$

$$\hat{B}\hat{A}\left|\psi\right\rangle = \hat{B}\hat{A}\left(\sum_i c_i\left|i\right\rangle\right) = \hat{B}\left(\sum_i c_i\hat{A}\left|i\right\rangle\right) = \hat{B}\left(\sum_i c_i a_i\left|i\right\rangle\right) = \sum_i c_i a_i\hat{B}\left|i\right\rangle = \sum_i c_i a_i b_i\left|i\right\rangle$$

$$\hat{A}\hat{B}\left|\psi\right\rangle = \hat{B}\hat{A}\left|\psi\right\rangle \Rightarrow \hat{A}\hat{B} - \hat{B}\hat{A} = \left[\hat{A}, \hat{B}\right] = 0$$

Proof

$$\left[\hat{A},\hat{B}\right]=0 \Rightarrow \hat{A}\hat{B}|\psi\rangle = \hat{B}\hat{A}|\psi\rangle$$

$$\hat{A}\left(\hat{B}|\psi\rangle\right)=\hat{B}\hat{A}|\psi\rangle = \hat{B}a|\psi\rangle = a\left(\hat{B}|\psi\rangle\right)$$

then $|\psi'\rangle = \hat{B}|\psi\rangle$ is an eigenstate of the operator A corresponding to the eigenvalue a

$\exists\ |\varphi\rangle$ that describes the same state as and is the eigenstate of A: $|\varphi\rangle = const\cdot\hat{B}|\psi\rangle$ $\hat{A}|\varphi\rangle = a|\varphi\rangle$

Thus $\hat{A}|\varphi\rangle = \hat{A}\left(const\cdot b|\psi\rangle\right) = const\cdot a|\psi\rangle \Rightarrow \hat{A}|\psi\rangle = \dfrac{a}{b}|\psi\rangle$

Time-dependent Schrodinger equation (TD-SE)

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

Separation of variables

$$\Psi(t,R) = \varphi(t)\psi(R)$$

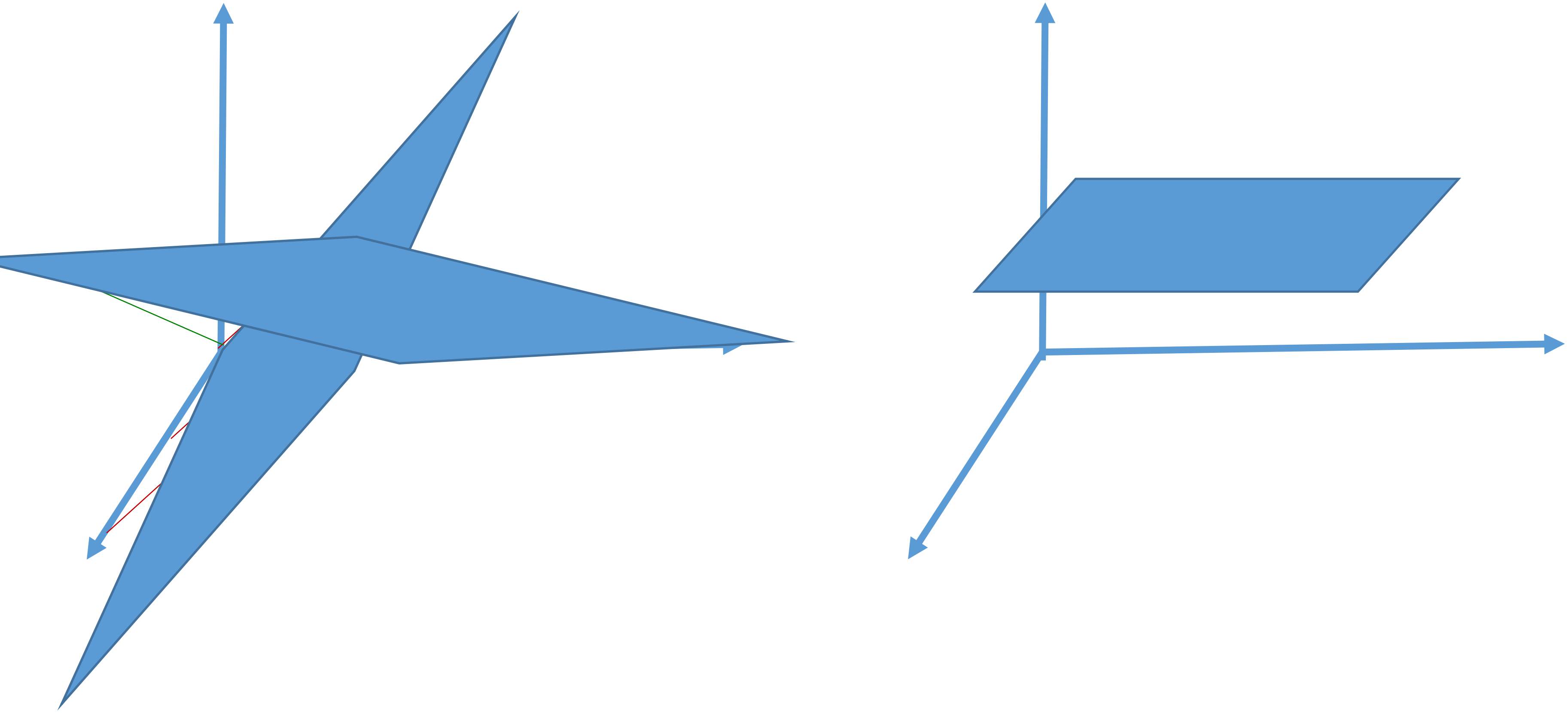
$$i\hbar \frac{\partial(\varphi(t)\psi(R))}{\partial t} = i\hbar \frac{\partial \varphi(t)}{\partial t}\psi(R) = \hat{H}(R)(\varphi(t)\psi(R)) = \varphi(t)\left(\hat{H}(R)\psi(R)\right)$$

Depends only on **t**

$$i\hbar \frac{\frac{\partial \varphi(t)}{\partial t}}{\varphi(t)} = \frac{\left(\hat{H}(R)\psi(R)\right)}{\psi(R)}$$

Depends only on **R**

When is this possible?



$$i\hbar\frac{\frac{\partial\varphi(t)}{\partial t}}{\varphi(t)}=\frac{\left(\hat{H}(R)\psi(R)\right)}{\psi(R)}=E=const$$

Time-dependent part of TD-SE

$$i\hbar \frac{\frac{\partial \varphi(t)}{\partial t}}{\varphi(t)} = E \Rightarrow i\hbar \frac{d\varphi}{\varphi} = Edt \Rightarrow \int_{\varphi(0)}^{\varphi(t)} d\ln\varphi = -i\int_0^t \frac{E}{\hbar} dt'$$

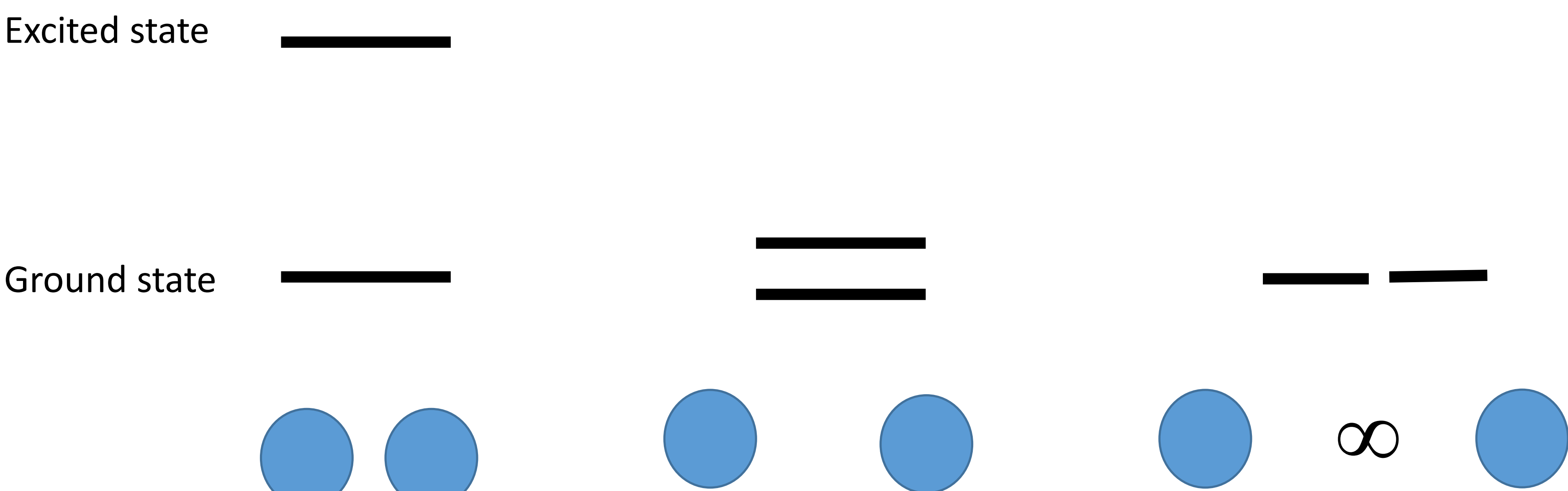
$$\varphi(t) = \exp\left(-\frac{i}{\hbar}\int_0^t Edt'\right)\varphi(0) = \exp\left(-\frac{iE}{\hbar}t\right)\varphi(0)$$

Phase factor

Stationary SE

$$\frac{\left(\hat{H}(R)\psi(R)\right)}{\psi(R)} = E \Leftrightarrow \hat{H}(R)\psi(R) = E\psi(R)$$

Produces energy spectrum at **fixed** positions



Chemical Dynamics

$$\Psi(t,R) = \sum_i c_i(t)\psi_i(R) = \sum_i c_i(t)|i(R)\rangle$$

$$i\hbar\sum_i \frac{\partial c_i(t)}{\partial t}|i(R)\rangle = \sum_i c_i(t)\hat{H}(R)|i(R)\rangle$$

$$i\hbar\langle i(R)|\sum_j \frac{\partial c_j(t)}{\partial t}|j(R)\rangle = \sum_j c_j(t)\langle i(R)|\hat{H}(R)|j(R)\rangle$$

$$i\hbar\frac{\partial c_i(t)}{\partial t} = \sum_j H_{ij}c_j(t)$$

Solve for $\{c_i(t)\}$

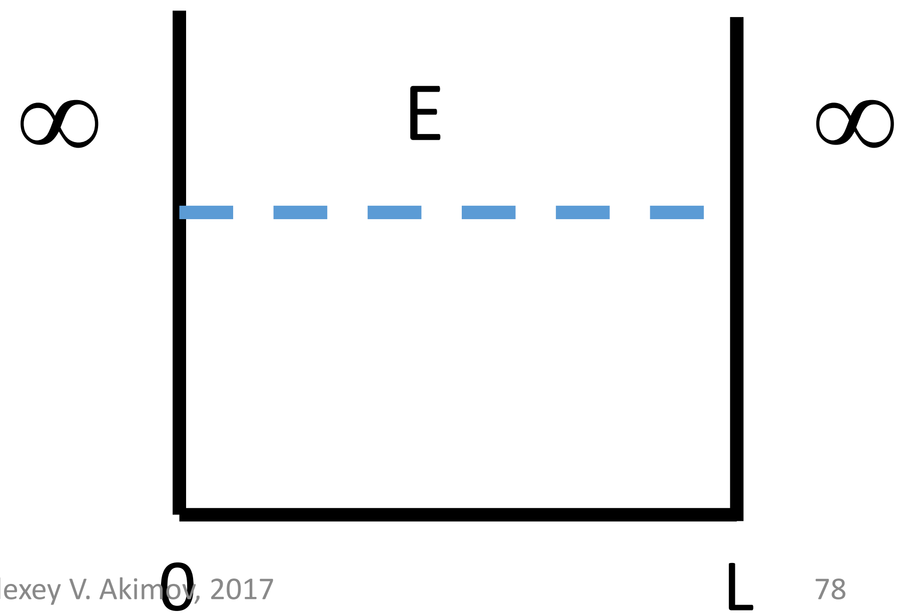
Stationary SE: Particle in the Box

$$\hat{H}\psi = E\psi \qquad \hat{H} = \sum_i -\frac{\hbar^2}{2m_i}\nabla_i^2 + V\left(\{\vec{r}\}\right)$$

1D $$-\frac{\hbar^2}{2m}\psi''(x) + \left(V(x) - E\right)\psi(x) = 0$$

Model problem (Hamiltonian)

$$V(x) = \begin{cases} 0, x \in [0, L] \\ \infty, x < 0, x > L \end{cases}$$



Stationary SE: Particle in the Box

$$\psi(0) = 0$$

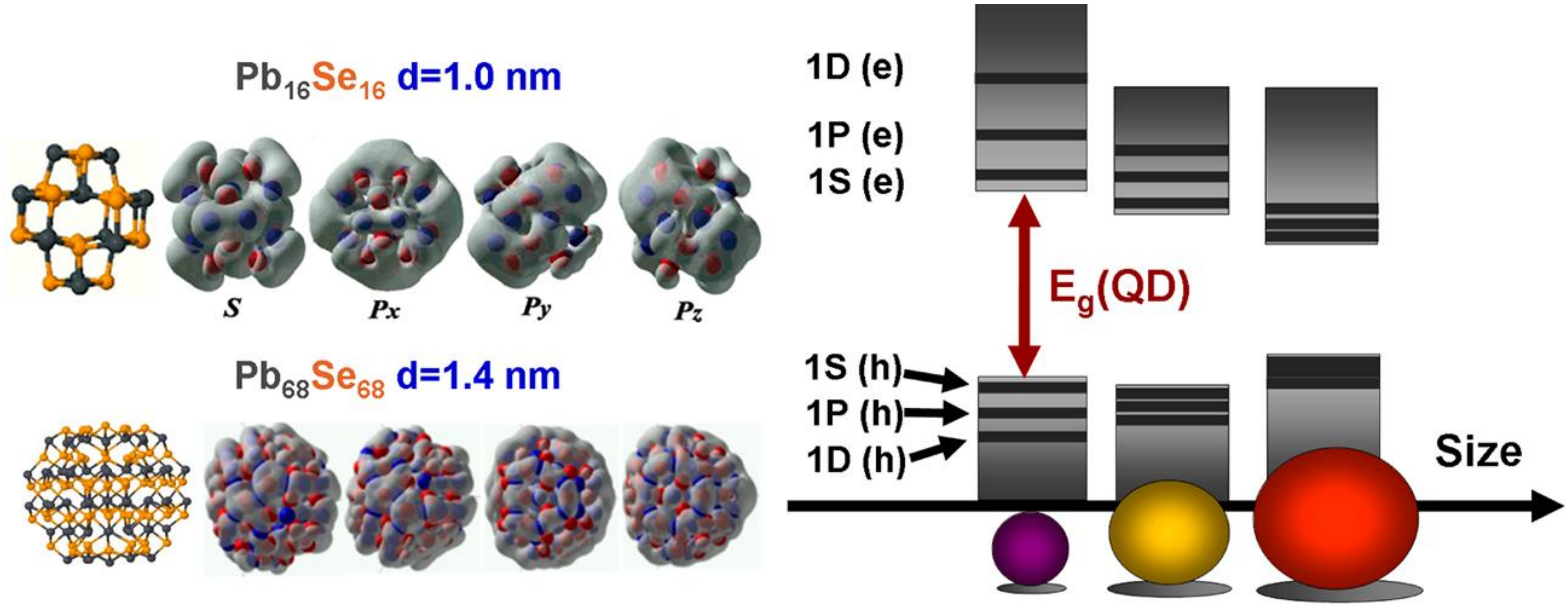
Because of the infinite potential

Particle confinement ➔ quantization

Spectrum: energy spacing quadratic

Eigenstates: nodal structure

Applications: Quantum Dots and Linear Polyenes



(a) (b)

$$E_{n,e} = E_{CBE} + \frac{\pi^2 \hbar^2}{2m_e^* L^2} n^2$$

$$E_g = 3.30 + \frac{0.293}{d} + \frac{3.94}{d^2}$$

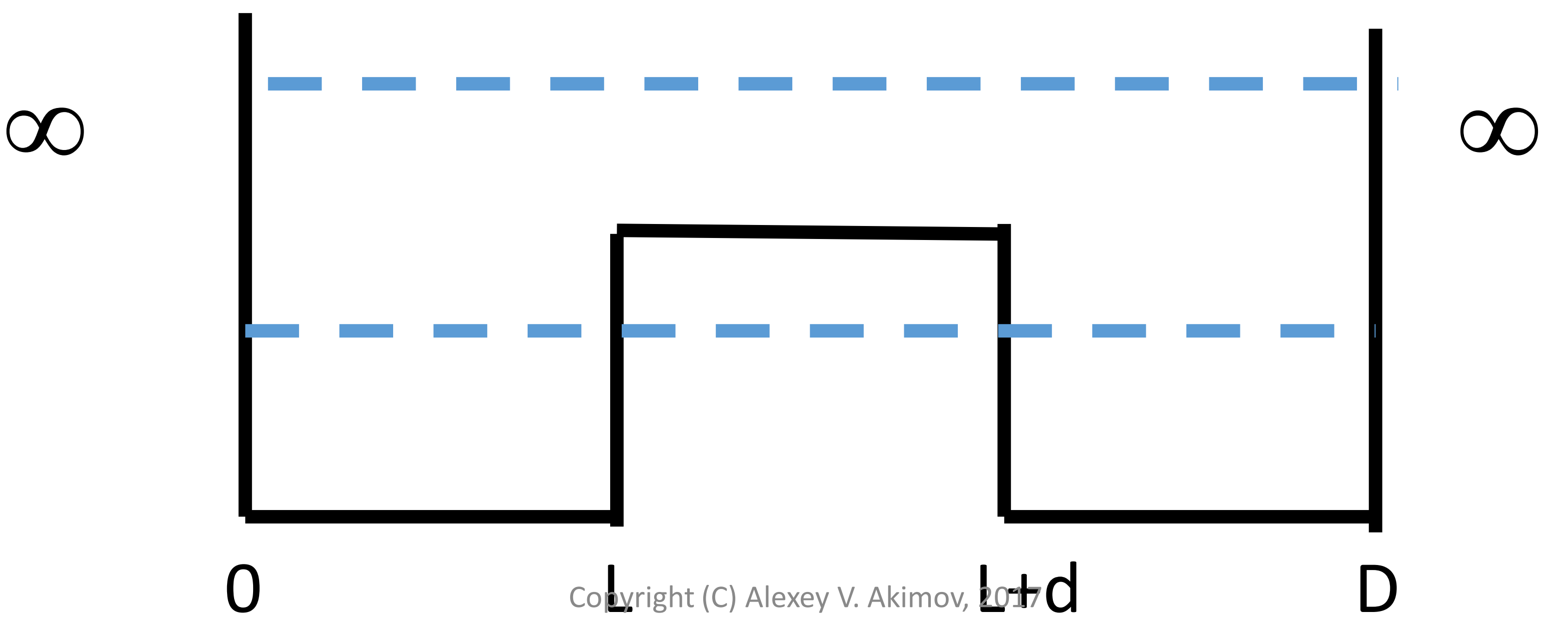
$$E_{n,h} = E_{VBE} - \frac{\pi^2 \hbar^2}{2m_h^* L^2} n^2$$

Tunneling

$$V(x)=\begin{cases} 0, x\in[0,L]\cup[L+d,D] \\ \infty, x\in(-\infty,0)\cup(D,\infty) \\ V, x\in(L,L+d) \end{cases}$$

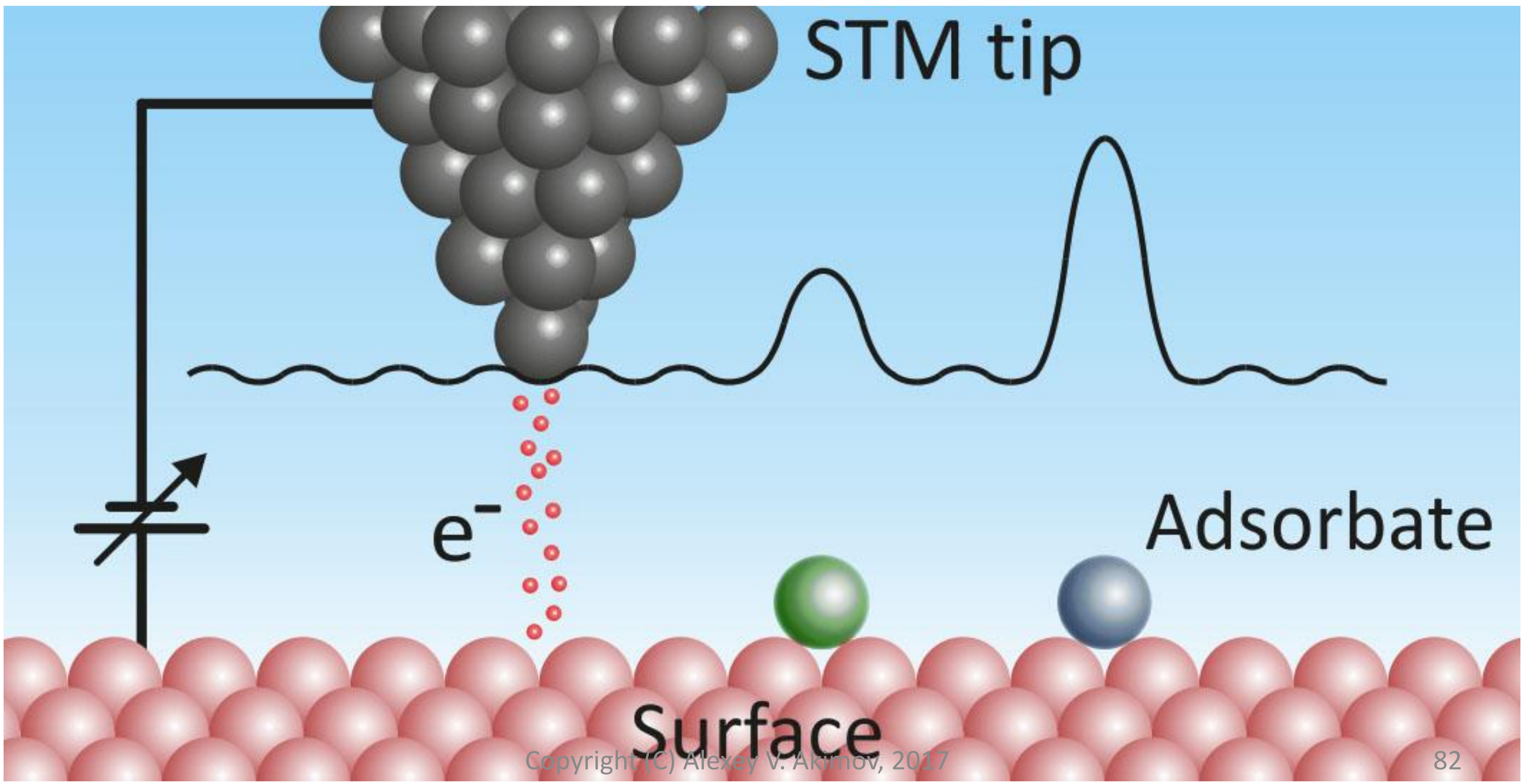
2 Cases:

1) E < V
2) E > V

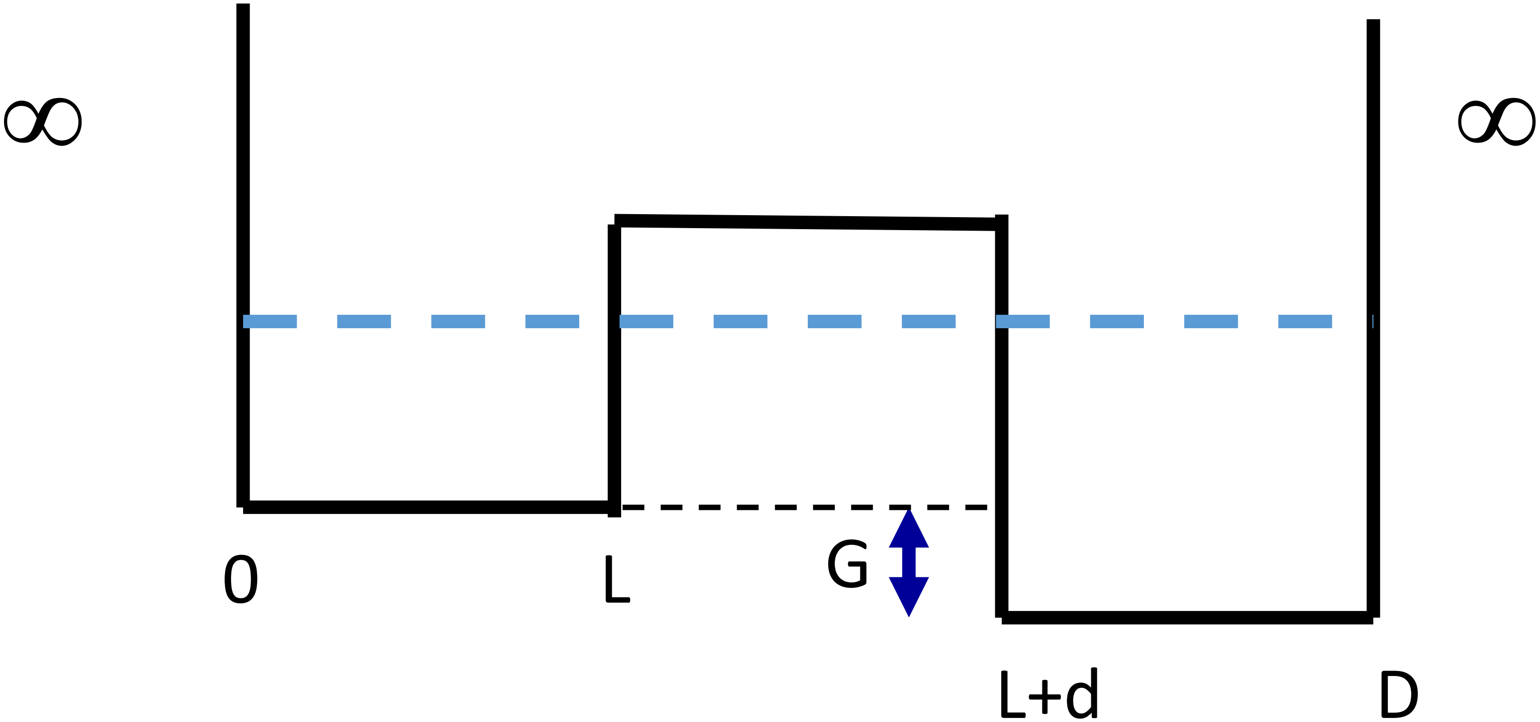


Solve. Applications: STM

$$\psi(z) \sim e^{-\alpha z}$$



The "WIN COURSE"



1) Get eigenstates of the problem above $\left\{ \left| \psi_i \right\rangle \right\}$ adiabatic basis

2) Get eigenstates of the problem Donor and Acceptor boxes

$\left\{ \left| \tilde{\psi}_i^A \right\rangle \right\}$ $\left\{ \left| \tilde{\psi}_i^D \right\rangle \right\}$ diabatic basis

3) Start in a given acceptor state, n, (with energy below the barrier)

$$\left\{ \left| \tilde{\psi}_n^A \right\rangle \right\}$$

4) This initial state can be expressed in the adiabatic basis, initially:

$$\left|\psi(0)\right\rangle = \left|\tilde{\psi}_n^A\right\rangle = \sum_i c_{in}(0)\left|\psi_i\right\rangle$$

5) … or at any time t:

$$\left|\psi(t)\right\rangle = \sum_i c_{in}(t)\left|\psi_i\right\rangle$$

6) To find the evolution of the coefficients, solve the TD-SE (see before)

7) To find how the population of the acceptor state, m, at any time t:

$$P_{A,m} = \left|\left\langle \psi_m^D \middle| \psi(t) \right\rangle\right|^2$$

Vibrational motion: Harmonic Oscillator

Reading assignment: Chapter 6
Prof. Autschbach Notes

Harmonic Oscillator: Another approach

$$\hat{H}\psi(x) = E\psi(x) \Leftrightarrow \left(\frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2\right)\psi(x) = E\psi(x)$$

Introduce: $a_+ = \dfrac{1}{\sqrt{2\hbar m\omega}}\left(-i\hat{p} + m\omega\hat{x}\right)$ $\quad a_- = \dfrac{1}{\sqrt{2\hbar m\omega}}\left(i\hat{p} + m\omega\hat{x}\right)$

$$a_-a_+ = \frac{H}{\hbar\omega} + \frac{1}{2} \qquad a_+a_- = \frac{H}{\hbar\omega} - \frac{1}{2}$$

so: $\left[a_-, a_+\right] = \hat{1}$

and: $\hat{H} = \hbar\omega\left(a_-a_+ - \dfrac{1}{2}\right) = \hbar\omega\left(a_+a_- + \dfrac{1}{2}\right)$

Raising and lowering operations

If: $\hat{H}\psi(x) = E\psi(x)$ then:

$$\hat{H}(a_+\psi(x)) = (E + \hbar\omega)(a_+\psi(x)) \qquad \hat{H}(a_-\psi(x)) = (E - \hbar\omega)(a_-\psi(x))$$

Prove it?

Raising/Creation operator:

$a_+ : \psi(x) \rightarrow \tilde{\psi}(x) = a_+\psi(x)$ new state with energy $E + \hbar\omega$

Lowering/Annihilation operator:

$a_- : \psi(x) \rightarrow \tilde{\psi}(x) = a_-\psi(x)$ new state with energy $E - \hbar\omega$

The Ground state

There a state, for which the energy is minimal ψ_0

a_- When acting on ψ_0 will try to lower its energy, but since there is no such state, the result is zero

$$a_- \psi_0(x) = 0$$

$$\hbar \psi'_0 + m\omega x \psi_0 = 0$$

Solve it?

Solution: $$\psi_0(x) = A \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

normalization: $$A = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

All other states

$$a_+ : \psi(x) \rightarrow \tilde{\psi}(x) = a_+ \psi(x)$$

$$\psi_n(x) = A_n (a_+)^n \psi_0(x)$$

The normalization of the operators (and switching to bra-ket)

$$a_+ |n\rangle = \sqrt{n+1} |n+1\rangle$$

$$a_- |n\rangle = \sqrt{n} |n-1\rangle$$

Many variables: **Factorization**

$$\hat{A}\psi_A = \lambda_A \psi_A \qquad \hat{B}\psi_B = \lambda_B \psi_B \qquad \hat{C}\psi_C = \lambda_C \psi_C$$

And: $\left[\hat{A},\hat{B}\right]=0 \qquad \left[\hat{A},\hat{C}\right]=0 \qquad \left[\hat{B},\hat{C}\right]=0$

Then for the operator: $\hat{X} = \hat{A}+\hat{B}+\hat{C}+\ldots$

$\psi_X = \psi_A \cdot \psi_B \cdot \psi_C$ is the eigenfunction

$\lambda_X = \lambda_A + \lambda_B + \lambda_C$ is the eigenvalue

Prove it!

Example

$$\hat{H}(x,y) = \left(\frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{1}{2}k\hat{x}^2 + \frac{1}{2}k\hat{y}^2 \right)$$

$$\hat{H}(x,y) = \hat{h}(x) + \hat{h}(y) = \left(\frac{\hat{p}_x^2}{2m} + \frac{1}{2}k\hat{x}^2 \right) + \left(\frac{\hat{p}_y^2}{2m} + \frac{1}{2}k\hat{y}^2 \right)$$

$$\psi_{n_1 n_2}(x,y) = \psi_{n_1}(x) \cdot \psi_{n_2}(y)$$

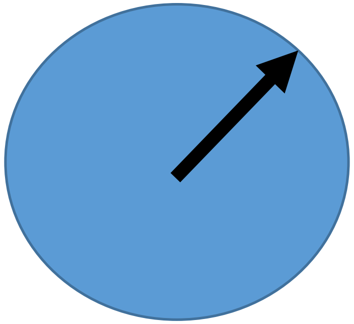
$$E_{n_1 n_2} = E_{n_1} + E_{n_2} = \hbar\omega\left(n_1 + \frac{1}{2} \right) + \hbar\omega\left(n_2 + \frac{1}{2} \right)$$

Room for degeneracies (symmetries!)

Particle in a spherically-symmetric potential

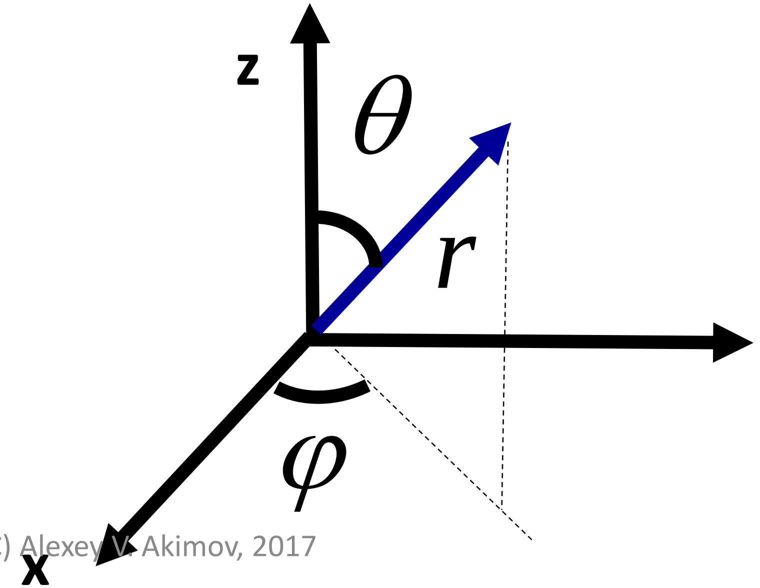
$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(|\vec{r}|)$$

$$|\vec{r}| = \sqrt{(\vec{r},\vec{r})}$$



$V(|\vec{r}|)$ Spheric symmetry

Forces are called central



Change of coordinate system:
spherical polar coordinates

Coordinates Transformations

$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$
$$z = r\cos\theta$$

$$r = |\vec{r}| = \sqrt{(\vec{r},\vec{r})} = \sqrt{x^2+y^2+z^2}$$

$$\varphi = \arctan\left(\frac{y}{x}\right) \qquad \theta = \arccos\left(\frac{z}{r}\right)$$

$$f(x,y,z) = f\left(x(r,\theta,\varphi), y(r,\theta,\varphi), z(r,\theta,\varphi)\right)$$

so, using the chain rule

$$\frac{\partial}{\partial x} f = \frac{\partial}{\partial r} f \cdot \frac{\partial r}{\partial x} + \frac{\partial}{\partial \theta} f \cdot \frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \varphi} f \cdot \frac{\partial \varphi}{\partial x} = \begin{pmatrix} \frac{\partial r}{\partial x} & \frac{\partial \theta}{\partial x} & \frac{\partial \varphi}{\partial x} \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \varphi} \end{pmatrix} f$$

Transformations and Jacobian

that is

$$\frac{\partial}{\partial x} = \begin{pmatrix} \frac{\partial r}{\partial x} & \frac{\partial \theta}{\partial x} & \frac{\partial \varphi}{\partial x} \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \varphi} \end{pmatrix}$$

For all components:

$$\vec{\nabla} = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} = \boxed{\begin{pmatrix} \frac{\partial r}{\partial x} & \frac{\partial \theta}{\partial x} & \frac{\partial \varphi}{\partial x} \\ \frac{\partial r}{\partial y} & \frac{\partial \theta}{\partial y} & \frac{\partial \varphi}{\partial y} \\ \frac{\partial r}{\partial z} & \frac{\partial \theta}{\partial z} & \frac{\partial \varphi}{\partial z} \end{pmatrix}} \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \varphi} \end{pmatrix}$$

Jacobian

Laplacian and Angular momentum

$$\Delta(x, y, z) = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\Delta(r, \theta, \varphi) = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \right) + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \varphi^2} \right)$$

$$\hat{L}_x = i\hbar\left(\frac{1}{\tan\theta}\cos\varphi\frac{\partial}{\partial\varphi} + \sin\varphi\frac{\partial}{\partial\theta} \right)$$

so:

$$\hat{L}_y = i\hbar\left(\frac{1}{\tan\theta}\sin\varphi\frac{\partial}{\partial\varphi} - \cos\varphi\frac{\partial}{\partial\theta} \right)$$

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \varphi^2} \right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

Then:

$$\Delta(r, \theta, \varphi) = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2}$$

Kinetic energy and Classification

$$\hat{T} = -\frac{\hbar^2}{2m}\Delta(r,\theta,\varphi) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2} = \hat{T}_R + \hat{T}_{ang}$$

Operator factorization: separation of radial and angular components

Particle **in** a Sphere

$$\hat{H} = \hat{T}_R + \hat{T}_{ang}$$

Particle **on** a Sphere

(a.k.a **rigid rotor**)

$$\hat{H} = \hat{T}_{ang}$$

$$r = const$$

Hydrogen-like

atoms

$$\hat{H} = \hat{T}_R + \hat{T}_{ang} + V(r)$$

with $V(r) = -\frac{1}{r}$

common form of solution

$$\Psi(r,\theta,\varphi) = R_{n,l}(r)Y_l^m(\theta,\varphi)$$

The difference in the Radial component

(a summary in advance)

Rigid rotor

$$R_{n,l}(r) = const$$

Particle-in-a-sphere

$$R_{n,l}(r) \sim j_l(k \cdot r)$$

Spherical **Bessel** functions of order l

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

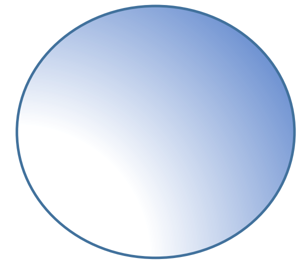
Hydrogen-like atoms

$$R_{n,l}(r) \sim L_{n-l-1}^{2l+1}(2\alpha \cdot r) \cdot e^{-\alpha r}$$

Laguerre polynomial
and
exponent

Angular kinetic energy

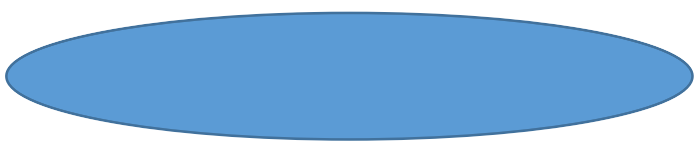
$$\hat{H} = \hat{T}_{ang} = \frac{\hat{L}^2}{2I}$$



Kinetic energy of rotational motion

I – moment of inertia

More general case:



$$\hat{H} = \frac{\hat{L}_x^2}{2I_x} + \frac{\hat{L}_y^2}{2I_y} + \frac{\hat{L}_z^2}{2I_z}$$

Lets looks at the commutation relationships first

Commutation of angular momentum components

$$\hat{L} = \hat{r} \times \hat{p} = \begin{pmatrix} \hat{y} \cdot \hat{p}_z - \hat{z} \cdot \hat{p}_y \\ \hat{z} \cdot \hat{p}_x - \hat{x} \cdot \hat{p}_z \\ \hat{x} \cdot \hat{p}_y - \hat{y} \cdot \hat{p}_x \end{pmatrix}$$

Using:

$$\left[\hat{x}, \hat{p}\right] = i\hbar$$

$$\left[A, BC\right] = B\left[A, C\right] + \left[A, B\right]C$$

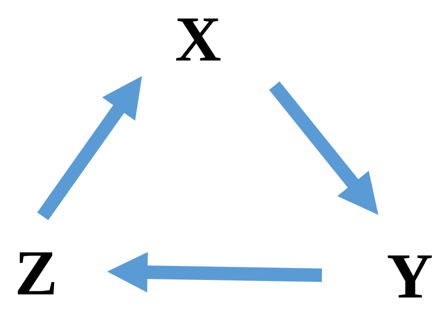
Show that

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar \hat{L}_z$$

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar \hat{L}_y$$

$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar \hat{L}_x$$

Mnemonics: cyclic permutations



Commutation with the total angular momentum

$$\left[\hat{L}_x, \hat{L}^2\right] = \left[\hat{L}_x, \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2\right] = \left[\hat{L}_x, \hat{L}_y^2 + \hat{L}_z^2\right]$$

$$\left[\hat{L}_x, \hat{L}_y^2\right] = \hat{L}_y\left[\hat{L}_x, \hat{L}_y\right] + \left[\hat{L}_x, \hat{L}_y\right]\hat{L}_y = i\hbar\left(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y\right)$$

$$\left[\hat{L}_x, \hat{L}_z^2\right] = \hat{L}_z\left[\hat{L}_x, \hat{L}_z\right] + \left[\hat{L}_x, \hat{L}_z\right]\hat{L}_z = i\hbar\left(\hat{L}_z\left(-\hat{L}_y\right) + \left(-\hat{L}_y\right)\hat{L}_z\right)$$

$$\left[\hat{L}_x, \hat{L}^2\right] = 0$$

Same for other components

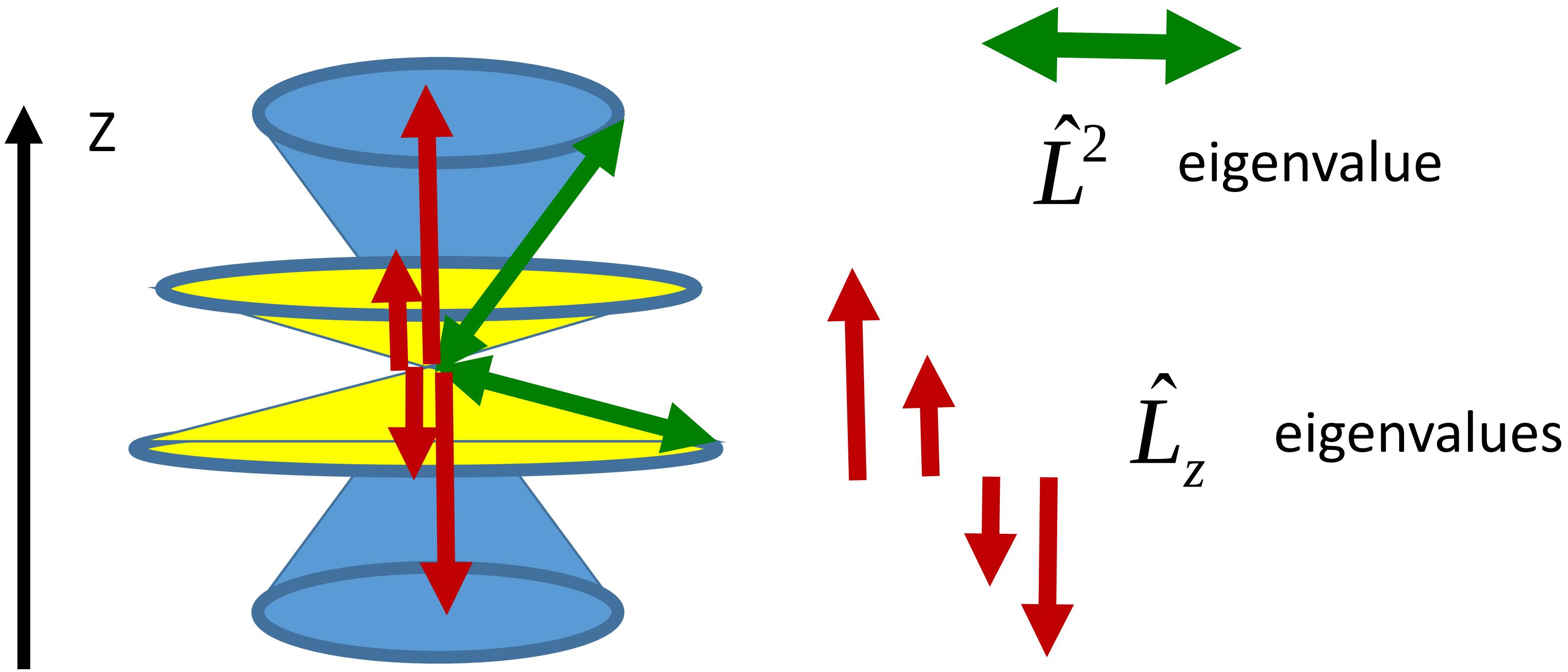
Summary: Quantization of Rotational DOF

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k$$

What does that mean?

$$\left[\hat{L}_i, \hat{L}^2\right] = 0, \forall i$$

What does that mean?



Back to the angular equation

$$\hat{H} = \frac{-\hbar^2}{2mr^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) = \hat{H}_\theta + \hat{H}_\varphi$$

We can separate variables then: $\Psi(\theta,\varphi) = f(\theta)\cdot g(\varphi)$

Because $\left[\hat{L}_z, \hat{L}^2\right] = 0$ $\Psi(\theta,\varphi) = f(\theta)\cdot g(\varphi)$

is also an eigenfunction of $\hat{L}_z$

which leads to

$$\hat{L}_z g(\varphi) = -i\hbar\frac{\partial}{\partial\varphi}g(\varphi) = \lambda g(\varphi) \Rightarrow g(\varphi) = Ne^{-i\frac{\lambda}{\hbar}\varphi}$$

Azimuthal part of wfc

Periodic boundary conditions: $$e^{i\frac{\lambda}{\hbar}(\varphi+2\pi)} = e^{i\frac{\lambda}{\hbar}\varphi} \Rightarrow e^{2\pi i\frac{\lambda}{\hbar}} = 1$$

$$\cos\left(2\pi\frac{\lambda}{\hbar}\right) = 1 \Leftrightarrow 2\pi\frac{\lambda}{\hbar} = 2\pi m, m \in Z$$

$$\Rightarrow \lambda = m\hbar$$

$$g(\varphi) = Ne^{-im\varphi}$$

Normalize!

$$g_m(\varphi) = \sqrt{\frac{1}{2\pi}}e^{-im\varphi}$$

$$m = 0, \pm 1, \pm 2, etc$$

Polar part of the wfc

$$\hat{H} f(\theta) e^{-im\varphi} = \frac{-\hbar^2}{2mr^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) f(\theta) e^{-im\varphi} = E f(\theta) e^{-im\varphi}$$

$$\frac{-\hbar^2}{2mr^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} - \frac{m^2}{\sin^2\theta} + \frac{2mr^2 E}{\hbar^2}\right) f(\theta) = 0$$

The solution is: **associated Legendre polynomial**

$$f_{l,m}(\theta) = P_l^{|m|}(\cos\theta) = \frac{1}{2^l l!}\sin^{|m|}\theta \frac{d^{l+|m|}}{d\cos(\theta)^{l+|m|}}\left(\cos^2\theta - 1\right)^l \qquad l = 0,1,2,\ldots$$

Overall solution: Spherical Harmonics

$$Y_l^m(\theta,\varphi)=(-1)^m\left(\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right)^{1/2}P_l^{|m|}(\cos\theta)e^{im\varphi}$$

The functions are **complex-valued**, but one can use real-valued linear combinations

Symmetries:

$$\left(Y_l^m\right)^*=(-1)^m Y_l^{-m}$$

Orthonormalization:

$$\int_0^{2\pi}d\varphi\int_0^{\pi}\left(Y_l^m\right)^* Y_{l'}^{m'}\sin\theta d\theta=\langle l,m|l',m'\rangle=\delta_{l,l'}\delta_{m,m'}$$

Note how the scalar product is defined (it contains an extra sin(theta))!

Eigenvalues:

$$\hat{L}^2 Y_l^m(\theta,\varphi)=l(l+1)\hbar^2 Y_l^m(\theta,\varphi)$$

$$\hat{L}_z Y_l^m(\theta,\varphi)=m\hbar Y_l^m(\theta,\varphi)$$

Some important points

$\hat{L}^2$ Defines the magnitude of the vector

$\hat{L}_z$ Defines the projection of the vector

so: $m^2 \leq l(l+1) \Rightarrow -l \leq m \leq l$

there are 2l+1 degenerate states for a given l

Total magnitude is always a bit large than the max. projection (uncertainty principle in action!!!)

Linear combinations of spherical harmonics "pre-Atomic orbitals"

S-states (spherically-symmetric)

$$Y_0^0 = \frac{1}{2\sqrt{\pi}}$$

P-states

$$Y_1^{-1} = \frac{1}{2}\sqrt{\frac{3}{2\pi}} e^{-i\varphi} \sin\theta \qquad Y_1^{1} = \frac{1}{2}\sqrt{\frac{3}{2\pi}} e^{i\varphi} \sin\theta$$

$$Y_1^0 = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta = \frac{1}{2}\frac{z}{r}\sqrt{\frac{3}{\pi}}$$

$$Y_1^{-1} + Y_1^{1} = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\left(e^{-i\varphi} + e^{i\varphi}\right)\sin\theta = \sqrt{\frac{3}{2\pi}}\cos\varphi\sin\theta = \frac{x}{r}\sqrt{\frac{3}{2\pi}}$$

$$i\left(Y_1^{-1} - Y_1^{1}\right) = \frac{i}{2}\sqrt{\frac{3}{2\pi}}\left(e^{-i\varphi} - e^{i\varphi}\right)\sin\theta = \sqrt{\frac{3}{2\pi}}\sin\varphi\sin\theta = \frac{y}{r}\sqrt{\frac{3}{2\pi}}$$

Raising/Lowering operators

$$L_+ = L_x + iL_y$$
$$L_- = L_x - iL_y$$

$$\left[L_\pm, L^2\right] = 0$$
$$\hat{L}^2 Y_l^m(\theta,\varphi) = l(l+1)\hbar^2 Y_l^m(\theta,\varphi)$$

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$$
$$\left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x$$

$$\left[\hat{L}_z, \hat{L}_+\right] = \left[\hat{L}_z, \hat{L}_x\right] + i\left[\hat{L}_z, \hat{L}_y\right] = i\hbar\hat{L}_y + \hbar\hat{L}_x = \hbar\hat{L}_+$$

$$\hat{L}^2\hat{L}_\pm Y_l^m(\theta,\varphi) = \hat{L}_\pm\hat{L}^2 Y_l^m(\theta,\varphi) = \hat{L}_\pm l(l+1)\hbar^2 Y_l^m(\theta,\varphi) = l(l+1)\hbar^2\left(\hat{L}_\pm Y_l^m(\theta,\varphi)\right)$$

same is for $\hat{L}_z$ **do not change L**

$$\hat{L}_z\hat{L}_\pm Y_l^m = \hat{L}_\pm\hat{L}_z Y_l^m + \left[\hat{L}_z, \hat{L}_\pm\right] Y_l^m = \hat{L}_\pm m\hbar Y_l^m \pm \hbar\hat{L}_\pm Y_l^m = \hbar(m \pm 1)\left(\hat{L}_\pm Y_l^m\right)$$

$\hat{L}_{\pm} Y_l^m$ is an eigenstate of $\hat{L}_z$ corresponding to m+/- 1

$$\hat{L}_{\pm} Y_l^m = C_{l,m}^{\pm} Y_l^{m\pm1}$$

$$\hat{L}_{+}\hat{L}_{-} = \hat{L}^2 - \hat{L}_z^2 \pm \hbar \hat{L}_z$$

$$\left\langle \hat{L}_{\pm} Y_l^m \middle| \hat{L}_{\pm} Y_l^m \right\rangle = \left\langle Y_l^m \middle| \hat{L}_{\mp}\hat{L}_{\pm} \middle| Y_l^m \right\rangle = \left\langle Y_l^m \middle| \hat{L}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z \middle| Y_l^m \right\rangle \geq 0$$

$$l(l+1) \geq m^2 \pm m \Rightarrow -l < m < l$$

$$\left| C_{l,m}^{\pm} \right|^2 = l(l+1) - m^2 \mp m \Rightarrow C_{l,m}^{\pm} = \sqrt{l(l+1) - m(m \pm 1)}$$

$$\hat{L}_{\pm} Y_l^m = \sqrt{l(l+1) - m(m \pm 1)}\, Y_l^{m\pm1}$$

Spin

$$\hat{S}_x = \frac{1}{2}\hat{\sigma}_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\hat{S}_y = \frac{1}{2}\hat{\sigma}_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\langle \alpha | \beta \rangle = \begin{pmatrix} 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0$$

$$\hat{S}_z = \frac{1}{2}\hat{\sigma}_x = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\hat{S}_x\alpha = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{2}\beta \qquad \hat{S}_y\alpha = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 0 \\ i \end{pmatrix} = \frac{i}{2}\beta \qquad \hat{S}_z\alpha = \frac{1}{2}\alpha$$

$$\hat{S}_x\beta = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}\alpha \qquad \hat{S}_y\beta = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} -i \\ 0 \end{pmatrix} = -\frac{i}{2}\alpha \qquad \hat{S}_z\beta = -\frac{1}{2}\beta$$

Non-collinear

$$S^2\alpha = \left(\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2\right)\alpha = \frac{3}{4}\alpha$$

$$S^2\beta = \left(\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2\right)\beta = \frac{3}{4}\beta$$

$$\left(\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1\hat{S}_2\right)\beta(1)\alpha(2) =$$
$$= \frac{3}{4}\beta(1)\alpha(2) + \beta(1)\frac{3}{4}\alpha(2) + 2\left(\frac{1}{2}\alpha(1)\frac{1}{2}\beta(2) + \frac{i}{2}\alpha(1)\frac{-i}{2}\beta(2) + \frac{-1}{2}\beta(1)\frac{1}{2}\alpha(2)\right) =$$
$$= \frac{3}{2}\beta(1)\alpha(2) + \alpha(1)\beta(2) - \frac{1}{2}\beta(1)\alpha(2) = \beta(1)\alpha(2) + \alpha(1)\beta(2)$$

$$\left(\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1\hat{S}_2\right)\alpha(1)\beta(2) = \alpha(1)\beta(2) + \beta(1)\alpha(2)$$

$$\left(\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1\hat{S}_2\right)[\beta(1)\alpha(2) - \alpha(1)\beta(2)] = [\beta(1)\alpha(2) + \alpha(1)\beta(2)] - [\alpha(1)\beta(2) + \beta(1)\alpha(2)] = 0$$