# Theoretical Biophysics
# -
# Quantum Theory and Molecular Dynamics

Pawel Romanczuk
WS 2017/18

**http://lab.romanczuk.de**/teaching/

# Introduction

Two pillars of classical theoretical physics
at the begin of 20th century:

| Matter | Radiation |
|---|---|
| particles / trajectories | waves / fields |
| • classical mechanics (Newton, Lagrange, Hamilton)<br>• statistical mechanics (Maxwell, Boltzmann,Gibbs,…)<br>• classical thermodynamics (Carnot, Maxwell, Clausius, Gibbs,...) | • classical electrodynamics (Maxwell, Faraday, Hertz,...) |

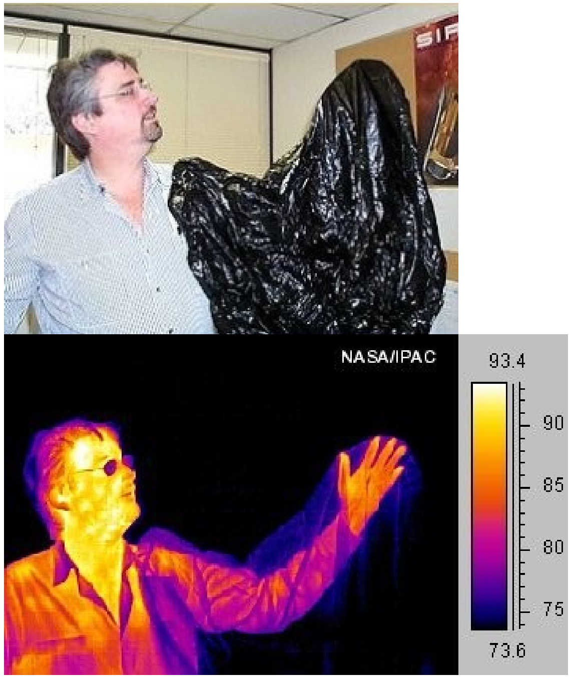
However, more and more experimental observations accumulated which could not be explained by these theories.

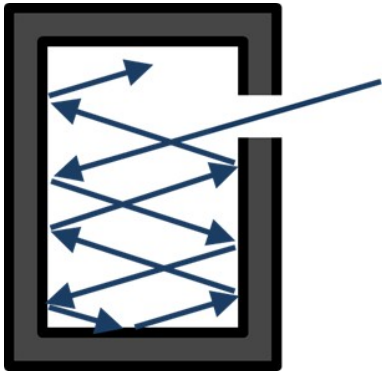
# Quantum nature of radiation

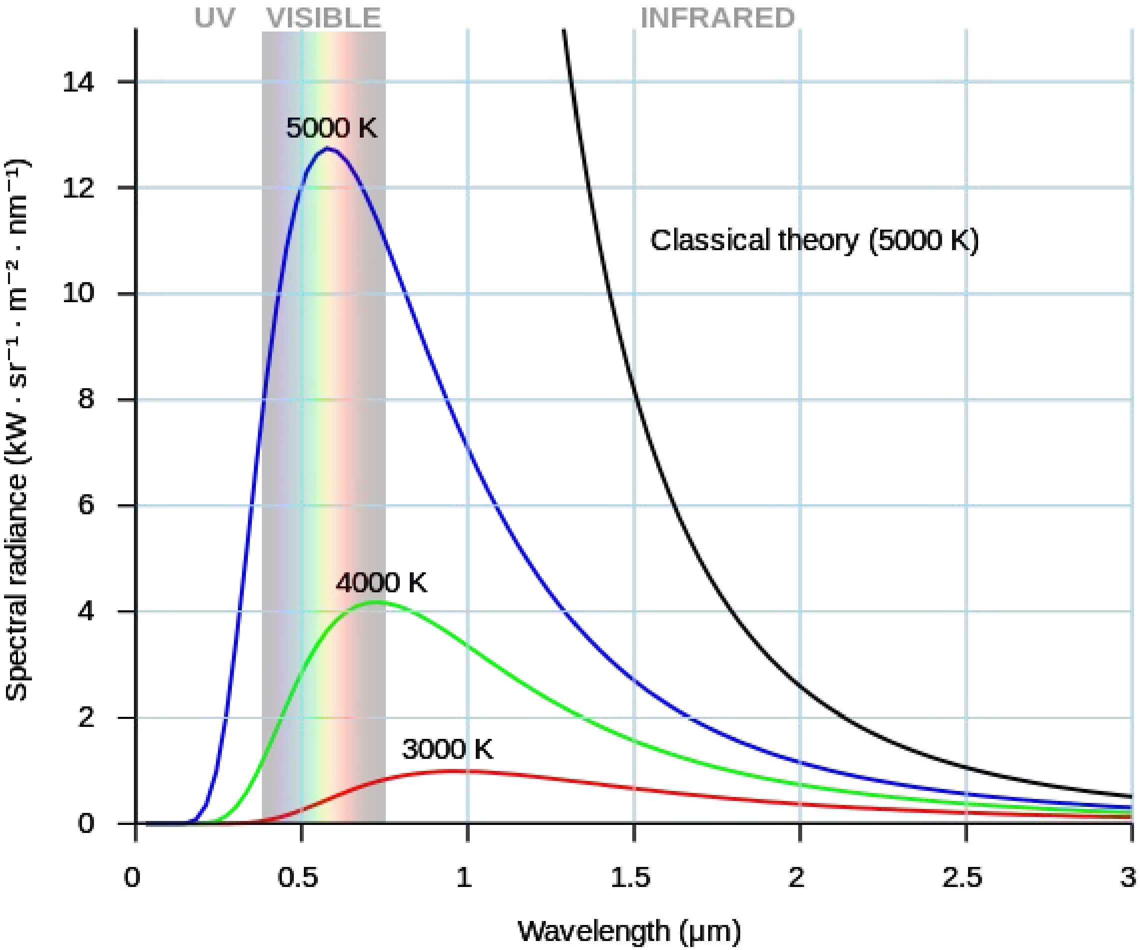
**particle-wave dualism**

- not explainable by classical electrodynamics
- radiation → electromagnetic waves
- many experimental observations

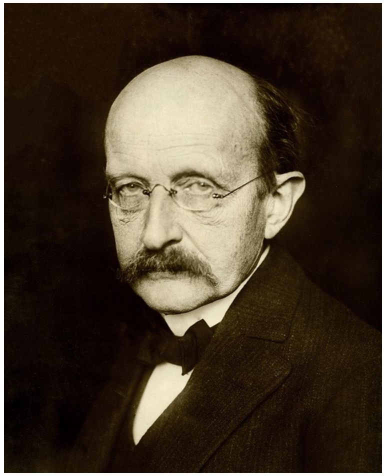
# Black body radiation







# Planck's law



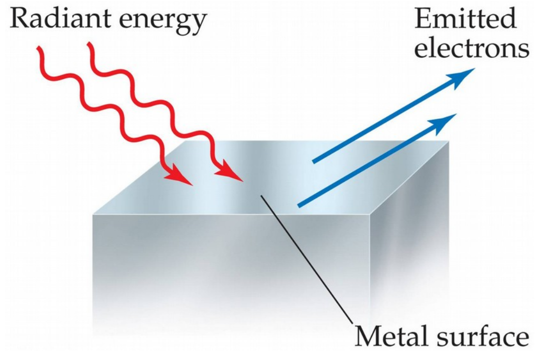
Planck's theory describing black body radiation (1900):

- phenomenological assumption → emission and absorption of energy only possible in packets (“quanta”)

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

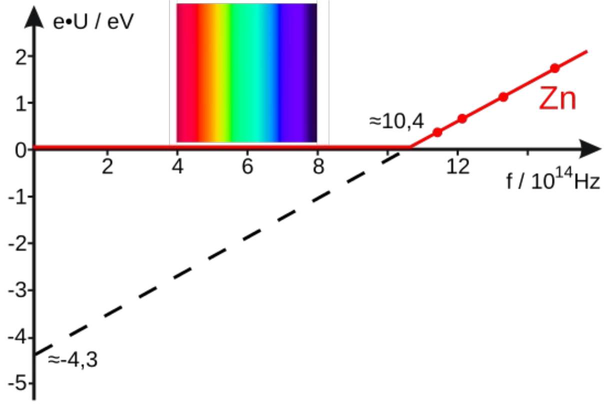
$$h = 6,63 \cdot 10^{-34} Js = 4.14 \cdot 10^{-15} eVs$$

# Photoelectric effect



Experimental observations:

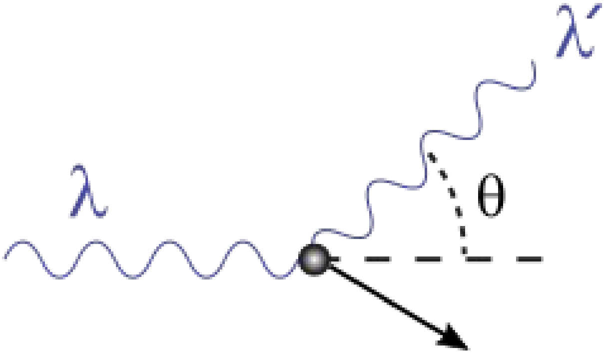
- there exists a threshold frequency for emission of electrons
- number of emitted electrons proportional to the intensity of light
- kinetic energy of electrons proportional to frequency of light but completely independent on intensity!



Theoretical explanation by Einstein (1905)
→radiation consists of photons with energy

$$E = h\nu$$

# Compton effect



X-ray scattering can be understood as inelastic collision of 'particles' (1923):

- energy of photons: $E = h\nu = pc$
- momentum of a photon: $p = \frac{h\nu}{c} = \frac{h}{\lambda}$

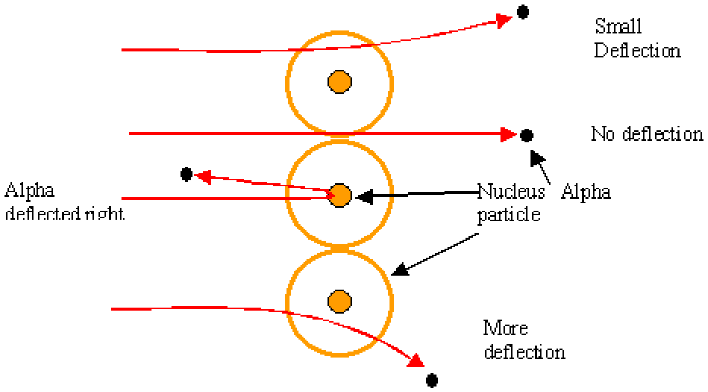
# Building blocks of matter

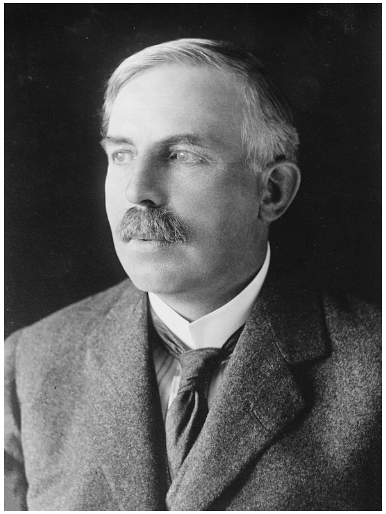
- Structure and stability of 'fundamental' units of matter (atoms) can not be explained by classical mechanics and electrodynamics.

# 'Planetary model' of an atom

Rutherford scattering (1911):

- radius of nucleus: $R_n \approx 10^{-14} m$
- radius of atom (electron orbit): $R_n \approx 10^{-10} m$





Classical electrodynamics → unstable configuration:

- accelerated charge (electron rotating around nucleus) must radiate and lose energy
- classically predicted life times: $\tau \approx 10^{-11} s$

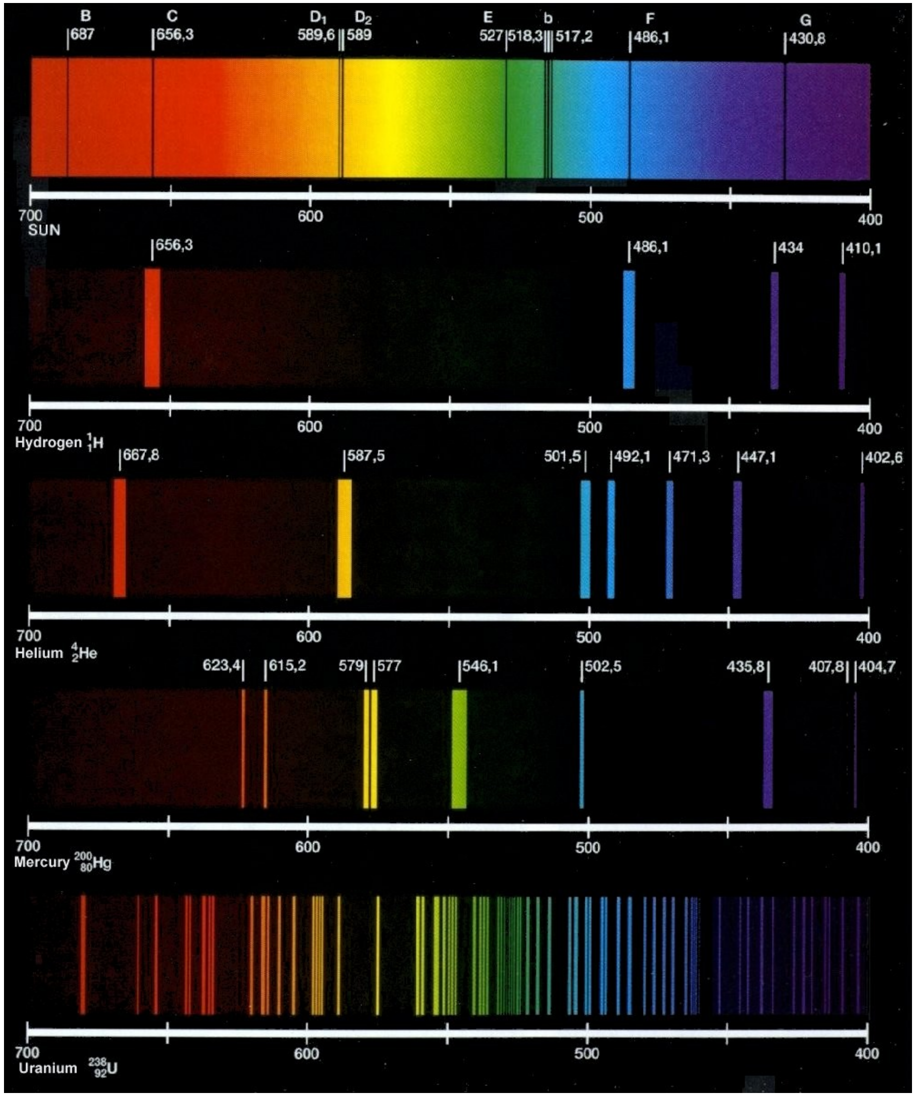
# Spectral lines

- Spectral lines (emission/absorption) - „fingerprints“ of atoms and molecules  cannot be explained by classical electrodynamics

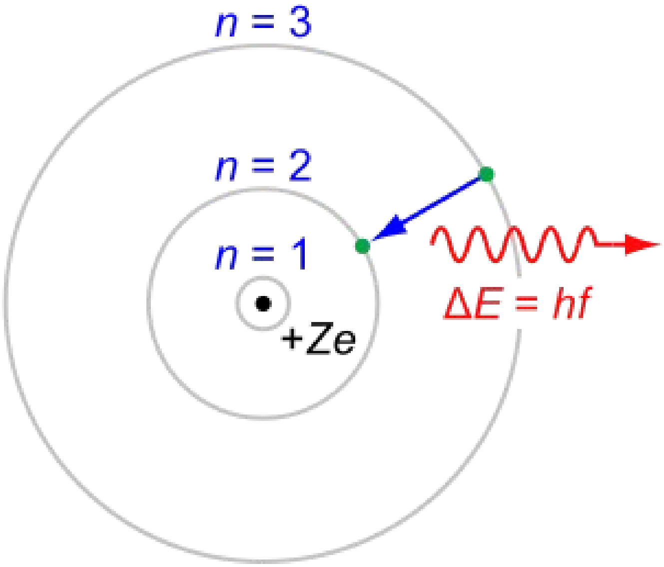
- only empirical formulas, e.g. for hydrogen Balmer/Rydberg:

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

$$n, m \in \mathbb{N},\ n > m$$



# Bohr model



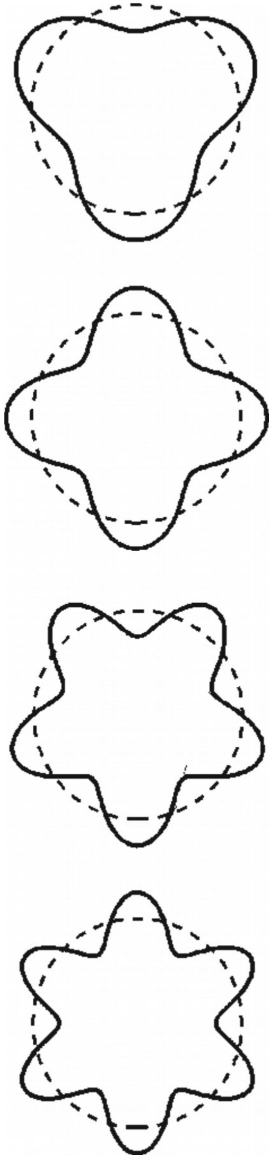
- atom model by Bohr (1913): classical mechanics + additional postulates
  1) stable quantized orbits (radiation free)
  2) emission/absorption → electron transitions between orbits

$$h\nu = \Delta E = E_n - E_m$$

→ Balmer/Rydberg formula

- fails for more complicated atoms (He)
- ad-hoc assumptions

# Matter Waves



- de Broglie hypothesis (1923/24): particles (electrons, protons etc) can be ascribed a wavelength (frequency) following Planck/Einstein formulae

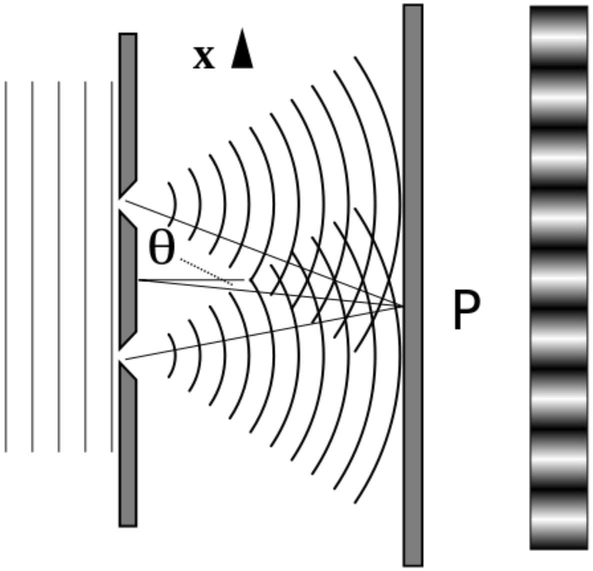
$$p = mv = \frac{h}{\lambda} \qquad E = h\nu$$

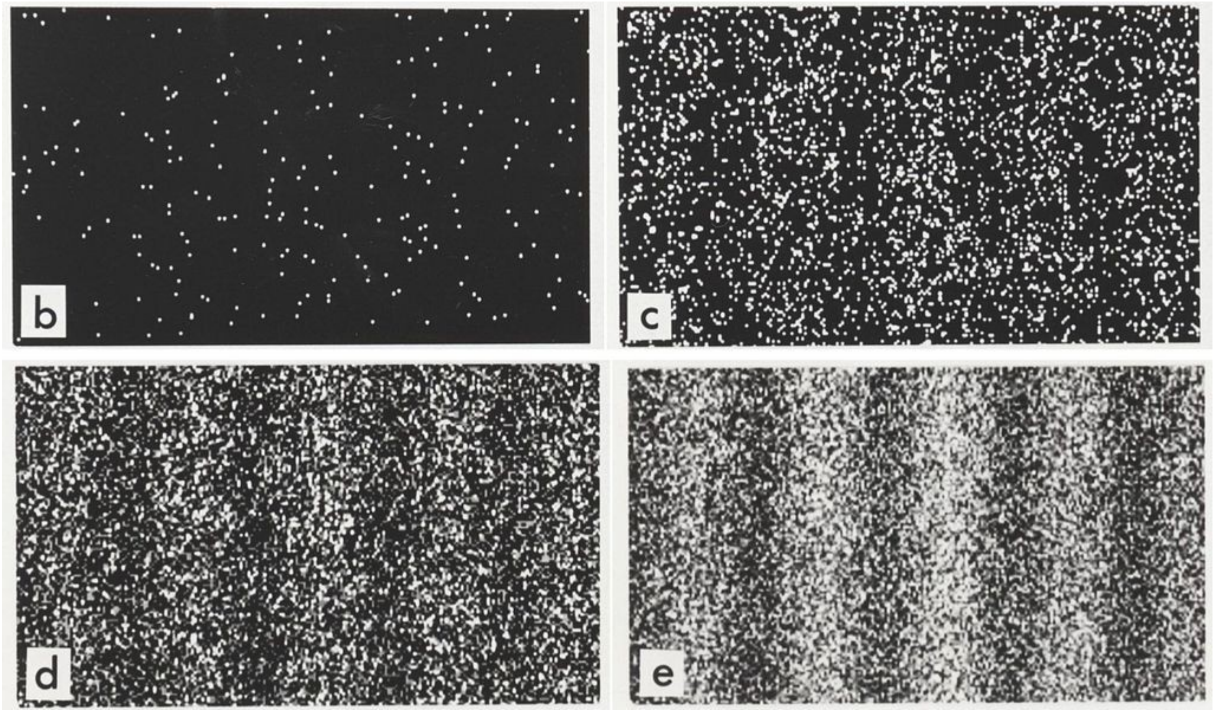
- combination with Bohrs first postulate allows interpretation of quantized orbits as standing waves.

**Can we observe wave nature of particles directly?**

# Electrons as Waves

- de Broglie hypothesis was confirmed experimentally with diffraction experiments in 1927 (Davisson/Germer, Thomson)





# Wave-particle dualism for radiation and matter

- Bad news: both pillars of theoretical physics affected
- Good news: similar phenomena & problems
→ theoretical solution maybe also similar

Final outcome a single unifying theory for both classical pillars: **Quantum Theory** (incl. Quantum Field Theory)

# Correspondence principle

- All (microscopic) objects obey quantum mechanics
- But for large systems and/or high energies classical mechanics & electrodynamics provide good quantitative prediction
- Classical theories → limiting cases for large systems (many coupled degrees of freedom) or large quantum numbers (high energies)

# Quantum Biophysics

Quantum Biophysics (Molecular Quantum Physics): Quantum approach to biophysical systems and biomolecules.

Theoretical foundation for:

- biochemistry (quantum chemistry)
- quantitative methods (photophysics, spectroscopy)
- biological function of quantum systems (e.g. photosynthesis, enzymatic activity, etc)

# Postulates of Quantum Mechanics

- Fundamental assumptions
- Cannot be derived from some more basic principles
- Whatever we do in quantum theory, must make sense in the light of these postulates.

# 1st Postulate – Quantum States

The state of a system is fully described by its **wave function**:

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}, t) = \psi(\mathbf{r_1}, t)\psi(\mathbf{r_2}, t), \ldots \psi(\mathbf{r_N}, t)$$

- The wave function depends on the coordinates of all particles in the system.
- it is complex and not directly measurable
- motivated by the wave-particle dualism
- for non-interacting particles it can be decomposed into a product of single particle functions:

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}, t) = \psi(\mathbf{r_1}, t)\psi(\mathbf{r_2}, t), \ldots \psi(\mathbf{r_N}, t)$$

# Wave Functions

- Probabilistic interpretation: The square of the wave function $|\psi(\mathbf{r},t)|^2$ is proportional to the probability to find the particle in the time interval $dt$ at position $\boldsymbol{r}+d\boldsymbol{r}$

As a consequence $\psi(\mathbf{r},t)$

- has unique definition $\mathbf{r},t \to \psi(\mathbf{r},t)$
- must be continuous
- must have a continuous first derivative
  (Exception: points in space with infinite potential)
- must be quadratically integrable (in space - not time!)

$$\int_\Omega |\psi(\mathbf{r},t)|^2 d\mathbf{r} < \infty$$

# $2^{\text{nd}}$ Postulate: Observables

Each quantity $A$ that can be "measured" is described by linear, self-adjoint (hermitian) **operator** $\hat{A}$:

Definition: A hermitian operator is an an operator $\hat{A}$ that is its own hermitian (complex) conjugate.

$$\hat{A}^\dagger = \hat{A}$$

An important consequence:

*All eigenvalues of hermitian operator are real numbers.*

# 3rd Postulate: Measurement results

In any measurement of the observable associated with operator $\hat{A}$, the only values that will be ever observed are the eigenvalues $a$, which satisfy:

$$\hat{A}\Psi = a\Psi$$

- analogy to linear algebra (!)
- real numbers (see previous postulate)
- values of dynamical variables can be quantized (discrete, bound states), but also continuum of eigenvalues is possible (unbound states).

# Quantum Measurements

- If the system is in a quantum state which is a pure eigenstate of $\hat{A}$ with eigenvalue $a$ then any measurement of quantity $A$ will yield the value $a$
- An arbitrary ("mixed") quantum state can be expressed as linear superpositions of eigenstates:

$$\Phi = \sum_{i}^{n} c_i \Psi_i$$

- The values $c_i$ will be measured with the probability $|c_i|^2$
- A measurement of $c_i$ results in "collapse" of the wave function onto the corresponding eigenstate $\Psi_i$

**Measurement affects the system!**

# 4th Postulate: Expectation value

If the system is described by a **normalized** wave function:

$$\langle\Psi|\Psi\rangle = \int_\Omega d\mathbf{r}\Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t) = \int_\Omega d\mathbf{r}|\Psi(\mathbf{r},t)|^2 = 1$$

Then the average of multiple measurements is given by the **expectation value**:

$$\langle A\rangle = \left\langle \Psi \middle| \hat{A}\Psi \right\rangle = \int_\Omega d\mathbf{r}\Psi^*(\mathbf{r},t)\hat{A}\Psi(\mathbf{r},t)$$

# 5th Postulate: Schrödinger Equation

The state function of the system (wave function) evolves according to the time dependent Schrödinger equation:

$$\mathrm{i}\hbar\partial_t\Psi(\mathbf{r_1},\ldots,\mathbf{r_N},t) = \hat{H}\Psi(\mathbf{r_1},\ldots,\mathbf{r_N},t)$$

$$= -\frac{\hbar^2}{2m}\Delta\Psi(\mathbf{r_1},\ldots,\mathbf{r_N},t) + V\Psi(\mathbf{r_1},\ldots,\mathbf{r_N},t)$$

Hamilton operator: $\hat{H} = -\frac{\hbar^2}{2m}\Delta + \hat{V}$

→ operator of the total energy of the system