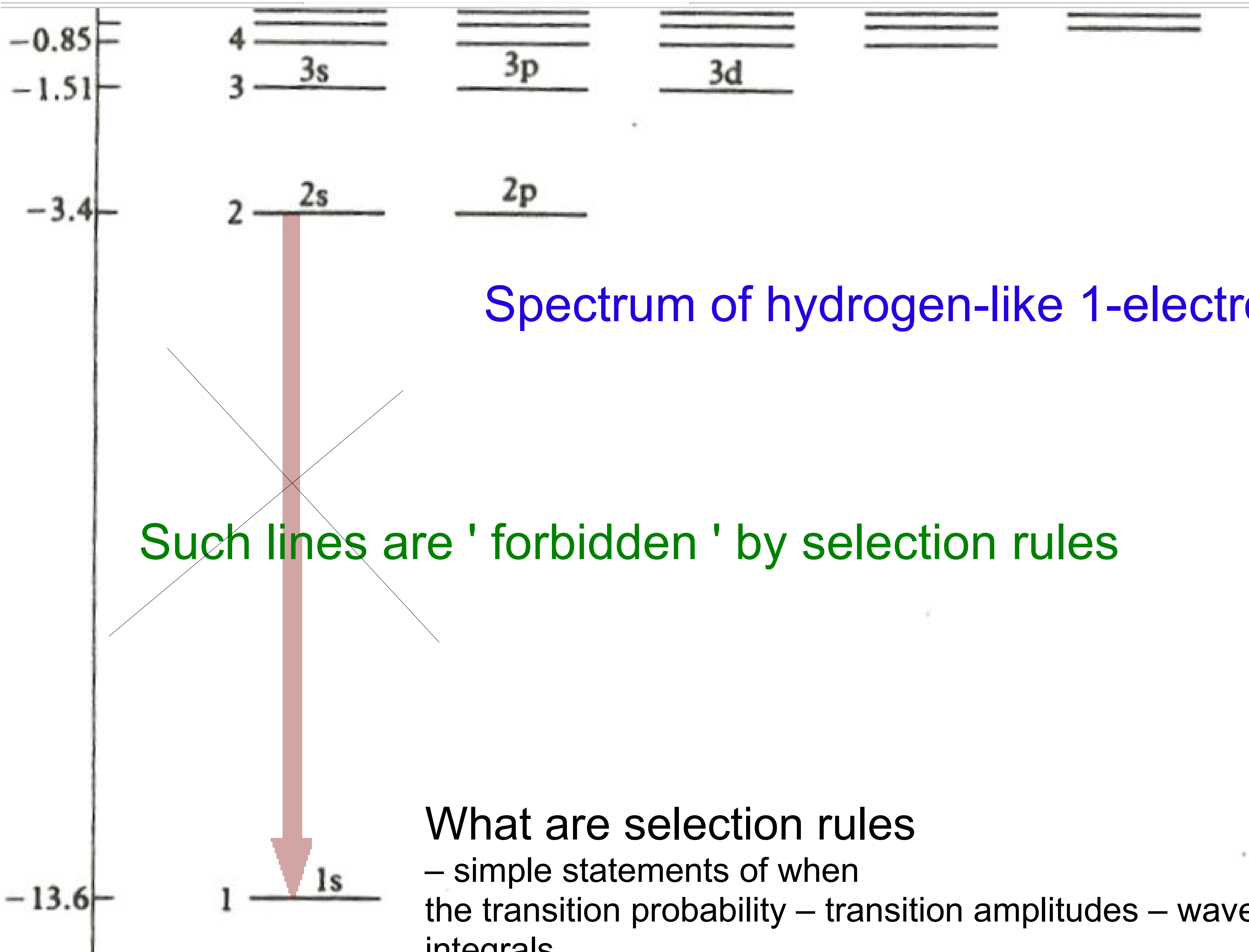
PHYS261 Atomic Physics and Physical Optics

Lecture Tuesday 2. September 2008

Topics:

1. Selection Rules, Parity – hydrogen-like levels
2. Helium Atom – starting the topic

Comment: Selection rules, transition probability ....
The theory of eletromagnetic transitions will be treated in detail later – in "Atoms and light" section

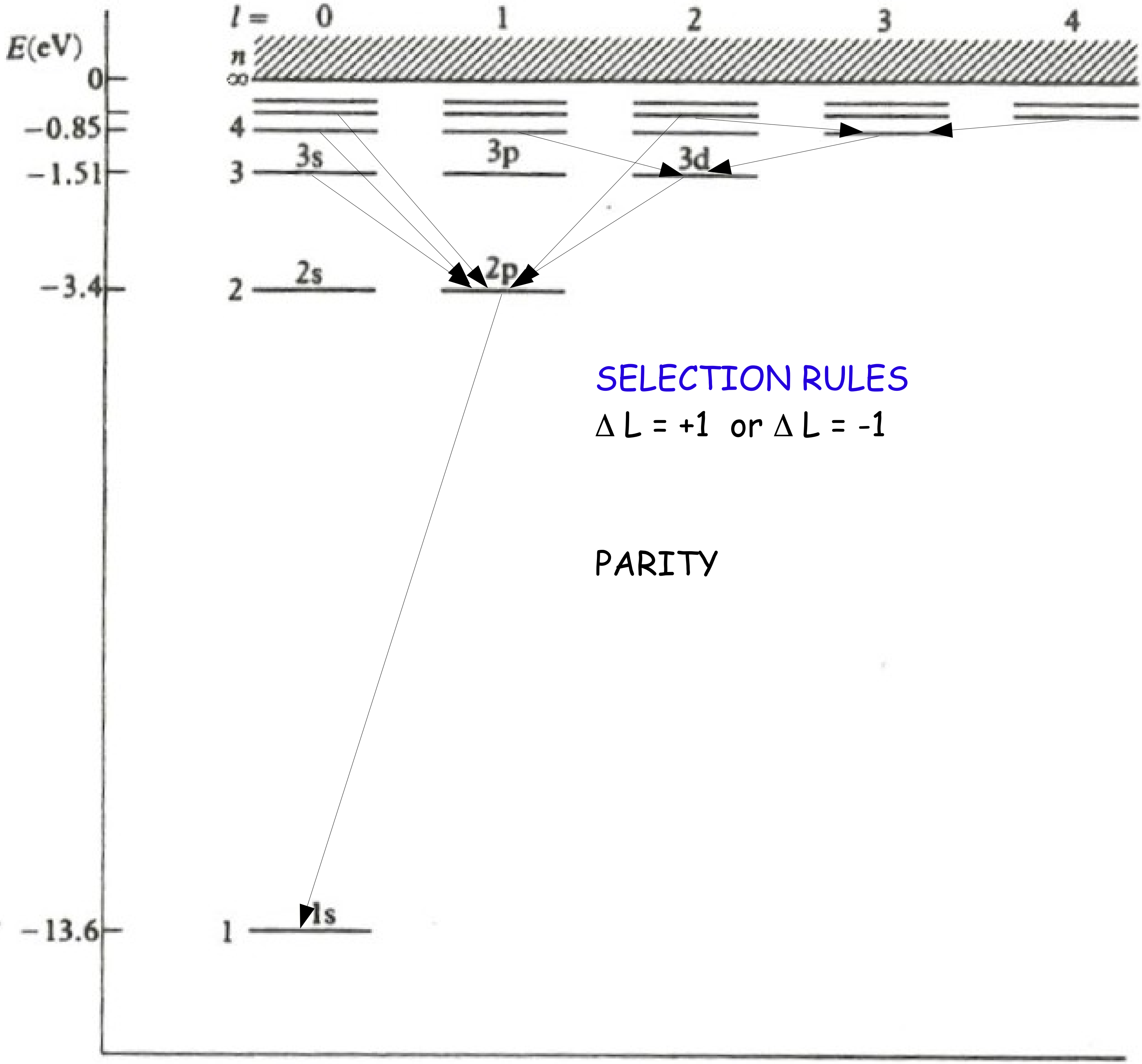


Spectrum of hydrogen-like 1-electron atom

Such lines are ' forbidden ' by selection rules

What are selection rules

– simple statements of when
the transition probability – transition amplitudes – wavefunction integrals
– are (non) zero



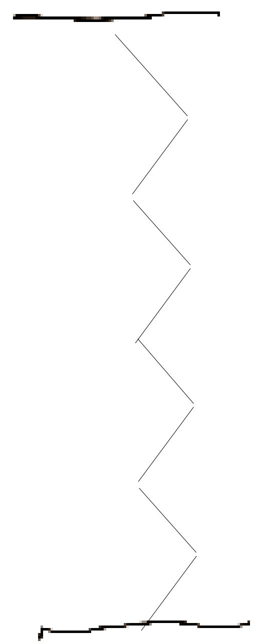
SELECTION RULES

$\Delta L = +1$ or $\Delta L = -1$

PARITY

Initial state (higher E)

$\psi_i(\vec{r})$



$\psi_f(\vec{r})$

lower E

Final state

total E conserved

Amplitude: $\langle \psi_f | H_I | \psi_i \rangle$

Simplified picture of a 'transition'

the transition probability – transition amplitudes – wavefunction integrals – are (non) zero

Amplitude: $\langle \psi_f | H_I | \psi_i \rangle$

Probabilities of transition $|\text{amplitude}|^2$

$$\langle \psi_f | H_I | \psi_i \rangle \equiv \int d^3\vec{r}\ \psi_f^*(\vec{r})\, H_I(\vec{r})\, \psi_i(\vec{r})$$

These must be different from 0

$H_i \propto \vec{r}$ (dipole)

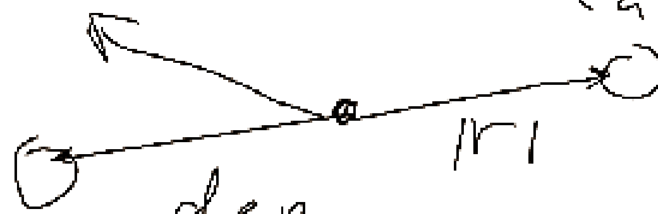
Simplified picture of a 'transition'

the transition probability – transition amplitudes – wavefunction integrals
– are (non) zero

The atom works as ' antenna ' - the dipole antenna is the simplest most efficient

$\underbrace{n, l=0}_{\text{const in angle}} \longrightarrow n, l=0$

const in angle



dep on absolute distance

$$\int \psi^*_{n_1 0} \, \vec{r} \, \psi_{n_2,0} \, d^3\vec{r} = 0$$

$$\int \psi^*_{n,l=1} \, \vec{r} \, \psi_{n_2 0} \, d^3 r \neq 0$$

$$\approx \int (\vec{r} \cdot \vec{r}) \, \psi_{n0} \, d\Omega \, dr$$

$|$to each minus contribution$|^2 \longrightarrow$ only ≥ 0

$z = a + ib \qquad z^* = a - ib$

$\Delta L = \pm 1$ gives nonzero

$\Delta L = l_f - l_i$

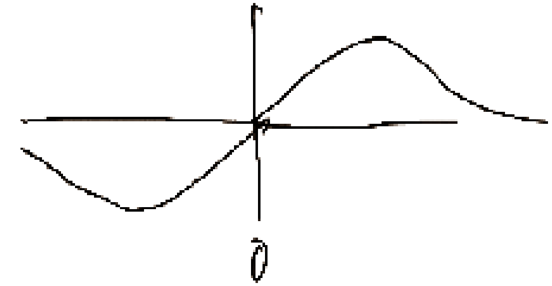
Parity of a function

1 dim

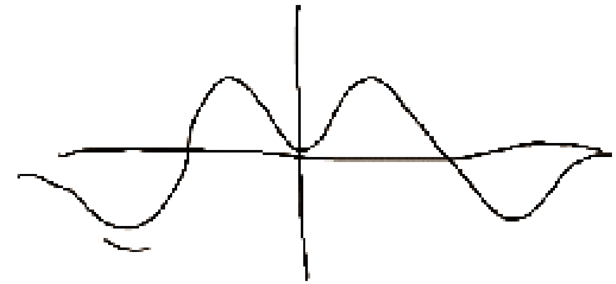
PARITY
is about relation

f(r) ?? f(-r)

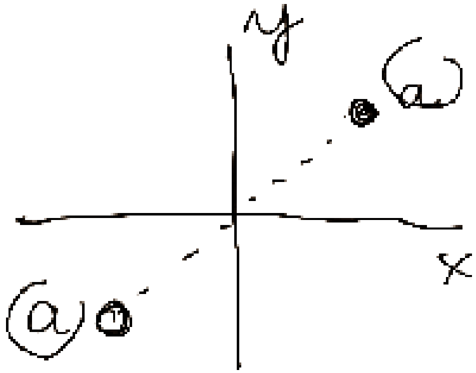
negative parity



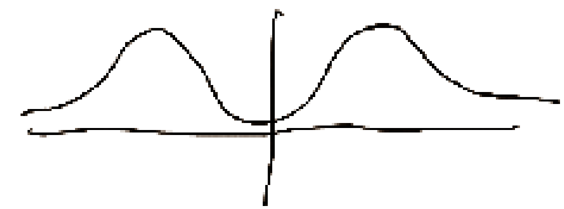
positive parity

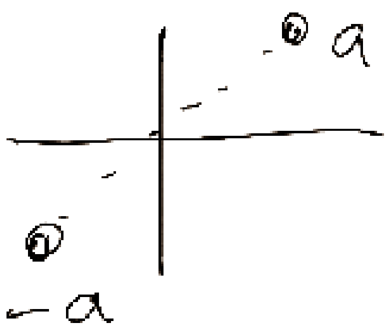


2 dim



positive parity





negative parity

mixed parity

$|f(x)| \neq |f(-x)|$

Find the decomposition $a^{+}(x) + b^{-}(x)$ in two parities

positive   negative

Homework on parity:

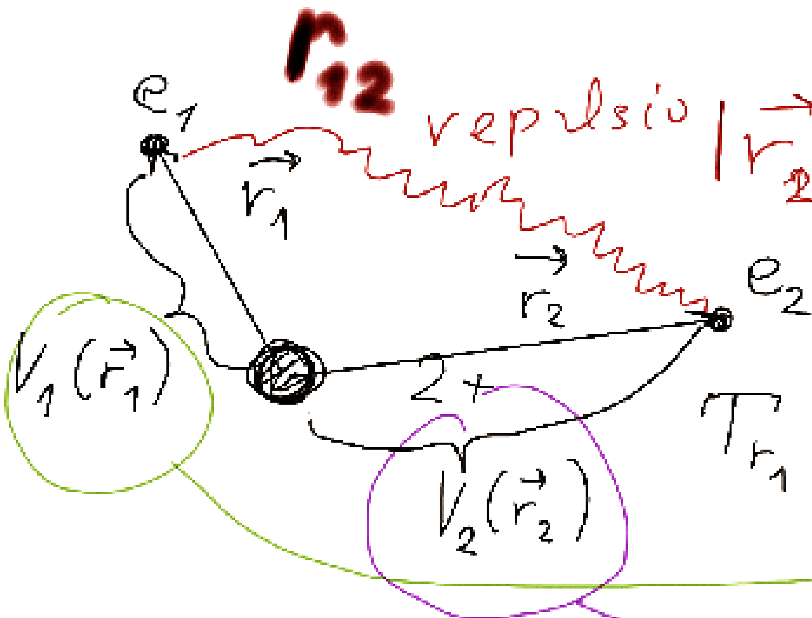
A mixed parity function is just any function $| f(x) |$ not equal to $| f(-x) |$

Find the decomposition of such general function f(x)
into a positive parity p(x) and negative parity n(x),
i.e. express p(x) and n(x) in terms of f(x)

Helium

2 electrons 2 charges -1

nucleus: 2 protons + 2 neutrons
total charge +2



Centre of mass of He is CM of $\underline{\underline{\alpha}}$

$$T_{r_1} + T_{r_2} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_2-\vec{r}_1|}$$

6-dimensional problem

$$T_{\vec{r}_1} \longrightarrow -\frac{\hbar^2}{2m_e}\nabla^2_{r_1} \qquad \frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}$$

$$T_{\vec{r}_2} \longrightarrow \nabla^2_{r_2} \cdots \qquad \frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}$$

$$r_1 = \sqrt{x_1^2+y_1^2+z_1^2}$$

$$r_{12} = |\vec{r}_1-\vec{r}_2| = \sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}$$

$$|r| = \sqrt{\vec{r}\cdot\vec{r}} \qquad = \sqrt{\vec{r}_1^{\,2}+\vec{r}_2^{\,2}-2\vec{r}_1\cdot\vec{r}_2}$$

$$H(\vec{r}_1, \vec{r}_2)\ \Psi(\vec{r}_1, \vec{r}_2) = E\ \Psi(\vec{r}_1, \vec{r}_2)$$

Start with <u>independent</u> electrons

(forget about $+\dfrac{e^2}{|\vec{r}_2 - \vec{r}_1|}$)

Probability density $\rho(\vec{r}) = |\psi(\vec{r})|^2$

$|\psi(\vec{r}_1, \vec{r}_2)|^2$ ...... e_1 at r_1 "at the
(correlation) e_2 at r_2 same time"

two independent events .... product of probabilities

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1)\ \psi_2(\vec{r}_2)$$

$$\rho(r_1 r_2) = \rho_1(r_1) \cdot \rho_2(r_2)$$

Independent probability densities

↓

Product of — " —

product of wave functions

$$\left[\underbrace{T_1 + V_1}_{r_1} + \underbrace{T_2 + V_2}_{r_2}\right] \psi_1(r_1)\, \psi_2(r_2) = E\, \psi_1(r_1)\, \psi_2(r_2)$$

$$\left[(T_1 + V_1)\, \psi_1(r_1)\right] \psi_2(r_2) + \left[(T_2 + V_2)\, \psi_1(r_1)\right] \psi_1(r_1) = E\, \psi_1(r_1)\, \psi_2(r_2)$$

$$\frac{(T_1 + V_1)\, \psi_1(r_1)}{\psi_1(r_1)} + \frac{(T_2 + V_2)\, \psi_2(r_2)}{\psi_2(r_1)} = E$$

Separation of variables

$\Downarrow$

2 independent equations

$$E = E_1 + E_2$$

$$(T_1 + V_1)\, \psi_1(r_1) = E_1\, \psi_1(r_1)$$

(and the same eq. for $\underline{\underline{2}}$)

Product wavefunction → still not the whole story
Because of the spin (Pauli)

So called Pauli Principle
Aufbau Prinzip (Build up) ....
In each state only 1 electron

Spin came from another "story"

The story of 1924-1930 development of
Quantum Mechanics
Atomic Theory
and Quantum Chemistry is fascinating!!
There were both Bohr and Heisenberg, but also Pauli, Heitler and London, and also Pauling