4) Many Particle Quantum Physics

So far (weeks 8 -10) we ever only dealt with **one** particle at a time

4.1.) Many particle wave function

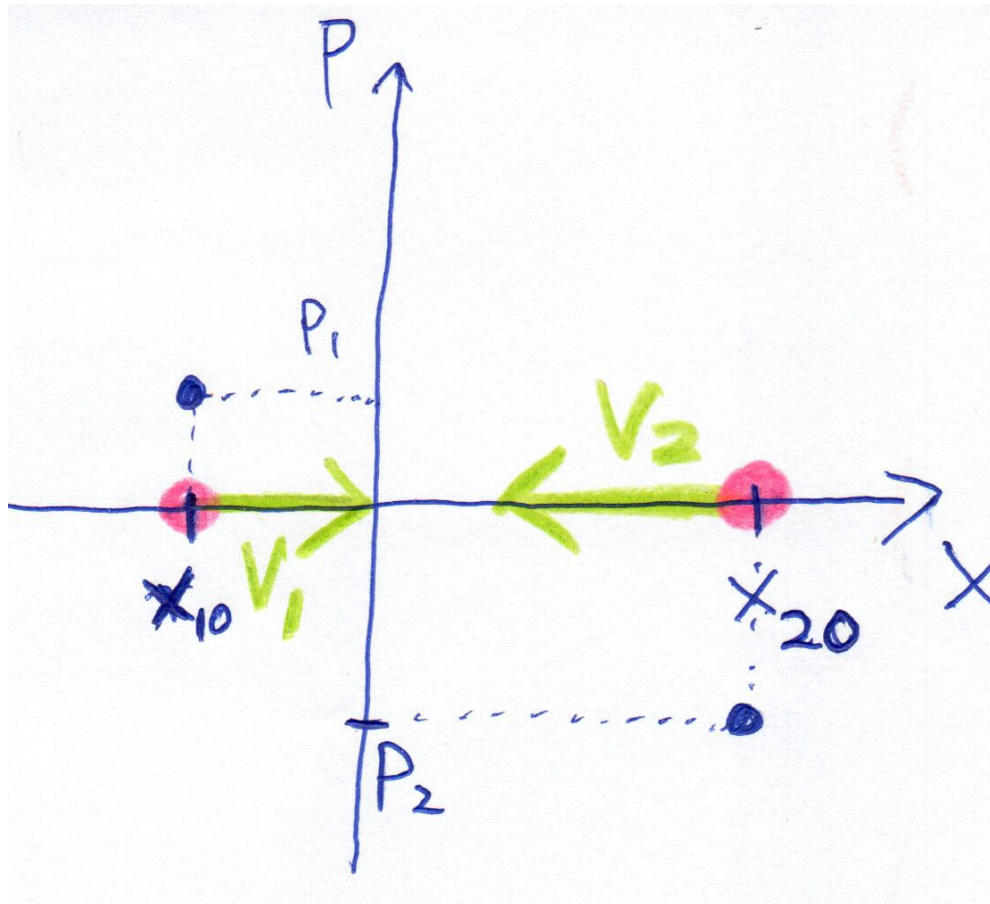Q: Classically,
two particles:

QM:

$$\vec{r}_1 \quad \vec{r}_2$$
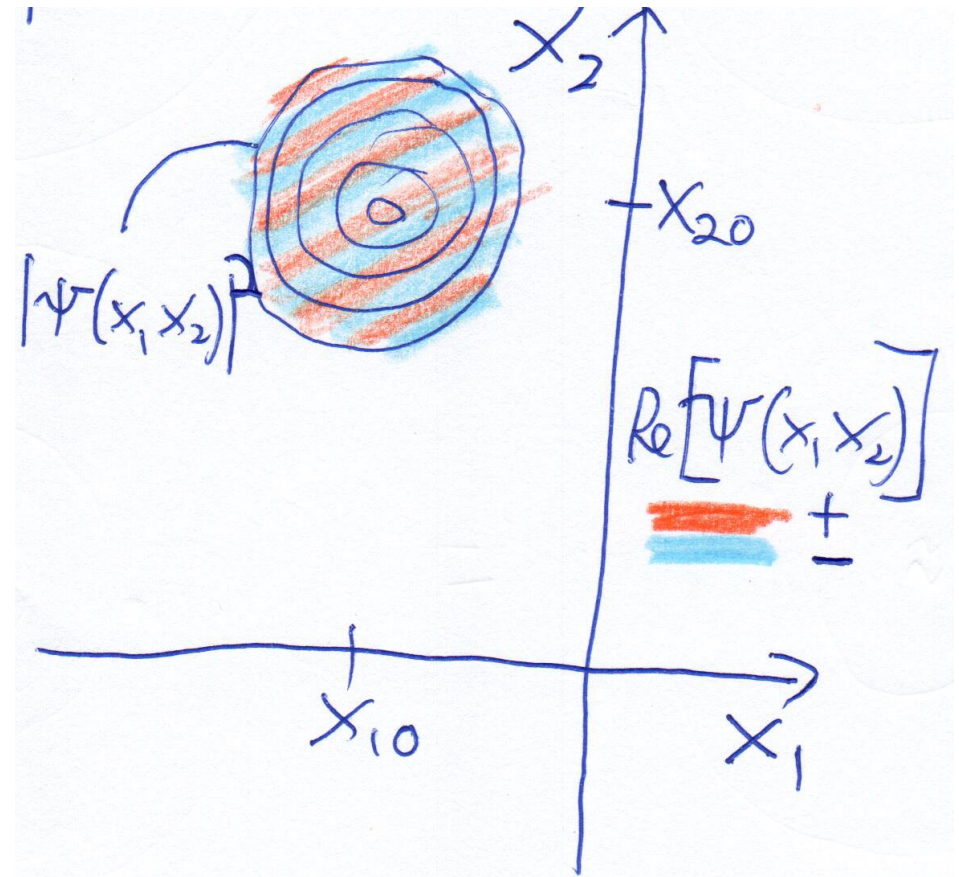
$$\vec{p}_1 \quad \vec{p}_2$$

$$\Psi(\vec{r}_1) \rightarrow \Psi(\vec{r}_1, \vec{r}_2)$$

Many particle wave function

Two particles treated **classically**, free to move in 1D
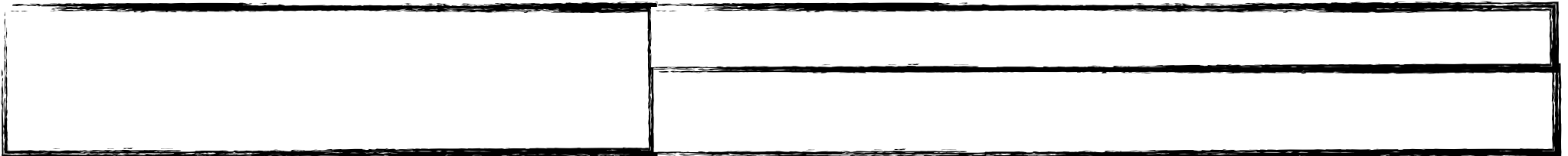
Two particles treated **quantum**, free to move in 1D

If free to move in 3D: 6D wave-function
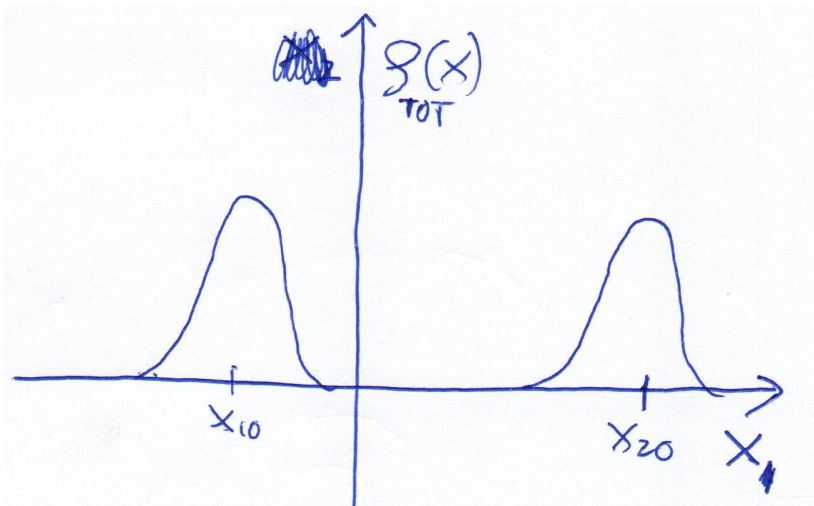
Many particle wave function

More details: two particles that can move in **one dimension** x

$$\Psi(x_1, x_2) = \mathcal{N} \exp(-(x_1 - 3)^2/\sigma_1^2)\exp(-(x_2 + 4)^2/\sigma_2^2)$$

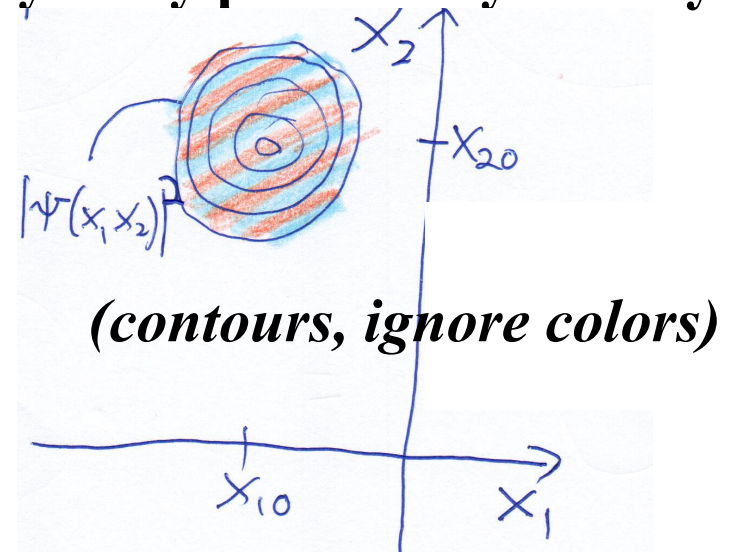Q: What does this example **mean?**

Total particle density

Many-body probability density

(contours, ignore colors)

4.1.1) Symmetries of the wave function

Consider now two identical particles (e.g. two electrons, or two gold atoms)

The Heisenberg uncertainty forces us to treat them as strictly **indistinguishable**

It turns out, this requires …

The two-particle wave function under **exchange** of the two particles must be either:

symmetric $\quad\quad\quad\quad \Psi(\vec{r}_1, \vec{r}_2) = + \Psi(\vec{r}_2, \vec{r}_1)$

or (142)

anti-symmetric $\quad\quad \Psi(\vec{r}_1, \vec{r}_2) = - \Psi(\vec{r}_2, \vec{r}_1)$

Symmetries of the wave function

The two-particle wave function under **exchange** of the two particles must be either:

$$\textbf{symmetric} \qquad \Psi(\vec{r}_1, \vec{r}_2) = + \Psi(\vec{r}_2, \vec{r}_1)$$
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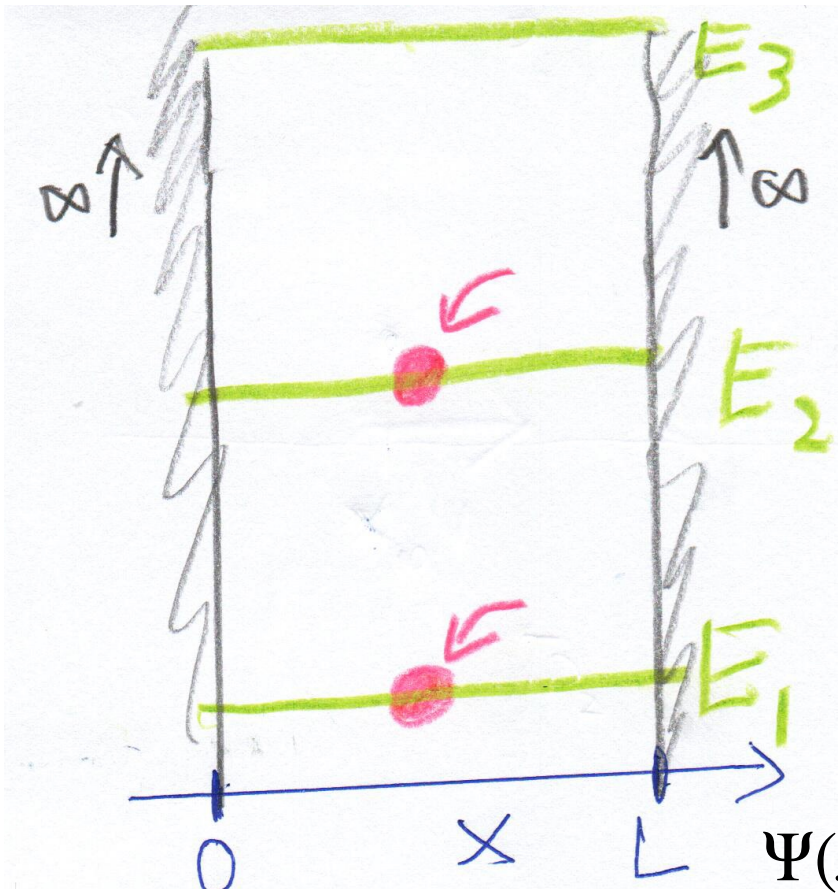
or (142)

It further turns out that….

symmetric $\qquad \leftrightarrow \qquad$ Bosons

anti-symmetric $\qquad \leftrightarrow \qquad$ Fermions

(143)

- These allocations follow from **relativistic quantum mechanics**

4.1.2) Pauli exclusion principle

Suppose we have two (non-interacting) Fermions in the infinite box (see Eq. 105).
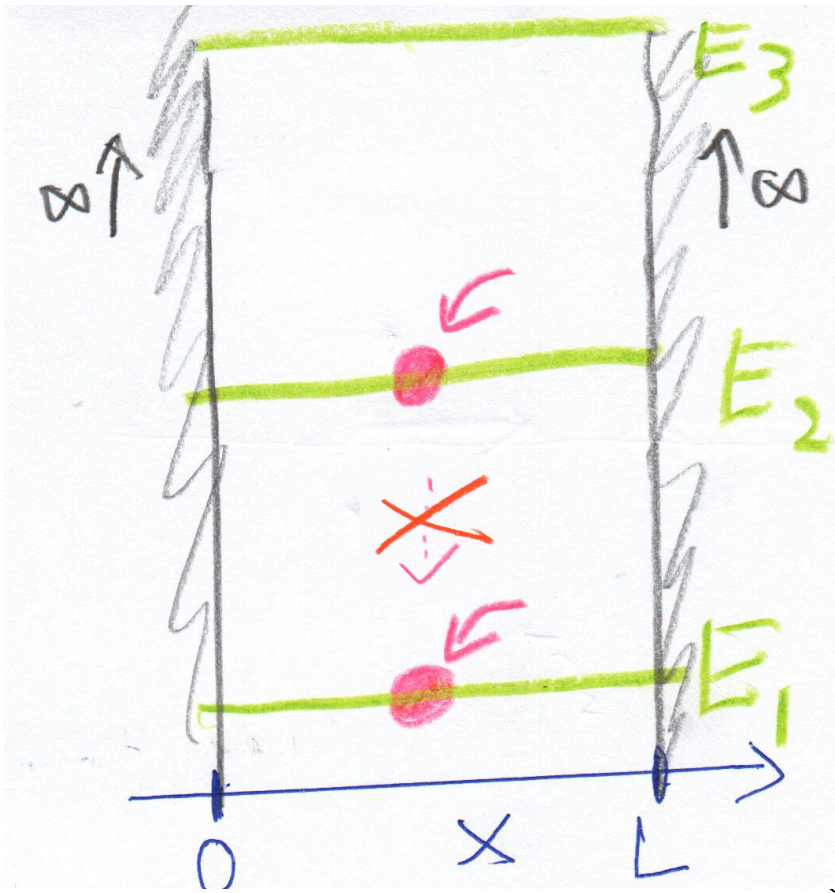

Each can be in one of the eigenstates, e.g.:

$$\Psi(x_1, x_2) = \phi_1(x_1)\phi_2(x_2) \quad \text{(144)}$$

But Eq. (144) is not **anti-symmetric** (142), we need:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)\right]$$

(145)

Pauli exclusion principle

Suppose we have two (non-interacting) Fermions in the infinite box (see Eq. 105).

Each can be in one of the eigenstates, e.g.:

$$\Psi(x_1, x_2) = \phi_1(x_1)\phi_2(x_2) \quad \textbf{(144)}$$

But Eq. (144) is not **anti-symmetric** (142), we need:

$$(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)\right]$$

$$\textbf{(145)}$$

Pauli exclusion principle

Q: now what happens if both Fermions are in the same state?

Again, this does not work due to wrong symmetry:

$$\Psi(x_1, x_2) = \phi_1(x_1)\phi_1(x_2) \qquad \textbf{(146)}$$

But now we also **cannot anti-symmetrize it!!!**

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\phi_1(x_1)\phi_1(x_2) - \phi_1(x_2)\phi_1(x_1)\right] = 0 \qquad \textbf{(147)}$$

This leads to the

Pauli-exclusion principle: **(148)**
Two identical Fermions, can never occupy the same quantum state.
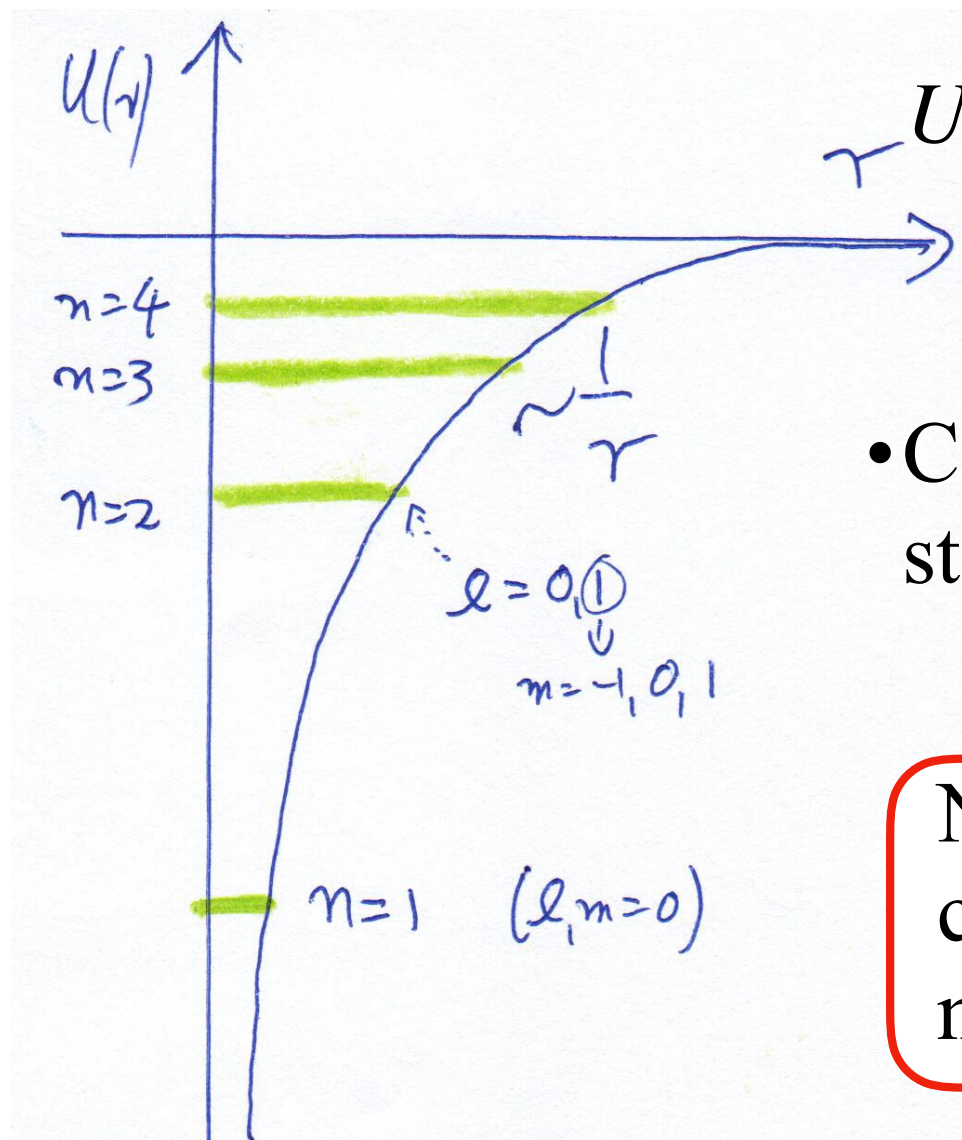
4.2) Many-Electron Atoms

From Helium upwards, atoms do contain many identical Fermions (electrons) $N_e \Rightarrow$ Pauli exclusion

Let us for the moment **assume** all electrons are attracted to the nucleus, but do not repel each other
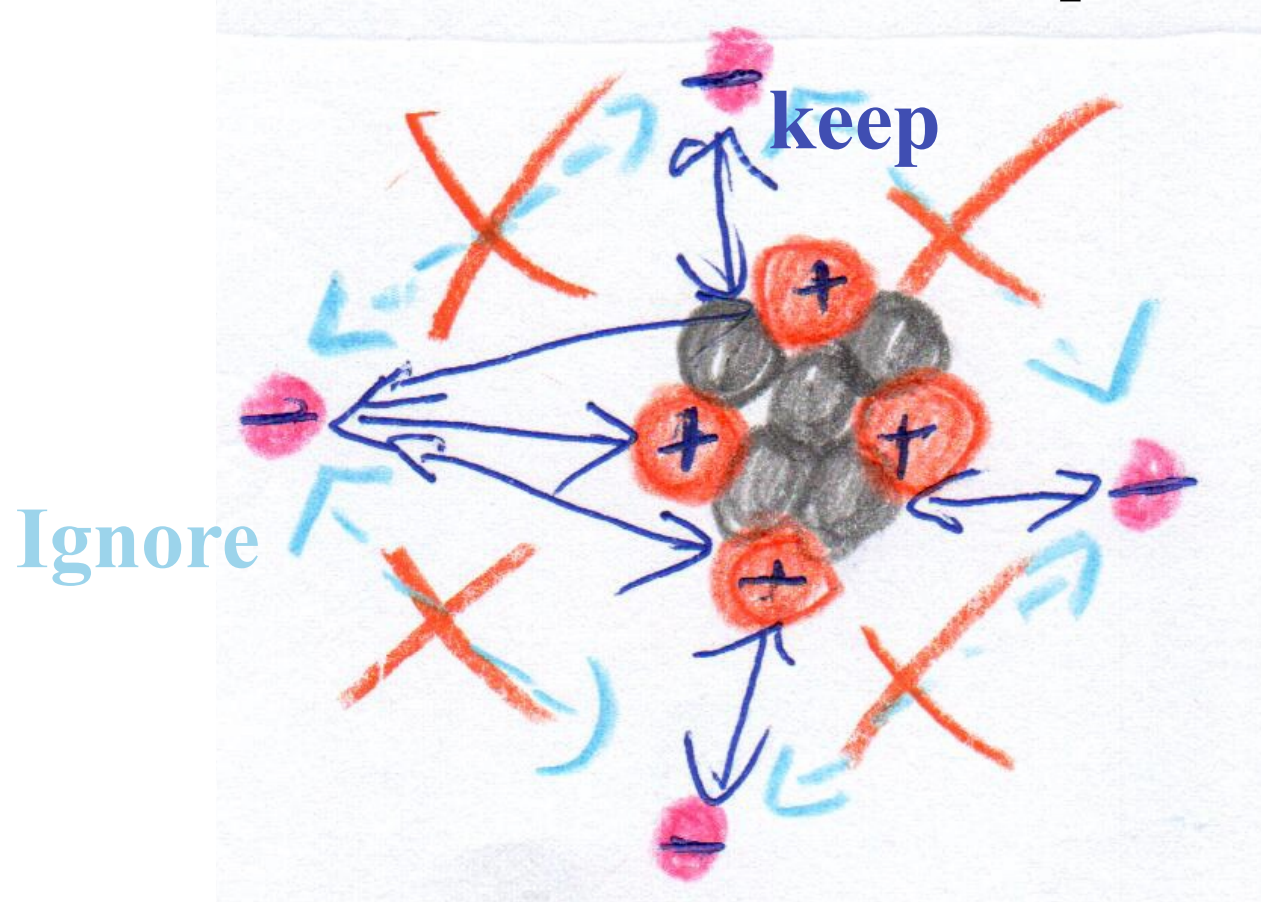
4.2.1) Atomic shells

This means each electron state can be calculated like for Hydrogen/week 10 (with higher nuclear charge Q=Ze).
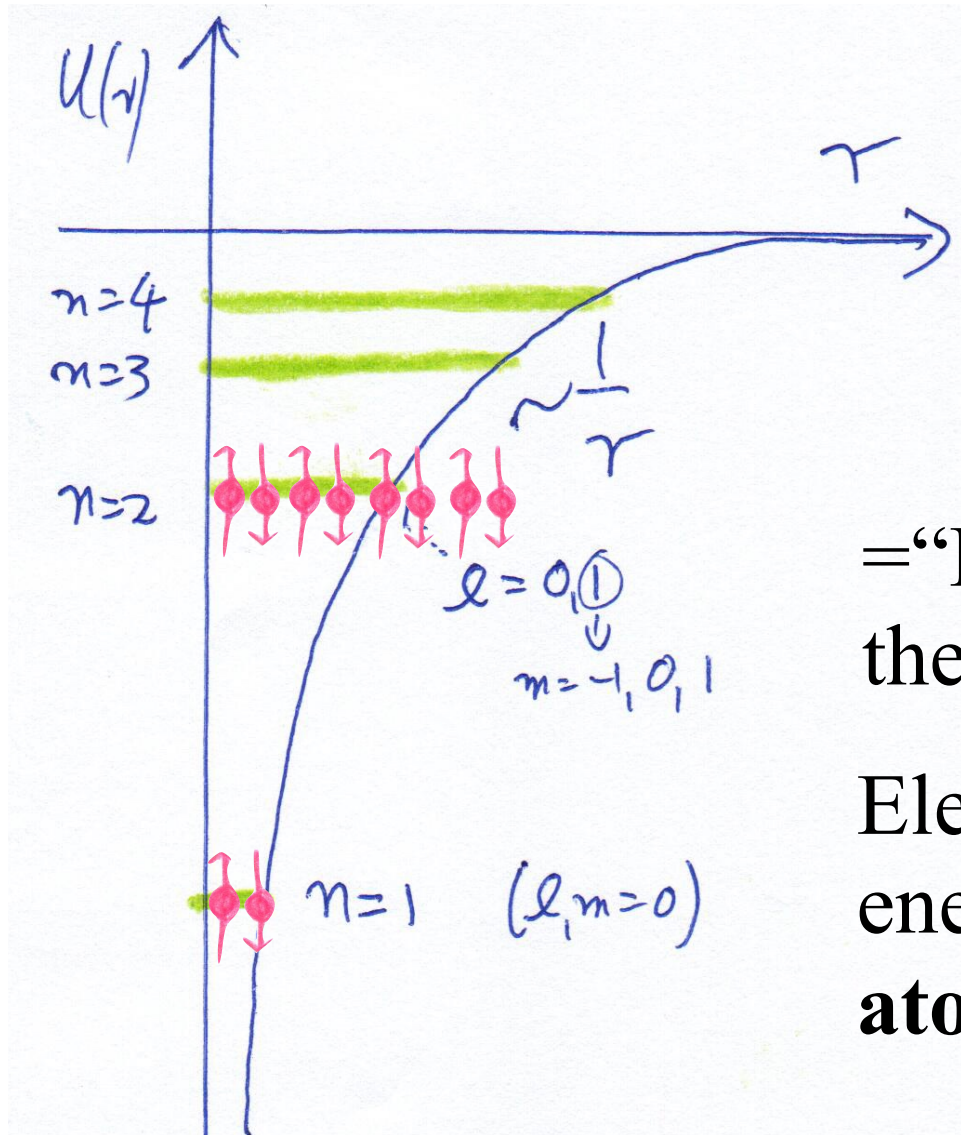

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}$$

[instead of Eq. (118b)]

- Cannot occupy same quantum state for (148) means here…

No two electrons in an atom can have all equal quantum numbers n,l,m,m_s **(149)**

Atomic shells

This means each electron state can be calculated like for Hydrogen/week 10 (with higher nuclear charge).

- Each of the states n,l,m of week 10 can thus host **two electrons** ($m_s=+1/2$, $m_s=-1/2$).

="Fill Hydrogen states up from the bottom"

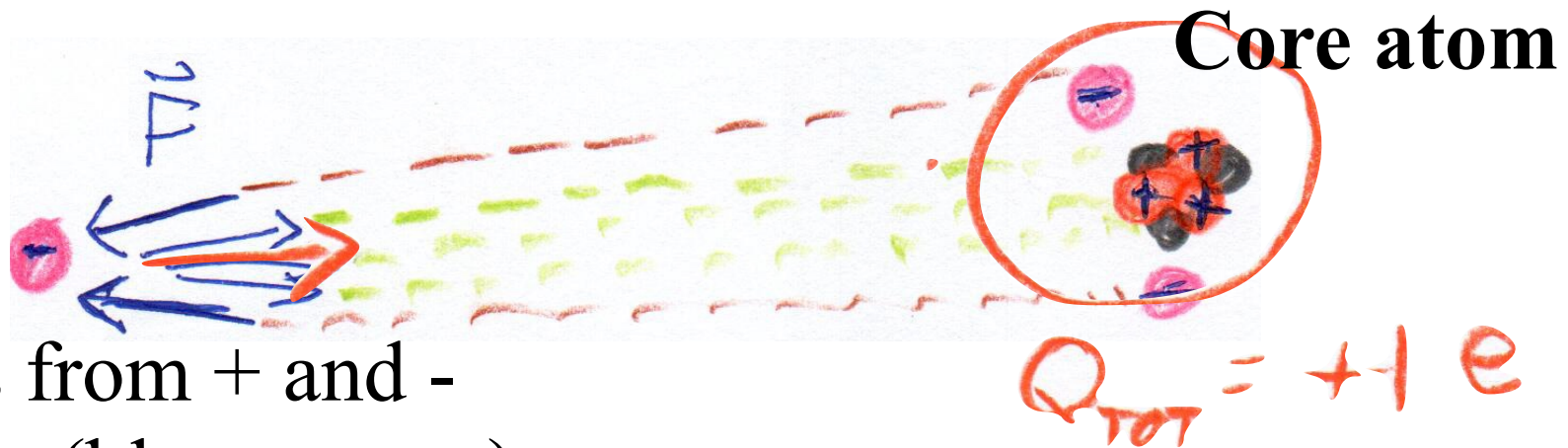Electrons of roughly similar energy are said to **form an atomic shell**

Atomic shells

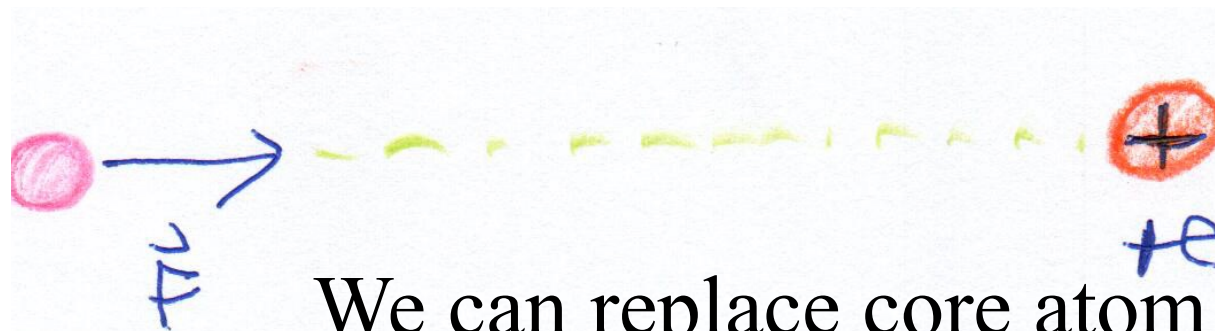Going to heavier atoms, we increase N_e but also $Q=Ze$, the **nuclear charge.** $\Rightarrow$ **Deeper Coulomb well**
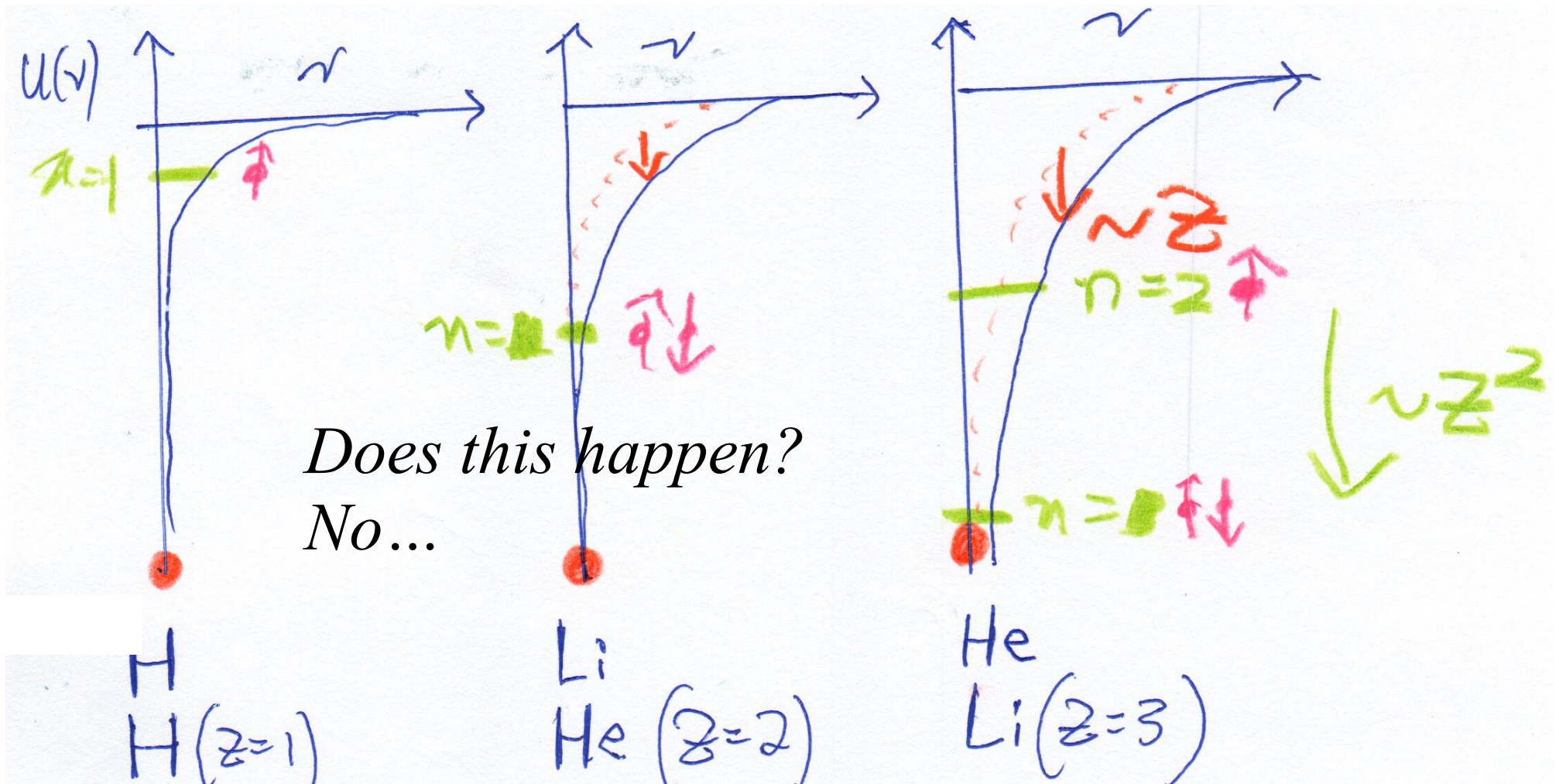
4.2.2) Screening

Now let us take care of electron-electron interactions. Most importantly they **screen** the nucleus

Core atom

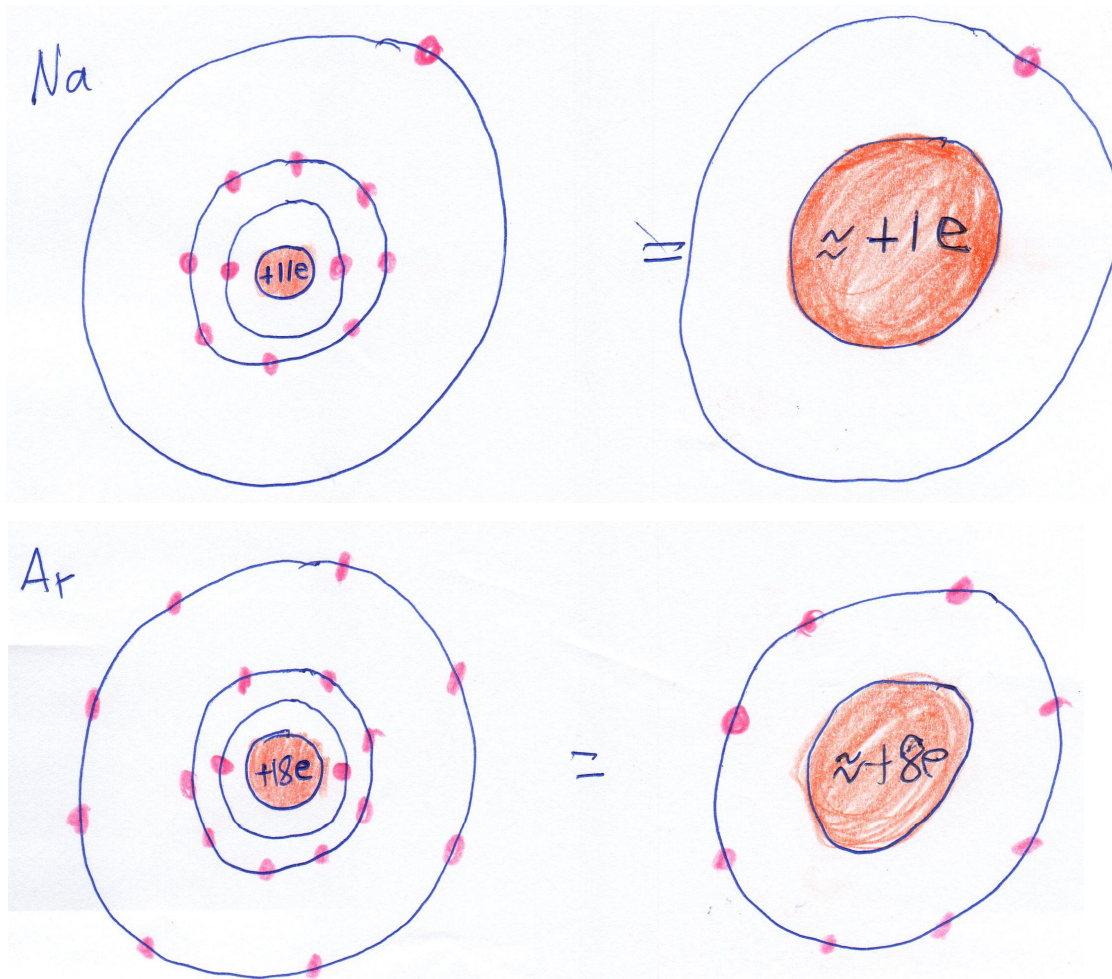$Q_{TOT} = +1\ e$

Forces from + and - charges (blue arrows) cancel except one.

$=$

$+e$

We can replace core atom by an effective charge $Q_{eff} = +1\ e$

4.2.2) Screening

In atom, lower shell electrons are closer to the nucleus, so they **screen** it (approximately completely) for all higher shell electrons:
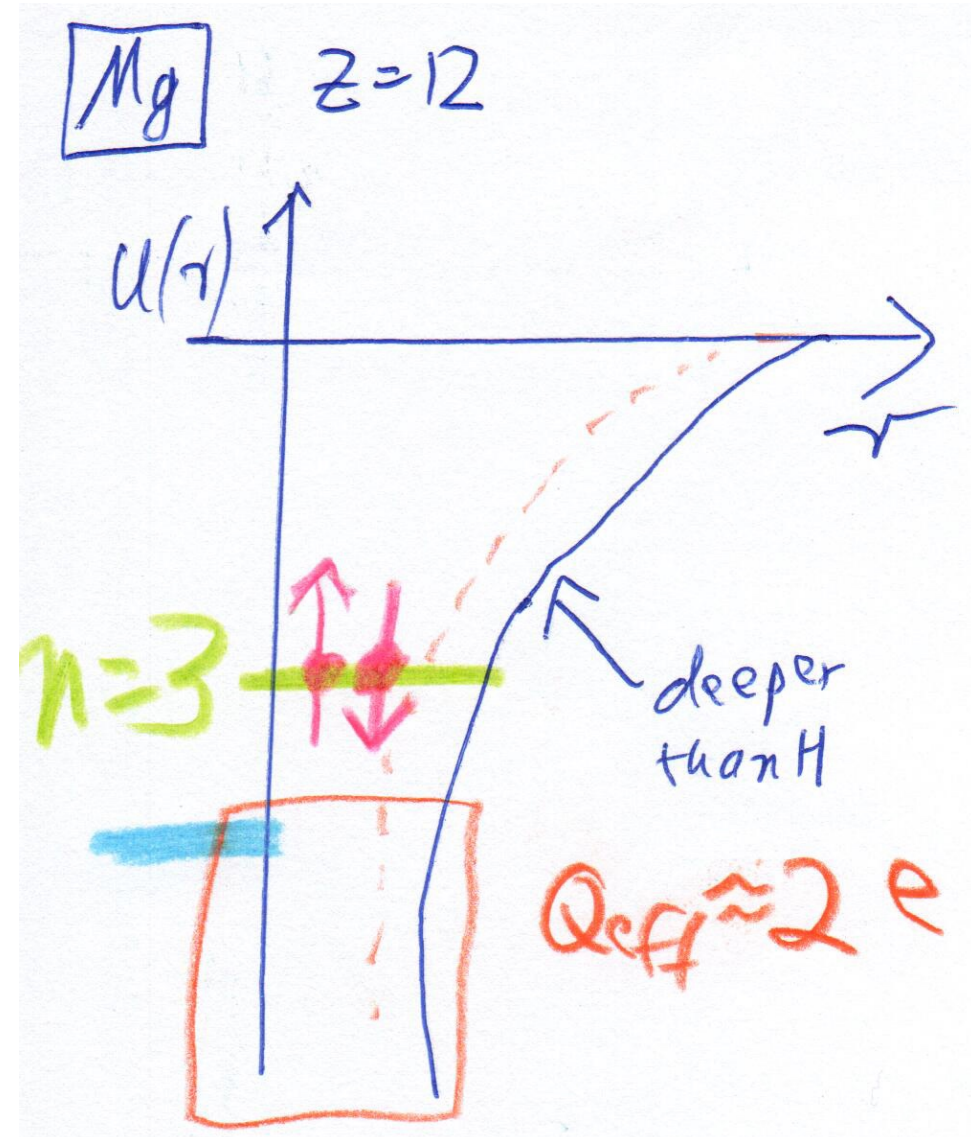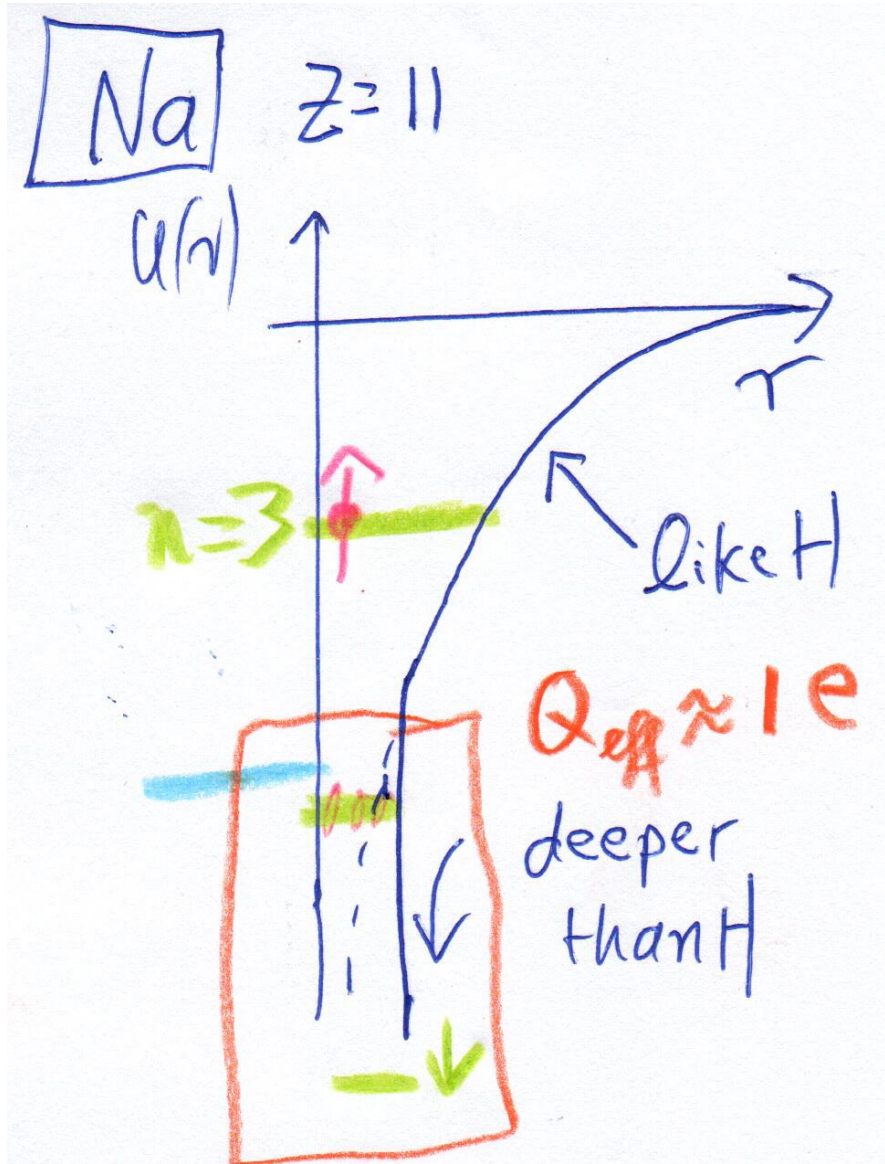

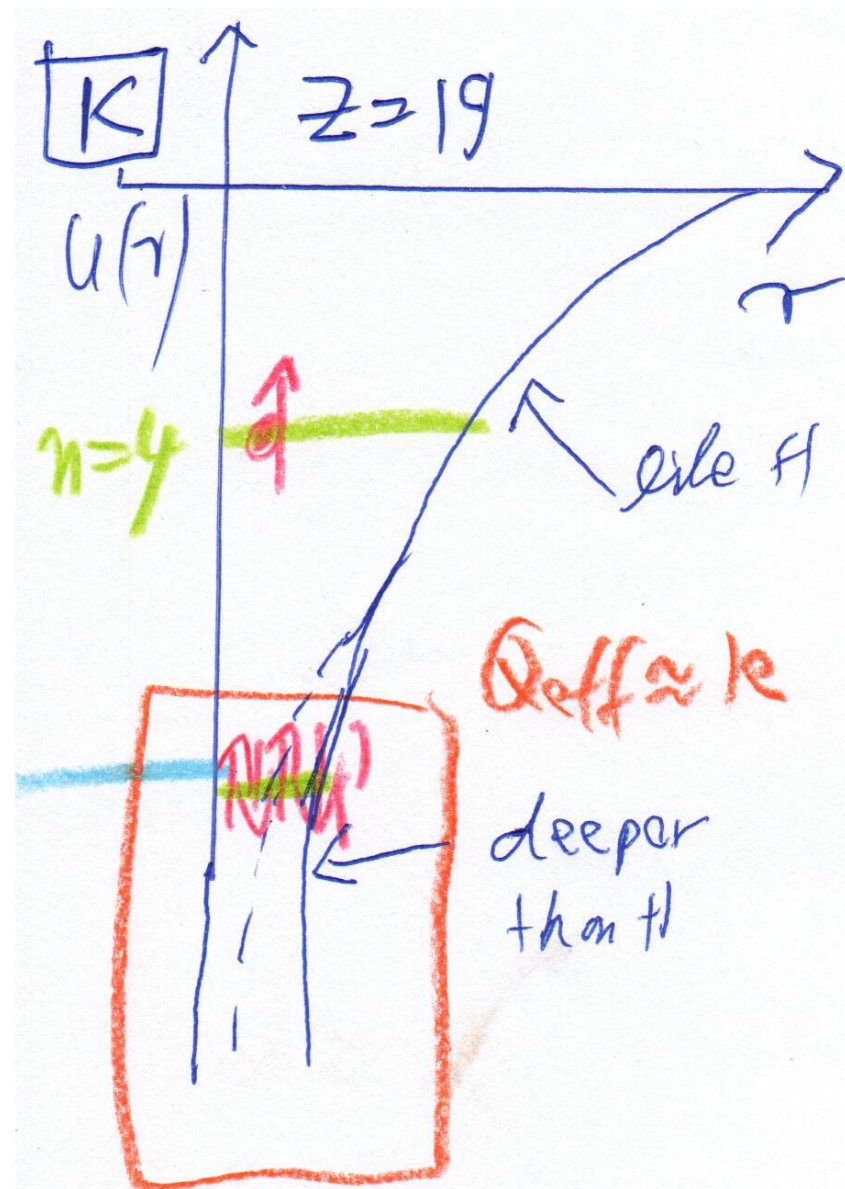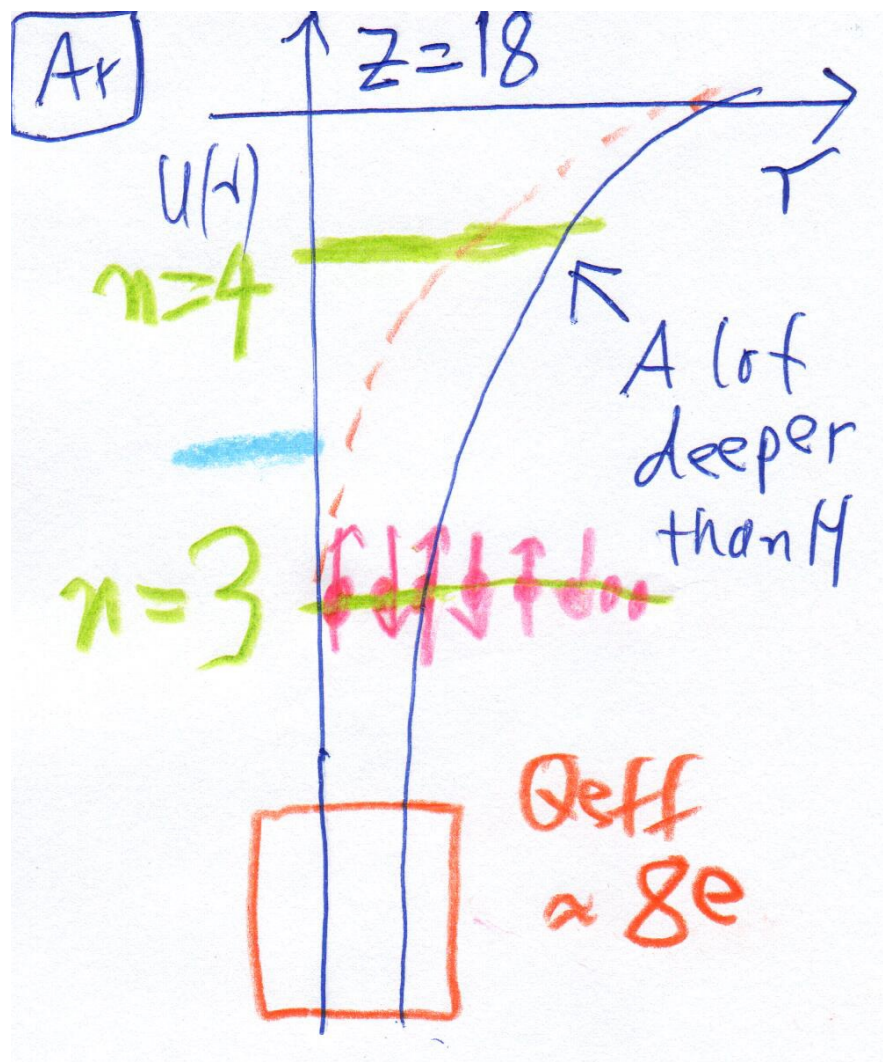**Alkali atoms** =1 electron on highest shell. **Screening:** Effectively a Q=1e nucleus

Noble gas atoms: many electrons on highest shell. **Less Screening since same shell electrons do not contribute**

4.2.3) Periodic table

The two pictures above (filling up Hydrogen+ screening) explain the most important properties of the periodic table

Periodic table

Ar, $Z = 18$

$U(r)$

$n = 4$

$n = 3$

A lot deeper than H

Qeff $\approx 8e$

K, $Z = 19$

$U(r)$

$n = 4$

erle H

Qeff $\approx 1e$

deeper than H

Periodic table   See also www.ptable.com

A new period starts once a shell is filled

Chemical properties ~ Ne on outer shell only: periodicity
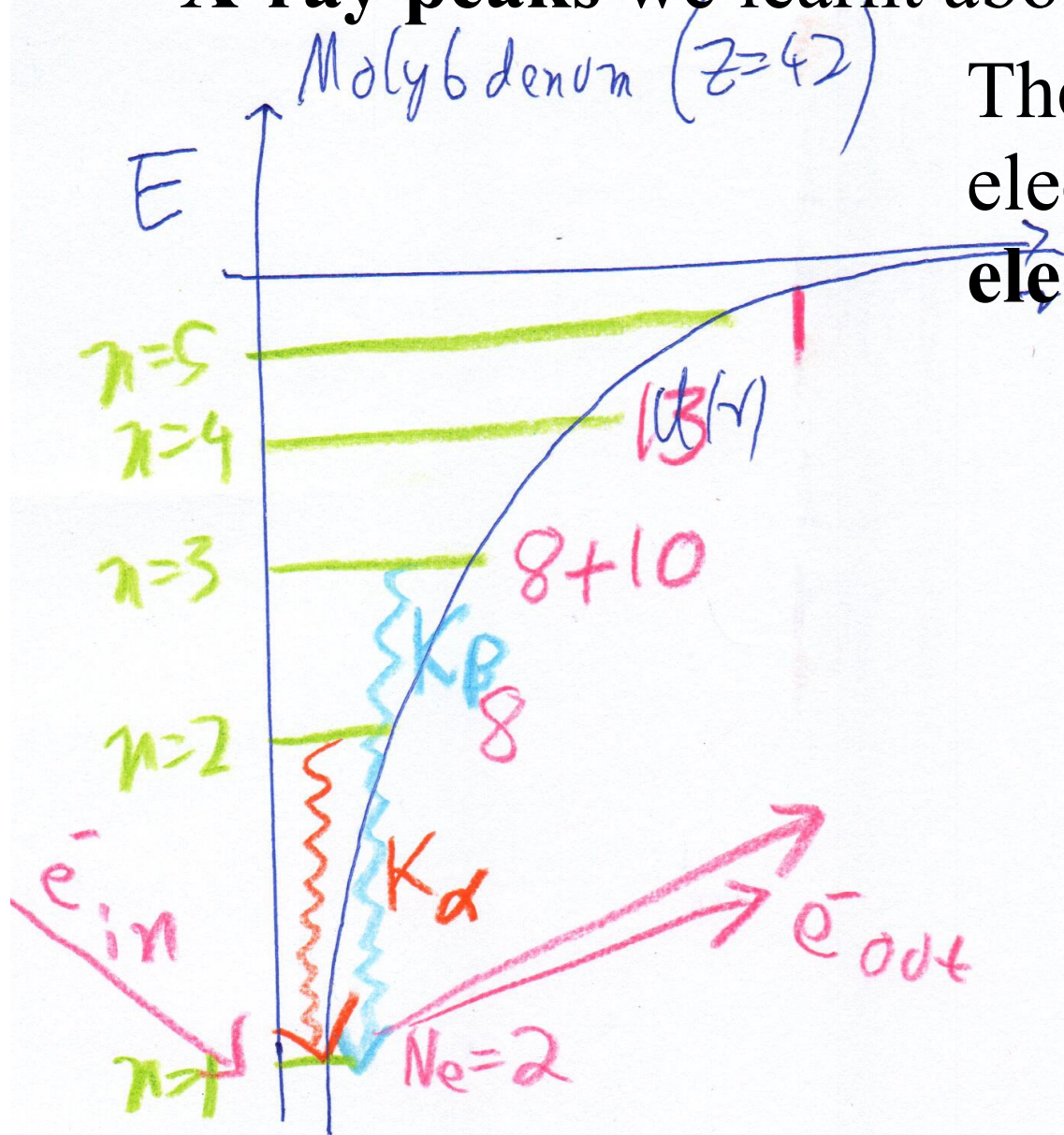
Periodic table
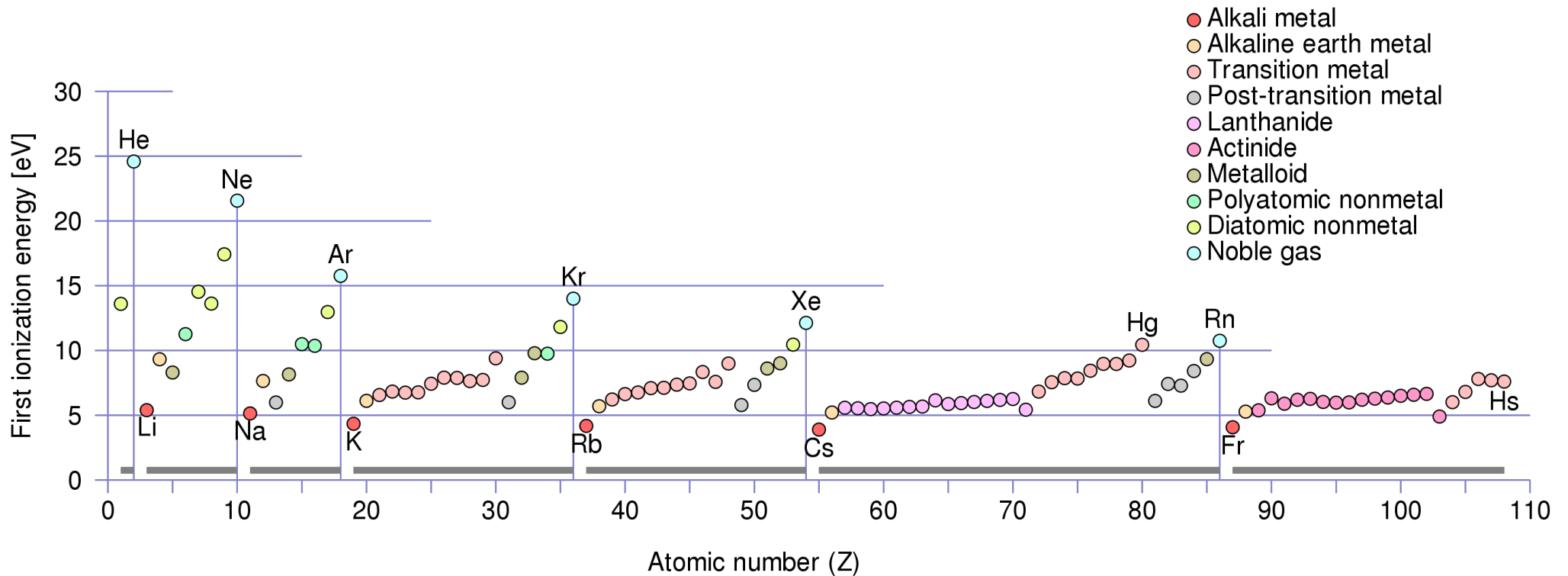
Ionisation energy of atoms in the period table = energy needed to rip out the **outermost** electron

Without the Pauli principle, all atoms would be functioning very similarly = **boring universe**

4.2.4) X-ray spectra, revisited.

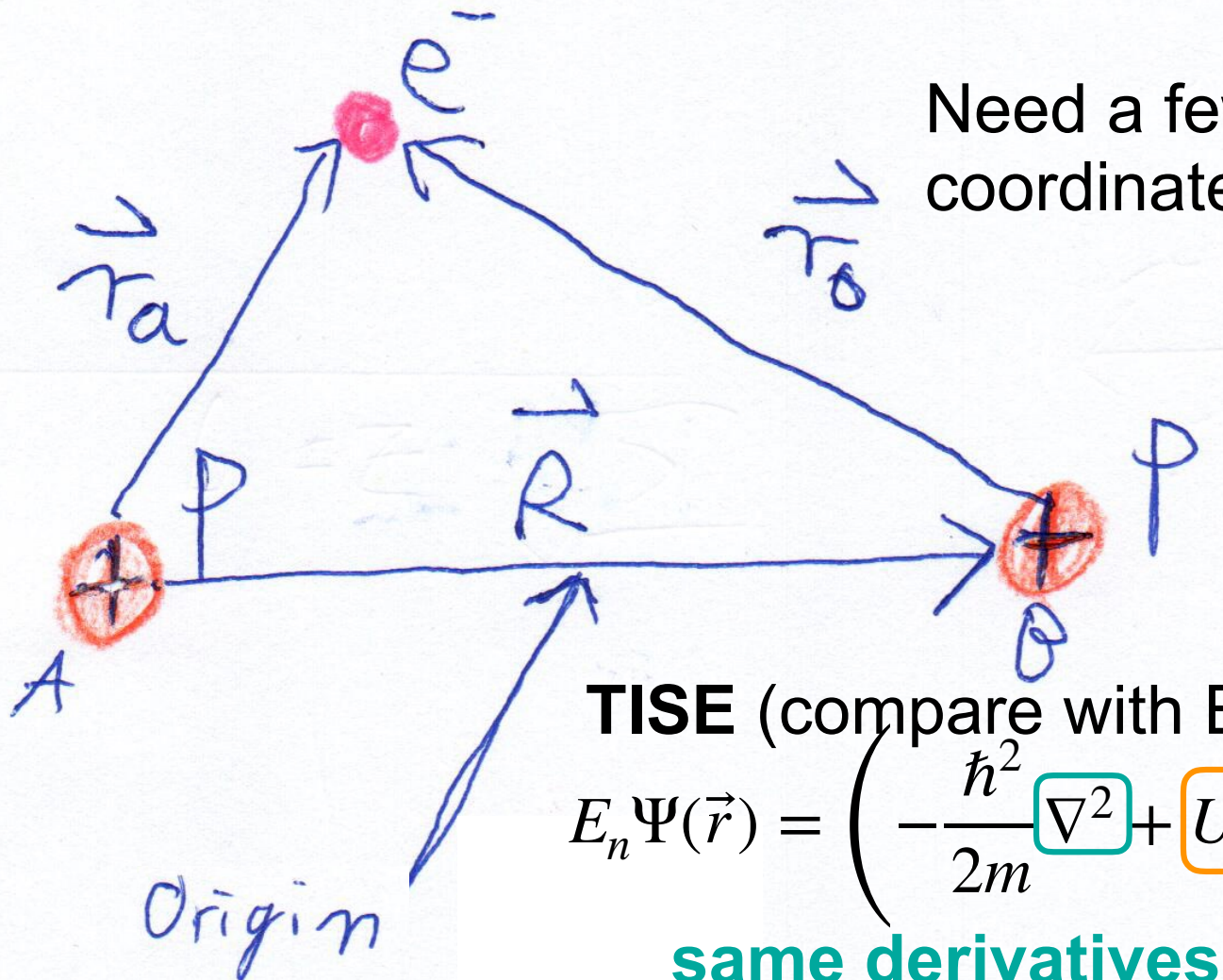We can now also understand the **characteristic X-ray peaks** we learnt about in section 2.2.4)

They occur when the incoming electron ejects an **inner shell electron from a target atom**

- Larger energy differences between inner shells $E \sim -k$eV and outer shells $E \sim -1..10$ eV.

- Sets photon energy, $\sim k$eV = X-ray

4.3.) Molecules and Chemistry
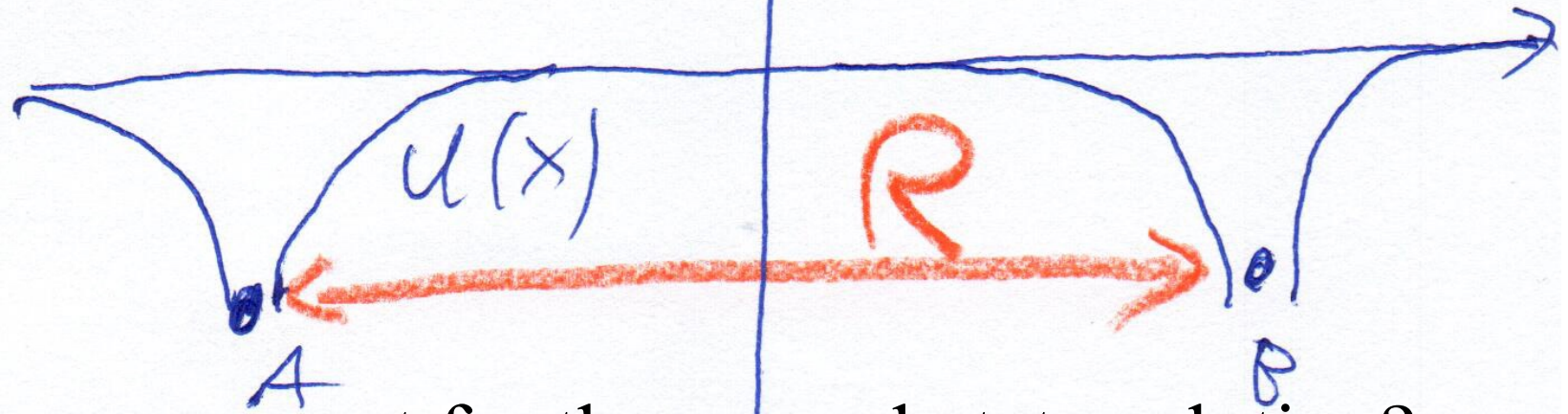
Understand molecules from TISE, similar to atoms.

Simplest: molecular ion H_2^+

Need a few more
coordinates than before

**potential from
nucleus A**

**potential from
nucleus B**

TISE (compare with Eq. 118)

$$E_n \Psi(\vec{r}) = \left(-\frac{\hbar^2}{2m} \boxed{\nabla^2} + \boxed{U(|\vec{r}_a|)} + \boxed{U(|\vec{r}_b|)} \right) \Psi(\vec{r})$$
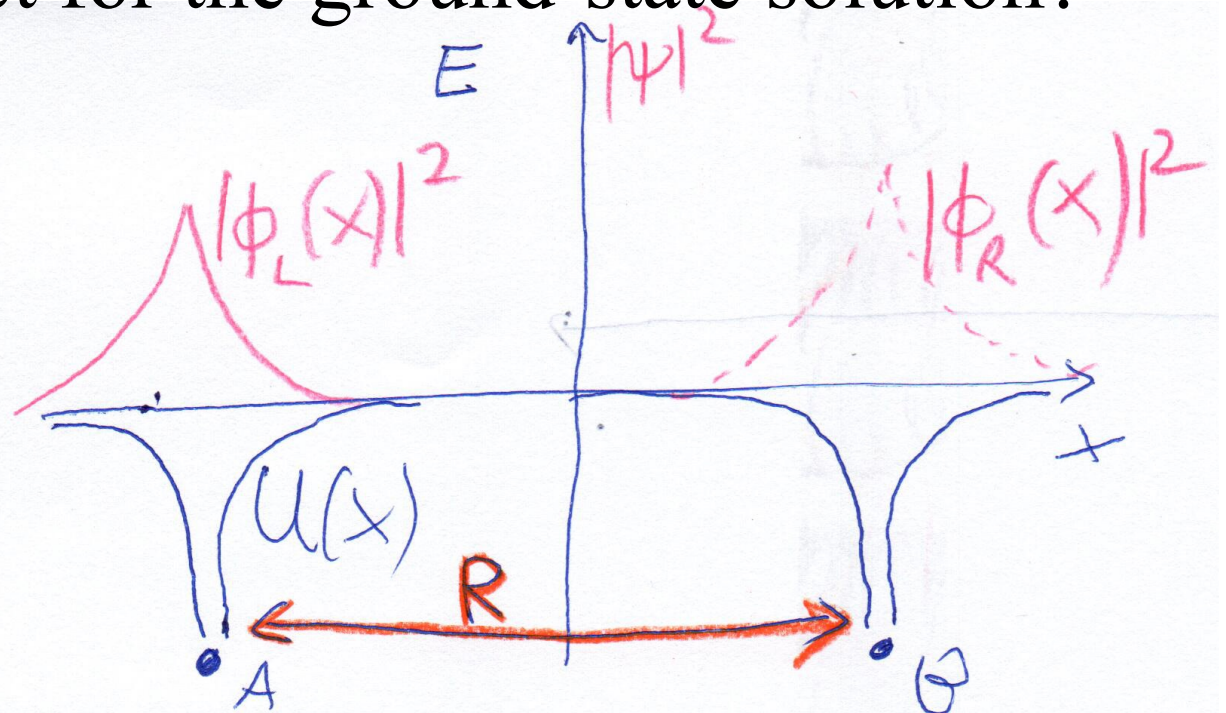
(150)

same derivatives

4.3.1) Molecular bonds

Let's assume far separated protons:

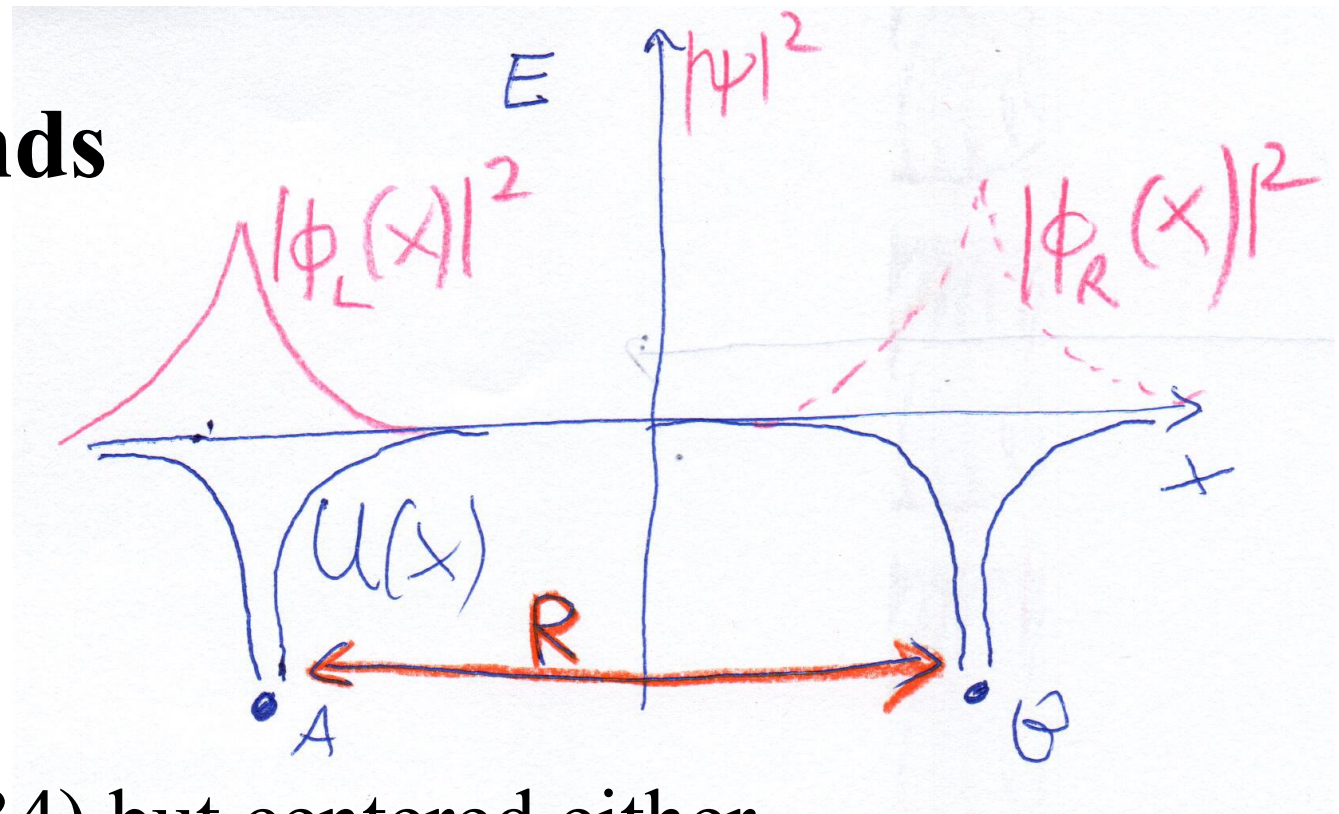Q: what do you expect for the ground-state solution?

A: two separate Hydrogen-like possibilities

Molecular bonds

Let's schematically write these as

$$\phi_L(\vec{r}) \qquad \phi_R(\vec{r})$$

Given by Eq. (134) but centered either on proton A or proton B.

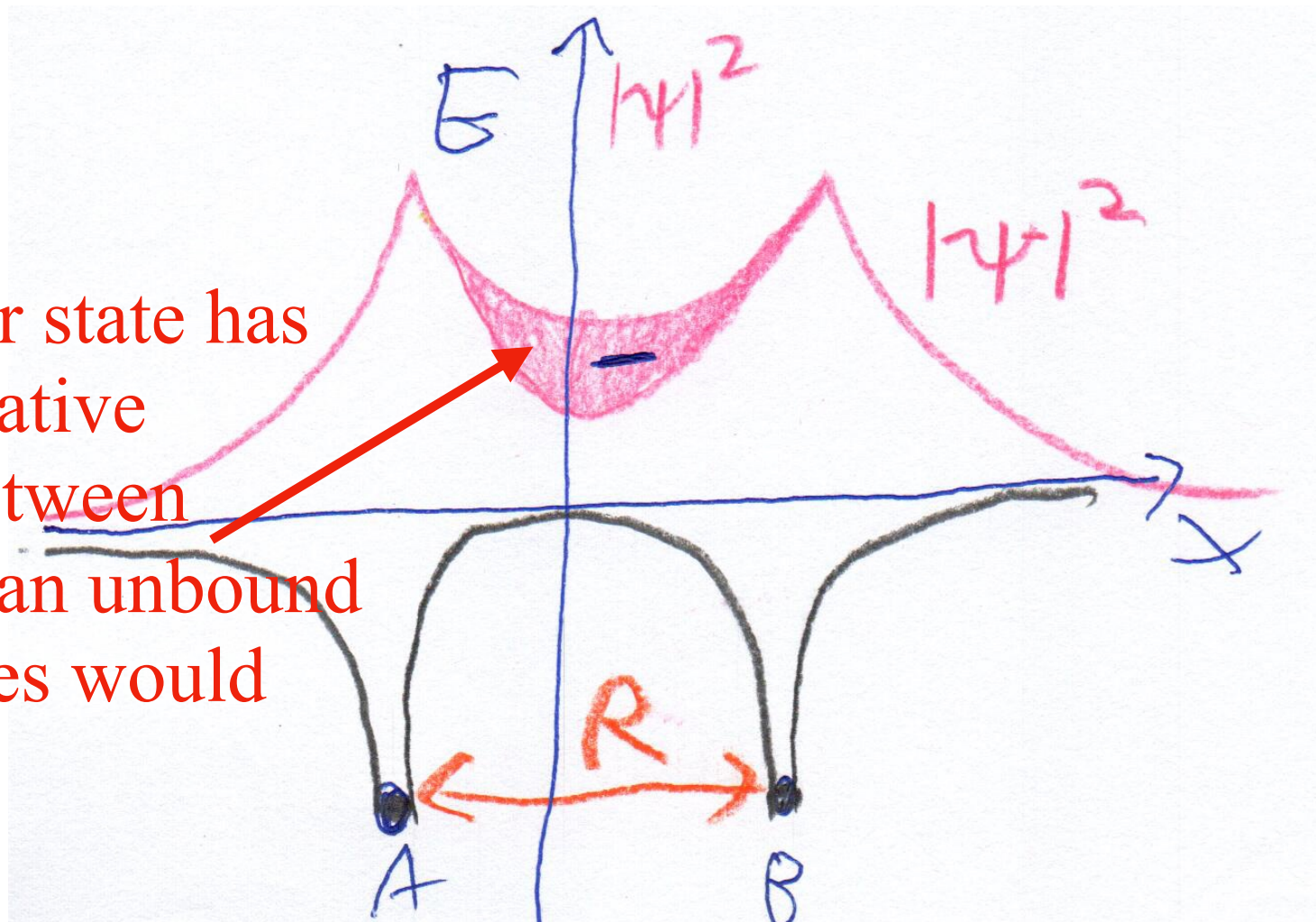Superposition principle: Should do both at the same time!!

Molecular electronic state: shared electron

$$\Psi(\vec{r}) = \frac{1}{\sqrt{2}}(\phi_L(\vec{r}) + \phi_R(\vec{r})) \qquad \text{(151)}$$
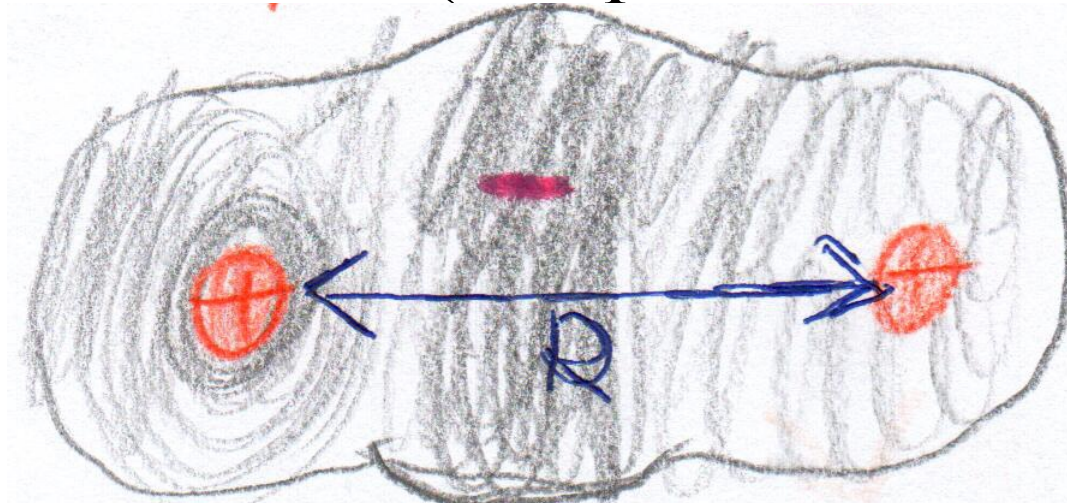
Molecular bonds

If we draw /calculate the electron density from this superposition state for **closer protons**

Molecular state has more negative charge between nucleii than unbound atom states would have

Molecular bonds

Now electron charge density has excess **between** the nucleii (compared to free atoms)
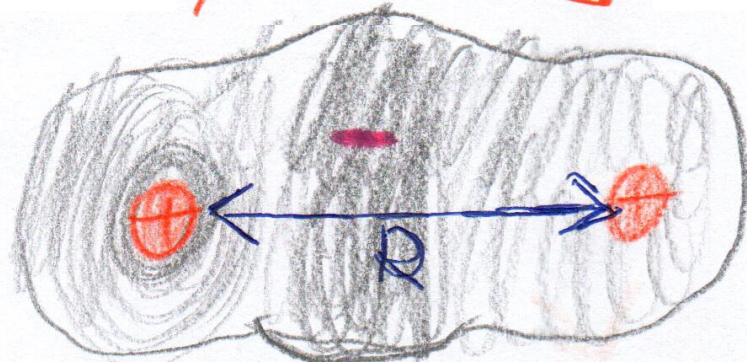

This is the essence of a

Covalent molecular bond: two nuclei share one (or more) electrons, placing the -ve electron charge more in-between the nucleii.

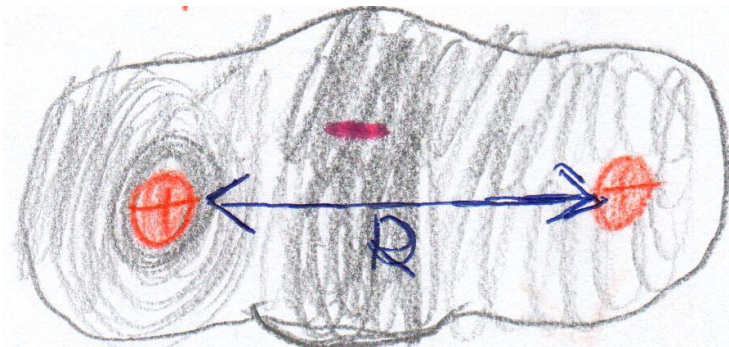*Q: molecules can do two things that atoms can't... which?*

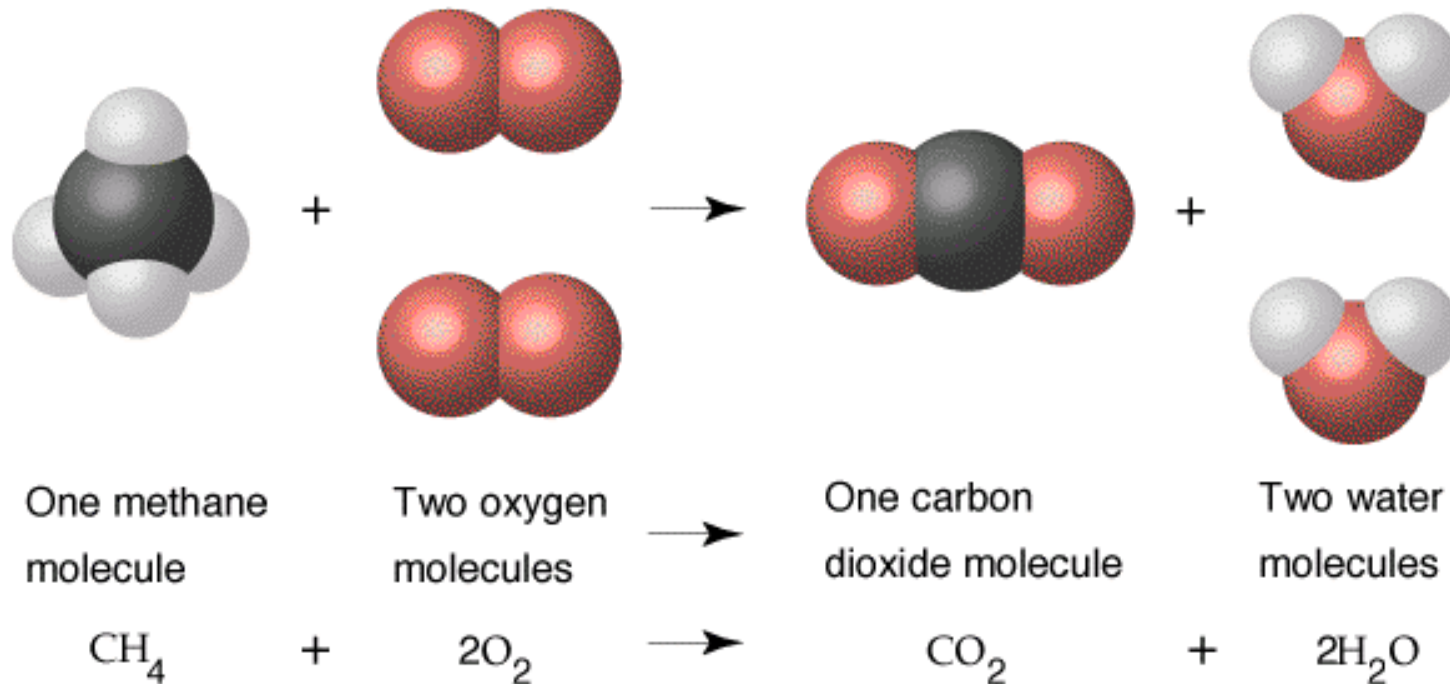# 4.3.2) Molecular vibrations and rotations

Rotations:

Q: QM?

Vibrations.

fill in lecture

fill in lecture

fill in lecture

4.3.3) Chemical Reactions

One methane molecule	Two oxygen molecules	One carbon dioxide molecule	Two water molecules

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

In principle we could predict all chemical reactions based on the TDSE (85), if we included **all nucleii** and **all electrons** in the problem.

In practice very high dimensional wave-function (section 4.1.), usually impossible to solve.

Tricks $\Rightarrow$ **Quantum Chemistry**