

We started with Hydrogen atom:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r, \theta, \varphi) - \frac{e^2}{4\pi\epsilon_0 r} \psi(r, \theta, \varphi) = E \psi(r, \theta, \varphi)$$

with the solution of the form:

$$\psi_{nlm}(r, \theta, \varphi) = \underbrace{R_n^l(r)}_{\text{radial part}} \underbrace{Y_l^m(\theta, \varphi)}_{\text{spherical harmonics}}$$

$$R(r) = f(r)/r$$

$f(r)$: solution of the following D.E.:

$$-\frac{\hbar^2}{2m} \frac{d^2 f}{dr^2} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r}}_{\text{Coulomb potential}} f(r) + \underbrace{\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}}_{\text{Angular potential}} f(r) = E f(r)$$

↓

Where does $l(l+1)$ come from:

$l(l+1)$ are the eigenvalues of the spherical harmonic eigenfunction for the angular parts of the ∇^2 in Schrödinger equation, $L(\theta, \varphi)$:

$$\nabla^2 \psi = \underbrace{\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right)}_{\text{Radial part}} + \underbrace{\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2}}_{\text{Angular part, } L(\theta, \varphi) \psi}$$

$$L(\theta, \varphi) Y_{\ell}^m = -\ell(\ell+1) Y_{\ell}^m$$

the angular term Y_{ℓ}^m is the same for all atoms.

It is only the radial part $R(r)$ that changes.

we also learned that ℓ gives the known atomic orbitals.

m is also an integer number such that: $-\ell \leq m \leq \ell$

	$\ell = 0$ $m = 0$	$\ell = 1$ $m = 0, \pm 1$	$\ell = 2$ $m = 0, \pm 1, \pm 2$
$n = 4$	<u>4s</u>	<u>4p</u>	<u>4d</u>
$n = 3$	<u>3s</u>	<u>3p</u>	<u>3d</u>
$n = 2$	<u>2s</u>	<u>2p</u>	
$n = 1$	<u>1s</u>		
↓	↓	↓	↓
	s level has no degeneracy	3-fold degenerate	5-fold degenerate

p and d levels have higher energy than s levels. why?

Because $\ell \neq 0$, there is an additional angular energy

of $\frac{\hbar^2 \ell(\ell+1)}{2m}$ that is repulsive (positive).

Note that the Coulomb potential is attractive (negative):

$$-\frac{e^2}{4\pi\epsilon_0 r}$$

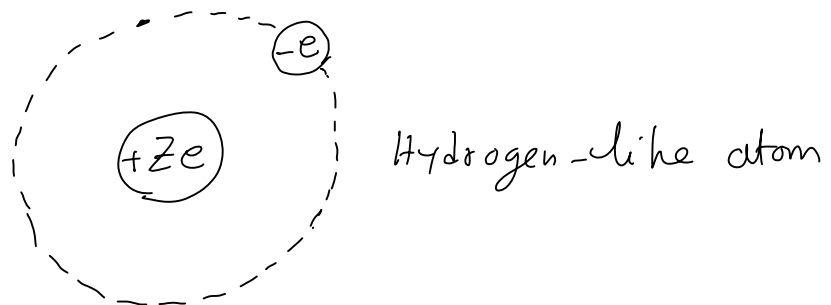
If we ignore higher order effects, 2s and 2p have equal energy. Similarly 3s, 3p, and 3d. This is unique to Hydrogen atom, which results in a simple equation of:

$$E_n = -\frac{E_0}{n^2}, \quad E_0 = \frac{e^2}{8\pi\epsilon_0 a_0}, \quad a_0 = 0.0529 \text{ nm}$$

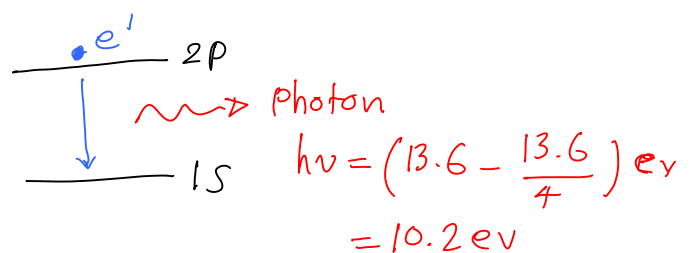
\uparrow -13.6 eV Bohr radius
 \uparrow

for all energy levels. For Hydrogen-like atom (like He^{2+})

we have: $E_n = -\frac{Z^2 E_0}{n^2}$ where Z is the atomic number.



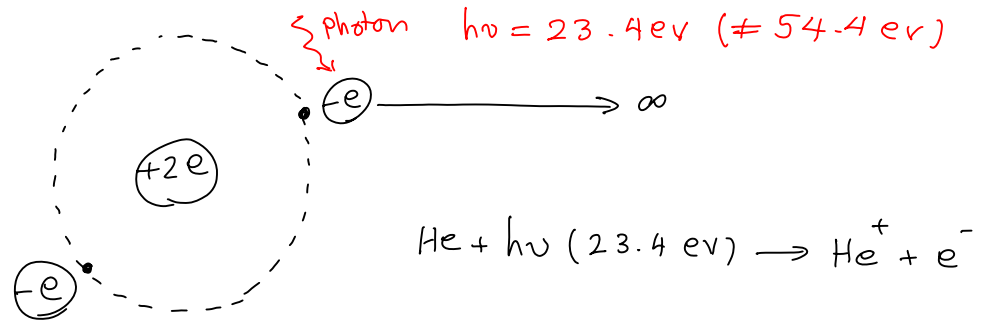
So an electron in 1s, has ionization energy of 13.6 eV and 2s an ionization energy of $\frac{13.6}{4}$ eV. This agrees well with experiments such as photoemission:



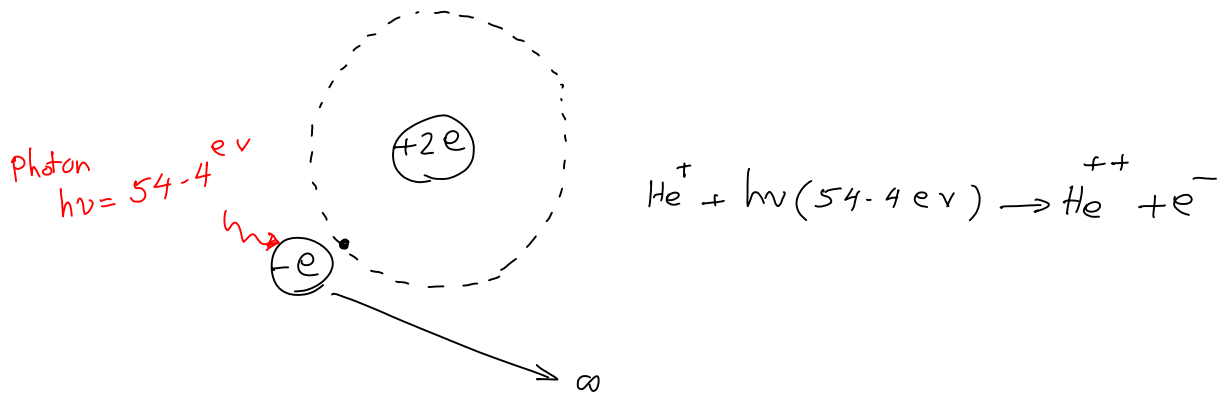
Let's see if it also works for He: $E_n = \frac{Z^2}{n^2} E_0 = \frac{4}{n^2} E_0$

The first ionization energy is: $E_1 = \frac{4}{1} (13.6) = 54.4 \text{ eV}$

However, in experiment, we measure 23.4 eV:



But for the 2nd ionization energy, we get 54.4 eV



Obviously, for the first ionization, we are not considering the effect of the other electron, which results in electron-electron repulsive potential.

How can we include this effect?

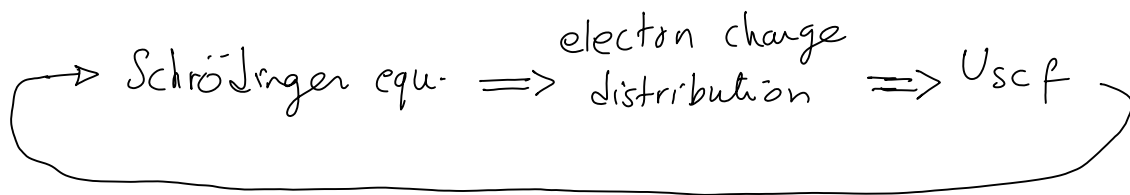
One way: Add the self-consistent field term $U_{scf}(r)$ to the radial Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2mr^2} + U_{scf}(r) \right] f(r) = E f(r)$$

Note that an electron doesn't feel its own potential. So U_{scf} is due to other $Z-1$ electrons.

But why we said again self-consistent potential?

Because we need to know the electron charge distribution to find $U_{scf}(r)$. But that depends on individual electron wavefunction that are derived from the Schrödinger equation. But the Schrödinger equation itself depends on U_{scf} . Therefore, the equation must be solved self-consistently.



Hartree Approximation

U_{scf} is approximately calculated from:

$$\nabla^2 U_{scf}(r) = -\frac{e^2}{\epsilon_0} n(r)$$

↓
electron density

In integral form, we can write this as:

$$U_{scf}(\vec{r}) = \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}') d\vec{r}'}{|\vec{r} - \vec{r}'|}$$

The total number of electrons is $N = \int n(\vec{r}) d^3r = \int |\Psi|^2 d^3r$

In spherical coordinate, we have:

$$\Psi = R(r) Y(\theta, \varphi) = \frac{f_n(r)}{r} Y(\theta, \varphi) \quad \text{for } n(r), \text{ we must}$$

Sum over all occupied states:

$$n(\vec{r}) = \sum_{\text{occupied } n, \ell, m} \left| \frac{f_n(r)}{r} \right|^2 \left| Y_{\ell}^m(\theta, \varphi) \right|^2$$

And for N , we have:

$$N = \int |\Psi|^2 d^3r = \int \overbrace{r^2 \sin\theta dr d\theta d\varphi}^{d^3r} \sum_{\text{occupied } n, \ell, m} \left| \frac{f_n(r)}{r} \right|^2 \left| Y_{\ell}^m(\theta, \varphi) \right|^2$$

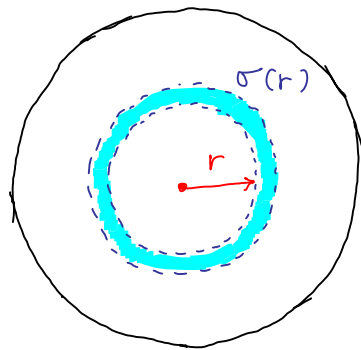
$$= \sum_{\text{occ. } n, \ell, m} \int |f_n(r)|^2 dr \underbrace{\int \sin\theta \left| Y_{\ell}^m(\theta, \varphi) \right|^2 d\theta d\varphi}_{=1 \text{ since } Y_{\ell}^m \text{ is normalized}}$$

$$= \int dr \sum_{\text{occ. } n, \ell, m} |f_n(r)|^2 = \int dr \sigma(r)$$

$$\equiv \sigma(r)$$

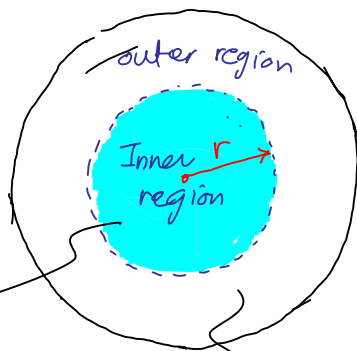
$$N = \int \sigma(r) dr$$

$\sigma(r)$ tells us how much charge we have in a given shell:



To simplify the computation of the integral $N = \int \sigma(r) dr$, we split the sphere in two parts of inner and outer regions:

Two region of charge at radius r :



The potential due to the inner region is:

$$\frac{e^2}{4\pi\epsilon_0 r} \int_0^r \sigma(r') dr'$$

We modeled the inner charge as a **point charge** at origin.

And the outer region:

$$\frac{e^2}{4\pi\epsilon_0} \int_r^\infty \frac{\sigma(r') dr'}{r'}$$

We modeled the outer charge as a constant external potential (no r)

So overallly we have:

$$U_{\text{self}} = \frac{Z-1}{Z} \left[\frac{e^2}{4\pi\epsilon_0 r} \int_0^\infty \sigma(r') dr' + \frac{e^2}{4\pi\epsilon_0} \int_r^\infty \frac{\sigma(r')}{r'} dr' \right]$$

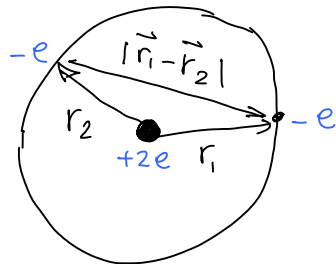
This is to account for the fact that electron doesn't feel its own potential.

Remember that overall we will solve this self-consistently:

1. Make a guess for U_{scf} (usually zero)
2. Find eigenvalues and eigenfunctions of the Sch. equ.
3. Calculate electron density $n(r)$
4. Calculate electron potential $U_{scf}(r)$
5. Check your U_{scf} and if it is different from the last value, go to step 2.

(A reasonable difference is $k_B T / 10$)

Our U_{scf} is formulated as a potential that one electron feels from all other electrons around it. However, this is not completely correct! Let's look at the Schrodinger equ. for Helium atom:



$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \underbrace{\frac{2e^2}{4\pi\epsilon_0 r_1}}_{U_N(r_1)} - \underbrace{\frac{2e^2}{4\pi\epsilon_0 r_2}}_{U_N(r_2)} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

potential due
to the nuclei

$$H \Psi(r_1, r_2) = E \Psi(r_1, r_2)$$

$$\left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + U_N(r_1) + U_{N'}(r_2) + \underbrace{\frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}} \right) \Psi(r_1, r_2) = E \Psi(r_1, r_2)$$

Coulomb interaction between two electrons

The difficulty comes from the fact that e-e interaction

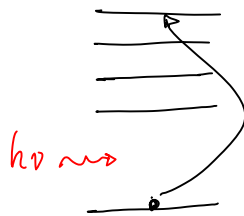
term is not separable. $U(\vec{r}) \neq U_x(x) + U_y(y) + U_z(z)$.

For example if we have 10 electrons, we will have a 30-dimension coordinate system (3 per electron), and the exact solution is not practical. That's why we implemented the U_{scf} approximation.

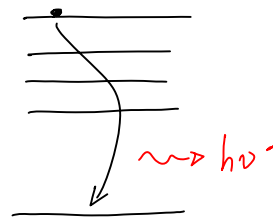
Ionization and Affinity energies

These energies are known from photoemission & inverse photoemission experiments.

Photoemission (PE)



Inverse Photoemission (IPE)



So ionization energies are found by knocking out an electron & the affinity energies by adding an electron.

For one electron ionization level, E_n :

$$E_n = E_G(N) - E_n(N-1)$$

Ground state energy of the neutral N -electron atom

n^{th} energy level of the positively ionized $(N-1)$ electron atom

For one electron affinity level, E_n :

$$E_n = E_n(n+1) - E_G(n)$$

\downarrow
 n^{th} energy level of the
negatively ionized $(N+1)$ electron atom

So what should we use to calculate U_{scf} ?

Intuitively, self-consistent field for ionization is:

$$U_{\text{scf}} = U_{ee}(N) - U_{ee}(N-1)$$

\downarrow
 U_{ee} is e-e interaction energy, which is generally difficult to find.

And for affinity levels:

$$U_{\text{scf}} = U_{ee}(N+1) - U_{ee}(N)$$

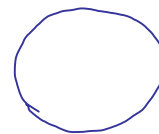
One simple model treats the interaction energy U_{ee} as that stored in a capacitor:

Simple capacitive model

$$U_{ee}(N) = \frac{1}{2} \frac{q^2}{C} = \frac{e^2 N^2}{2C}$$



to eliminate "self interaction":



$$U_{ee}(N) = \frac{e^2 N(N-1)}{2C}$$

So for ionization levels, we have:

$$U_{\text{scf}} = \frac{e^2 N(N-1)}{2C} - \frac{e^2 (N-1)(N-2)}{2C} = \frac{e^2}{C} (N-1)$$

And for affinity levels :

$$U_{scf} = \frac{e^2(N+1)N}{2C} - \frac{e^2N(N-1)}{2C} = \frac{e^2}{C} N$$

So for affinity levels, add an electron and potential is felt due to N existing electron.

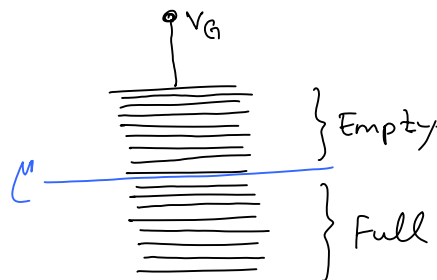
For ionization levels, removed electron feels potential due to $(N-1)$ electrons.

Note that ionization and affinity levels are different by a single electron charging energy $\frac{e^2}{C}$

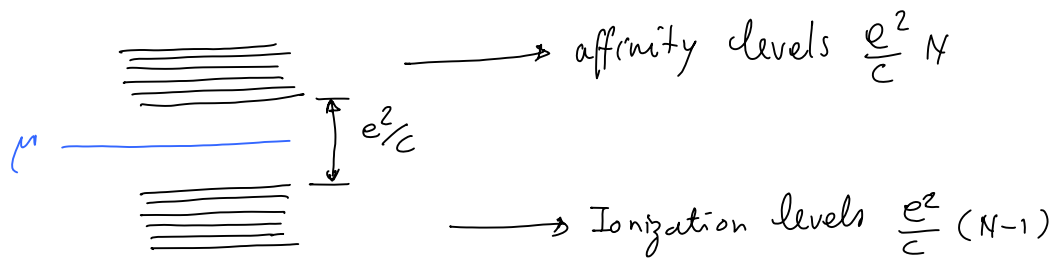
But for large systems which by nature have large capacitances they are almost equal.

This difference of $\frac{e^2}{C}$ has an important consequence as it results in Coulomb gap or **Coulomb blockade** as we discussed before.

For example, consider a conductor that presumably has closely spaced levels:



But in reality we will have a Coulomb gap at μ :



So if $\frac{e^2}{C} > k_B T$, then a conductor, which one thinks would conduct well, will not necessarily do so!

Large Conductors

For relatively large conductors we can write:

$$U_{scf} = \frac{\partial U_{ee}}{\partial N}$$

and for a big conductor with spacial dependent electron density $n(\vec{r})$:

$$U_{scf}(\vec{r}) = \frac{\partial U_{ee}}{\partial [n(\vec{r})]}$$

However, again, finding U_{ee} is the most difficult part.

Approximations such as:

$$U_{ee} = \frac{1}{2} \iint \frac{e^2}{4\pi\epsilon_0} \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}d\vec{r}'$$

are usually used. This classical electrostatics.

If we know make a derivative and calculate U_{scf} , we get the Hartree U_{scf} approximation:

$$U_{scf}(\vec{r}) = \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' = U_H(r)$$

In reality, the correct U_{scf} is less than the approximate U_H . Why?

Theoretically, we should have a two electron probability distribution $g(r, r')$ such that:

$$U_{ee} = \frac{1}{2} \int \frac{e^2 g(r, r')}{4\pi\epsilon_0 |\vec{r}-\vec{r}'|} dr dr'$$

But $g(r, r') < n(r)n(r')$, because electrons try to avoid each other and their motion is not independent (or truly random).

So the actual U_{ee} is somewhat smaller than that from classical electrostatics. For correction, often

a negative **correlation energy**, U_{xc} , is added to U_H :

There are many theories as how to estimate U_{xc} .

One common simple approximation gives:

$$U_{xc}(\vec{r}) = -c \frac{e^2}{4\pi\epsilon_0} \sqrt[3]{n(r)} \quad U_{scf} = U_H + U_{xc}$$

where $c \approx 1$. This is called **Local density approximation (LDA)**.

LDA agrees well with experiments on atoms. For molecules, of course, we have to use alternate $U_{xc}(\vec{r})$.