# Quantum Transport: Atom to Transistor

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Lecture 10: Self Consistent Field: Relation to the Multi-Electron Picture

Ref. Chapter 3.2

*Network for Computational Nanotechnology*

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# Retouch on Concepts

00:00

• Last time we looked at the self-consistent field method, altering the Schrödinger equation to include a self-consistent potential $U_{scf}$:

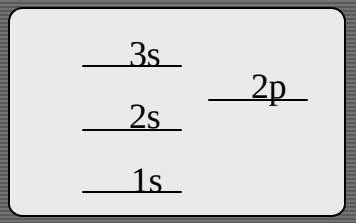
$$E\Psi = \left[\frac{-\hbar^2}{2m}\nabla^2 + U_N + U_{\text{scf}}\right]\Psi,$$

where $U_N$ is the potential due to the nucleus.

• If the energy levels of the helium atom are calculated without taking into account electron-electron interactions incorrect ionization energies are predicted.

• For example –54.4 eV for the first ionization with respect to the experimental value of –23.4 eV.

Helium Energy Levels




• To get the correct ionization energies $U_{scf}$ is added. $U_{scf}$ approximates electron-electron interactions.

# Why the self-consistent field method?

04:00

• $U_{scf}$ is formulated, in essence, from the idea that each electron feels a potential due to all other electrons around it. This, however, is not completely correct and we will look at this today.

• The Schrödinger equation for Helium looks like :

$$E\Psi(r_1, r_2) = \begin{bmatrix} \frac{-\hbar^2}{2m}\nabla_1^2 - \frac{-\hbar^2}{2m}\nabla_2^2 \\ +U_N(r_1) + U_N(r_2) \\ + \frac{q^2}{4\pi\varepsilon_0 \left|\vec{r}_1 - \vec{r}_2\right|} \end{bmatrix} \Psi(r_1, r_2)$$

where the last term represents coulomb interaction between two electrons.

• If $\frac{q^2}{4\pi\varepsilon_0 \left|\vec{r}_1 - \vec{r}_2\right|}$ is excluded and the overall nuclear potential is separable (i.e)

$$U(\vec{r}) = U_X(x) + U_Y(y) + U_Z(z)$$

then the equation is solvable.

• The electron-electron interaction term is inseparable.

• For example consider a 10 electron atom, for this a 30 dimension coordinate system exists (3 per electron) and the exact solution becomes prohibitive if not impossible.

• So this is why we implement the $U_{scf}$ approximation.

# Interpreting Energy Levels

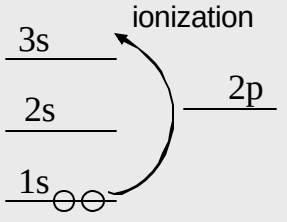
11:01

• Suppose we could solve the analytical problem. In the case of the Helium how would we represent it's energy levels, that of a two electron problem, and relate them to the one electron energy level diagram?

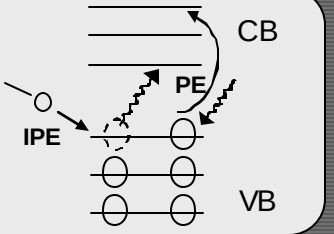
• One method, following the approach we have been using so far, is to view our one - electron energy levels as ionization and affinity energies.

• Recall, these energies are known from photoemission and inverse photoemission experiments.

One Electron Energy Level diagram: Helium




Photoemission (PE) and Inverse Photoemission(IPE)

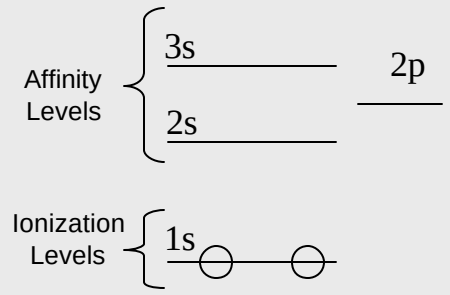


# $U_{scf}$ for Ionization and Affinity Levels

15:00

• So, ionization levels are found by knocking out an electron and affinity levels by adding an electron.

Affinity and Ionization Levels




• The one electron ionization levels, $E_n$, are given by:
$E_n = E_G(N) - E_n(N-1)$, where $E_G(N)$ is the ground state energy of the neutral N-electron atom and
$E_n(N-1)$ the nth level of the positively ionized (N-1) atom.

• Similarly the one electron affinity level, $E_n$, are given by:
$E_n = E_n(N+1) - E_G(N)$ where $E_G(N)$ is the ground state energy of the neutral N-electron atom and
$E_n(N+1)$ the nth level of the negatively ionized atom.

• So the basic question is: What should we use to calculate $U_{scf}$?

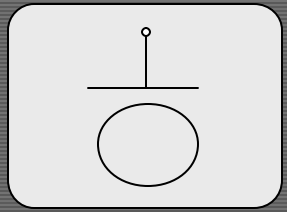
# $U_{scf}$ Using the Capacitive Model

18:31

Simple Capacitive Model

- Intuitively, it follows that the self-consistent field for ionization levels is given by:
  $U_{scf} = U_{ee}(N) - U_{ee}(N-1)$, where $U_{ee}$ is the electron-electron interaction energy.
- And for affinity levels:
  $U_{scf} = U_{ee}(N+1) - U_{ee}(N)$
- In general finding the electron-electron interaction energy, $U_{ee}$ is quite difficult.

- One simple method treats the interaction energy as that stored in a capacitor.



- So, we take: $U_{ee}(N) = \dfrac{q^2 N^2}{2C}$

And to correct for "self-interaction":

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

# Uscf Using the Capacitive Model

23:20

• For ionization levels, using the capacitive model, we get:

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

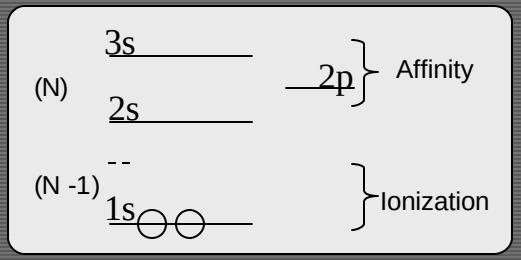
$$= \frac{q^2}{C}(N-1)$$

• But for the affinity levels, N gets replaced by N+1:

$$U_{scf} = \frac{q^2}{C} N$$

• Affinity Levels: Add an electron and potential is felt due to N existing electrons.

Helium Levels




• Ionization Levels: Removed electron feels potential due to other N -1 electrons.

• So we must treat ionization and affinity levels differently. Note: This distinction is not so important for large systems which by nature have large capacitances.

# Coulomb Blockade

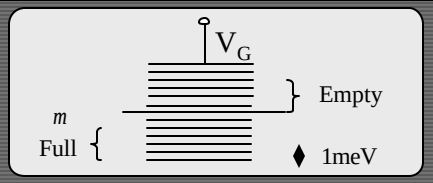
29:35

- Overall it is important to note that [$U_{scf}$] ionization and [$U_{scf}$] affinity differ by the single electron charging energy by $q^2/C$.

- An important consequence of this property is the coulomb gap or coulomb blockade.

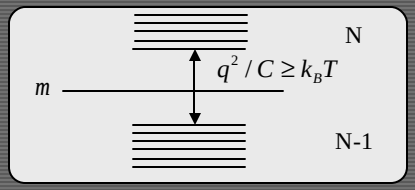
- This can occur even in conductors (which have levels that are very closely spaced).

Conductor with closely spaced levels




- If $q^2 / C \geq k_B T$ then a conductor, which one might think would conduct well, will not necessarily do so.

Coulomb Gap



# Large Conductors

33:00

For relatively large conductors we write:

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

(the change in Uee being so small that it can be written as a derivative with respect to N).

For a big conductor depending on r:

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

where n (r) is the electron density.

However Uee remains the most difficult problem, approximations such as:

$$U_{ee} = \frac{1}{2}\int \int \frac{q^2}{4pe} \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}d\vec{r}'$$

are usually used.

- This particular approximation gives rise to the **Hartree** $U_{scf}$ approximation:

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

- The correct $U_{scf}$ (r) is infact less than this classical approximation ( $U_H$ (r) ). Why is this? Theoretically, there is two electron probability distribution g(r,r') such that :

$$U_{ee} = \frac{1}{2}\int \frac{q^2 g(\vec{r},\vec{r}')d\vec{r}d\vec{r}'}{4pe|\vec{r}-\vec{r}'|},$$

but g(r,r') is less than n(r)n(r'). Electrons try to avoid each other and their motion is not truly random.

# Correlation Energy

42:40

- So, Uee will be somewhat less than then that given by classical electrostatics.
- Thus, a negative correlation energy term is often added to UH:
- Uscf = UH + UXC
- There are many theories as to what exactly what UXC(r) is, one common simple approximation gives:

$$U_{xc}(\vec{r}) = -C\frac{q^2}{4\pi\varepsilon_0}[n(\vec{r})]^{1/3}$$

- Where $C \approx 1$ .This is often called the 'Local Density Approximation' (LDA).

• A physical justification for this approximation is the near exact experimental agreement with virtually all atoms. See F. Herman and Skillman, "Atomic Structure Calculations", p. 3-9, Prentice-Hall (1963).

• Of course this is harder to do with molecules and so alternate $U_{xc}(\vec{r})$ approximations are needed. More on this later.

•Next Lecture: The Energetics of Bonding.