

Quantum Transport:

Atom to Transistor

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Lecture 9: Self Consistent Field, Basic Concept

Ref. Chapter 3.1



Network for Computational Nanotechnology





Retouch on Concepts

00:00

- The time independent Schrödinger Equation:

$$E\Psi = \left[\frac{-\hbar^2}{2m} \nabla^2 \Psi + U(r) \right] \Psi$$

- Last time we talked about the Hydrogen atom and how to calculate both the eigen wave functions and energy levels numerically
- Solving 3D problems directly can be difficult, but by applying of separation of variables problems can be made easier

- Separation of variables in spherical coordinates can be done with all atoms

- Atomic solutions can be written in the form

$$\Psi = R(r)Y_l^m(\mathbf{q}, \Phi) = \frac{f(r)}{r} Y_l^m(\mathbf{q}, \Phi)$$

- Remember $R(r) = f(r)/r$ is used to simplify the radial separable equation to the form:

$$Ef = \left[\frac{-\hbar^2}{2m} \frac{d^2}{dr^2} + U(r) + \frac{l(l+1)\hbar^2}{2mr^2} \right] f$$

Hydrogen Orbitals

05:10

- For any particular value of l we can solve the radial Schrödinger Equation
- l comes from the spherical harmonics $Y_l^m(\theta, \Phi)$
- For Hydrogen, l gives the known atomic orbitals
 - $l = 0$: s levels
 - $l = 1$: p levels
 - $l = 2$: d levels
- Note: for $l = 0$, $m = 0$
 - $l = 1$, $m = -1, 0, 1$
 - $l = 2$, $m = -2, -1, 0, 1, 2$Therefore, s levels have no degenerate states, p levels have 3, and d five, etc.

- Usually we only care about the lowest energy levels, as seen here:

	$l = 0$	$l = 1$	$l = 2$
	4s	4p	4d
	3s	3p	3d
	2s	2p	
	1s		
Energy ↑			

Hydrogen Orbitals

08:00

	$l = 0$	$l = 1$	$l = 2$
	4s	4p	4d
	3s	3p	3d
	2s	2p	
	1s		
Energy ↑			

- To solve for the s levels ($l = 0$), p levels ($l = 1$), d levels ($l = 2$) we need to solve a different version of the Schrödinger Equation in each case!

- There is no 1p level, counting begins at 2p. Similarly, there are no 1d and 2d levels

- Why do the p and d levels have more energy?

- Because the term $\frac{\hbar^2 l(l+1)}{2mr^2}$ is repulsive (positive)

unlike the $\frac{-Zq^2}{4\pi\epsilon_0 r}$ coulomb potential (or $\frac{-q^2}{4\pi\epsilon_0 r}$ for Hydrogen-like atoms)

- Don't forget, the s levels are not degenerate, the p levels 3-fold degenerate, and the d levels 5-fold.

Hydrogen Orbitals

12:00

	$l = 0$	$l = 1$	$l = 2$
	4s	4p	4d
	3s	3p	3d
	2s	2p	
	1s		
Energy ↑			

- Ignoring higher order effects, the 2s and 2p levels have the same energy. Similarly, so do the 3s, 3p, and 3d levels, etc.

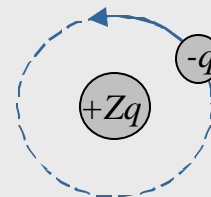
- This effect is unique to Hydrogen-like atoms
- It explains why a simple equation such as $E_n = (-Z^2 / n^2) E_0$ can give all the energy levels of Hydrogen-like atoms with good accuracy

- Recall:
 $E_0 = (q^2) / (8\pi \epsilon_0 a_0)$
 $a_0 = 0.0529\text{nm}$ and the equations of derivation are: $2pr = n(\hbar / mv)$

$$\frac{Zq^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}$$

$$E = -\frac{Zq^2}{4\pi\epsilon_0 r} + \frac{mv^2}{2}$$

Hydrogen-like Atom

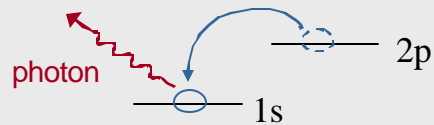


Hydrogen and Onto Helium

23:49

- $a_0 = 0.0529\text{nm}$ is often referred to as the "Bohr Radius". Also, $E_0 = -13.6\text{ eV}$. So an electron in the 1s level has an ionization energy of $E = -13.6\text{ eV}$ and 2s an ionization energy of $E = \frac{1}{4} (-13.6\text{ eV})$

- Energy levels such as these are measured by optical emission:



- Or with more difficulty by the photo-electric effect. Meaning, the photon energy is needed to knock an electron into the vacuum

- What would happen if we did such experiments on Helium?

- Using the Bohr model, one would expect all energy levels to be expressed by $E_n = (Z^2/n^2) E_0$ and the ground state ionization energy to be $(4)(-13.6\text{eV}) = -54.4\text{eV}$

- However, experimentally this turns out to be wrong; the first ionization energy is approximately $+23.4\text{eV}$
 $(\text{He} + h\nu = \text{He} + 23.4\text{V}) \rightarrow \text{He}^+ + \text{e}^-$

- But the quantity 54.4eV is not completely irrelevant, it is the second ionization energy:
 $(\text{He}^+ + h\nu = \text{He}^+ + 54.4\text{eV}) \rightarrow \text{He}^{++} + \text{e}^-$



Atomic Self Consistent Field

33:00

- We are getting the incorrect ionization energies because we are not accounting for **electron-electron** repulsive potentials

- How do we include electron-electron interactions?

- A first step is to add a self-consistent field term $U_{\text{scf}}(r)$ to the radial Schrödinger Equation:

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

- $U_{\text{scf}}(r)$ is due to the other (Z-1) electrons. An electron does not feel a potential due to itself

- Why must electron-electron interactions be calculated self-consistently?

- To calculate $U_{\text{scf}}(r)$ electronic charge is needed but electronic charge distribution depends on the individual electron wave functions that are derived from the Schrödinger Equation which in turn depends on $U_{\text{scf}}(r)$. Therefore, the equations must be solved self-consistently

Hartree Approximation

36:00

- The Hartree approximation treats the self-consistent field as:

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

Where $n(\vec{r})$ is the electron density. Or in integral form:

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

- In spherical coordinates the total number of electrons is therefore:

$$N = \int \left[dr' r'^2 \sin \theta' d\theta' d\Phi' \times \sum_{\text{occ. } m, l, m} \left| \frac{f_n(\vec{r}')}{r'} \right|^2 \left| Y_l^m \right|^2 \right]$$

- And since Y_l^m is normalized...

$$N = \int dr' S(r') \quad \text{where} \quad S(r) = \sum_{\text{occ. } m, l, m} |f_n(r)|^2$$

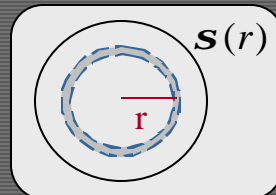
- Summed over all occupied states, the $n(\vec{r})$ may be expressed as:

$$n(\vec{r}') = \sum_{\text{occ. } n, l, m} \left| \frac{f_n(\vec{r}')}{r'} \right|^2 \left| Y_l^m(\theta, \Phi) \right|^2$$

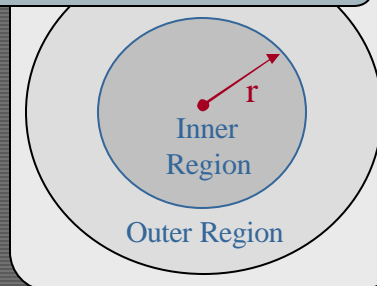
Hartree Approximation

44:30

- $s(r)$ tells us how much charge exists in a particular shell at a particular radius. To visualize ...



- Two regions of charge at radius r :



- To simplify the computation of the integral:

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

we split the spherical space of charge into two regions

- Using this approach we can simplify the potential due to the inner region to a point charge at the origin. Likewise, we can treat the outer shell of charge as a constant external potential

Hartree Approximation

49:00

- So the potential due to the inner region is:

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

- And the outer region:

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

- Remember, overall this must be solved self-consistently. A rough sketch of this process:

1. Make a guess for $U_{\text{scf}}(r)$ (usually zero)
2. Find eigenvalues and eigenfunctions of the Schrödinger Equation
3. Calculate the electron density $n(r)$
4. Calculate the electronic potential $U_{\text{scf}}(r)$
5. If the new $U_{\text{scf}}(r)$ differs significantly from the last guess, go back to step 2, else exit the self-consistent loop. A reasonable difference for terminating the loop is say $k_B T/10$.

- Overall, they contribute to the final self-consistent field which is:

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

where the scaling factor $(Z-1)/Z$ is added to account for the fact that an electron feels no repulsion due to itself