

# Fundamentals of Nanoelectronics

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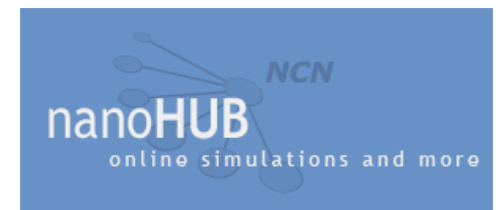
09.27.2004

## Lecture 14: Covalent Bonds

Ref. Chapter 3.3



*Network for Computational Nanotechnology*



## Solution of Schrödinger Equation in 3D

00:03

- Last session we talked about finding energy levels of Hydrogen atom. To find energy levels of any material, the Schrödinger equation is the first step:

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

- Since  $U(r) \sim 1/r$  and as the result  $U$  does not depend on theta or phi (spherical symmetry), the solution can be written as:

$$\Phi = \frac{f(r)}{r} Y_l^m(\theta, \varphi)$$

- Putting this solution in the Schrödinger equation gives us the energy levels:

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

- “l” can take integer values and “m” can take values from -l to l in steps of 1:

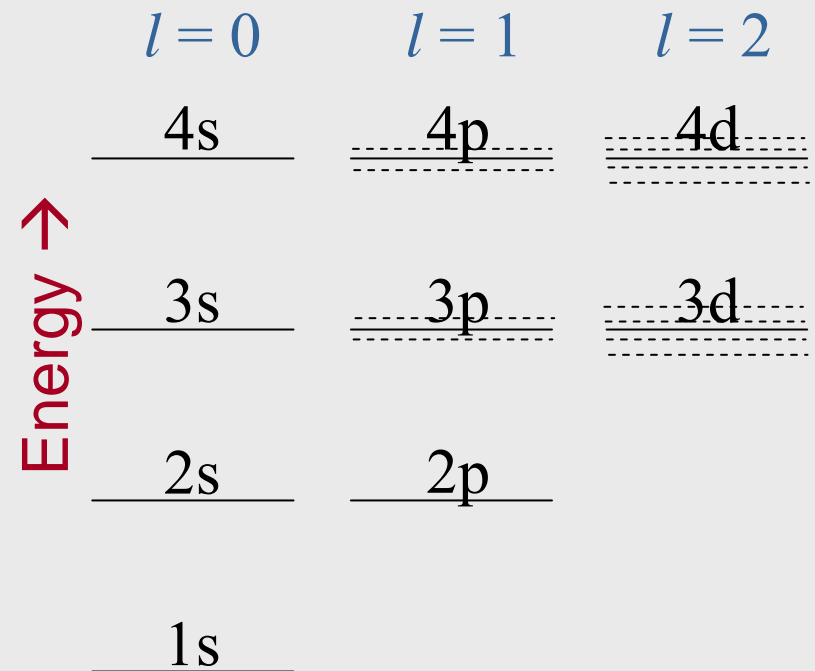
$$l = 0, 1, 2, \dots$$

$$m = -l, -l+1, \dots, 0, \dots, l-1, l$$

# Atomic Energy Levels and Self Consistent Solution

02:13

- Since the potential in Hydrogen atom has the form of  $1/r$ , the levels 2s and 2p are at the same energy. This does not have to be the case for other atoms. In all other atoms, the p levels will be a little higher than s levels and the d levels will be higher than p levels. Equation 1 can be used to solve for the energy levels. The equation can be turned into a matrix equation and the eigenvalues and eigenvectors can be found from there.
- Solving 1 for any other atom becomes a lot harder because then it has to be solved self consistently. This is because the potential  $U(r)$  has two parts: nuclear potential and the electron cloud potential. Since the potential of each electron affects the other ones, the problem must be solved self consistently.

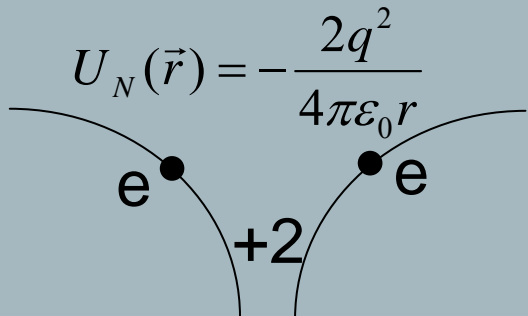


$$U(\vec{r}) = U_N + U_{ee}$$

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

# Self Consistent Field (SCF)

- Consider Helium for example. It has 2 positive charges at the origin.

$$U_N(\vec{r}) = -\frac{2q^2}{4\pi\epsilon_0 r}$$


The diagram illustrates a Helium atom. At the center is a nucleus labeled '+2'. Two electrons, represented by black dots and labeled 'e', are shown in elliptical orbits around the nucleus. The equation  $U_N(\vec{r}) = -\frac{2q^2}{4\pi\epsilon_0 r}$  is written above the diagram, representing the nuclear potential energy.

- But for electronic energy levels we also have to include the potential due to the other electron which is a repulsive potential. So we need to add something to  $U_N$ . But we do not know that potential unless we know the electron's wave function. The electron wavefunction has to be found from Schrödinger equation which requires the electron potential to be solved. This is why self consistency is coming to play. In all:  $U = U_N + U_{scf}$

- One starts with a reasonable guess for  $U_{scf}$ . Then solves the Schrödinger equation and finds the wavefunctions which in turn give the electron density:

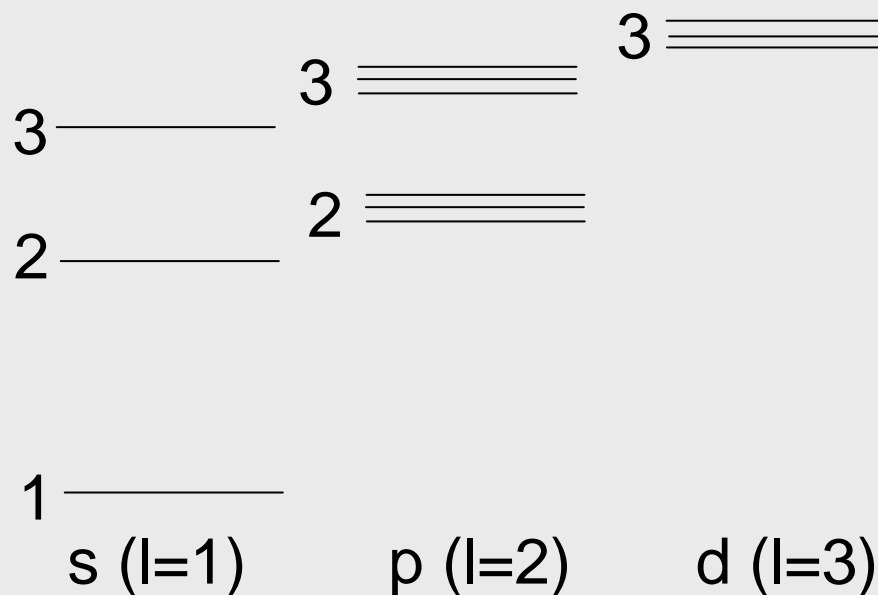
$$n(\vec{r}) = \sum_{\text{occupied } \alpha} \Psi_{\alpha}^* \Psi_{\alpha}$$

- From electron density one finds the corresponding potential and compares it with the initial guess and modifies the guess to match the calculated result better. This process goes on till the answer converges. That is to say the guessed value and the calculated value are very close to each other.
- This is very important because without it, one gets results that are very wrong. Solving for He 1s level without  $U_{scf}$  we get -54.4eV. But the experimental value is measured to be -23.4eV. The difference is coming from the repulsive potential:  $U_{scf}$ .

# Atoms and Energy Levels

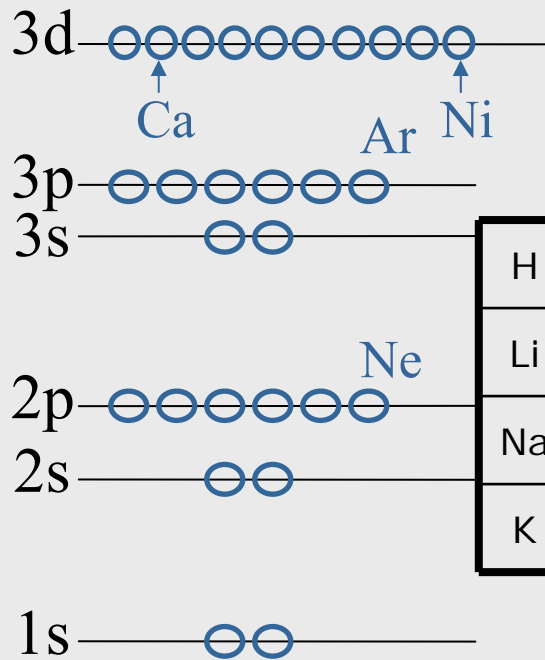
15:08

- The energy levels can be cataloged as illustrated:



- As one goes through the periodic table these energy levels get filled by electrons. See next slide...

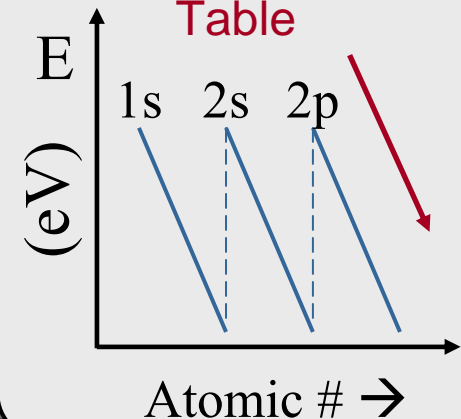




## Filling up Valence Electrons

## Valence Electrons

Towards the right  
along the Periodic  
Table



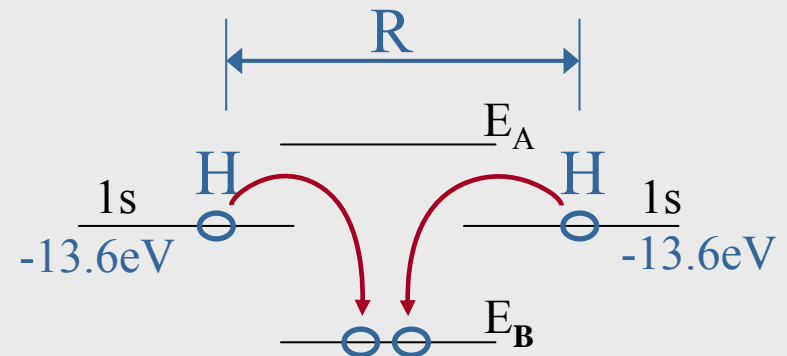
- As we go down the rows the valence levels fill. As a level fills, going along left to right, energy levels become more negative.
- Usually ionic bonds are formed between atoms on opposing sides of the periodic table. Take for example Na and Cl. Since the valence level in chlorine is more negative compared to sodium, the valence electron in Na tends to go the Cl level to form an ionic bond.
- Electrical and optical properties are all about the valence electrons! Not concerned with core electrons. Although, core electrons are valuable for diagnostic purposes (e.g. knowing what impurities are present in silicon) Note that core electrons do not get affected by the surroundings.

# Covalent Bonding

29:35

- As far as valence electrons are concerned we want to understand the nature of energy levels of solids. On the way to solids we will talk about the energy levels in molecules today.
- As was mentioned before, ionic bonds are formed between atoms on opposing sides of the periodic table. An electron in a higher level energy in one atom goes to a lower energy in another atom. However...
- All the solids that we are interested in like silicon are formed by covalent bonds which are very different from ionic bonds. For the example why two H atoms bond together to form H<sub>2</sub> molecule. The generic reason is that H<sub>2</sub> has a lower energy than 2 H atoms. But how can that be understood? One realizes that the argument of ionic bonding does not work here because the electron in the two H atom are at the same energy level.

## Two Hydrogen Atoms



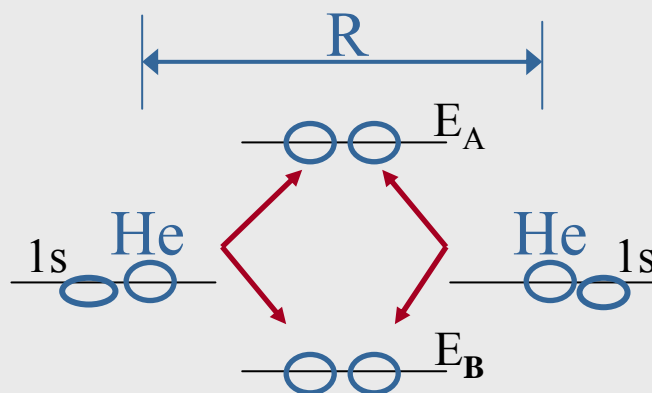
- As the two atoms get close together one, solution of Schrödinger equation shows that there will be two available levels. One level forms a little lower,  $E_B$ , and another a little higher,  $E_A$ . In this way, energy can be gained through bonding

# Why isn't there a covalent bond for Helium?

35:31

- Why doesn't this work for He?

## Helium Bonding?

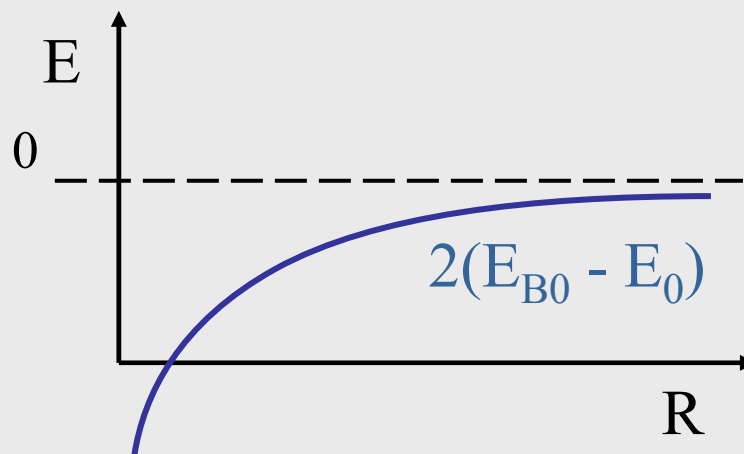
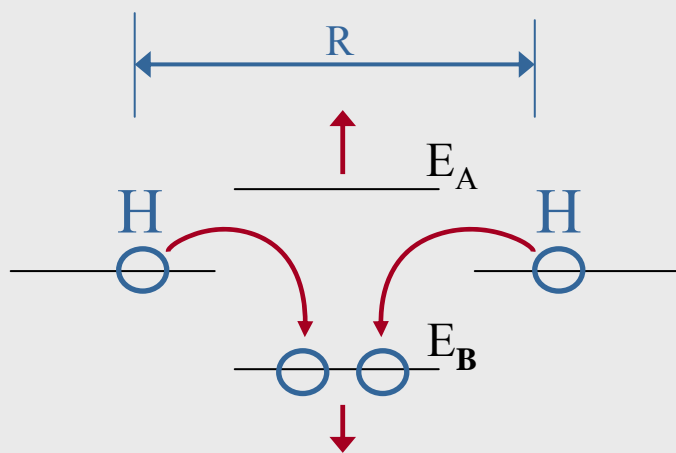


Since electrons must fill the top and bottom bonding levels, no energy can be gained in the process and so bonding does not occur. Covalent bonding works best with partially filled valence bands. For example the group 4 elements: C, Si, Ga, etc.



# H<sub>2</sub> Collapse?

37:49



- Since the objective is to minimize energy, a total collapse to  $R=0$  seems to make sense. However, we are ignoring key electron and nuclear interactions:

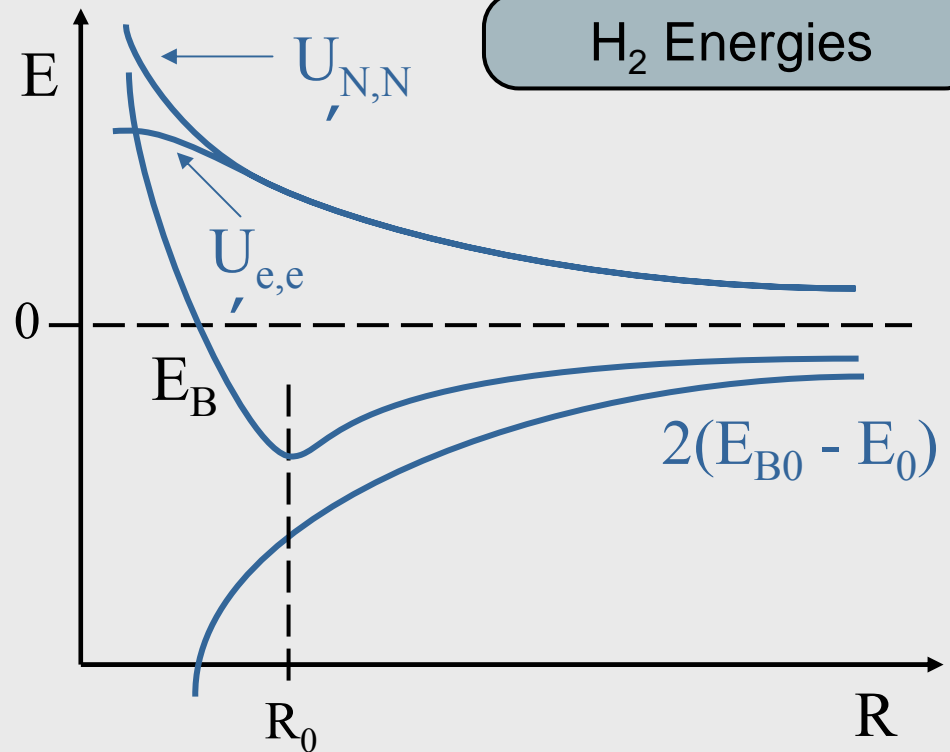
$$E(2H) = U_{e,N} + U_{e',N'} = 2E_0 \quad \text{and}$$

$$E(H_2) = U_{e,N} + U_{e,N'} + U_{e,e'} + U_{N,N'} + U_{e',N} + U_{e',N'}$$

# Interaction in an H<sub>2</sub> Molecule

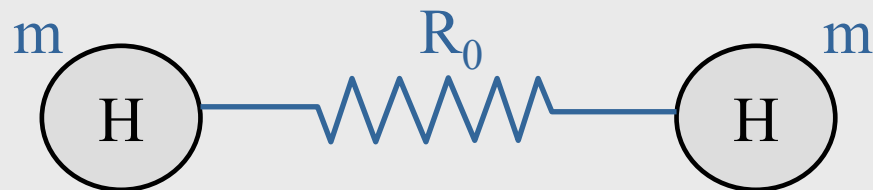
- If we include all the interactions involved, then we get a curve like the one marked by  $E_B$ . So there is actually an optimum distance at which the energy is minimum and that is the actual bond distance of H<sub>2</sub> molecule.

- So, it is important to consider the full energetic...



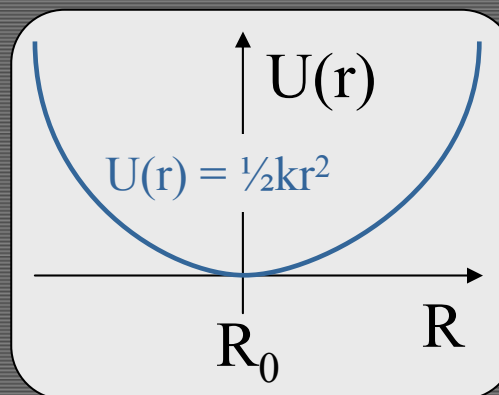
# Spring Mass Visualization

- One can visualize this as a a spring mass system.
- Consider the covalent bond as a spring connecting the two masses in H<sub>2</sub> molecule:
- $R_0$  is the equilibrium length of the spring



As known, the curve of an ideal spring looks like:

- The bonding curve, as with Hydrogen molecule, is usually not parabolic but for the small region around  $R_0$  we can approximate  $E_B$  with an appropriate parabola that describes the energy of a two mass and a spring system.



- Finally, this bonding picture can be extended to large systems such as solids. In silicon we can have silicon atoms be represented by masses and the bonding between them by springs.

