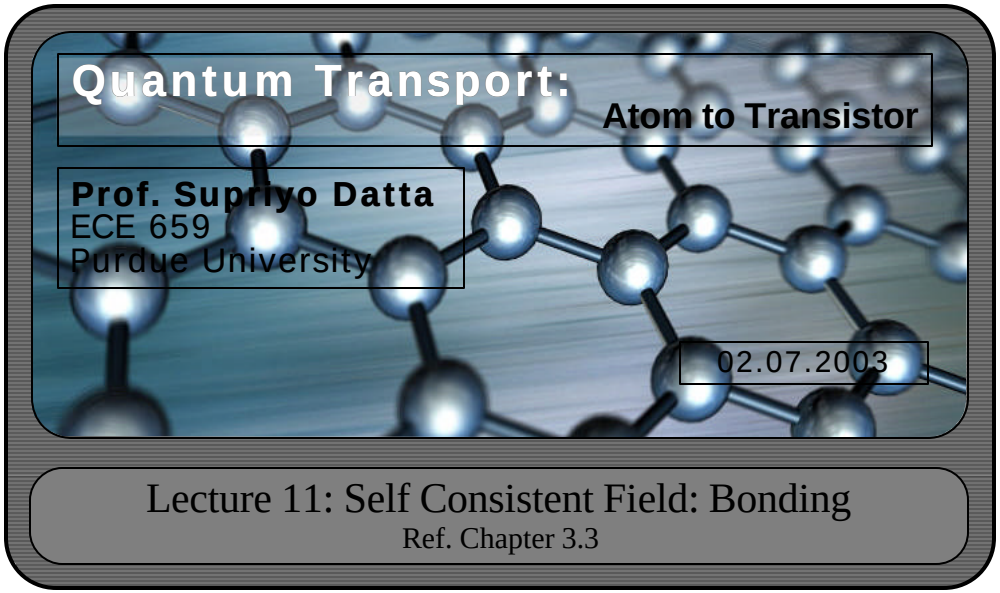


Lecture 11: Self Consistent Field: Bonding

Ref. Chapter 3.3

Network for Computational Nanotechnology

nanoHUB
online simulations and more

Retouch on Concepts

00:00

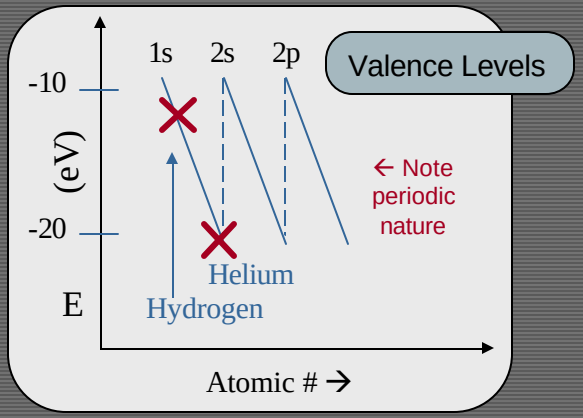
• Last time we talked about the self consistent field method, recall:

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + U_N(r) + U_{scf}(r)\right]\Psi_a = E_a\Psi_a$$

• Basic Ideas:
– Solve Schrödinger Eq. with added U_{scf} term
– U_{scf} accounts for electron-electron interactions
– Simplest method is the Hartree Approximation (U_H)
– It is recognized that there should be an additional negative term, U_{XC}, such that
$U_{scf} = U_H + U_{XC}$

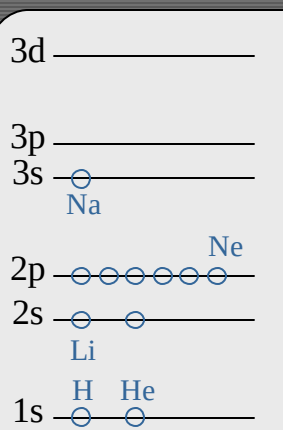
• So, using this approach, one can more or less understand all observed atomic spectra

• However, it is valence electrons that really matter, for which energy levels tend to go periodically up and down

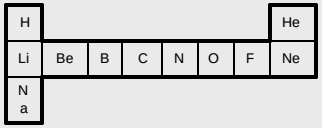


How the energy levels fill up

04:45

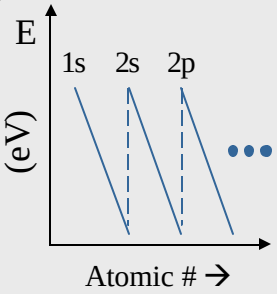


Filling up Valence Electrons



- Outermost levels are relevant to the chemical properties of an element

Valence Electrons

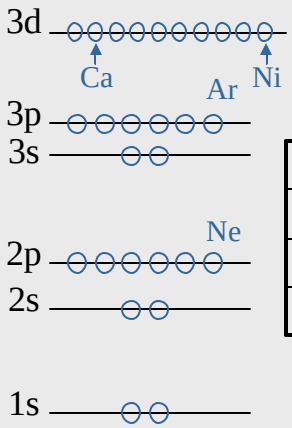


- Not concerned with core electrons. Although, core electrons are valuable for diagnostic purposes (e.g. knowing what impurities are present in silicon)

- Electrical and optical properties are all about the valence electrons!

More of the table

11:17

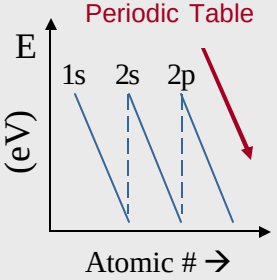


Filling up Valence Electrons

H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr

Valence Electrons

Towards the right along the Periodic Table



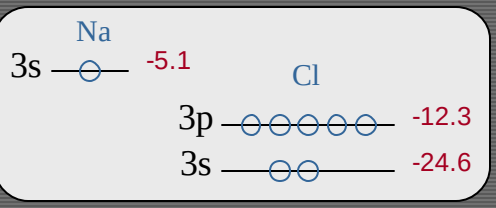
- As we go down the rows and right along the columns the valence levels fill
- Note: as a level fills, going along left to right, energy levels become more negative

Ionic Bonding

14:53

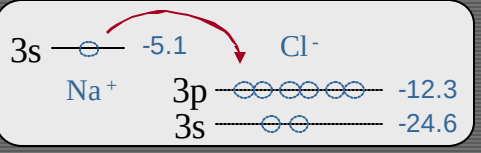
• Usually ionic bonds are formed between atoms on opposing sides of the periodic table. Take for example Na and Cl

Na and Cl



• When they come together you'd expect $Na^+ Cl^-$, with the Na electron dropping 7.2eV

$Na^+ Cl^-$, 7.2eV drop



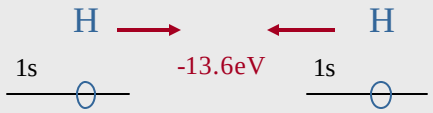
• However, this is **wrong**! The actual bonding energy is ~ 4eV. To get the correct answer one must consider how the electrostatic energy lowers as $Na^+ Cl^-$ are brought close together: ie.

Covalent Bonding: H_2

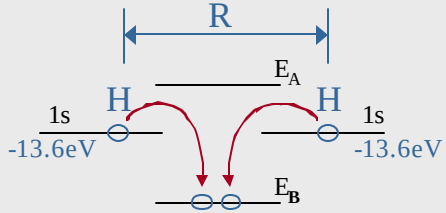
19:28

- Ionic bonding illustrates that careful considerations are needed to understand the energetics of electron transfer on an atomic scale.
- Onto covalent bonding … Many electrical materials, such as Silicon, form through covalent bonding
- A simple example of covalent bonding: H_2

Two Hydrogen Atoms



- Why do two Hydrogen atoms want to come together and form a bond?
- First, solve the Schrödinger Equation for two Hydrogen atoms at a distance R…



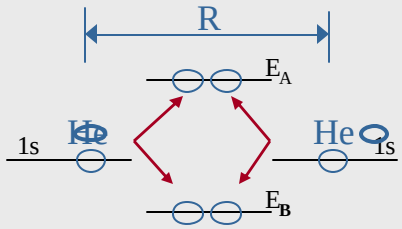
- And we see that one level forms a little lower, E_B, and another a little higher, E_A. In this way, energy can be gained through bonding

Covalent Bonding

24:30

• Why doesn't this occur with Helium?

Helium Bonding?



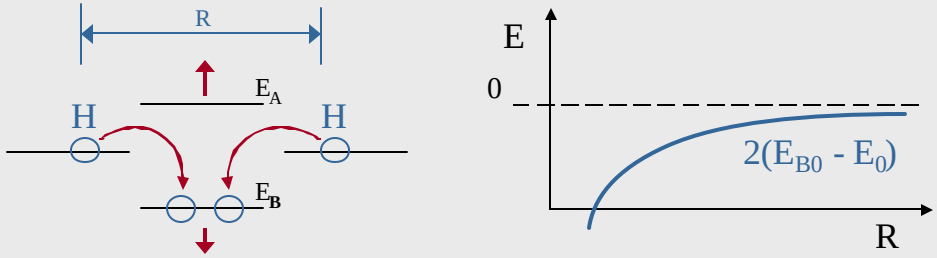
• Since electrons must fill the top and bottom bonding levels, no energy can be gained in the process and so bonding does not occur

• Covalent bonding works best with partially filled valence band. For example the group 4 elements: C, Si, Ga, etc.

• Note: in the case of the Hydrogen molecule it is not exactly obvious why the two atoms do not collapse since E_B continues falling and E_A continues rising as the atoms approach each other.

H_2 Collapse

H_2 Collapse



• 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:

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

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

H_2 Covalent Interactions

- Just solving for 2-nuclei we get:

$U_{e,N} + U_{e,N}' = E_{B0}$

$U_{e}',_{N} + U_{e}',_{N}' = E_{B0}$

- Thus,

$E(H_2) - E(2H) =$

$2(E_{B0} - E_0) + U_{e,e}' + U_{N,N}'$

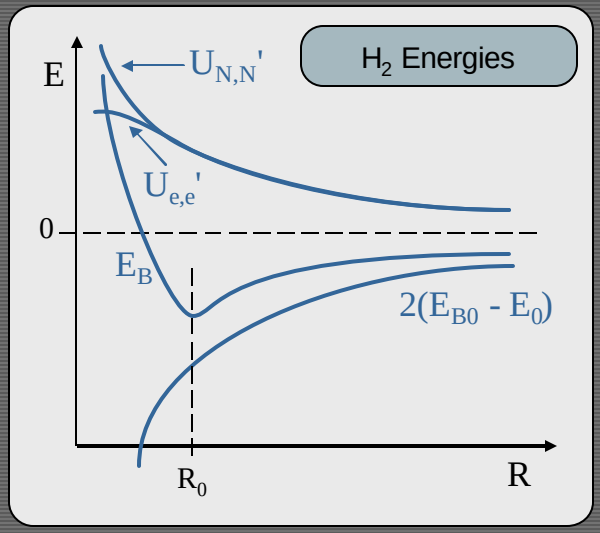
- Solving for $U_{N,N}'$ is easy:

$$U_{N,N'} = q^2 / (4\pi\varepsilon_0 R)$$

- Solving for Uee is the difficult part, so we approximate:

$$U_{e,e'} = \frac{q^2}{4\pi\varepsilon_0 \sqrt{R^2 + a_0^2}}$$

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



H_2 Ionization

35:48

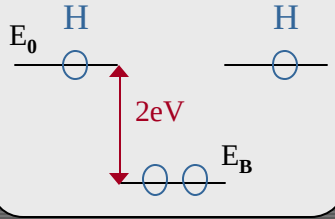
• What is the ionization energy of H_2^+ or $E(H_2) - E(H_2^+)$

• We know that
$E(H_2^+) = U_{e,N} + U_{e,N}' + U_{N,N}'$
Therefore
$E(H_2) - E(H_2^+) = E_{B0} + U_{e,e}' = E_B$

• So, the ionization or binding energy, E_B, is greater than the non-interacting value E_{B0}. Meaning that if we leave out $U_{e,e}'$ in our calculations the incorrect value will be obtained

• Also, conceptually it is tempting to view the binding energy as $E_{bin} = 2(E_B - E_0) + U_{N,N}'$

Binding Energy



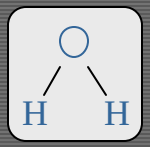
• Or simply, $E_{bin} = 2(2eV) + U_{N,N}'$
but this is wrong! We are double counting the electron-electron interaction energy. Corrected:
$E_{bin} = 2(E_B - E_0) + U_{N,N}' - U_{e,e}'$

Ground State Structure

43:30

• There is a great deal of work that has gone on, and continues to go on, examining the ground state structure of covalent molecules and lattices.

e.g. Why the water molecule is not linear?

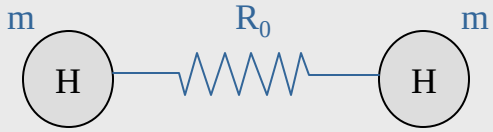


• In this course we will assume the molecular structure is known and look at current conduction only

• Next lecture: Basis Functions

• However, one more point remains to be addressed, visualization of bonding as a spring mass system

• Consider the covalent bond as a spring connecting the two masses:

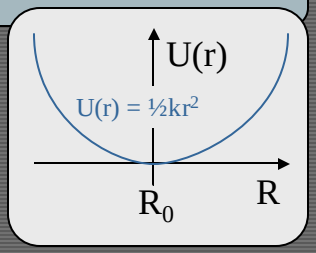


• Where R_0 is the equilibrium length of the spring

Equilibrium Structure as a Mass-Spring System

46:00

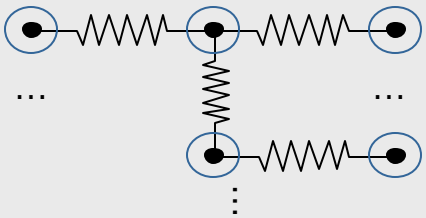
• As known, the potential curve of an ideal spring looks like:



• The vibrational frequency of H_2 can be accurately estimated from the resonant frequency

$$f_0 = \sqrt{\frac{2k}{m}}$$

• Finally, this bonding picture can be extended to large systems such as solids …



• The bonding curve, as with Hydrogen, is usually not parabolic but for the small region around R_0 we can approximate E_B with an appropriate spring constant k estimated from the curvature

$$\left[\frac{d^2U}{dR^2}\right]_{R=R_0}$$