Physics 0551 Lecture #7

The bonding of atoms

If a thorough discussion of the properties in the periodic arrangements of atoms is to be performed, then it is clearly necessary to justify the existence of these solids and discuss the interactions which mediate their formation. In general, it is energetically favorable for atoms to aggregate. (It is not immediately obvious that this collection of particles should form into an ordered structure!)

There are five basis classes of bonding which are traditionally discussed.

NAME	STRENGTH	ORIGIN
1. Van der Waals (e.g., N_2,H_2,Ne,Kr,Xe)	Very weak ($\sim$.1 eV/atom)	Dipole-Dipole interactions
2. Metallic (e.g., metals)	Weak to moderate ($\sim$1 eV/atom)	Global sharing of valence electrons
3. Ionic (e.g., NaCl, CaO, salts)	Strong	Electrostatic attraction of charged ions
4. Covalent (e.g., Si, Ge, Diamond)	Very strong ($\sim$5eV/atom)	Local sharing of electrons
5. Hydrogen (e.g., NH_3,H_2O)	Strong	Shared protons

The aforementioned bonding types are not mutually exclusive; there are intermediates to and combinations of the various bonding types.

For example:

1. Graphite - Covalent bonding within graphite layers and VdW between them.
2. N_2 - Covalently bonded pairs in a VdW solid.

Covalent Bonding

The nature of the covalent bond can be understood in the context of Quantum Mechanics using the Born-Oppenheimer approximation.

Main Points:

1: The time dependence of the electronic wave function [exp(iωt), E=$\hbar\omega$] is much faster than the motion of the atomic nuclei.

2: The Schrödinger wave equation can be solved for the electronic energy in the potential of these nucleii with the nuclear coordinates R as the comparison parameter.

Time-dependent Schrödinger Wave Equation:

$$-\frac{\hbar^2}{2m}\bigtriangledown^2\psi(\vec{r},t)+U(\vec{r},t)\psi(\vec{r},t)=i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)$$

m is the mass of the electron
ψ is the wave function
U is the potential

Now $\psi(\vec{r},t) = \psi(\vec{r})f(t)$ where these two terms are the spatial and temporal parts of the wave function respectively.

$$f(t)\propto e^{i\omega t}, \quad \text{thus}$$

$$|\psi(\vec{r},t)|^2=\psi^*\psi=|\psi(\vec{r})|^2, \quad E=\hbar\omega$$

Time-independent Schrödinger Wave Equation:

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

What is U($\vec{r}$)?

The potential energy for a single electron:

$$U_1\left(\vec{r}\right)=-\frac{e^2}{4\pi\varepsilon_0}\sum_i\frac{Z_i}{|\vec{r}-\vec{R}_i|}$$

electron-nucleus interaction

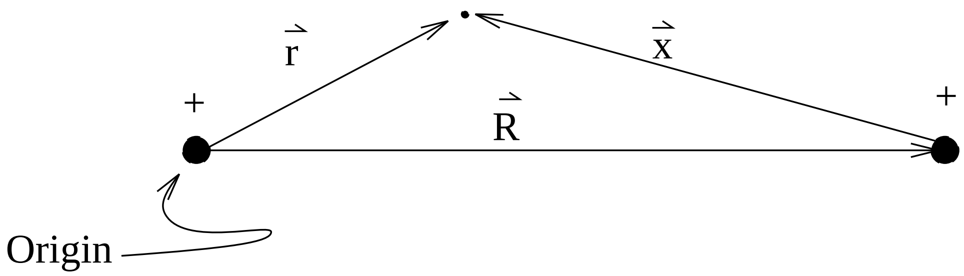
$\vec{R}_i$ is the position of the ith nucleus

$$U_2\left(\vec{r}\right)=\frac{e^2}{4\pi\varepsilon_0}\int\frac{\rho\left(\vec{r}\,'\right)}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,' \qquad \rho\left(\vec{r}\,'\right)=\sum_i|\psi_i\left(\vec{r}\,',t\right)|^2$$

electron-electron interaction

In general, the solution to the previous expression is not immediately obvious or trivial. However, we will examine the solution for an H_2^+ ion.

$$U\left(\vec{r}\right)=-\frac{e^2}{4\pi\varepsilon_0}\left[\frac{1}{|\vec{r}|}+\frac{1}{|\vec{r}-\vec{R}|}\right]$$



Approximation: Assume $\vec{R}$ is sufficiently large, so that near each proton $\psi(\vec{r})$ will closely resemble the H 1s wave-function.

$$\psi_H(r) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} \qquad a_0 = .53\text{Å, Bohr radius}$$

$$\int_{\text{all space}} \psi_{\text{H}}^{*}\psi_{\text{H}}\; d^3r = 1 \qquad \text{Normalization condition}$$

So

$$\psi_{\text{H}_2^+} = C[\psi_{\text{H}}(|\vec{r}|) + \psi_{\text{H}}(|\vec{r} - \vec{R}|)]$$

is one possible solution

Note:

$$C = |\frac{1}{2(1+\Delta)}|^{1/2}; \quad \Delta = \int \psi_{\text{H}}(|\vec{r}|)\,\psi_{\text{H}}(|\vec{r} - \vec{R})|d\vec{r}$$

Since

$$\begin{aligned} \textstyle\int \psi_{H_2^+}^{*}\psi_{H_2^+}\,d\vec{r} &= 1 \\ &= C^2 \textstyle\int d\vec{r}\;[\psi_{\text{H}}^2(\vec{r}) + 2\psi_{\text{H}}(\vec{r})\,\psi_{\text{H}}\left(\vec{r} - \vec{R}\right) + \psi_{\text{H}}^2\left(\vec{r} - \vec{R}\right)] \end{aligned}$$

Now

$$\int d\vec{r}\;\psi_{\text{H}}^2(|\vec{r}|) = 1 = \int d\vec{r}\;\psi_{\text{H}}^2(|\vec{r} - \vec{R}|)$$

$$1 = C^2[1 + 2\int d\vec{r}\;\psi_{\text{H}}(|\vec{r}|)\psi_{\text{H}}(|\vec{r} - \vec{R}|) + 1]$$

$$C = |\;\frac{1}{2(1+\Delta)}\;|^{1/2}$$

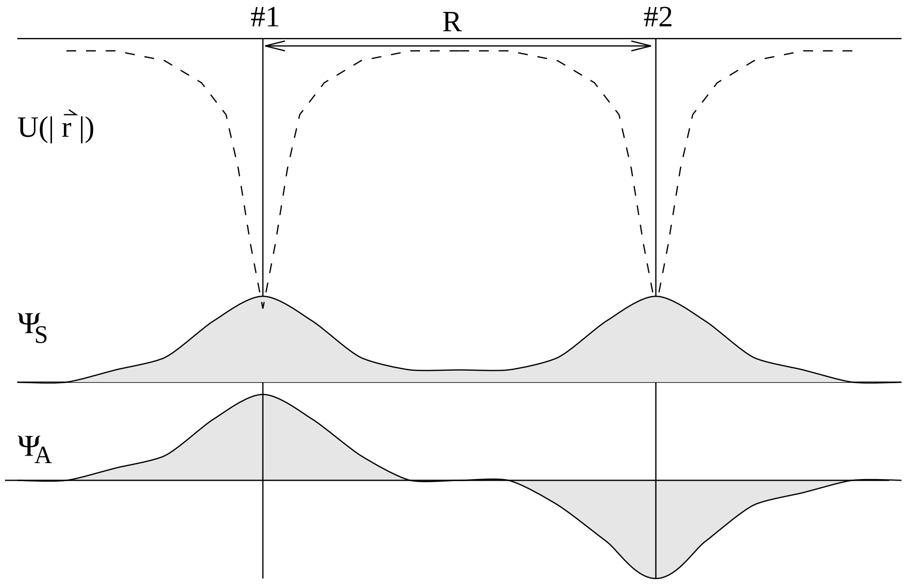
Call this the symmetric solution $\psi_S(|\vec{r}|)$.

An anti-symmetric solution

$$\psi_A(|\vec{r}|) = C'[\psi_{\text{H}}|\vec{r} - \psi_{\text{H}}(|\vec{r} - \vec{R}|)] \quad \text{also exists.}$$

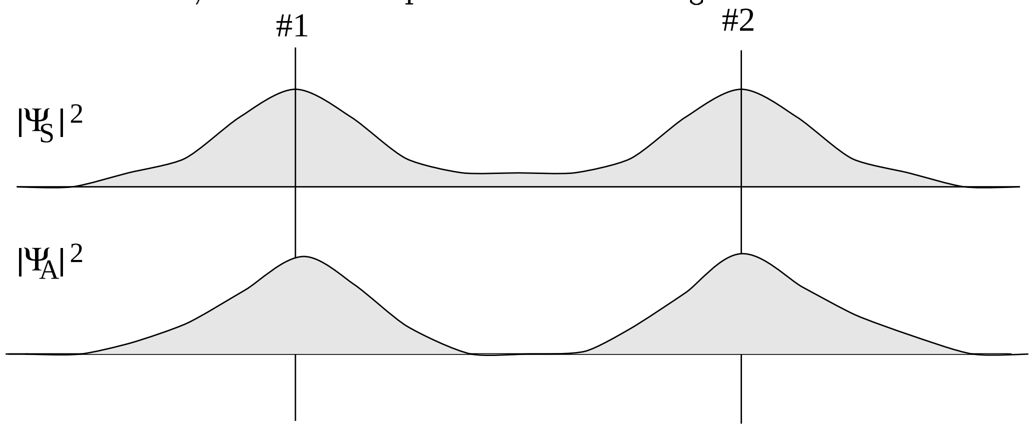
$$C' = |\frac{1}{2(1-\Delta)}|^{1/2}$$

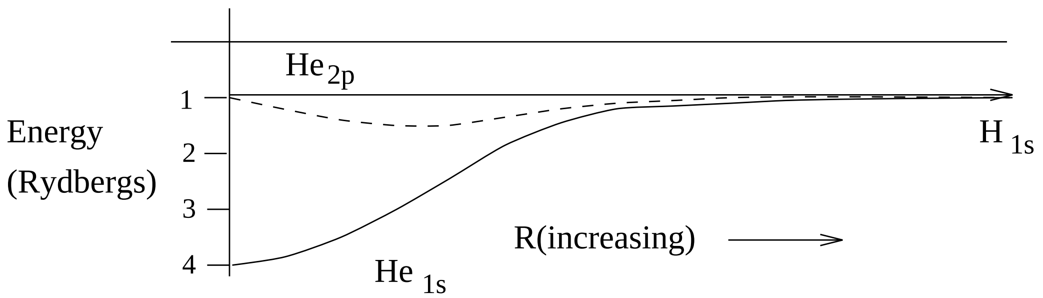
So for



Rather than ψ_S, ψ_A, plot $|\psi_S|^2, |\psi_A|^2$

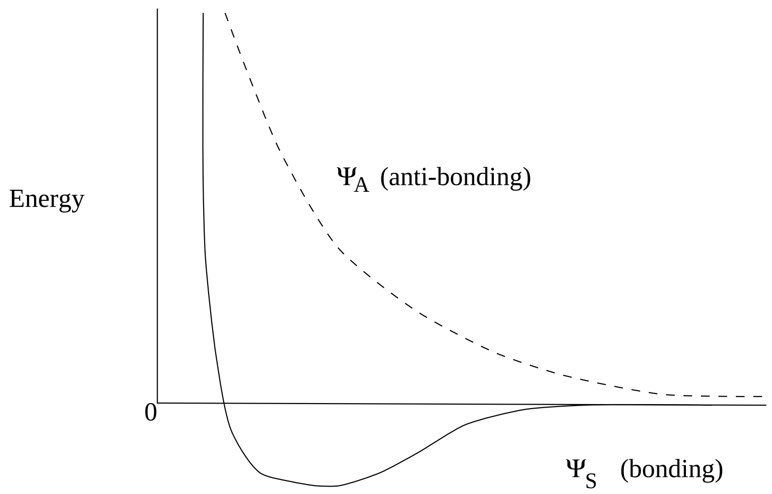
Notice that for $|\psi_S|^2$, there is increased electron density in a region where the charge is "shared". Hence, it should be expected that this configuration has the lower energy.





At R=0, the problem reduces to that of the He^+ ion solution.

To get the total energy, the $+e^2/R$ nuclear repulsion should be included. Thus



These states can be occupied by $2e$'s, one $\uparrow$ and one $\downarrow$. For the higher Z elements, the repulsion of the core electrons must be included. This result is still only an approximation, for the electron-electron interactions have been neglected!

For Group IV elements the electron configuration is more complicated since there are 4 electrons in the valence shell.

For Carbon, $2s2$, $2p2$ is the ground state. When carbon atoms are brought together, the total energy can be lowered with sp^3 hybridization.

$2p \searrow$ — — — — sp^3 anti-bonding (antisymmetric)

A sp^3– – – – B sp^3– – – – $\nearrow$ $\searrow$

$2s \nearrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ sp^3 bonding (symmetric)

$2s + 2p_x + 2p_y + 2p_z$ $\uparrow\downarrow$
$2s - 2p_x + 2p_y + 2p_z$ $\uparrow\downarrow$
$2s + 2p_x - 2p_y + 2p_z$ $\uparrow\downarrow$
$2s + 2p_x + 2p_y - 2p_z$ $\uparrow\downarrow$

Covalently bound solids

1. High melting point - large cohesive energy
2. Loose packing
3. Insulators - non magnetic
4. Brittle

C 170 Kcal/mole
(7.4 eV/atom)
Si 101 Kcal/mole