4/11/01

Lecture 34 Chemical Binding

Pauli Exclusion Principle

Overall Spin + Space Wave function is antisymmetric.

$\Rightarrow$ (symmetric in space) (antisym. in spin)

or

(antisymmetric in space) (symmetric in spin)

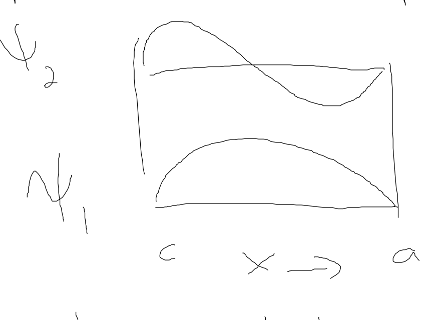
Note

antisym in spin $\Rightarrow S=0$ $\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

sym. in spin $\Rightarrow S=1$ $\begin{cases} \uparrow\uparrow \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ \downarrow\downarrow \end{cases}$

IN general symmetric spatial states have lowe energy than antisym. states.

Example two particles in a square well



Symmetric state $\psi_1(x_1)\,\psi_1(x_2)$
both particles in ground state

antisym. state: Need at least one particle in first excited state

$$\psi_1(x_1)\,\psi_2(x_2) - \psi_1(x_2)\,\psi_2(x_1)$$

because $\psi_1(x_1)\,\psi_1(x_2) - \psi_1(x_2)\,\psi_1(x_1) \equiv 0$

H_2 Molecule and Chemical Binding

How does energy of H atom depend on its size?

$$E = \langle T \rangle + \langle V \rangle$$

$$\sim \frac{\hbar^2}{2m}\left(\frac{1}{\Delta x}\right)^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{\Delta x}$$

From $p \sim \Delta p \sim \frac{\hbar}{2}\frac{1}{\Delta x}$

Now consider H_2 molecule. If we spread the electron cloud out over both H atoms one can increase Δx and therefore decrease kinetic energy of cloud.

Large Kinetic Energy

Smaller Kinetic energy

At the same time the distance from one or the other of the nuclei is not any greater. Therefore delocalizing the electron on both nuclei does not increase the potential energy

Note need to put two electrions in this one spatial orbital. However you can do this if you use an antisymmetric $S=0$ spin state.

Two electrions in ground state of H_2 molecule have $S=0$.

This same basic idea works for many bounds in chemistry.

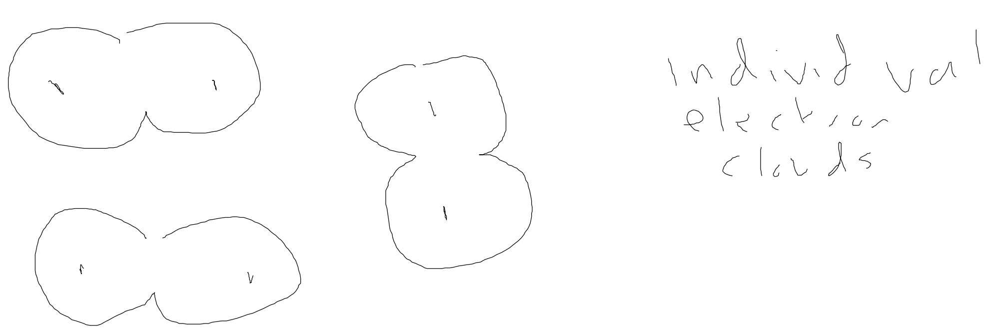
The energy of the two H atoms is lower when they are nearby and share the electrions.

Pressure Melting

Metalic Hydrogen, Other metals and White Dwarfs and neutron stars.

Liquid Hydrogen

At lower densities one has molecular hydrogen. Electrions are bound to individual H_2 molecules. Not so easy for an electrion to jump from one molecule to the next. $\Rightarrow$ Electrical conductivity is low.



At high density under great pressure (millions of atm.) Electron clouds merge into one big electron cloud.

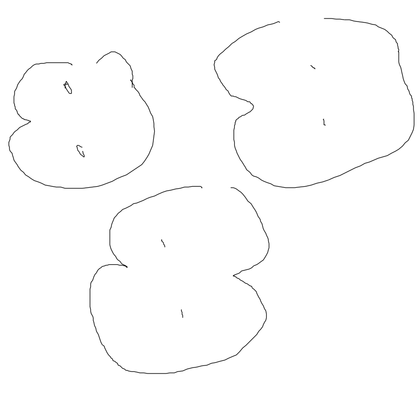
Electrons become delocalized over all of the molecules inside to reduce their kinetic energy.

If electrons are delocalized they can hop from one molecule to the next and the electrical conductivity is high.

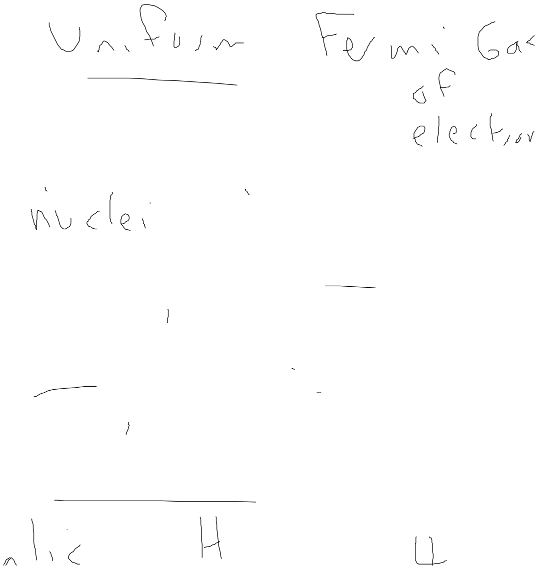
⟹ Phase transition to Metalic hydrogen. This is the interior of Jupiter and Saturn.

Experiments in lab which use explosives to compress samples have produced metalic H for very short time.

At very high density electrons are free to move about whole sample in more or less uniform background of positively charged nuclei



Molecular H



Metalic H

Squeeze even harder and get very high density electron gas.

Old stars can "die" as white dwarfs. They burn nuclear fuel H to He to C or O then nuclear reactions stop. Star starts to cool and collapse all the way to an object about the size of the earth. Called a White Dwarf.

Bright star Sirius has a small companion that is a white dwarf.

$\rho = 1\ g/cm^3$ water

$\sim 10\ g/cm^3$ heavy things like Pb or Uranium

$\rho \sim 10^5\ g/cm^3$ white dwarf.

The pressure in a white dwarf is dominated by the zero point motions of the electrons

$\Rightarrow$ Fermi gas.