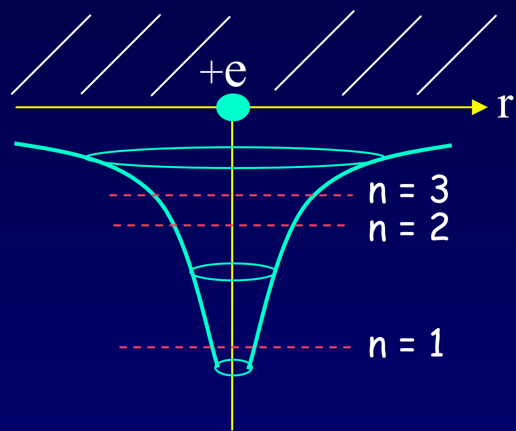
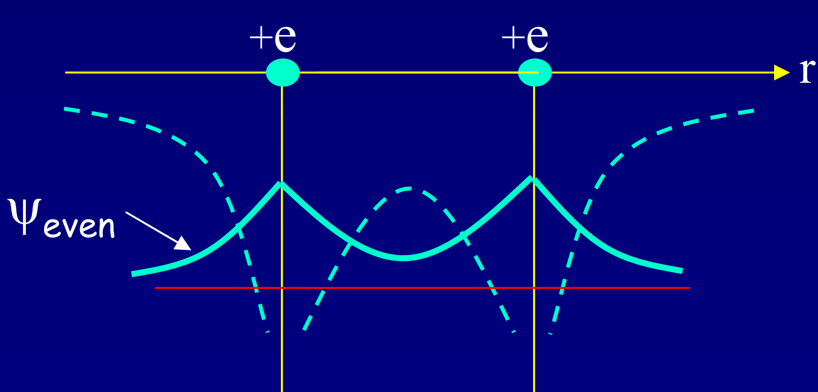
Lecture 19:
Building Atoms and Molecules





Today

Nuclear Magnetic Resonance

Using RF photons to drive transitions between nuclear spin orientations in a magnetic field

Atomic Configurations

States in atoms with many electrons –
filled according to the Pauli exclusion principle

Molecular Wave Functions: origins of covalent bonds

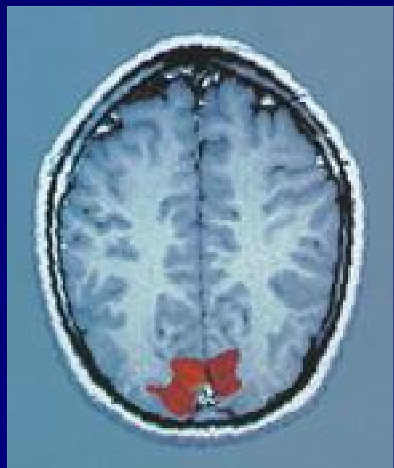
Example: $\mathbf{H + H \rightarrow H_2}$

Nuclear Magnetic Resonance

Just like electrons, the proton in the H atom also has a spin, which is described by an additional quantum number, m_p, and therefore also a magnetic moment. However, it is several orders of magnitude smaller than that of the electron.

- The energy difference between the two proton spin states in a magnetic field is 660 times smaller than for electron spin states!
- But… There are many more unpaired proton spins than unpaired electron spins in ordinary matter. Our bodies have many unpaired protons in H_2O. Detect them ……

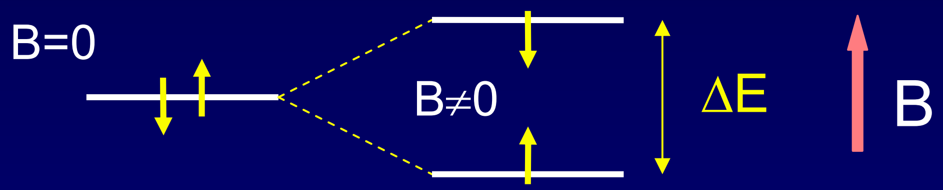
In order to image tissue of various types, Magnetic Resonance Imaging detects the small difference in the numbers of "up" and "down" hydrogen proton spins generated when the object studied is placed in a magnetic field.
Nobel Prize (2003): Lauterbur (UIUC)



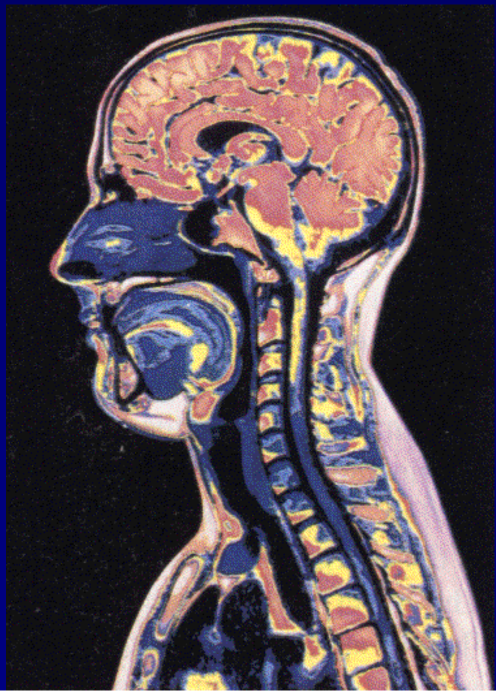
www.beckman.uiuc.edu/research/mri.html

Example: Nuclear Spin and MRI

Magnetic resonance imaging (MRI) depends on the absorption of electromagnetic radiation by the nuclear spin of the hydrogen atoms in our bodies. The nucleus is a proton with spin ½, so in a magnetic field B there are two energy states. The proton's magnetic moment is
$\mu_p = 1.41 \times 10^{-26}$ J /Tesla.



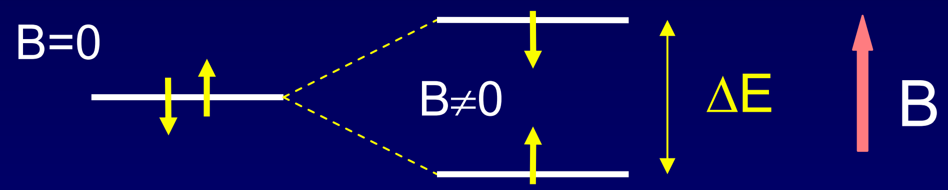
1) The person to be scanned by an MRI machine is placed in a strong (1 Tesla) magnetic field. What is the energy difference between spin-up and spin-down proton states in this field?

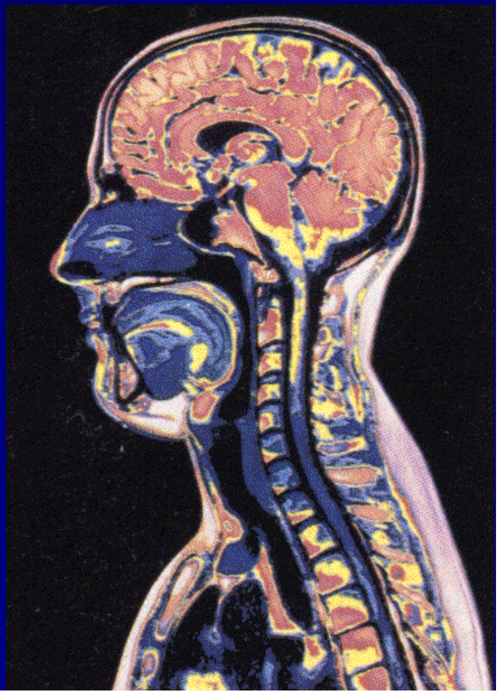


2) What photon frequency, f, will be absorbed?

Solution

Magnetic resonance imaging (MRI) depends on the absorption of electromagnetic radiation by the nuclear spin of the hydrogen atoms in our bodies. The nucleus is a proton with spin ½, so in a magnetic field B there are two energy states. The proton's magnetic moment is $\mu_p = 1.41 \times 10^{-26}$ J /Tesla.





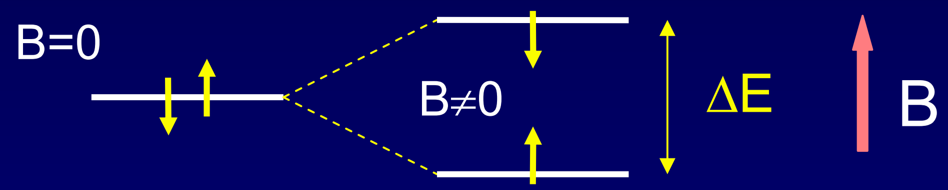
1) The person to be scanned by an MRI machine is placed in a strong (1 Tesla) magnetic field. What is the energy difference between spin-up and spin-down proton states in this field?

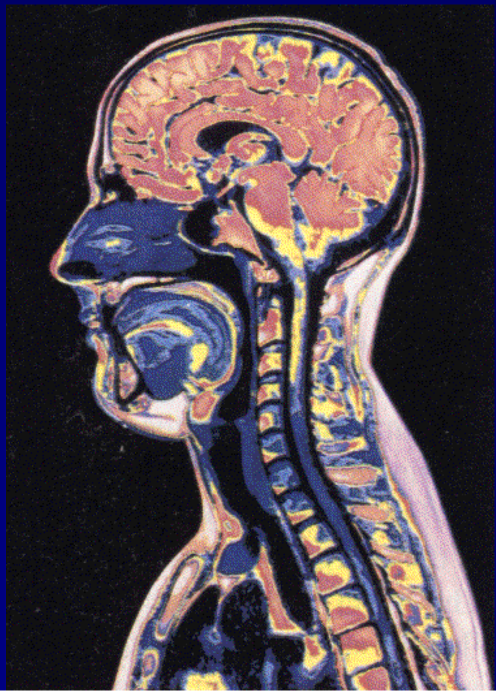
$$\Delta E = 2\mu_p B$$
$$= 2 \cdot (1.41 \times 10^{-26}\ \text{J/T}) \cdot (1\ \text{T})$$
$$= 2.82 \times 10^{-26}\ \text{J} = 1.76 \times 10^{-7}\ \text{eV}$$

2) What photon frequency, f, will be absorbed?

Solution

Magnetic resonance imaging (MRI) depends on the absorption of electromagnetic radiation by the nuclear spin of the hydrogen atoms in our bodies. The nucleus is a proton with spin ½, so in a magnetic field B there are two energy states. The proton's magnetic moment is μ_p = 1.41 x 10^{-26} J /Tesla.





1) The person to be scanned by an MRI machine is placed in a strong (1 Tesla) magnetic field. What is the energy difference between spin-up and spin-down proton states in this field?

$$\Delta E = 2\mu_p B$$
$$= 2\cdot(1.41\times10^{-26}\text{ J/T})\cdot(1\text{ T})$$
$$= 2.82\times10^{-26}\text{ J} = 1.76\times10^{-7}\text{ eV}$$

2) What photon frequency, f, will be absorbed?

$$f = E/h$$
$$= (2.82\times10^{-26}\text{ J})/(6.63\times10^{-34}\text{ J}\cdot\text{s})$$
$$= 4.26\times10^{7}\text{ Hz}$$

Act 1

We just saw that radio frequency photons can cause a nuclear spin to flip.
What is the angular momentum of each photon?

a. 0 b. $\hbar/2$ c. $\hbar$

Solution

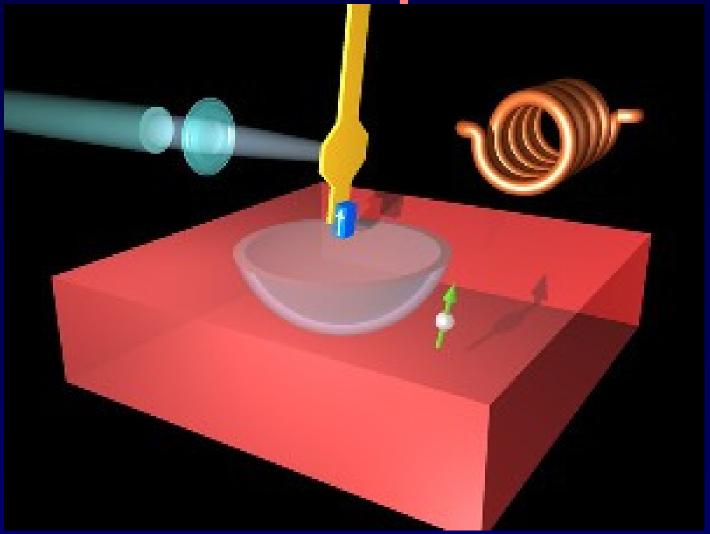
We just saw that radio frequency photons can cause a nuclear spin to flip.
What is the angular momentum of each photon?

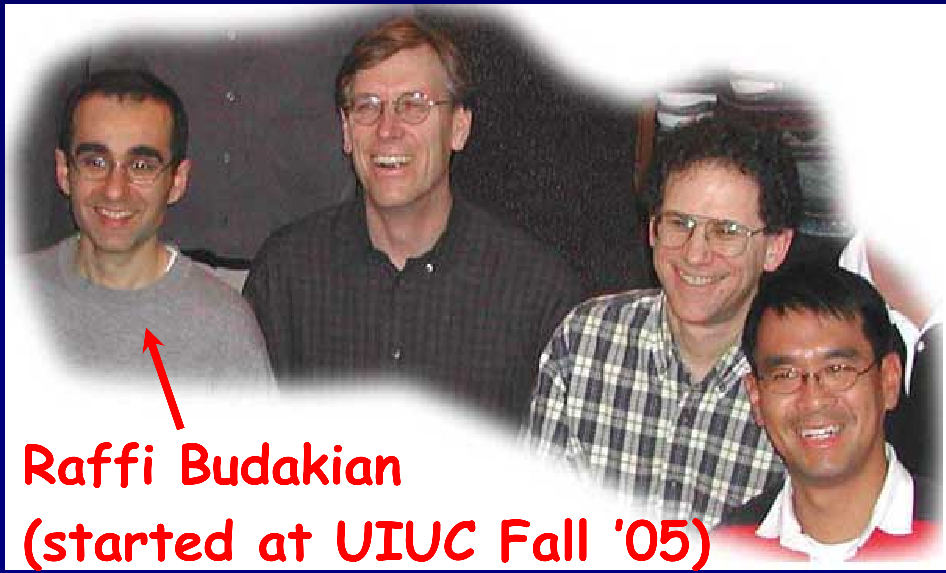
a. 0　　　b. ħ/2　　　c. ħ

The nuclear spin has flipped from ↑ to ↓ (or vice versa).
That is, its z-component has changed by ħ. Conservation of angular momentum requires that the photon have brought (at least) this much in.

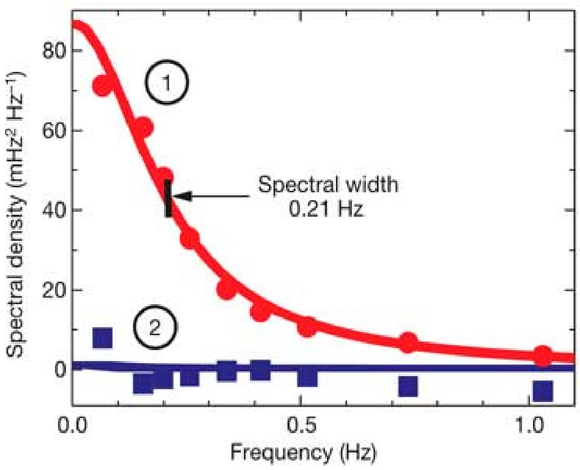
FYI: Recent Breakthrough – Detection of a *single* electron spin!

- (Nature July 14, 2004) -- IBM scientists achieved a breakthrough in nanoscale magnetic resonance imaging (MRI) by directly detecting the faint magnetic signal from a single electron buried inside a solid sample.





Raffi Budakian (started at UIUC Fall '05)



Next step – detection of single nuclear spin (660x smaller).

Pauli Exclusion Principle

Let's start building more complicated atoms to study the Periodic Table.
For atoms with many electrons (e.g., carbon: 6, iron: 26, etc.) …
What energies do the electrons have?

"Pauli Exclusion Principle" (1925)

No two electrons can be in the same quantum state.

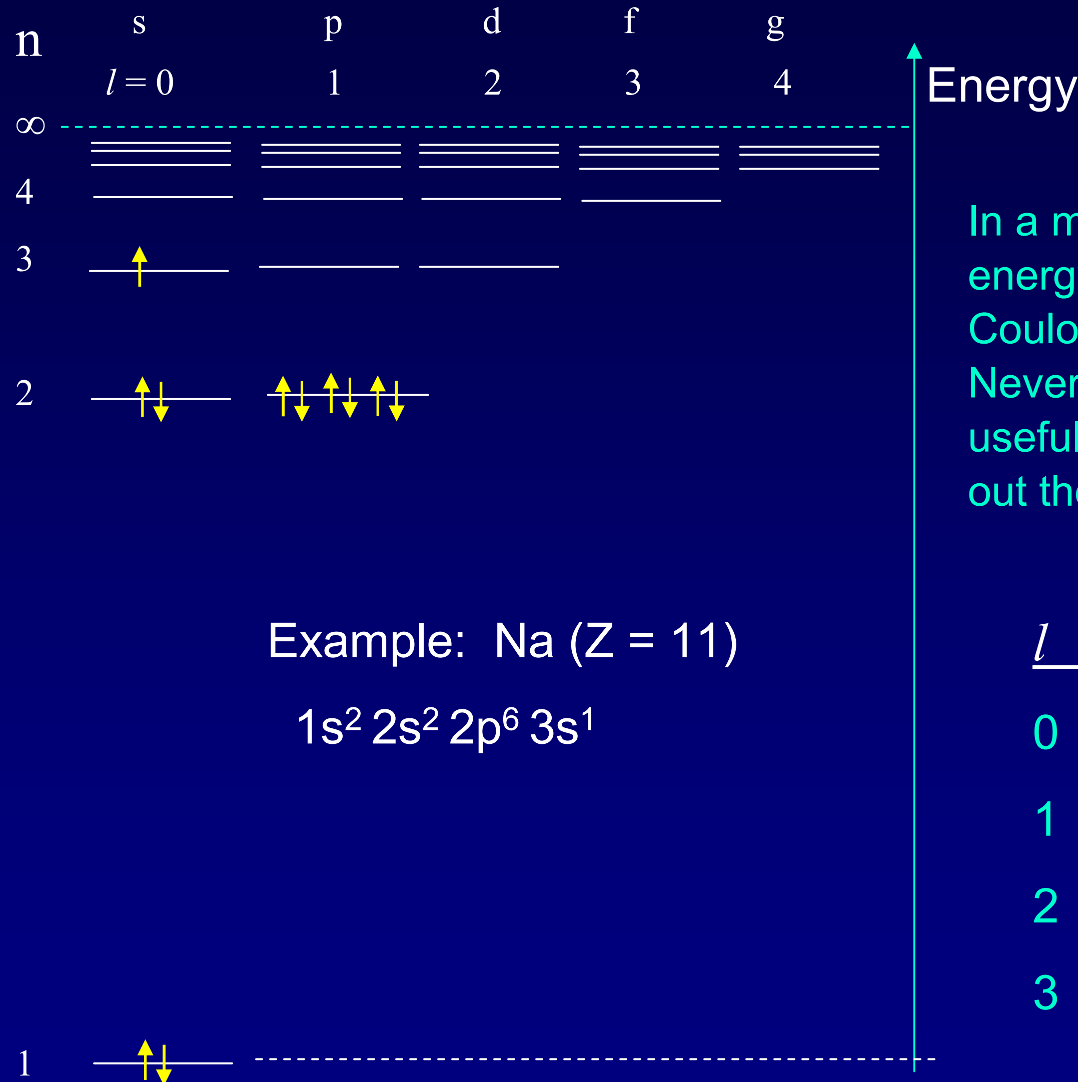
For example, in a given atom they cannot have the same set of quantum numbers n, l, m_l, m_s.

This means that each atomic orbital (n,l,m_l) can hold 2 electrons: $m_s = \pm½$.

Important consequence:

- Electrons do not pile up in the lowest energy state.
  It's more like filling a bucket with water.
- They are distributed among the energy levels
  according to the Exclusion Principle.
- Particles that obey this principle are called "fermions".
  Protons and neutrons are also fermions, but photons are not.

Filling Atomic Orbitals According to the Exclusion Principle



$$E_n = \frac{-13.6\ eV}{n^2} Z^2$$

In a multi-electron atom, the H-atom energy level diagram is distorted by Coulomb repulsion between electrons. Nevertheless, the H-atom diagram is useful (with some caveats) for figuring out the order in which orbitals are filled.

Example: Na (Z = 11)

$1s^2\ 2s^2\ 2p^6\ 3s^1$

l	label	#orbitals $(2l+1)$
0	s	1
1	p	3
2	d	5
3	f	7

Z = atomic number = # protons

Act 2

1. Which of the following states (n, l, m_l, m_s) is/are NOT allowed?

   a. (2, 1, 1, -1/2)
   b. (4, 0, 0, 1/2)
   c. (3, 2, 3, -1/2)
   d. (5, 2, 2, 1/2)
   e. (4, 4, 2, -1/2)

2. Which of the following atomic electron configurations violates the Pauli Exclusion Principle?

   a. $1s^2, 2s^2, 2p^6, 3s^2, 3d^8$
   b. $1s^2, 2s^2, 2p^6, 3s^2, 3d^4$
   c. $1s^2, 2s^2, 2p^8, 3s^2, 3d^8$
   d. $1s^1, 2s^2, 2p^6, 3s^2, 3d^9$
   e. $1s^2, 2s^2, 2p^3, 3s^2, 3d^{11}$

Solution

1. Which of the following states (n,l,m_l,m_s) is/are NOT allowed?

a. (2, 1, 1, -1/2)
b. (4, 0, 0, 1/2)
c. (3, 2, 3, -1/2) $m_l > l$
d. (5, 2, 2, 1/2)
e. (4, 4, 2, -1/2) $l = n$

2. Which of the following atomic electron configurations violates the Pauli Exclusion Principle?

a. $1s^2, 2s^2, 2p^6, 3s^2, 3d^8$
b. $1s^2, 2s^2, 2p^6, 3s^2, 3d^4$
c. $1s^2, 2s^2, 2p^8, 3s^2, 3d^8$
d. $1s^1, 2s^2, 2p^6, 3s^2, 3d^9$
e. $1s^2, 2s^2, 2p^3, 3s^2, 3d^{11}$

Solution

1. Which of the following states (n, l, m_l, m_s) is/are NOT allowed?

a. (2, 1, 1, -1/2)
b. (4, 0, 0, 1/2)
c. (3, 2, 3, -1/2) — $m_l > l$
d. (5, 2, 2, 1/2)
e. (4, 4, 2, -1/2) — $l = n$

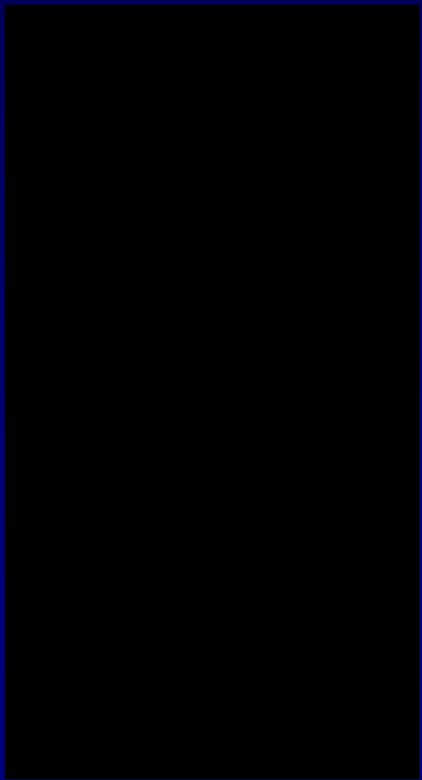
2. Which of the following atomic electron configurations violates the Pauli Exclusion Principle?

a. $1s^2, 2s^2, 2p^6, 3s^2, 3d^8$
b. $1s^2, 2s^2, 2p^6, 3s^2, 3d^4$
c. $1s^2, 2s^2, 2p^8, 3s^2, 3d^8$
d. $1s^1, 2s^2, 2p^6, 3s^2, 3d^9$
e. $1s^2, 2s^2, 2p^3, 3s^2, 3d^{11}$

Filling Procedure for Atomic Orbitals

Due to electron-electron interactions, the hydrogen levels fail to give us the correct filling order as we go higher in the periodic table.

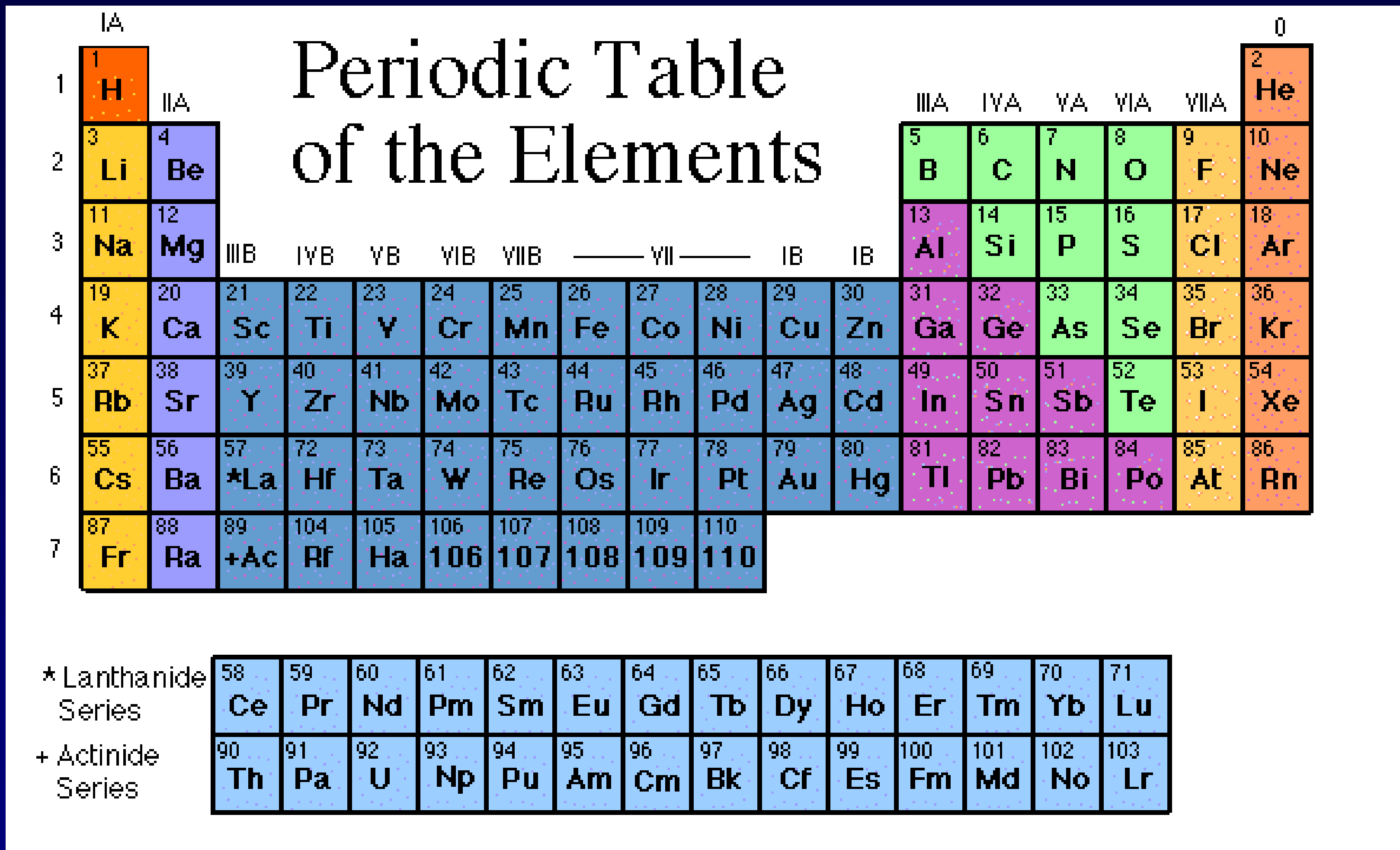
The actual filling order is given in the table below. Electrons are added by proceeding along the arrows shown.



This is just a mnemonic.

Home exercise:
Bromine is an element with Z = 35. Find its electronic configuration (e.g., $1s^2\ 2s^2\ 2p^6$ …).

Note:
The chemical properties of an atom are determined by the electrons in the orbitals with the largest n, because they are on the "surface" of the atom.

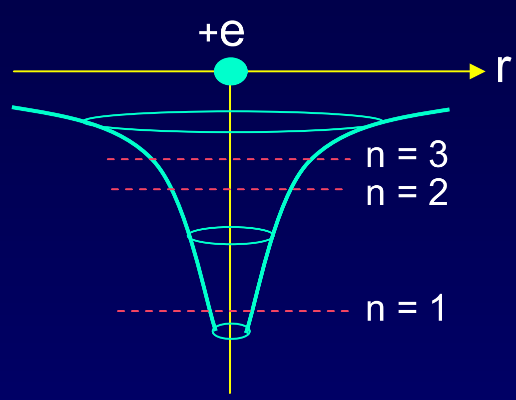


As you learned in chemistry, the various behaviors of all the elements (and all the molecules made up from them) is all due to the way the electrons organize themselves, according to quantum mechanics.

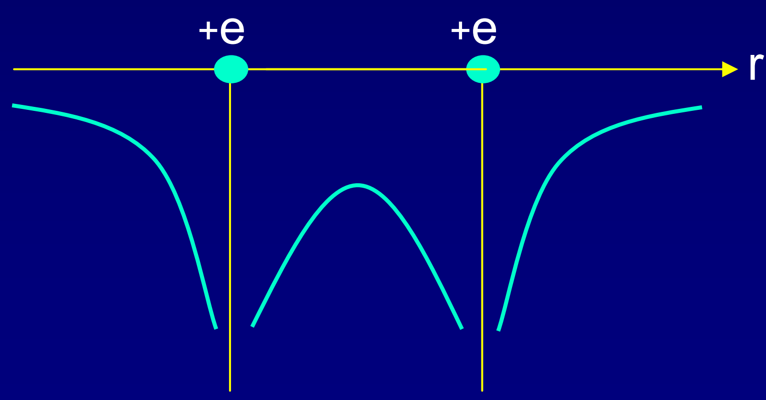
Bonding Between Atoms

How can two neutral objects stick together? $H + H \leftrightarrow H_2$

Let's represent the atom in space by its Coulomb potential centered on the proton (+e):



The potential energy due to the two protons in an H_2 molecule looks something like this:

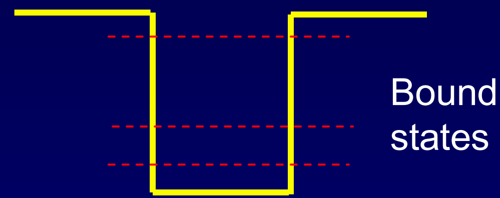


The energy levels for this potential are complicated, so we consider a simpler potential that we already know a lot about.

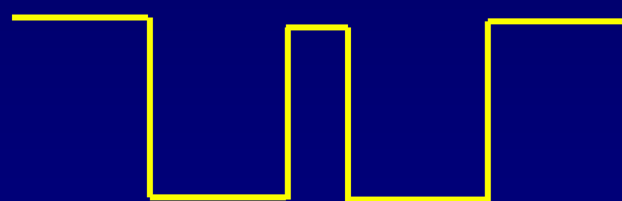
Particle in a Finite Square Well Potential

This has all of the qualitative features of molecular bonding, but is easier to analyze..

The 'atomic' potential:



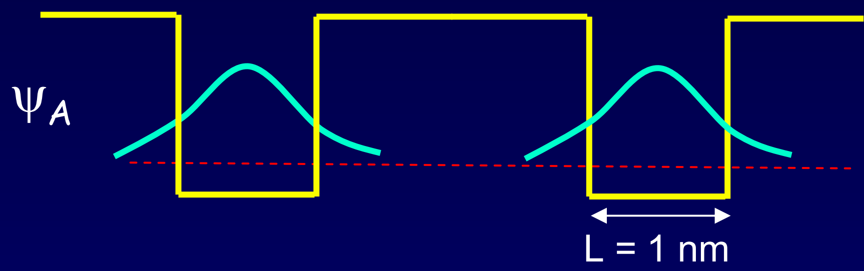
The 'molecular' potential:



Consider what happens when two "atoms" approach one other.
There is one electron, which can be in either well (or both!).
This is a model of the H_2^+ molecule.
We'll worry about the second electron later...

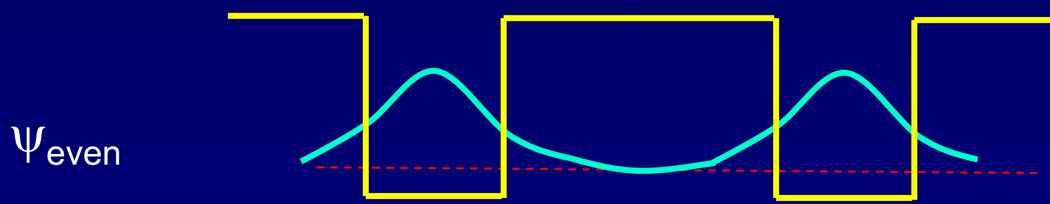
'Molecular' Wave functions and Energies

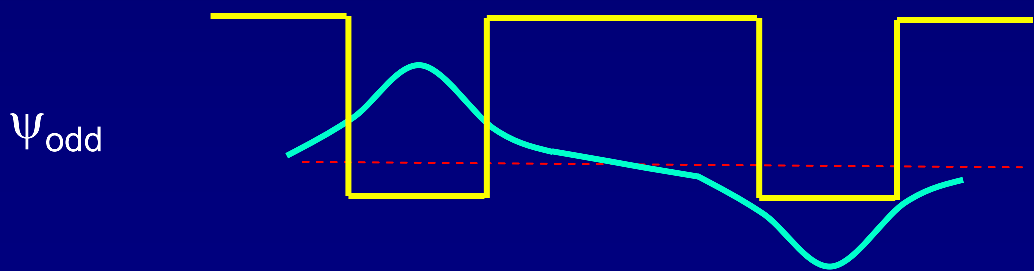
"Atomic' wave functions:



$$E \approx \frac{1.505\ \text{eV} \cdot \text{nm}^2}{(2L)^2} = 0.4\ eV$$

'Molecular' Wavefunctions: 2 'atomic' states $\rightarrow$ 2 'molecular' states

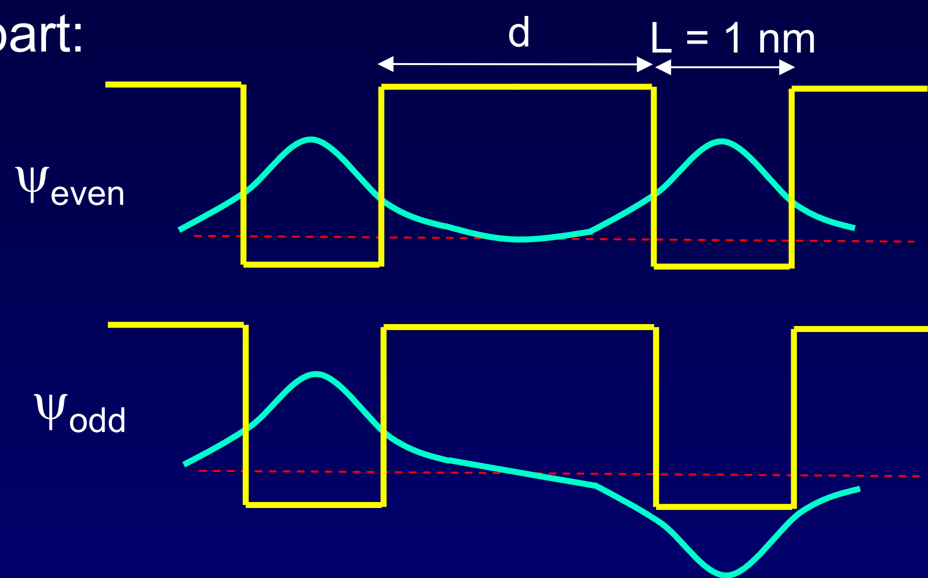




When the wells are far apart, the 'atomic' functions don't overlap.
The single electron can be in either well with E = 0.4 eV.

'Molecular' Wave Functions and Energies

Wells far apart:

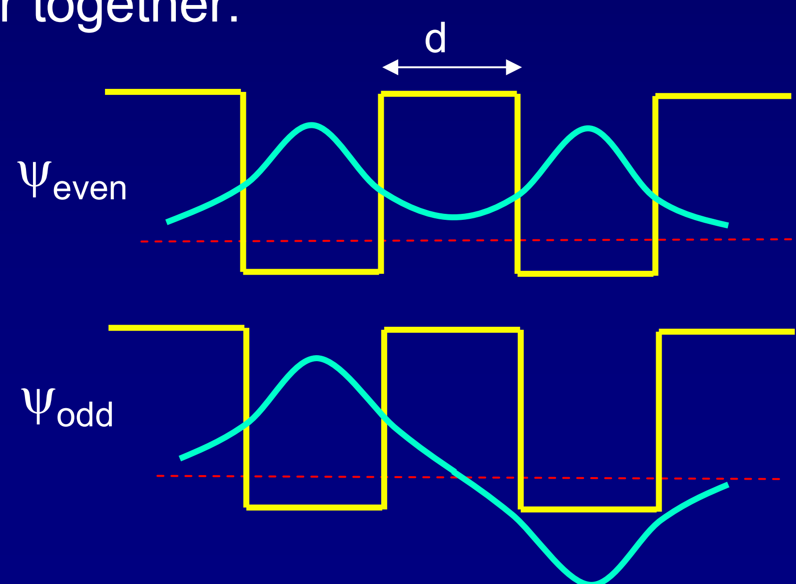


Degenerate states:

$$E \approx \frac{1.505\ \text{eV}\cdot\text{nm}^2}{(2\text{L})^2} = 0.4\ eV$$

$$E \approx \frac{1.505\ \text{eV}\cdot\text{nm}^2}{(2\text{L})^2} = 0.4\ eV$$

Wells closer together:

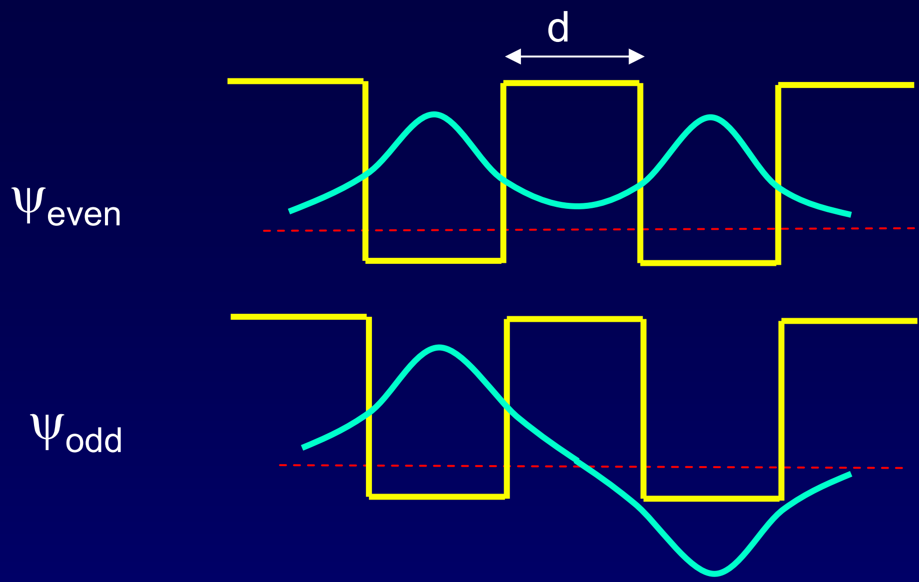


'Atomic' states are beginning to overlap and distort. ψ_{even} and ψ_{odd} are not the same. The degeneracy is broken:

$E_{even} < E_{odd}$

ψ_{even}: no nodes
ψ_{odd} : one node

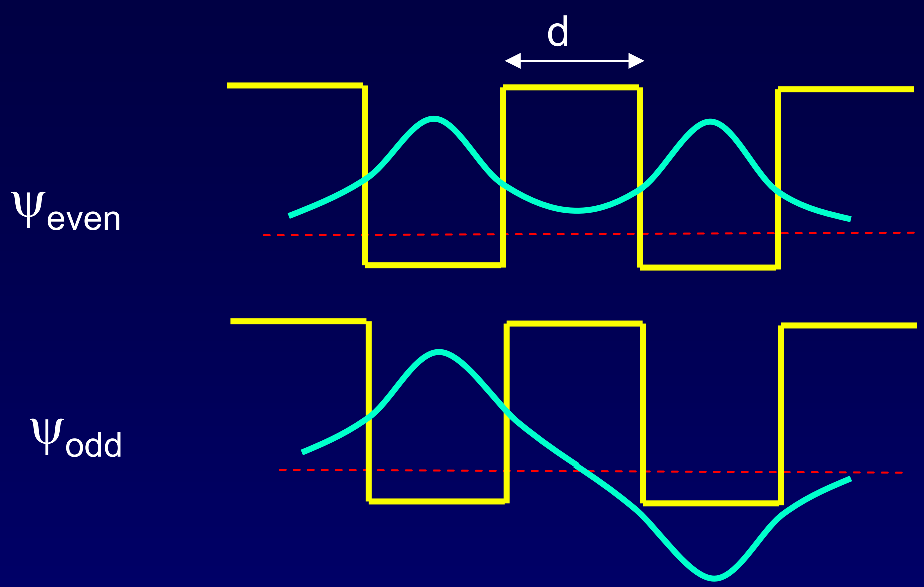
Act 3



What will happen to the energy of ψ_{even} as the two wells come together (i.e., as d is reduced)? [Hint: think of the limit as d → 0]

a. E_{even} decreases.
b. E_{even} stays the same.
c. E_{even} increases.

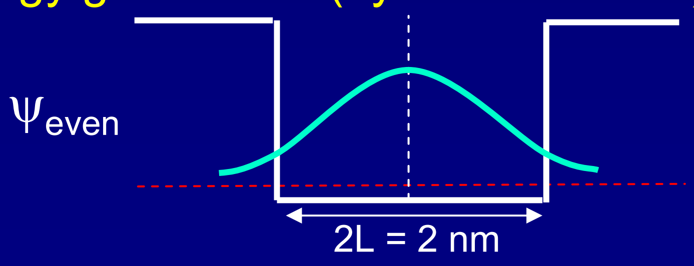
Solution



What will happen to the energy of ψ_{even} as the two wells come together (i.e., as d is reduced)? [Hint: think of the limit as d → 0]

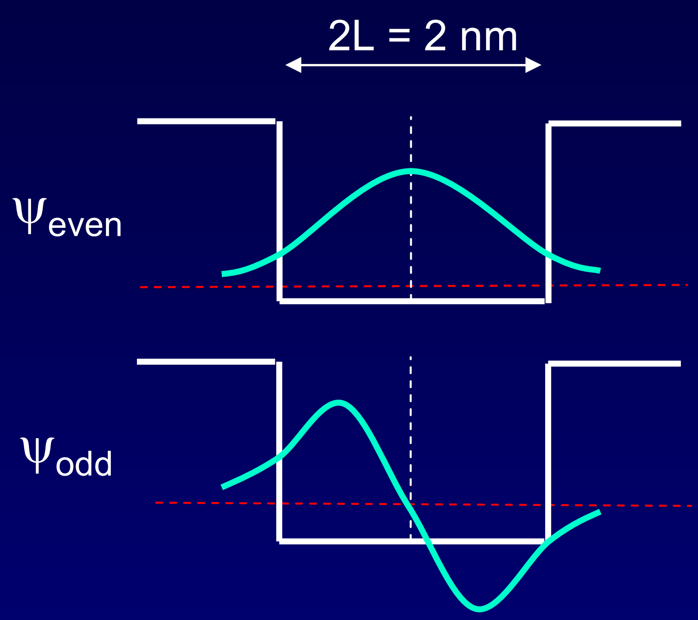
a. E_{even} decreases.
b. E_{even} stays the same.
c. E_{even} increases.

As the two wells come together, the barrier disappears, and the wave function spreads out over a single double-width well. Therefore the energy goes down (by a factor of ~4).



Energy as a Function of Well Separation

When the wells just touch (d = 0, becoming one well) we know the energies:



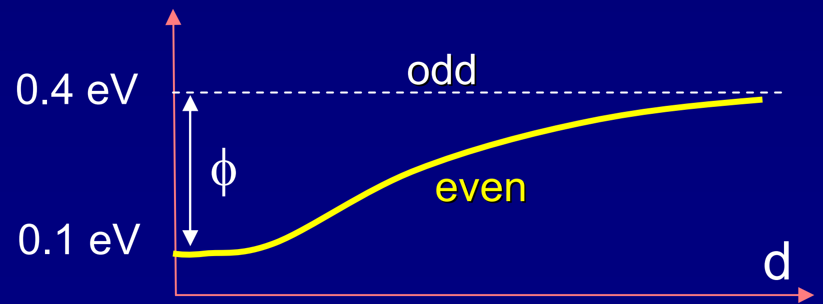
$$E_1 \approx \frac{1.505\ \mathrm{eV \cdot nm^2}}{(4L)^2} = 0.1\ eV$$

(n = 1 state)

$$E_2 \approx \frac{1.505\ \mathrm{eV \cdot nm^2}}{(4L)^2} \cdot 2^2 = 0.4\ eV$$

(n = 2 state)

As the wells are brought together, the even state always has lower kinetic energy (smaller curvature, because it spreads out). The odd state stays at about the same energy. The node prevents it from spreading.



Splitting between even and odd states:

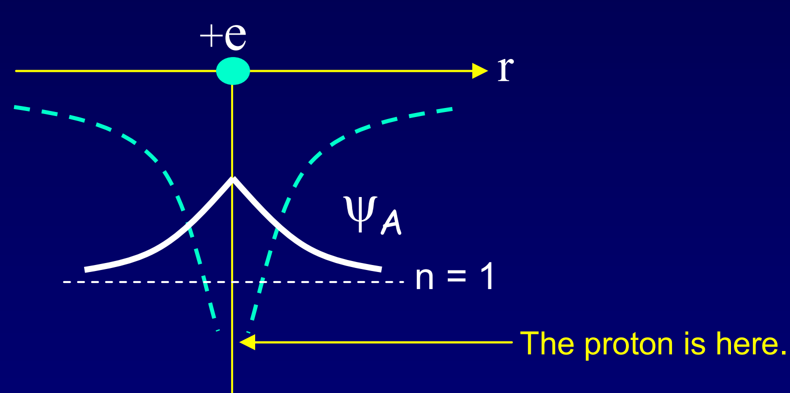
$$\Delta E = 0.4 - 0.1\ \mathrm{eV} = 0.3\ \mathrm{eV}$$

Molecular Wave functions and Energies with the Coulomb Potential

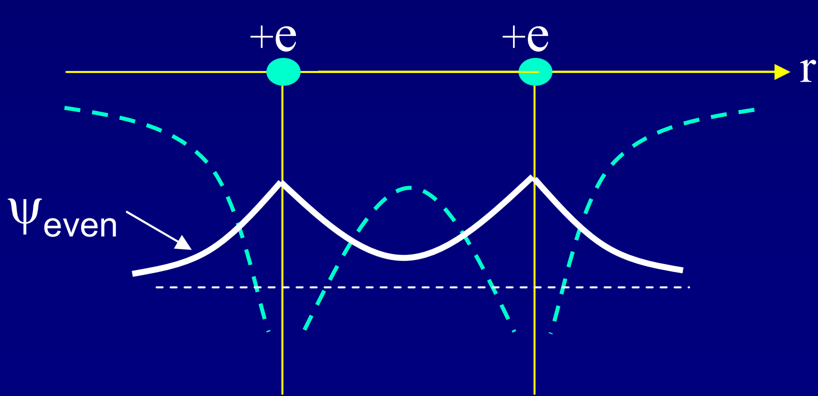
To understand real molecular bonding, we must deal with two issues:

- The atomic potential is not a square well.
- There is more than one electron in the well.

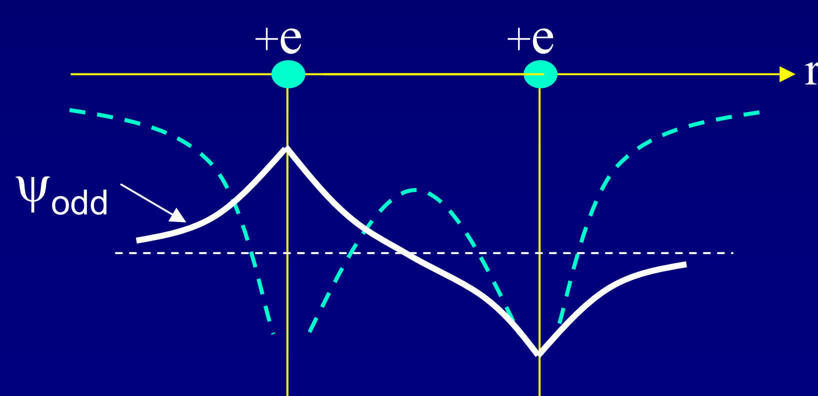
Atomic ground state (1s):



Molecular states:



Bonding state

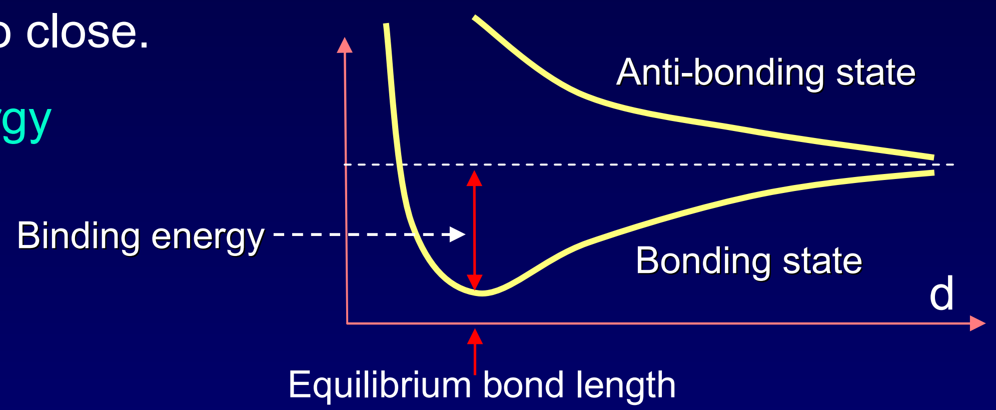


Antibonding state

Energy as a Function of Atom Separation

The even and odd states behave similarly to the square well, but there is also repulsion between the nuclei that prevents them from coming too close.

Schematic picture for the total energy of two nuclei and one electron:



Let's consider what happens when there is more than one electron:

- 2 electrons (two neutral H atoms): Both electrons occupy the bonding state (with different m_s). This is neutral H_2.
- 4 electrons (two neutral He atoms). Two electron must be in the anti-bonding state. The repulsive force cancels the bonding, and the atoms don't stick. The He_2 molecule does not exist!

Summary

Atomic configurations

- States in atoms with many electrons
- Filled according to the Pauli exclusion principle

Molecular wave functions: origins of covalent bonds

- Example: $H + H \rightarrow H_2$

Electron energy bands in crystals

- Bands and band gaps are properties of waves in periodic systems.
- There is a continuous range of energies for “allowed” states of an electron in a crystal.
- A Band Gap is a range of energies where there are no allowed states

  Bands are filled according to the Pauli exclusion principle

Next time

Some practical uses of QM:

- Why do some solids conduct – others do not
- Solid-state semiconductor devices
- Lasers
- Superconductivity