Tentative content material to be covered for Exam 2 (Wednesday, November 2, 2005)

Chapter 16 Quantum Mechanics and the Hydrogen Atom

16.1 Waves and Light
16.2 Paradoxes in Classical Physics
16.3 Planck, Einstein, and Bohr
16.4 Waves, Particles, and the Schrödinger Equation
16.5 The Hydrogen Atom

Chapter 17 Many-Electron Atoms and Chemical Bonding

17.1 Many-Electron Atoms and the Periodic Table
17.2 Experimental Measures of Orbital Energies
17.3 Sizes of Atoms and Ions
17.4 Properties of the Chemical Bond
17.5 Ionic and Covalent Bonds
17.6 Oxidation States and Chemical Bonding

Chapter 18 Molecular Orbitals, Spectroscopy, and Chemical Bonding

18.1 Diatomic Molecules
18.2 Polyatomic Molecules
18.3 The Conjugation of Bonds and Resonance Structures
18.4 The Interaction of Light with Molecules
18.5 Atmospheric Chemistry and Air Pollution.

Today’s lecture will be combination ppt and “chalk” lecture on how to create molecular orbital configurations of electrons by the appropriate combination of atomic orbitals.

First there will be a ppt review of the key ideas of Chapter 17 on how atomic electron configurations can be employed to understand the properties of elements

Followed by a chalk talk introduction to molecular orbital theory

The chemical behavior of atoms

An atom's chemical behavior depends strongly on how many valence electrons it has and one the electronic configuration of the valence electrons.

For the representative elements, the key valence electrons are the ns and np electrons which build up to a final core ns^2np^6 noble gas configuration.

Closed shells, core electrons and effective nuclear charge

Electrons in closed shells are inert because they are "buried" close to the nucleus

Closed shells are "core" electrons of an atom because they "screen" electrons in the "outer" orbitals outside the closes shell from the nuclear charge Z

The electrons in the outer orbitals see an effective nuclear charge, Z_{eff}, not the full nuclear charge, Z

The outer electrons are the valence electrons

The Bohr one electron atom as a starting point for the electron configurations of multielectron atoms.

Replace Z (actual charge) with Z_{eff} (effective charge)

$$E_n = -(Z_{eff}^2/n^2)Ry$$
$$r_n = (n^2/Z_{eff})a_0$$
$$E_n \sim -1/r_n$$

Key ideas:

(1) Larger Z_{eff} more energy required (IE) to remove e^-

(2) Smaller r more energy required (IE) to remove e^-

(3) Larger Z_{eff} more energy gained (EA) when adding a e^-

(4) Smaller r more energy gained (EA) when adding a e^-

Key formulae are derived from the one electron Bohr atom:

$E \sim Z/n$ $r \sim n/Z$ $E \sim 1/r$

n is roughly the same along a period

Z increases: IE increases, r decreases

Z is roughly the same down a column:

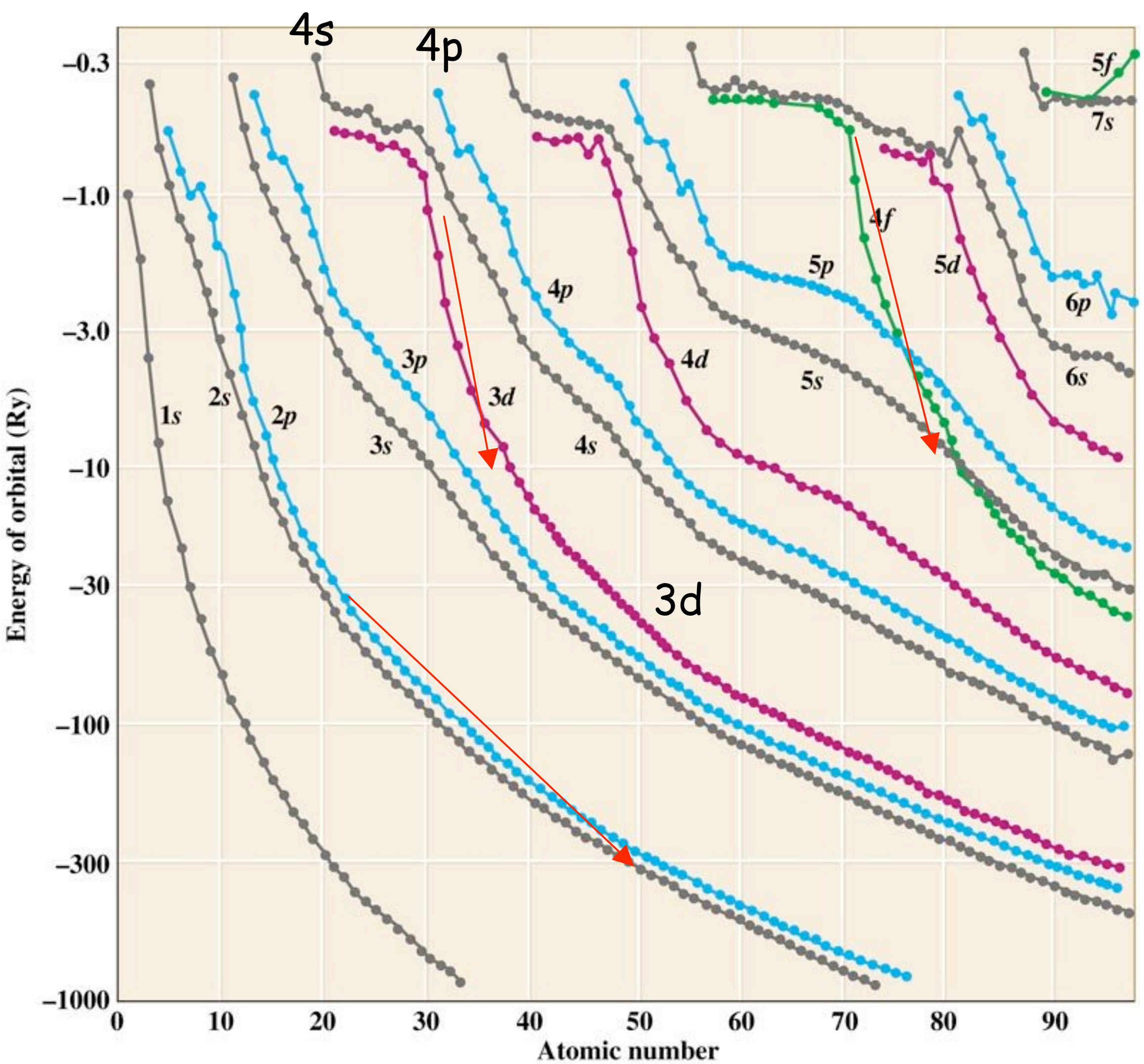
r, n increases
IE decreases

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
1 **H** $1s^1$																	2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^45s^1$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 ***La** $5d^16s^2$	72 **Hf** $5d^26s^2$	73 **Ta** $5d^36s^2$	74 **W** $5d^46s^2$	75 **Re** $5d^56s^2$	76 **Os** $5d^66s^2$	77 **Ir** $5d^76s^2$	78 **Pt** $5d^96s^1$	79 **Au** $5d^{10}6s^1$	80 **Hg** $5d^{10}6s^2$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **†Ac** $6d^17s^2$	104 **Rf** $6d^27s^2$	105 **Db** $6d^37s^2$	106 **Sg** $6d^47s^2$	107 **Bh**	108 **Hs**	109 **Mt**	110	111	112	Unknown	114	Unknown	††116	Unknown	††118

*	58 **Ce** $4f^26s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^16s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$	71 **Lu** $4f^{14}5d^16s^2$
†	90 **Th** $6d^27s^2$	91 **Pa** $5f^26d^17s^2$	92 **U** $5f^36d^17s^2$	93 **Np** $5f^46d^17s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^17s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$	103 **Lr** $5f^{14}6d^17s^2$

Orbital energies from photoelectron spectroscopy

Note the steeper slope of the drop of increasing stability with the 3d and 4f orbitals:



Note the big drop in the energy of the 3d orbitals starting at Z = 30 for Zn: $4s^2d^{10}$

This energy drop leaves the 4s and 4p as the valence electrons

Chapter 18 Molecular orbitals and spectroscopy

18.1 Diatomic molecules

Constructing molecular orbitals from atomic orbitals

Constructive and destructive interference of waves

Bonding and anti-bonding molecular orbitals

Orbital correlation diagrams

MO energies, AO parentage, Bond order

Homonuclear and heteronuclear diatomic molecules

Diamagnetism of N_2 and paramagnetism of O_2

Molecular Orbitals and Diatomic Molecules

Atomic orbitals: orbitals that are localized on single atoms.

Molecular orbitals: orbitals that span two or more atoms.

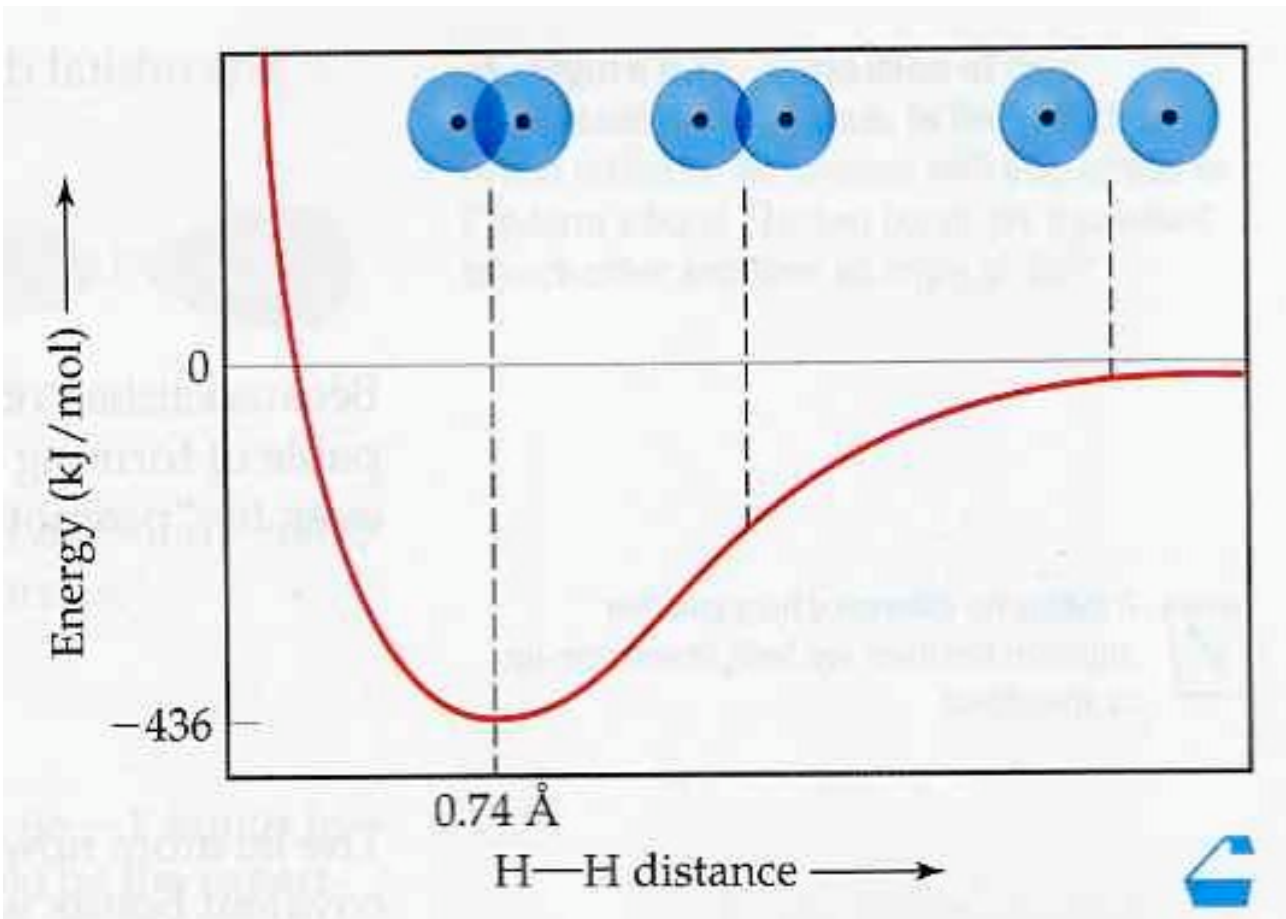
Constructing molecular orbitals (MOs) by overlapping atomic orbitals (AOs)

σ bonds: electron density of MO directed along bond axis

π bonds: electron density of MO has a nodal plane that contains the bond axis

H_2 is more stable than 2 H atoms. Why?

Quantum mechanics and molecular orbital theory provide an explanation: the overlap of atomic orbitals (waves)



Constructing MOs

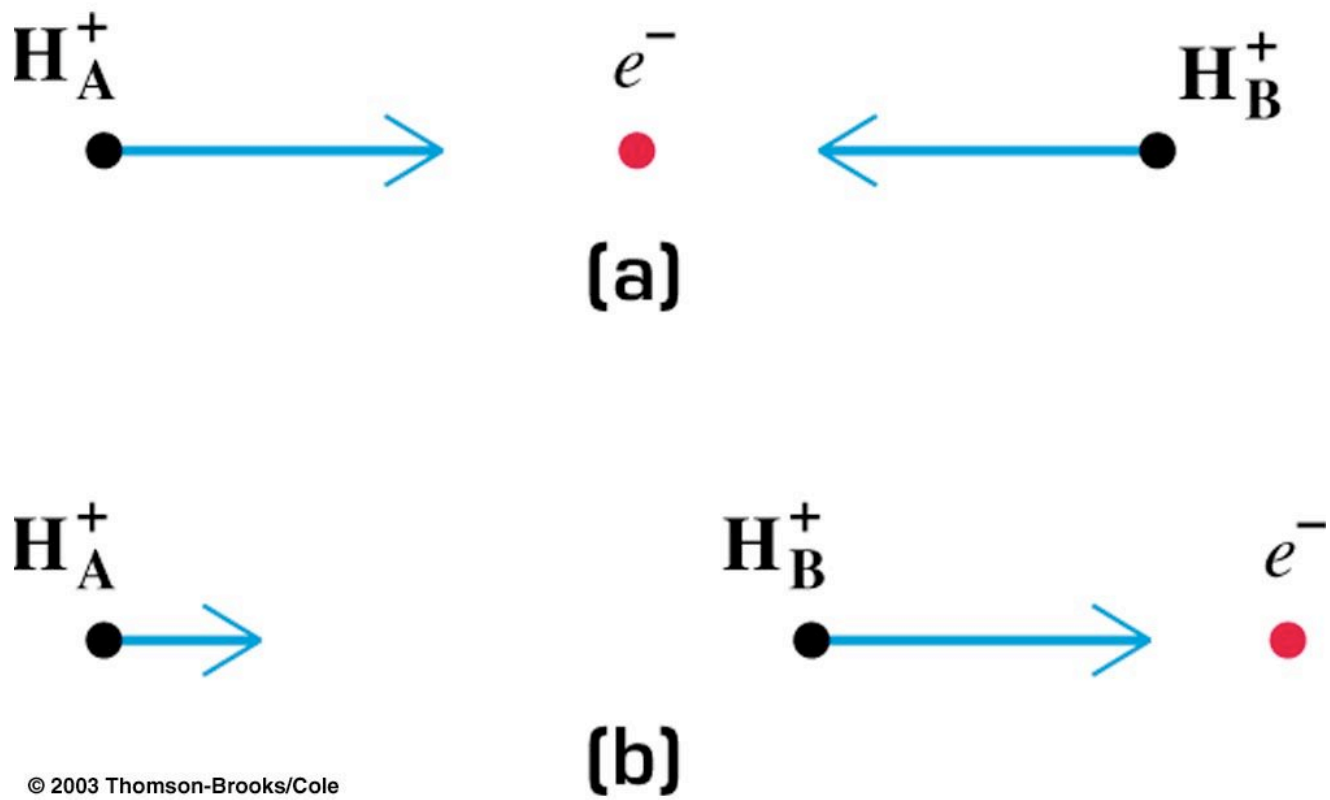
The overlap Two AOs is treated as the overlap and interference of two waves

If the waves are in phase the interference is constructive and add to give a larger total amplitude

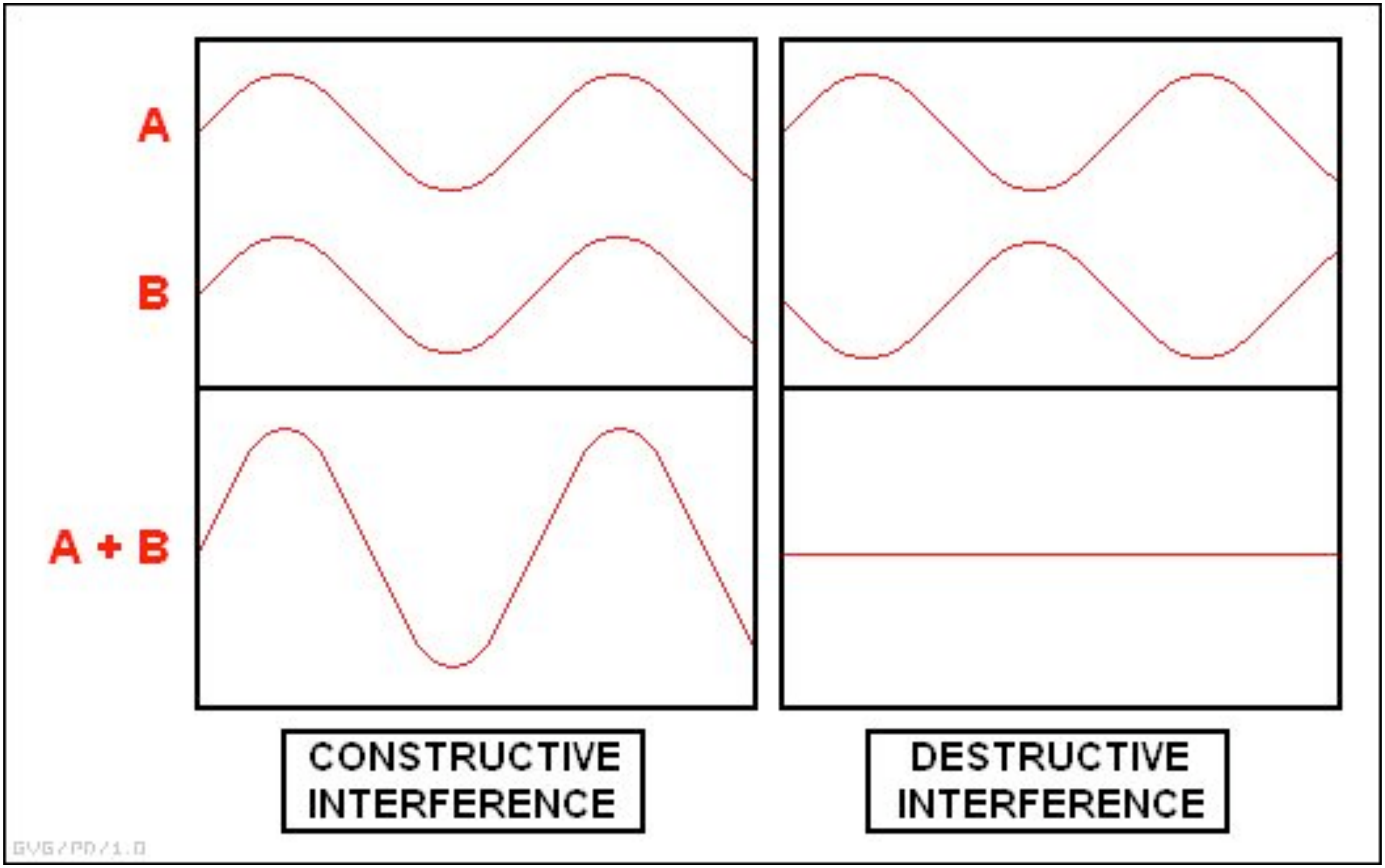
If the waves are out of phase the interference is destructive and add to cancel a smaller total amplitude or a zero amplitude (node)

An electron between two nuclei pulls the nuclei together and is bonding.

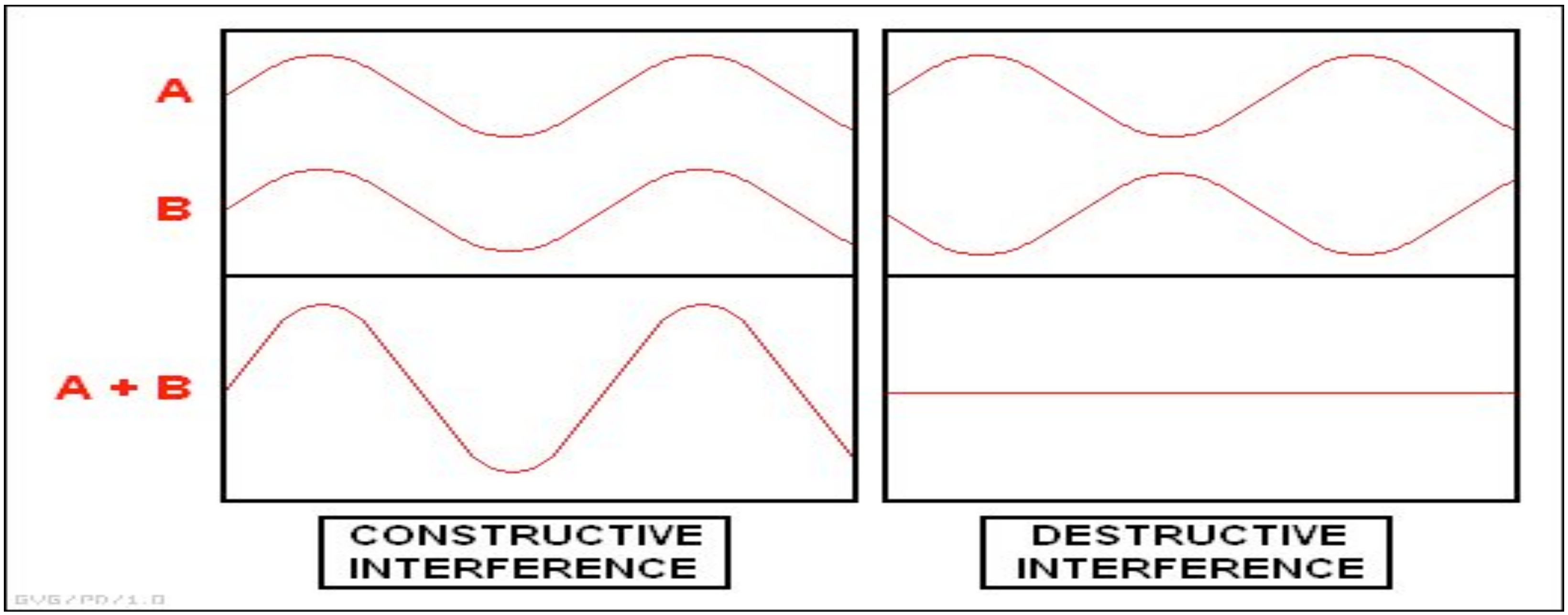
An electron beyond two nuclei pulls the nuclei apart and is anti-bonding.



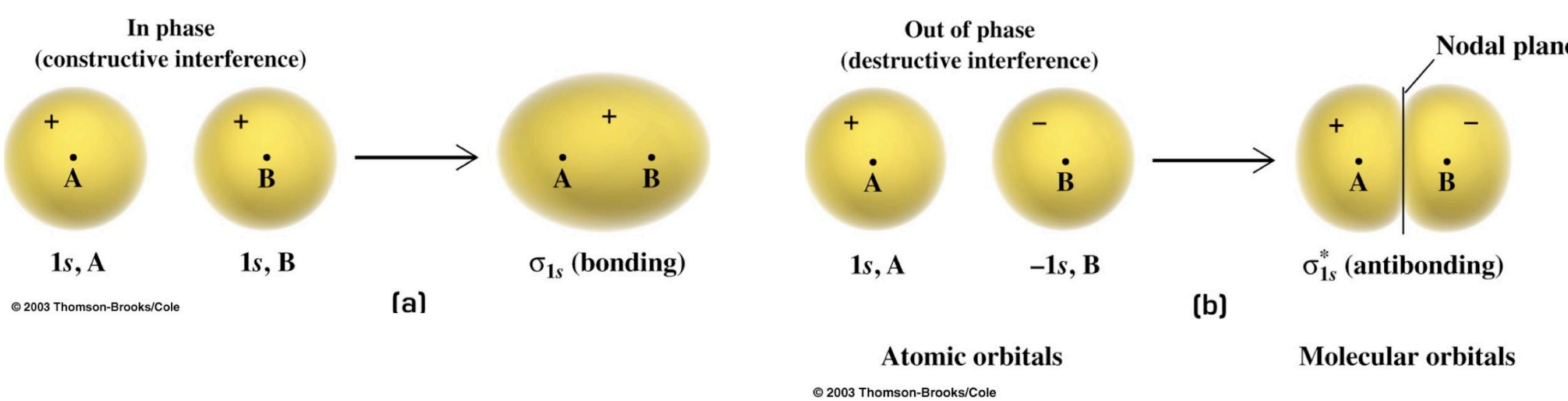
A signature property of waves in the phenomena of constructive and destructive interference



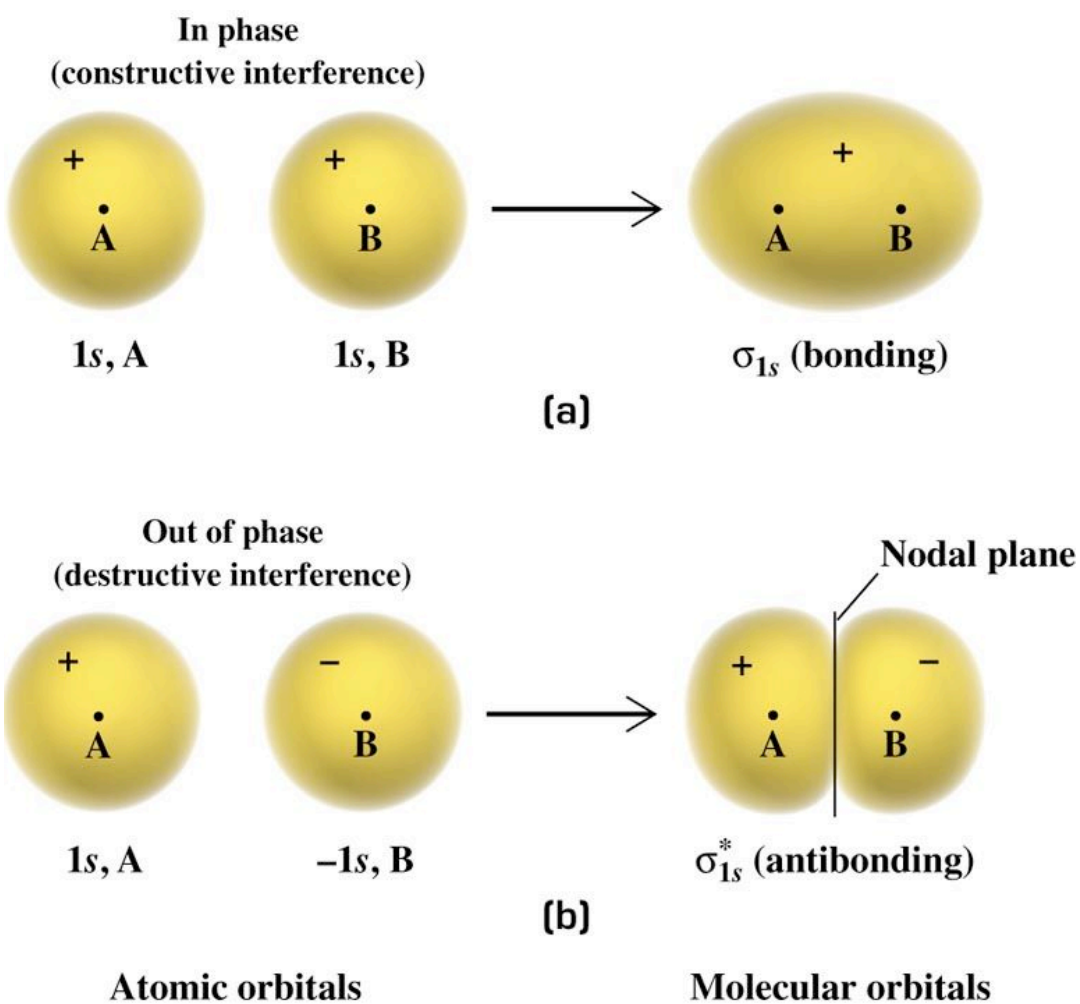
Constructive and destructive interference of waves:constructive (bonding), destructive (anti-bonding)



1s orbitals: wave interference



Constructive (top) and destructive (bottom) interference of two 1s orbitals



An electron in a σ_{1s} orbital has an enhanced probability of being found between the nuclei.

An electron in a σ^*_{1s} Orbital has a reduced probability of being found between the nuclei.

Rules for constructing ground state electronic configurations of homonuclear diatomic orbitals

Combine AOs to generate a set of molecular orbital from constructive and destructive interference of the AOs

The number of final MO's must equal the number of combined AO's

Order the MO's by energy from lowest to highest (in a manner analogous to the procedure for AO's

Put the available electrons in the MO's following the Aufbau principle, the Pauli principle and Hund's rule

Why are molecules more stable than the separated atoms?

Because there is more bonding than anti-bonding

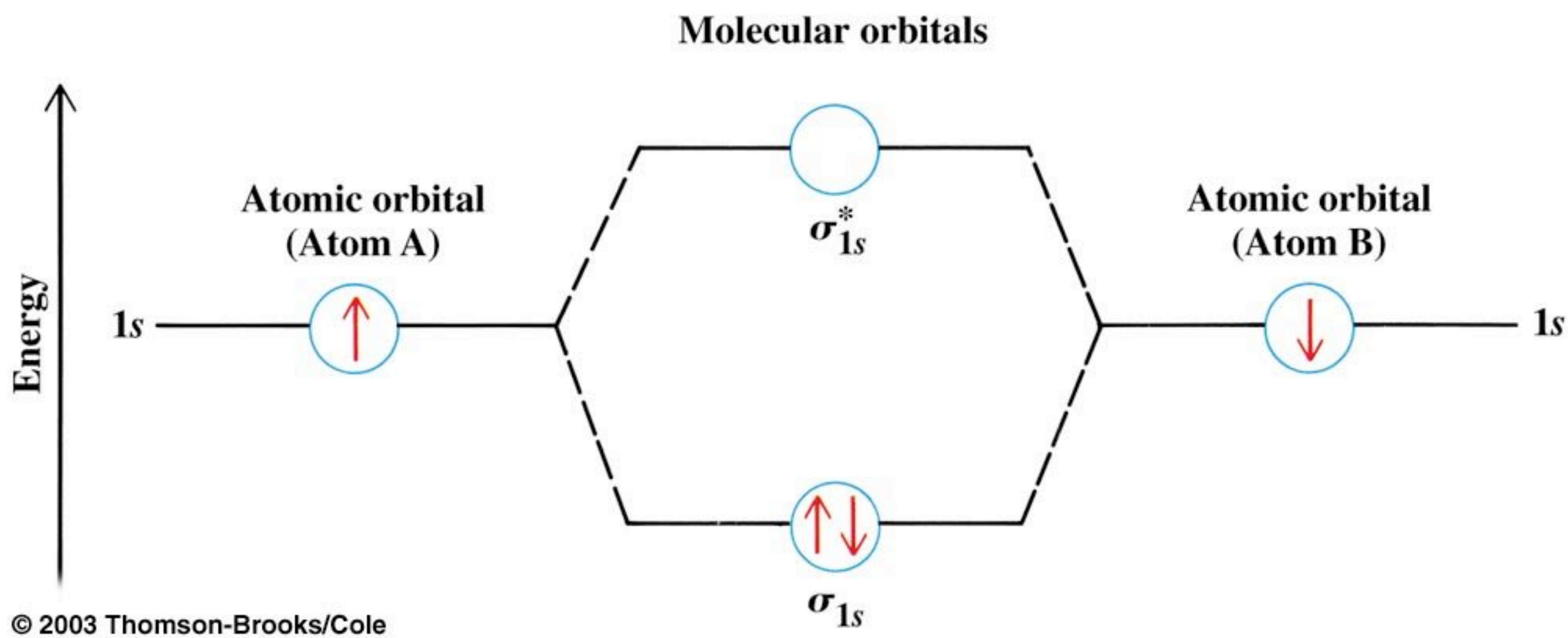
How can you predict the stability of simple molecular species?

Through orbital correlation diagrams

Which of the following are stable or unstable?

H_2, H_2^+, He_2, He_2^+

Correlation diagram for the overlap of two 1s orbitals



The electronic configuration of a H_2 molecule is σ_{1s}^2

The subscript ($_{1s}$) tells which AOs are combined, the superscript (^{2}) tells how many electrons are in the MO

A shared pair of electrons make a single covalent bond

Electrons in bonding orbitals enhance bonding, electrons in anti-bonding orbitals reduce bonding

Bond order is a measure of the bonding between two atoms: 1/2[(e in bonding MOs) - [(e in anti-bonding MOs)]

TABLE 18–1 Configurations and Bond Orders for First-Row Homonuclear Diatomic Molecules

Species	Electron Configuration	Bond Order	Bond Enthalpy (kJ mol^{-1})	Bond Length (Å)
H_2^+	$(\sigma_{1s})^1$	$\frac{1}{2}$	255	1.06
H_2	$(\sigma_{1s})^2$	1	431	0.74
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	$\frac{1}{2}$	251	1.08
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	Not observed	

What is the bond order of the first electronically excited state of H_2?

The electronic configuration of the first excited state of H_2 is $(\sigma_{1s})^1(\sigma^*_{1s})^1$.

Bond order = 1/2(1 - 1) = 0

Photochemical excitation of H_2 makes it fly apart into 2 H atoms.