SOE: Symmetry–Overlap–Energy
Notes on General Chemistry

■ Bonding and antibonding molecular orbitals
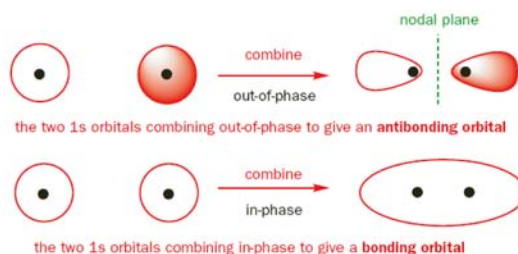
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Atoms interact by overlap of their atomic orbitals (AO's). If the AO's overlap in-phase, electron density is *enhanced* between the atoms and so the Coulomb energy *decreases* as the atoms approach. If the AO's overlap out-of-phase, electron density is *depleted* between the atoms and so the Coulomb energy *increases* as the atoms approach. For both in-phase and out-of-phase overlap, since the molecular orbital (MO) electron wave is confined to smaller region, and so has smaller wavelength, as the atoms approach the kinetic energy *increases*.
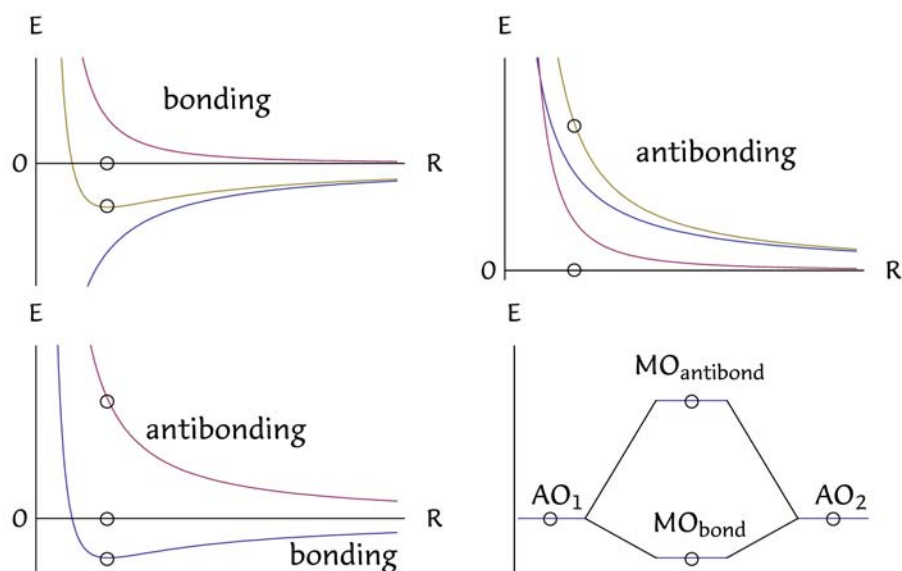
Upper left: In-phase (bonding) AO combination energies: Coulomb contribution (lower, blue curve); kinetic energy contribution (upper, red curve); and total energy (middle, yellow curve). Upper right: Out-of-phase (antibonding) AO combination: Coulomb contribution (middle, blue curve); kinetic energy contribution (lower red curve); and total energy (upper, yellow curve). The small circles compare the energies of the separated atoms (the zero of energy) and total energy at the placed at the bond length (the minimum of the total energy of the in-phase total energy). Lower left: In-phase (bonding) AO combination total energy (blue, lower curve), :and out-of-phase (antibonding) AO combination (red, upper curve). The small circles compare the energies of the separated atoms (the zero of energy) and total energy at the placed at the bond length (the minimum of the total energy of the in-phase total energy). Lower right: Correlation diagram relating the energies of the AO's when the atoms are wide apart with the energies of the MO's formed from the in-phase (MO_{bond}) and out-of-phase ($MO_{antibond}$) overlap.

The small circles on the diagrams compare the energies of the separated atoms (the zero of energy) and total energy at the bond length (the minimum of the in-phase total energy). The *correlation diagram* (lower right) is a compact way of representing this comparison. The middle part of the correlation diagram corresponds to the atoms separated by the bond distance; the left and right parts corresponds to the atoms far enough apart that there is no overlap of their AO's and so no bonding or antibonding effect on total energy.

Here are questions about the energy of MO's formed from the combination of AO's as atoms approach one another.

1. The kinetic energy of the antibonding combination of a pair of AO's is ...

A greater than that for the bonding combination

B about the same that for the bonding combination

C less than that for the bonding combination

2 The total energy of the antibonding combination of a pair of AO's is ...

A   never negative

B   has a minimum near the bond distance

C   about the same as for the bonding combination

D   is smaller the larger the separation

E   A and D

3 The potential energy of the antibonding combination of a pair of AO's is ...

A   never negative   B   about zero   C   about the same as for the bonding combination

4 As a pair of atoms approach from a large separation, initially the energy resulting from in-phase overlap of their AO's ...

A   goes up, due to increased kinetic energy.

B   goes down, due to enhancement of electron density between

C   goes up, due to depletion of electron density between the

D   None of the above

5 As a pair of atoms approach from a large separation, initially the energy of the MO resulting from out-of-phase overlap of their AO's ...
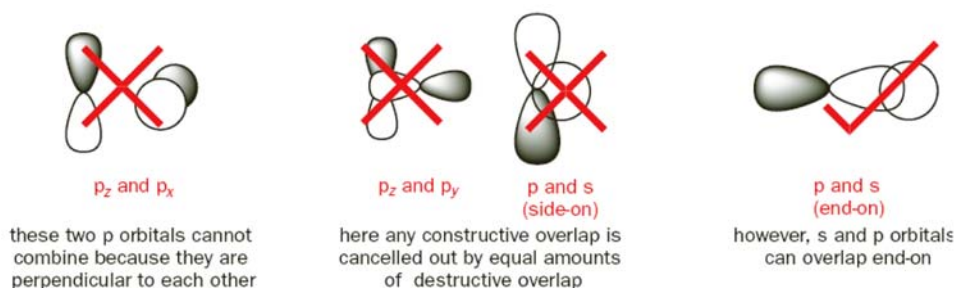
A   goes down, due to decreased kinetic energy.

B   goes down, due to enhancement of electron density between

C   goes up, due to depletion of electron density between the

D   None of the above

6 A pair of atoms approach from a large separation, and the resulting MO has equal amounts of in-phase and out-of-phase overlap of their AO's. The result is that initially the total energy ...

   A goes up, due to increased kinetic energy.

   B goes down, due to enhancement of electron density between

   C goes up, due to depletion of electron density between the

   D None of the above

■ Symmetry

If AO's have only in-phase or only out-of-phase overlap, we say they have *correct symmetry*. If AO's have equal amounts of in-phase and out-of-phase overlap, we say they have *incorrect symmetry*.

p_z and p_x

these two p orbitals cannot combine because they are perpendicular to each other

p_z and p_y p and s (side-on)

here any constructive overlap is cancelled out by equal amounts of destructive overlap

p and s (end-on)

however, s and p orbitals can overlap end-on

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7 Which pairs of AO's on different atoms have correct symmetry?
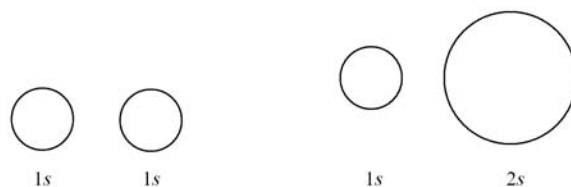
$1s$ $1s$ $1s$ $2s$

   A 1s + 1s   B 1s + 2s   C both   D neither

8 Which pairs of AO's on different atoms have correct symmetry? Assume *z* is along bond axis.

$1s$ $2p_z$ $1s$ $2p_y$
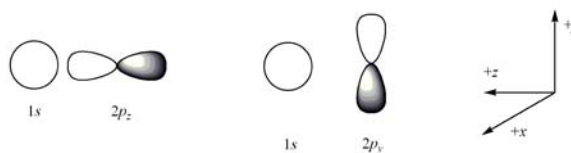
   A 1s + 2pz   B 1s + 2py   C both   D neither

9 Which pairs of AO's on different atoms have correct symmetry? Assume *z* is along bond axis.

  A   2s + 2pz   B   2s + 2py   C   both   D   neither

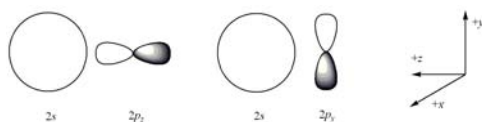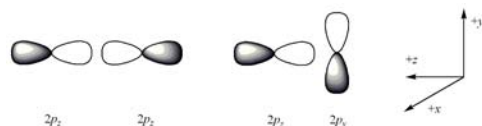**10 Which pairs of AO's on different atoms have correct symmetry? Assume *z* is along bond axis.**

  A   2pz + 2pz   B   2pz + 2py   C   both   D   neither

11 Which pairs of AO's on different atoms have correct symmetry? Assume *z* is along bond axis.
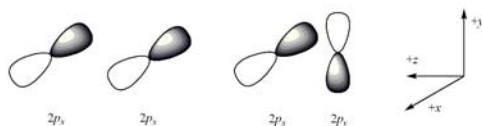
  A   2px + 2py   B   2px + 2px   C   both   D   neither

■ Overlap

If AO's have correct symmetry, then we consider next how much they overlap. The greater the overlap, the greater the energy change, relative to the AO energies, when the atoms are at the bond length separation.

12 Arrange the pairs of AO's in Li$_2$ according to increasing overlap when the atoms are at the lowest energy separation (the bond length).

  A   1s + 1s < 2s + 2s < 1s + 2s   B   1s + 2s < 1s + 1s < 2s + 2s   C   1s + 1s < 1s + 2s < 2s + 2s

■ Energy

Finally, once we know the pair of AO's with correct symmetry and greatest overlap, we consider relative AO energies. The bonding/antibonding effect will be greatest for AO's closest in energy.

Energies of AOs both the same	AO on atom B is a *little* lower in energy than AO on atom A	AO on atom B is a *lot* lower in energy than AO on atom A
large interaction between AOs	less interaction between AOs	AOs are too far apart in energy to interact
bonding MO much lower in energy than AOs	bonding MO is lowered only by a small amount relative to AO on atom B	the filled orbital on the anion has the same energy as the AO on atom B
antibonding MO is much higher in the energy than the AOs	antibonding MO is raised in energy by only a small amount relative to AO on atom B	the empty orbital on the cation has same energy as the AO on atom A
both AOs contribute equally to the MOs	the AO on B contributes more to the bonding MO and the AO on A	only one AO contributes to each 'MO'
electrons in bonding MO are shared equally between the two atoms	electrons in bonding MO are shared between atoms but are associated more with atom B than A	electrons in the filled orbital are located only on atom B
bond between A and B would classically be described as purely covalent	bond between A and B is covalent but there is also some electrostatic (ionic) attraction between atoms	bond between A and B would classically be described as purely ionic
easiest to break bond into two radicals (homolytic fission). Heterolytic fission of bond is possible and could give either A^+ and B^- or A^- and B^+	easiest to break bond into two ions, A^+ and B^-, although it is also possible to give two radicals	compound already exists as ions A^+ and B^-

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13 Arrange the pairs of AO's in Li_2 according to increasing energy change at the bond length.

A $1s + 1s < 2s + 2s < 1s + 2s$ B $1s + 2s < 1s + 1s < 2s + 2s$ C $1s + 1s < 1s + 2s < 2s + 2s$

14 Which pair of AO's in HF will interact most strongly? Assume *z* is along the bond axis.

A   H $1s$ + F $1s$ B   H $1s$ + F $2s$ C   H $1s$ + F $2p_z$ D   H $1s$ + F $2p_y$ E   C and D

15 Assume AO$_1$ and AO$_2$ have correct relative symmetry, greatest overlap, and are closest in energy. AO$_1$ has IE = 5 eV and AO$_2$ has IE = 6 eV. Which of the following is true?
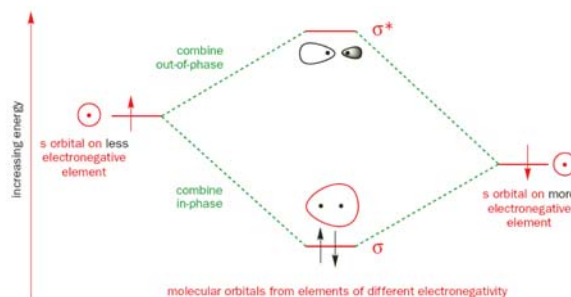
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A Bonding MO has more AO$_1$ than AO$_2$ B Bonding MO has more AO$_2$ than AO$_1$

C Antibonding MO is almost entirely AO$_1$ D Antibonding MO is almost entirely AO$_2$

E A and D   F B and C

16 AO$_1$ has IE = 3 eV and AO$_2$ has IE = 12 eV. Which of the following is true?
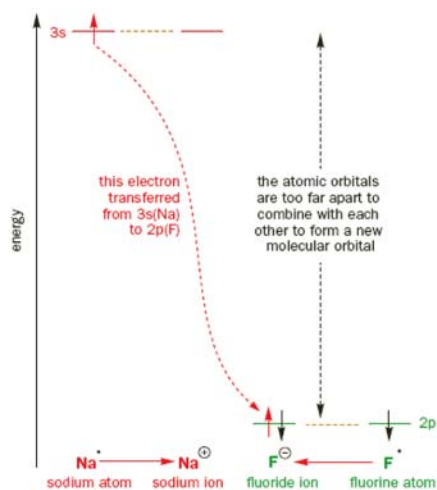
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A Bonding MO is almost entirely AO$_1$

B Bonding MO is has a little more AO$_2$ than AO$_1$

C Antibonding MO is almost entirely AO$_1$

D Antibonding MO has a little more AO$_1$ than AO$_2$

E None of the above

F B and C

17 The bond pair in Na:F is in the Na 3s + F 2pz MO. The bond pair in H:F is in the H 1s + F 2pz MO. Which of the following is true?

A   The bond pair is almost entirely on the F of HF.

B   The bond pair is almost entirely on the H of HF.

C   The bond pair is almost entirely on the F of NaF.

D   The bond pair is almost entirely on the Na of NaF.

E   A and D

18 Na 3s has IE = 5.1 eV. H 1s has IE = 13.6 eV. F has IE = 17.4 eV. NaF is more ionic than HF because ...

A   Na 3s has lower IE than does H 1s

B   F 2pz has higher IE than does H 1s

C   Na 3s has lower IE than does F 2pz

D   F 2pz has higher IE than does Na 3s

19 A key concept in chemistry is that it is the *valence* electrons on different atoms that interact with one another, rather than the *core* electrons. What is the best explanation for this?

A   Adjacent valence electron waves have the greatest in-phase or out-of-phase overlap.

B   Adjacent valence electron waves have the same energy.

C   Core electron clouds have the wrong symmetry.

D   Core electron clouds move with the wrong frequency.