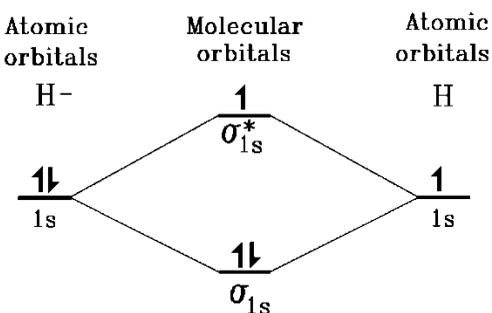


Chapter 3

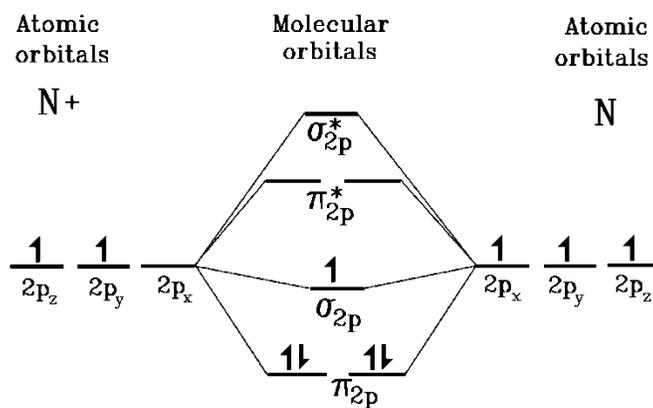
COVALENT BONDING

Exercises

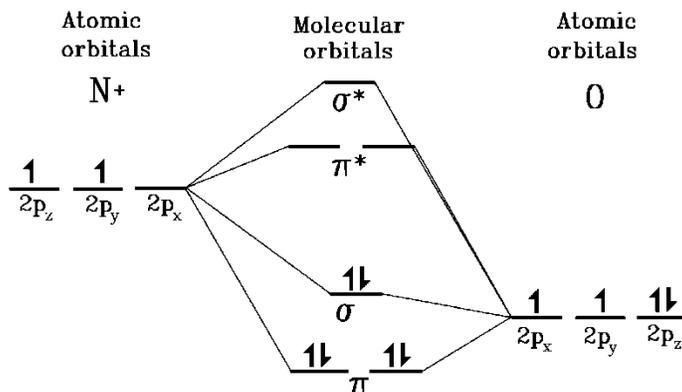
- 3.1 (a) The acronym for linear combination of atomic orbitals; it is a sophisticated theory for the representation of bonding in covalent molecules.
- (b) A molecular orbital in which the increased electron density lies between the two nuclei involved in the bonding.
- (c) The acronym for valence shell electron pair repulsion, a method of predicting molecular shape using simple electron pair concepts of bonding.
- (d) Hybridization involves the concept of mixing atomic orbitals on a central atom to give hybrid orbitals that have the directions to give the maximum overlap with the atomic orbitals of the surrounding atoms.
- (e) The principal axis is the axis containing the highest n -fold rotation axis.
- 3.3 The bond order would be $\frac{1}{2}$ and the ion would be paramagnetic.



3.5 Bond order $2\frac{1}{2}$. Electron configuration: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$.

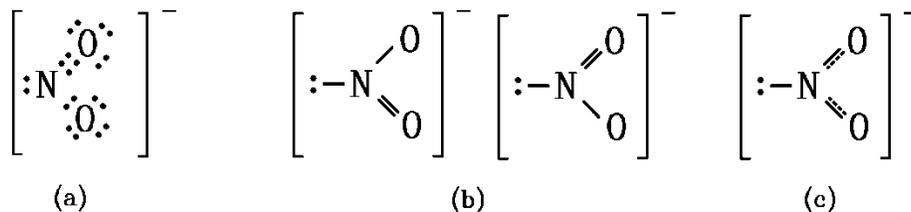


3.7 Triple bond.

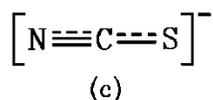
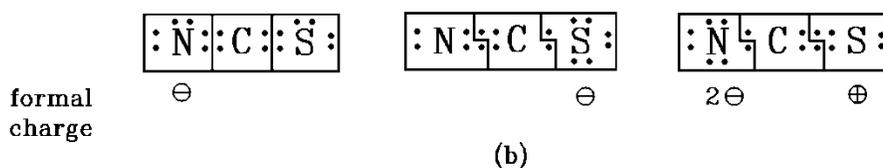
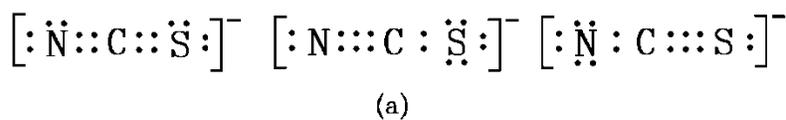


3.9 Single bond. The ordering for the earlier elements predicts two unpaired electrons, while that for the later elements predicts paired electrons. Hence if the former ordering is correct, the molecule should be paramagnetic, but the latter ordering would be diamagnetic [diboron is actually paramagnetic].

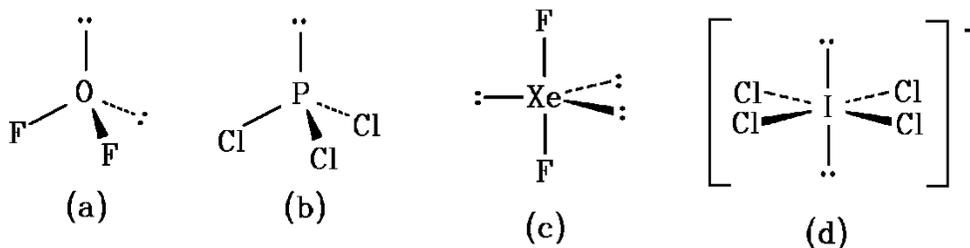
- 3.13 (a) Electron-dot diagram; (b) resonance structures; (c) partial bond representation. Bond order approximately $1\frac{1}{2}$.



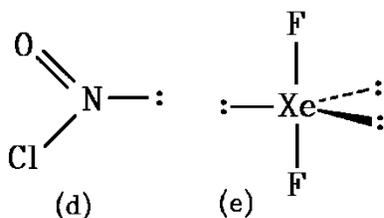
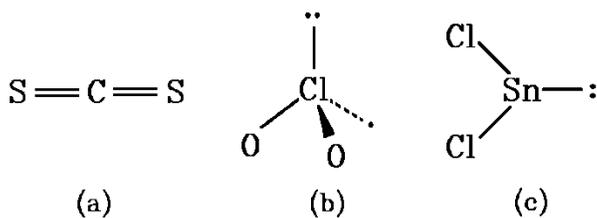
- 3.15 (a) Electron dot diagrams; (b) formal charge structures; (c) partial bond representation



- 3.17 (a) tetrahedral, V-shaped; (b) tetrahedral, trigonal pyramidal; (c) trigonal bipyramidal, linear; (d) octahedral, square planar.



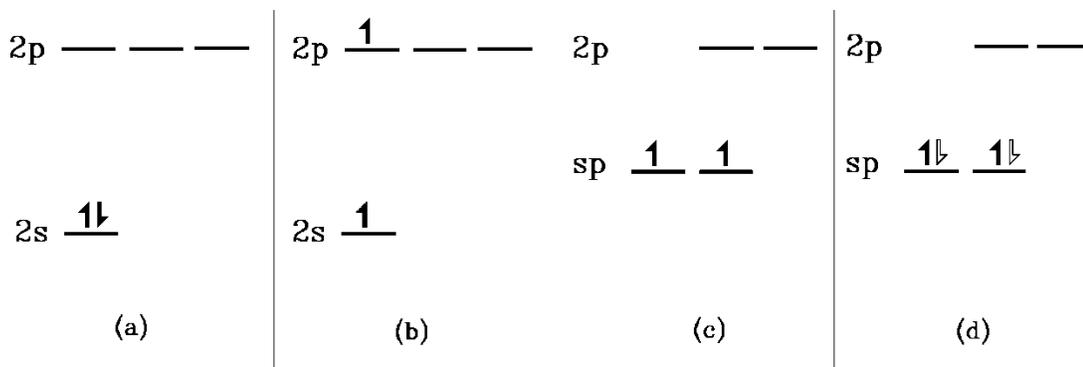
- 3.19 Linear: carbon disulfide and xenon difluoride; V-shaped: chlorine dioxide ($< 109\frac{1}{2}^\circ$) [in fact, the bonding is not so simple, as we discuss in Chapter 16], tin(II) chloride ($< 120^\circ$), and nitrosyl chloride ($< 120^\circ$).



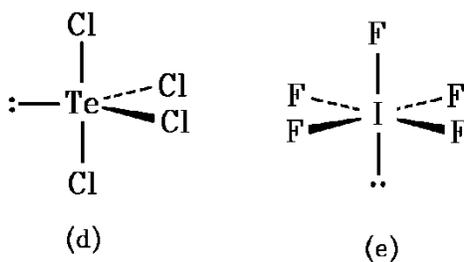
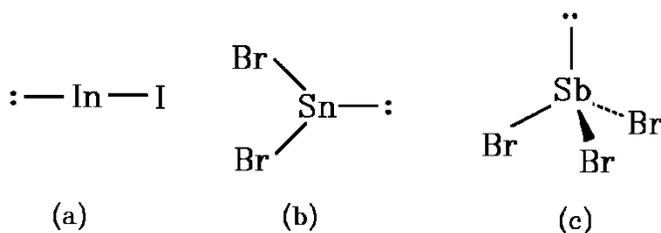
- 3.21 Oxygen difluoride and phosphorus trichloride. The bond angles will be reduced as a result of the presence of the lone pairs.

- 3.23 (a) sp^3 ; (b) sp^3 ; (c) sp^3d ; (d) sp^3d^2 .

- 3.25 The hybrid orbitals used would be sp , accounting for the linear arrangement.



- 3.27 Hydrogen selenide, because with more electrons, the dispersion forces would be greater (the slightly weaker dipole-dipole interaction than that of hydrogen sulfide is a less important factor).
- 3.29 Polar: oxygen difluoride and phosphorus trichloride; nonpolar: xenon difluoride and the tetrachloroiodate ion.
- 3.31 Ammonia, because neighboring molecules will hydrogen-bond to each other, providing a strong intermolecular force and hence a higher boiling point than phosphine, which has the weaker dipole-dipole interactions.
- 3.33 The possible hybridization: (a) sp ; (b) sp^2 ; (c) sp^3 ; (d) sp^3d ; (e) sp^3d^2 .



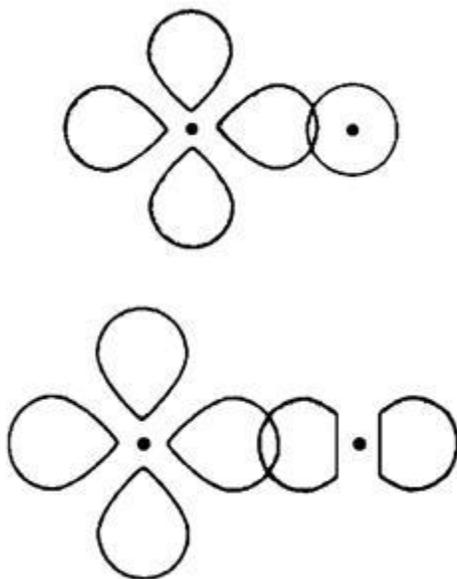
- 3.35 Because methane is nonlinear, it will have $(3N-6)$ vibrational modes. With five atoms, then it will have nine vibrational modes.
- 3.37 (a) There will be one C_3 axis, three C_2 axes, three σ_v planes, one σ_h plane, one improper S_6 axis, and three S_2 axes. The molecule would have D_{3h} symmetry.
- (b) There will be one C_4 axis and two σ_v planes. The molecule will have C_{4v} symmetry.

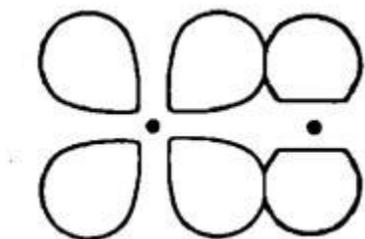
(c) There will be one C_4 axis, four C_2 axes, one σ_h plane, four σ_v planes, a center of symmetry, one improper S_4 axis, and four S_2 axes.

- 3.39 (a) Trigonal pyramidal. One C_3 axis and three σ_v planes. The point group will be C_{3v} .
- (b) Trigonal planar. One C_3 axis, three C_2 axes, one σ_h plane, and three σ_v planes. The point group will be D_{3h} .
- (c) Tetrahedral. Four C_3 axes, three C_2 axes, and six σ_v planes. The point group will be T_d .
- (d) Octahedral. Three C_4 axes, four C_3 axes, six C_2 axes, nine σ_v planes, and a center of symmetry.

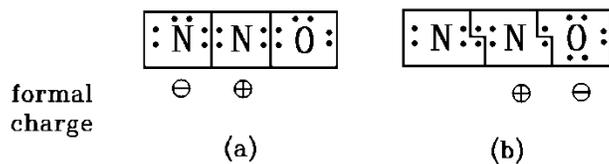
Beyond the Basics

- 3.41 The following figures show the overlap of an s orbital with a typical d orbital to form a σ bond; overlap of a p orbital with a typical d orbital to form a σ bond; and overlap of a p orbital with a typical d orbital to form a π bond. Black dots indicate the location of the nuclei.

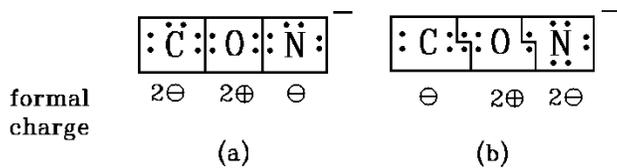




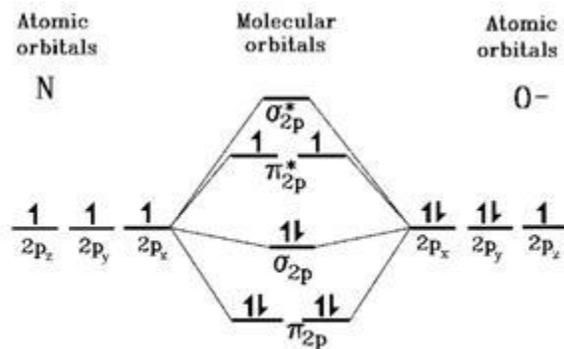
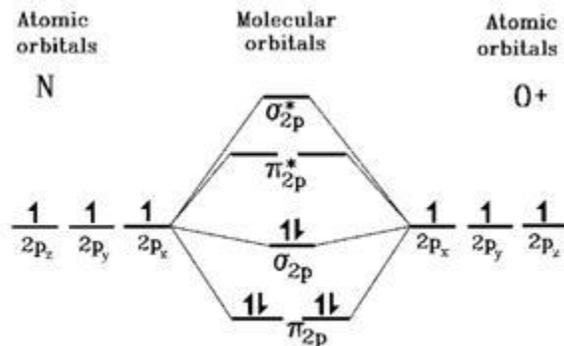
- 3.43 Using formal charge structures, we see that the NNO arrangement provides two possibilities with only one formal charge per atom. The two feasible formal charge structures for NON both have double charges.

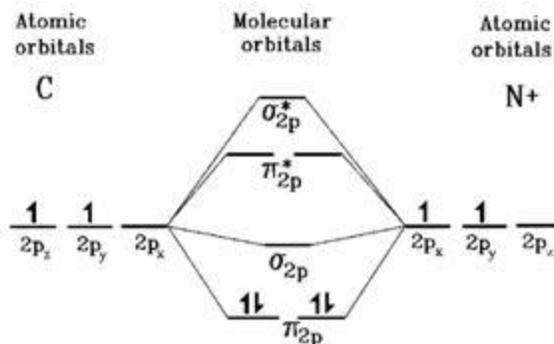
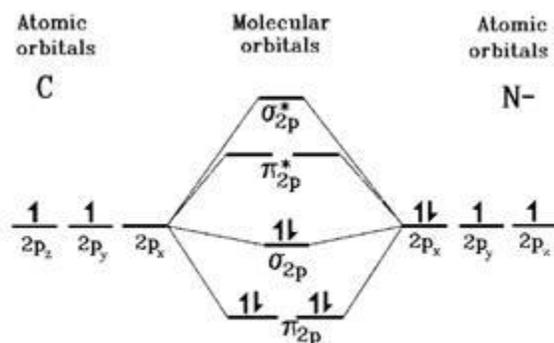


- 3.45 The two feasible formal charge electron arrangements for the CON^- ion have five formal charges! This is a very unlikely structure.



- 3.47 Let us look at the bond order of the product molecules in each case. NO^+ and CN^- are both triply bonded while NO^- and CN^+ will be double bonded. The former combination will therefore be energetically preferred.





- 3.49 One would expect the halide with the larger number of halogen atoms to have the higher boiling point as a result of the greater number of electrons and hence the stronger dispersion forces. A possible answer (but not necessarily the correct one!) would be that antimony has an electronegativity comparable to some metals. As a result, there may be a significant ionic character to the bonding in SbCl_3 (the lower oxidation state and hence lower charge density species) resulting in a higher boiling point than otherwise expected.
- 3.51 One C_5 axis, five C_2 axes, one σ_h plane, and five σ_v planes.
- 3.53 To have an infrared active absorption, a bond vibration must involve a change in dipole moment. For diatomic dioxygen, there can be no vibration that results in a change of dipole moment. For triatomic molecules, such as trioxygen, an asymmetrical stretch involves a change in dipole moment. Thus ozone will be infrared absorbing.

- 3.55 With the low planetary mass, the atmospheric gases on Mars would be lost comparatively quickly. Volcanoes provided a replenishment of the carbon dioxide into the atmosphere. Carbon dioxide is a strong radiation trapper. When the core solidified, volcanic activity ceased and no more of the 'greenhouse gas' was being pumped into the atmosphere to replace that lost due to the low gravitational field of the planet. Hence the remaining atmosphere cooled.

