

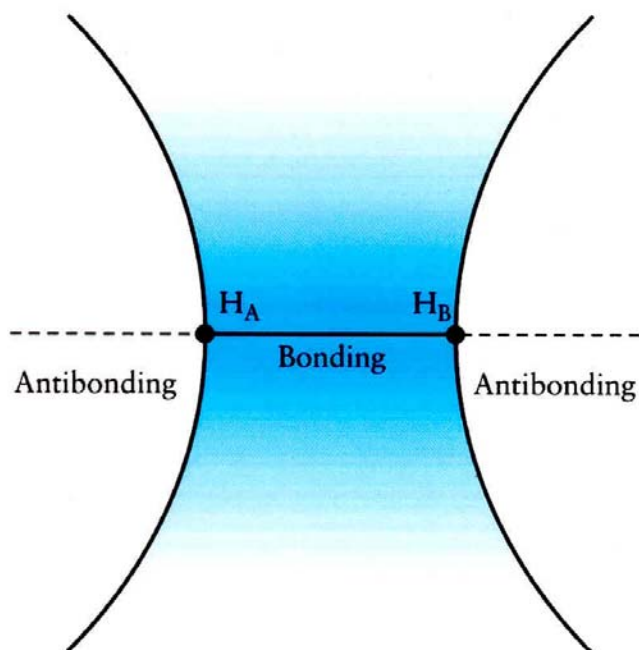
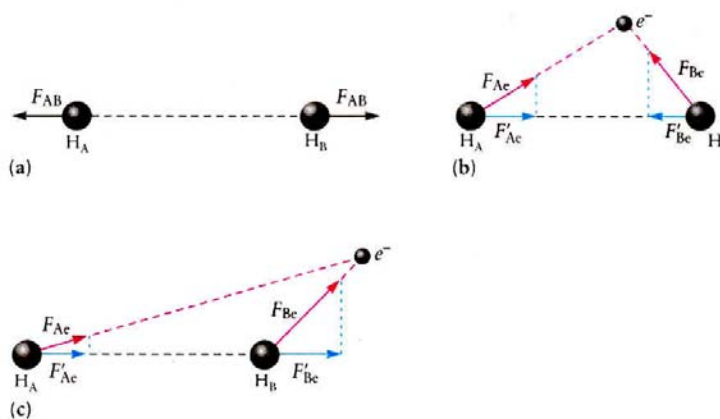
## Topic 2B - Covalent Bonding

### Topic 2C - Beyond the Octet Rule

## Covalent Bond Formation

**FIGURE 3.11** The forces between the particles in  $H_2^+$ . (a) The internuclear repulsion always opposes bonding the nuclei together. (b) An electron positioned in a region that will tend to bond the nuclei together. (c) An electron positioned in a region that will tend to pull the nuclei apart.

(Adapted from G.C. Pimentel and R.D. Spratley, *Chemical Bonding Clarified through Quantum Mechanics*, Holden-Day Inc., San Francisco, 1969, Page 74.)

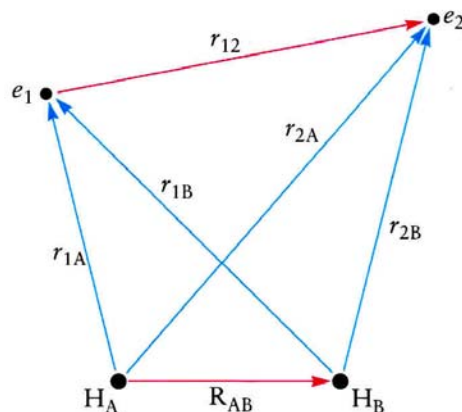


**FIGURE 3.12** Bonding and antibonding regions in a homonuclear diatomic molecule. An electron located within the bonding region will tend to pull the nuclei together, whereas an electron in the antibonding regions will tend to pull the nuclei apart.

(Adapted from G.C. Pimentel and R.D. Spratley, *Chemical Bonding Clarified through Quantum Mechanics*, Holden-Day Inc., San Francisco, 1969, Page 75.)

## Chemical Bond Formation

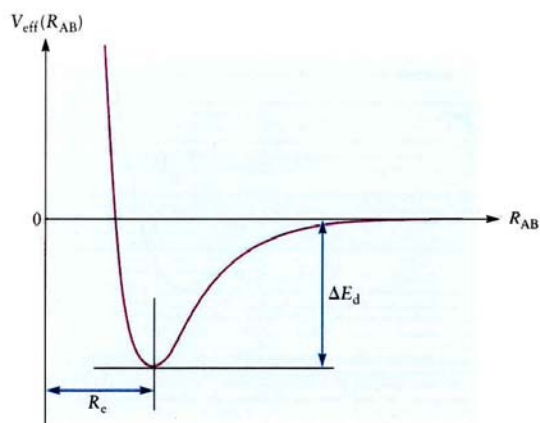
**FIGURE 3.8** Coordinates for the hydrogen molecule. The nuclei are assumed stationary at fixed positions separated by the distance  $R_{AB}$ . The distance of electron 1 from nuclei A and B is given by  $r_{1A}, r_{1B}$ ; the distance of electron 2 from nuclei A and B is given by  $r_{2A}, r_{2B}$ ; the distance between the electrons is given by  $r_{12}$ .

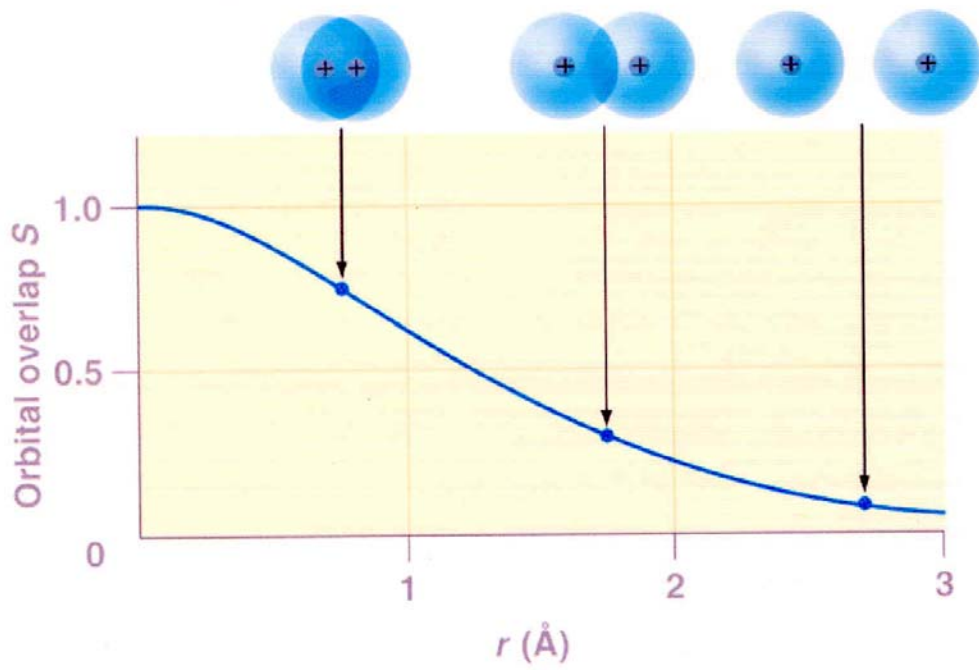
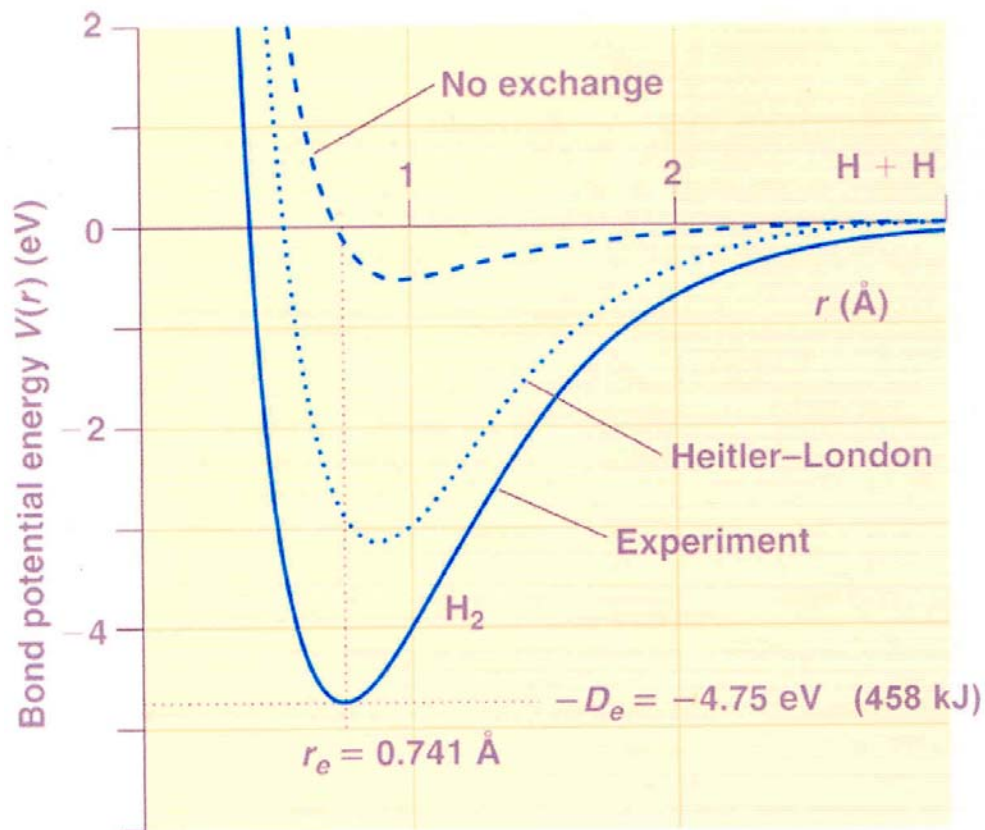


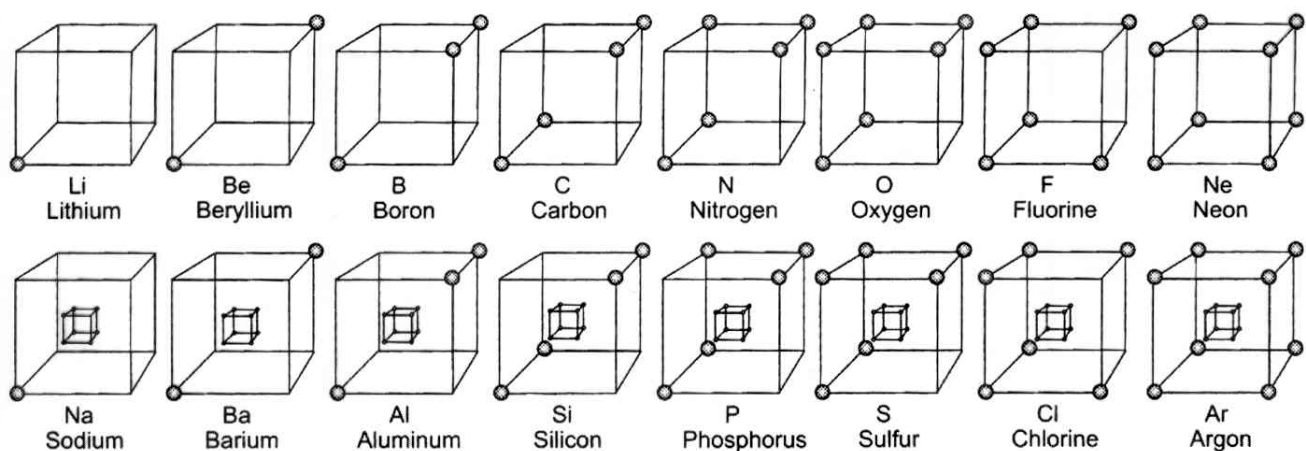
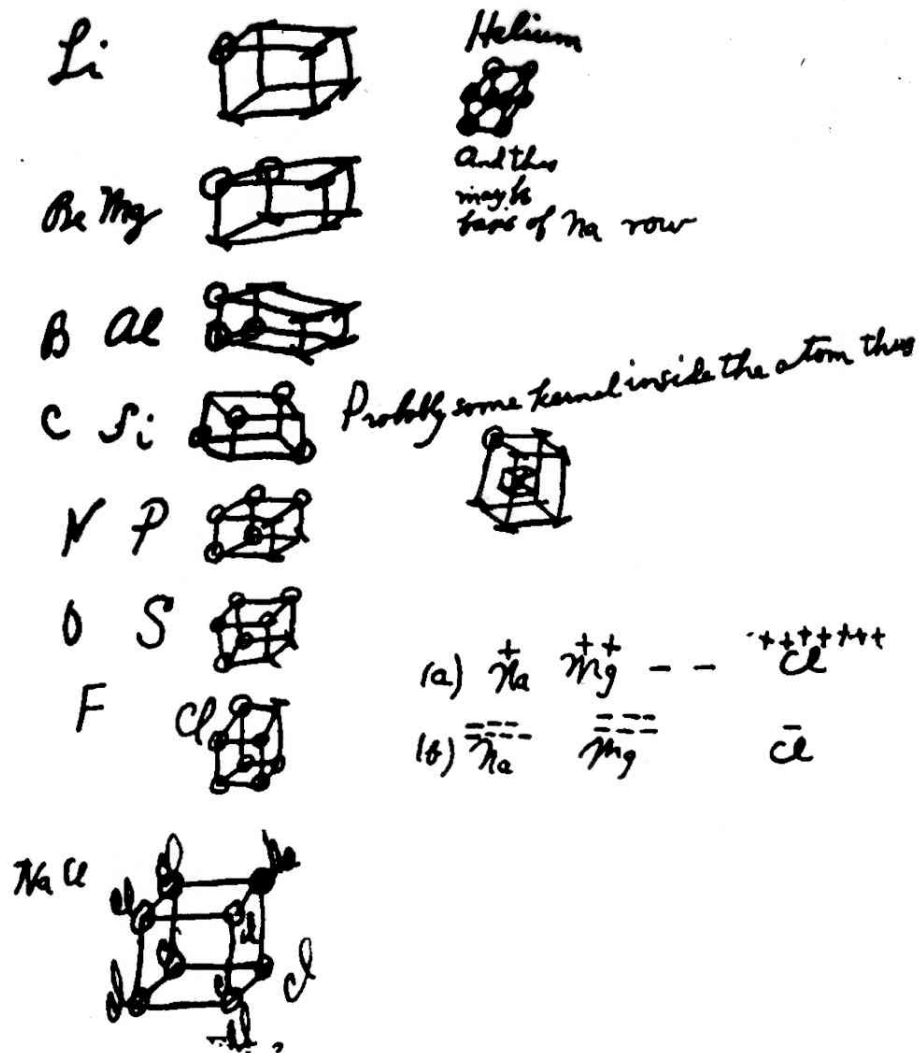
$$V = -\frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{1A}} + \frac{1}{r_{2A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2B}} \right) + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{12}} \right) + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R_{AB}} \right)$$

$$V = V_{en} + V_{ee} + V_{nn}$$

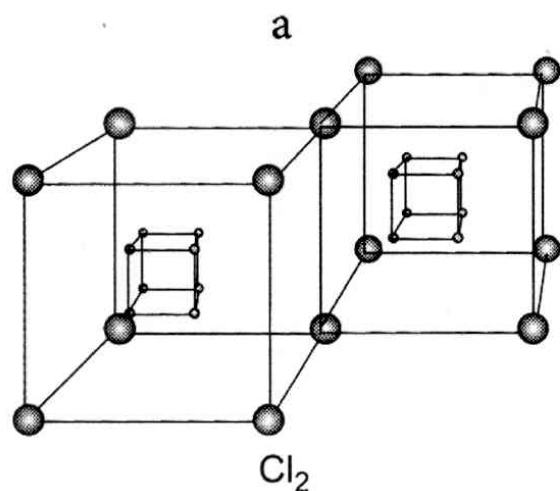
**FIGURE 3.9** Dependence of the effective potential energy  $V_{eff}$  for a diatomic on the internuclear distance  $R_{AB}$ . The location of the minimum corresponds to the equilibrium bond length. The depth of the well relative to the separated atoms is the energy required to dissociate the molecule to form the atoms, and it measures the stability of the molecule.



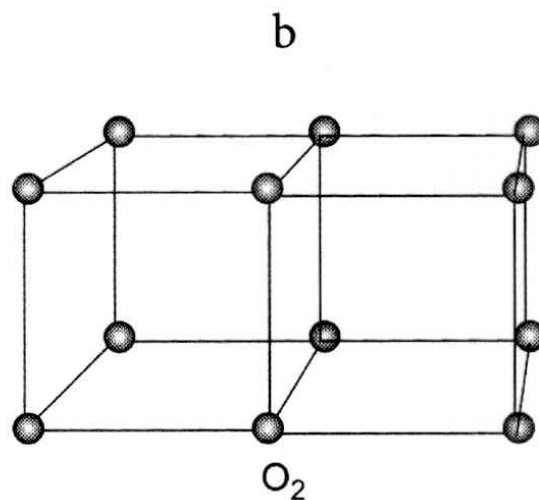




As early as 1902, in a course taught with T.W. Richards at Harvard, G.N. Lewis was developing a cubic model for atoms that placed an electron at the corner of the cube, increasing by one electron in steps across the second and third period of the Periodic Table. With the filling of the 8 electrons in neon of the second period, that cube moved to the inside of the cube representing the sites for electron placement in building up the third period of the Periodic Table.

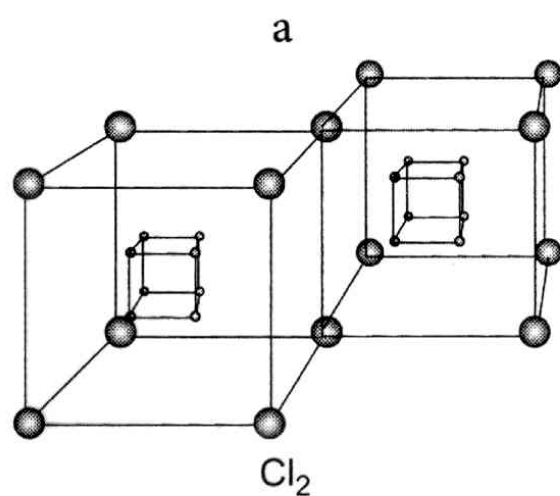


Chlorine Molecule

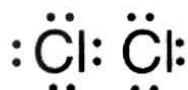
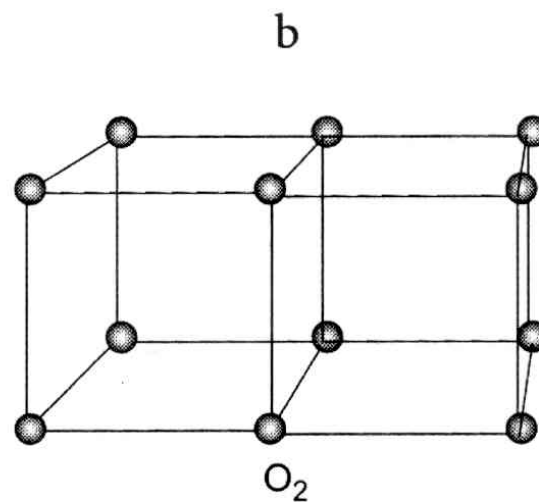


Oxygen Molecule

It was the union of the cubic model for atoms to form molecules by sharing electron pairs that lead G.N. Lewis to propose his theory of the sharing of a pair, or pairs, of electrons to form a stable molecular bond.



Chlorine Molecule

*Cl<sub>2</sub> chlorine molecule*

Oxygen Molecule

*O<sub>2</sub> oxygen molecule*

Simplification of the cubic model of molecular bond formation lead Lewis to develop his electron dot formation of bonding structure. It was the simplified



## Summary

### Writing Lewis Structures

- Sum the valence electrons from all the atoms. Do not worry about keeping track of which electrons come from which atoms. It is the *total* number of electrons that is important.
- Use a pair of electrons to form a bond between each pair of bound atoms.
- Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements.

## Summary

### Lewis Structures and the Octet Rule

- The second-row elements C, N, O, and F should always be assumed to obey the octet rule.
- The second-row elements B and Be often have fewer than eight electrons around them in their compounds. These electron-deficient compounds are very reactive.
- The second-row elements never exceed the octet rule, since their valence orbitals ( $2s$  and  $2p$ ) can accommodate only eight electrons.
- Third-row and heavier elements often satisfy the octet rule but are assumed in the simplest model to exceed the octet rule by using their empty valence  $d$  orbitals.
- When writing the Lewis structure for a molecule, first draw single bonds between all bonded atoms, and then satisfy the octet rule for all the atoms. If electrons remain after the octet rule has been satisfied, place them on the elements having available  $d$  orbitals (elements in the third period or beyond).

Give the Lewis structure for each of the following.

- a. HF    b. N<sub>2</sub>    c. NH<sub>3</sub>    d. CH<sub>4</sub>    e. CF<sub>4</sub>    f. NO<sup>+</sup>

### Solution

In each case we apply the three rules for writing Lewis structures. Recall that lines are used to indicate shared electron pairs and that dots are used to indicate nonbonding pairs (lone pairs). We have the following tabulated results:

	Total Valence Electrons	Draw Single Bonds	Calculate Number of Electrons Remaining	Use Remaining Electrons to Achieve Noble Gas Configurations
a. HF	$1 + 7 = 8$	H—F	6	H— $\ddot{\text{F}}:$
b. N <sub>2</sub>	$5 + 5 = 10$	N—N	8	:N≡N:
c. NH <sub>3</sub>	$5 + 3(1) = 8$	H—N—H   H	2	H— $\ddot{\text{N}}$ —H   H
d. CH <sub>4</sub>	$4 + 4(1) = 8$	H   H—C—H   H	0	H   H—C—H   H
e. CF <sub>4</sub>	$4 + 4(7) = 32$	F   F—C—F   F	24	: $\ddot{\text{F}}$ :   : $\ddot{\text{F}}$ —C— $\ddot{\text{F}}$ :   : $\ddot{\text{F}}$ :
f. NO <sup>+</sup>	$5 + 6 - 1 = 10$	N—O	8	[: $\text{N}\equiv\text{O}$ :] <sup>+</sup>

Write the Lewis structure for PCl<sub>5</sub>.

### Solution

We can follow the same stepwise procedure we used previously for sulfur hexafluoride.

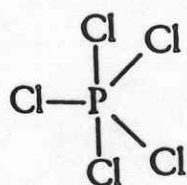
#### STEP 1

Sum the valence electrons.

$$\begin{array}{r} 5 + 5(7) = 40 \text{ electrons} \\ \uparrow \quad \uparrow \\ \text{P} \quad \text{Cl} \end{array}$$

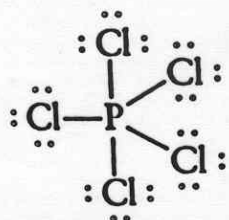
#### STEP 2

Indicate single bonds between bound atoms.



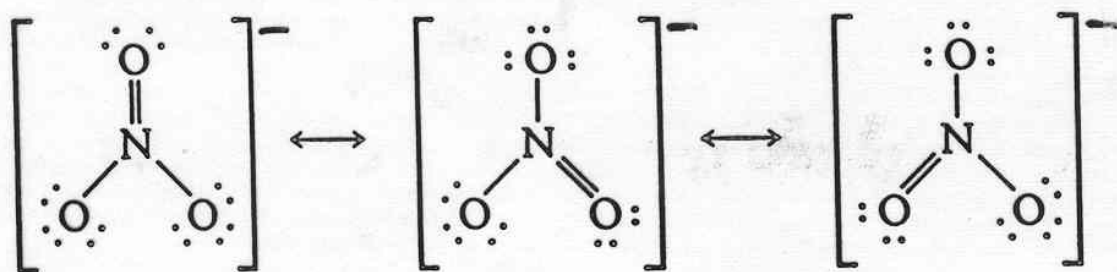
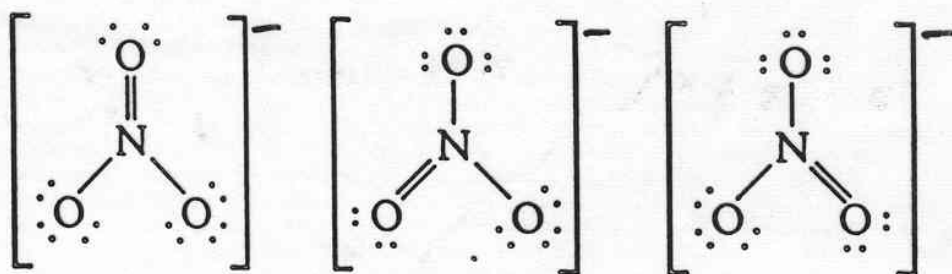
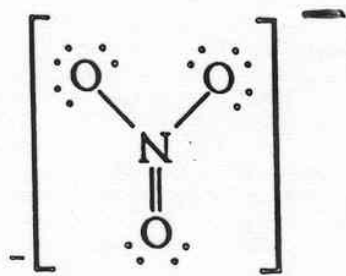
#### STEP 3

Distribute the remaining electrons. In this case, 30 electrons (40 – 10) remain. These are used to satisfy the octet rule for each chlorine atom. The final Lewis structure is



Note that phosphorus, which is a third-row element, exceeds the octet rule by two electrons.





The concept of formal charge derives from Pauling's **Electroneutrality Principle**: *Electrons in a molecule are distributed in such a way as to make the “residual charge” on each atom as close to zero as possible.*

The **Formal Charge** on any atom in a given Lewis structure is the hypothetical “charge” it would have if the bonding were perfectly covalent and the atom had a  $\frac{1}{2}$ -“share” of its bonding electrons and all of its lone pairs.

### Summary

#### Rules Governing Formal Charge

- To calculate the formal charge on an atom:
  1. Take the sum of the lone pair electrons and one-half of the shared electrons. This is the number of valence electrons assigned to a given atom in the molecule.
  2. Subtract the number of assigned electrons from the number of valence electrons on the free, neutral atom to obtain the formal charge.
- The sum of the formal charges of all atoms in a given molecule or ion must equal the overall charge on that species.
- If nonequivalent Lewis structures exist for a species containing second-row atoms, those with formal charges closest to zero and with any negative formal charges on the most electronegative atoms are considered to best describe the bonding in the molecule or ion.

This results in the least “distortion” of each atom’s electron density distribution, compared to that of the isolated, neutral atom.

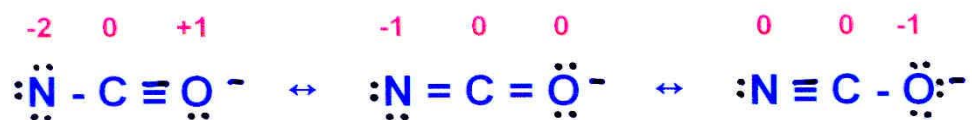
## Application of Formal Charge Principal

Possible Bonding Arrangements for (C,N,O)<sup>-</sup> Ionic Species containing 16 valence electrons:



Cyanate Ion (NCO<sup>-</sup>):

Resonance Forms:



Fulminate Ion (CNO<sup>-</sup>):

Resonance Forms:

