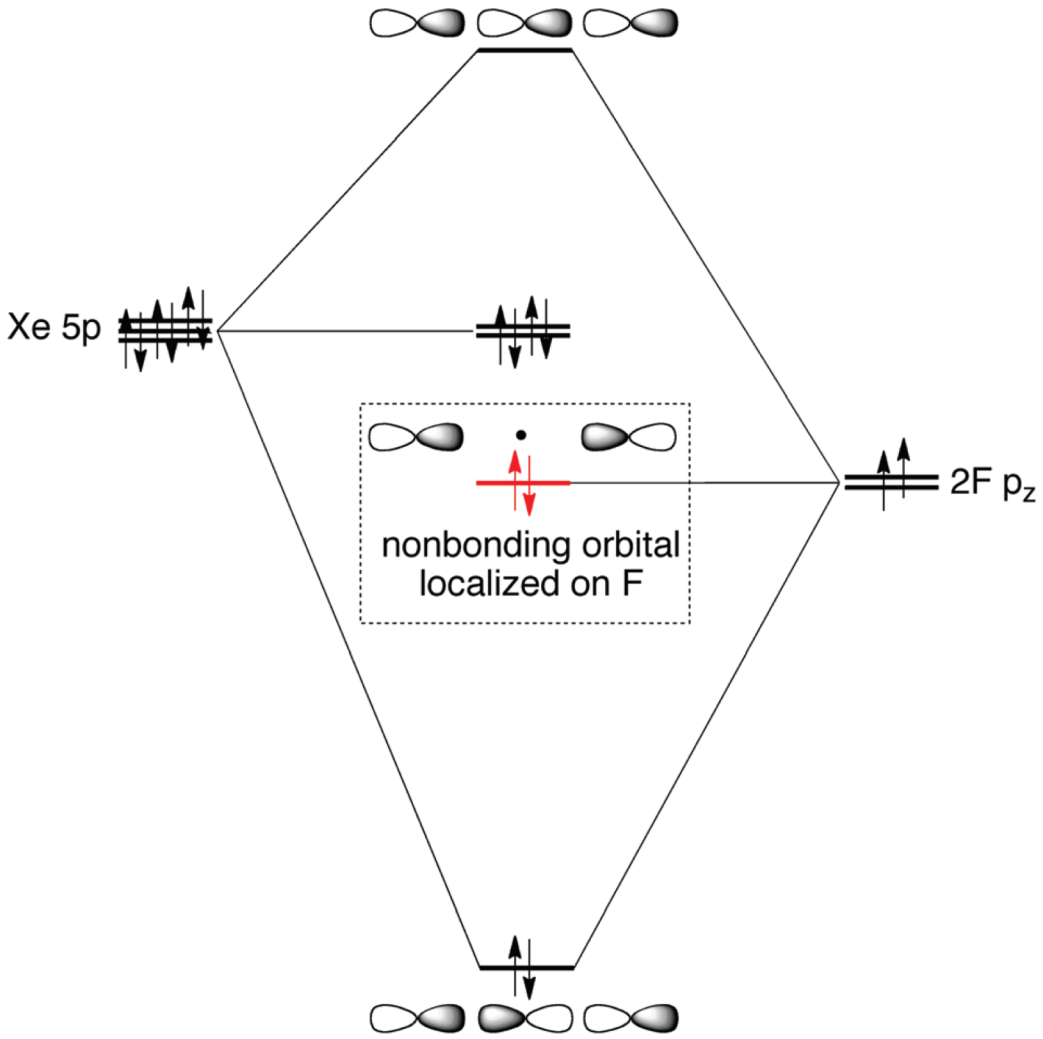
Hypervalent Molecules: 1

Examples of molecules with three centre four electron bonds

And their representation within the covalent bond classification

XeF_2 – an example of a 3c-4e bond



Xe uses its 5s and three 5p orbitals for bonding

The molecule is linear

The Xe $5p_\sigma$ orbital and two F $2p_\sigma$ orbitals form a 3 centre bond

The inphase combination of the two F $2p_\sigma$ orbitals are nonbonding

Occupancy of these two orbitals results in a build up of charge on the fluorines

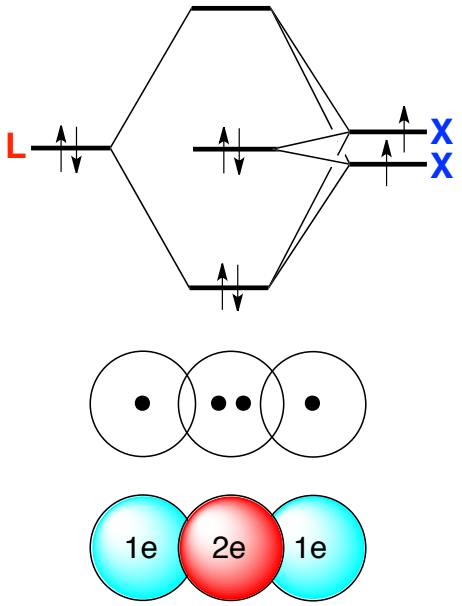
The equivalent Lewis formulation is given below

$$F—Xe^+\ \ F^- \longleftrightarrow F^-\ \ Xe^+—F$$

Xe contributes 2 electrons to the bonding and retains its octet.
The XeF bond order is ½.

3c–4e Interactions

X ····· L ····· X



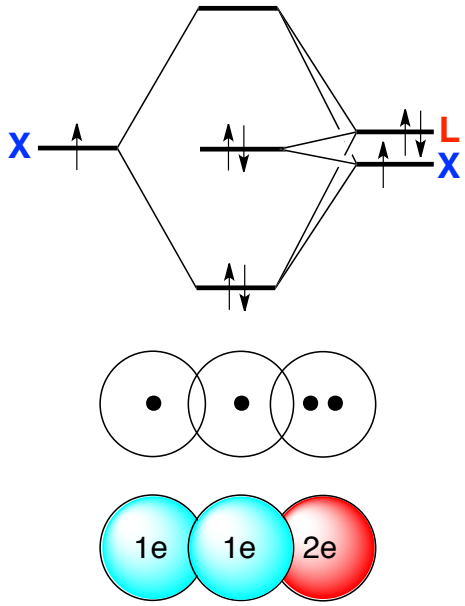
X–μ-L–X

$(X_2)^H$

number of electrons contributed to the central atom (L): 0

contribution to the valence of the central atom (L): 2

X ····· X ◄····· L



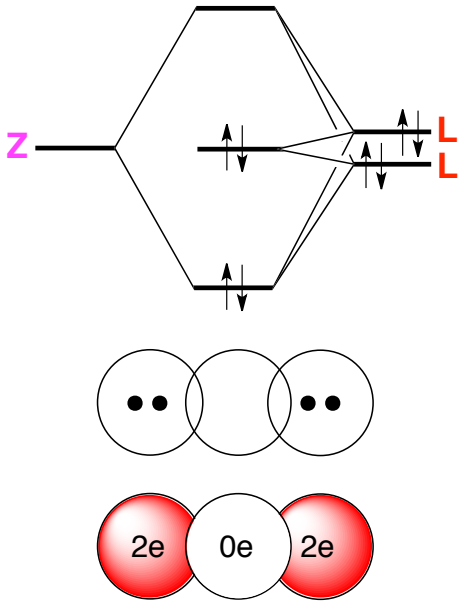
X–μ-X–L

$(LX)^H$

number of electrons contributed to the central atom (X): 1

contribution to the valence of the central atom (X): 1

L ·····►Z◄····· L



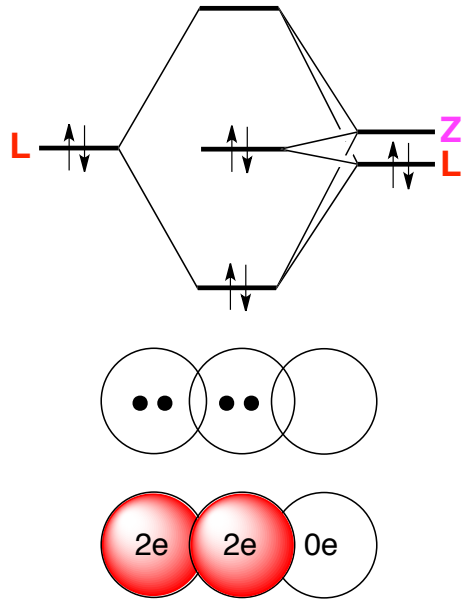
L–μ-Z–L

$(L_2)^H$

number of electrons contributed to the central atom (Z): 2

contribution to the valence of the central atom (Z): 0

L ·····►L·····►Z



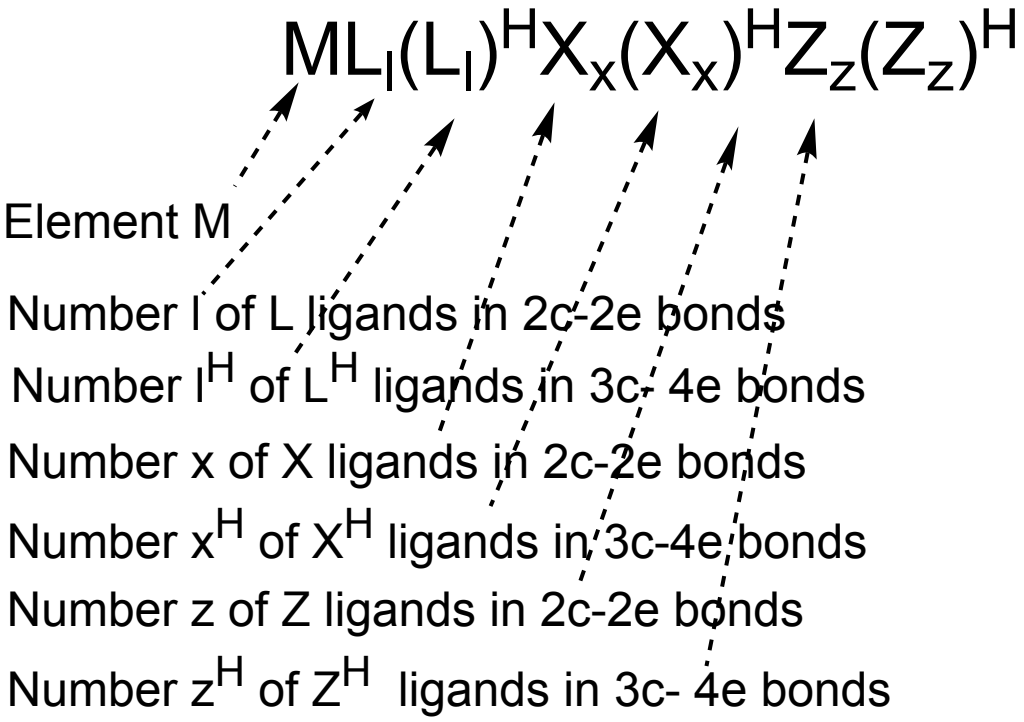
L–μ-L–Z

$(LZ)^H$

number of electrons contributed to the central atom (L): 0

contribution to the valence of the central atom (L): 2

Method of Writing Formula of Covalent Molecules that contain 3 center - 4 electron bonds



This may be condensed to

$$ML_{2l}X_{2x}Z_{2z}H_{l+x+z}$$

The general formula being

$$ML_lX_xH_h$$

H indicates a hypervalent interaction
h is the number of hypervalent interactions

Counting using the general formulae

	X^H–M–X^H	X^H–M–L^H	L^H–M–L^H	L^H–M–Z^H
number of electrons contributed to the central atom	0	1	2	0
contribution to the valence of the central atom	2	1	0	2

Class: $ML_l(L_l)^HX_x(X_x)^HZ_z(Z_z)^H$ **or** $ML_lX_xZ_zH_h$

Electron number(EN) = nb + 2(l + x) + (l + x)^H **or** = m + 2l + x - 2h

Valence number (VN) = (x + x^H) + 2(z + z^H) **or** = x + 2z

Ligand bond number (LBN) = (x + l + z) + (x + l + z)^H **or** = l + x + z

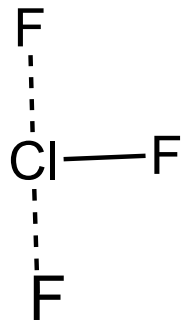
m = the number of electrons in the valency shell of the element
nb = number of nonbonding electrons on M = m - VN

The use of the superscript ^{H} as in L^H, X^H and Z^H indicates the bond is hypervalent (3c-4e)

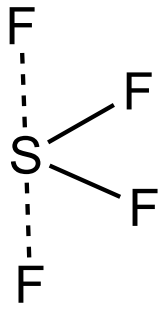
H is not to be confused with H for hydrogen

Non-metal fluoride examples of $(X_2)^H$ 3c-4e bonds

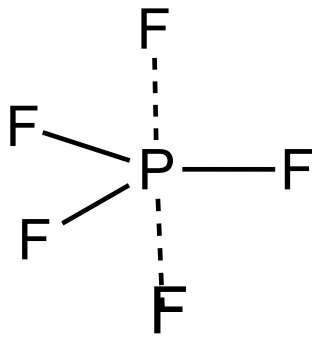
$XeF_2{}^H$
VN = 2, EN = 8



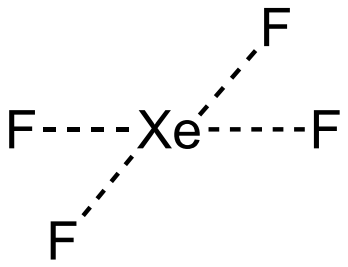
$ClFF_2{}^H$
VN = 3, EN = 8



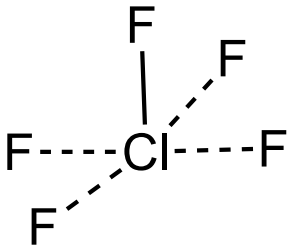
$SF_2F_2{}^H$
VN = 4, EN = 8



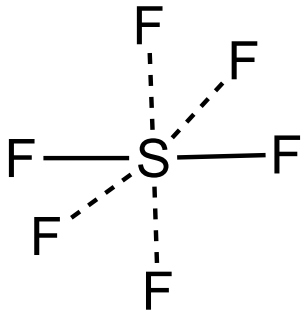
$PF_3F_2{}^H$
VN = 5, EN = 8



$XeF_4{}^H$
VN = 4, EN = 8



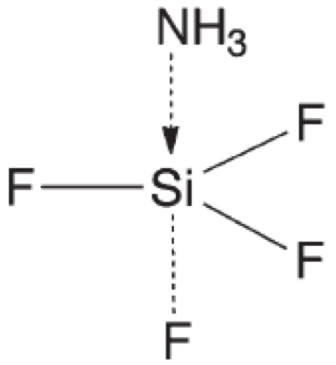
$ClFF_4{}^H$
VN = 5, EN = 8

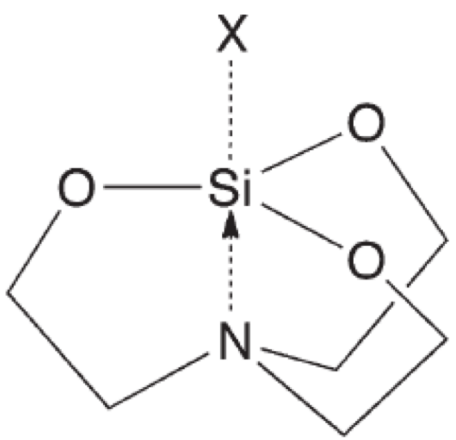


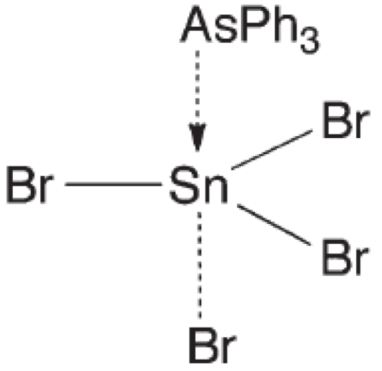
$SF_2F_4{}^H$
VN = 6, EN = 8

The 3c-4e bonds are linear being formed by a p orbital which favours linear overlap. They are longer than the 2c-2e bonds having a bond order of ½ rather than 1.

Examples of $(LX)^H$ 3c-4e bonds



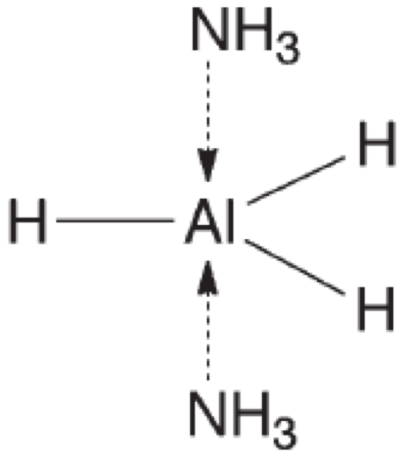


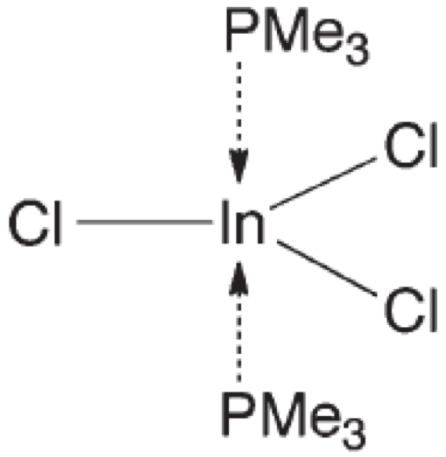


$SiF_3F^{H(}NH_3)^H$
VN = 4 EN = 8

$SnBr_3Br^{H(}AsPh_3)^H$
VN = 4 EN = 8

Examples of $(L_2)^H$ 3c-4e bonds





$AlH_3(NH_3)_2{}^H$
VN = 3 EN = 8

$InCl_3(PMe_3)_2{}^H$
VN = 4 EN = 8

3c-4e bonds with first and second period elements as the central atom

Most examples of 3c-4e bonds are from the 3rd period and below. However the classic example from the first period is the bifluoride ion, $[HF_2]^-$.

Some more exotic examples with B and C are shown below