

VSEPR

- Le **formule di Lewis** servono per tenere la contabilità degli elettroni di valenza in semplici molecole, ma **non** sono in grado di dire assolutamente nulla sulla **forma delle molecole**, cioè su come gli atomi costituenti una molecola sono disposti nello spazio.
- Una teoria in grado di prevedere la geometria di semplici molecole è la cosiddetta teoria **VSEPR** (Valence Shell Electron Pair Repulsion). Anche questa teoria, come il metodo di Lewis, è estremamente semplice: ciò spiega da un lato la sua popolarità e utilità, dall'altro i suoi limiti.
- Anche la teoria VSEPR è applicabile solo a molecole composte da atomi dei blocchi s e p.
- Il concetto di base della teoria VSEPR è il seguente: **In una molecola costituita da un atomo centrale legato ad altri atomi terminali, le coppie elettroniche attorno all'atomo centrale (sia le coppie di legame che quelle di non legame) tendono a respingersi e quindi si dispongono in modo tale da rendere minima questa repulsione.**

VSEPR

- Siccome le **coppie di legame corrispondono a degli atomi legati all'atomo centrale**, il vincolo della repulsione minima determina la disposizione nello spazio degli atomi costituenti la molecola in esame.
- Definiamo **coppie strutturali** l'insieme delle **coppie elettroniche di legame e non legame attorno all'atomo centrale**. I **legami multipli**, pur contenendo più di una coppia di elettroni, **contano per una sola coppia** strutturale, in quanto le coppie elettroniche di un legame multiplo sono confinate nella **stessa regione di spazio** e quindi, ai fini della repulsione elettrostatica con le altre coppie, vanno prese tutte assieme.



VSEPR

- Sulla base di quanto detto e di intuitive considerazioni di simmetria, è possibile prevedere la geometria delle coppie strutturali dal loro numero:

- La **geometria molecolare** è quella degli **atomi** costituenti una molecola. Ne segue che, una volta determinata la **geometria delle coppie strutturali**, bisogna associare ad ogni coppia di legame il corrispondente atomo terminale ed analizzare la geometria molecolare risultante.

n. coppie	Geometria
2	lineare
3	trigonale piana
4	tetraedrica
5	bipiramidale trigonale
6	ottaedrica

La geometria delle coppie strutturali per la molecola di H₂O è di tipo tetraedrico, ma la geometria molecolare è di tipo angolato.

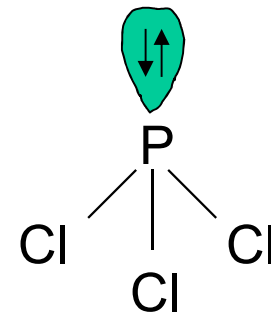
Come si determina il numero di coppie elettroniche di valenza, ovvero come si determina la geometria?

Innanzitutto bisogna determinare l'atomo centrale della molecola o ione per il quale facciamo il conto delle coppie elettroniche. (Es. NO_3^- , PCl_3 , PCl_5 , H_2O , NH_3)

Per contare tutte le coppie di valenza di natura σ intorno all'atomo centrale si considerano gli elettroni dell'atomo e quelli derivanti dai legami con gli atomi che stanno intorno:

N.B. I cloruri formalmente si comportano come datori di $1e^-$, infatti hanno valenza 1 ovvero basta che formino un legame singolo per completare l'ottetto.

Es: PCl_3 : $5e^-$ (per il P) + $3 \cdot 1e^-$ (per ogni Cl) = $8e^-$
che corrisponde a **4 coppie** σ .



Poiché nel nostro sistema a 4 coppie abbiamo solamente 3 atomi che si legano al P, il sistema è uno di tipo AX_3E dove X indica **gli atomi legati all'atomo centrale** mentre E indica una coppia **elettronica solitaria** ovvero una coppia di elettroni non impegnata nella formazione di legami. Ora in base alla teoria VSEPR, i **4 doppietti elettronici** assumono una disposizione **tetraedrica**.

*N.B. La geometria della molecola è **piramide a base triangolare**. Infatti la geometria molecolare, come abbiamo visto, è definita dalle distanze di legame e dagli angoli di legame tra gli atomi. Non si considerano ai fini della geometria le coppie solitarie!*

Qual'è la struttura dei legami? Sappiamo che alla disposizione tetraedrica delle coppie corrisponde l'ibridizzazione sp^3 .

Facendo un conto formale delle coppie di valenza siamo in grado di prevedere la disposizione delle coppie e quindi la geometria molecolare ed infine la struttura dei legami. E' importantissimo da notare che il conto degli elettroni ai fini della VSEPR è puramente formale e serve unicamente a determinare il numero di coppie di valenza indipendenti!

Consideriamo ora il caso di molecole o ioni che contengono atomi che possono formare **legami multipli**:

NO_3^- : Ai fini della VSEPR si considera l'ossigeno come un atomo che può formalmente formare legame **doppio**. Di conseguenza egli è un $2e^-$ datore. Bisogna però considerare che il **secondo legame è formalmente di tipo π** , e noi sappiamo che un legame π non può esistere in una direzione indipendente ma esso esiste sempre coassiale ad un legame σ . Di conseguenza per determinare le coppie di valenza indipendenti è necessario sottrarre il contributo π . Il contributo π è $2e^-$ per ogni legame per cui ogni O contribuisce con $2e^-$, ma allo stesso tempo per ogni O dobbiamo sottrarre un contributo π di $2e^-$. **In totale O non contribuisce.**

$\text{NO}_3^- : 5 e^- (\text{N}) + 3 \cdot 2e^- (\text{O}) + 1e^- (\text{carica}) - 3 \cdot 2e^- (\text{contributo } \pi) = 6 e^-$

3 coppie \rightarrow sistema $\text{AX}_3 \rightarrow$ ibrido $sp^2 \rightarrow$ Geometria trigonale planare, in accordo con i dati sperimentali:

Si noti che a causa del fatto che N non può utilizzare orbitali di tipo d, essendo del II periodo, possiamo considerare uno dei legami di tipo dativo, ovvero un legame in cui ambedue gli provengono dallo stesso atomo.

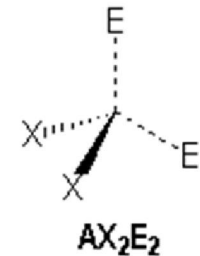
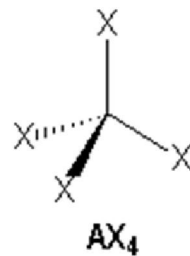
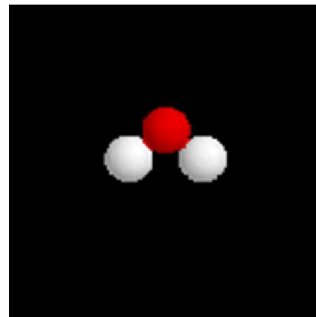
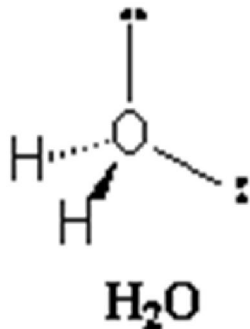
Riassumendo quindi le regole per descrivere una molecola/ione semplice sono:

1. individuare l'atomo centrale
 2. sommare gli elettroni dell'atomo centrale con il contributo degli atomi che lo circondano e la carica ionica.
 3. Sottrarre contributo degli e^- di tipo π (sottrarre 2 e^- per ogni legame π che formalmente si può formare) e calcolare il numero delle coppie a simmetria σ .
 4. Individuare la configurazione ibridizzata utilizzando lo schema AX_mE_n e quindi la disposizione spaziale delle coppie
 5. Disporre le coppie di legame e le coppie solitarie in modo da minimizzare la repulsione.
 6. Applicare la teoria di "Valence Bond" per descrivere il legame chimico.
- E' chiaro a questo punto che per capire come è fatta una molecola o ione semplici, è assolutamente necessario prima determinare la geometria molecolare, utilizzando VSEPR e successivamente determinare la struttura dei legami mediante la teoria del legame di valenza.

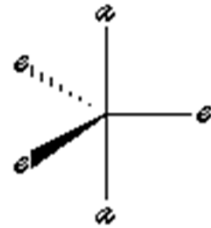
N° coppie strutturali	N° coppie solitarie	VSEPR	Geometria coppie strutturali	Geometria molecola	Esempi
2	0	AX2	Lineare	Lineare	BeCl ₂ , CO ₂ , CS ₂ , COS, C ₂ H ₂ , HCN
3	0	AX3	Trigonale planare	Trigonale planare	BF ₃ , BCl ₃ , SO ₃ , H ₂ CO, COCl ₂ , C ₂ H ₄ , C ₂ H ₂ F ₂ , (CO ₃) ²⁻
	1	AX2E		Angolata	SnCl ₂ , SO ₂ , O ₃ , NSF
4	0	AX4	Tetraedrica	Tetraedrica	CH ₄ , SiF ₄ , (NH ₄) ⁺ , POF ₃ , POCl ₃ , SNF ₃ , (SO ₄) ²⁻ , (S ₂ O ₃) ²⁻
	1	AX3E		Piramidale trigonale	NH ₃ , PH ₃ , AsH ₃ , PF ₃ , PCl ₃ , PBr ₃ , PI ₃ , (H ₃ O) ⁺
	2	AX2E2		Angolata	H ₂ O, H ₂ S, Cl ₂ O, OF ₂ , (NH ₂) ⁻
5	0	AX5	Bipiramide trigonale	Bipiramide trigonale	PCl ₅ , PF ₃ Cl ₂ , XeO ₃ F ₂ , PF ₃ Cl ₂ , SOF ₄ , (IO ₅) ³⁻
	1	AX4E		Tetraedrica distorta	SF ₄ , (IO ₂ F ₂) ⁻ , XeO ₂ F ₂
	2	AX3E2		a T	ClF ₃
	3	AX2E3		Lineare	(I ₃) ⁻ , XeF ₂
6	0	AX6	Ottaedrica	Ottaedrica	SF ₆ , XeF ₆ , IOF ₅
	1	AX5E		Piramide a base quadrata	XeOF ₄ , BrF ₅
	2	AX4E2		Planare quadrata	(ICl ₄) ⁻ , XeF ₄

L'effetto sterico delle coppie di non legame.

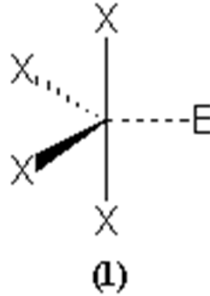
- Nella teoria VSEPR, le **coppie di non legame** vengono considerate più **“repulsive”** di quelle di legame. Una semplicistica spiegazione di ciò è data dal fatto che una coppia di legame risente dell'attrazione di due nuclei (contrariamente ad una coppia di non legame, che è attratta da un solo nucleo) e risulta perciò più “stirata”. Il fatto che le coppie di non legame siano più “ingombranti” spiega le deformazioni dagli angoli teorici in molecole come H₂O: l'angolo H-O-H dovrebbe essere di **109.28°** mentre si trova sperimentalmente che esso è di **104.5°**.
- Il maggiore ingombro delle coppie di non legame determina la loro posizione in quei casi in cui ci sono diverse possibilità non equivalenti. Es. geometria bipiramidale trigonale o ottaedrica con due coppie di non legame.



L'effetto coppie di legame e di non legame.

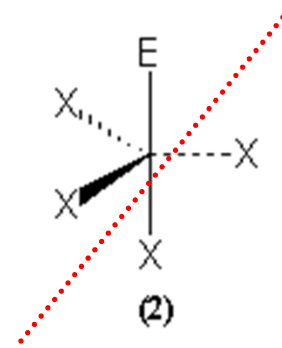


AX5



AX4E

Lone pair
equatoriale



AX4E

Lone pair
assiale

Ordine di repulsione $E-E > E-X > X-X$

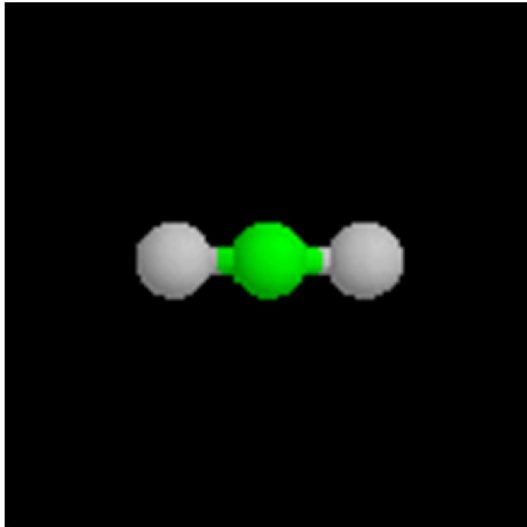
(1) AX4E

2 interazioni $\alpha \leq 90^\circ$ e 2 interazioni $\geq 120^\circ$

(2) AX4E

3 interazioni $\alpha \leq 90^\circ$

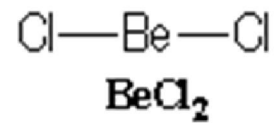
VSEPR: Lineare AX2 BeCl_2



$\text{Be } 1s^2 2s^2$

$2e^- (\text{Be}) + 2e^- (2 \text{ legami } \sigma) =$

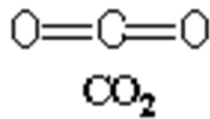
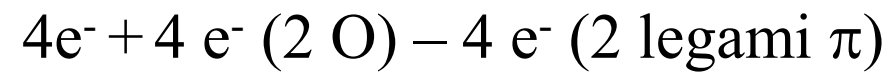
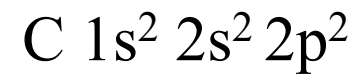
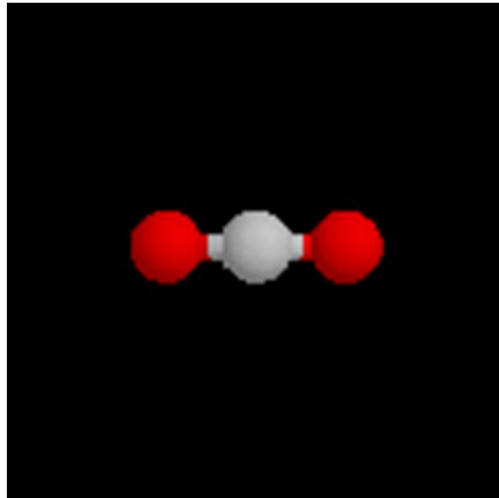
$4 = 2 \text{ coppie} = \text{AX2}$



$d(\text{Be-Cl}) = 0,117 \text{ nm}$

$\alpha = 180^\circ$

VSEPR: Lineare AX₂ CO₂

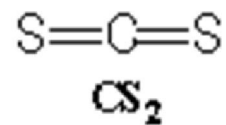
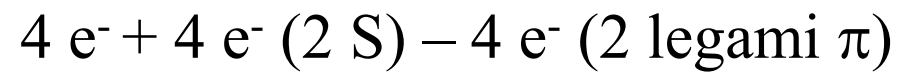
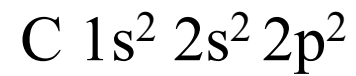
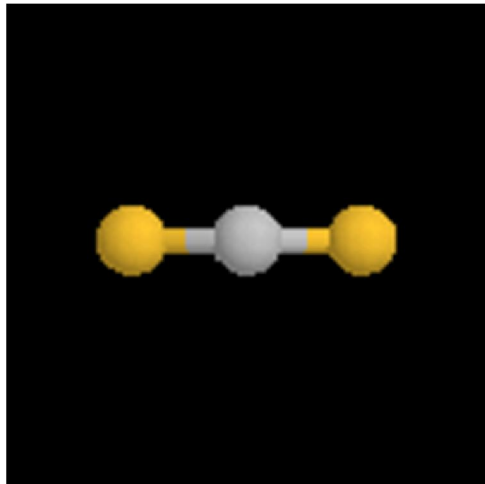


Co2.pdb

d(C-O) = 0,116 nm

$\alpha = 180^\circ$

VSEPR: Lineare AX₂ CS₂

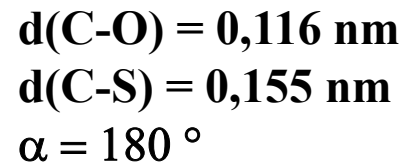
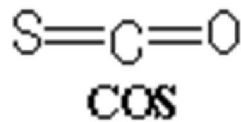
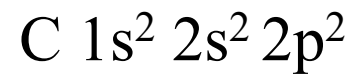
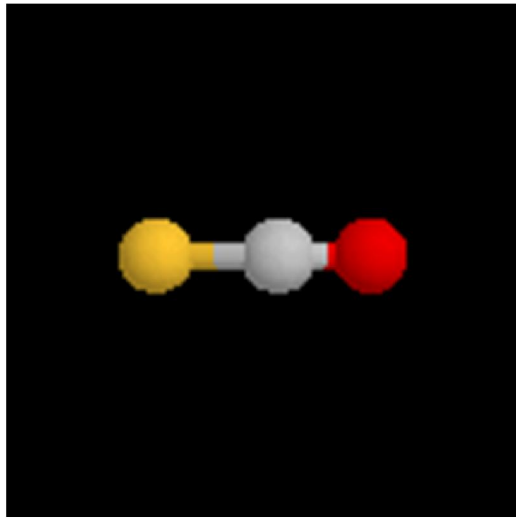


Cs2.pdb

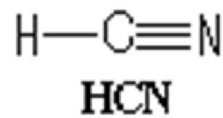
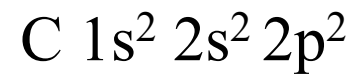
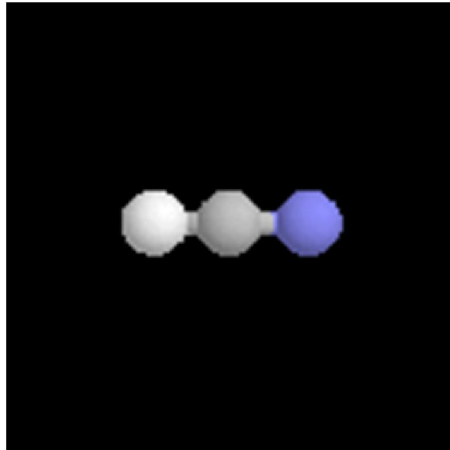
d(C-S) = 0,155 nm

$\alpha = 180^\circ$

VSEPR: Lineare AX₂ COS



VSEPR: Lineare AX2 HCN

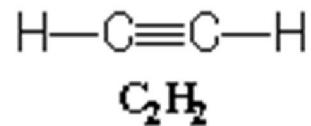
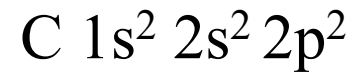
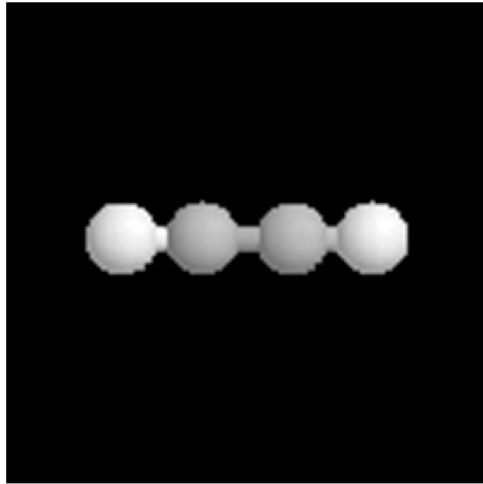


d(H-C) = 0,107 nm

d(C-N) = 0,116 nm

$\alpha = 180^\circ$

VSEPR: Lineare AX2 C_2H_2



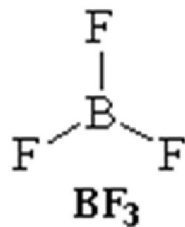
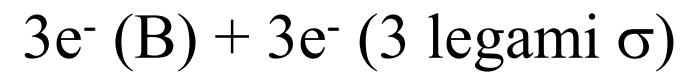
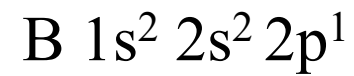
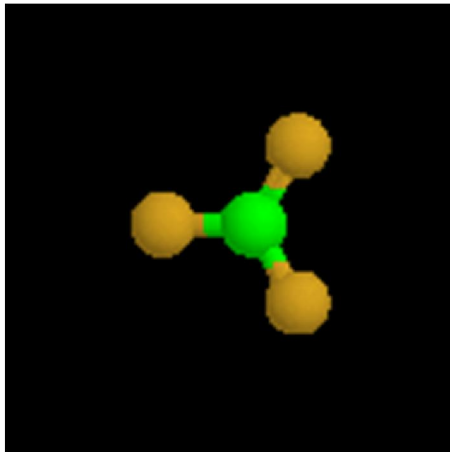
C2h2.pdb

$$d(C-C) = 0,1204 \text{ nm}$$

$$d(C-H) = 0,1058 \text{ nm}$$

$$\alpha = 180^\circ$$

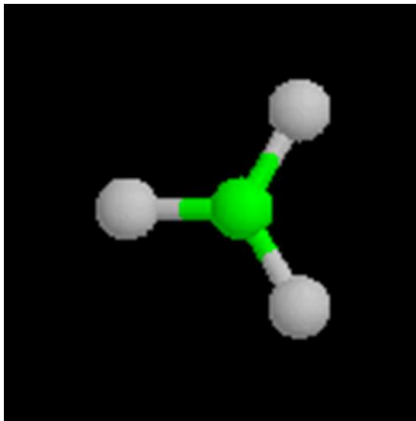
VSEPR: trigonale planare AX3 BF_3



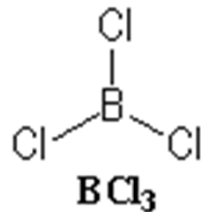
$d(\text{B-F}) = 0,130 \text{ nm}$

$\alpha = 120^\circ$

VSEPR: trigonale planare AX3 BCl₃

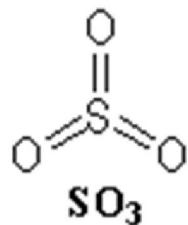
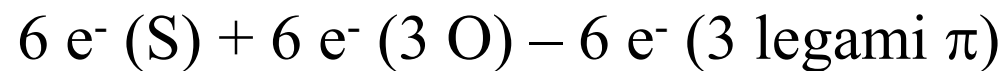
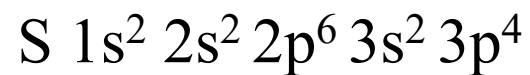
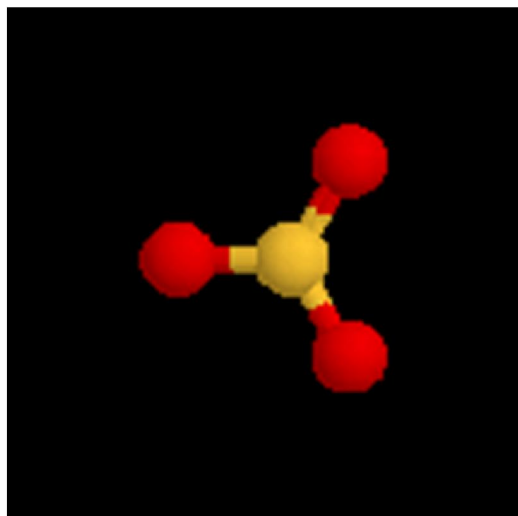


B $1s^2 2s^2 2p^1$
 $3e^-$ (B) + $3e^-$ (3 legami σ)
 $6 = 3$ coppie = AX3



$d(\text{B-Cl}) = 0,176 \text{ nm}$
 $\alpha = 120^\circ$

VSEPR: trigonale planare AX3 SO₃

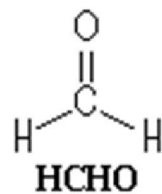
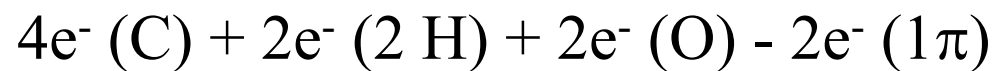
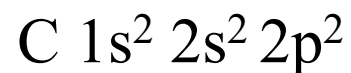
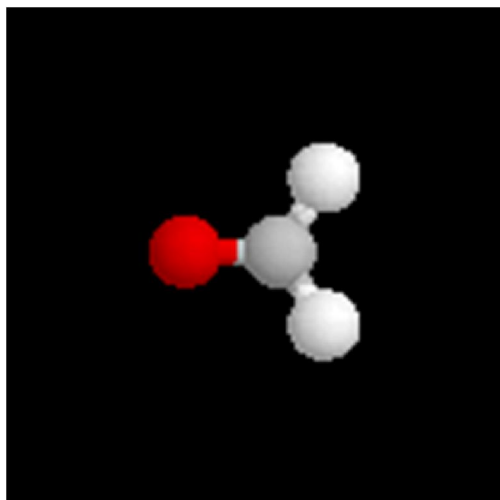


Fase gassosa :

d(S-O) = 0,143 nm

$\alpha = 120^\circ$

VSEPR: trigonale planare AX3 HCHO

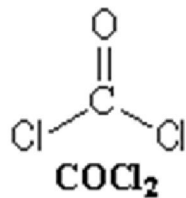
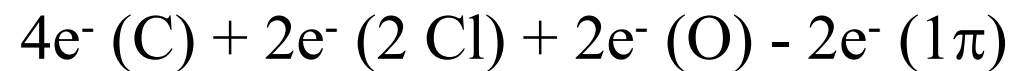
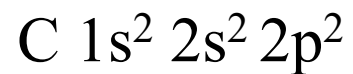
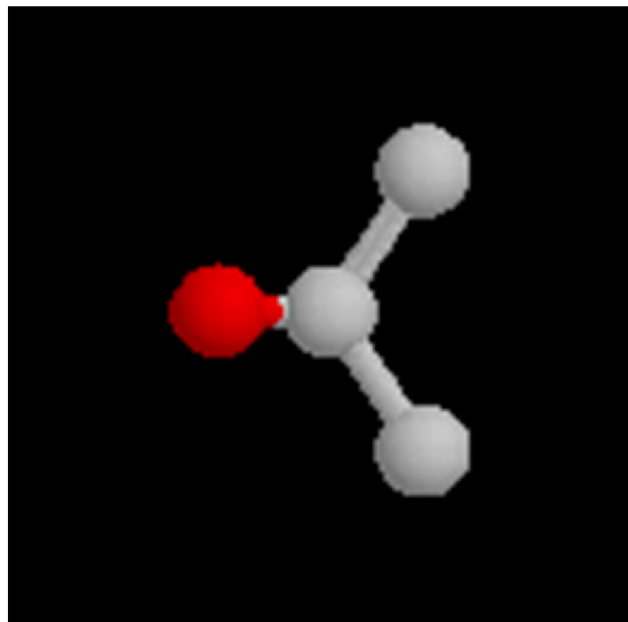


d(C-H) = 0,112 nm

d(C-O) = 0,121 nm

$\alpha = 116,5^\circ$

VSEPR: trigonale planare AX3 COCl_2



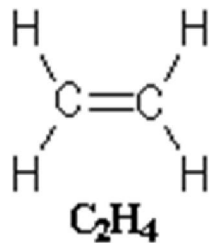
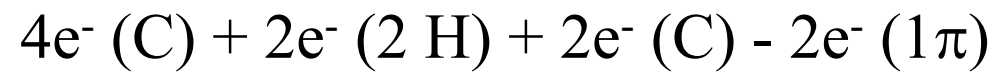
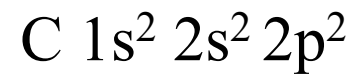
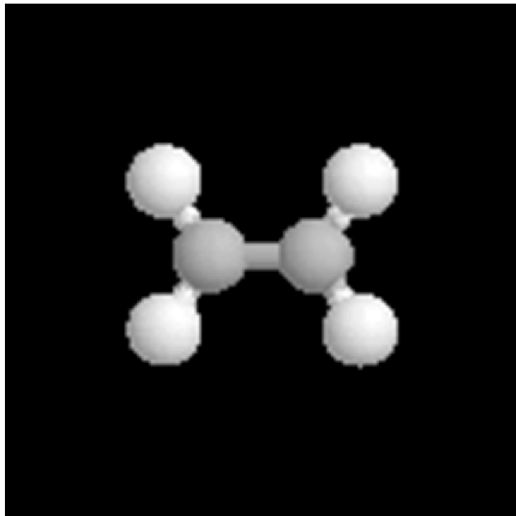
Coh2.pdb

$$d(\text{C-Cl}) = 0,174 \text{ nm}$$

$$d(\text{C-O}) = 0,117 \text{ nm}$$

$$\alpha = 113,2^\circ$$

VSEPR: trigonale planare AX3 C₂H₄

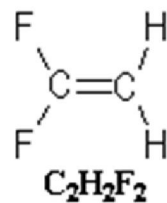
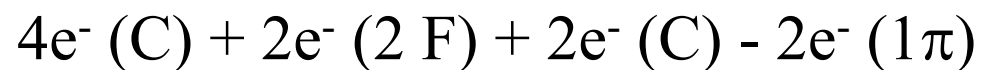
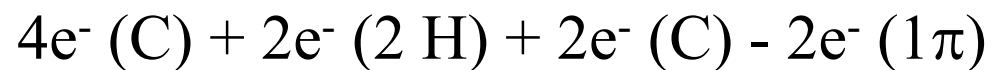
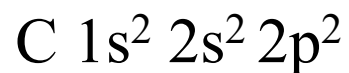
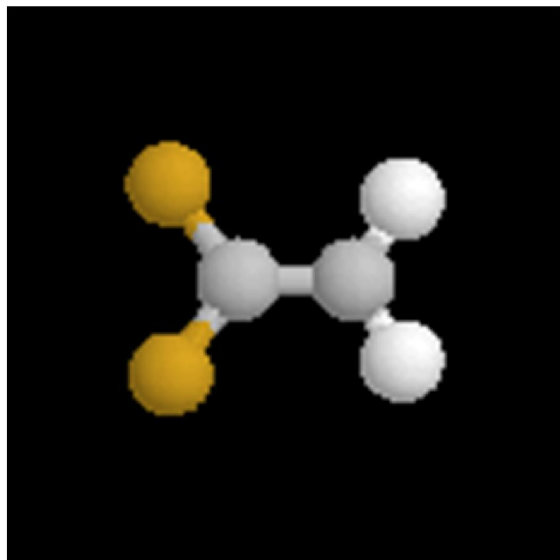


d(C-H) = 0,110 nm

d(C-C) = 0,134 nm

$\alpha = 118^\circ$

VSEPR: trigonale planare AX3 $C_2H_2F_2$



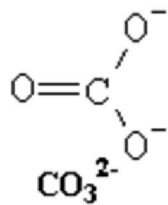
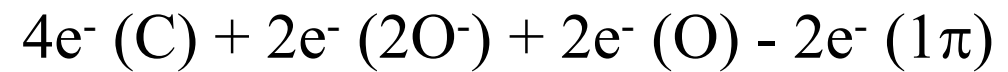
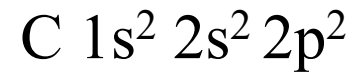
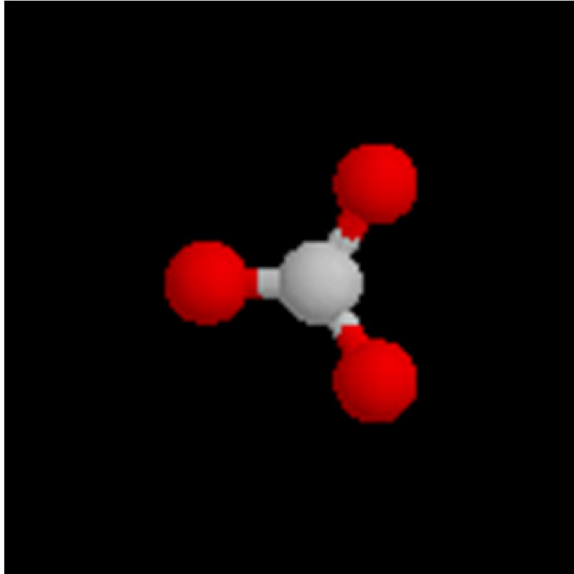
d(C-H) = 0,110 nm

d(C-C) = 0,134 nm

d(C-F) = 0,135 nm

α (FCF) = 109,3 °

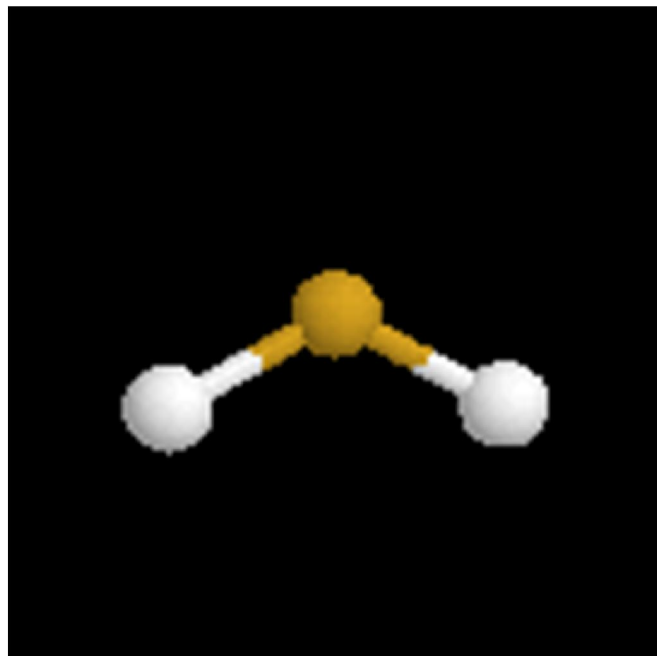
VSEPR: trigonale planare AX3 CO_3^{2-}



$d(\text{C-O}) = 0,129 \text{ nm}$

$\alpha = 120^\circ$

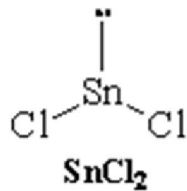
VSEPR: angolata AX2E SnCl₂



Sn [Kr] 4d¹⁰ 5s² 5p²

4e⁻ (Sn) + 2e⁻ (2Cl)

6 = 3 coppie ma 2 legami = AX2E

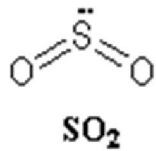
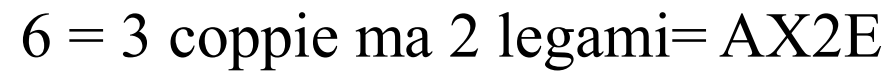
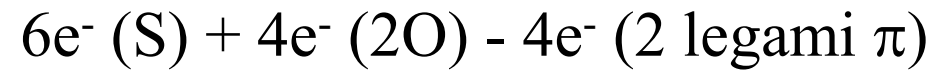
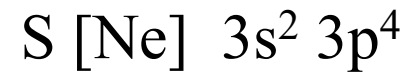
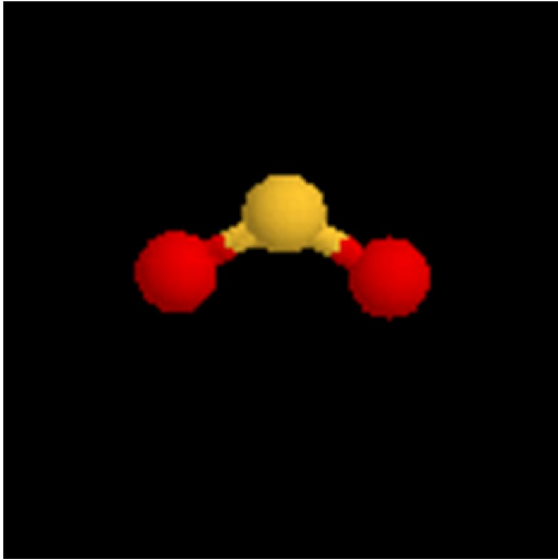


Sncl2.pdb

d(Sn- Cl) = 0,242 nm

$\alpha = 95^\circ$

VSEPR: angolata AX2E SO₂

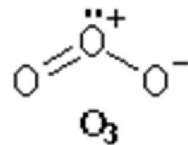
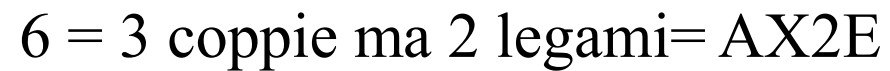
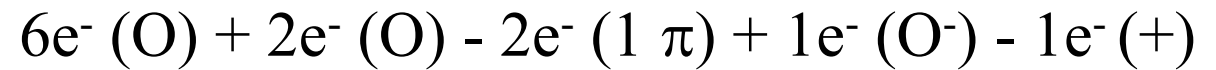
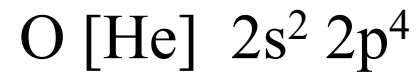
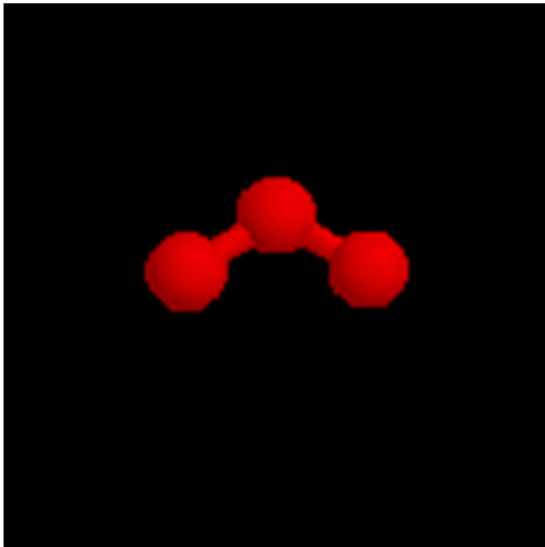


So2.pdb

d(S-O) = 0,143 nm

$\alpha = 119,5^\circ$

VSEPR: angolata AX2E O₃

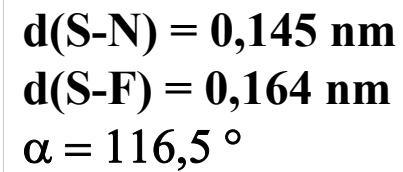
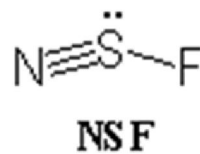
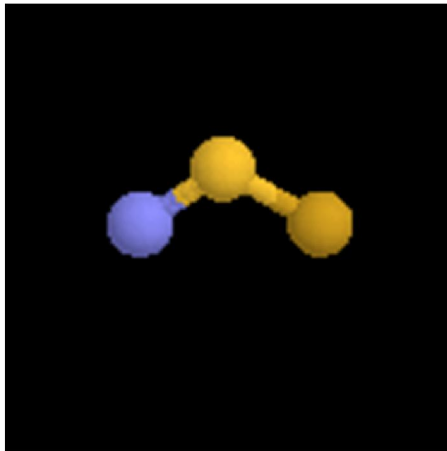
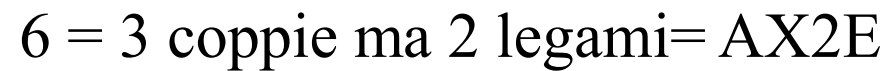
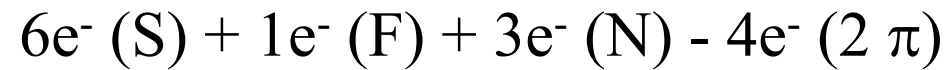
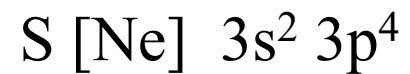


O3.pdb

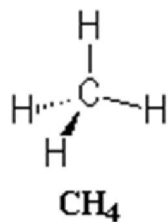
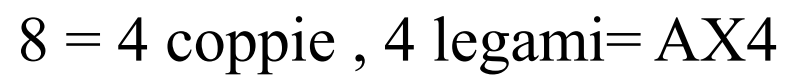
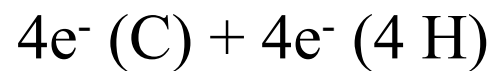
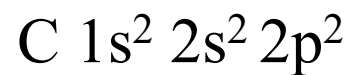
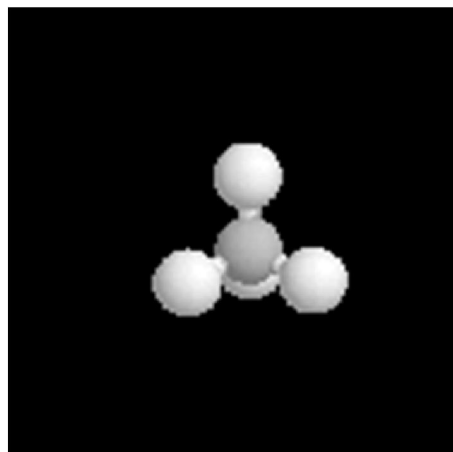
d(O-O) = 0,128 nm

α = 116,8 °

VSEPR: angolata AX2E NSF



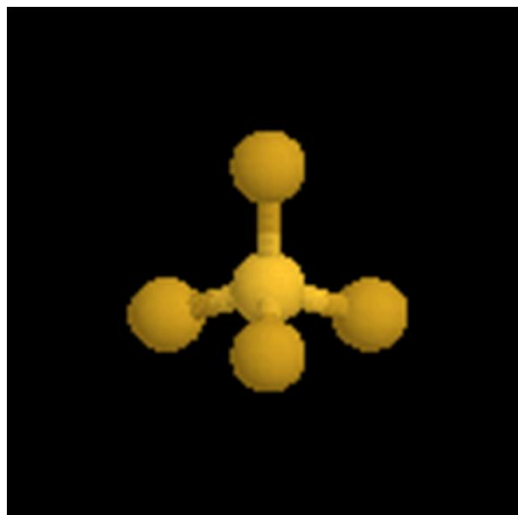
VSEPR: tetraedrica AX₄ CH₄



d(C-H) = 0,1094 nm

$\alpha = 109,5^\circ$

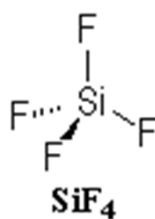
VSEPR: tetraedrica AX4 SiF_4



Si [Ne] $3s^2 3p^2$

$4e^-$ (Si) + $4e^-$ (4 F)

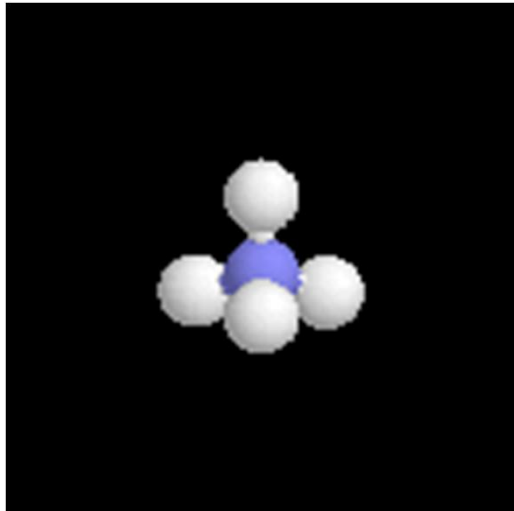
8 = 4 coppie , 4 legami = AX4



$d(\text{Si-F}) = 0,154 \text{ nm}$

$\alpha (\text{FSiF}) = 109,5^\circ$

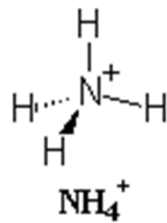
VSEPR: tetraedrica AX4 NH_4^+



N [He] $2s^2 2p^3$

$5e^-$ (N) + $4e^-$ (4 H) - $1e^-$ (+)

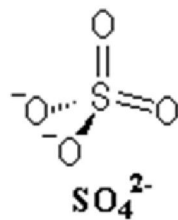
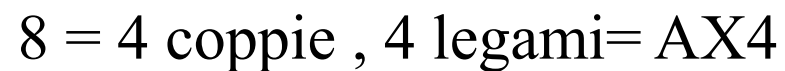
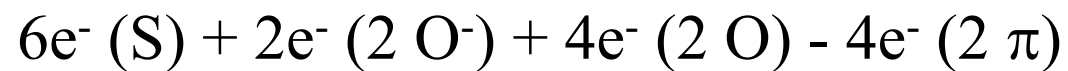
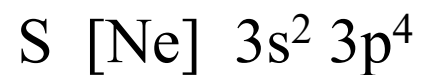
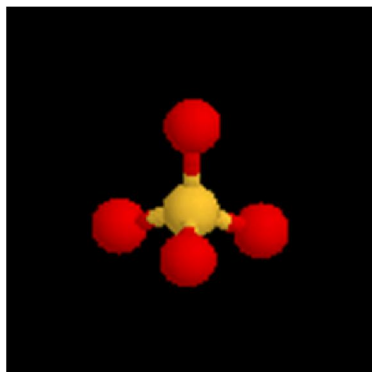
8 = 4 coppie , 4 legami = AX4



d(N-H) = 0,103 nm

$\alpha = 109,5^\circ$

VSEPR: tetraedrica AX4 SO_4^{2-}

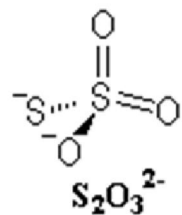
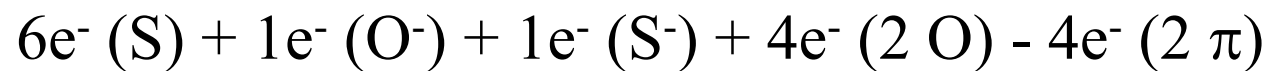
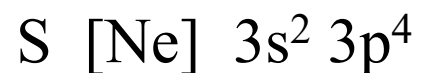
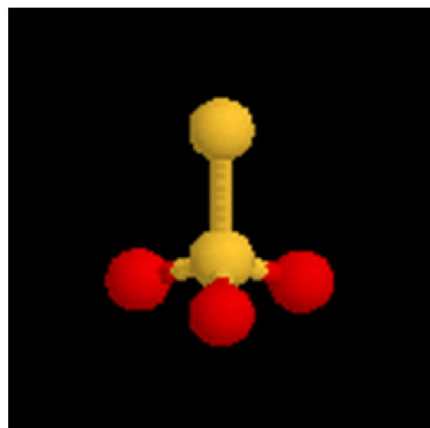


So42m.pdb

d(S-O) = 0,150 nm

$\alpha = 109^\circ$

VSEPR: tetraedrica AX4 $\text{S}_2\text{O}_3^{2-}$

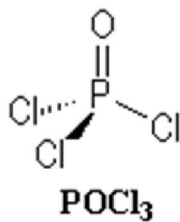
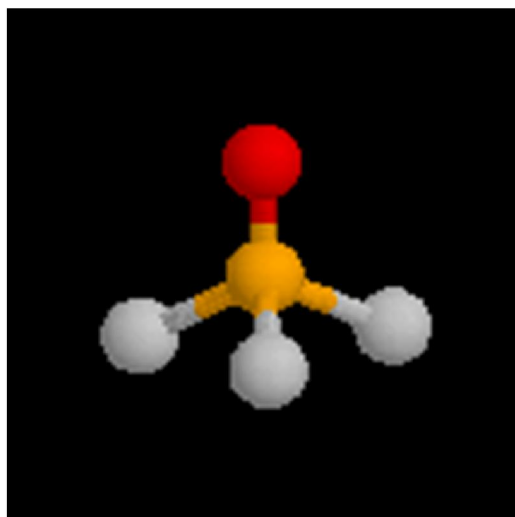
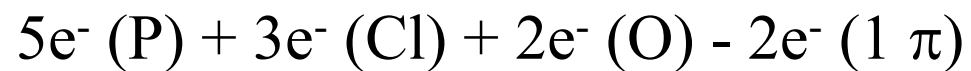
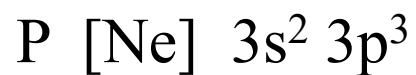


$d(\text{S-O}) = 0,150 \text{ nm}$

$d(\text{S-S}) = 0,201 \text{ nm}$

$\alpha = 109^\circ$ (valore stimato)

VSEPR: tetraedrica AX4 POCl_3



Poc13.pdb

$d(\text{P-Cl}) = 0,199 \text{ nm}$

$d(\text{P-O}) = 0,145 \text{ nm}$

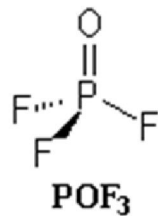
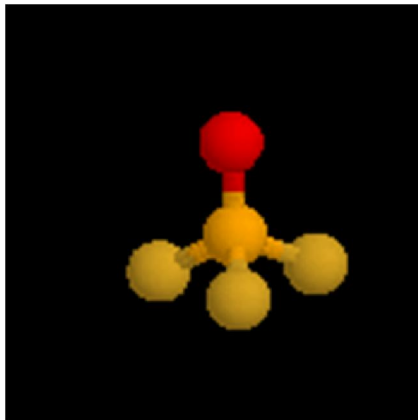
$\alpha (\text{ClPCl}) = 103,5^\circ$

VSEPR: tetraedrica AX4 POF_3

P [Ne] $3s^2 3p^3$

$5e^-$ (P) + $3e^-$ (F) + $2e^-$ (O) - $2e^-$ (1 π)

8 = 4 coppie , 4 legami = AX4

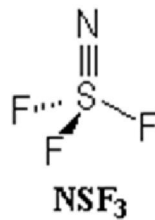
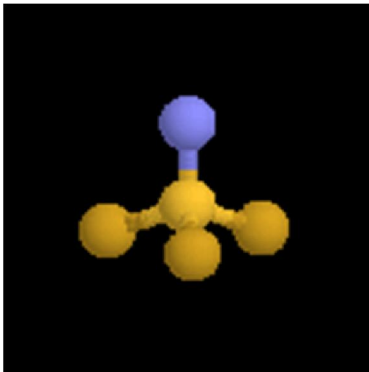
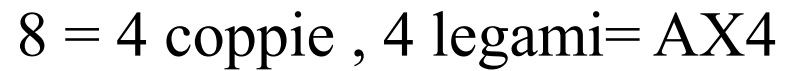
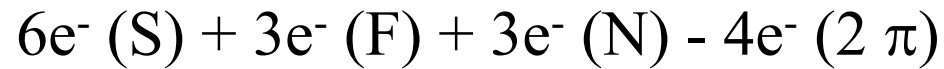
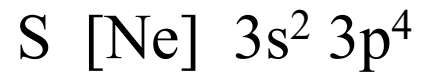


$d(\text{P-F}) = 0,154 \text{ nm}$

$d(\text{P-O}) = 0,145 \text{ nm}$

$\alpha (\text{FPF}) = 102^\circ$

VSEPR: tetraedrica AX4 NSF₃

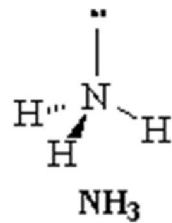
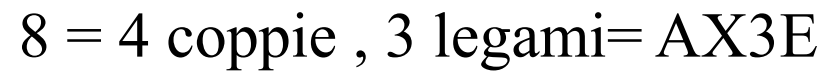
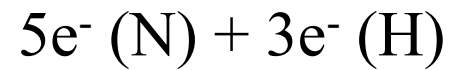
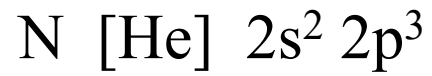
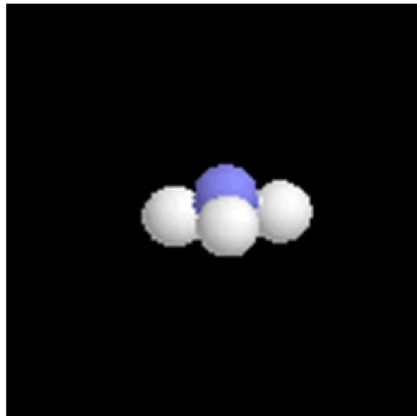


$$d(\text{S-N}) = 0,14 \text{ nm}$$

$$d(\text{S-F}) = 0,16 \text{ nm}$$

$$\alpha(\text{FSF}) = 98^\circ$$

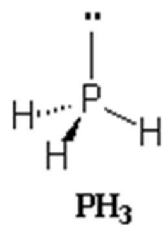
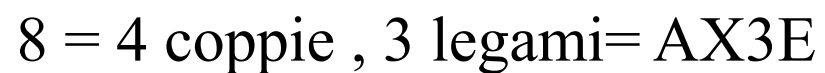
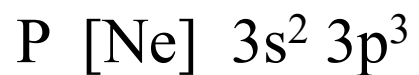
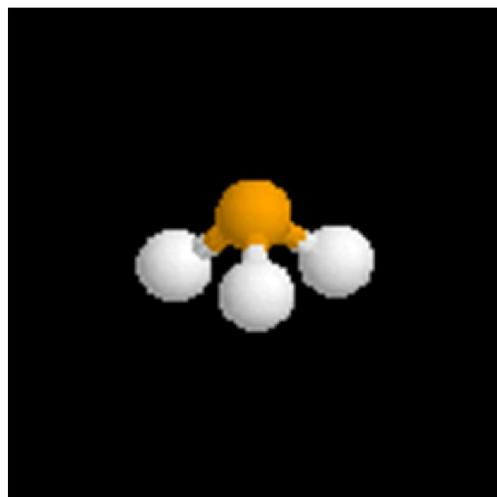
VSEPR: piramide trigonale AX3E NH₃



d(N-H) = 0,102 nm

$\alpha = 107,8^\circ$

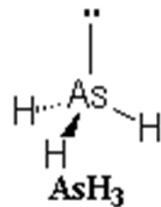
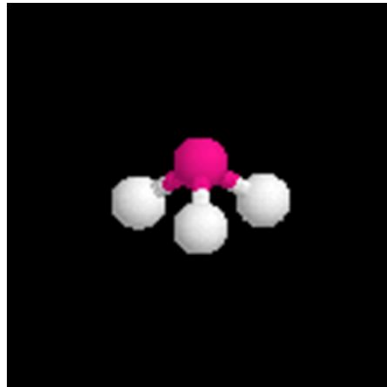
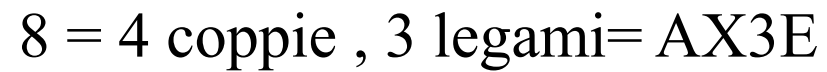
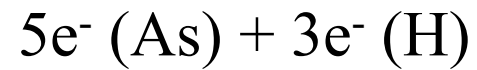
VSEPR: piramide trigonale AX3E PH₃



d(P-H) = 0,144 nm

$\alpha = 93,3^\circ$

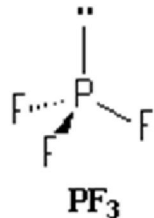
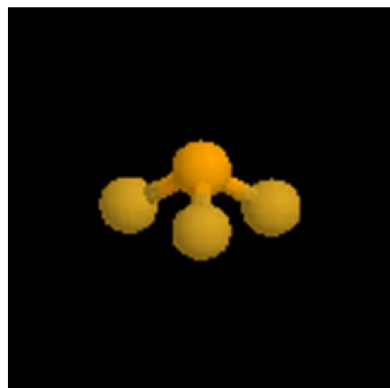
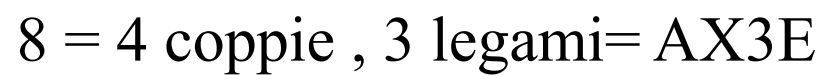
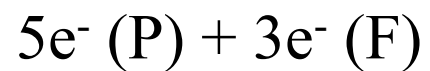
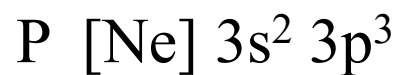
VSEPR: piramide trigonale AX3E AsH_3



$d(\text{As-H}) = 0,144 \text{ nm}$

$\alpha = 91,8^\circ$

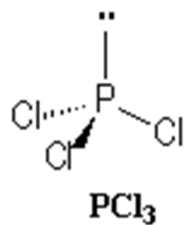
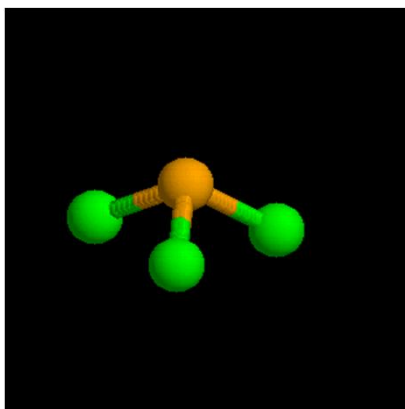
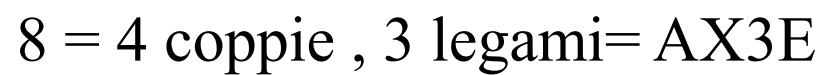
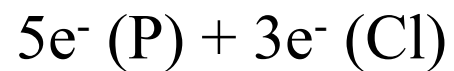
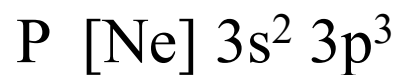
VSEPR: piramide trigonale AX3E PF₃



d(P-F) = 0,157 nm

$\alpha = 97,8^\circ$

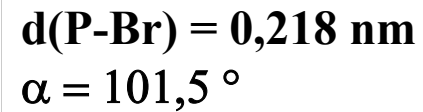
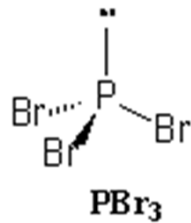
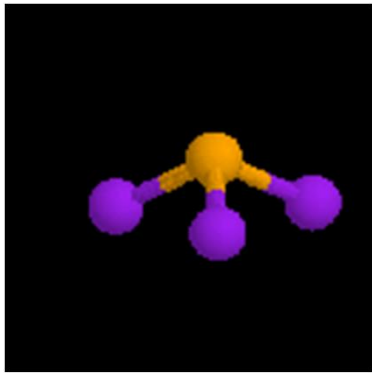
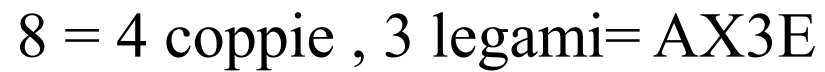
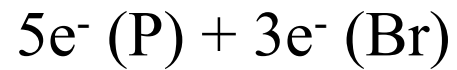
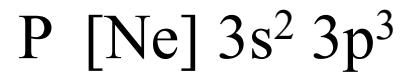
VSEPR: piramide trigonale AX3E PCl_3



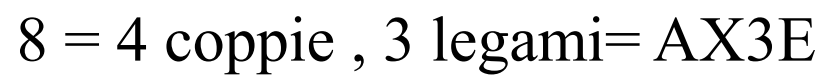
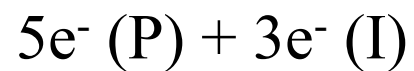
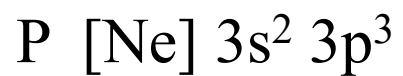
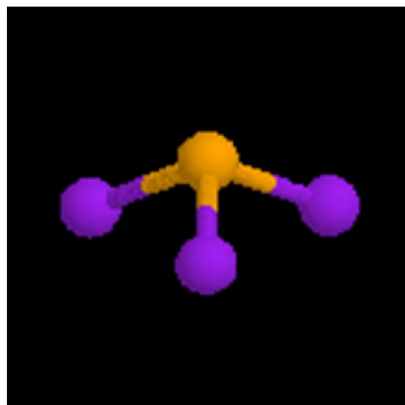
$d(\text{P-Cl}) = 0,204 \text{ nm}$

$\alpha = 100,1^\circ$

VSEPR: piramide trigonale AX3E PBr₃



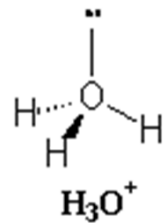
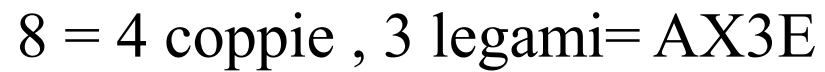
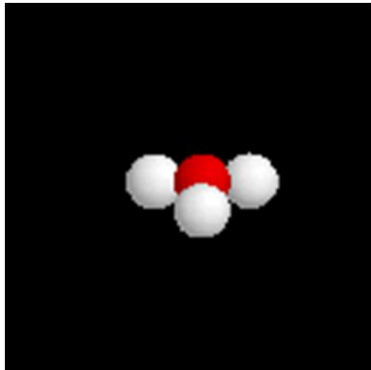
VSEPR: piramide trigonale AX3E PI_3



$d(\text{P-I}) = 0,243 \text{ nm}$

$\alpha = 102^\circ$

VSEPR: piramide trigonale AX3E H₃O⁺

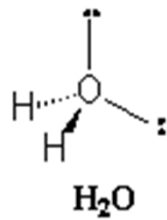
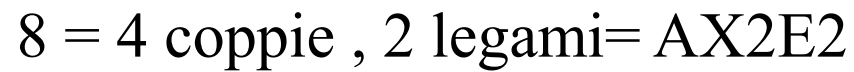
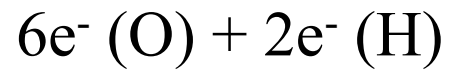
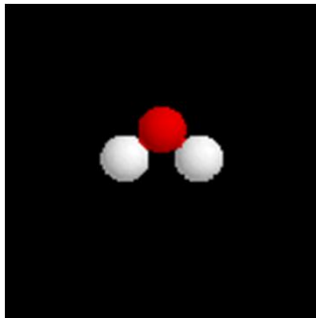


**Valori ottenuti con Cl⁻ come
controione**

d(O-H) = 0,096 nm

α = 117 °

VSEPR: angolata AX₂E₂ H₂O

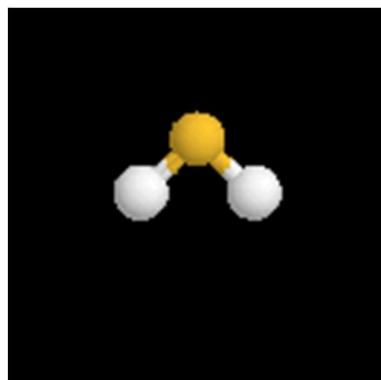


H2o.pdb

d(O-H) = 0,096 nm

$\alpha = 104,5^\circ$

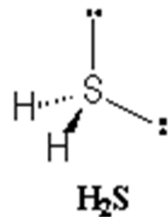
VSEPR: angolata AX₂E₂ H₂S



S [Ne] 3s² 3p⁴

6e⁻ (S) + 2e⁻ (H)

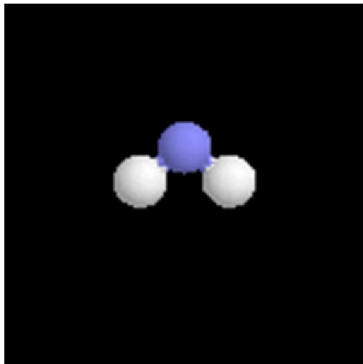
8 = 4 coppie , 2 legami= AX₂E₂



d(S-H) = 0,135 nm

$\alpha = 93,3^\circ$

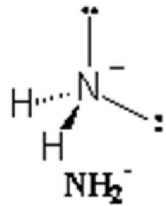
VSEPR: angolata AX₂E₂ NH₂⁻



N [He] 2s² 2p³

5e⁻ (N) + 2e⁻ (H) + 1e⁻ (-)

8 = 4 coppie , 2 legami= AX₂E₂



Nh2m.pdb

d(N-H) = 0,103 nm

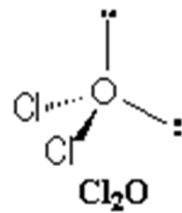
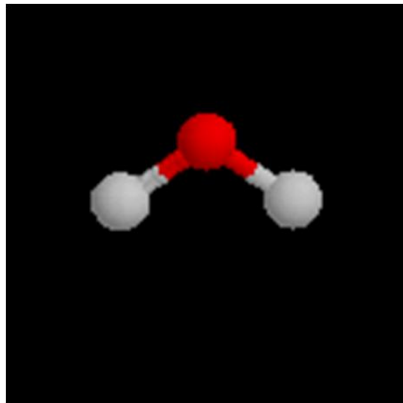
$\alpha = 104^\circ$

VSEPR: angolata AX₂E₂ Cl₂O

O [He] 2s² 2p⁴

6e⁻ (O) + 2e⁻ (Cl)

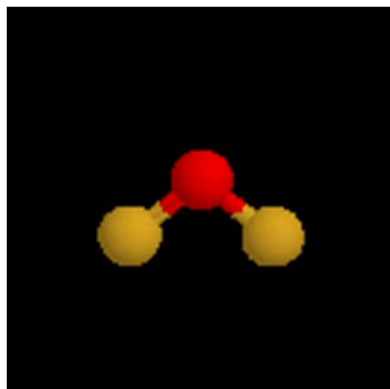
8 = 4 coppie , 2 legami= AX₂E₂



d(O-Cl) = 0,170 nm

$\alpha = 110,9^\circ$

VSEPR: angolata AX₂E₂ OF₂



O [He] 2s² 2p⁴

6e⁻ (O) + 2e⁻ (F)

8 = 4 coppie , 2 legami= AX₂E₂

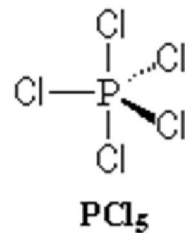
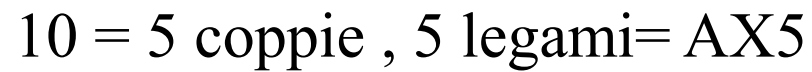
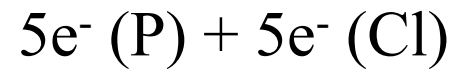
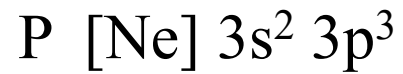
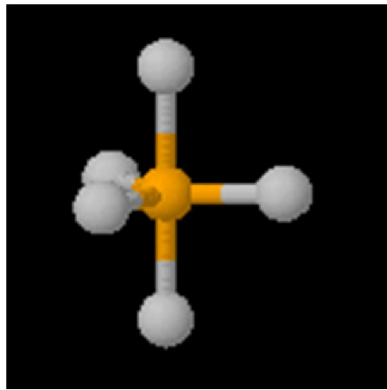


Of2.pdb

d(O-F) = 0,140 nm

$\alpha = 103^\circ$

VSEPR: bipiramide a base trigonale AX5 PCl_5

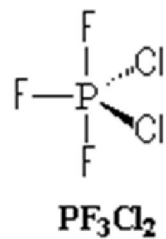
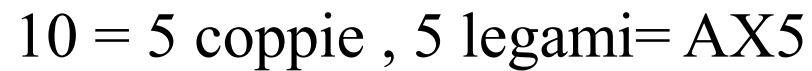
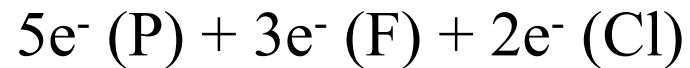
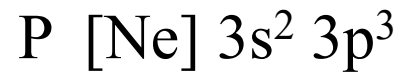
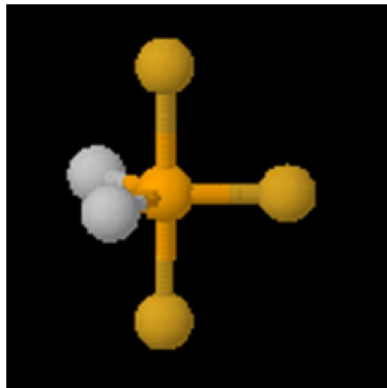


$d(\text{P}-\text{Cl}_{\text{eq}}) = 0,202 \text{ nm}$

$d(\text{P}-\text{Cl}_{\text{ax}}) = 0,214 \text{ nm}$

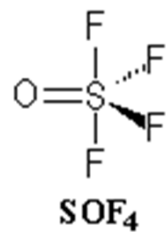
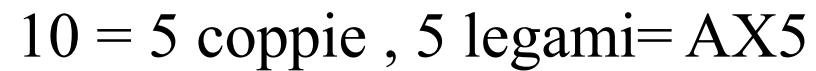
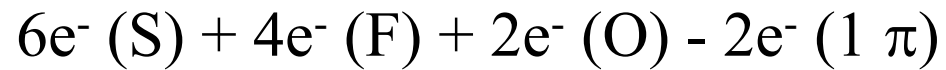
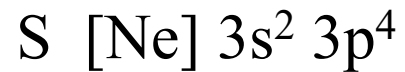
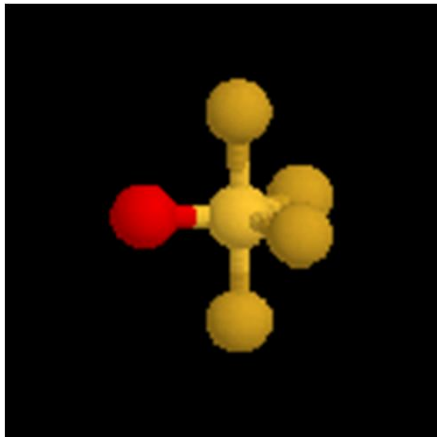
$\alpha(\text{ClPCl}) = 90^\circ$; $\alpha(\text{ClPCl}) = 120$

VSEPR: bipiramide a base trigonale AX5 PF₃Cl₂



d(P-Cl_{stim}) = 0,2 nm ; d(P-F) = 0,15 nm
α(FPF) = 90° ; α (ClPCL) = 120°
(valore stimato)

VSEPR: bipiramide a base trigonale AX5 SOF_4



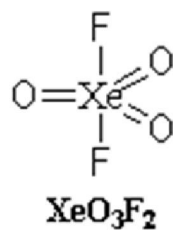
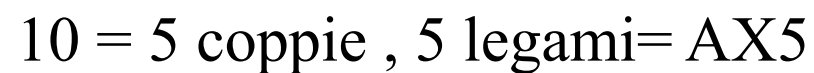
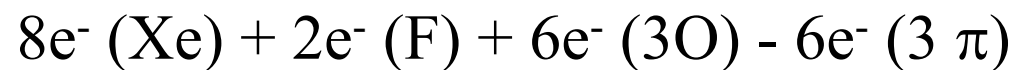
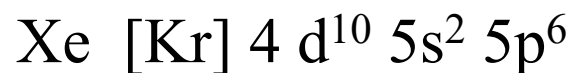
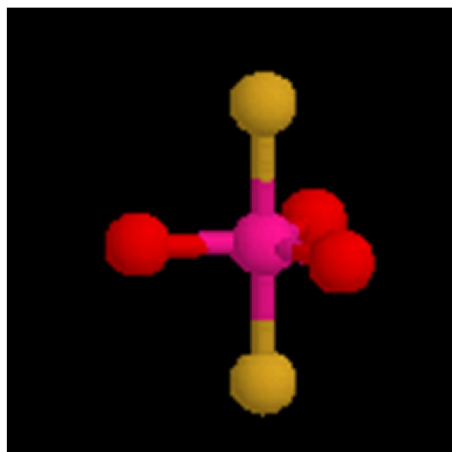
$$d(\text{S-O}) = 0,140 \text{ nm}$$

$$d(\text{S-F}_{\text{eq}}) = 0,155 \text{ nm}$$

$$d(\text{S-F}_{\text{ax}}) = 0,157 \text{ nm}$$

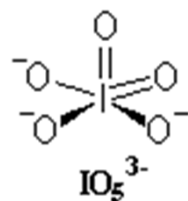
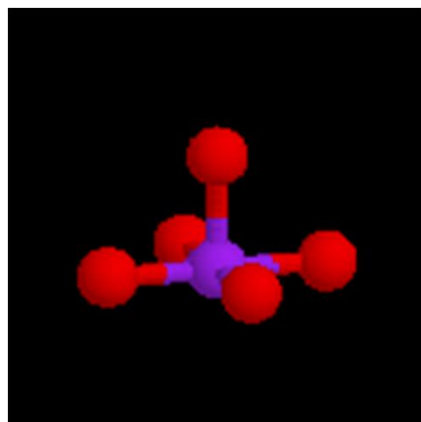
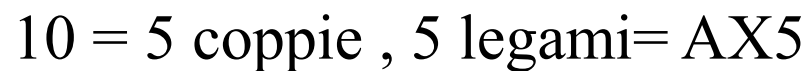
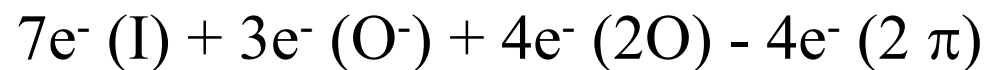
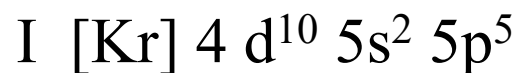
$$\alpha (\text{F}_{\text{eq}}\text{S}\text{F}_{\text{eq}}) = 110^\circ$$

VSEPR: bipiramide a base trigonale AX5 XeF₂O₃



$d(\text{Xe-O}) = 0,180 \text{ nm}$
 $d(\text{Xe-F}) = 0,200 \text{ nm}$
 $\alpha (\text{OXeO}) = 120^\circ$
(valore stimato)

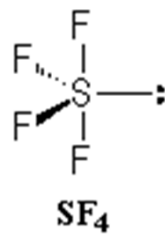
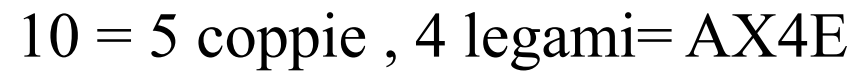
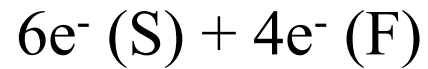
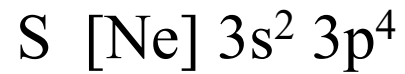
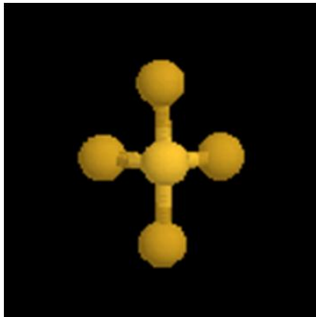
VSEPR: bipiramide a base trigonale AX5 IO₅³⁻



Io53m.pdb

d(I-O) = 0,180 nm
 α (OIO) = 90 °
(valore approssimato)

VSEPR: tetraedrica distorta AX4E SF₄



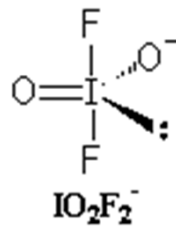
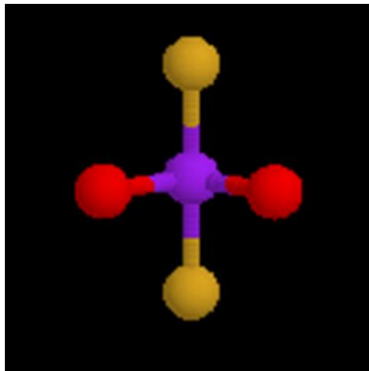
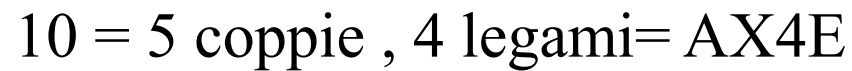
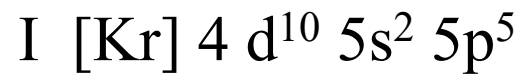
d(S-F_{eq}) = 0,154 nm

d(S-F_{ax}) = 0,164 nm

α(F_{eq}SF_{eq}) = 101,6 °

α(F_{ax}SF_{ax}) = 173,6 °

VSEPR: tetraedrica distorta AX4E IO₂F₂⁻



d(I-O) = 0,193 nm

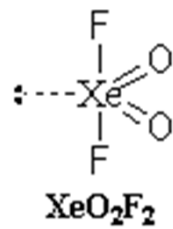
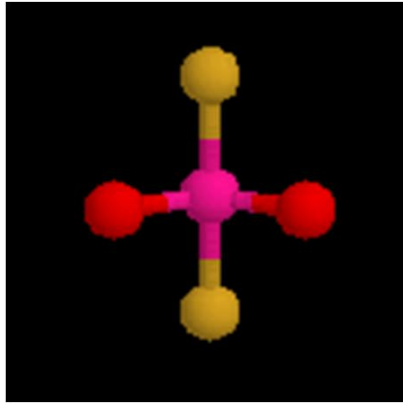
d(I-F) = 0,200 nm

VSEPR: tetraedrica distorta AX4E XeO_2F_2

$\text{Xe} [\text{Kr}] 4d^{10} 5s^2 5p^6$

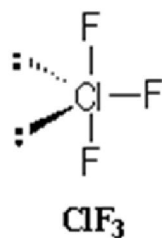
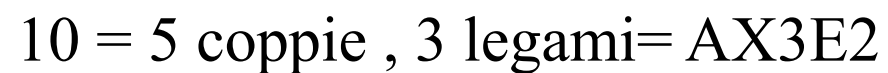
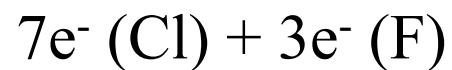
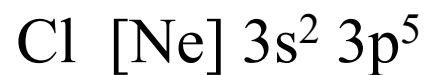
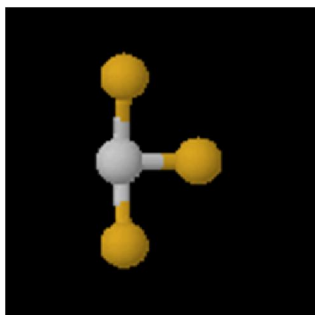
$8e^- (\text{Xe}) + 2e^- (\text{F}) + 2e^- (\text{O}) - 2e^- (1 \pi)$

$10 = 5 \text{ coppie} , 4 \text{ legami} = \text{AX}_4\text{E}$



$d(\text{Xe-O}) = 0,180 \text{ nm}$
 $d(\text{Xe-F}) = 0,200 \text{ nm}$
(valore stimato)

VSEPR: a T AX3E2 ClF₃

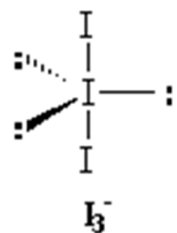
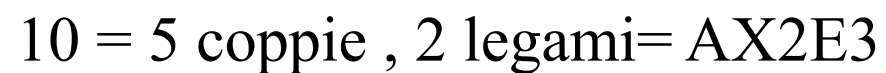
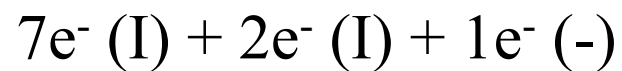
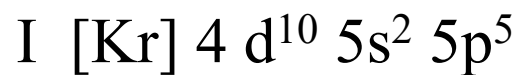
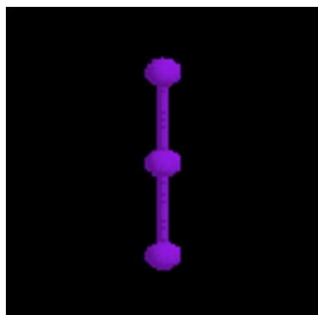


d(Cl-F_{eq}) = 0,1596 nm

d(Cl-F_{ax}) = 0,1696 nm

α (FCIF) = 87,5 °

VSEPR: lineare AX₂E₃ I₃⁻



I3m.pdb

**Valori ottenuti con NEt₄⁺ come
controione**

d(I-I) = 0,294 nm

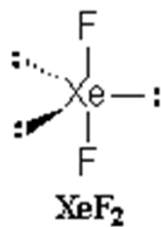
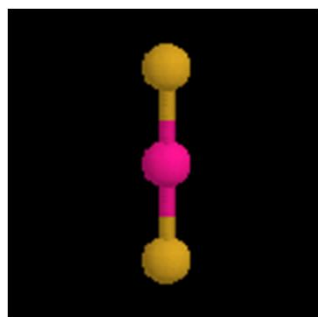
a = 180°

VSEPR: lineare AX₂E₃ XeF₂

Xe [Kr] 4 d¹⁰ 5s² 5p⁶

8e⁻ (Xe) + 2e⁻ (F)

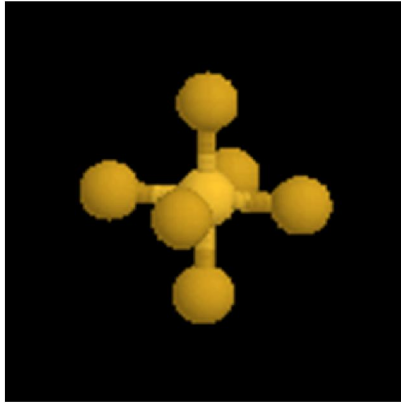
10 = 5 coppie , 2 legami= AX₂E₃



d(Xe-F) = 0,200 nm

$\alpha = 180^\circ$

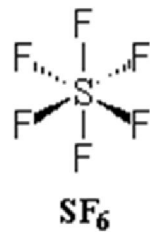
VSEPR: ottaedrica AX₆ SF₆



S [Ne] 3s² 3p⁴

6e⁻ (S) + 6e⁻ (F)

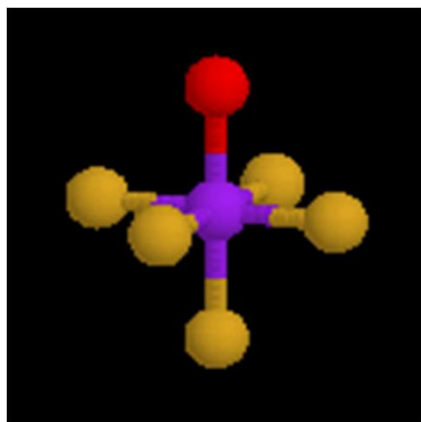
12 = 6 coppie , 6 legami= AX₆



d(S-F) = 0,1564 nm

$\alpha = 90^\circ$

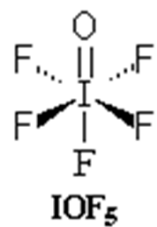
VSEPR: ottaedrica AX6 IOF₅



I [Kr] 4 d¹⁰ 5s² 5p⁵

7e⁻ (I) + 5e⁻ (F) + 2e⁻ (O) - 2e⁻ (1 π)

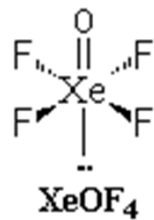
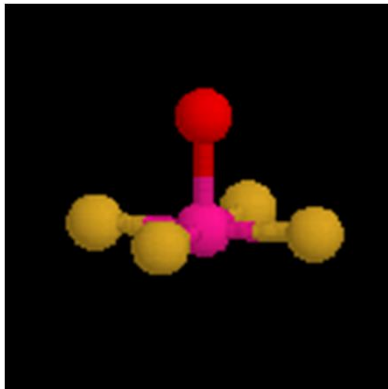
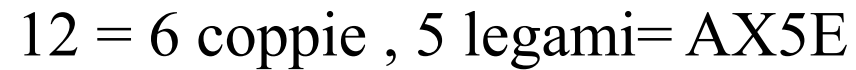
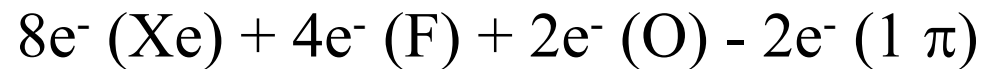
12 = 6 coppie , 6 legami= AX6



d(I-O) = 0,19 nm (valore stimato)

d(I-F) = 0,20 nm (valore stimato)

VSEPR: piramide a base quadrata AX5E XeOF₄



d(Xe-F) = 0,19 nm (valore medio)

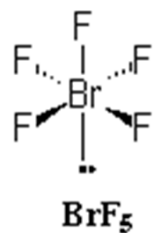
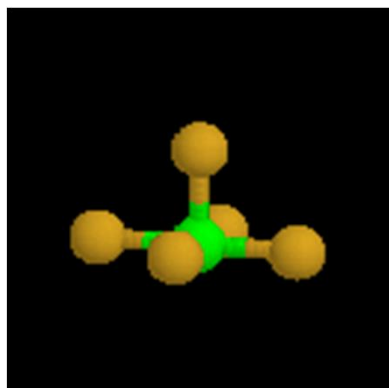
d(Xe-O) = 0,18 nm (valore medio)

VSEPR: piramide a base quadrata AX5E BrF₅

Br [Kr] 4 d¹⁰ 5s² 5p⁶

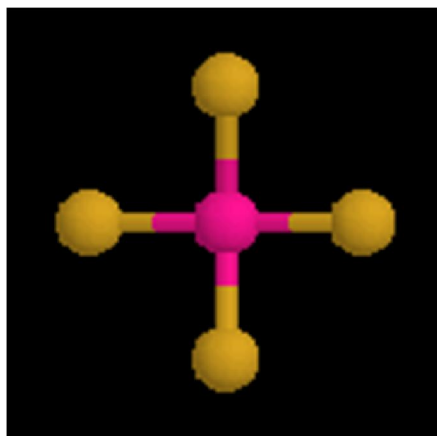
7e⁻ (Br) + 5e⁻ (F)

12 = 6 coppie , 5 legami= AX5E



$d(\text{Br-F}_{\text{ax}}) = 0,169 \text{ nm}$
 $d(\text{Br-F}_{\text{eq}}) = 0,178 \text{ nm}$
 $\alpha (\text{F}_{\text{eq}}, \text{Br}, \text{F}_{\text{ax}}) = 84,9^\circ$
(fase gassosa)

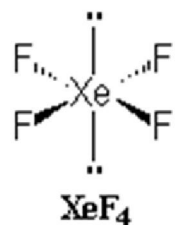
VSEPR: planare quadrata AX₄E₂ XeF₄



Xe [Kr] 4 d¹⁰ 5s² 5p⁶

8e⁻ (Xe) + 4e⁻ (F)

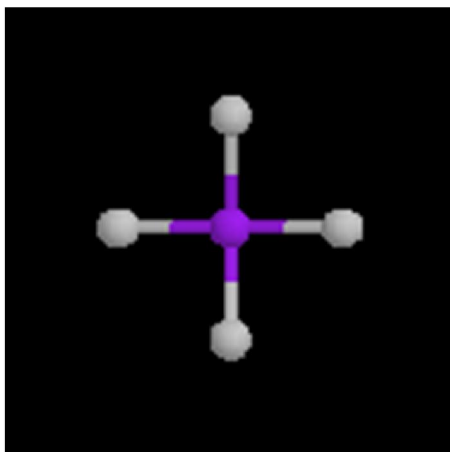
12 = 6 coppie , 4 legami= AX₄E₂



d(Xe-F) = 0,195 nm (valore medio)

$\alpha = 90^\circ$ (valore medio)

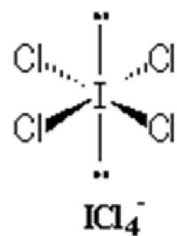
VSEPR: planare quadrata AX₄E₂ ICl₄⁻



I [Kr] 4 d¹⁰ 5s² 5p⁵

7e⁻ (I) + 4e⁻ (Cl) + 1e⁻ (-)

12 = 6 coppie , 4 legami = AX₄E₂

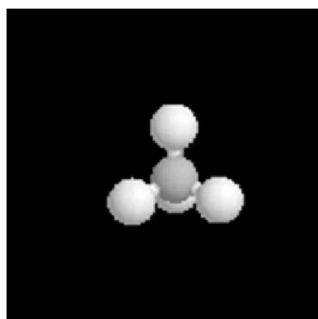


Icl4m.pdb

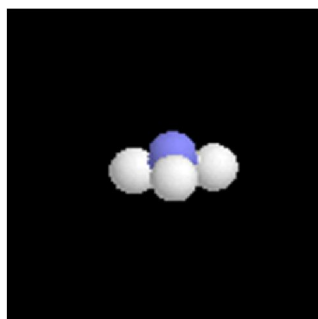
d(I-Cl) = 0,250 nm (valore medio)

$\alpha = 90^\circ$ (valore medio)

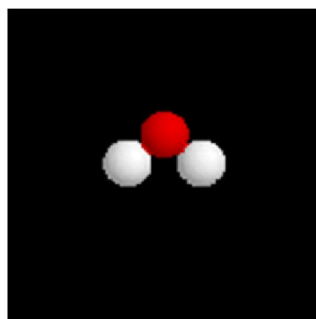
VSEPR: influenza coppie di legame sugli angoli di legame



109,5°



107°



104,5°

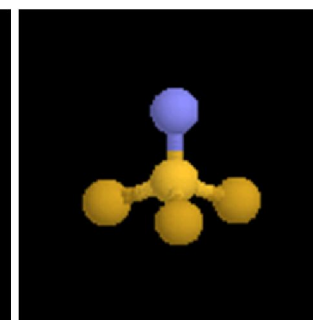
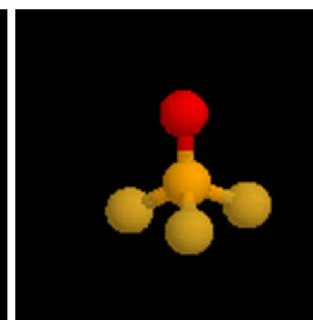
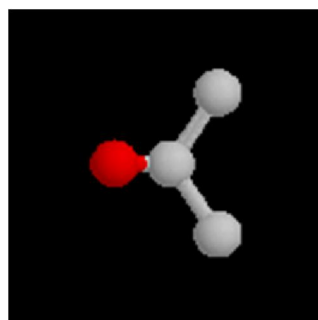
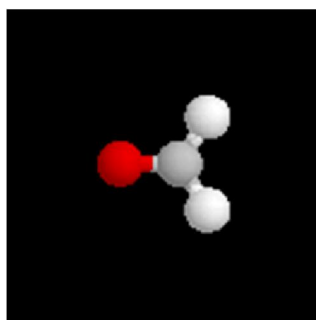
CH₄, NH₃ e H₂O

Stesso andamento per i derivati ionici dell'ammoniaca

NH ₄ ⁺	NH ₃	NH ₂ ⁻
109,5°	107°	104°

VSEPR: influenza del volume dei legami multipli sugli angoli di legame

La forma geometrica dipende solamente dai legami σ . Pertanto possiamo considerare le molecole con legami π come se possedessero solo legami σ . Il volume occupato dagli elettroni dipende però dal numero di legami π , e conseguentemente ci si deve aspettare (e si osserva sperimentalmente) una diminuzione dell'angolo che si trova opposto al legame π .



115,8°

111,3°

109,5°

102°

98°

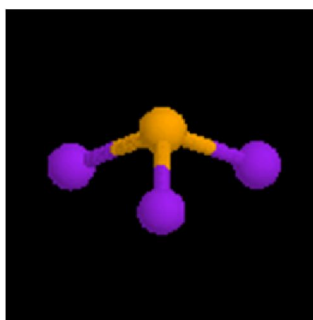
1 π

2 π

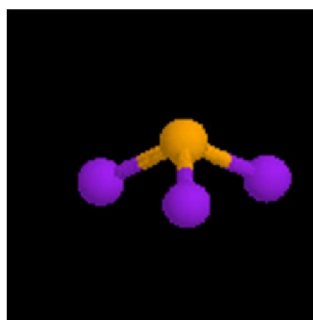
VSEPR: influenza dell'elettronegatività sugli angoli di legame (I)

χ (I)	χ (Br)	χ (Cl)	χ (F)
2,66	2,96	3,16	3,98

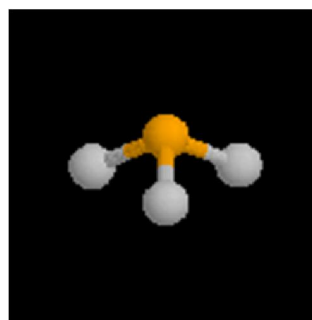
$$\chi (\text{I}) < \chi (\text{Br}) < \chi (\text{Cl}) < \chi (\text{F})$$



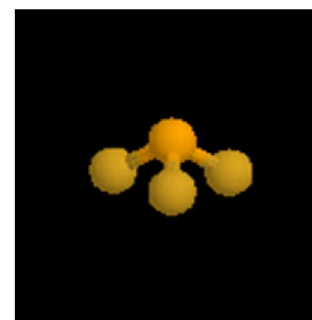
102°



101,5°



100,3°



97,8°

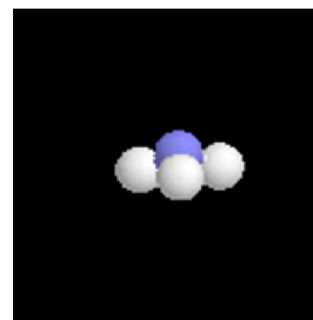
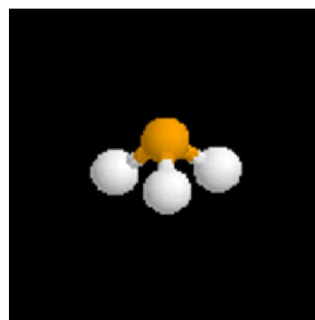
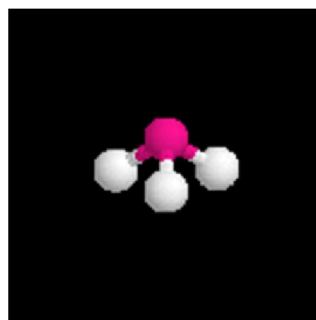
VSEPR: influenza dell'elettronegatività sugli angoli di legame (I)

A parità di atomo centrale (A), all'aumentare dell'elettronegatività degli atomi terminali (X) le coppie elettroniche di legame risultano maggiormente delocalizzate sugli atomi terminali (X). Pertanto, maggiore sarà la loro delocalizzazione verso l'atomo X, minore sarà la loro repulsione reciproca e quindi l'angolo diminuisce.

VSEPR: influenza dell'elettronegatività sugli angoli di legame (II)

χ (As)	χ (P)	χ (N)
2,17	2,19	3,04

$$\chi (\text{As}) < \chi (\text{P}) < \chi (\text{N})$$



91,58°

93,83°

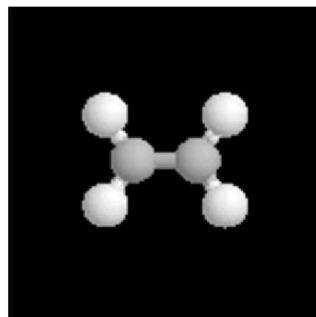
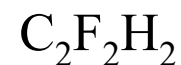
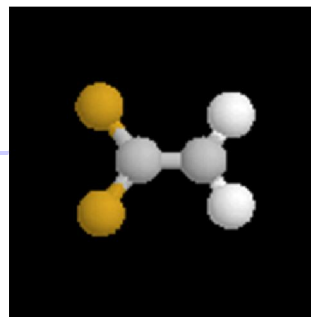
107°

VSEPR: influenza dell'elettronegatività sugli angoli di legame (II)

A parità di atomo terminale (X), all'aumentare dell'elettronegatività dell'atomo centrale (A) le coppie elettroniche di legame risultano maggiormente delocalizzate sull'atomo centrale (A). Pertanto, maggiore sarà la loro delocalizzazione verso l'atomo A, maggiore sarà la loro repulsione reciproca e quindi l'angolo aumenta.

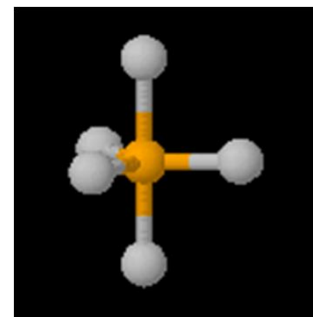
VSEPR: influenza del volume e dell'elettronegatività sugli angoli di legame

In molecole quali C_2H_4 e $C_2F_2H_2$, si osserva che gli angoli tra i legami singoli sono inferiori a 120° . Si interpreta tale osservazione immaginando che il “volume” dei legami doppi sia maggiore di quello dei legami singoli. Nel caso di $C_2F_2H_2$ tale diminuzione è maggiore che nel caso di C_2H_4 poiché F ha una elettronegatività maggiore rispetto a H e pertanto le coppie di legame sono maggiormente confinate vicino a F presentando una minore repulsione.

 118°  109°

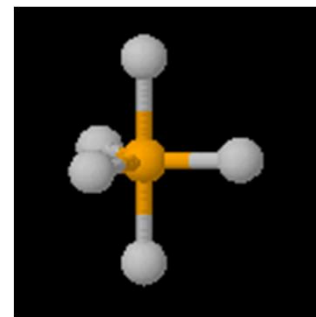
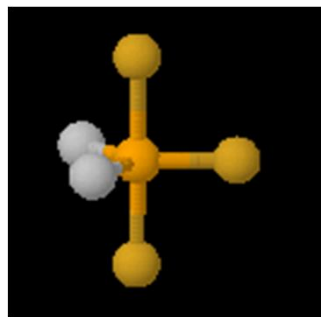
VSEPR: non equivalenza tra posizioni assiali ed equatoriali

Bond	P-Cl_{éq}	P-Cl_{ax}
d (nm)	0,202	0,214



Le posizioni equatoriali ed assiali non sono equivalenti in molecole quali PF₅ o PCl₅. Infatti l'interazione tra coppie elettroniche di legame in posizione equatoriale risulta inferiore rispetto alla situazione assiale. Pertanto ci si aspetta e si osserva) una diminuzione della lunghezza di legame in posizione equatoriale e un aumento della lunghezza di legame in posizione assiale.

VSEPR: non equivalenza tra posizioni assiali ed equatoriali



La non equivalenza delle posizioni assiali ed equatoriali è visibile quando sono presenti atomi terminali X differenti. Per esempio, in PF_3Cl_2 , Cl ha una minore elettronegatività rispetto a F e pertanto i doppietti elettronici che formano i legami tra P e Cl occupano un volume maggiore rispetto a quelli tra P e F e pertanto pertanto la molecola con i 2 Cl in posizione equatoriale è la più stabile.

NB. Cl ha anche dimensioni maggiori rispetto a F

VSEPR: Limiti

La teoria VSEPR permette spesso di predire la corretta geometria delle coppie elettroniche attorno ad un atomo centrale in numerose molecole, ioni o composti semplici. Essa però fallisce quando cresce la complessità delle molecole (composti organici e biologici).

Inoltre, va ricordato che le molecole non sono entità statiche, ma sono presenti tutta una serie di moti termici che possono portare a fenomeni di scambio tra posizioni assiali ed equatoriali.