

Ligações Químicas

Os átomos se ligam porque, quando ligados, estão em um **estado mais estável** do que quando "separados"

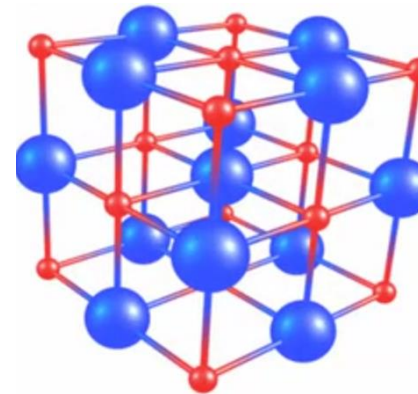


$$\Delta G = \Delta H - T\Delta S \quad \text{Processo Exotérmico}$$

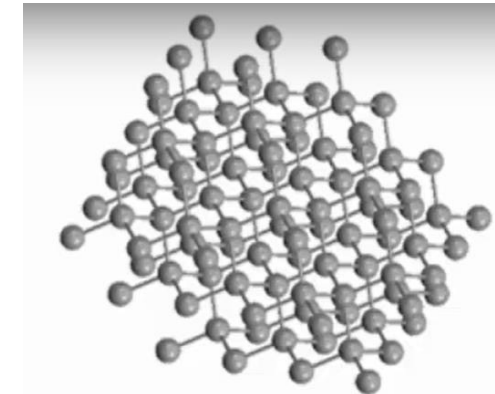
Ligação Iônica → **Atração eletrostática** entre os íons

Ligação Covalente → **Compartilhamento** de elétrons, através da sobreposição de orbitais

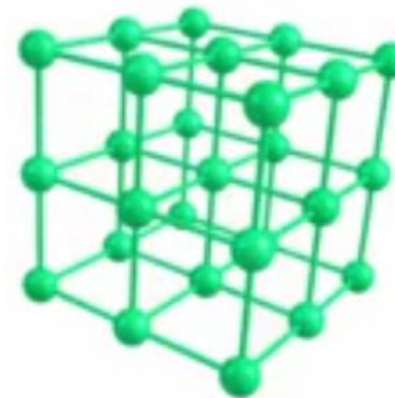
Ligação Metálica → Agregado de cátions, coesos por **elétrons livres**



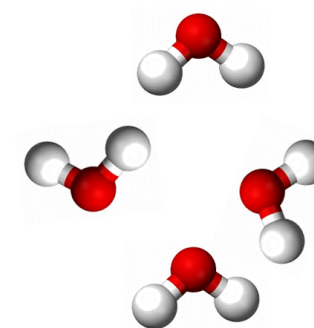
NaCl, CaF₂, AlBr₃



C_G, C_D, SiO₂



Au, Fe, Al



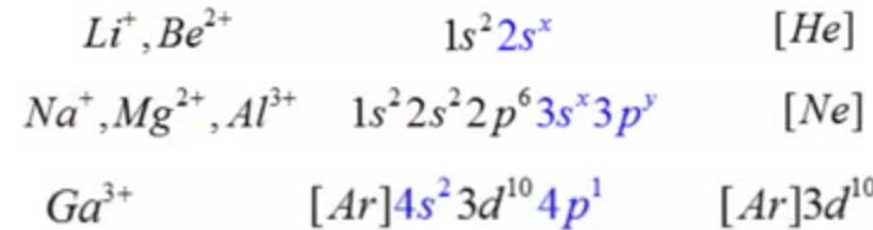
H₂O, CH₄, O₂

Ligação Iônica

É a **atração eletrostática** entre cátions e ânions



Os átomos tendem a formar íons com configuração eletrônica **similar a um gás nobre**



Metais →

Possuem **baixa** afinidade eletrônica
e **baixa** energia de ionização



Tendem a formar **cátions**

Elementos pesados dos **grupos 13, 14, 15**
possuem **valência variável**

Elementos de transição possuem **valência variável**

Ametais →

Possuem **alta** afinidade eletrônica
e **alta** energia de ionização

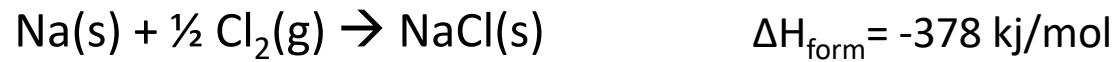


Tendem a formar **ânions**

Elementos de transição **pesados** existem
em sua **forma atômica**

Formação de um cristal iônico

Para formar um **cristal iônico**, é necessário que a energia dos íons no cristal seja **menor** que das substâncias separadas.

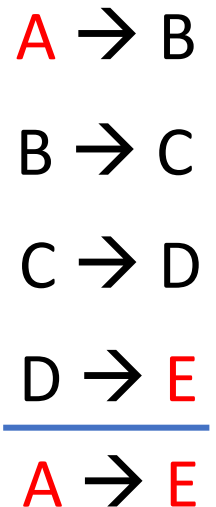
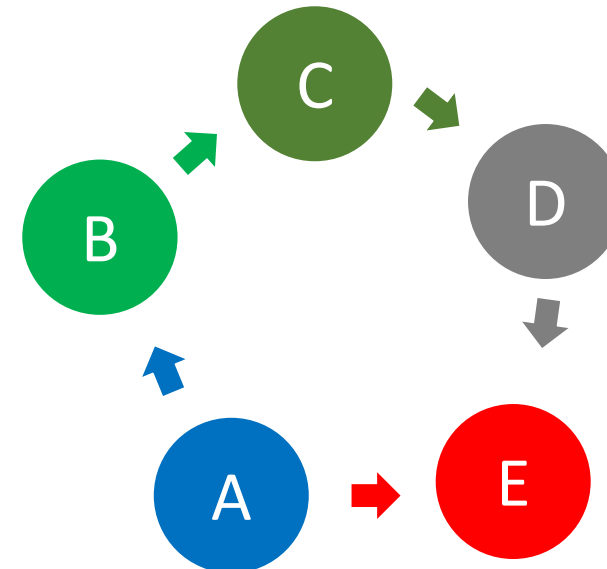


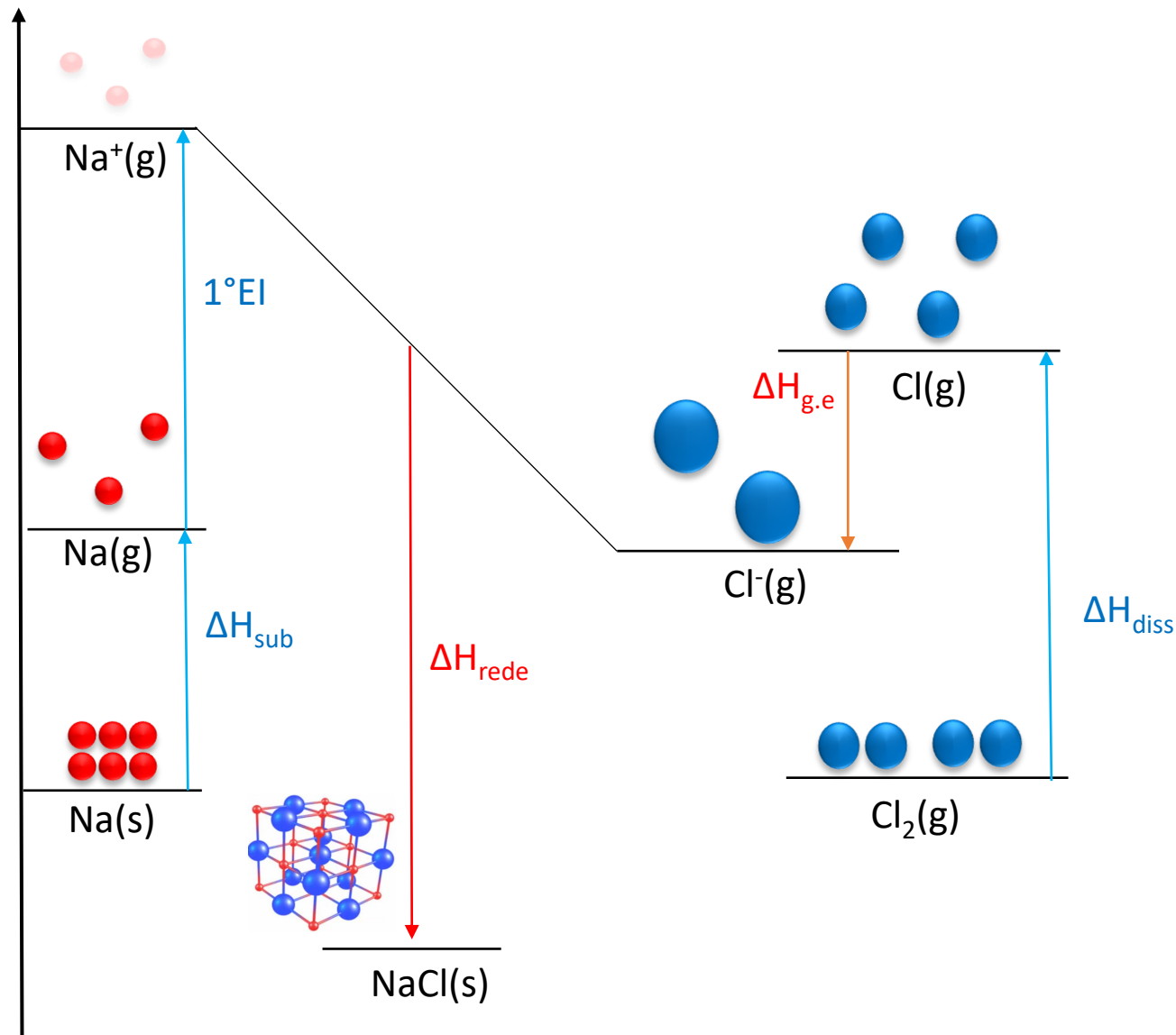
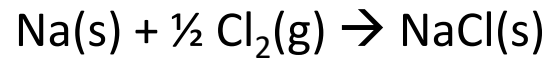
Como é possível a formação dos compostos iônicos ?



Alguma etapa do processo deve **compensar o gasto de energia!**

Ciclo de Born-Haber

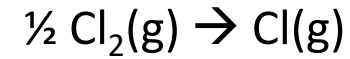




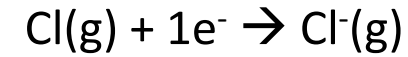
$$\Delta H_{\text{sub}} = +104 \text{ kJ/mol}$$



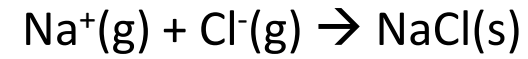
$$1^\circ \text{EI} = +495,4 \text{ kJ/mol}$$



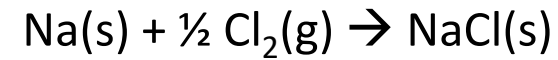
$$\Delta H_{\text{diss}} = \frac{1}{2} (242) \text{ kJ/mol}$$



$$\Delta H_{\text{g.e}} = -349 \text{ kJ/mol}$$



$$\Delta H_{\text{rede}} = -754 \text{ kJ/mol}$$



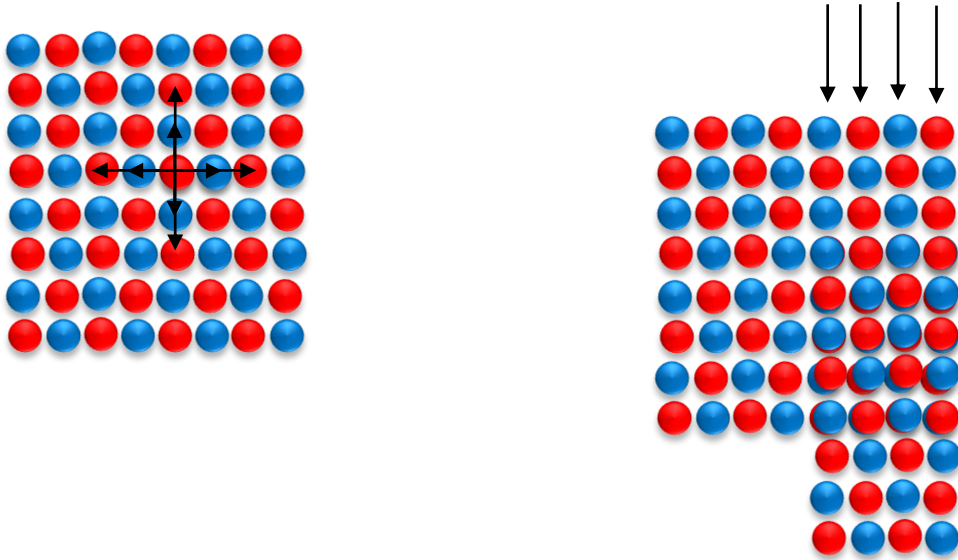
$$\Delta H_{\text{form}} = -382,6 \text{ kJ/mol}$$

Energia Reticular

Um sólido iônico não é formado por pares iônicos, e sim por um **agregado de cátions e ânions**



Todos os cátions interagem com todos os ânions, em maior ou menor grau (**interação global**)



Lei de Coulomb

$$E_p = -\frac{1}{4\pi\epsilon_0} \frac{Z_1 Z_2 e^2}{r_{12}}$$

Par de íons

$$E_p = -N_A \frac{1}{4\pi\epsilon_0} \frac{Z_1 Z_2 e^2}{r_{12}}$$

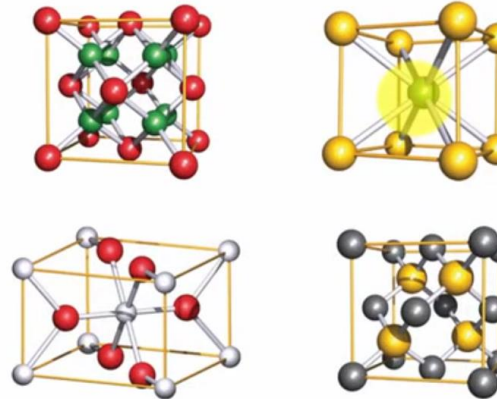
Mol de íons

$$E_p = -A N_A \frac{1}{4\pi\epsilon_0} \frac{Z_1 Z_2 e^2}{r_{12}}$$

Constante de Madelung (A)

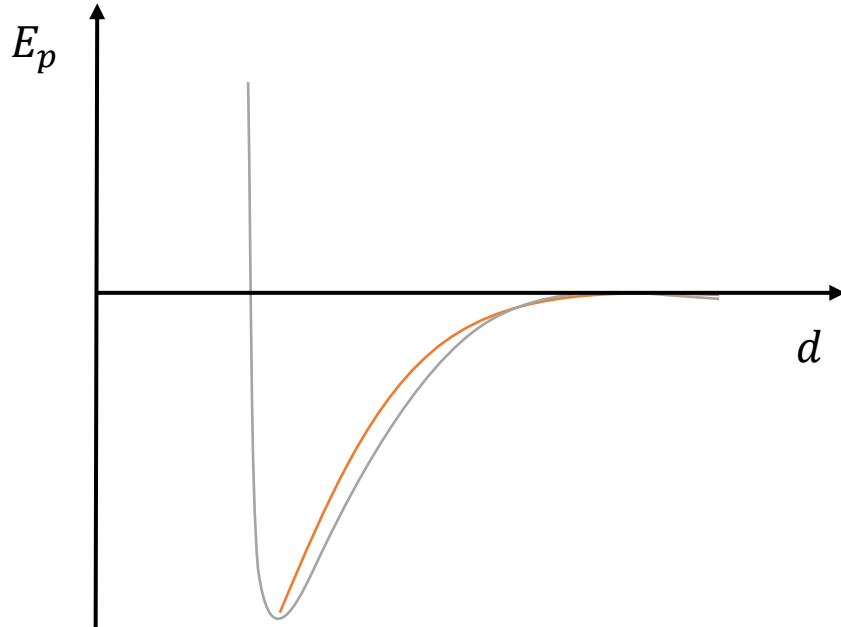


Parâmetro estrutural (calculado)
próprio de cada tipo de sistema



Tipo de Estrutura	A
Cloreto de Césio	1,763
Fluorita	2,519
Halita	1,748
Rutilo	2,408

$$E_p = -A N_A \frac{1}{4\pi\epsilon_0} \frac{Z_1 Z_2 e^2}{d}$$



$$\Delta H_{rede} = -A N_A \frac{1}{4\pi\epsilon_0} \frac{Z_1 Z_2 e^2}{d} \left(1 - \frac{d^*}{d} \right)$$

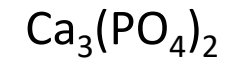
Equação de Born-Meyer

Quanto **mais negativo** for o ΔH_{rede} , **mais “estável”** será o sólido iônico



Baixa **solubilidade**; elevado **ponto de fusão**

Compostos iônicos com **carga elevada**, e **raio pequeno**, levam a uma **grande entalpia de rede**



Sais insolúveis

Calcule, através do ciclo de Born-Haber, a energia do retículo cristalino par ao óxido de magnésio.

$$\Delta H_{\text{sub}}(\text{Mg}) = 146,3 \text{ kJ} / \text{mol}$$

$$1^\circ EI(\text{Mg}) = 737,7 \text{ kJ} / \text{mol}$$

$$2^\circ EI(\text{Mg}) = 1450,7 \text{ kJ} / \text{mol}$$

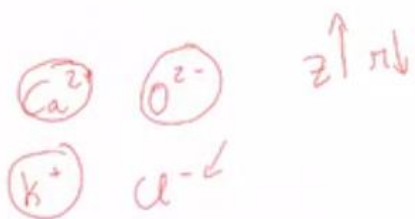
$$\Delta H_{\text{diss}}(\text{O}_2) = 494 \text{ kJ} / \text{mol}$$

$$1^\circ A.E = 141 \text{ kJ} / \text{mol}$$

$$2^\circ A.E = -780 \text{ kJ} / \text{mol}$$

$$\Delta H_{\text{form}}^\circ(\text{MgO}) = -617,5 \text{ kJ} / \text{mol}$$

Os sólidos iônicos CaO e KCl cristalizam no mesmo tipo de estrutura. Em que composto as interações entre os íons são mais fortes?



$$\Delta H_{\text{sub}}(\text{Mg}) = 146,3 \text{ kJ/mol}$$

$$1^{\circ} \text{EI}(\text{Mg}) = 737,7 \text{ kJ/mol}$$

$$2^{\circ} \text{EI}(\text{Mg}) = 1450,7 \text{ kJ/mol}$$

$$\Delta H_{\text{diss}}(\text{O}_2) = 494 \text{ kJ/mol}$$

$$1^{\circ} \text{A.E.} = 141 \text{ kJ/mol}$$

$$2^{\circ} \text{A.E.} = -780 \text{ kJ/mol}$$

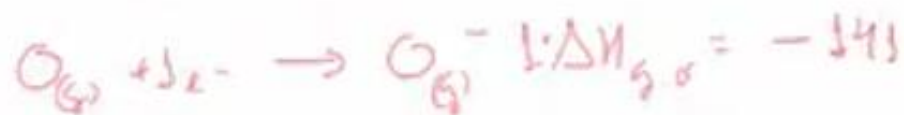
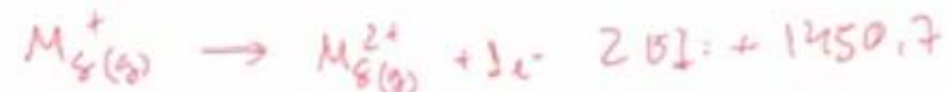
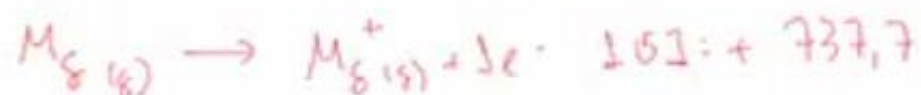
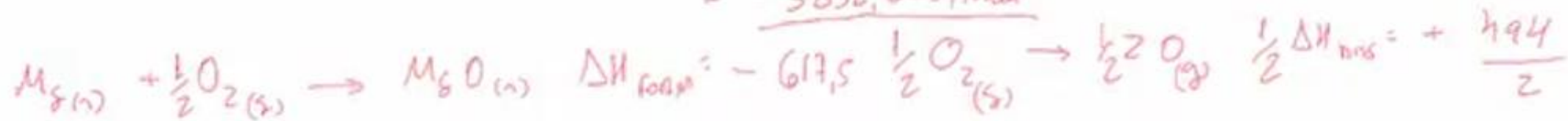
$$\Delta H_{\text{form}}^{\circ}(\text{MgO}) = -617,5 \text{ kJ/mol}$$

$$\Delta H_{\text{form}} = \Delta H_{\text{sub}} + 1 \text{EI} + 2 \text{EI} + \frac{1}{2} \Delta H_{\text{diss}} + 1 \cdot \Delta H_{\text{G.O.}} + 2 \Delta H_{\text{G.O.}} + \Delta H_{\text{recomb}}$$

$$\Delta H_{\text{recomb}} = \Delta H_{\text{form}} - \left(\Delta H_{\text{sub}} + 1 \text{EI} + 2 \text{EI} + \frac{1}{2} \Delta H_{\text{diss}} + 1 \Delta H_{\text{G.O.}} + 2 \Delta H_{\text{G.O.}} \right)$$

$$= -617,5 - \left(146,3 + 737,7 + 1450,7 + \frac{494}{2} - 141 + 780 \right)$$

$$= -3838,2 \text{ kJ/mol}$$



Estrutura de Lewis

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE ATOM AND THE MOLECULE.

By GILBERT N. LEWIS.
Received January 26, 1916.

In a paper entitled "Valence and Tautomerism"¹ I took occasion
¹ THIS JOURNAL, 35, 1448 (1913); see also the important article of Bray and Branch, *Ibid.*, 35, 1440 (1913).

THE ATOM AND THE MOLECULE.

763

to point out the great importance of substituting for the conventional classification of chemical substances, as inorganic or organic, the more general classification which distinguishes between polar and nonpolar substances. The two classifications roughly coincide, since most inorganic substances are distinctly polar, while the majority of organic substances belong to the nonpolar class; thus potassium chloride represents the extreme polar type and methane the nonpolar. Nevertheless, there are many inorganic substances which, under ordinary circumstances, are predominantly nonpolar, and many organic substances which, at least in a certain part of the molecule, are strongly polar.

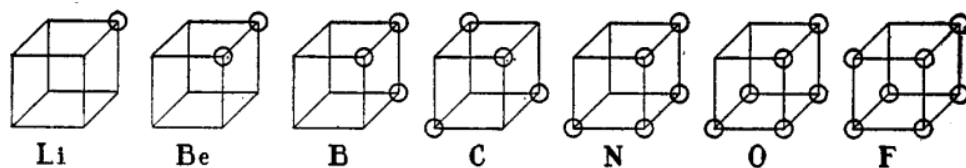


Fig. 2.

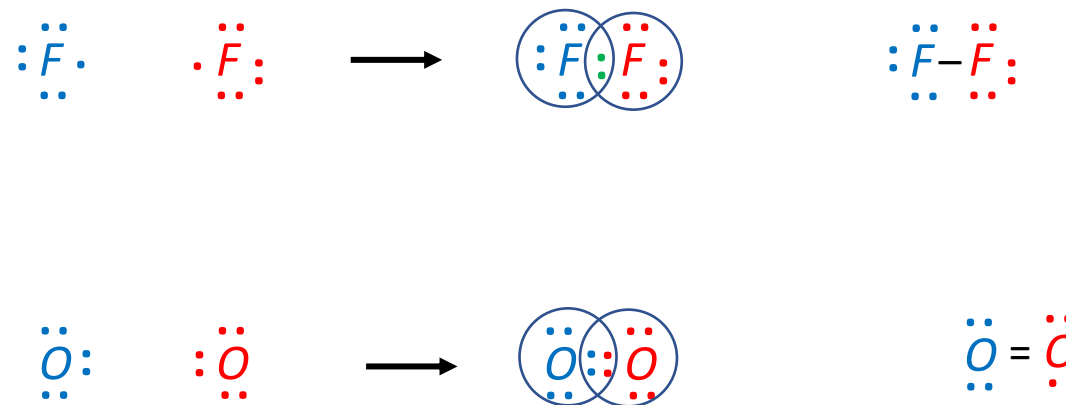
É uma representação pictográfica que indica quantos **elétrons** um átomo tem em sua **camada de valência**



A **Ligação Covalente** né formada pelo compartilhamento de um par de elétrons

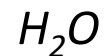


Com o objetivo de completar o **octeto**



Moléculas Poliatômicas

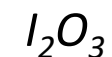
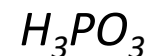
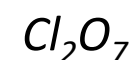
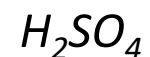
- **Conta-se todos** os elétrons de valência
 - Leva-se em conta a carga do íon
- **Liga-se todos** os átomos ao átomo central
 - O menos eletronegativo
- Distribui-se os elétrons nos **átomos periféricos**
- Distribui-se os elétrons no **átomo central**
 - Completou o octeto ?
- Usa-se ligações **duplas** ou **triplas**



Oxiácidos



Anidridos moleculares



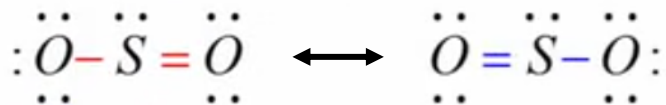
Ressonância

Ocorre quando uma molécula **não pode** ser representada adequadamente por **uma única Estrutura de Lewis**

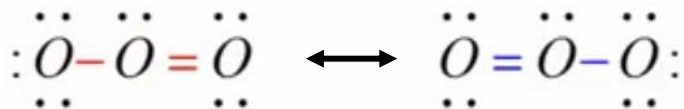


Ligações duplas e simples **alternadas**

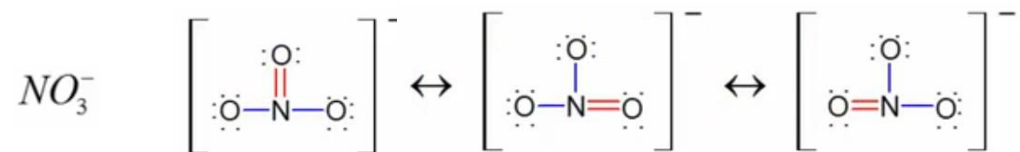
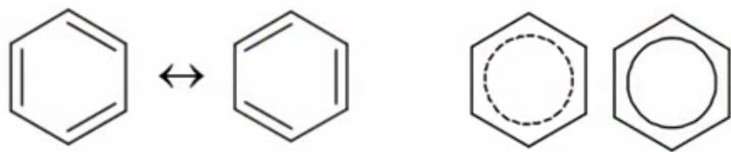
SO_2



O_3

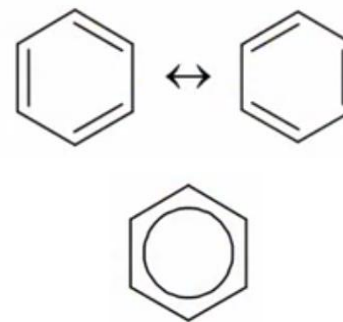


C_6H_6

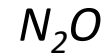


Estruturas de ressonância sugerem uma **deslocalização eletrônica**

O **Híbrido de Ressonância** indica a **coexistência** de Estruturas de Lewis



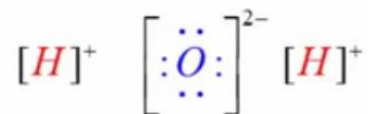
Estruturas de Lewis **não equivalentes**



A análise da **carga formal** ajuda a determinar a melhor estrutura de Lewis

Carga Formal

É a **carga** que um átomo teria caso as ligações fossem rompidas e fossem 100 covalente



Uma Estrutura de Lewis será mais **representativa (menor energia)**, se:

- A que tiver **menor quantidade** de cargas formais
 - A que tiver a carga **negativa** sobre o átomo mais **eletronegativo**

$$CF_a = V_a - N_a - \frac{B_a}{2}$$

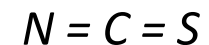
V_a — elétrons de valência

N_a — elétrons não ligantes

B_a — elétrons ligados



Qual seria a distribuição dos átomos do íon tiocianato (SCN^-) ?

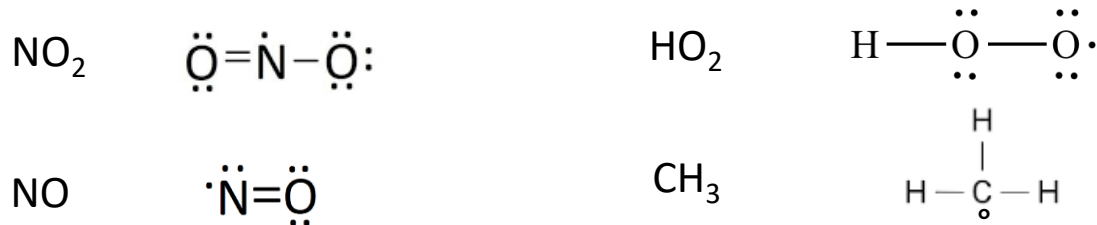


Regra do Octeto

Elementos como metais alcalinos, metais alcalinos terrosos, C, N, O e F costuma obedecer à regra do octeto



E quando o número de elétrons é **ímpar** ?



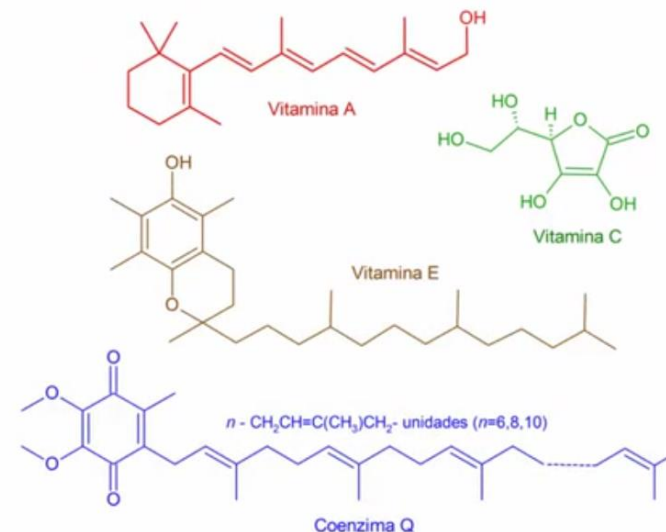
Radicais

Espécies altamente **reativas**!

Presentes em reações de **combustão**

Provocam a **oxidação**/destruição das células

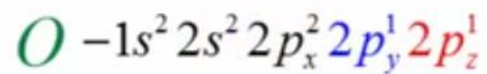
Antioxidantes



Radicais → Espécies que possuem um elétron desemparelhado



Paramagnéticos



Birradical



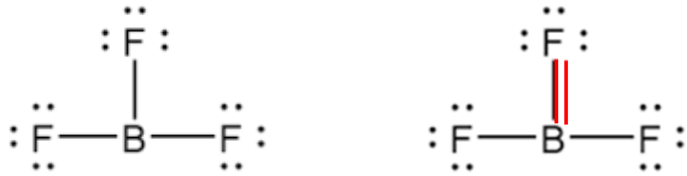
Compostos do Grupo 13

Existe, de maneira mais estável, com **6 elétrons** na camada de valência

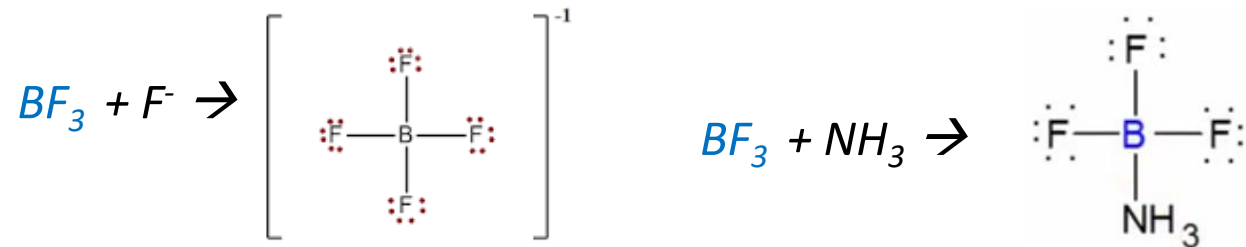


Boro

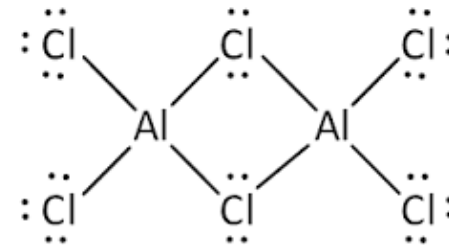
BF_3



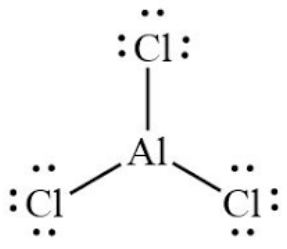
Ácido de Lewis



$AlCl_3$

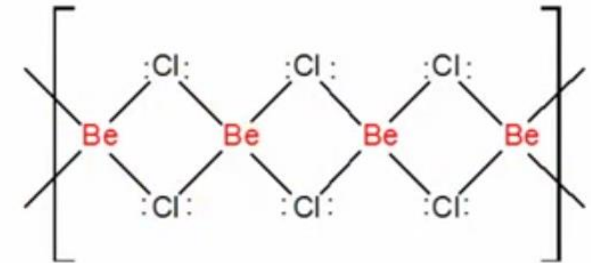


180 °C



200 °C

$BeCl_2$

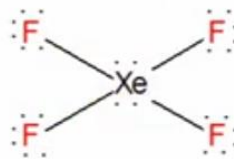
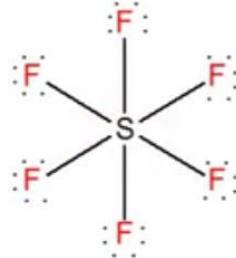
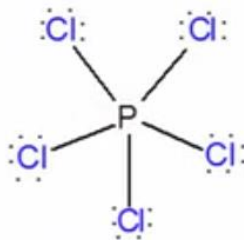
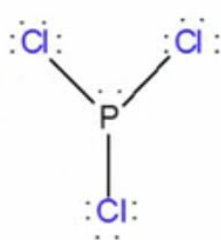
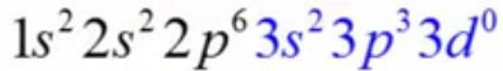


“Expansão do Octeto”

Elementos do **terceiro período** em diante, podem expandir sua camada de valência (**usam orbitais d**)



Possuem **tamanho adequado** para acomodar mais átomos ao seu redor



Desenhe **três** estruturas de Lewis possíveis para o íon sulfato e determine qual seria a mais representativa.

GDCh

Communications

Angewandte
International Edition
Chemie

International Edition: DOI: 10.1002/anie.201608795
German Edition: DOI: 10.1002/ange.201608795

Carbocations

Crystal Structure Determination of the Pentagonal-Pyramidal Hexamethylbenzene Dication $\text{C}_6(\text{CH}_3)_6^{2+}$

Moritz Malischewski* and K. Seppelt

Dedicated to Professor Karl Otto Christe on the occasion of his 80th anniversary

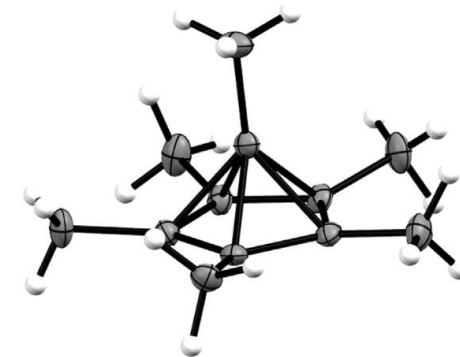
Abstract: In contrast to the well-known 2-norbornyl cation, the structure of which was a matter of long debate until its pentacoordinated nature was recently proven by an X-ray structure, the pentagonal-pyramidal dication of hexamethylbenzene has received considerably less attention. This species was first prepared by Hogeveen in 1973 at low temperatures in magic acid ($\text{HSO}_3\text{F}/\text{SbF}_5$), for which he proposed a non-classical structure (containing a hexacoordinated carbon) based on NMR spectroscopy and reactivity studies, but no X-ray crystal structure has been reported. $\text{C}_6(\text{CH}_3)_6^{2+}$ can be obtained through the dissolution of hexamethyl Dewar benzene epoxide in $\text{HSO}_3\text{F}/\text{SbF}_5$ and crystallized as the SbF_6^- salt upon addition of excess anhydrous hydrogen fluoride. The crystal structure of $\text{C}_6(\text{CH}_3)_6^{2+} (\text{SbF}_6^-)_2 \cdot \text{HSO}_3\text{F}$ confirms the pentagonal pyramidal structure of the dication. The apical carbon is bound to one methyl group (distance 1.479(3) Å) and to the five basal carbon atoms (distances 1.694(2)–1.715(3) Å).

The tetravalency of carbon and the hexagonal-planar ring structure of benzene are fundamental axioms of organic chemistry, and were developed 150 years ago by Kekulé.^[1,2] Chemists have long been fascinated by finding exceptions from these rules. Starting in the 1960s, valence isomers of benzene were prepared through elaborate organic syntheses,^[3–6] while hypercoordinated carbon compounds entered the stage through the pioneering work of Olah on superacids and non-classical cations.^[7,8]

different approach, Akiba and co-workers prepared formally hypercoordinated organic species through special ligand design, where an electrophilic carbon atom is intramolecularly coordinated by two/four neighboring methoxy groups. The C–O distances are in the range of 2.43(1)–2.45(1) Å and 2.641(5)–2.750(5) Å, respectively,^[12,13] thus indicating only weak interactions. In stark contrast, hypercoordinated carbon with much shorter bonds can be found in carboranes. Nevertheless, these common structural motives of boron chemistry are only subtly changed by replacing boron with an isolobal carbon fragment. Surprisingly, even hexagonal-planar carbon has been considered viable (based on theoretical calculations by Exner and Schleyer) in boron compounds, for example, in CB_6^{2-} .^[14]

Recently, the isolation of the non-classical norbornyl cation and its crystal structure analysis was achieved by Scholz et al.^[15] In this species, a C–C double bond (bond length of 1.39 Å) interacts with a carbocationic methylene group at a distance of 1.80 Å, which can be rationalized as a 3-center 2-electron bond. These results encouraged us to attempt the isolation of $\text{C}_6(\text{CH}_3)_6^{2+}$, where the hexacoordinated carbon is exclusively bound to carbon atoms.

In analogy to electron-deficient boron clusters, the Wade rules predict a pentagonal-pyramidal geometry (nido cluster) for $\text{C}_6\text{H}_6^{2+}$. In 2014, the group of Roithova detected this species after double ionization in the gas phase by infrared predissociation spectroscopy at temperatures below 4 K, in



Eletronegatividade

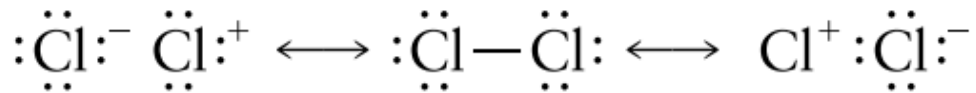
Correção do modelo covalente



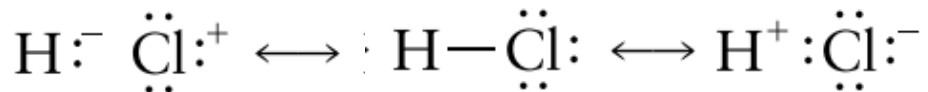
Adiciona **caráter iônico** à ligação covalente



Todas as ligações podem ser representadas como um híbrido de ressonância



As contribuições iônicas são **idênticas**



As contribuições iônicas são **diferentes**

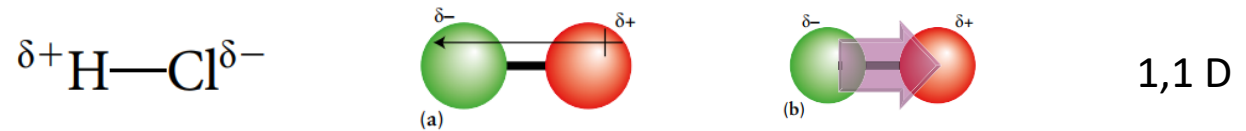
Formação de
cargas parciais



Ligação Covalente Polar



Momento de
Dipolo Elétrico (μ)



Quanto maior a **diferença de eletronegatividade**, maior será o caráter iônico de uma ligação covalente

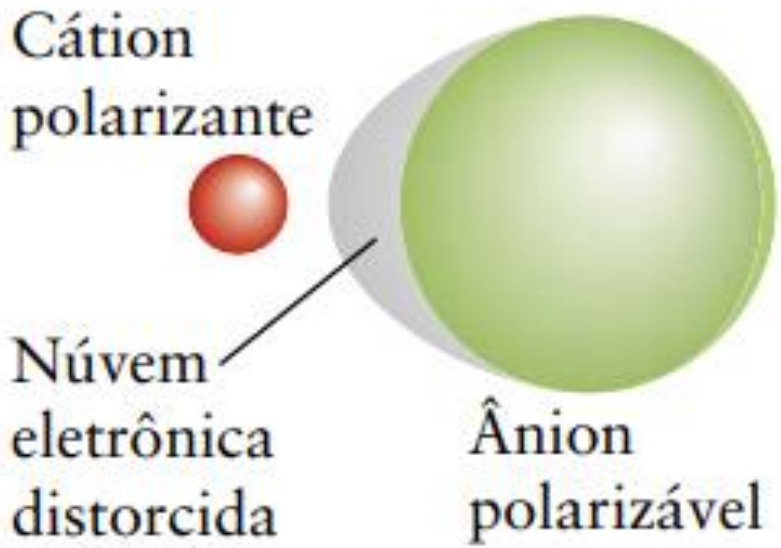
$$\Delta x_p \geq 2,0 \quad \text{Iônica}$$

$$\Delta x_p \leq 1,5 \quad \text{Covalente Polar}$$

Todas as **ligações iônicas** possuem um certo caráter **Polarizabilidade** → Capacidade de ter uma nuvem eletrônica distorcida

covalente
↓
O cátion é capaz de distorcer a nuvem eletrônica do ânion

↓
Aumenta a densidade eletrônica na região internuclear



Poder Polarizante → Capacidade de distorcer a nuvem eletrônica

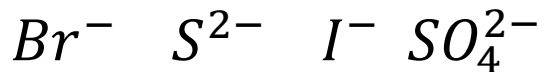
↓
Cátions com raio pequeno e Carga elevada



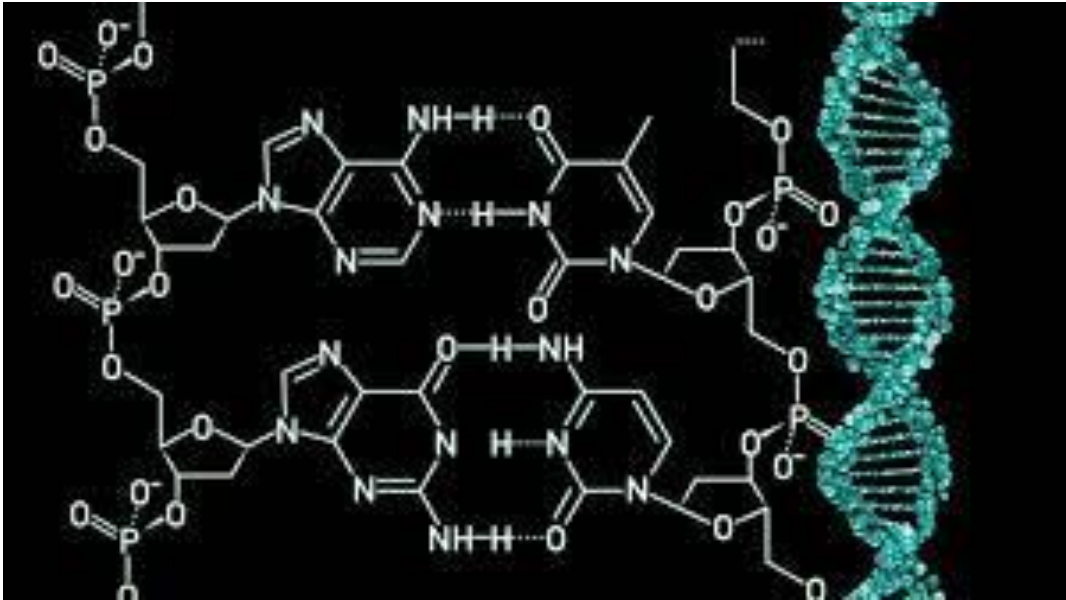
Falha no Modelo Eletrostático (Eq. De Born-Meyer)

Enfraquecimento do retículo cristalino

Ânions com raio e carga elevada



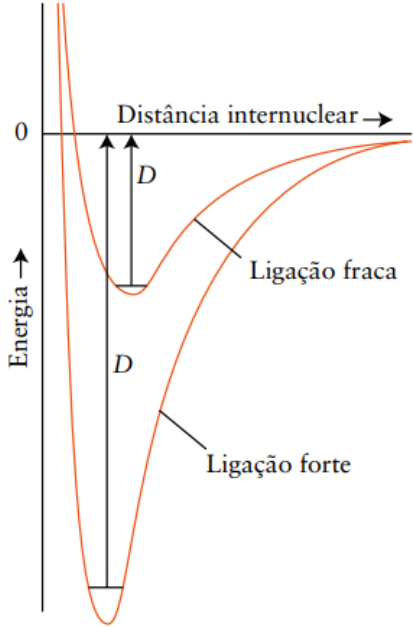
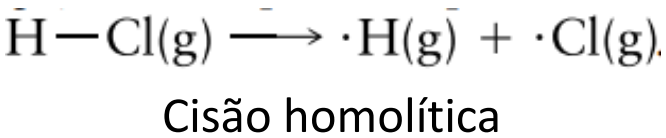
As propriedades de uma ligação química, dependem essencialmente dos **átomos envolvidos** na ligação



Força de Ligação

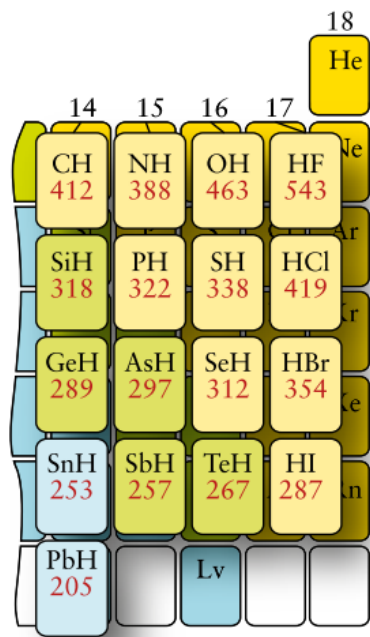
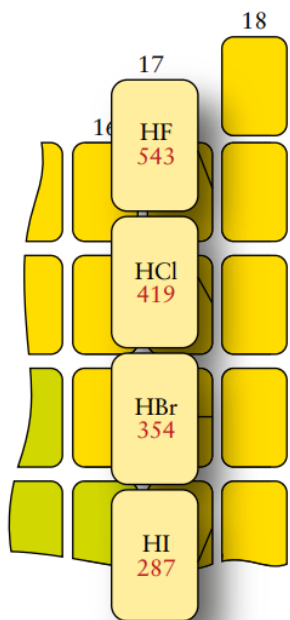
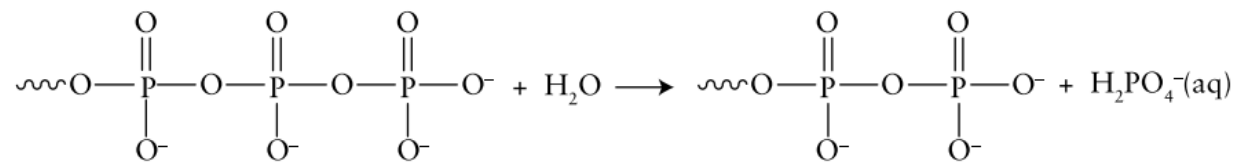
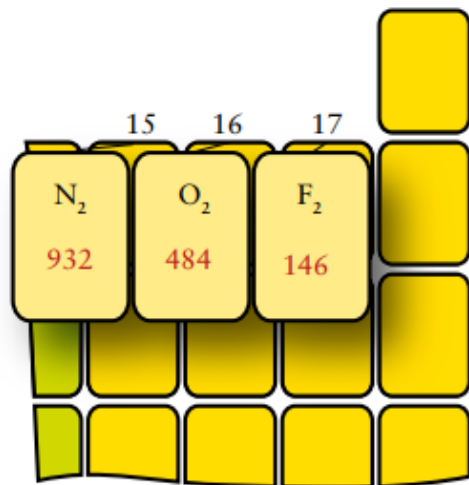
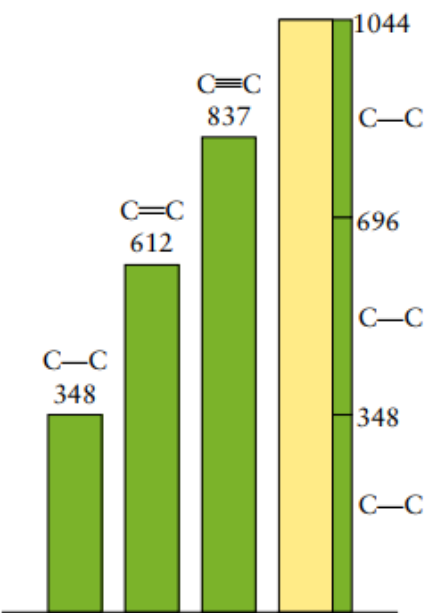


Energia de Dissociação



Molécula	Energia de dissociação (kJ · mol ⁻¹)
H ₂	424
N ₂	932
O ₂	484
CO	1062
F ₂	146
Cl ₂	230
Br ₂	181
I ₂	139
HF	543
HCl	419
HBr	354
HI	287

Ligação	Energia de dissociação média (kJ · mol ⁻¹)	Ligação	Energia de dissociação média (kJ · mol ⁻¹)
C—H	412	C—I	238
C—C	348	N—H	388
C=C	612	N—N	163
C≡C*	518	N=N	409
C=C	837	N—O	210
C—O	360	N=O	630
C=O	743	N—F	270
C—N	305	N—Cl	200
C—F	484	O—H	463
C—Cl	338	O—O	157
C—Br	276		



Comprimento de ligação

É a distância entre os centros de dois átomos em ligação covalente no mínimo de energia potencial



É **aproximadamente** igual à soma dos raios covalentes

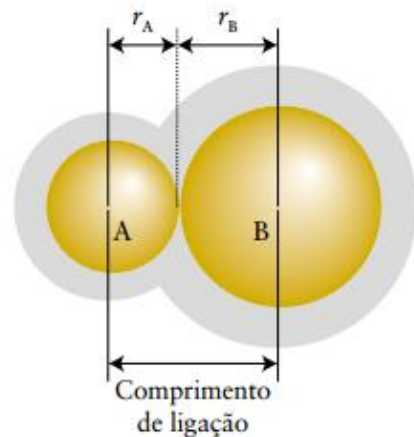
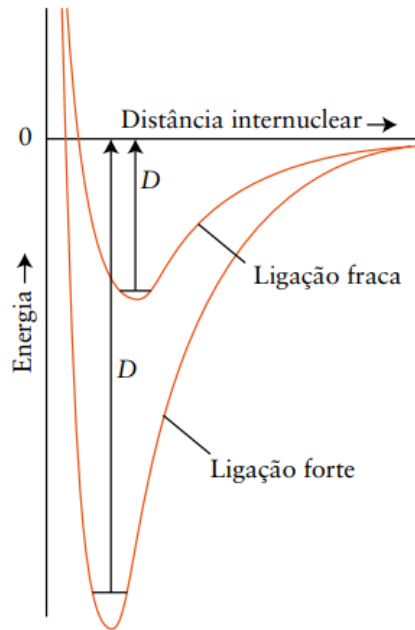


TABELA 2D.3 Comprimentos de ligação médios e experimentais

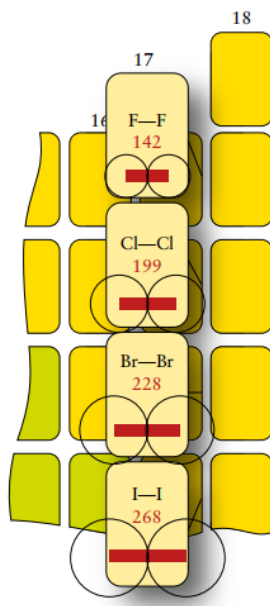
Ligação	Comprimento de ligação médio (pm)	Molécula	Comprimento de ligação experimental (pm)
C—H	109	H ₂	74
C—C	154	N ₂	110
C=C	134	O ₂	121
C≡C*	139	F ₂	142
C≡C	120	Cl ₂	199
C—O	143	Br ₂	228
C=O	112	I ₂	268
O—H	96		
N—H	101		
N—O	140		
N=O	120		

Entre os mesmo dois elementos, as ligações **múltiplas** são mais **curtas** do que as ligações simples



Para o mesmo par de átomos, a ligação mais **curta** é a mais **forte**

				<div>H 37</div>				18 He
	1	2	13	14	15	16	17	
2	Li	Be	<div>B 82</div>	<div>C 60 67 77</div>	<div>N 55 60 75</div>	<div>O 60 66</div>	<div>F 58</div>	Ne
3	Na	Mg	<div>Al 118</div>	<div>Si 111</div>	<div>P 110</div>	<div>S 102</div>	<div>Cl 98</div>	Ar
4	K	Ca	<div>Ga 126</div>	<div>Ge 122</div>	<div>As 121</div>	<div>Se 117</div>	<div>Br 114</div>	Kr
5	Rb	Sr	<div>In 144</div>	<div>Sn 141</div>	<div>Sb 138</div>	<div>Te 137</div>	<div>I 134</div>	Xe
6	Cs	Ba	Tl	Pb	Bi	Po	At	Rn

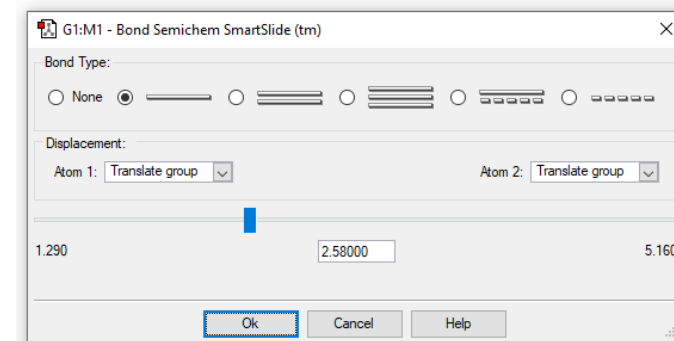
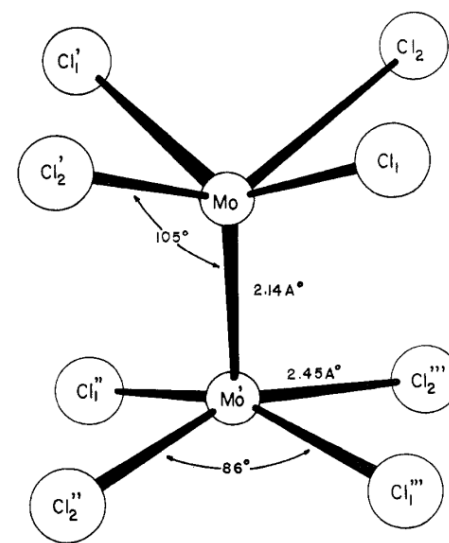


The Octachlorodimolybdate(II) Ion. A New Species with a Quadruple Metal-Metal Bond¹

BY JURIJ V. BRENCIC² AND F. A. COTTON

Received July 22, 1968

The compound $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ has been prepared as a red, crystalline solid and definitively characterized by X-ray crystallography as a compound containing the $\text{Mo}_2\text{Cl}_8^{4-}$ ion, isostructural with the $\text{Re}_2\text{Cl}_8^{3-}$ and $\text{Tc}_2\text{Cl}_8^{3-}$ ions. The $\text{Mo}_2\text{Cl}_8^{4-}$ ion consists of an approximately cubic array of eight chlorine atoms, within which a pair of molybdenum atoms is centered along one fourfold axis. The Mo—Mo distance is 2.138 (4) Å while the mean Mo—Cl bond length is 2.45 Å. The water molecules are bound to the K^+ ions and not to the $\text{Mo}_2\text{Cl}_8^{4-}$ ions. The eclipsed configuration, the short Mo—Mo bond (*cf.* $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, Mo—Mo = 2.11 Å), and the fact that $\text{Mo}_2\text{Cl}_8^{4-}$ is isoelectronic as well as isostructural with $\text{Re}_2\text{Cl}_8^{3-}$ leave no doubt that it has the type of quadruple bond (σ , 2π , δ) previously discussed for $\text{Re}_2\text{X}_8^{3-}$ compounds and their derivatives. The principal crystallographic data are as follows: space group, Pbam ; unit cell edges: $a = 8.005 \pm 0.004$ Å, $b = 13.267 \pm 0.006$ Å, $c = 8.059 \pm 0.004$ Å; measured density, 2.54 ± 0.05 g cm⁻³; density calculated for $Z = 2$, 2.60 g cm⁻³. The structure was solved and refined using 510 statistically significant nonzero reflections measured with a counter diffractometer. Absorption corrections were applied and anisotropic refinement was carried out to final unweighted and weighted residuals of 0.055 and 0.076, respectively.



Ligação covalente

Qualquer que seja a teoria que vamos utilizar para descrever a ligação covalente, é preciso conhecer previamente a **geometria** dessa molécula.

O principal fator que determina a estabilidade de um sistema químico é o **princípio de mínima energia**;

Isso implica, que se uma dada molécula pode ter várias geometrias, ela optará pela geometria à qual corresponde a energia mínima.

Geometria molecular

É o *arranjo tridimensional* dos átomos numa molécula, que é determinado pela orientação relativa das suas ligações covalentes. Esta estrutura é mantida quer a substância seja sólida, líquida ou gasosa.

É um parâmetro fundamental para a *previsão* da polaridade da molécula;

Permite inferir sobre o *tipo* e *intensidade* das interações intermoleculares e como tal prever as propriedades físicas e químicas dos compostos.

Geometria molecular

INORGANIC STEREOCHEMISTRY

By R. J. GILLESPIE, D.Sc., and R. S. NYHOLM, M.Sc., D.Sc.

(UNIVERSITY COLLEGE, LONDON, W.C.1)

DURING the past few years there have been several developments in theoretical chemistry which have led to a much better understanding of the factors responsible for the shapes of inorganic molecules. These developments have also made it clear that some apparently different approaches to stereochemistry can be integrated and, indeed, shown to be complementary. This Review attempts to bring together these approaches and to apply them to elements over the whole of the Periodic Table. Perhaps the most important result emerging from this unification is the conclusion that the simple qualitative Sidgwick-Powell¹ theory of electron-pair repulsions is of great value in accounting for the stereochemistry of practically all inorganic compounds.

Valence-Shell Electron-Pair Repulsion (VSEPR) Theory

Teoria da repulsão eletrônica dos pares de elétrons da camada de valência

Geometria molecular

Depende:

- Disposição espacial dos núcleos dos átomos;
- Repulsão dos pares eletrônicos das ligações ou pares livres nos átomos.

Prediz a geometria de uma molécula com base:

i) Na natureza eletrostática;

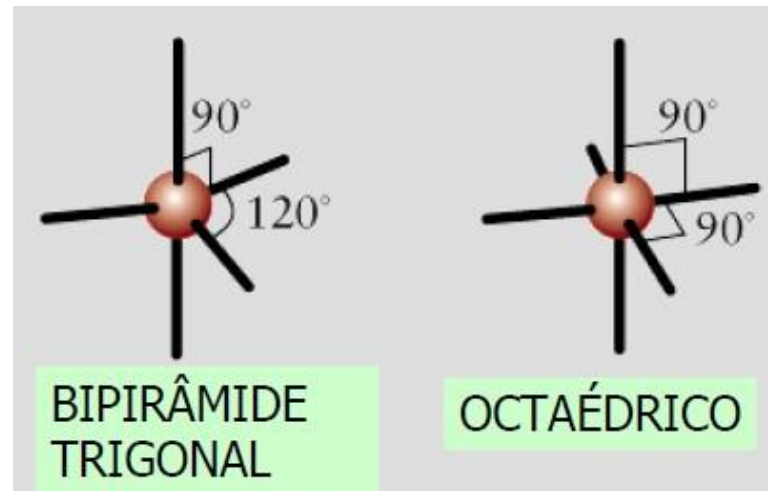
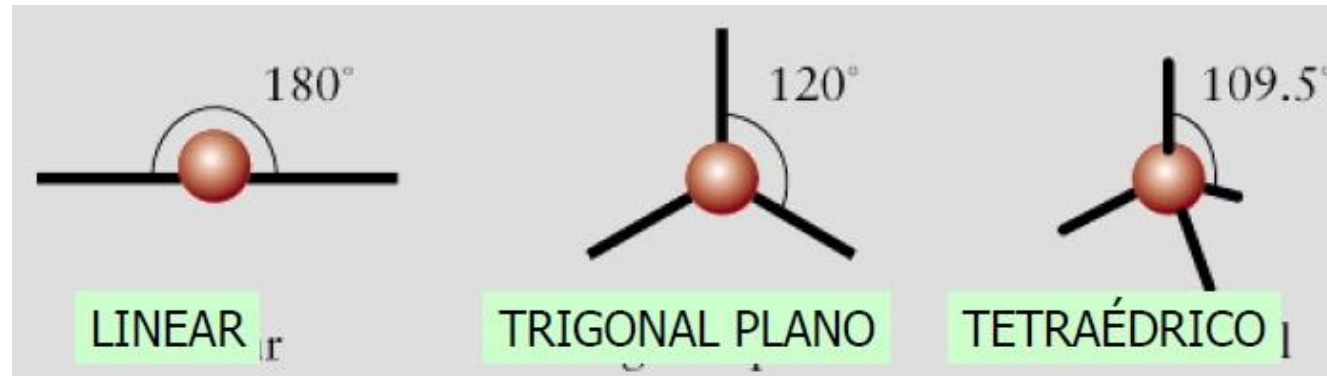
ii) Na natureza quântica

Previsão da geometria molecular

Repulsão por pares de elétrons de valência RPEV

PV	GEOMETRIA	PAR ELETRÔNICO
2	LINEAR	2 a 180°
3	TRIG.PLANO	3 a 120°
4	TETRAÉDRICO	4 a $109,5^\circ$
5	BIPIRÂMIDE TRIG.	2 axiais a 180° 3 equat. a 120°
6	OCTAÉDRICO	6 a 90°

Geometria molecular



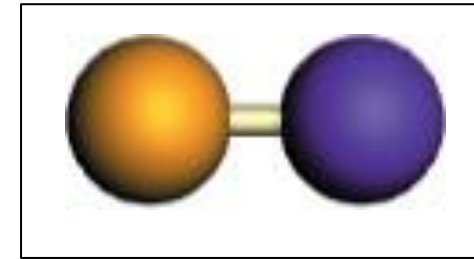
- I. Desenhe a estrutura de pontos para mostrar os elétrons de valência.
- II. Conte o número de "nuvens eletrônicas" ao redor do átomo central.
- III. Faça uma predição da geometria das nuvens eletrônicas ao redor do átomo central.
- IV. Ignore qualquer par solitário de elétrons e faça a predição da geometria da molécula/ion.

Geometria molecular

1) Molécula formada por 2 átomos:

- **Geometria linear.**

Ex: HBr, HCl, H_2 , N_2 , O_2 .

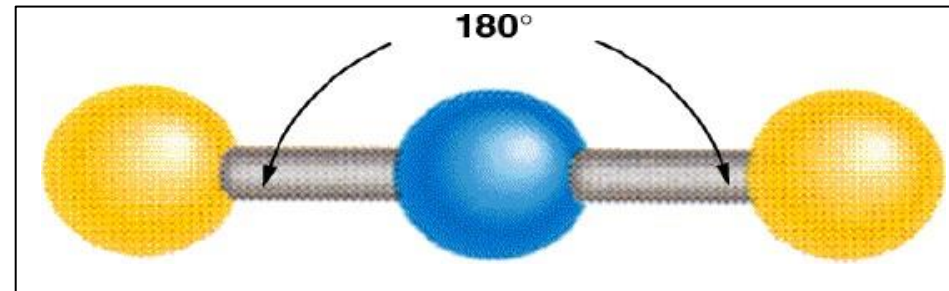


2) Molécula formada por 3 átomos:

a) Geometria linear - Se o átomo central não apresentar par de elétrons livre.

Ex: CO_2 , CS_2 ,

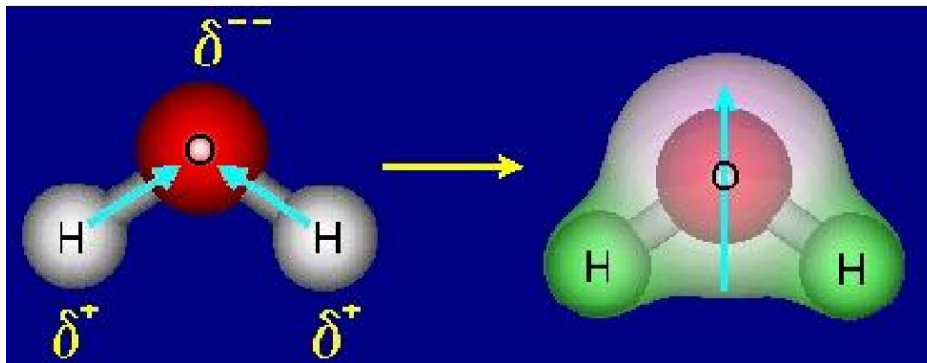
N_2O , HCN.



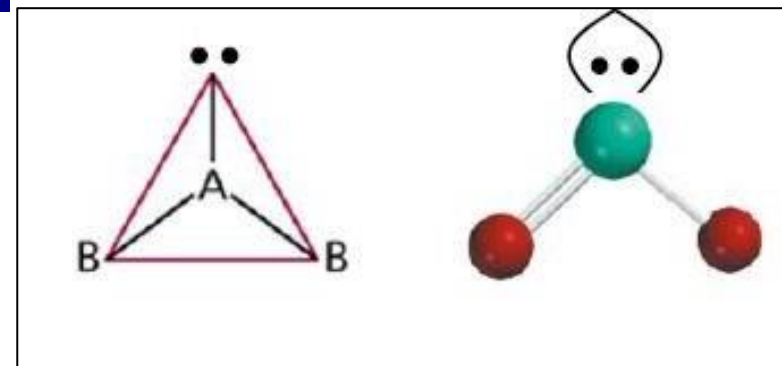
Geometria molecular

b) Geometria angular. Se o átomo central possuir par de elétrons emparelhados disponíveis.

Ex: H_2O (ângulo de $104,5^\circ$).



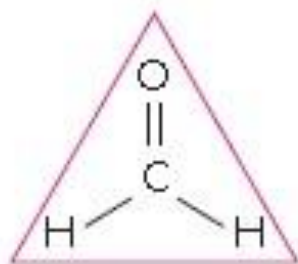
Ex: H_2S ; SO_2 ; NOCl



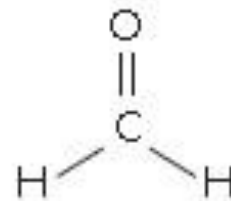
Geometria molecular

3) Molécula formada por 4 átomos

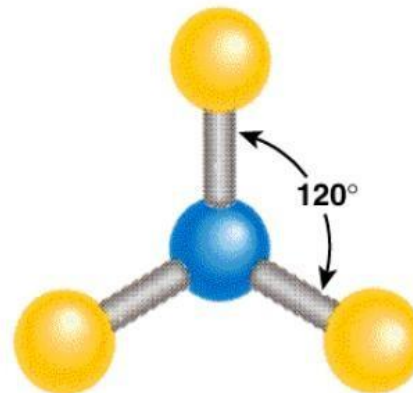
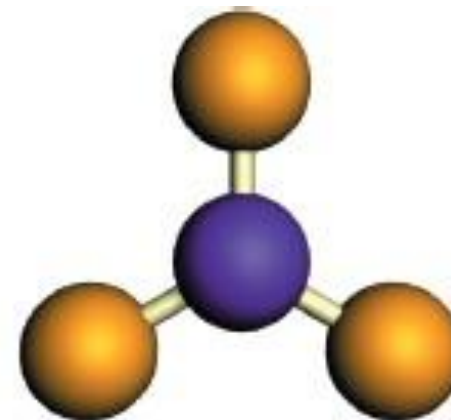
a) Trigonal plana: Átomo central não possui elétrons livres. SO_3 ; CH_2O ; COCl_2 ; NO_2Cl .



Triângulo equilátero

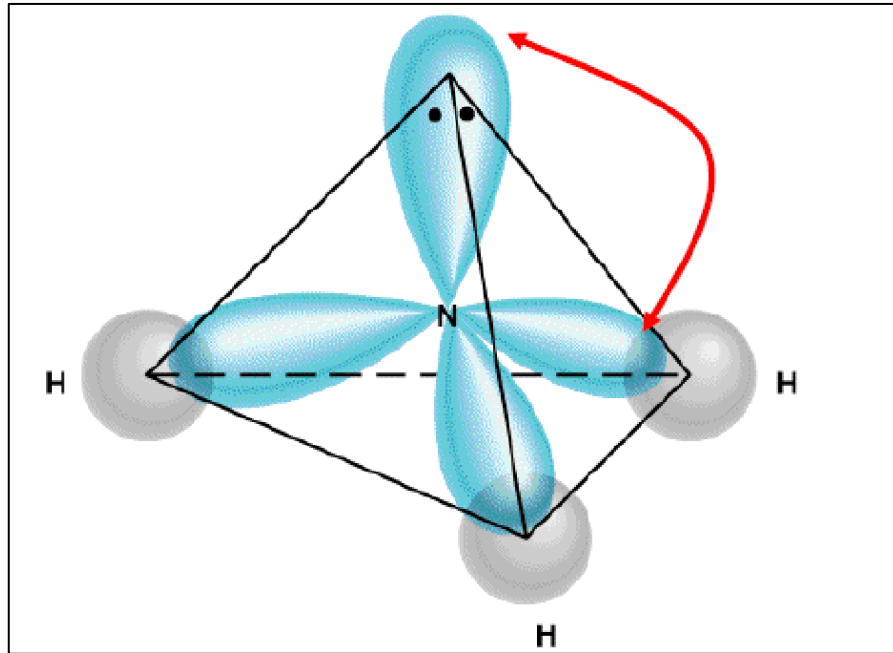


Trigonal plana

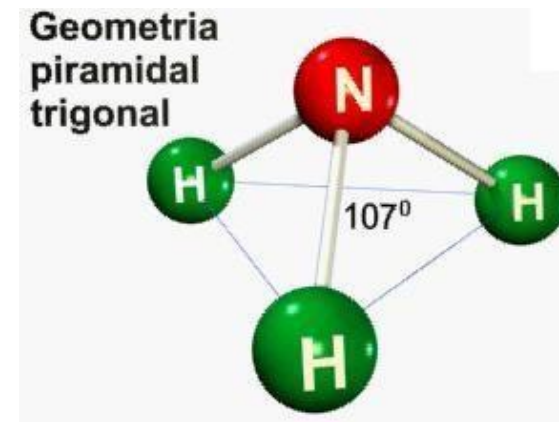


Geometria molecular

b) Piramidal ou pirâmide trigonal: Átomo central possuir elétrons livres. Ex: NH_3 ; NCl_3 ; PI_3 ; SOCl_2 .



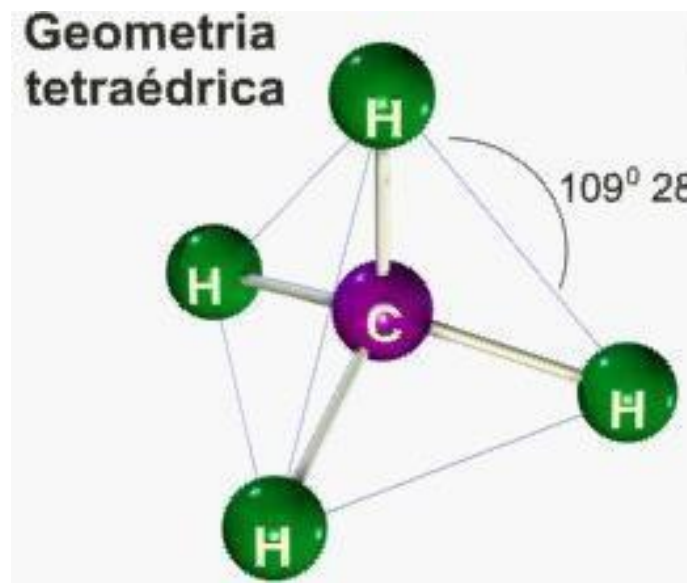
Ângulo: 107° .



Geometria molecular

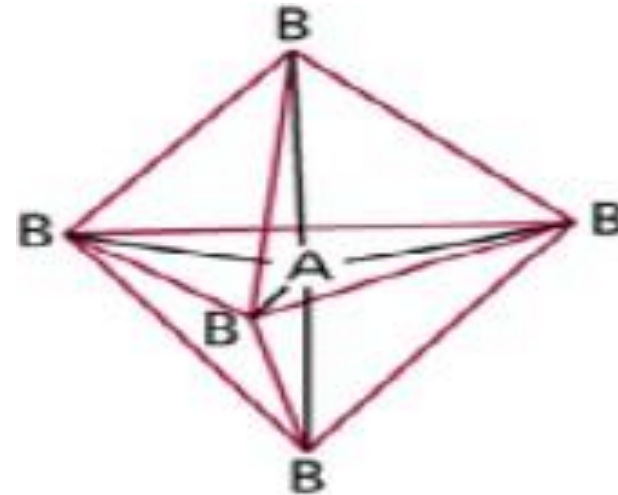
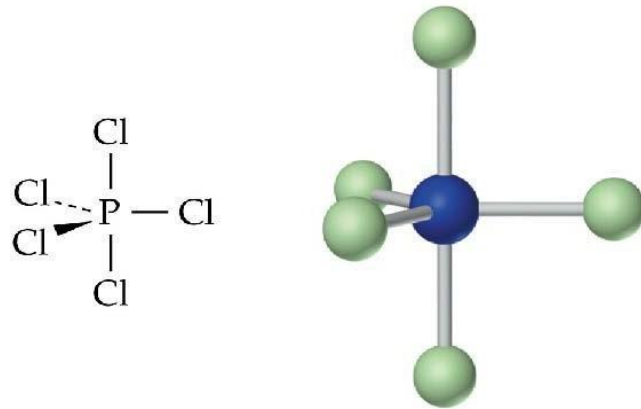
4) Molécula formada por 5 átomos

Geometria tetraédrica independente dos átomos envolvidos. Ex: CH_4 ; CHCl_3 ; SiCl_4 ; POCl_3 .

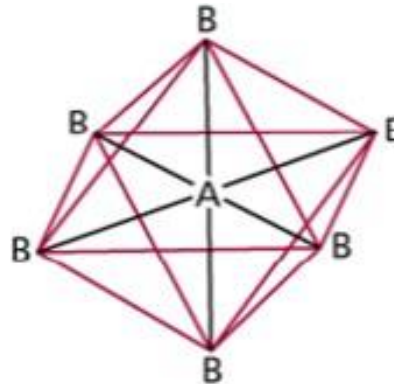


Geometria molecular

5) Molécula formada por 6 átomos: **Bipirâmide trigonal ou bipirâmide triangular.** PCl_5 ; PI_5 .



6) Molécula formada por 7 átomos: **Octaédrica.** Ex: SF_6 .



Geometria Macromolécula



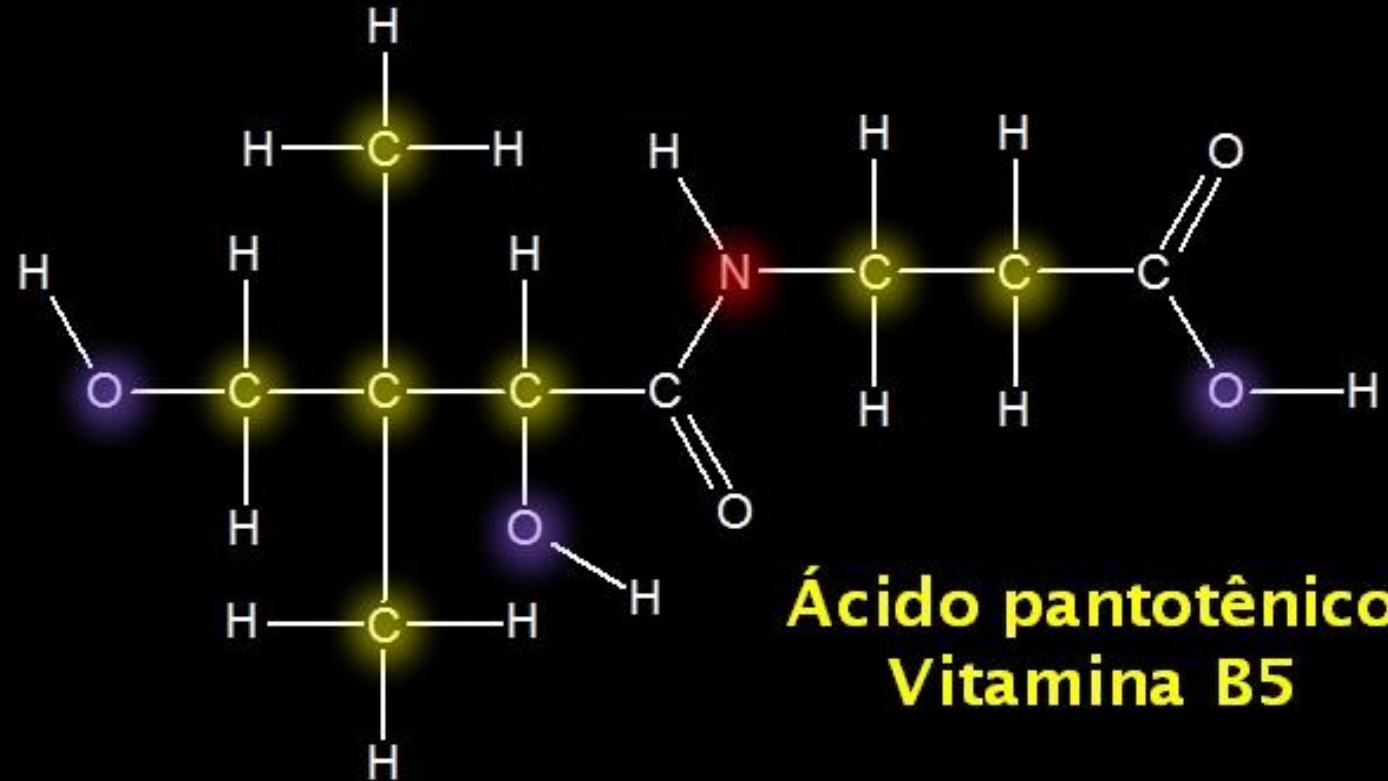
tetraédrica;



piramidal;



angular.

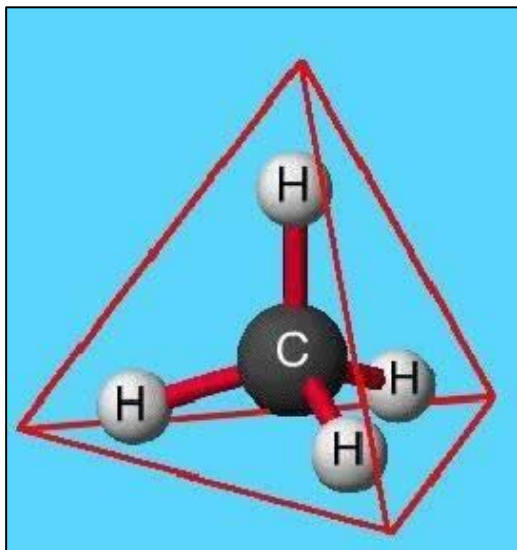


**Ácido pantotênico
Vitamina B5**

Geometria e polaridade das moléculas

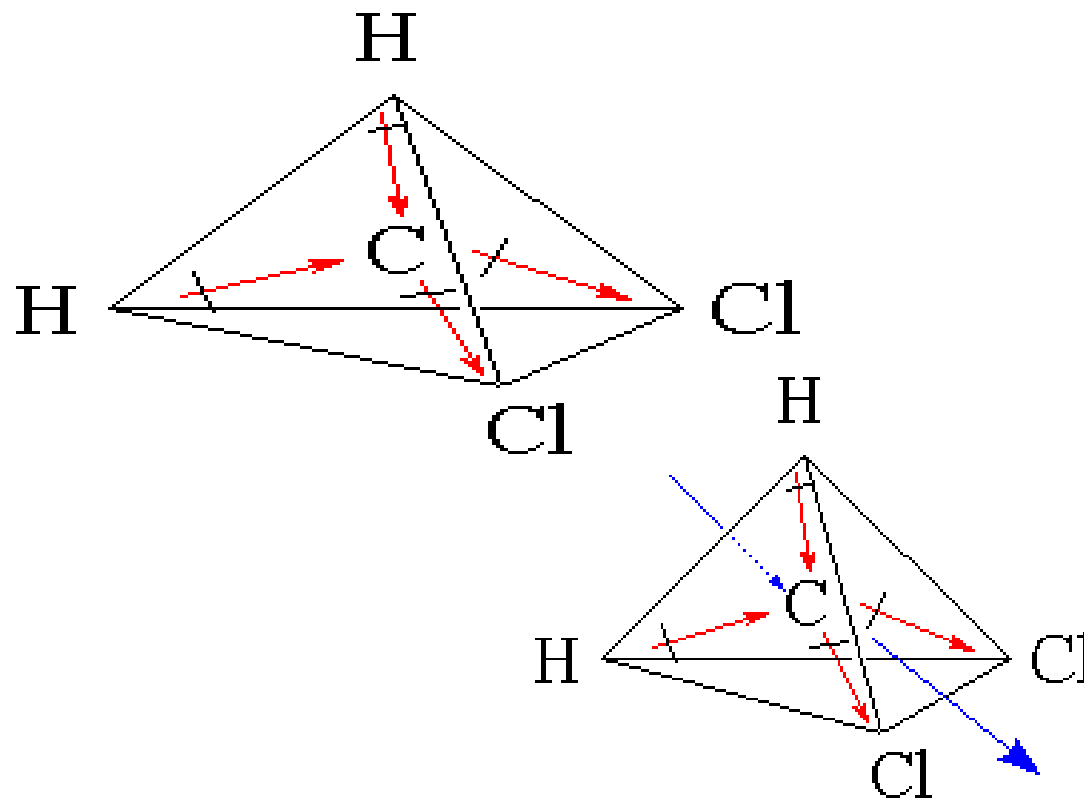
Metano CH_4 :

- estrutura tetraédrica;
- molécula apolar.



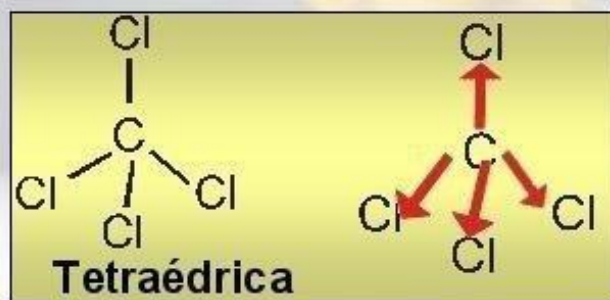
Dicloro metano CH_2Cl_2 :

- estrutura tetraédrica;
- molécula polar.

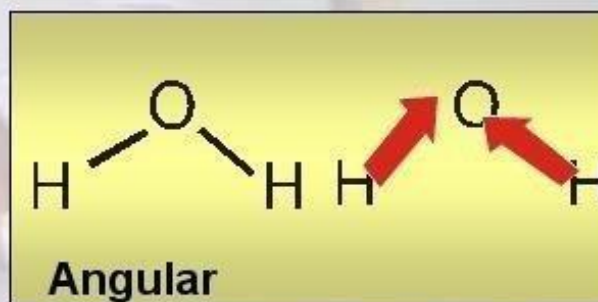


Polaridade das Moléculas

Moléculas Apolares



Moléculas Polares



Limitações e Excessões

Há uma série de exceções aparentes ao modelo VSEPR, a maioria das quais pode ser classificada devido às **interações ligante-ligante**.

The Geometry of Nonmetal Hydrides and the Ligand Radius of Hydrogen

E. A. Robinson[†] and R. J. Gillespie^{*}

Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1 Canada

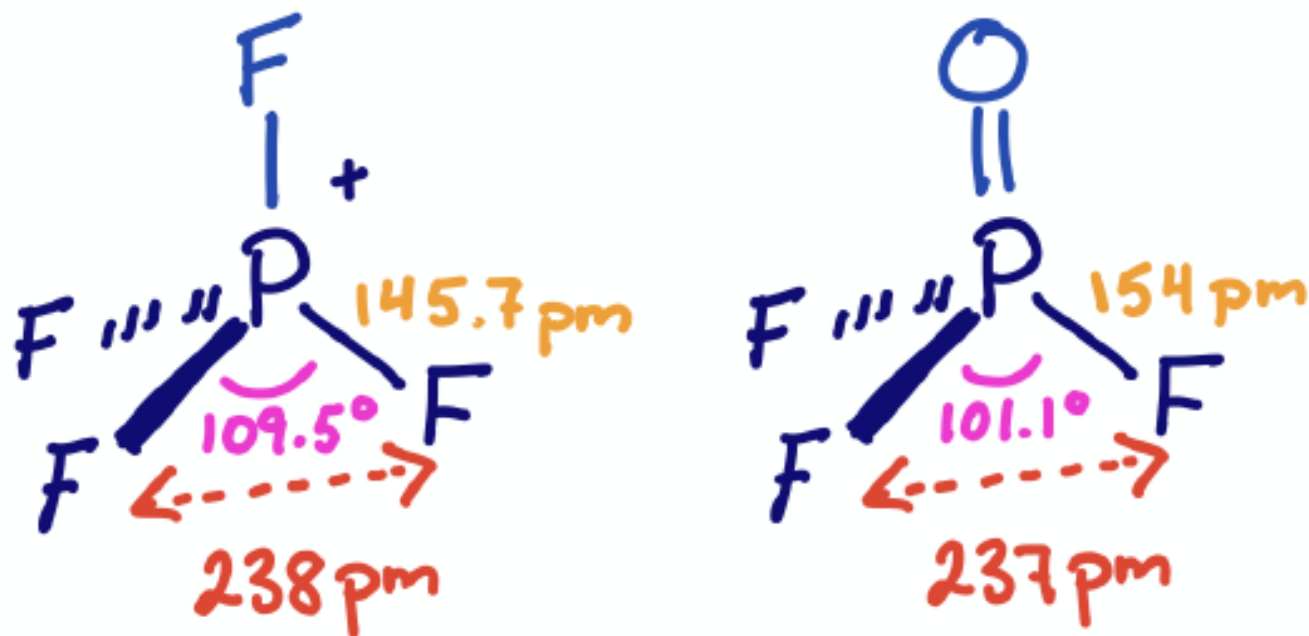
Received October 6, 2003

The aim of this paper was to investigate why the geometries of nonmetal hydrides are often not in accordance with the VSEPR model. From a consideration of interligand distances in a variety of BX_4 , CX_4 , and NX_4 molecules where X is a ligand or a lone pair and in which there are at least two H ligands we have shown that the hydrogen ligands are essentially close-packed. For each of the central atoms we have obtained a value for the ligand radius of hydrogen. These radii decrease with decreasing negative charge and increasing positive charge of the hydrogen ligand as the electronegativity of the central atom increases, as has been found previously for other ligands such as F and Cl. We show that ligand–ligand interactions are an important factor in determining bond angles in hydrides and that the ligand close-packing (LCP) model gives a better explanation of bond angles than the VSEPR model according to which bond angles depend on the electronegativity of the ligand rather than on its size. For example, although the very small angles in PH_3 and SH_2 are not in accord with the VSEPR model, they are consistent with the LCP model in that they are a consequence of the small size of hydrogen ligands which are pushed together by the lone pairs until they are almost close-packed.

Ligand Close-Packing (LCP)

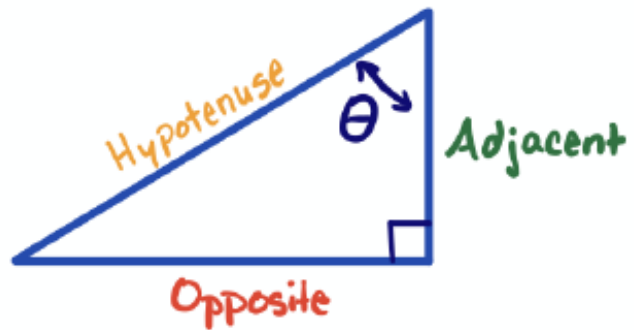
- LCP se concentra em repulsões entre **átomos ligantes**;
- O modelo LCP assume que os ligantes se **"compactam"** o mais próximo possível em torno de um átomo central.
- Para um conjunto específico de ligantes em torno de um átomo central específico, as distâncias **ligante-ligante são constantes**.

Limitações e Excessões

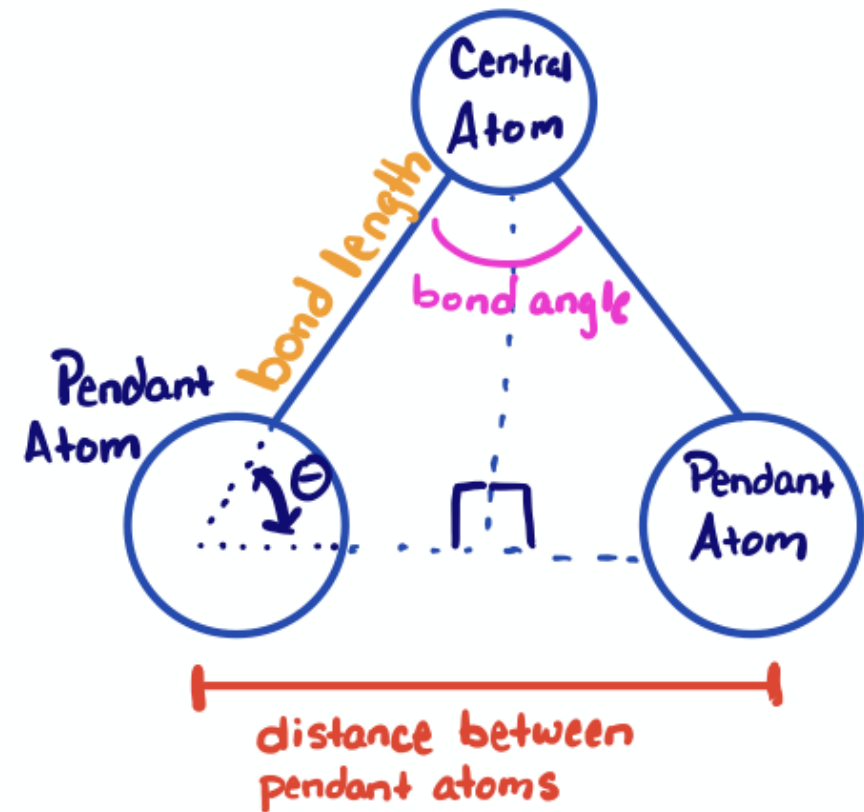


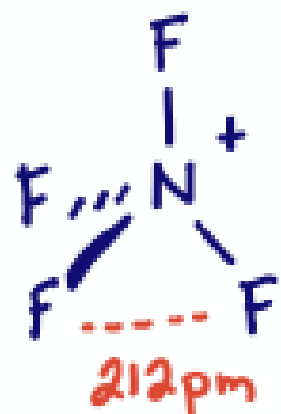
Há uma série de exceções aparentes ao modelo VSEPR, a maioria das quais pode ser classificada devido às **interações ligante-ligante**

- é razoável substituir a regra de eletronegatividade do modelo VSEPR original pela regra de que os ângulos de ligação aumentam com o tamanho do ligante.
- o modelo LCP adiciona um aspecto semiquantitativo ao modelo VSEPR



$$\begin{aligned}\sin \theta &= \frac{\text{opposite}}{\text{hypotenuse}} \\ \cos \theta &= \frac{\text{adjacent}}{\text{hypotenuse}} \\ \tan \theta &= \frac{\text{opposite}}{\text{adjacent}}\end{aligned}$$



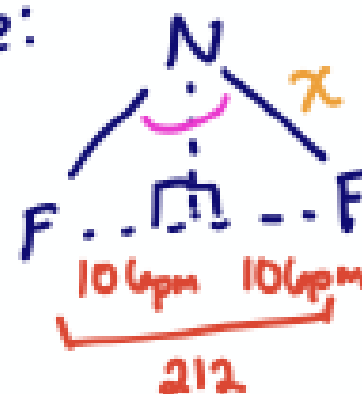


$$\sin \theta = \frac{\text{opposite}}{\text{hypotenuse}}$$

$$\sin\left(\frac{1}{2} \cdot 109.5^\circ\right) = \frac{106 \text{ pm}}{x}$$

$$x = 130 \text{ pm}$$

Triangle:



$$\sin \theta = \frac{\text{opposite}}{\text{hypotenuse}}$$

$$\sin\left(\frac{1}{2} \cdot 102.3^\circ\right) = \frac{106 \text{ pm}}{x}$$

$$x = 136 \text{ pm}$$

- TEORIA DA LIGAÇÃO DE VALÊNCIA

- TEORIA DA LIGAÇÃO DE VALÊNCIA

- TEORIA DA LIGAÇÃO DE VALÊNCIA

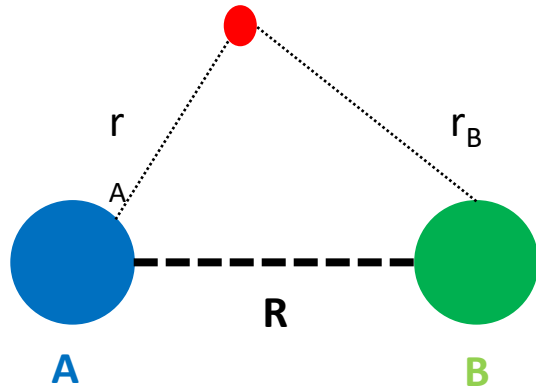
- TEORIA DA LIGAÇÃO DE VALÊNCIA

Orbitais Moleculares de Moléculas Diatômicas

A Origem dos Orbitais Atômicos

• H_2^+

$$\hat{H}_e \Psi_e = E_e \Psi_e$$



$$1s_A \equiv (a_0)^{-3/2} \pi^{-1/2} e^{-r_A/a_0}$$

$$1s_B \equiv (a_0)^{-3/2} \pi^{-1/2} e^{-r_B/a_0}$$



$$\hat{H} = \hat{K}_N + \hat{K}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee}$$

$$\hat{H}_e = \hat{K}_e + \hat{V}_{NN} + \hat{V}_{Ne}$$

$$\Phi = c_A 1s_A + c_B 1s_B$$

$$\hat{H}_e = \frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\epsilon_0 R} - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B}$$

A Origem dos Orbitais Atômicos

Densidade de Probabilidade

$$\Phi = c_A 1s_A + c_B 1s_B$$

$$\Phi^2 = (c_A 1s_A + c_B 1s_B)^2$$

$$\Phi^2 = c_A^2 (1s_A)^2 + c_B^2 (1s_B)^2 + 2c_A c_B 1s_A 1s_B$$

$$W = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau} \quad \text{Integral Variacional}$$

$$\frac{dW}{dc_A} = 0 = \frac{dW}{dc_B} \quad \text{São gerados dois conjuntos de coeficiente } c_A \text{ e } c_B.$$

Devido a simetria da molécula

$$c_B = c_A$$

$$c_B = -c_A$$

$$\Phi_+ = c_A (1s_A + 1s_B)$$

$$\Phi_+^2 = c_A^2 (1s_A^2 + 1s_B^2 + 2 \cdot 1s_A 1s_B)$$

$$\Phi_- = c_A (1s_A - 1s_B)$$

$$\Phi_-^2 = c_A'^2 (1s_A^2 + 1s_B^2 - 2 \cdot 1s_A 1s_B)$$

Condição de Normalização

$$\int \Psi^* \Psi d\tau = 1$$

$$\int \Phi_+^2 d\tau = 1$$

$$c_A^2 \left(\int 1s_A^2 d\tau + \int 1s_B^2 d\tau + \int 2 \cdot 1s_A 1s_B \right) = 1$$

$$S \equiv \int 2 \cdot 1s_A 1s_B$$

Integral de Sobreposição

$$c_A^2 (1 + 1 + 2S) = 1$$

$$\longrightarrow c_A = (2 + 2S)^{-1/2}$$

$$c_A'^2 (1 + 1 - 2S) = 1$$

$$\longrightarrow c_A' = (2 - 2S)^{-1/2}$$

A Origem dos Orbitais Atômicos

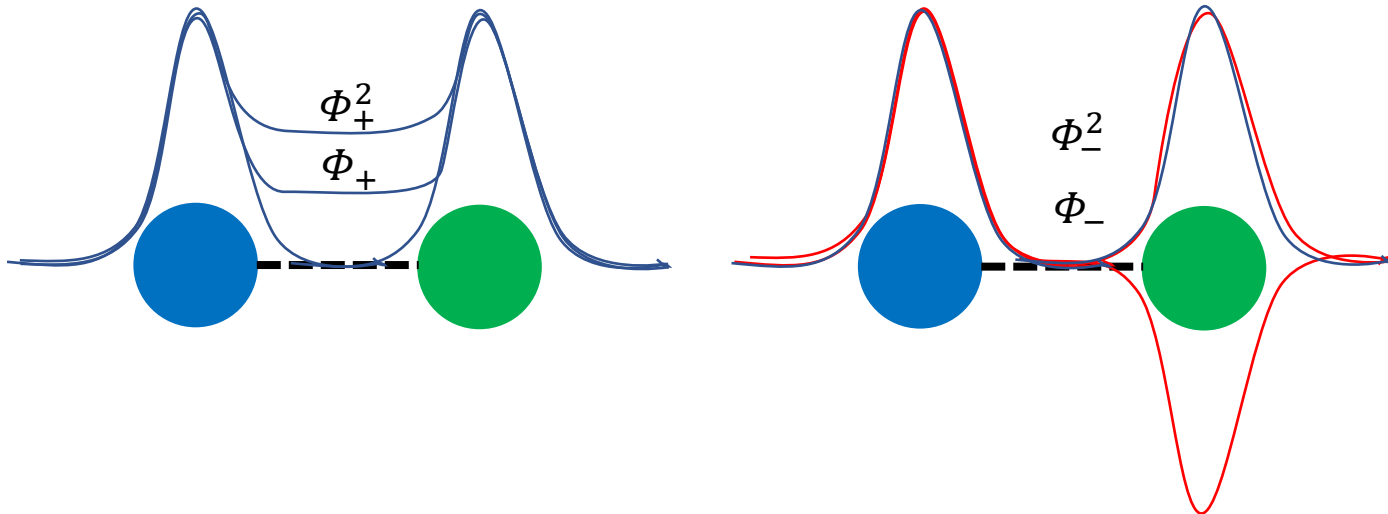
$$\Phi_+ = c_A(1s_A + 1s_B)$$

$$\Phi_- = c_A(1s_A - 1s_B)$$

$$\Phi_+ = (2 + 2S)^{-1/2} (1s_A + 1s_B)$$

$$\Phi_- = (2 + 2S)^{-1/2} (1s_A - 1s_B)$$

OM-CLOA



$$\hat{H}_e \Psi_e = E_e \Psi_e$$

$$\Phi_+ = (2 + 2S)^{-1/2} (1s_A + 1s_B)$$

$$\Phi_- = (2 + 2S)^{-1/2} (1s_A - 1s_B)$$

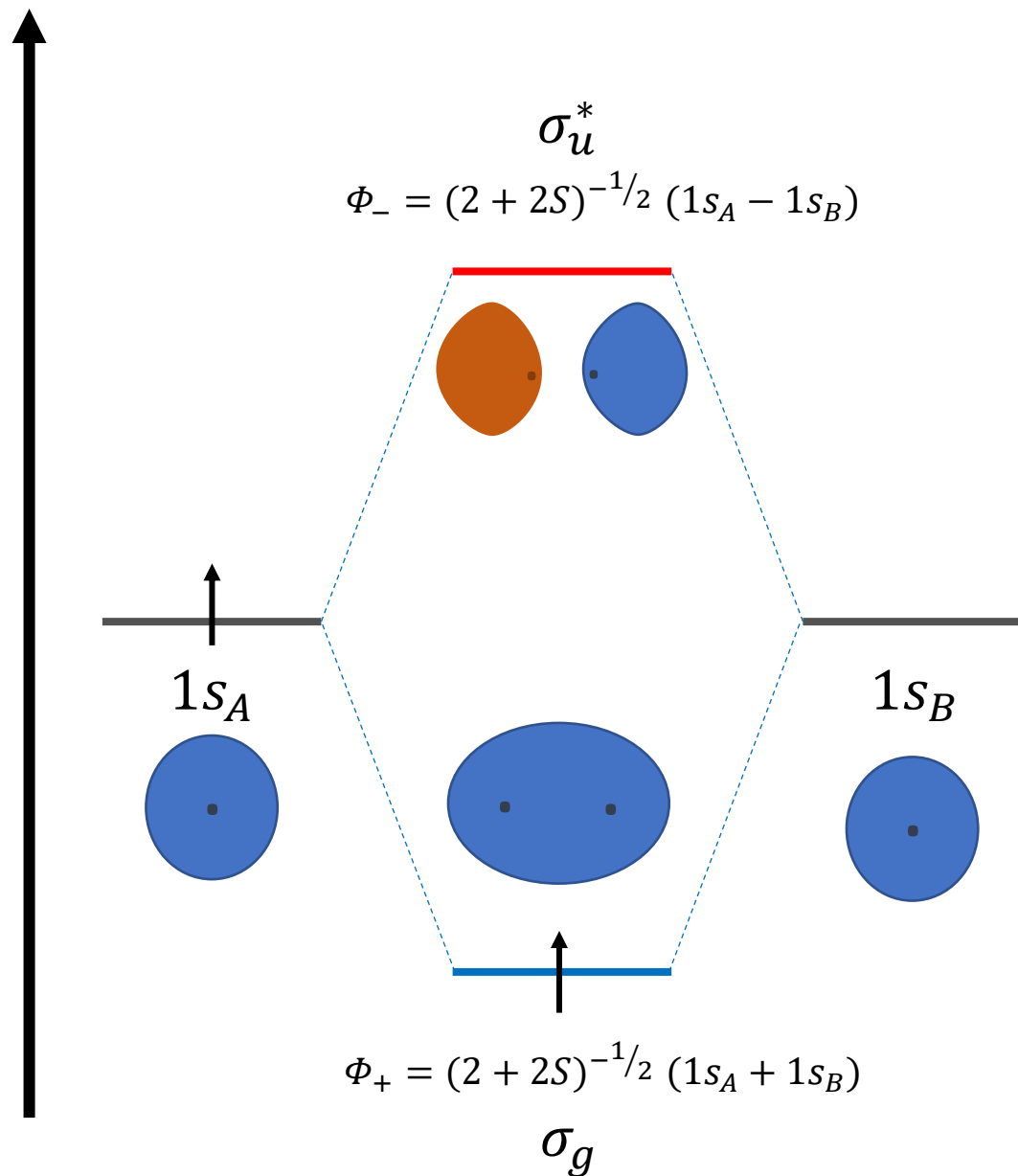
$$E_- = E_{H1s} + \frac{j_0}{R} - \frac{j - k}{1 - S}$$

$$E_+ = E_{H1s} + \frac{j_0}{R} - \frac{j + k}{1 + S}$$

$$s = \int \Phi_A \Phi_B d\tau \quad \text{Integral de Sobreposição}$$

$$j = j_0 \int \frac{\Phi_A^2}{r_B} d\tau$$

$$k = \int \frac{\Phi_A \Phi_B}{r_B} d\tau$$



Orbital ligante	→	Energia relativa
Orbital antiligante		
Orbital σ	→	Simetria ao longo do eixo internuclear
Orbital π		
Orbital "gerade"	→	Simetria ao longo do centro de inversão
Orbital "ungerade"		