



QUÍMICA ARISTOCRÁTICA: ESPÉCIES METAESTÁVEIS DE GASES NOBRES

Thiago Messias Cardozo

Instituto de Química - UFRJ

Os Gases Nobres

Periodic Table of the Elements

1 H Hydrogen 1.008	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012
11 Na Sodium 22.990	12 Mg Magnesium 24.305
19 K Potassium 39.998	20 Ca Calcium 40.078
21 Sc Scandium 44.956	22 Ti Titanium 47.88
23 V Vanadium 50.942	24 Cr Chromium 51.996
25 Mn Manganese 54.938	26 Fe Iron 55.933
27 Co Cobalt 58.933	28 Ni Nickel 58.693
29 Cu Copper 63.546	30 Zn Zinc 65.39
31 Ga Gallium 69.732	32 Ge Germanium 72.61
33 As Arsenic 74.992	34 Se Selenium 78.09
35 Br Bromine 84.80	36 Kr Krypton 83.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62
39 Y Yttrium 88.906	40 Zr Zirconium 91.224
41 Nb Niobium 92.906	42 Mo Molybdenum 95.94
43 Tc Technetium 98.907	44 Ru Ruthenium 101.07
45 Rh Rhodium 102.906	46 Pd Palladium 106.42
47 Ag Silver 107.868	48 Cd Cadmium 112.411
49 In Indium 113.818	50 Sn Tin 114.818
51 Sb Antimony 121.760	52 Te Tellurium 126.904
53 I Iodine 131.29	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327
57-71 La Lanthanum 138.906	72 Hf Hafnium 178.49
73 Ta Tantalum 180.948	74 W Tungsten 183.85
75 Re Rhenium 186.207	76 Os Osmium 190.23
77 Ir Iridium 192.22	78 Pt Platinum 195.08
79 Au Gold 196.967	80 Hg Mercury 200.59
81 Tl Thallium 204.383	82 Pb Lead 207.2
83 Bi Bismuth 208.980	84 Po Polonium [208.982]
85 At Astatine 209.987	86 Rn Radium 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025
89-103 Ac Actinium 227.028	104 Rf Rutherfordium [261]
105 Db Dubnium [262]	106 Sg Seaborgium [266]
107 Bh Bohrium [266]	108 Hs Hassium [269]
109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]
111 Rg Roentgenium [272]	112 Cn Copernicium [277]
113 Uut Ununtrium unknown	114 Fl Flerovium [289]
115 Uup Ununpentium unknown	116 Lv Livermorium [298]
117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown
58 Ce Cerium 140.115	59 Pr Praseodymium 140.908
60 Nd Neodymium 144.24	61 Pm Promethium 144.913
62 Sm Samarium 150.36	63 Eu Europium 151.966
64 Gd Gadolinium 157.25	65 Tb Terbium 158.925
66 Dy Dysprosium 162.50	67 Ho Holmium 164.930
68 Er Erbium 167.26	69 Tm Thulium 168.934
70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
89 Ac Actinium 227.028	90 Th Thorium 232.038
91 Pa Protactinium 231.036	92 U Uranium 238.029
93 Np Neptunium 237.048	94 Pu Plutonium 244.064
95 Am Americium 243.061	96 Cm Curium 247.070
97 Bk Berkelium 247.070	98 Cf Californium 251.080
99 Es Einsteinium [254]	100 Fm Fermium 257.095
101 Md Mendelevium 258.1	102 No Nobelium 259.101
103 Lr Lawrencium [262]	

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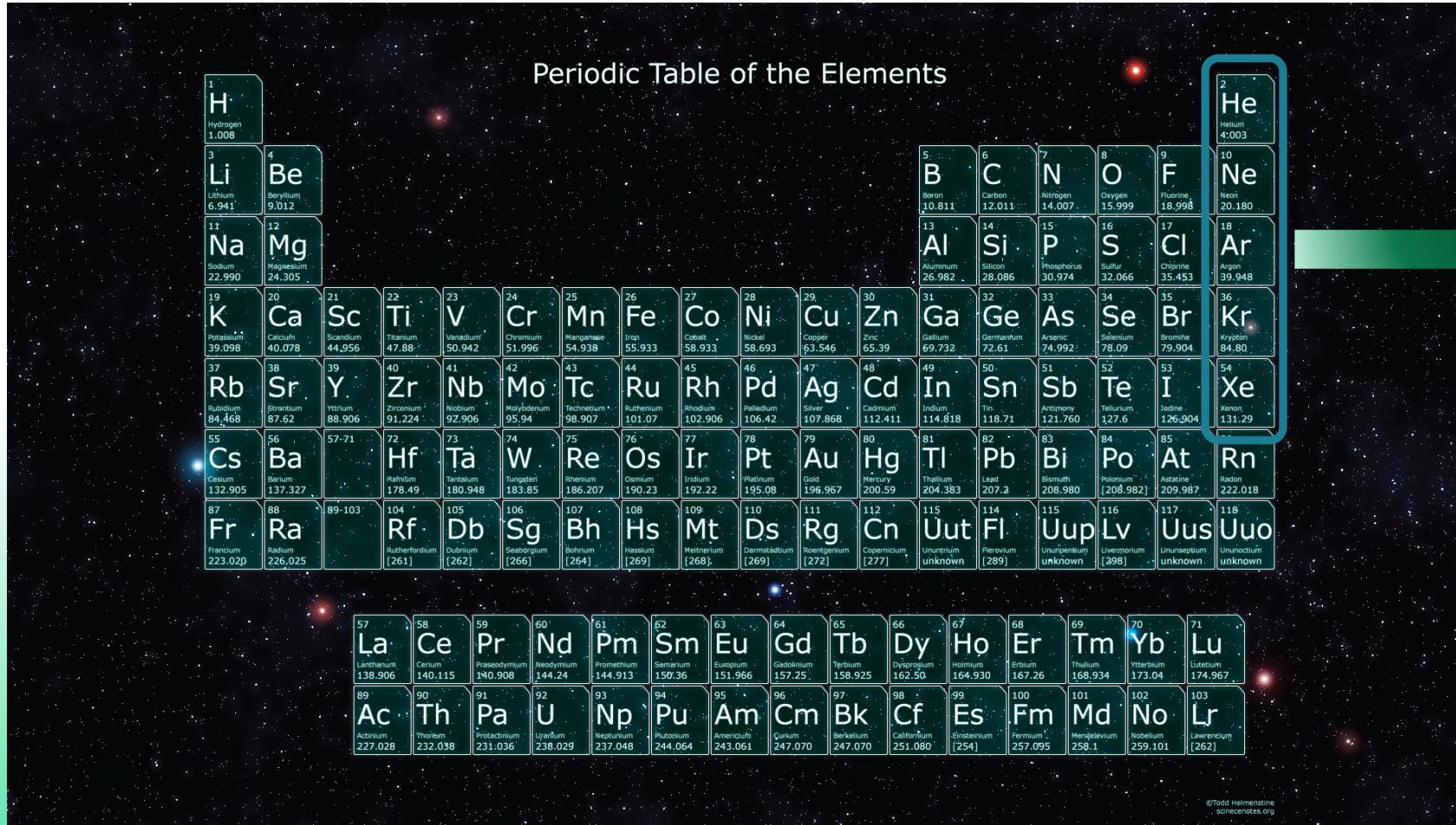
Os Gases Nobres



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117	Uuo	Ununoctium unknown
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63	Eu	Europium 151.966
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Os Gases Nobres



Os Gases Nobres

GASES MONOATÔMICOS,
INCOLORES E
“QUÍMICAMENTE INERTES”

Os Gases Nobres

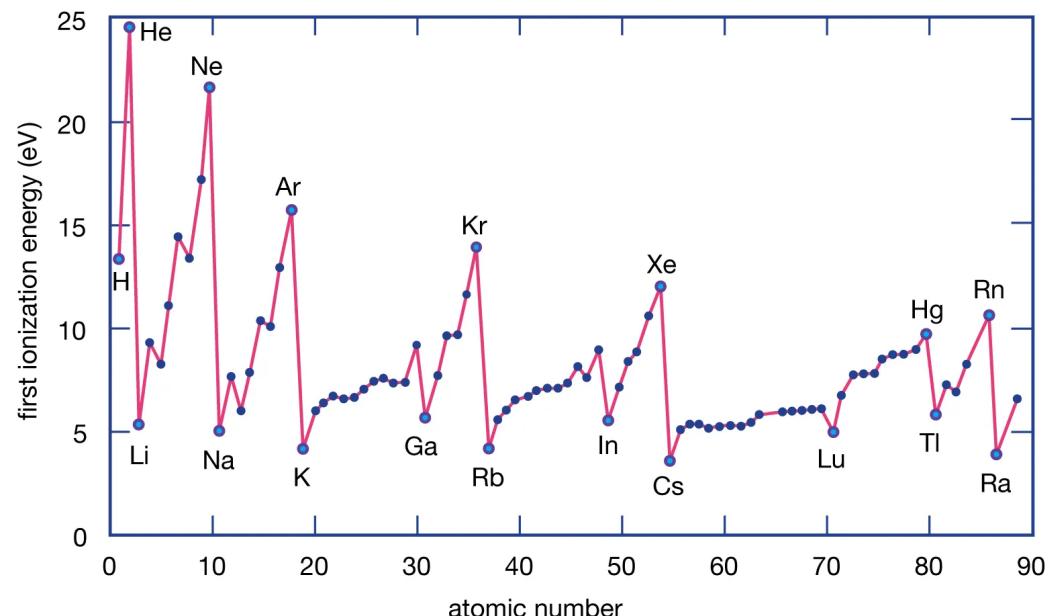
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MAIORES POTENCIAIS DE
IONIZAÇÃO NOS PERÍODOS
RESPECTIVOS

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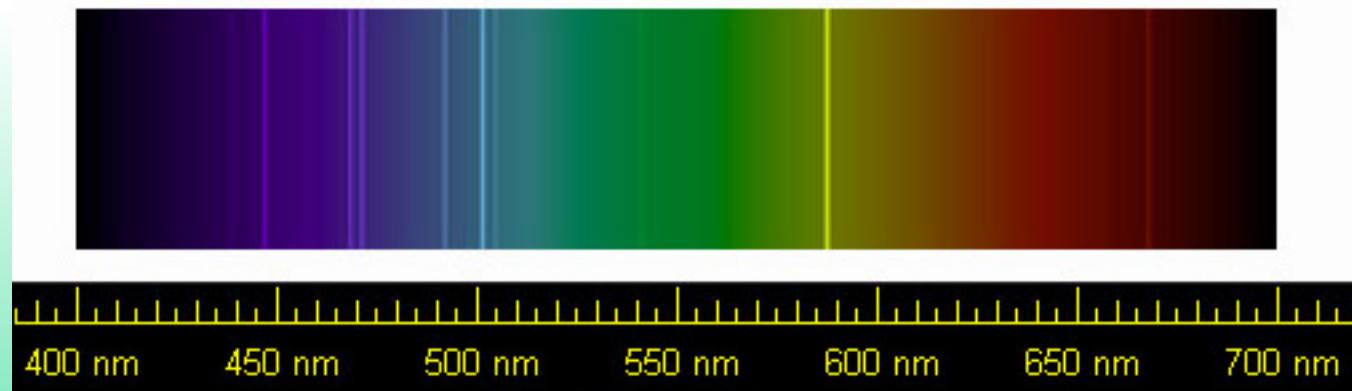
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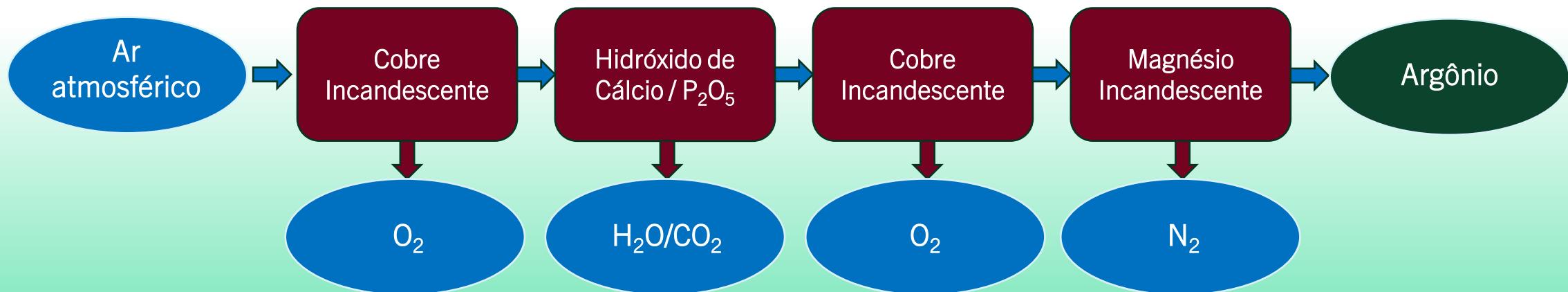
Os Gases Nobres

- 1868 - Detecção do **Helio** no espetro
solar por Jansen e Lockyer



Os Gases Nobres

- 1894 - Isolamento do **Argônio**, “O Preguiçoso”, por Ramsay e Rayleigh.



Os Gases Nobres

- 1895-1898 - Isolamento dos elementos He, Ne, Kr e Xe por Ramsay.

- 1899 - Obtenção do Radônio por Rutherford e Owens.

- 1902 – Isolamento e caracterização do Radônio por Soddy e... Ramsay.

A Química dos Gases Nobres

- 1962 - Bartlett



A Química dos Gases Nobres

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$$\text{P.I.}(\text{O}_2) = 12.1 \text{ eV}$$

A Química dos Gases Nobres

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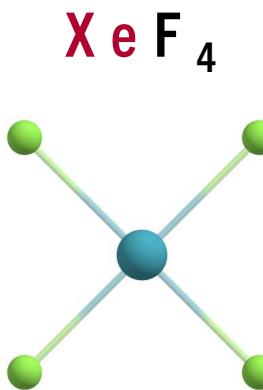
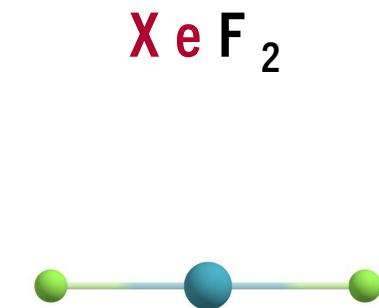


A Química dos Gases Nobres

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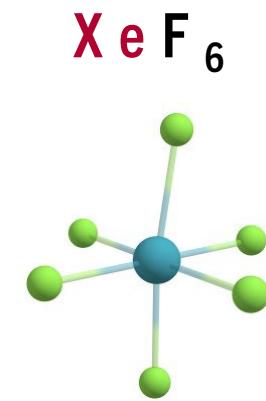
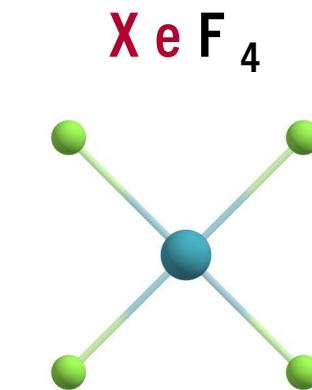
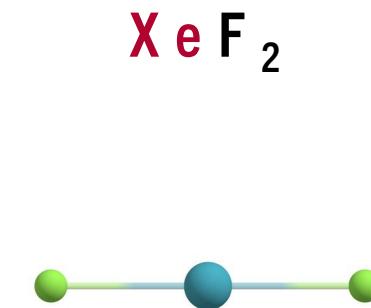


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A Química dos Gases Nobres

- 1925 – Hoggness e Lund

Obtenção de HHe^+ via impacto de elétrons

A Química dos Gases Nobres

- 1925 – Hoggness e Lund

Obtenção de HHe^+ via impacto de elétrons

- 1961 – Giese e Maier



A Química dos Gases Nobres

- 1925 – Högness e Lund

Obtenção de HHe^+ via impacto de elétrons

- 1961 – Giese e Maier



- 1963 – Munson, Franklin, Field

Obtenção de espécies $(\text{Ng})(\text{Ng}')^+$

Compostos de Inserção

X-**N**g-Y com Ng=He, Ne são particularmente difíceis de se obter.

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$$P.I.(He) = 24.59 \text{ eV}$$

$$A.E.(He) = 0.08 \text{ eV}$$

$$\chi(He) = 12.30 \text{ eV}$$

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$$P.I.(He^+) = 54.42 \text{ eV}$$

$$A.E.(He^+) = 24.59 \text{ eV}$$

$$\chi(He^+) = 39.51 \text{ eV}$$



Compostos de Inserção

Ng⁺-Ng-Ng⁺

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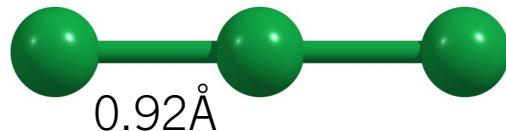


Metodologia

- Cálculos exploratórios: DSD-BLYP/aug-cc-pVTZ
- Confirmação: CCSD(T)/aug-cc-pVTZ
- Análise da Ligação: SCGVB/cc-pVTZ
 - GPF Energy Partitioning

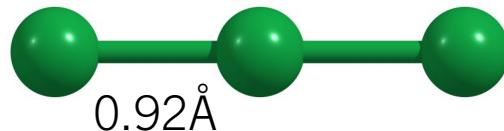
O Ion Molecular He_3^{2+}

- GEOMETRIA LINEAR, $D_{\infty\nu}$



O Íon Molecular He_3^{2+}

- GEOMETRIA LINEAR, $D_{\infty\nu}$



- MODOS NORMAIS:

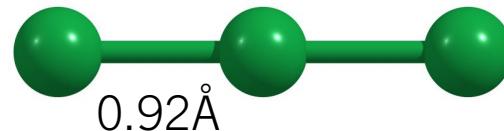
- ESTIRAMENTO ASSIMÉTRICO ($\tilde{\nu} = 2213.1 \text{ cm}^{-1}$)

- ESTIRAMENTO SIMÉTRICO ($\tilde{\nu} = 1187.7 \text{ cm}^{-1}$)

- DEFORMAÇÃO ANGULAR (DEG.) ($\tilde{\nu} = 942.6 \text{ cm}^{-1}$)

O Íon Molecular He_3^{2+}

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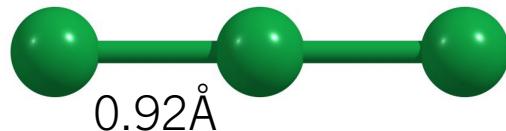
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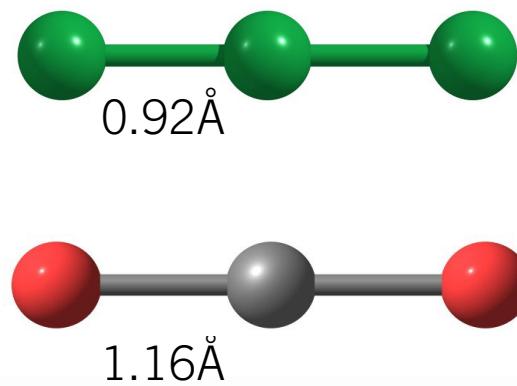
O Íon Molecular He_3^{2+}

- Comparação com CO_2

Propriedades calculadas com CCSD(T)/cc-pV6Z

Espécie	v [asym. stretch] (cm ⁻¹)	v [sym. stretch] (cm ⁻¹)	v [bending] (cm ⁻¹)
He_3^{2+}	2213.1	1187.7	942.6
CO_2	2350 ^(a)	1330 ^(a)	667 ^(a)

(a) NIST



O Íon Molecular He_3^{2+}

- Canais de Dissociação

Propriedades calculadas com CCSD(T)/aug-cc-pVTZ

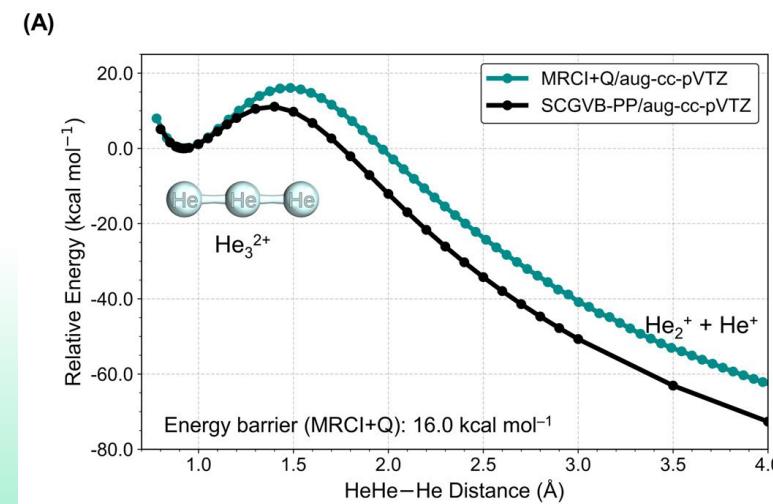
Canal	Energia de Dissociação (kcal/mol)
$\text{He}_3^{2+} \rightarrow \text{He} + 2\text{He}^+$	-96.97
$\text{He}_3^{2+} \rightarrow \text{He}^+ + \text{He}_2^+$	-151.10
$\text{He}_3^{2+} \rightarrow \text{He} + \text{He}_2^{2+}$	108.89

O Íon Molecular He_3^{2+}

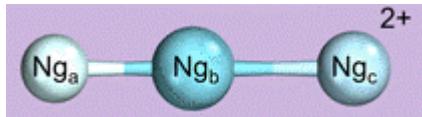
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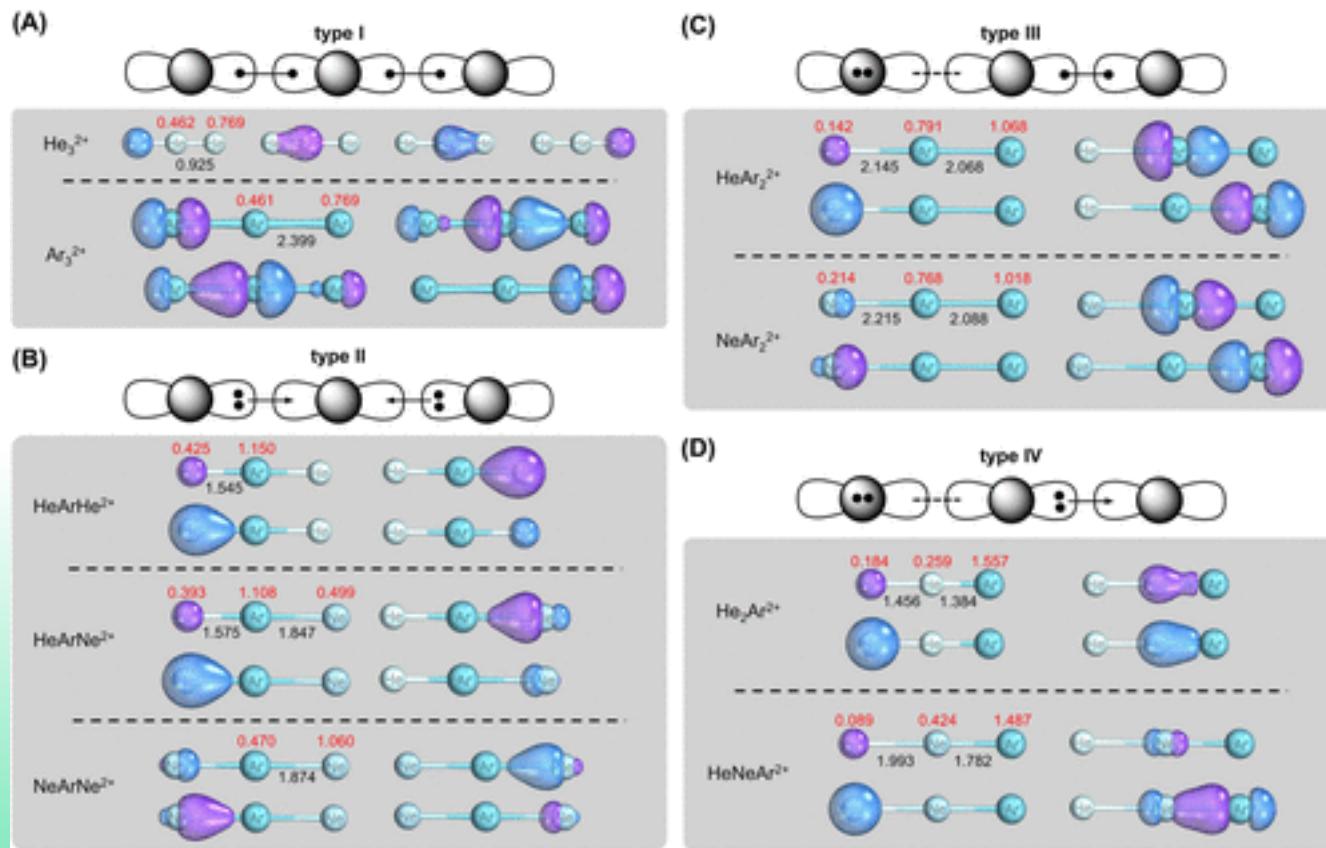
Outras Espécies



Propriedades calculadas com CCSD(T)/aug-cc-pVTZ

Espécie	Distâncias de Ligação (Å)		Gap S-T (eV)	v [asym. stretch] (cm ⁻¹)	v [sym. stretch] (cm ⁻¹)	v [angular] (cm ⁻¹)
	Ng _a -Ng _b	Ng _b -Ng _c				
He ₃ ²⁺	0.93	0.93	6.43	2207.9	1169.8	942.9
He ₂ Ne ²⁺	-	-				
He ₂ Ar ²⁺	1.46	1.38	2.28	1194.9	429.2	265.2
HeNeAr ²⁺	1.99	1.78	0.61	476.9	253.3	95.3
HeArHe ²⁺	1.55	1.55	2.84	995.5	690.9	519.1
HeArNe ²⁺	1.58	1.85	2.20	783.6	477.7	361.5
HeAr ₂ ²⁺	2.15	2.07	2.04	378.4	280.0	122.7
NeHeAr ²⁺	-	-				
NeArNe ²⁺	1.87	1.87	1.72	502.9	394.7	203.1
NeAr ₂ ²⁺	2.22	2.09	2.08	359.3	213.5	108.3
Ar ₃ ²⁺	2.40	2.40	1.55	289.3	118.1	104.0

Os quatro tipos de aristocratas



Orbitais da função de onda SCGVB-PP/aug-cc-pVTZ

Interferência e a Ligação Química

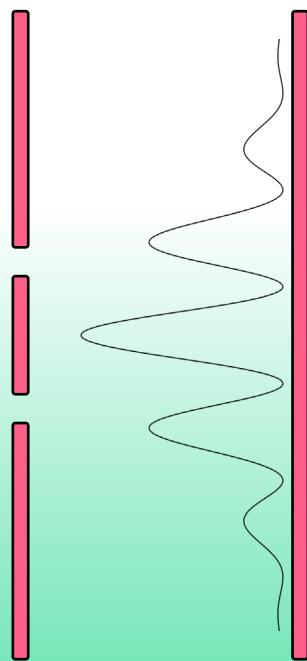
- Ruedenberg, 1962

"The Nature of the Chemical Bond"

Interferência e a Ligação Química

- Ruedenberg, 1962

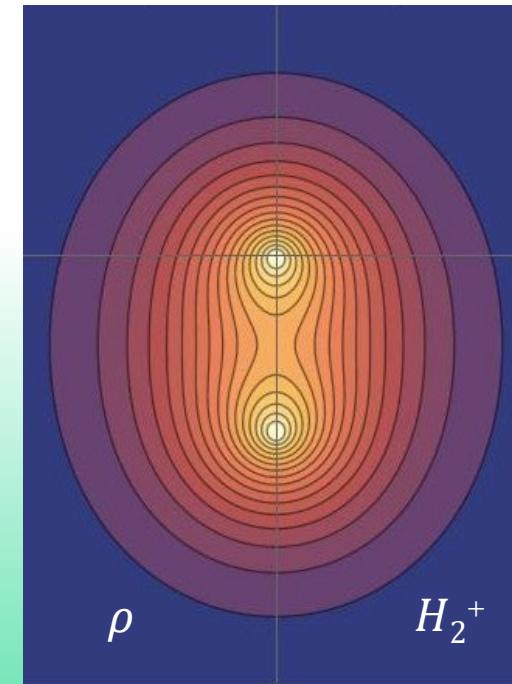
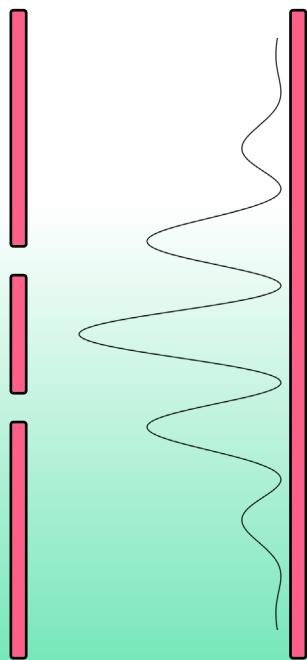
"The Nature of the Chemical Bond"



Interferência e a Ligação Química

- R u e d e n b e r g , 1 9 6 2

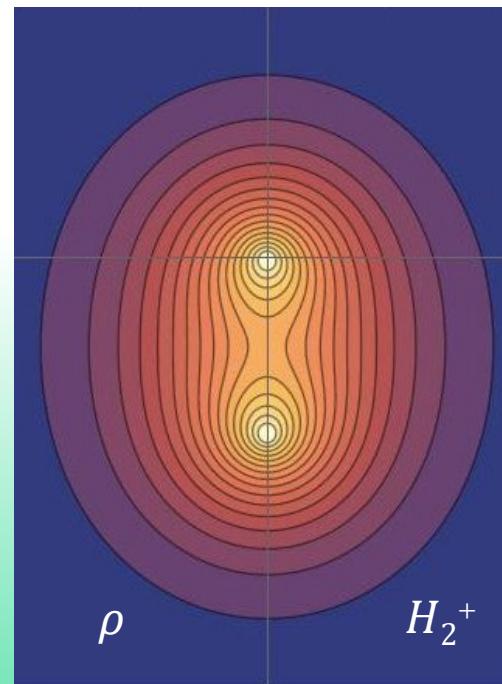
" T h e N a t u r e o f t h e C h e m i c a l B o n d "



Interferência e a Ligação Química

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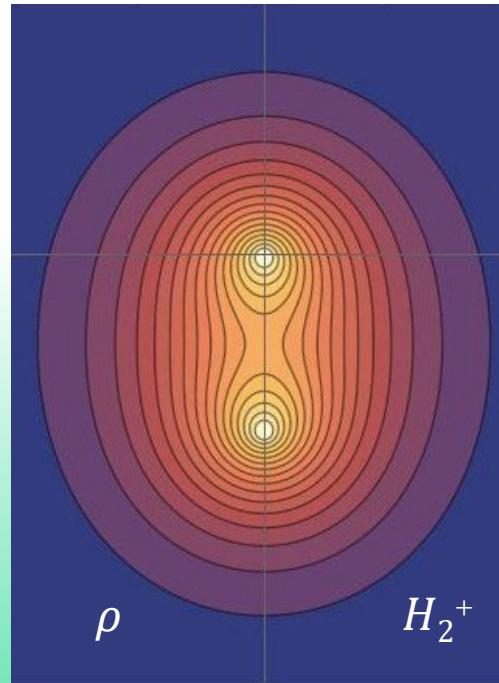
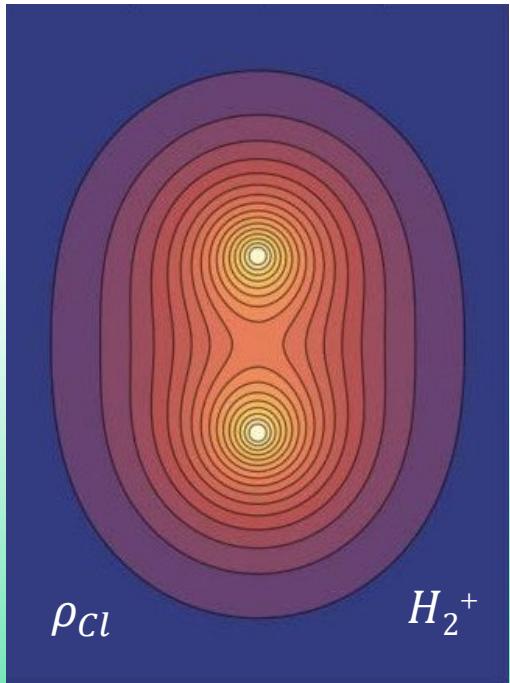
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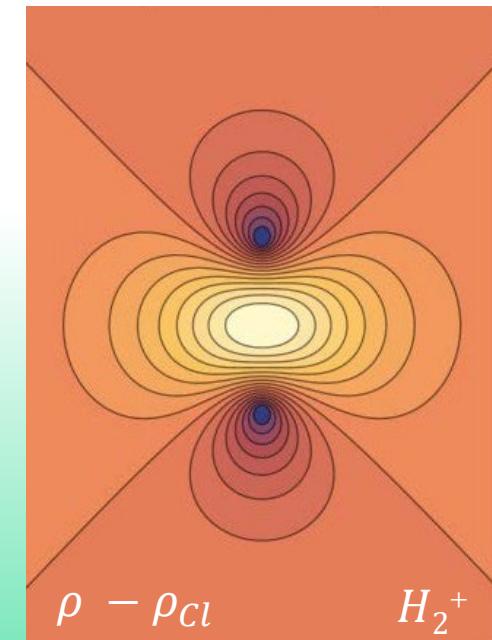
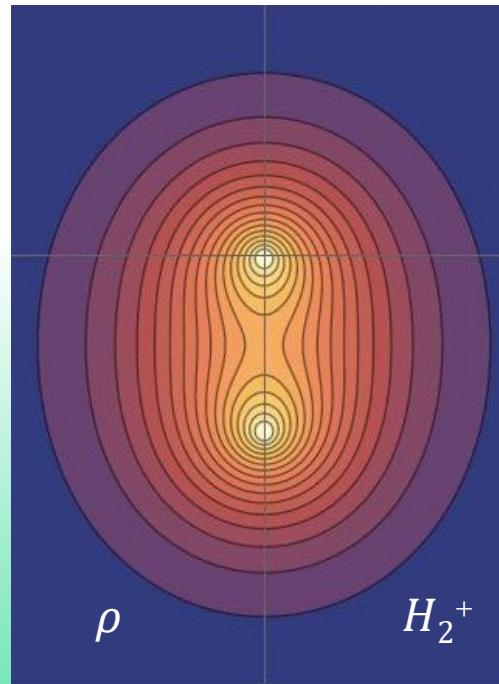
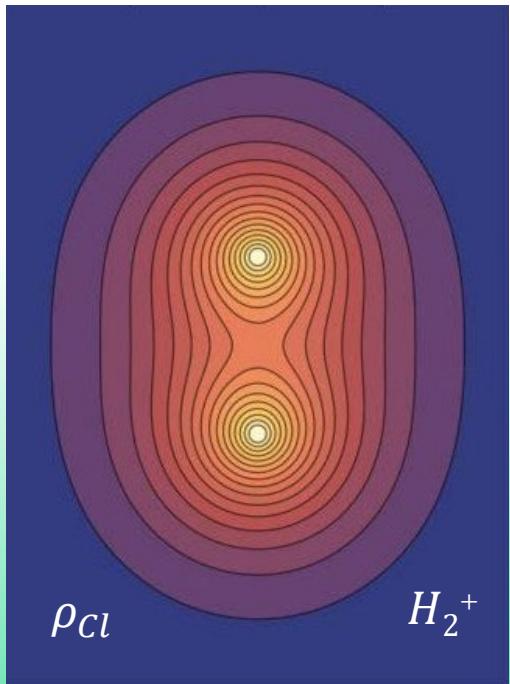
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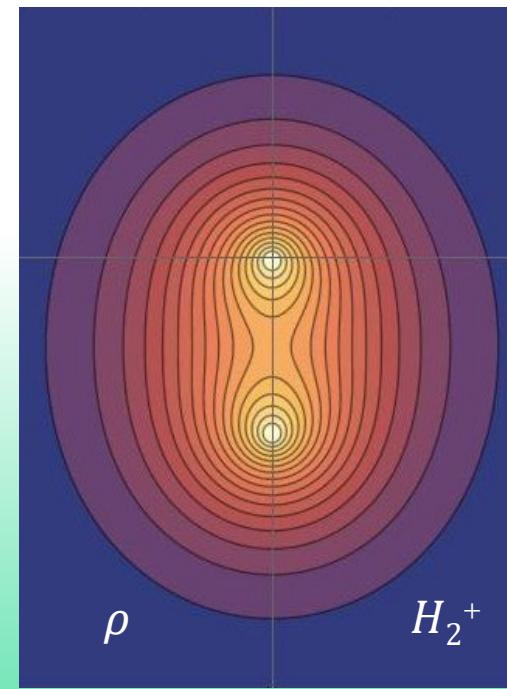
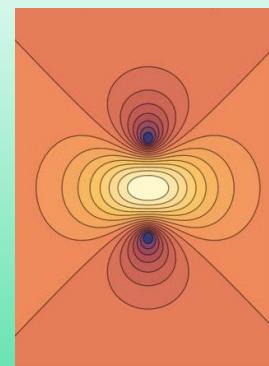
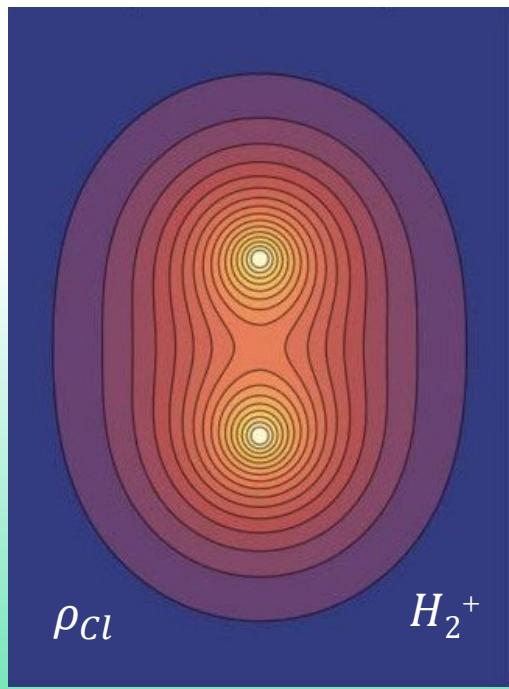
" T h e N a t u r e o f t h e C h e m i c a l B o n d "



Interferência e a Ligação Química

- Ruedenberg, 1962

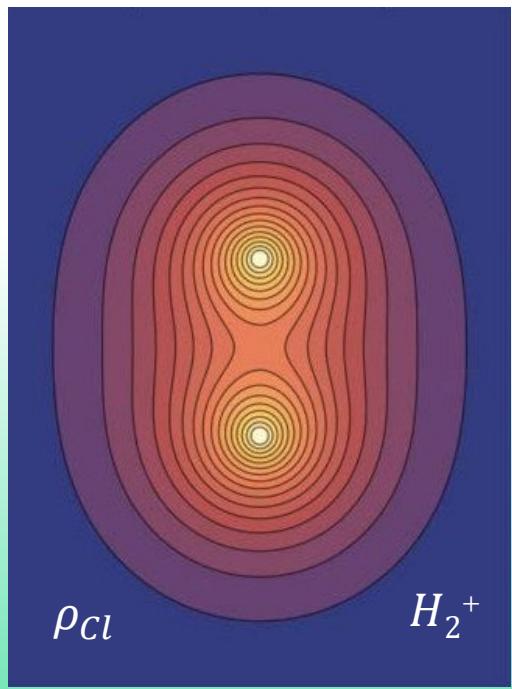
"The Nature of the Chemical Bond"



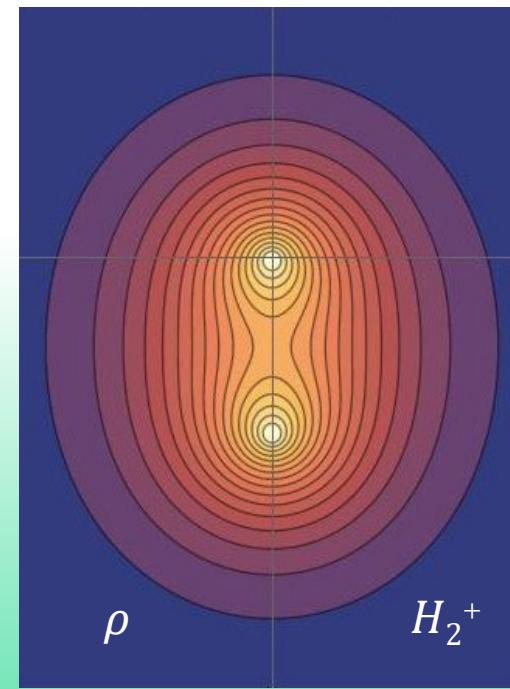
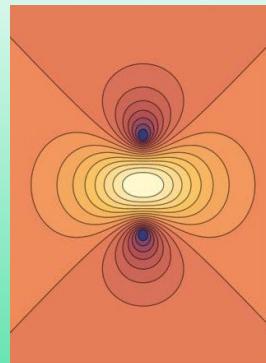
Interferência e a Ligação Química

- R u e d e n b e r g , 1 9 6 2

" T h e N a t u r e o f t h e C h e m i c a l B o n d "



$< T >$ diminui
 $< V >$ aumenta



Interferência no Íon Molecular He_3^{2+}

$$\psi = \frac{1}{\sqrt{2(1 + \xi_{12})}} (\phi_1 + \phi_2) \quad \xi_{12} = \langle \phi_1 | \phi_2 \rangle$$

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$$\rho = \left(\frac{1}{\sqrt{2(1 + \xi_{12})}} (\phi_1 + \phi_2) \right)^2 = \frac{1}{2(1 + \xi_{12})} |\phi_1|^2 + \frac{1}{2(1 + \xi_{12})} |\phi_2|^2 + \frac{1}{(1 + \xi_{12})} \phi_1 \phi_2$$

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$$\rho_{INT} = \frac{1}{(1 + \xi_{12})} \phi_1 \phi_2 - \frac{\xi_{12}}{2(1 + \xi_{12})} [|\phi_1|^2 + |\phi_2|^2]$$

Partição da Interferência

- Decomposição da Densidade

$$\phi_i \phi_j = c \left[|\phi_i|^2 + |\phi_j|^2 \right] + Int(\phi_i, \phi_j)$$

$$\int_{-\infty}^{+\infty} Int(\phi_i, \phi_j) d\tau_1 = 0$$

$$c = \frac{\xi_{12}}{2}$$

$$Int(\phi_i, \phi_j) = \phi_i \phi_j - \frac{\xi_{12}}{2} \left[|\phi_i|^2 + |\phi_j|^2 \right]$$

Matrizes de Densidade Reduzidas

- Matrizes de Densidade Reduzidas de
Primeira e Segunda Ordem

$$\rho(\tau_1; \tau'_1) = N \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \psi^*(\tau_1, \tau_2, \dots, \tau_N) \psi(\tau'_1, \tau_2, \dots, \tau_N) d\tau_2 \dots d\tau_N \quad \text{MDR - 1}$$

$$\rho(\tau_1) = N \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \psi^*(\tau_1, \tau_2, \dots, \tau_N) \psi(\tau_1, \tau_2, \dots, \tau_N) d\tau_2 \dots d\tau_N$$

$$\pi(\tau_1, \tau_2) = N(N-1) \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \psi^*(\tau_1, \tau_2, \tau_3, \dots, \tau_N) \psi(\tau_1, \tau_2, \tau_3, \dots, \tau_N) d\tau_3 \dots d\tau_N \quad \text{MDR - 2}$$

Matrizes de Densidade Reduzidas

- MDR-1 E MDR-2 em uma Base Discreta

$$\rho(1) = \sum_i^N \sum_j^N \phi_i(1)\phi_j(1)p(i|j)$$

$$\pi(1,2) = \sum_i^N \sum_j^N \sum_k^N \sum_l^N \phi_i(1)\phi_j(1)\phi_k(2)\phi_l(2)P(ij|kl)$$

Matrizes de Densidade Reduzidas

- MDR-1 E MDR-2 EM UMA BASE DISCRETA

$$\rho(1) = \sum_i^N \sum_j^N \phi_i(1)\phi_j(1)p(i|j)$$

$$\phi_i\phi_j = c \left[|\phi_i|^2 + |\phi_j|^2 \right] + Int(\phi_i, \phi_j)$$

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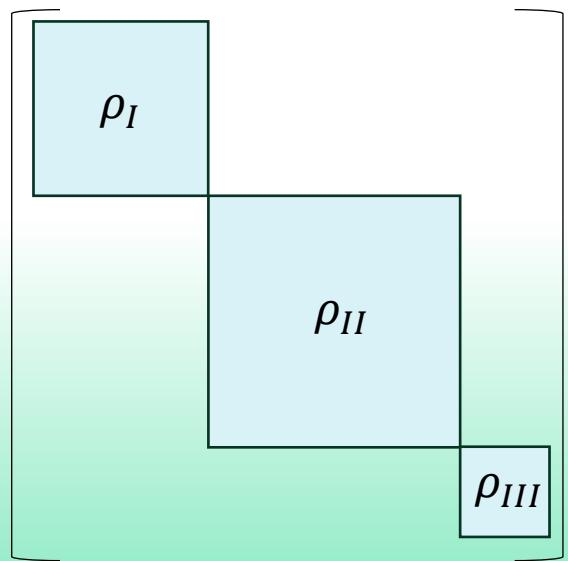
As Funções Produto Generalizadas

$$\psi = \widehat{A}_{inter}\{\psi_I(1, 2, \dots, n_I) \times \psi_{II}(n_I + 1, n_I + 2, \dots, n_{II}) \dots \psi_{NG}(n_{II} + 1, n_{II} + 2, \dots, n_{III})\}$$

As Funções Produto Generalizadas

$$\psi = \hat{A}_{inter}\{\psi_I(1, 2, \dots, n_I) \times \psi_{II}(n_I + 1, n_I + 2, \dots, n_{II}) \dots \psi_{NG}(n_{II} + 1, n_{II} + 2, \dots, n_{III})\}$$

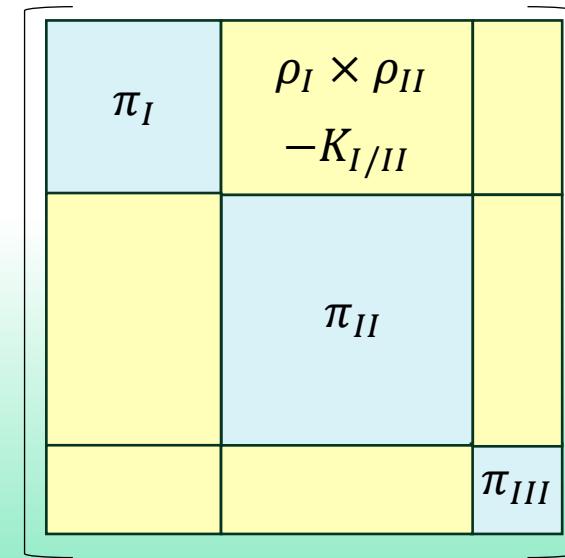
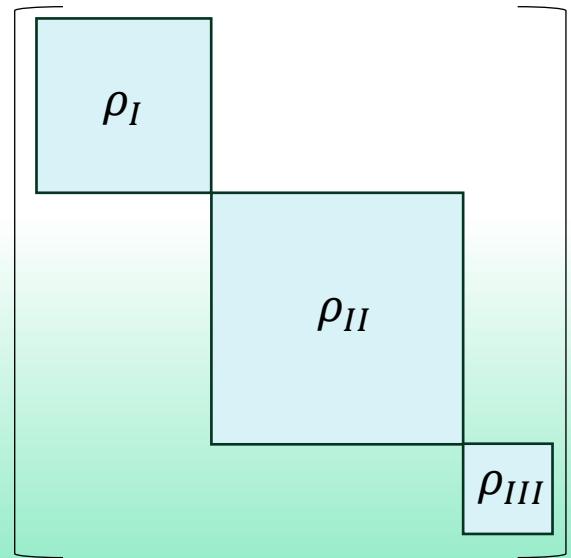
Ex.: G = 3



As Funções Produto Generalizadas

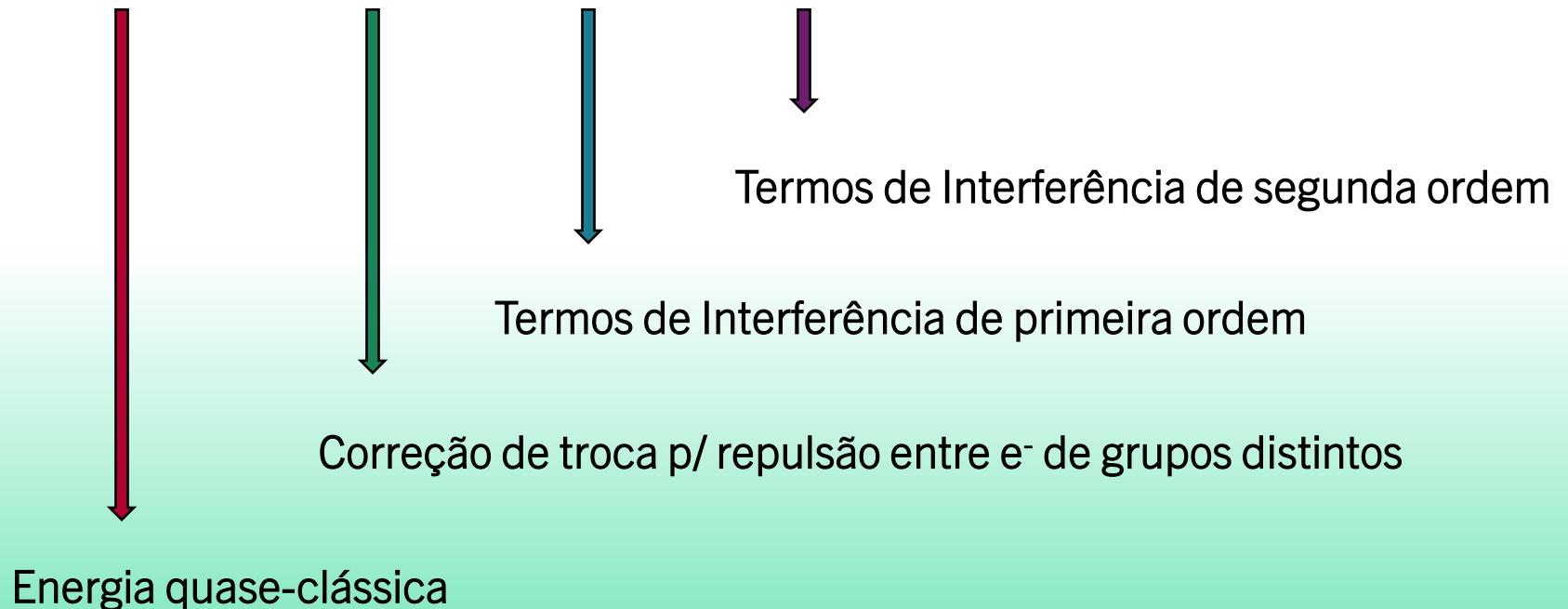
$$\psi = \widehat{A}_{inter}\{\psi_I(1, 2, \dots, n_I) \times \psi_{II}(n_I + 1, n_I + 2, \dots, n_{II}) \dots \psi_{NG}(n_{II} + 1, n_{II} + 2, \dots, n_{III})\}$$

Ex.: G = 3



A Partição de Energia em GPFs

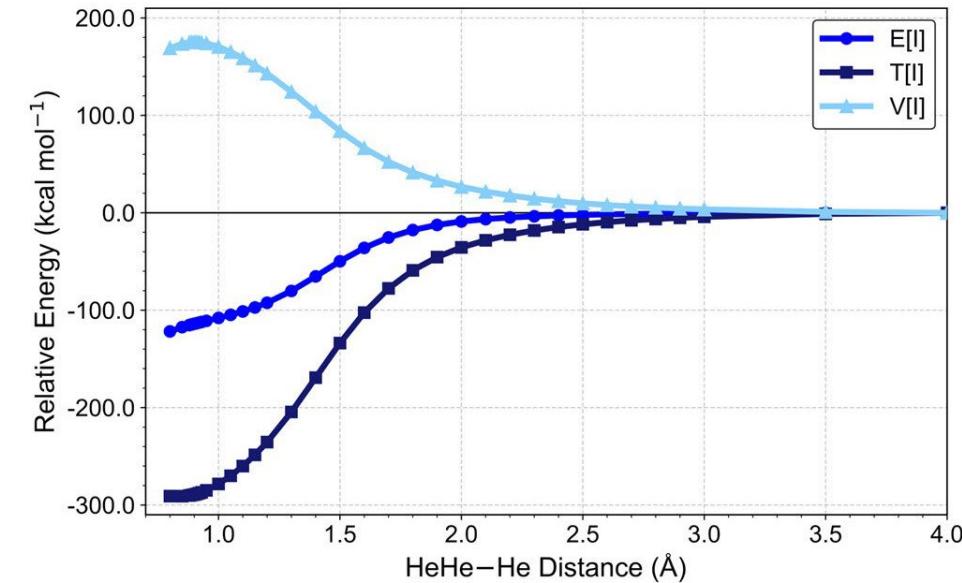
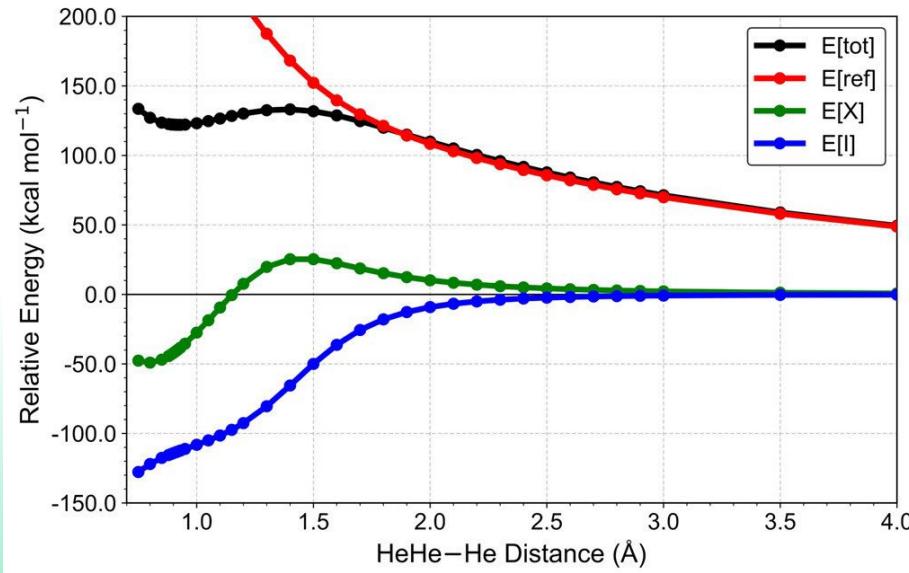
$$E[tot] = E[Ref] + E[X] + E[I] + E[II]$$



A Origem do Poço na SEP do He_3^{2+}

Partição GPF-EP obtida para função de onda SCGVB-PP/aug-cc-pVTZ

b)



Publicações – Gases Nobres



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Chemical Aristocracy: He₃ Dication and Analogous Noble-Gas-Exclusive Covalent Compounds

Lucas Araujo, Felipe Fantuzzi,* and Thiago M. Cardozo*



Cite This: *J. Phys. Chem. Lett.* 2024, 15, 3757–3763



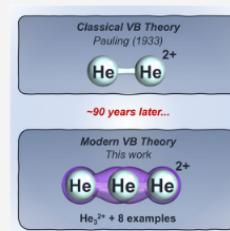
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ABSTRACT: Herein, we predict the first set of covalently bonded triatomic molecular compounds composed exclusively of noble gases. Using a combination of double-hybrid DFT, CCSD(T), and MRCI+Q calculations and a range of bonding analyses, we explored a set of 270 doubly charged triatomics, which included various combinations of noble gases and main group elements. This extensive exploration uncovered nine noble-gas-exclusive covalent compounds incorporating helium, neon, argon, or combinations thereof, exemplified by cases such as He₃²⁺ and related systems. This work brings to light a previously uncharted domain of noble gas chemistry, demonstrating the potential of noble gases in forming covalent molecular clusters.



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Unveiling distinct bonding patterns in noble gas hydrides via interference energy analysis†

Lucas Araujo, ab Marco A. C. Nascimento, a Thiago M. Cardozo *a and Felipe Fantuzzi *c

Received 20th October 2024,
Accepted 4th November 2024

DOI: 10.1039/d4cp04028g

rsc.li/pccp

Despite their apparent simplicity, the helium hydride ion (HeH⁺) and its analogues with heavier noble gas (Ng) atoms present intriguing challenges due to their unusual electronic structures and distinct ground-state heterolytic bond dissociation profiles. In this work, we employ modern valence bond calculations and the interference energy analysis to investigate the nature of the chemical bond in NgH⁺ (Ng = He, Ne, Ar). Our findings reveal that the energy well formation in their ground-state potential energy curves is driven by a reduction in kinetic energy caused by quantum interference, identical to cases of homolytic bond dissociation. However, clear differences in bonding situation emerge: in HeH⁺ and ArH⁺, electron charge transfer leads to Ng⁺-H covalent bonds, while in NeH⁺, a preferred Ne + H⁺ valence bond structure suggests the formation of a dative bond. This study highlights the distinct bonding mechanisms within the NgH⁺ series, showcasing the interplay between quantum interference and quasi-classical effects in molecules featuring noble gases.

Perspectivas

- Cálculo de frequências vibracionais com correções anarmônicas, incluindo acoplamentos entre modos vibracionais;

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- Ampliar análise da ligação nas outras espécies;
- Buscar colaborações para detecção da espécie;

Equipe do Projeto

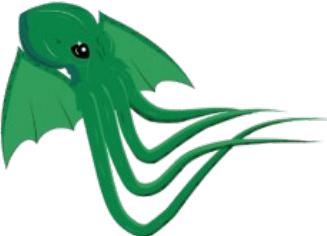


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(RUHR UNIVERSITY,
BOCHUM - GERMANY)



Prof. FELIPE FANTUZZI
(UNIVERSITY OF KENT)

Nosso Grupo

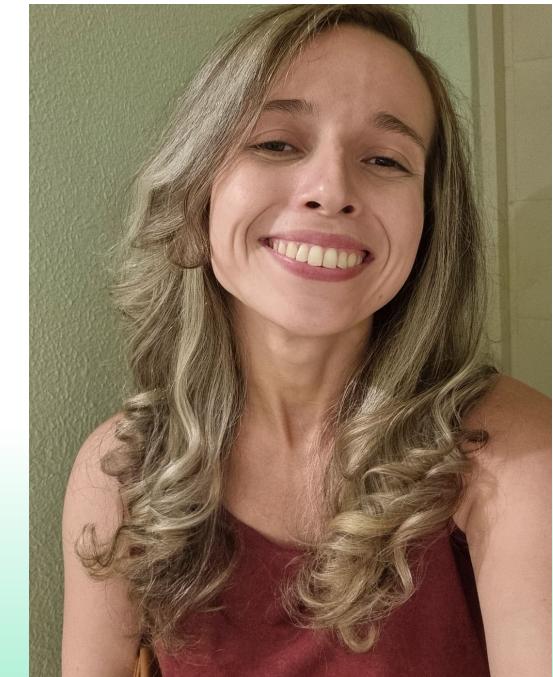


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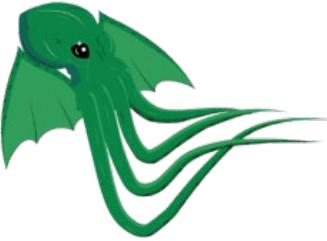
STEVAN MATHEUS (IC)

CÁLCULO DAS
PROPRIADES
ESPECTROSCÓPICAS DO
 HE_3^{2+}

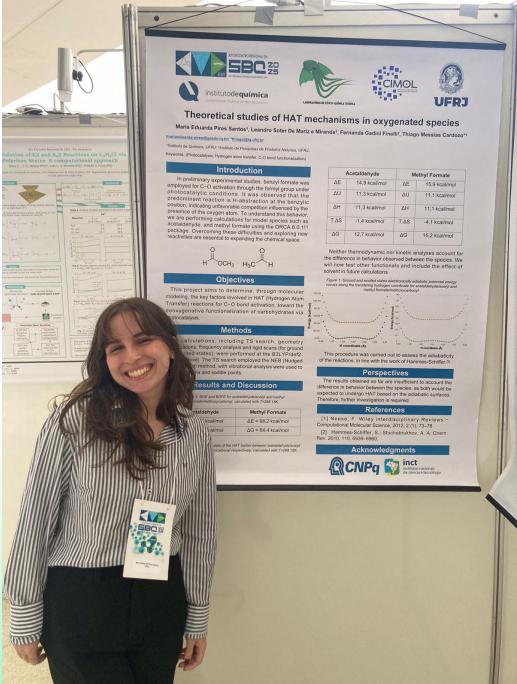


ALANE SOUZA (IC)

Nosso Grupo



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MECANISMOS FOTOCATALÍTICOS NA QUÍMICA DE CARBOIDRATOS

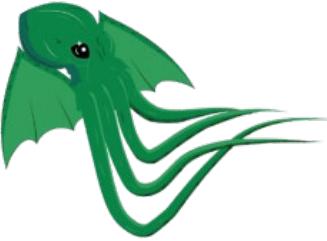
BUSCA DE COMPOSTOS MgC_xN DE INTERESSE ASTROQUÍMICO

MARIA EDUARDA
PIRES (IC)



VICTOR HUGO (IC)

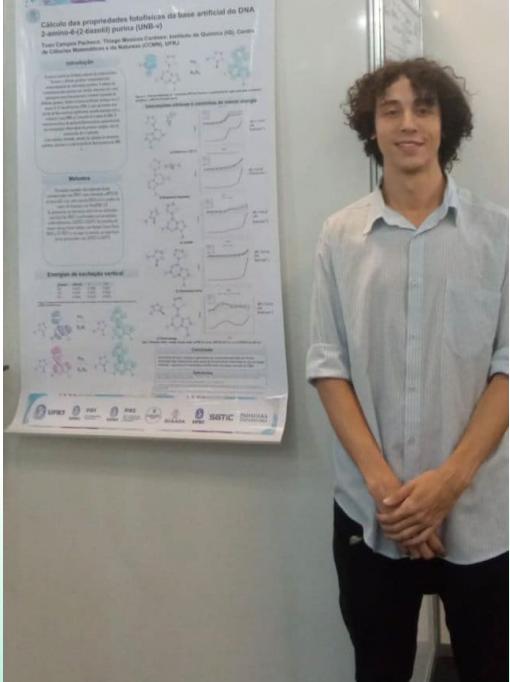
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LABORATÓRIO DE FÍSICO-QUÍMICA TEÓRICA

MECANISMOS DE DESATIVAÇÃO
NÃO-RADIATIVA EM
NUCLEOBASES NÃO-NATURAIS

PROPRIEDADES ÓTICAS NÃO-
LINEARES EM CLUSTERS DE
OURO QUIRAIS



TUAN PACHECO
(MESTRADO)



MARIO GUTFILEN
(MESTRADO)

Agradecimentos



Rede de Teoria, Modelagem e Simulação
de Materiais para Nanotecnologia



Obrigado!

Energy partitioning for generalized product functions: The interference contribution to the energy of generalized valence bond and spin coupled wave functions

Thiago Messias Cardozo and Marco Antonio Chaer Nascimento^{a)}

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Rio de Janeiro, 21949-900 RJ, Brazil*

(Received 23 October 2008; accepted 29 January 2009; published online 9 March 2009)

The main driving force for the formation of the covalent bond is the quantum-mechanical interference effect among one-electron states, as has been suggested in several works by the use of partition schemes to calculate the interference contributions to the energy. However, due to some difficulties associated with the original approaches, calculations were only carried out for a few, mostly diatomic molecules. In this work, we propose a general approach of partitioning based on generalized product functions with generalized valence bond at the perfect pairing approximation and spin-coupled groups, which should allow the investigation of a broader array of molecules, and hopefully, shed light on the nature of the chemical bond in molecules with unusual chemical features. Among other things, this approach lends itself naturally to the investigation of interference in individual bonds or groups of bonds in a molecule. © 2009 American Institute of Physics.
[DOI: [10.1063/1.3085953](https://doi.org/10.1063/1.3085953)]

Fig. S2: Laplacian of the electron density of all minimum structures at the CCSD(T)/aug-cc-pVTZ level. Bond critical points (BCPs) are shown as red dots.

