

# Coesão Cristalina

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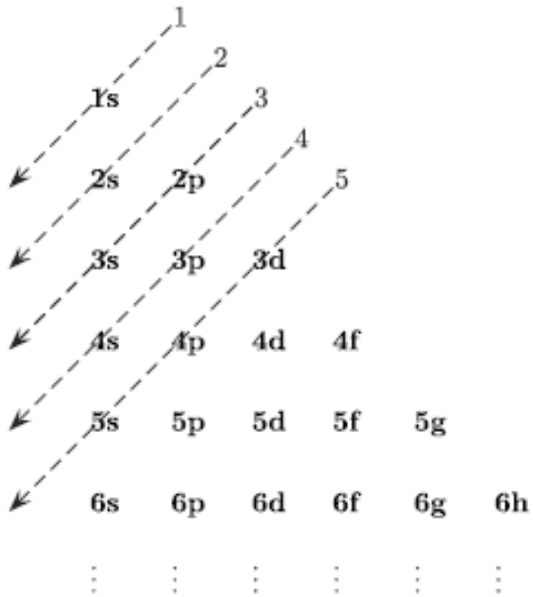
## Periodic table of the elements

$$n = 1, 2, \dots$$

$$l = 0, 1, \dots, n - 1$$

$$l_z = -l, \dots, l$$

$$\sigma_z = -1/2 \text{ or } +1/2.$$



| group<br>1*         | 2               | 3               | 4                | 5                | 6                | 7                | 8                | 9                | 10               | 11               | 12               | 13               | 14               | 15               | 16               | 17               | 18               |
|---------------------|-----------------|-----------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 1<br><b>H</b>       |                 |                 |                  |                  |                  |                  |                  |                  |                  |                  |                  |                  |                  |                  |                  |                  | 2<br><b>He</b>   |
| 3<br><b>Li</b>      | 4<br><b>Be</b>  |                 |                  |                  |                  |                  |                  |                  |                  |                  |                  | 5<br><b>B</b>    | 6<br><b>C</b>    | 7<br><b>N</b>    | 8<br><b>O</b>    | 9<br><b>F</b>    | 10<br><b>Ne</b>  |
| 11<br><b>Na</b>     | 12<br><b>Mg</b> |                 |                  |                  |                  |                  |                  |                  |                  |                  |                  | 13<br><b>Al</b>  | 14<br><b>Si</b>  | 15<br><b>P</b>   | 16<br><b>S</b>   | 17<br><b>Cl</b>  | 18<br><b>Ar</b>  |
| 19<br><b>K</b>      | 20<br><b>Ca</b> | 21<br><b>Sc</b> | 22<br><b>Ti</b>  | 23<br><b>V</b>   | 24<br><b>Cr</b>  | 25<br><b>Mn</b>  | 26<br><b>Fe</b>  | 27<br><b>Co</b>  | 28<br><b>Ni</b>  | 29<br><b>Cu</b>  | 30<br><b>Zn</b>  | 31<br><b>Ga</b>  | 32<br><b>Ge</b>  | 33<br><b>As</b>  | 34<br><b>Se</b>  | 35<br><b>Br</b>  | 36<br><b>Kr</b>  |
| 37<br><b>Rb</b>     | 38<br><b>Sr</b> | 39<br><b>Y</b>  | 40<br><b>Zr</b>  | 41<br><b>Nb</b>  | 42<br><b>Mo</b>  | 43<br><b>Tc</b>  | 44<br><b>Ru</b>  | 45<br><b>Rh</b>  | 46<br><b>Pd</b>  | 47<br><b>Ag</b>  | 48<br><b>Cd</b>  | 49<br><b>In</b>  | 50<br><b>Sn</b>  | 51<br><b>Sb</b>  | 52<br><b>Te</b>  | 53<br><b>I</b>   | 54<br><b>Xe</b>  |
| 55<br><b>Cs</b>     | 56<br><b>Ba</b> | 57<br><b>La</b> | 72<br><b>Hf</b>  | 73<br><b>Ta</b>  | 74<br><b>W</b>   | 75<br><b>Re</b>  | 76<br><b>Os</b>  | 77<br><b>Ir</b>  | 78<br><b>Pt</b>  | 79<br><b>Au</b>  | 80<br><b>Hg</b>  | 81<br><b>Tl</b>  | 82<br><b>Pb</b>  | 83<br><b>Bi</b>  | 84<br><b>Po</b>  | 85<br><b>At</b>  | 86<br><b>Rn</b>  |
| 87<br><b>Fr</b>     | 88<br><b>Ra</b> | 89<br><b>Ac</b> | 104<br><b>Rf</b> | 105<br><b>Db</b> | 106<br><b>Sg</b> | 107<br><b>Bh</b> | 108<br><b>Hs</b> | 109<br><b>Mt</b> | 110<br><b>Ds</b> | 111<br><b>Rg</b> | 112<br><b>Cn</b> | 113<br><b>Nh</b> | 114<br><b>Fl</b> | 115<br><b>Mc</b> | 116<br><b>Lv</b> | 117<br><b>Ts</b> | 118<br><b>Og</b> |
| lanthanoid series 6 |                 | 58<br><b>Ce</b> | 59<br><b>Pr</b>  | 60<br><b>Nd</b>  | 61<br><b>Pm</b>  | 62<br><b>Sm</b>  | 63<br><b>Eu</b>  | 64<br><b>Gd</b>  | 65<br><b>Tb</b>  | 66<br><b>Dy</b>  | 67<br><b>Ho</b>  | 68<br><b>Er</b>  | 69<br><b>Tm</b>  | 70<br><b>Yb</b>  | 71<br><b>Lu</b>  |                  |                  |
| actinoid series 7   |                 | 90<br><b>Th</b> | 91<br><b>Pa</b>  | 92<br><b>U</b>   | 93<br><b>Np</b>  | 94<br><b>Pu</b>  | 95<br><b>Am</b>  | 96<br><b>Cm</b>  | 97<br><b>Bk</b>  | 98<br><b>Cf</b>  | 99<br><b>Es</b>  | 100<br><b>Fm</b> | 101<br><b>Md</b> | 102<br><b>No</b> | 103<br><b>Lr</b> |                  |                  |

\*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

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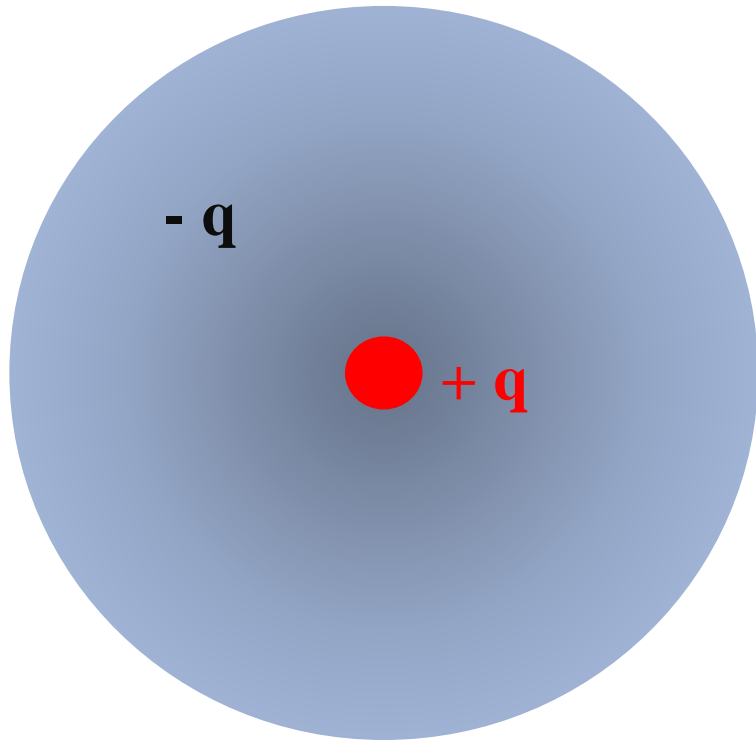
**The Atomic Mac™** Registered to: GREGORY TETRAULT  
For use only on a single machine

|  |    |   |    |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |
|--|----|---|----|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|---|----|----|----|----|----|----|----|----|----|----|----|
| H  | Li | Be  |    |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    | He |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |
| Na   | Mg | Hexagonal<br>Cubic body centered<br>Rhombohedral<br>Cubic                                       |    | Cubic face centered<br>Monoclinic<br>Orthorhombic<br>Tetragonal |    | B  | C  | N  | O  | F  | Ne |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |
| K  | Ca | Sc  | Ti | V   | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |
| Rb   | Sr | Y   | Zr | Nb  | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I  | Xe |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |
| Cs   | Ba | Hf<br>Ta<br>W<br>Re<br>Os<br>Ir<br>Pt<br>Au<br>Hg<br>Tl<br>Pb<br>Bi<br>Po<br>At<br>Rn           |    |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |
| Fr   | Ra | Rf<br>Db<br>Sg<br>Bh<br>Hs<br>Mt<br>Uun<br>Uuu<br>Uub<br>Uut<br>Uuq<br>Uup<br>Uuh<br>Uus<br>Uuo |    |   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |
| <table border="1"> <tr> <td>La</td> <td>Ce</td> <td>Pr</td> <td>Nd</td> <td>Pm</td> <td>Sm</td> <td>Eu</td> <td>Gd</td> <td>Tb</td> <td>Dy</td> <td>Ho</td> <td>Er</td> <td>Tm</td> <td>Yb</td> <td>Lu</td> </tr> <tr> <td>Ac</td> <td>Th</td> <td>Pa</td> <td>U</td> <td>Np</td> <td>Pu</td> <td>Am</td> <td>Cm</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lr</td> </tr> </table> |    |   |    |   |    |    |    |    |    |    |    |    |    |    |    |    |    | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
| La   | Ce | Pr  | Nd | Pm  | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |
| Ac   | Th | Pa  | U  | Np  | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |



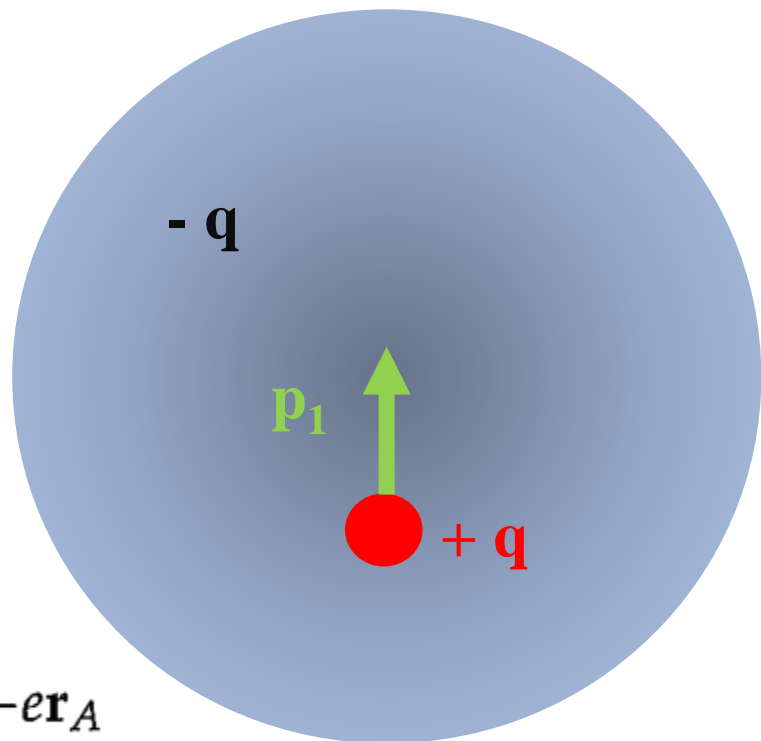
# Coessão Cristalina

Interação de van der Waals



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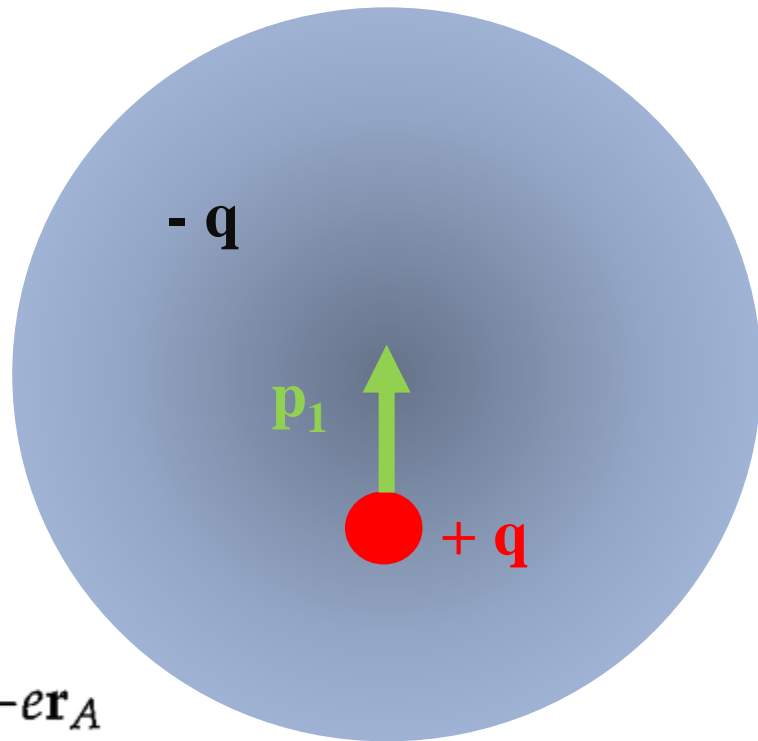
Interação de van der Waals



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Interação de van der Waals

$$V(\mathbf{R}) = \frac{1}{4\pi\epsilon_0} \frac{\mathbf{p}_A \cdot \mathbf{R}}{R^3}$$

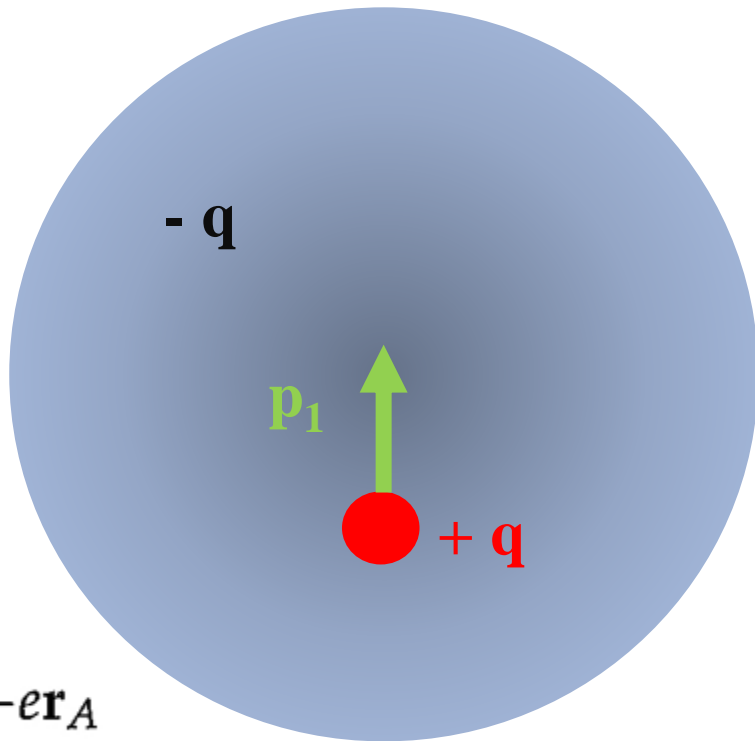


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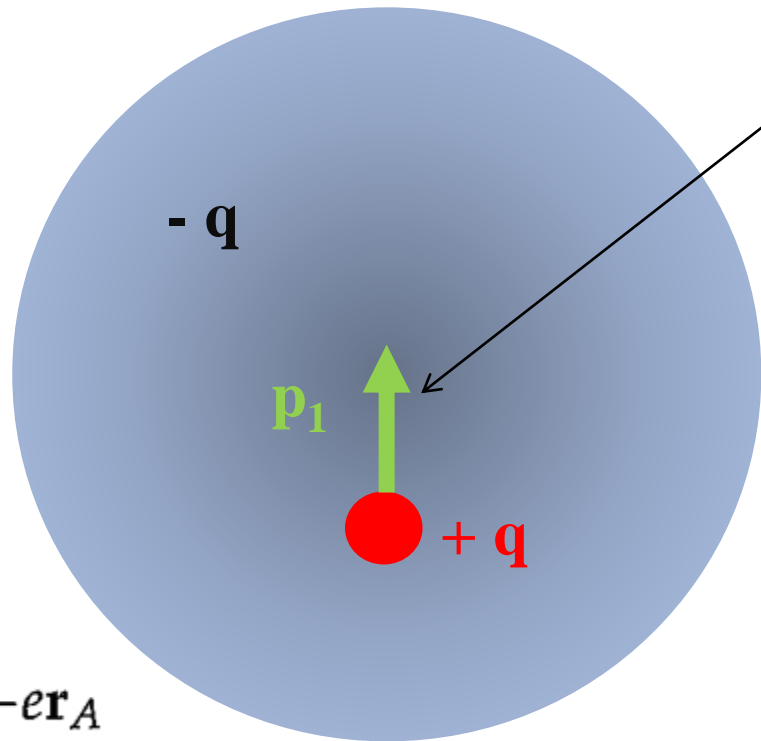


$$\mathbf{E} = -\nabla_{\mathbf{R}} V(\mathbf{R}) = \frac{e}{4\pi\epsilon_0} \frac{1}{R^3} [\mathbf{r}_A - 3(\mathbf{r}_A \cdot \mathbf{n})\mathbf{n}]$$

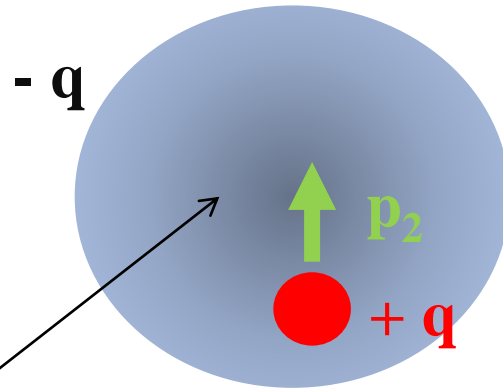


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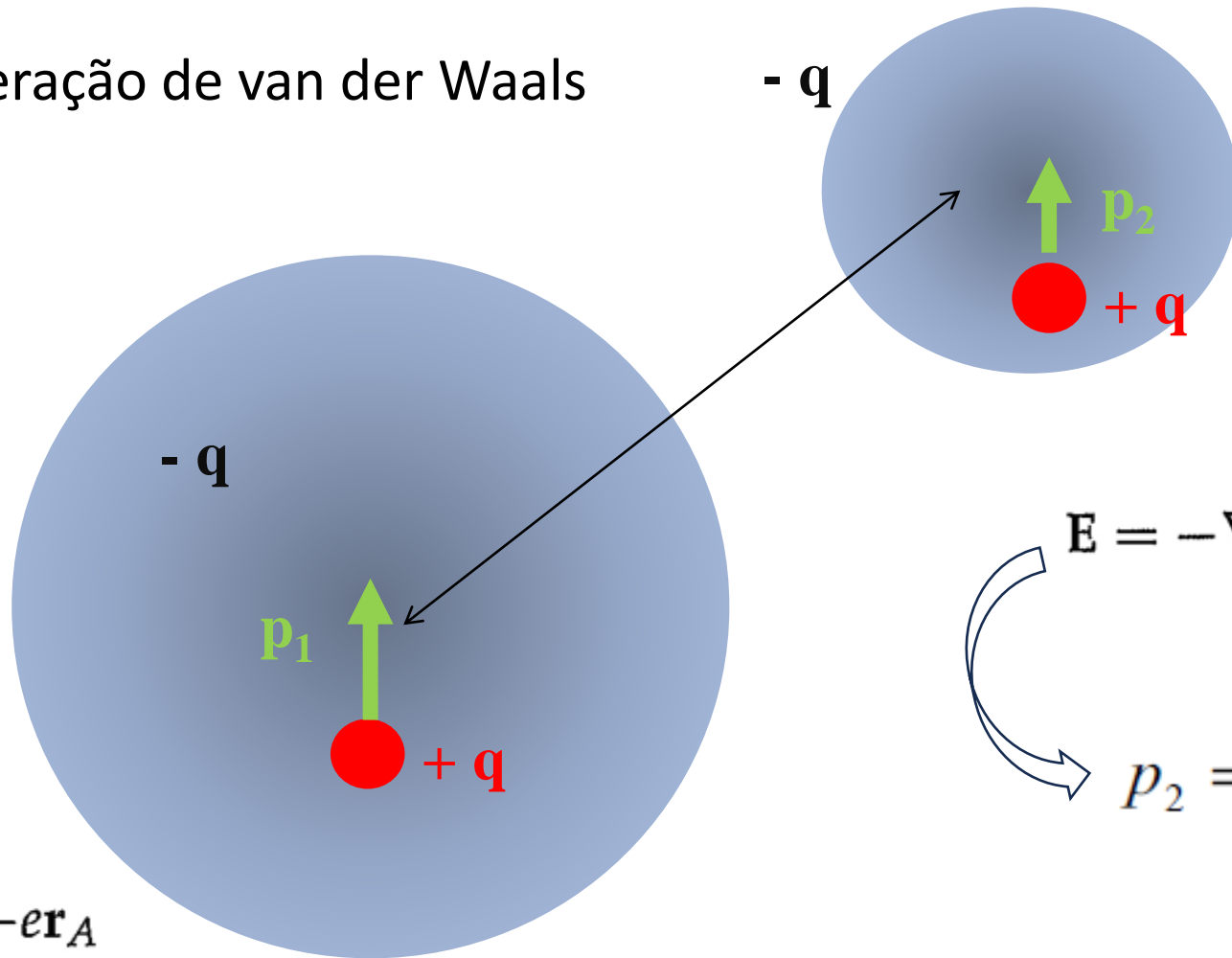
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$p_2 = \alpha E \propto \frac{\alpha p_1}{r^3}$  Momento de dipolo induzido

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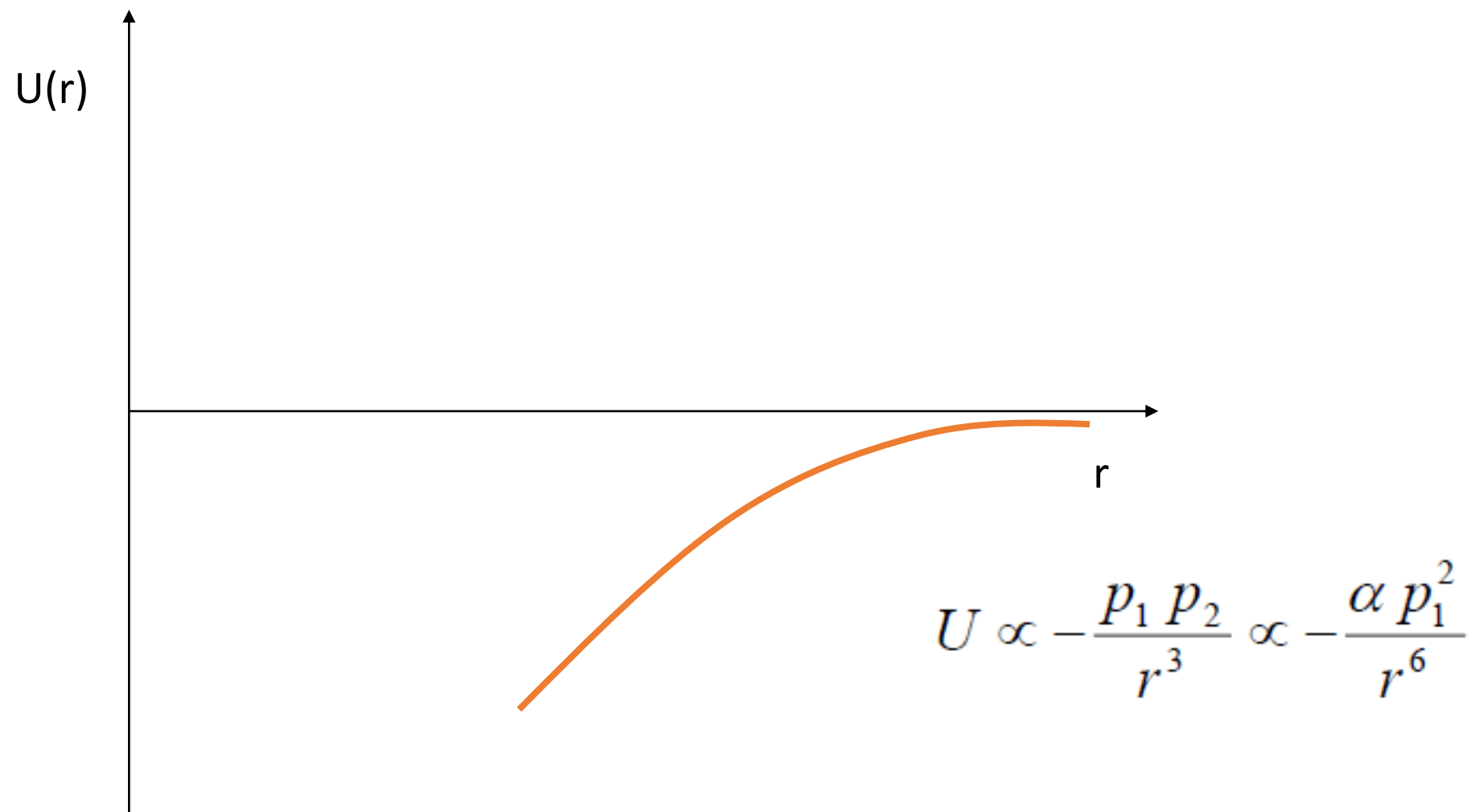
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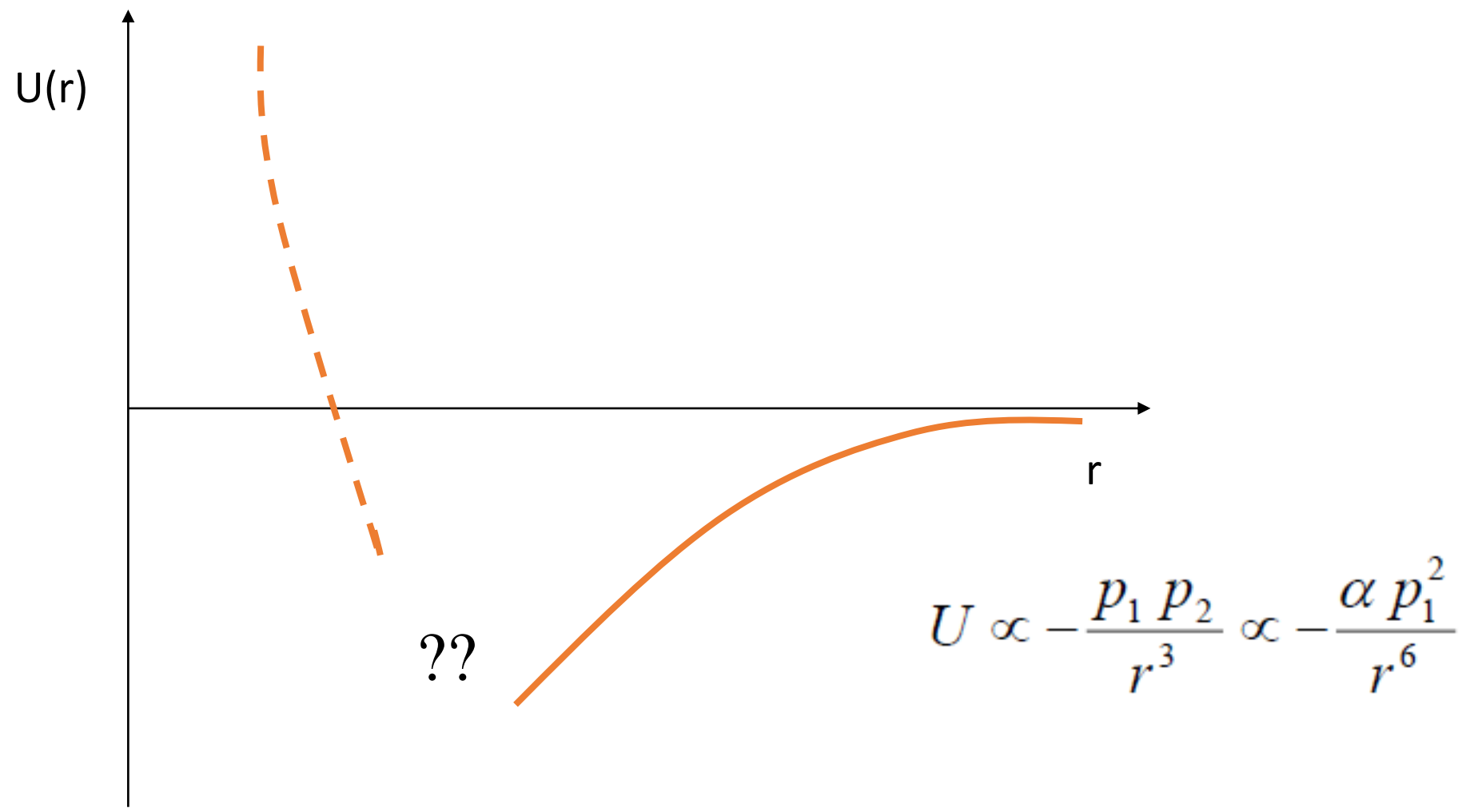
$$p_2 = \alpha E \propto \frac{\alpha p_1}{r^3} \quad \text{Momento de dipolo induzido}$$

$$U \propto -\frac{p_1 p_2}{r^3} \propto -\frac{\alpha p_1^2}{r^6}$$

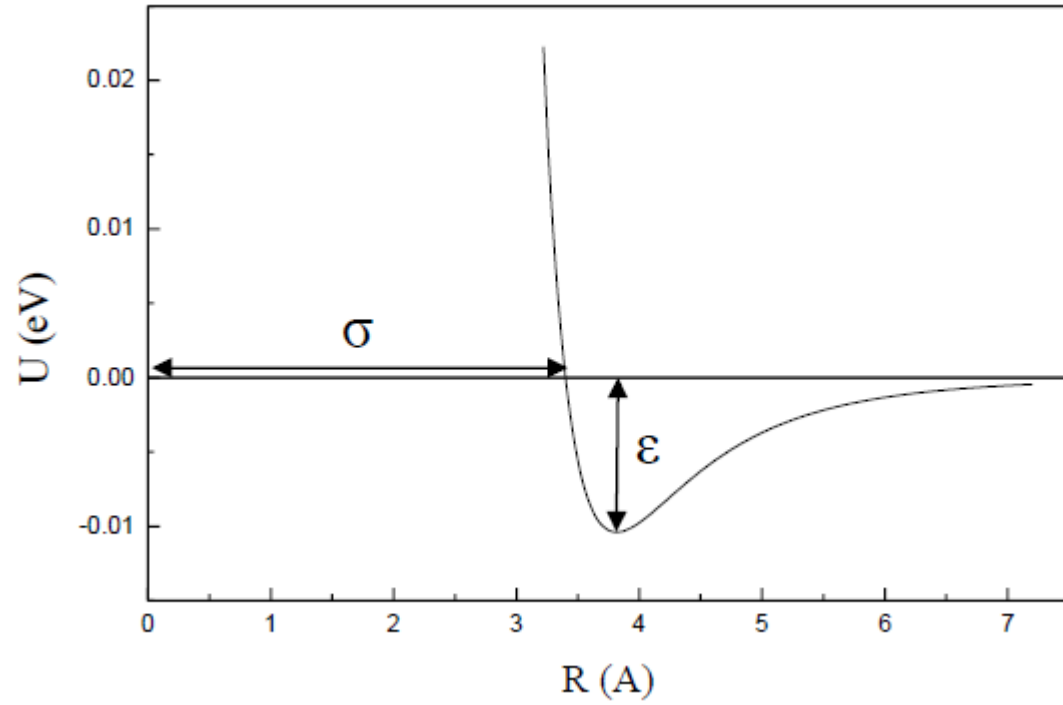
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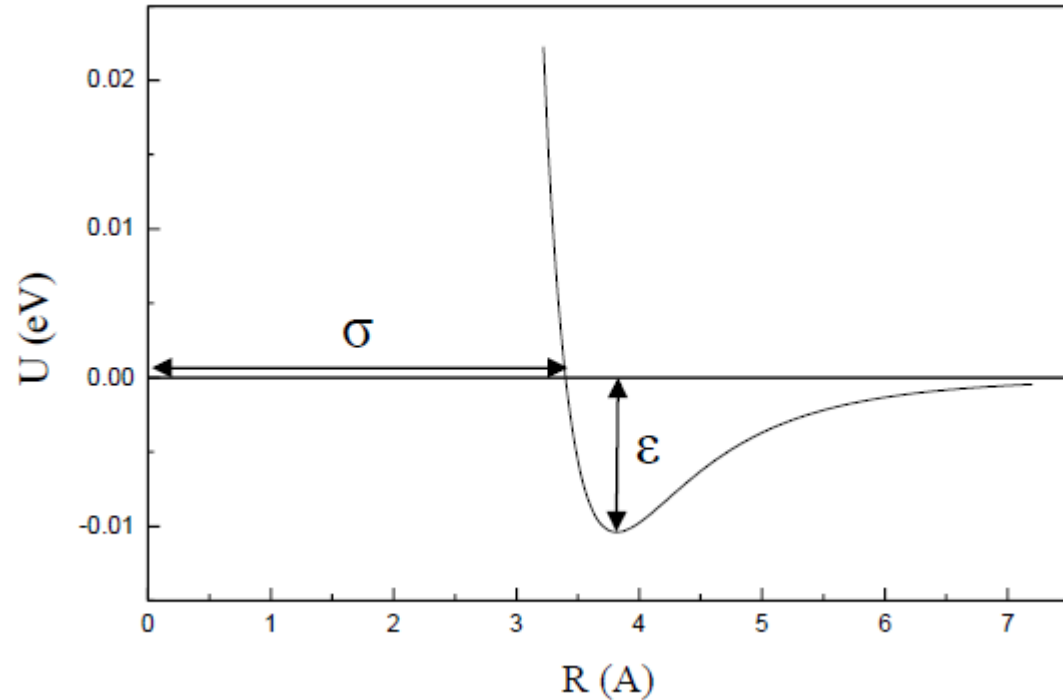
# Interação de van der Waals



# Potencial de Lennard-Jones

$$v_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

# Interação de van der Waals



## Potencial de Lennard-Jones

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| Elemento | Distância Interatômica (Å)             | Energia de Coesão (eV/átomo) | Ponto de Fusão (K) | Parâmetros de Lennard-Jones |              |
|----------|--|------------------------------|--------------------|-----------------------------|--------------|
|          |  |                              |                    | $\epsilon$ ( $10^{-4}$ eV)  | $\sigma$ (Å) |
| He       | líquido a $T=0\text{K}$ e pressão nula |                              |                    | 8,7                         | 2,56         |
| Ne       | 3,13                                   | 0,02                         | 24                 | 31                          | 2,74         |
| Ar       | 3,76                                   | 0,080                        | 84                 | 104                         | 3,40         |
| Kr       | 4,01                                   | 0,116                        | 117                | 140                         | 3,65         |
| Xe       | 4,35                                   | 0,17                         | 161                | 200                         | 3,98         |

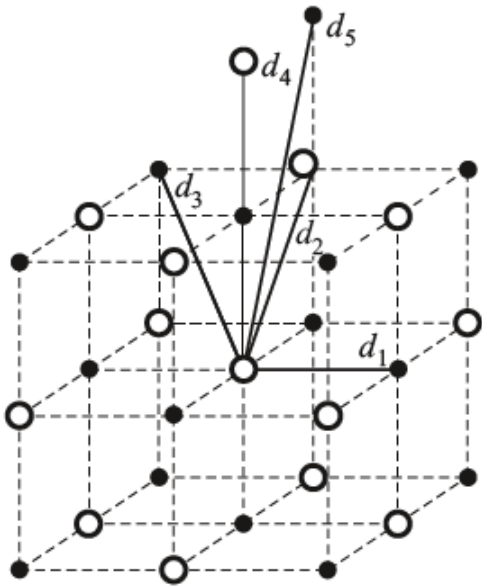
Energia de coesão: diferença de energia entre a situação de átomos isolados em relação a um sólido.

$$U = \frac{1}{N} \sum_{\langle ij \rangle} u(r_{ij}) = \frac{1}{2N} \sum_{i \neq j} u(r_{ij}) = \frac{1}{2} \sum_{j=2}^N u(r_j)$$

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Exemplo: rede cúbica



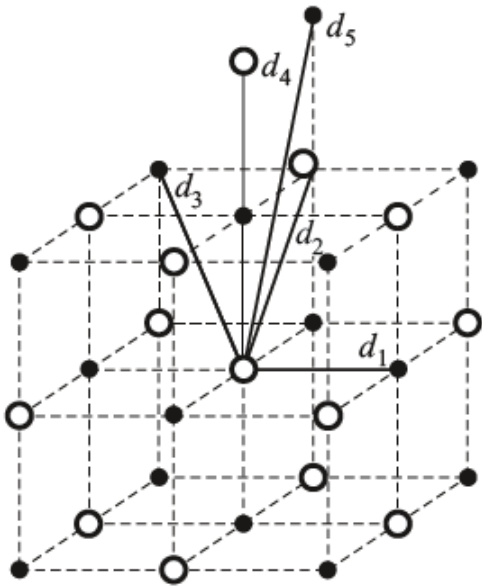
$$U(a) = \frac{1}{2} \left[ 6v_{LJ}(a) + 12v_{LJ}(\sqrt{2}a) + 8v_{LJ}(\sqrt{3}a) + \dots \right]$$



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$$p(v) = -\frac{dU}{dv}$$

$$p(\nu) = -\frac{dU}{d\nu} \quad \Rightarrow \quad B_0 = -\nu_0 \left. \frac{dp}{d\nu} \right|_{\nu_0} = \nu_0 \left. \frac{d^2U}{d\nu^2} \right|_{\nu_0}$$

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Table 20.3  
NEAREST-NEIGHBOR DISTANCE  $r_0$ , COHESIVE ENERGY  $u_0$ , AND  
BULK MODULUS  $B_0$  AT ZERO PRESSURE FOR THE SOLID NOBLE  
GASES<sup>a</sup>

|   |              | Ne     | Ar     | Kr     | Xe     |
|---|--------------|--------|--------|--------|--------|
| $r_0$ (angstroms)                                     | (Experiment) | 3.13   | 3.75   | 3.99   | 4.33   |
| $r_0 = 1.09\sigma$                                    | (Theory)     | 2.99   | 3.71   | 3.98   | 4.34   |
| $u_0$ (eV/atom)                                       | (Experiment) | -0.02  | -0.08  | -0.11  | -0.17  |
| $u_0 = -8.6\epsilon$                                  | (Theory)     | -0.027 | -0.089 | -0.120 | -0.172 |
| $B_0$ ( $10^{10}$ dyne/cm <sup>2</sup> ) <sup>b</sup> | (Experiment) | 1.1    | 2.7    | 3.5    | 3.6    |
| $B_0 = 75\epsilon/\sigma^3$                           | (Theory)     | 1.81   | 3.18   | 3.46   | 3.81   |

Fonte: Ashcroft, p.401

$$p(v) = -\frac{dU}{dv} \quad \Rightarrow \quad B_0 = -v_0 \left. \frac{dp}{dv} \right|_{v_0} = v_0 \left. \frac{d^2U}{dv^2} \right|_{v_0}$$

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| Material | Módulo de <i>bulk</i> (Pa) |
|----------|----------------------------|
| Diamante | $442 \times 10^9$          |
| Aço      | $160 \times 10^9$          |
| Vidro    | $35-55 \times 10^9$        |
| Água     | $2,2 \times 10^9$          |
| Ar       | $1,01 \times 10^5$         |

# Interação de van der Waals

- **Onde entra a Mecânica Quântica?**

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Vamos supor um átomo no nível 1s:

$$\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

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Mas, o quadrado do momento de dipolo é não nulo:

$$\langle p^2 \rangle = e^2 \langle r^2 \rangle = \frac{e^2}{\pi a_0^3} 4\pi \int_0^\infty r^4 e^{-2r/a_0} dr = 3e^2 a_0^2 \neq 0$$

**O dipolo flutua!!!**

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Mas, o quadrado do momento de dipolo é não nulo:

$$\langle p^2 \rangle = e^2 \langle r^2 \rangle = \frac{e^2}{\pi a_0^3} 4\pi \int_0^\infty r^4 e^{-2r/a_0} dr = 3e^2 a_0^2 \neq 0$$

**O dipolo flutua!!!**

- Como resolver esse problema via MQ?

# Interação de van der Waals

- Onde entra a Mecânica Quântica?

Vamos supor um átomo no nível 1s:

$$\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

Note que o momento de dipolo elétrico é nulo:

$$\langle p \rangle = -e \langle r \rangle = -\frac{e}{\pi a_0^3} 4\pi \int_0^\infty r^3 e^{-2r/a_0} dr = 0$$

Mas, o quadrado do momento de dipolo é não nulo:

$$\langle p^2 \rangle = e^2 \langle r^2 \rangle = \frac{e^2}{\pi a_0^3} 4\pi \int_0^\infty r^4 e^{-2r/a_0} dr = 3e^2 a_0^2 \neq 0$$

**O dipolo flutua!!!**

- Como resolver esse problema via MQ?



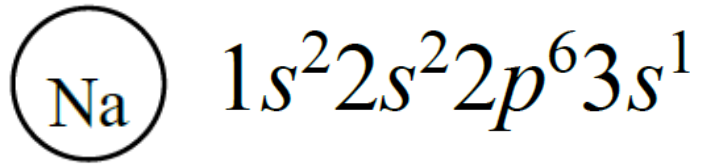
Retornaremos a esse problema no final da aula!

# Ligação Iônica

*O curioso caso do NaCl ...*

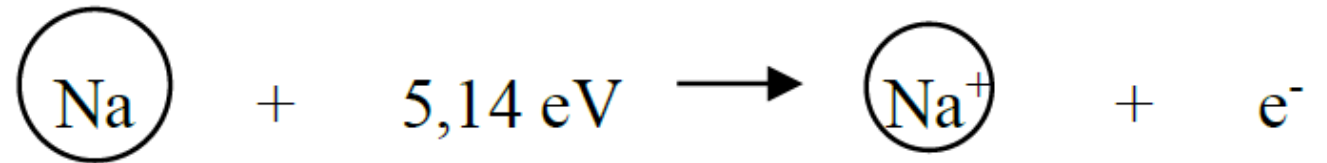
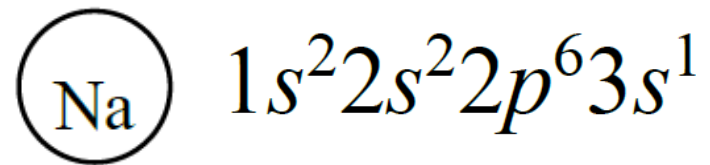
# Ligação Iônica

*O curioso caso do NaCl ...*



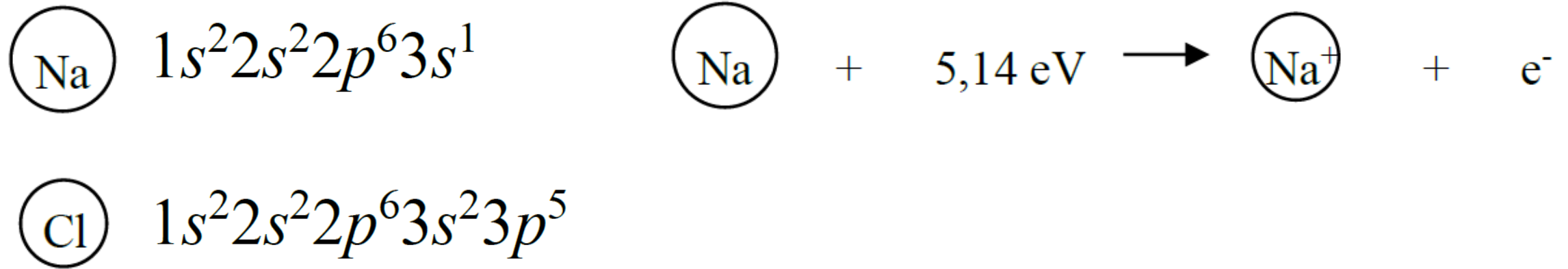
# Ligação Iônica

*O curioso caso do NaCl ...*



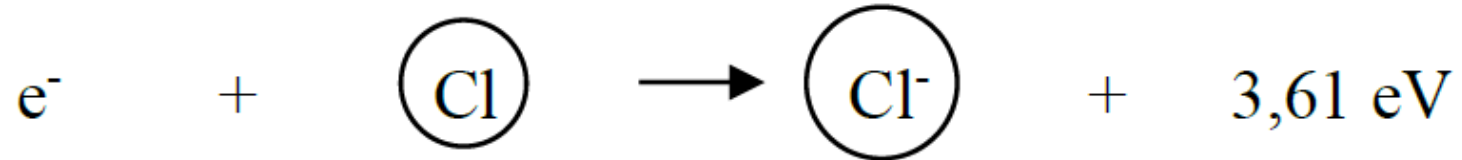
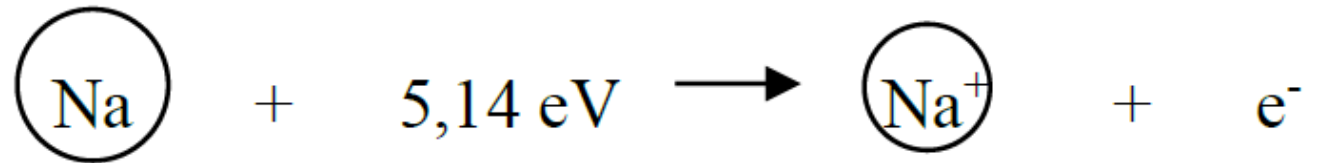
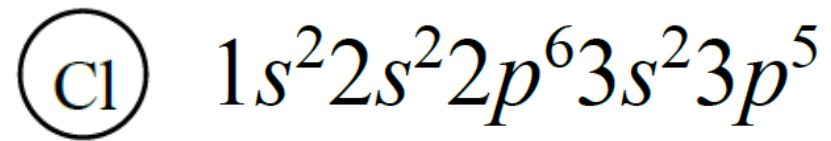
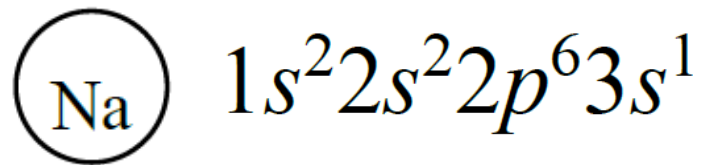
# Ligação Iônica

*O curioso caso do NaCl ...*



# Ligação Iônica

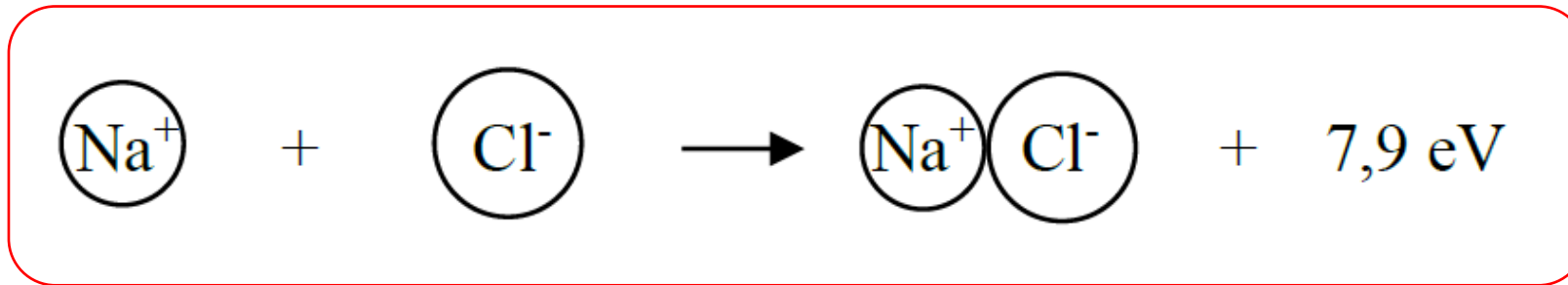
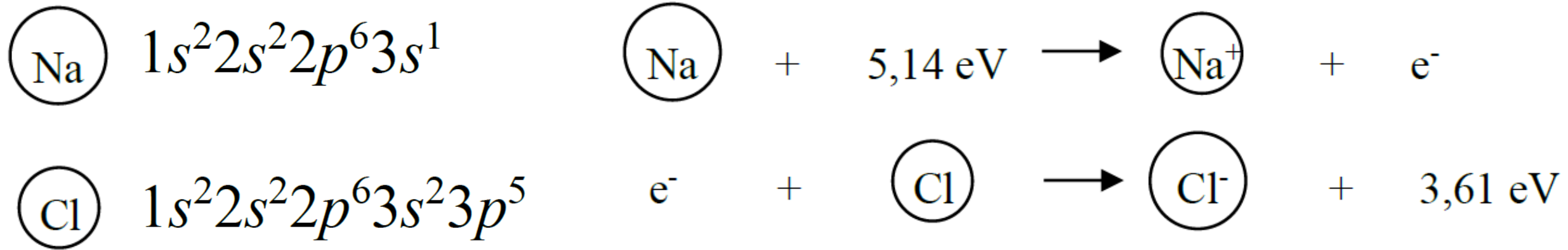
*O curioso caso do NaCl ...*





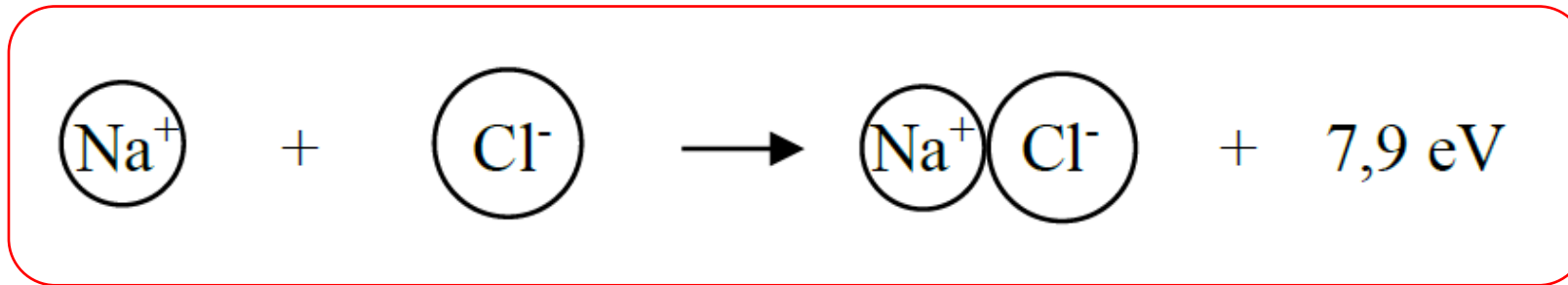
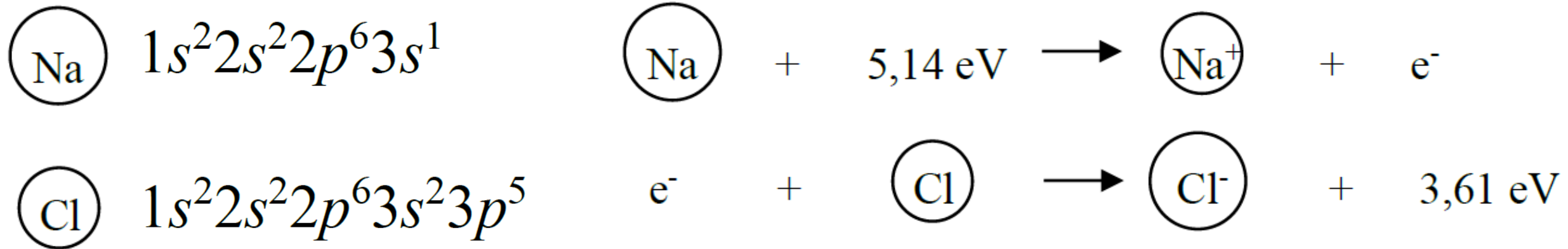
# Ligação Iônica

*O curioso caso do NaCl ...*



# Ligação Iônica

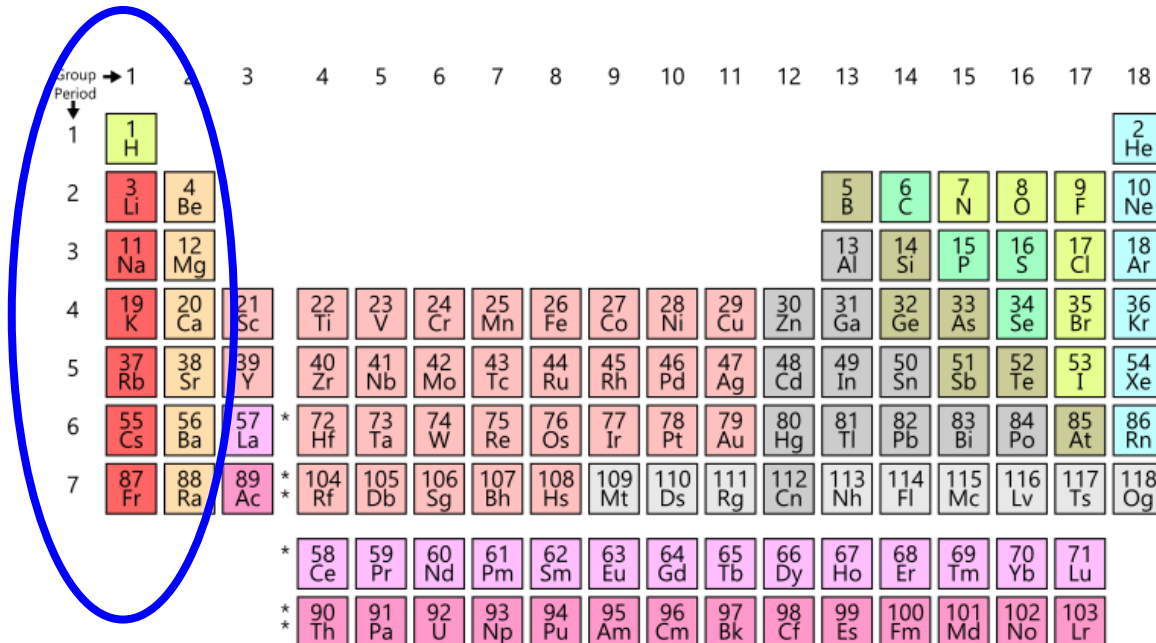
*O curioso caso do NaCl ...*



**Ganho energético eletrostático**

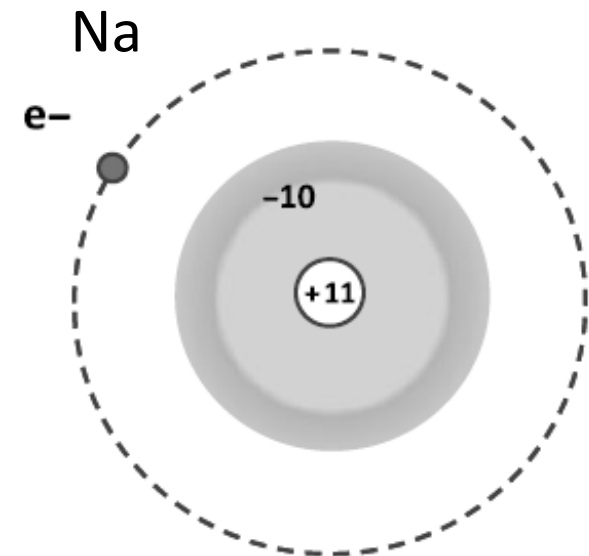
# Ligação Iônica

- Há átomos ansiosos por **perder** elétrons



The periodic table shows elements grouped by columns (Groups 1-18) and rows (Periods 1-7). A blue oval highlights the elements in Group 1: Hydrogen (H), Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs), and Francium (Fr).

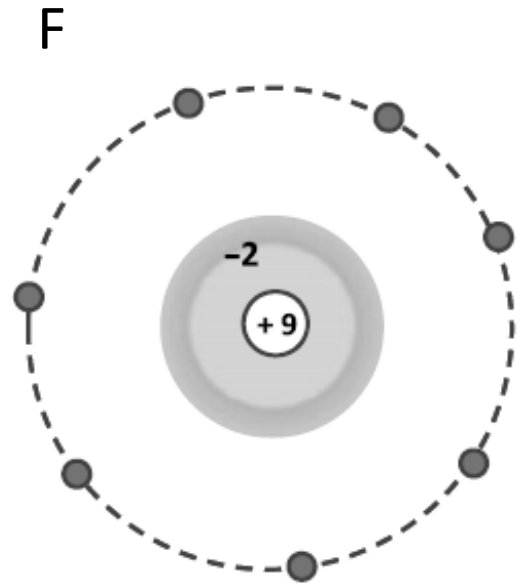
| Group    | 1     | 2     | 3      | 4      | 5      | 6      | 7      | 8      | 9      | 10     | 11     | 12     | 13     | 14     | 15     | 16     | 17     | 18     |  |
|----------|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--|
| Period 1 | 1 H   |       |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        | 2 He   |  |
| Period 2 | 3 Li  | 4 Be  |        |        |        |        |        |        |        |        |        | 5 B    | 6 C    | 7 N    | 8 O    | 9 F    | 10 Ne  |        |  |
| Period 3 | 11 Na | 12 Mg |        |        |        |        |        |        |        |        |        | 13 Al  | 14 Si  | 15 P   | 16 S   | 17 Cl  | 18 Ar  |        |  |
| Period 4 | 19 K  | 20 Ca | 21 Sc  | 22 Ti  | 23 V   | 24 Cr  | 25 Mn  | 26 Fe  | 27 Co  | 28 Ni  | 29 Cu  | 30 Zn  | 31 Ga  | 32 Ge  | 33 As  | 34 Se  | 35 Br  | 36 Kr  |  |
| Period 5 | 37 Rb | 38 Sr | 39 Y   | 40 Zr  | 41 Nb  | 42 Mo  | 43 Tc  | 44 Ru  | 45 Rh  | 46 Pd  | 47 Ag  | 48 Cd  | 49 In  | 50 Sn  | 51 Sb  | 52 Te  | 53 I   | 54 Xe  |  |
| Period 6 | 55 Cs | 56 Ba | 57 La* | 72 Hf  | 73 Ta  | 74 W   | 75 Re  | 76 Os  | 77 Ir  | 78 Pt  | 79 Au  | 80 Hg  | 81 Tl  | 82 Pb  | 83 Bi  | 84 Po  | 85 At  | 86 Rn  |  |
| Period 7 | 87 Fr | 88 Ra | 89 Ac* | 104 Rf | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 Ds | 111 Rg | 112 Cn | 113 Nh | 114 Fl | 115 Mc | 116 Lv | 117 Ts | 118 Og |  |
| * 58 Ce  |       |       |        | 59 Pr  | 60 Nd  | 61 Pm  | 62 Sm  | 63 Eu  | 64 Gd  | 65 Tb  | 66 Dy  | 67 Ho  | 68 Er  | 69 Tm  | 70 Yb  | 71 Lu  |        |        |  |
| * 90 Th  |       |       |        | 91 Pa  | 92 U   | 93 Np  | 94 Pu  | 95 Am  | 96 Cm  | 97 Bk  | 98 Cf  | 99 Es  | 100 Fm | 101 Md | 102 No | 103 Lr |        |        |  |



# Ligação Iônica

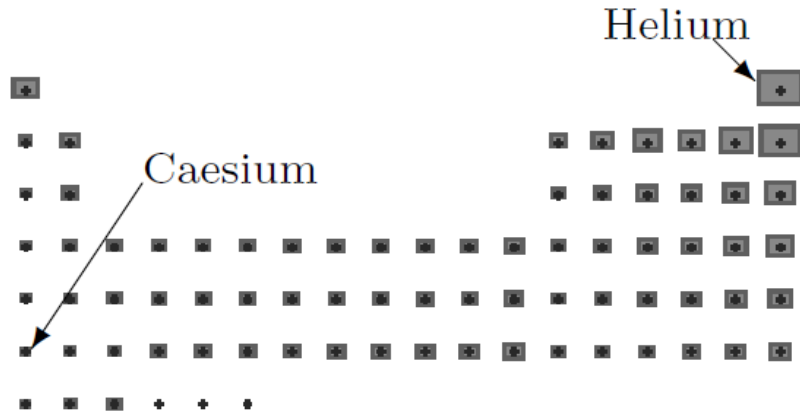
- Há átomos ansiosos por **perder** elétrons e outros por **ganhar**.

| Group    | 1        | 2        | 3          | 4          | 5         | 6         | 7         | 8         | 9         | 10        | 11        | 12        | 13        | 14        | 15        | 16        | 17        | 18        |
|----------|----------|----------|------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Period 1 | 1<br>H   |          |            |            |           |           |           |           |           |           |           |           |           |           |           |           |           | 2<br>He   |
| Period 2 | 3<br>Li  | 4<br>Be  |            |            |           |           |           |           |           |           |           | 5<br>B    | 6<br>C    | 7<br>N    | 8<br>O    | 9<br>F    | 10<br>Ne  |           |
| Period 3 | 11<br>Na | 12<br>Mg |            |            |           |           |           |           |           |           |           | 13<br>Al  | 14<br>Si  | 15<br>P   | 16<br>S   | 17<br>Cl  | 18<br>Ar  |           |
| Period 4 | 19<br>K  | 20<br>Ca | 21<br>Sc   | 22<br>Ti   | 23<br>V   | 24<br>Cr  | 25<br>Mn  | 26<br>Fe  | 27<br>Co  | 28<br>Ni  | 29<br>Cu  | 30<br>Zn  | 31<br>Ga  | 32<br>Ge  | 33<br>As  | 34<br>Se  | 35<br>Br  | 36<br>Kr  |
| Period 5 | 37<br>Rb | 38<br>Sr | 39<br>Y    | 40<br>Zr   | 41<br>Nb  | 42<br>Mo  | 43<br>Tc  | 44<br>Ru  | 45<br>Rh  | 46<br>Pd  | 47<br>Ag  | 48<br>Cd  | 49<br>In  | 50<br>Sn  | 51<br>Sb  | 52<br>Te  | 53<br>I   | 54<br>Xe  |
| Period 6 | 55<br>Cs | 56<br>Ba | 57<br>La * | 72<br>Hf   | 73<br>Ta  | 74<br>W   | 75<br>Re  | 76<br>Os  | 77<br>Ir  | 78<br>Pt  | 79<br>Au  | 80<br>Hg  | 81<br>Tl  | 82<br>Pb  | 83<br>Bi  | 84<br>Po  | 85<br>At  | 86<br>Rn  |
| Period 7 | 87<br>Fr | 88<br>Ra | 89<br>Ac * | 104<br>Rf  | 105<br>Db | 106<br>Sg | 107<br>Bh | 108<br>Hs | 109<br>Mt | 110<br>Ds | 111<br>Rg | 112<br>Cn | 113<br>Nh | 114<br>Fl | 115<br>Mc | 116<br>Lv | 117<br>Ts | 118<br>Og |
|          |          |          |            | * 58<br>Ce | 59<br>Pr  | 60<br>Nd  | 61<br>Pm  | 62<br>Sm  | 63<br>Eu  | 64<br>Gd  | 65<br>Tb  | 66<br>Dy  | 67<br>Ho  | 68<br>Er  | 69<br>Tm  | 70<br>Yb  | 71<br>Lu  |           |
|          |          |          |            | * 90<br>Th | 91<br>Pa  | 92<br>U   | 93<br>Np  | 94<br>Pu  | 95<br>Am  | 96<br>Cm  | 97<br>Bk  | 98<br>Cf  | 99<br>Es  | 100<br>Fm | 101<br>Md | 102<br>No | 103<br>Lr |           |



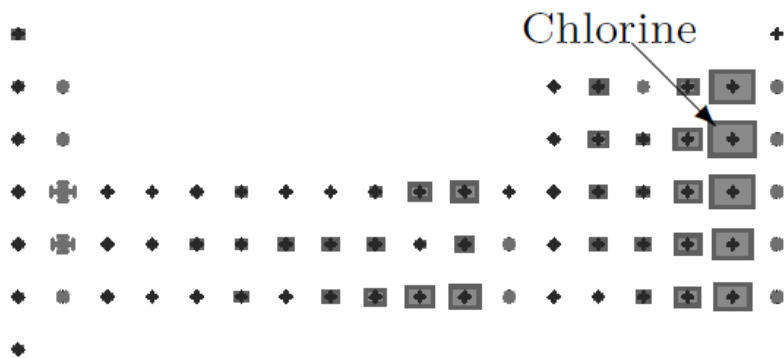
# Ligação Iônica

## First Ionization Energies



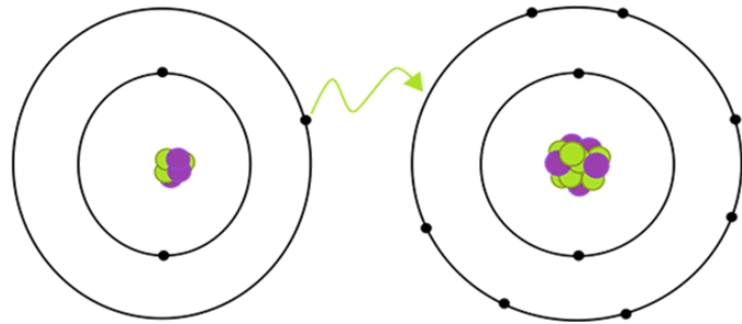
**Energia de Ionização:** Energia necessária para remover um elétron de um átomo neutro para criar um cátion.

## First Electron Affinities



**Afinidade eletrônica:** Ganho de energia ao adicionar um elétron a um átomo neutro para criar um ânion.

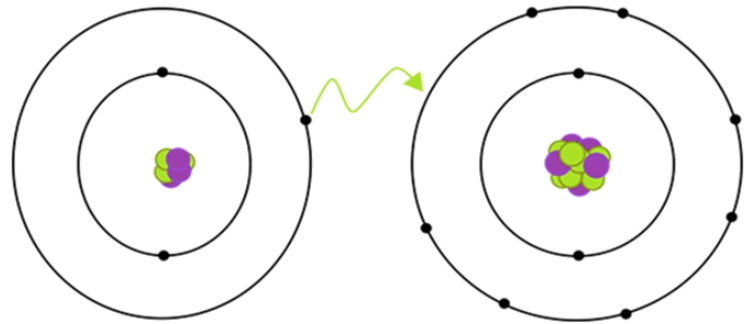
# Ligação Iônica



<https://byjus.com/chemistry/ionic-bond-or-electrovalent-bond/>

$$\Delta E_{A+B \rightarrow A^+ + B^-} = (\text{Energia de Ionização})_A - (\text{Afinidade eletrônica})_B$$

# Ligação Iônica



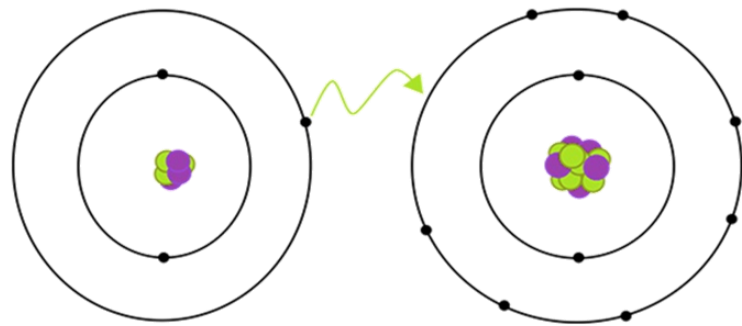
<https://byjus.com/chemistry/ionic-bond-or-electrovalent-bond/>

$$\Delta E_{A+B \rightarrow A^+ + B^-} = (\text{Energia de Ionização})_A - (\text{Afinidade eletrônica})_B$$

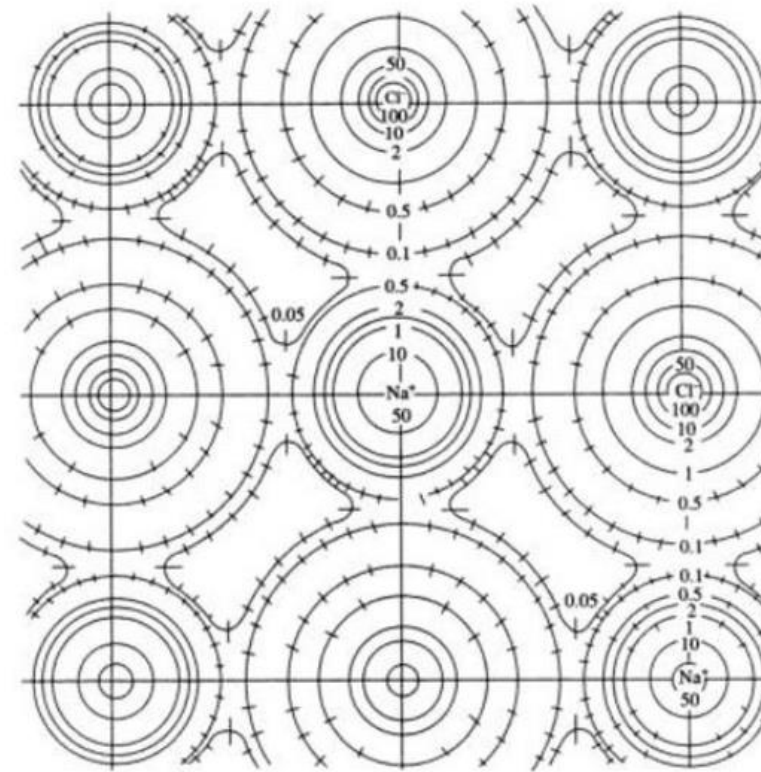
$$\Delta E_{A+B \rightarrow AB} = \Delta E_{A+B \rightarrow A^+ + B^-} - (\text{Energia de Coesão})$$

$$E_{\text{coesão}} = \sum_{i < j} \frac{Q_i Q_j}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

# Ligação Iônica



<https://byjus.com/chemistry/ionic-bond-or-electrovalent-bond/>



$$\Delta E_{A+B \rightarrow A^+ + B^-} = (\text{Energia de Ionização})_A - (\text{Afinidade eletrônica})_B$$

$$\Delta E_{A+B \rightarrow AB} = \Delta E_{A+B \rightarrow A^+ + B^-} - (\text{Energia de Coesão})$$

$$E_{\text{coesão}} = \sum_{i < j} \frac{Q_i Q_j}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$



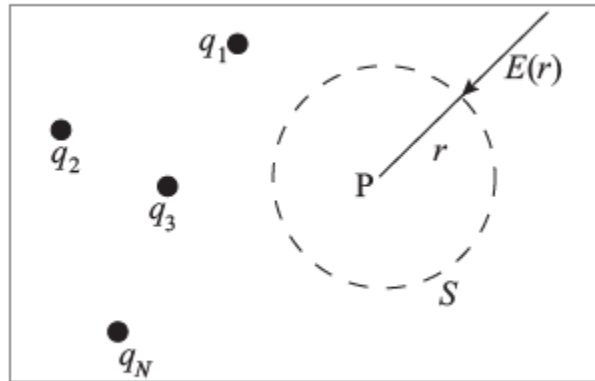
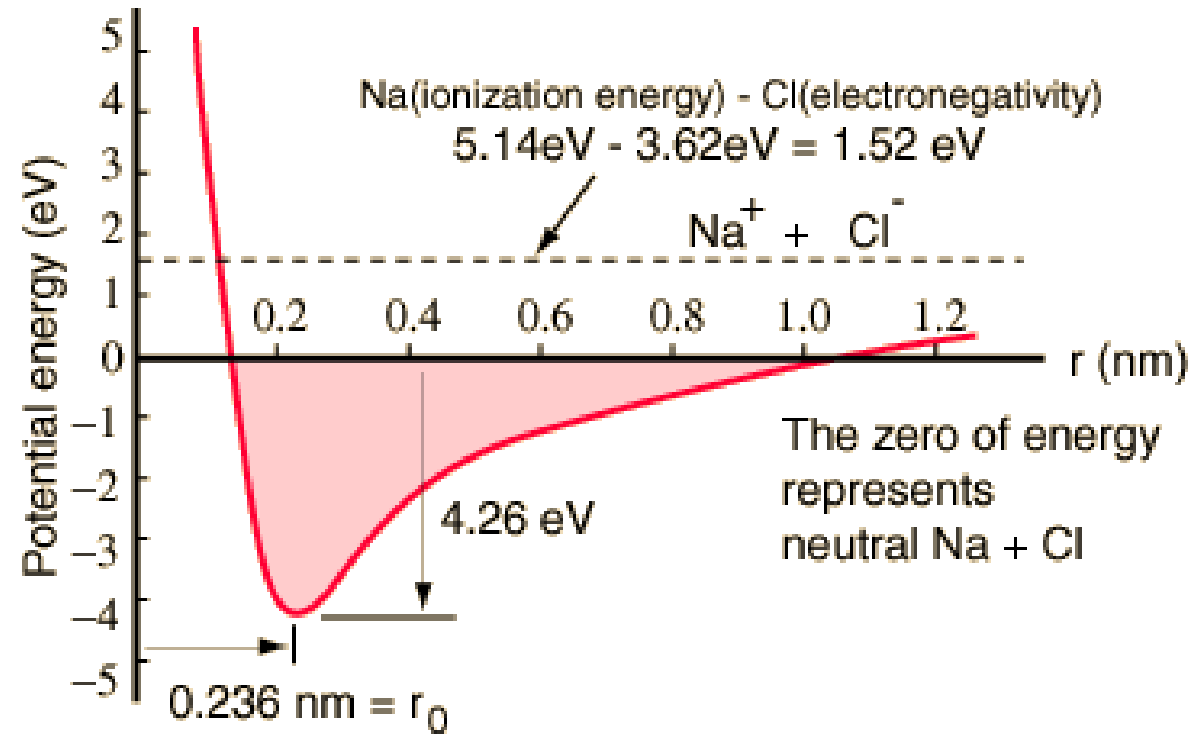


Figura 3.21 Teorema de Earnshaw.

### O teorema de Earnshaw

Um conjunto de cargas puntiformes  $q_1, q_2, \dots, q_N$ , em posições fixas, criam um campo eletrostático no vácuo. Seja  $P$  um ponto qualquer, não ocupado por nenhuma dessas cargas (Figura 3.21). Se colocarmos em  $P$  outra carga puntiforme  $q$ , poderá ela permanecer em equilíbrio *estável* nessa posição, sob a ação do campo criado pelas demais cargas? O *teorema de Earnshaw* diz que isso não acontece.

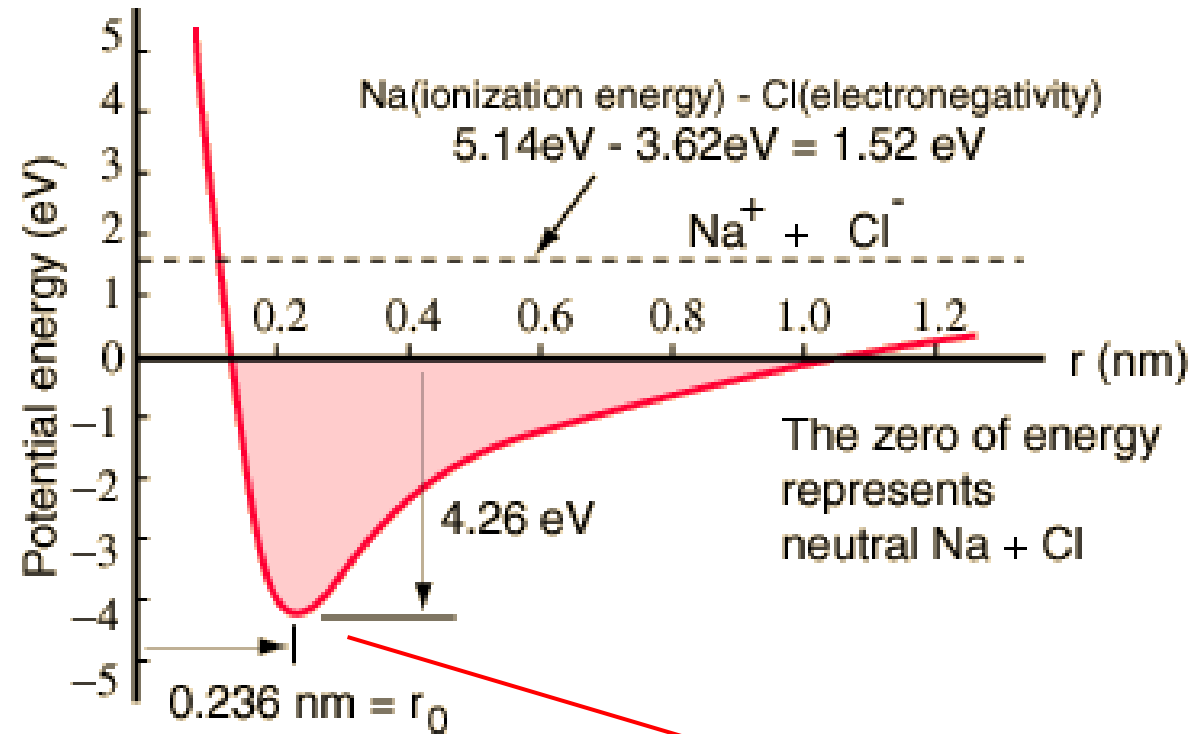
# Ligação Iônica



Born-Mayer approximation

$$\frac{E}{N} = -\alpha \frac{Z_1 Z_2 \tilde{e}^2}{r} + B \exp(-r/l)$$

# Ligação Iônica



Born-Mayer approximation

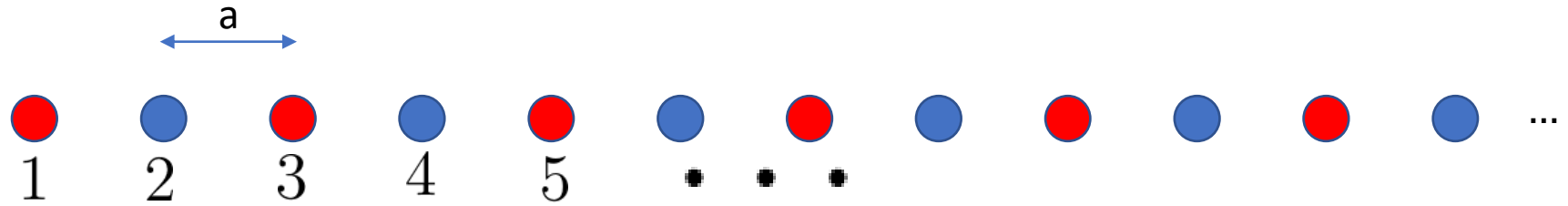
$$\frac{E}{N} = -\alpha \frac{Z_1 Z_2 \tilde{e}^2}{r} + B \exp(-r/l)$$

$$\alpha \frac{Z_1 Z_2 \tilde{e}^2}{d_1^2} - \frac{B}{l} \exp(-d_1/l) = 0$$

# Cristal iônico unidimensional

● =  $+e$

● =  $-e$



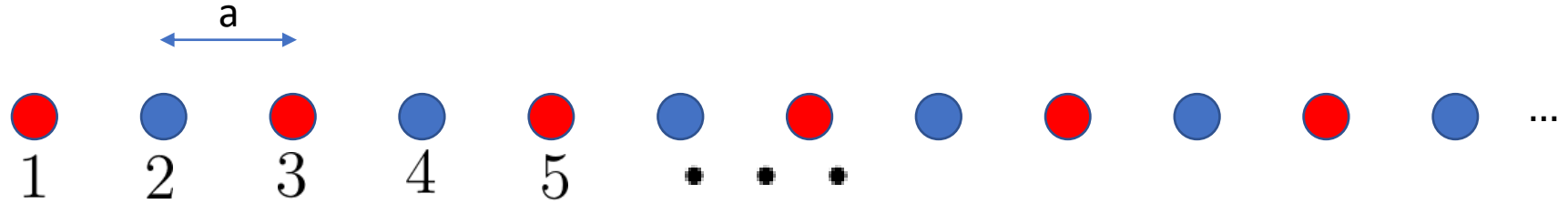
$$E_{\text{coesão}} = \sum_{i < j} \frac{Q_i Q_j}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

# Cristal iônico unidimensional

$$E_{\text{coesão}} = \sum_{i < j} \frac{Q_i Q_j}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

● = +e

● = -e



$$E_1 = E_{1 \rightarrow 2} + E_{1 \rightarrow 3} + E_{1 \rightarrow 4} + E_{1 \rightarrow 5} + \dots$$

$$= -\frac{e^2}{4\pi\epsilon_0 a} \left( 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \dots \right)$$

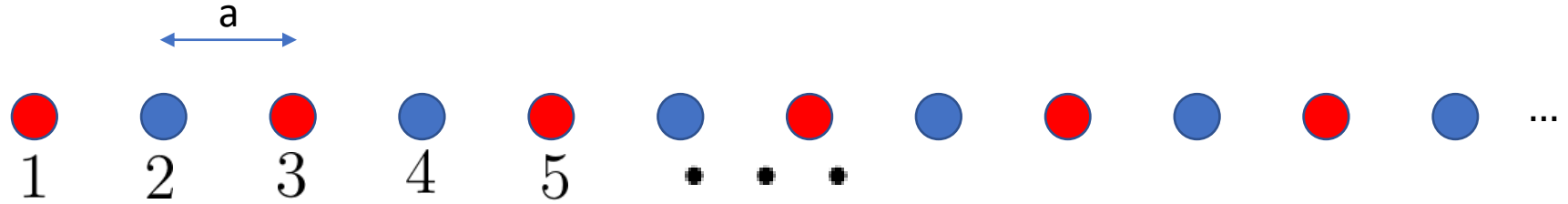


# Cristal iônico unidimensional

$$E_{\text{coesão}} = \sum_{i < j} \frac{Q_i Q_j}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

● = +e

● = -e



$$E_1 = E_{1 \rightarrow 2} + E_{1 \rightarrow 3} + E_{1 \rightarrow 4} + E_{1 \rightarrow 5} + \dots$$

$$= -\frac{e^2}{4\pi\epsilon_0 a} \left( 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \dots \right)$$

Constante de Madelung

$$U = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{q^2}{R} \sum_{j \neq 0} \frac{\pm 1}{|j|} = -\frac{1}{8\pi\epsilon_0} \frac{q^2 \alpha}{R}$$

$$\alpha = R \sum_{j \neq 0} \frac{\mp 1}{r_j} = \sum_{j \neq 0} \frac{\mp 1}{|j|}$$

# Cristal iônico unidimensional

## Constante de Madelung

Constante de Madelung

$$\alpha = R \sum_{j \neq 0} \frac{\bar{\varphi} 1}{r_j} = \sum_{j \neq 0} \frac{\bar{\varphi} 1}{|j|}$$



$$\alpha = 2 \left[ \frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right]$$

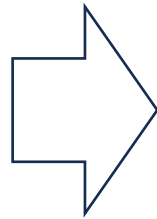


# Cristal iônico unidimensional

## Constante de Madelung

Constante de Madelung

$$\alpha = R \sum_{j \neq 0} \frac{\bar{\mp} 1}{r_j} = \sum_{j \neq 0} \frac{\bar{\mp} 1}{|j|}$$



$$\alpha = 2 \left[ \frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right]$$

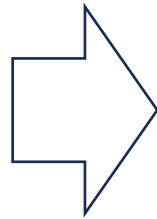
$$\ln(2) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots$$

# Cristal iônico unidimensional

## Constante de Madelung

Constante de Madelung

$$\alpha = R \sum_{j \neq 0} \frac{\bar{\mp} 1}{r_j} = \sum_{j \neq 0} \frac{\bar{\mp} 1}{|j|}$$



$$\alpha = 2 \left[ \frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right]$$

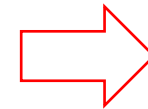
$$\ln(2) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots$$

$$\alpha = R \sum_{j \neq 0} \frac{\bar{\mp} 1}{r_j} = \sum_{j \neq 0} \frac{\bar{\mp} 1}{|j|} = 2 \ln 2$$

## Constante de Madelung

**Table 4.4.** The Madelung constant for some typical ionic crystals

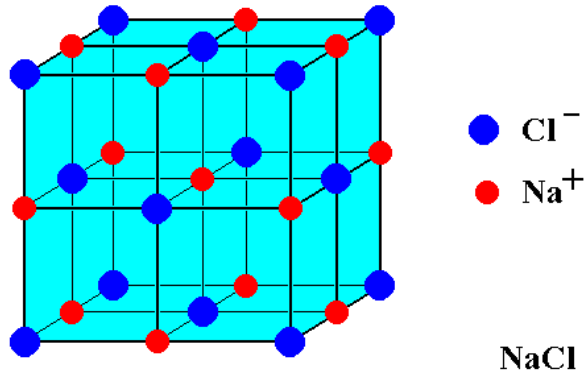
| Structure                                  |                 |      | Ionic composition  | Madelung constant |
|--|-----------------|------|--------------------|-------------------|
| Name                                       | Notation        |      |                    |                   |
| Sodium chloride (NaCl)                     | B1              | cF8  | $M^+X^-$           | 1.74756           |
| Cesium chloride (CsCl)                     | B2              | cP2  | $M^+X^-$           | 1.76267           |
| Sphalerite (ZnS)                           | B3              | cF8  | $M^{2+}X^{2-}$     | 1.63806           |
| Wurtzite (ZnS)                             | B4              | hP4  | $M^{2+}X^{2-}$     | 1.64132           |
| Fluorite (CaF <sub>2</sub> )               | C1              | cF12 | $M^{2+}X_2^-$      | 2.51939           |
| Cuprite (Cu <sub>2</sub> O)                | C3              | cP6  | $M_2^+X^{2-}$      | 2.22124           |
| Corundum (Al <sub>2</sub> O <sub>3</sub> ) | D5 <sub>1</sub> | hR10 | $M_2^{3+}X_3^{2-}$ | 4.1719            |



Rede cúbica?  
Lista ou prova!!!

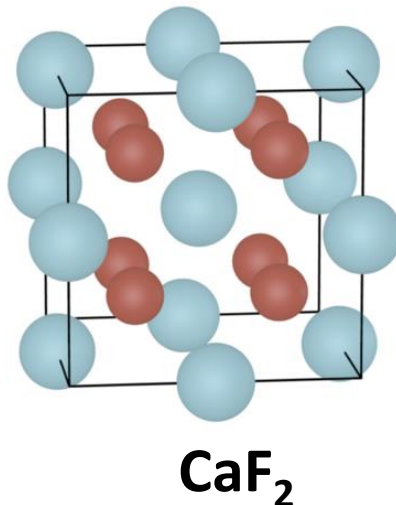
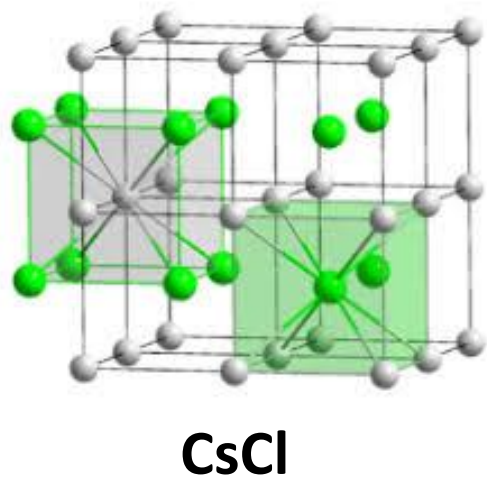
# Sólidos Iônicos

- Ligação típica entre elementos das famílias 1A/2A com elementos das famílias 6A/7A.



- Duros. (5-10 eV/átomo)
- Altas temperaturas de fusão.
- Pouco densos.
- Ligações sem orientação.
- Isolantes Elétricos.

NaCl derrete a  $\sim 800^\circ \text{C}$ .

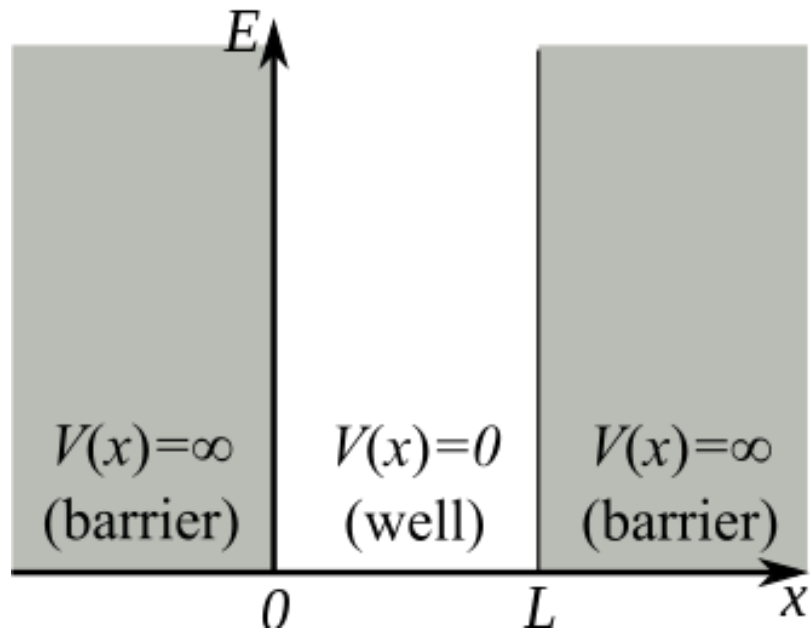


| Substance | Cohesive energy |             | Substance | Cohesive energy |             |
|-----------|-----------------|-------------|-----------|-----------------|-------------|
|           | kJ/mol          | eV/molecule |           | kJ/mol          | eV/molecule |
| LiF       | 1036            | 10.74       | LiCl      | 853             | 8.84        |
| NaF       | 923             | 9.57        | NaCl      | 786             | 8.15        |
| KF        | 821             | 8.51        | KCl       | 715             | 7.41        |
| RbF       | 785             | 8.14        | RbCl      | 689             | 7.14        |
| CsF       | 740             | 7.67        | CsCl      | 659             | 6.83        |

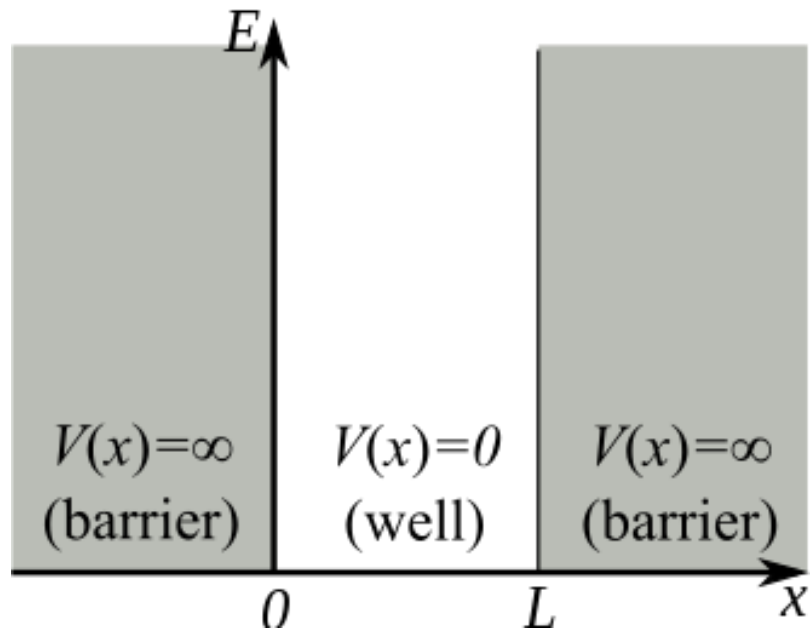
# Ionicidade de materiais

| <b>Cristal</b> | <b>Ionicidade</b> | <b>Cristal</b> | <b>Ionicidade</b> | <b>Cristal</b> | <b>Ionicidade</b> |
|----------------|-------------------|----------------|-------------------|----------------|-------------------|
| <b>Si</b>      | 0,00              | <b>CdSe</b>    | 0,70              | <b>AgBr</b>    | 0,85              |
| <b>SiC</b>     | 0,18              | <b>CdTe</b>    | 0,67              | <b>AgI</b>     | 0,77              |
| <b>Ge</b>      | 0,00              | <b>InP</b>     | 0,42              | <b>MgO</b>     | 0,84              |
| <b>ZnO</b>     | 0,62              | <b>InAs</b>    | 0,36              | <b>MgS</b>     | 0,79              |
| <b>ZnSe</b>    | 0,62              | <b>InSb</b>    | 0,32              | <b>MgSe</b>    | 0,79              |
| <b>ZnTe</b>    | 0,63              | <b>GaAs</b>    | 0,31              | <b>LiF</b>     | 0,92              |
| <b>CdO</b>     | 0,79              | <b>GaSb</b>    | 0,26              | <b>NaCl</b>    | 0,94              |
| <b>CdS</b>     | 0,69              | <b>AgCl</b>    | 0,86              | <b>RbF</b>     | 0,96              |

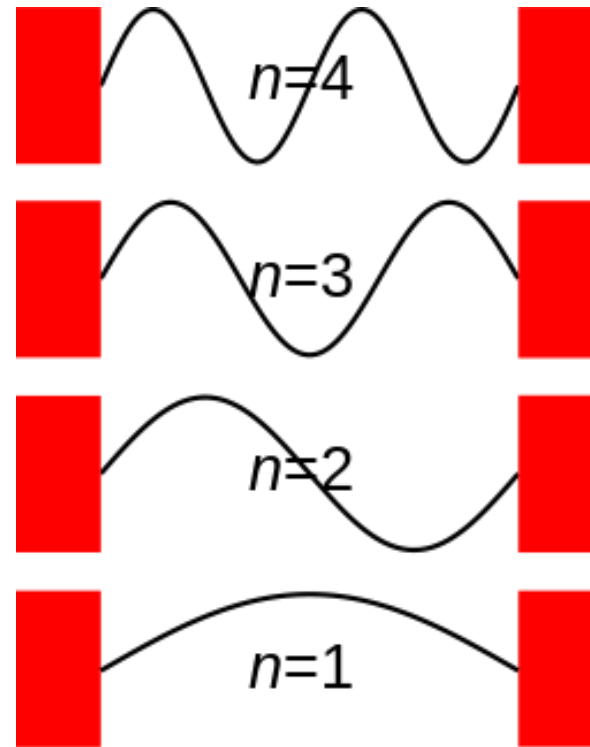
# Ligação Covalente



# Ligação Covalente



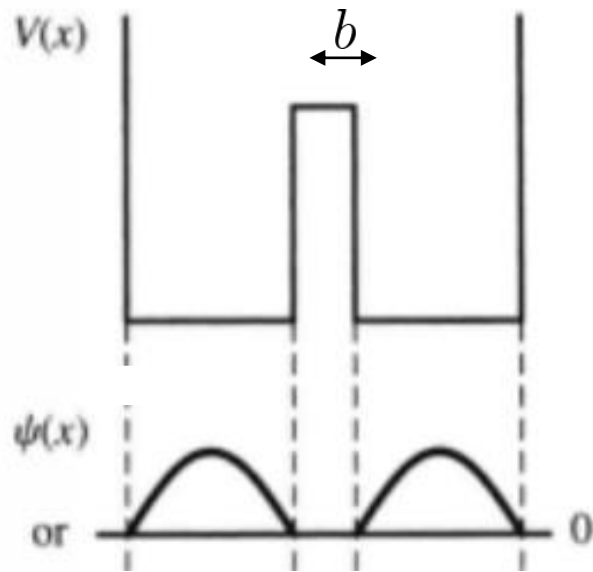
$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$



# Ligação Covalente

- Intuição de porque a combinação antissimétrica tem a maior energia.

Soluções de menor energia para  $b$  grande.



Se  $b \rightarrow 0$ , então

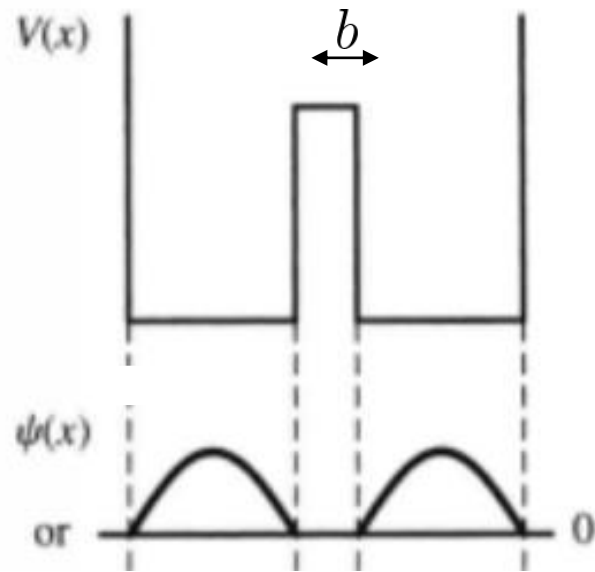
$$E = \frac{\hbar^2 \pi^2}{2m(2L)^2}$$



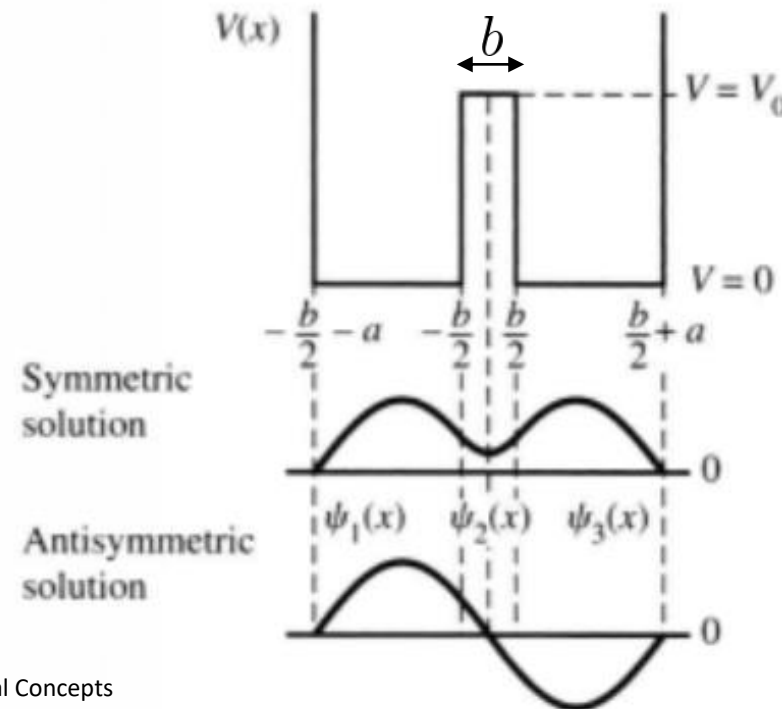
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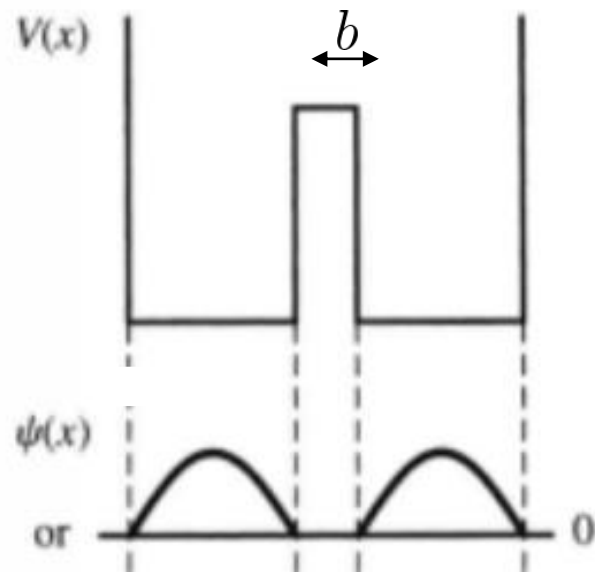
Soluções de menor energia para  $b$  pequeno.



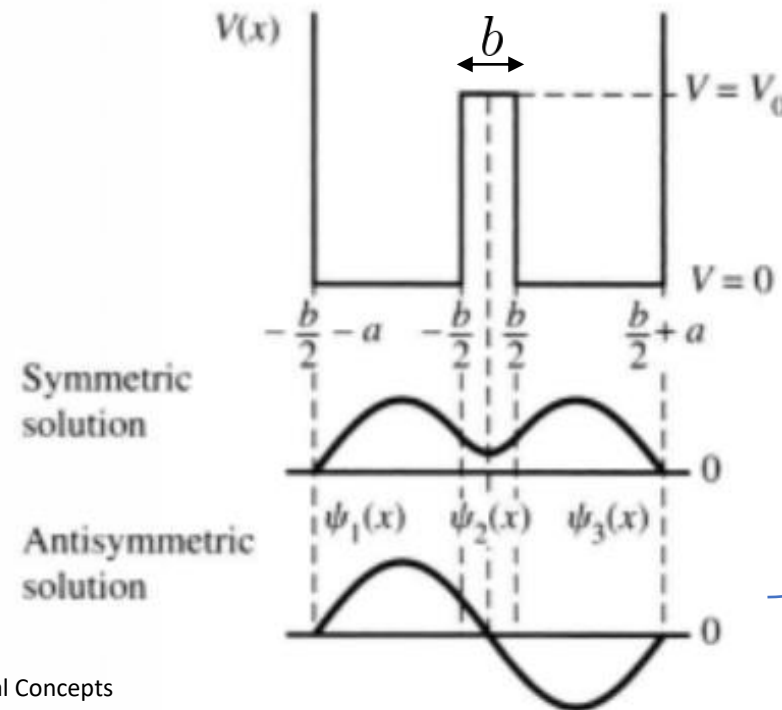
# Ligação Covalente

- Intuição de porque a combinação antissimétrica tem a maior energia.

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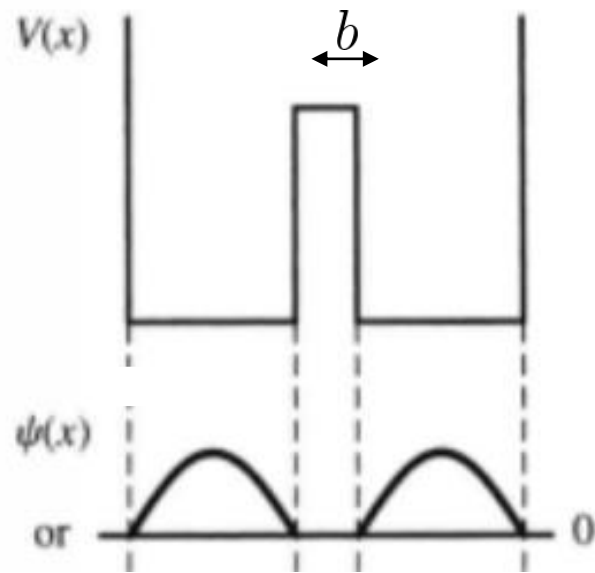
Maior variação com a posição

⇒  
Maior energia

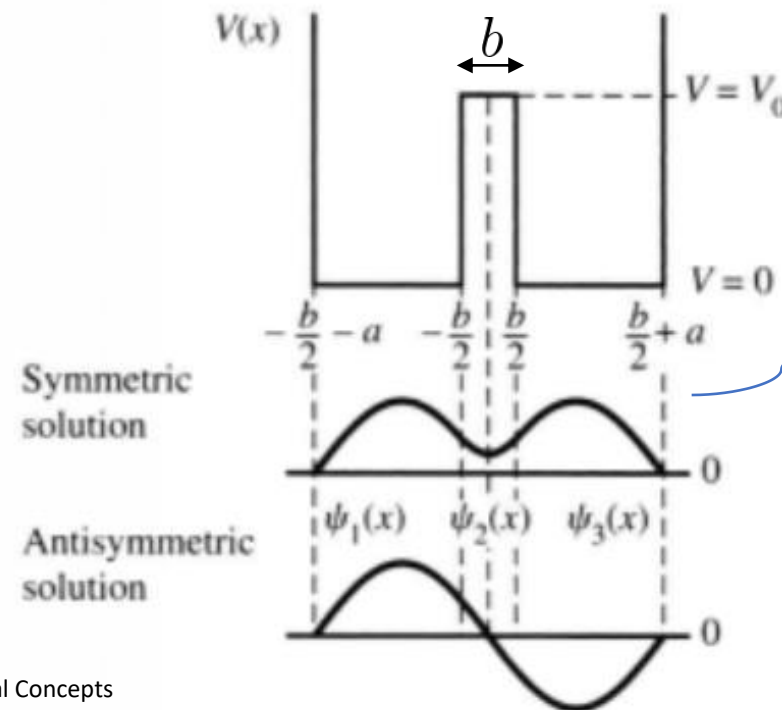
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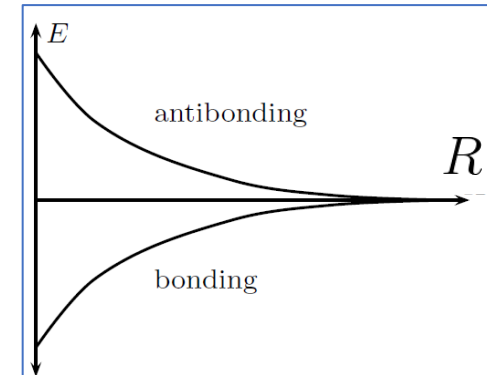


Quanto menor  $b \Rightarrow$   
menor a variação espacial  $\Rightarrow$

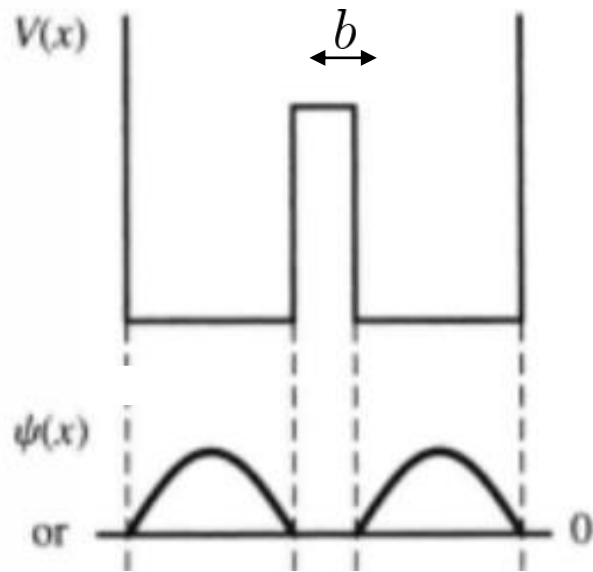
**maior a diferença de energia  
entre os dois estados!**

# Ligação Covalente

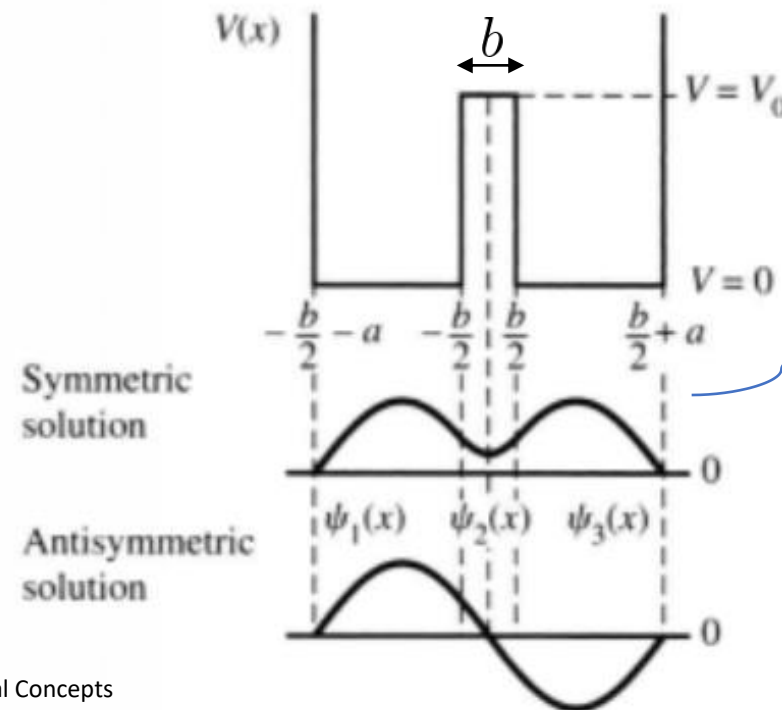
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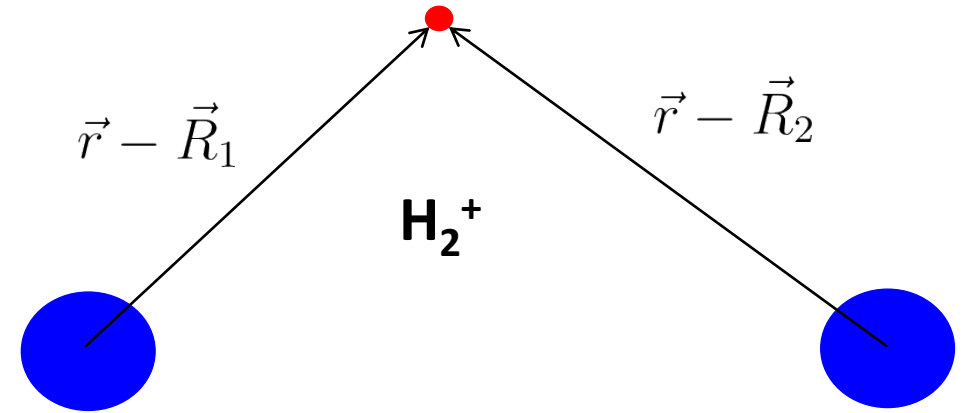


Quanto menor  $b \Rightarrow$   
menor a variação espacial  $\Rightarrow$

**maior a diferença de energia  
entre os dois estados!**

# Teoria do orbital molecular

- Tratamento quântico orbital para  $\text{H}_2^+$ . (Born-Oppenheimer)



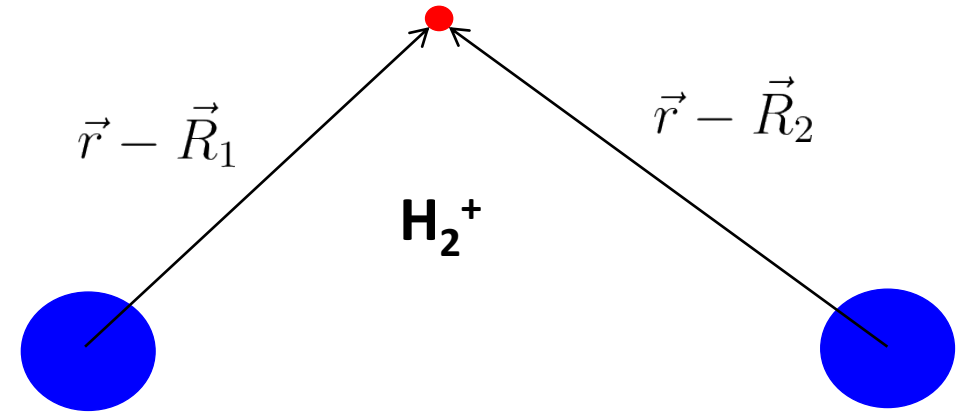
# Teoria do orbital molecular

- Tratamento quântico orbital para  $\text{H}_2^+$ . (Born-Oppenheimer)

$$H = K + V_1 + V_2$$

$$K = \frac{p^2}{2m}$$

$$V_i = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{R}_i|}$$



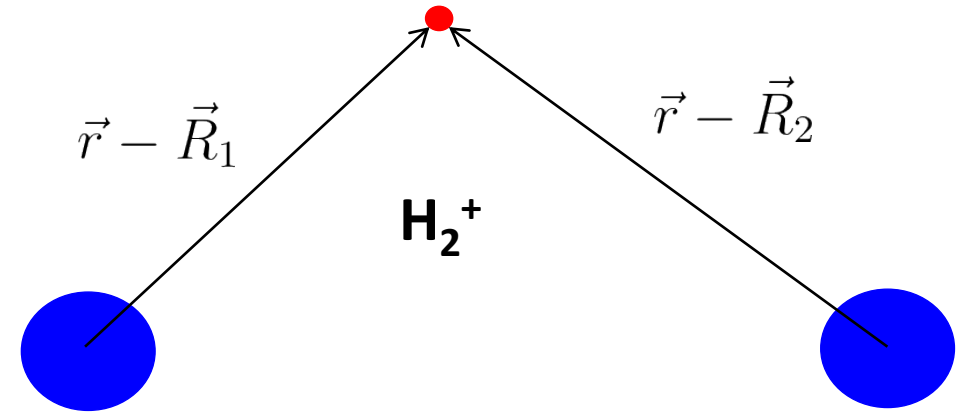
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- Seja o auto-estado fundamental do átomo de H conhecido:

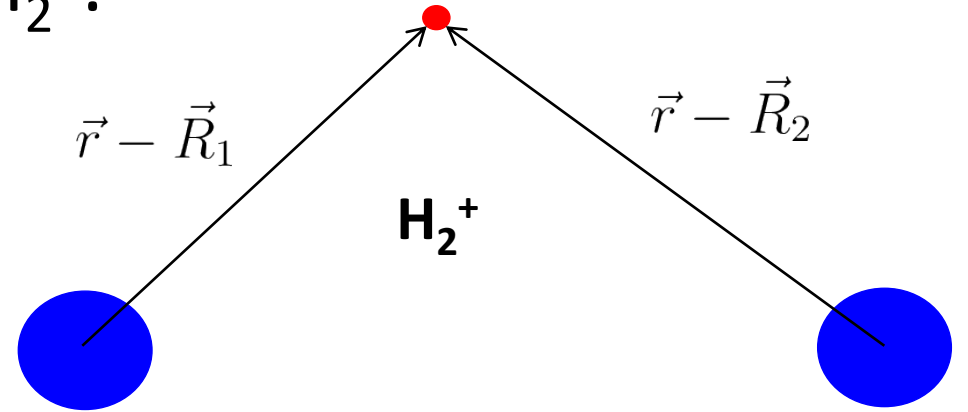
$$(K + V_1)|1\rangle = \epsilon_0|1\rangle$$

$$(K + V_2)|2\rangle = \epsilon_0|2\rangle$$

- Busquemos o estado fundamental de  $H_2^+$ .

$$H = K + V_1 + V_2$$

|  |
|--|
| $(K + V_1) 1\rangle = \epsilon_0 1\rangle$ |
| $(K + V_2) 2\rangle = \epsilon_0 2\rangle$ |





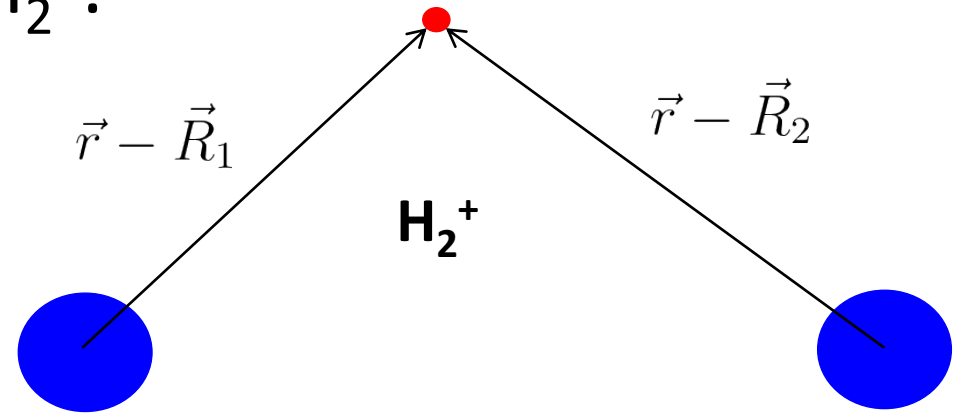
- Busquemos o estado fundamental de  $\text{H}_2^+$ .

$$H = K + V_1 + V_2$$

$$\begin{aligned} (K + V_1)|1\rangle &= \epsilon_0|1\rangle \\ (K + V_2)|2\rangle &= \epsilon_0|2\rangle \end{aligned}$$

Sendo  $|\psi\rangle = \phi_1|1\rangle + \phi_2|2\rangle$

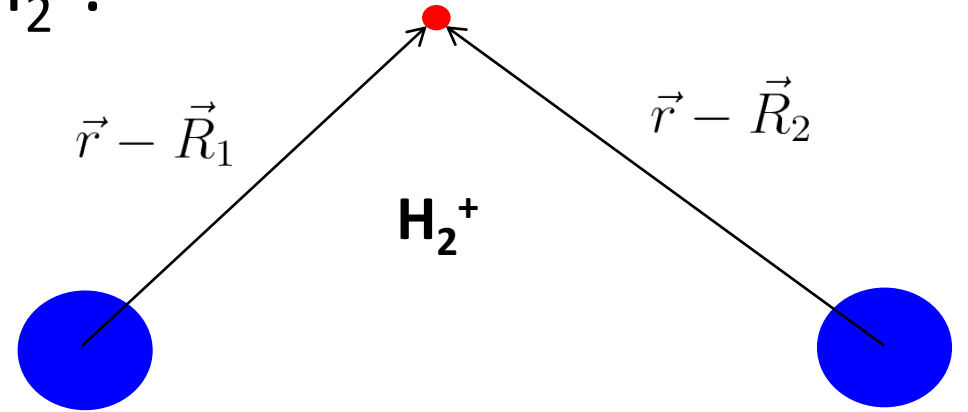
$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = E \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$



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Então  $H_{11} = \langle 1|H|1\rangle = \langle 1|K + V_1|1\rangle + \langle 1|V_2|1\rangle$

$$H_{11} = \epsilon_0 + V_{\text{cross}}$$

$$H_{22} = \epsilon_0 + V_{\text{cross}}$$

$$H_{12} = \langle 1|H|2\rangle = \langle 1|K + V_2|2\rangle + \langle 1|V_2|2\rangle$$

$$H_{12} = \epsilon_0 \langle 1|2\rangle + \langle 1|V_2|2\rangle$$

$$H_{12} = \langle 1|H|2\rangle = \langle 1|K + V_2|2\rangle + \langle 1|V_2|2\rangle$$

$$H_{12} = \epsilon_0 \langle 1|2\rangle + \langle 1|V_2|2\rangle$$

Aproximando  $\langle i|j\rangle = \delta_{ij} \Rightarrow \boxed{H_{12} = -t = H_{21}^*}$

$$\boxed{\langle 1|2\rangle = \int d^3\mathbf{r} \psi_1^*(\mathbf{r}) \psi_2(\mathbf{r})}$$

$$H_{12} = \langle 1|H|2\rangle = \langle 1|K + V_2|2\rangle + \langle 1|V_2|2\rangle$$

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$$E_{\pm} = \epsilon_0 + V_{\text{cross}} \pm t \approx \epsilon_0 \pm t$$

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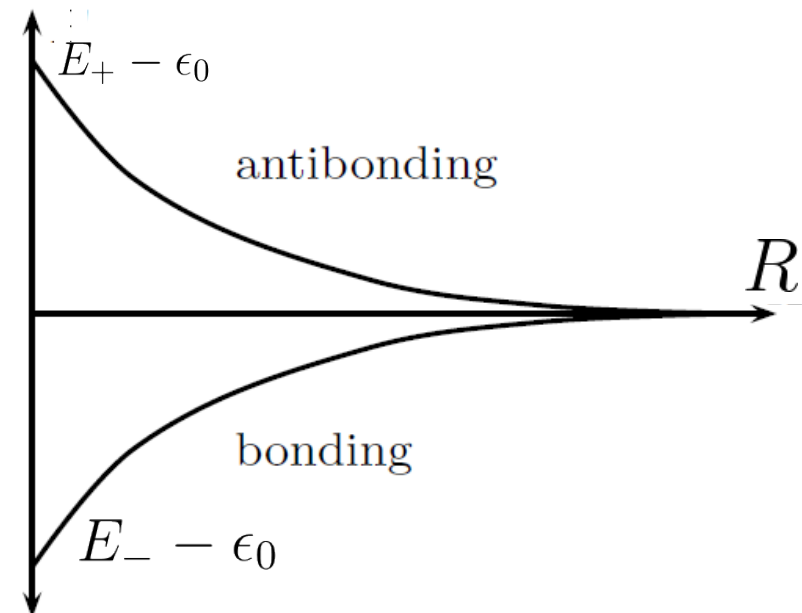
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# Teoria do orbital molecular

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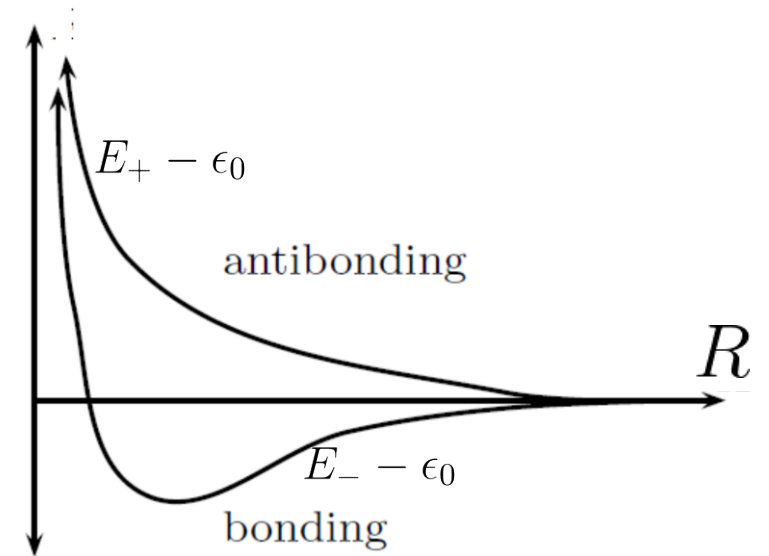
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$$|\psi\rangle = \phi_1|1\rangle + \phi_2|2\rangle$$

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- Autovalores:

$$E_{\pm} \approx \epsilon_0 \pm t$$



# Teoria do orbital molecular

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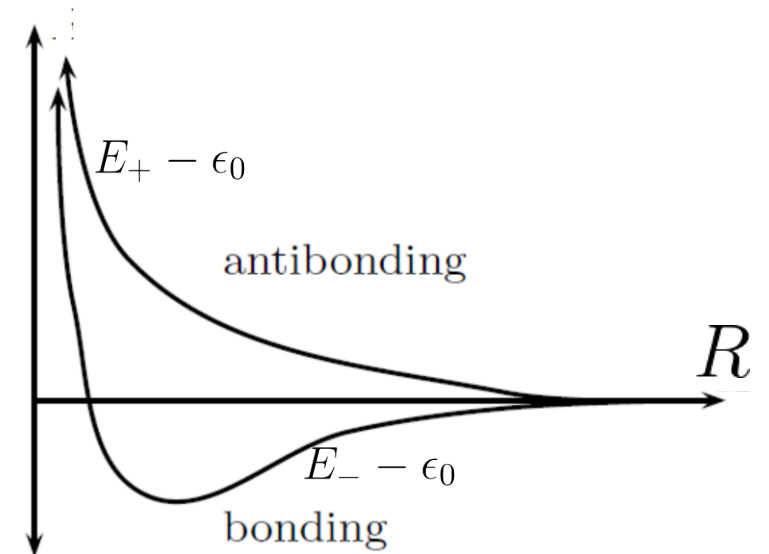
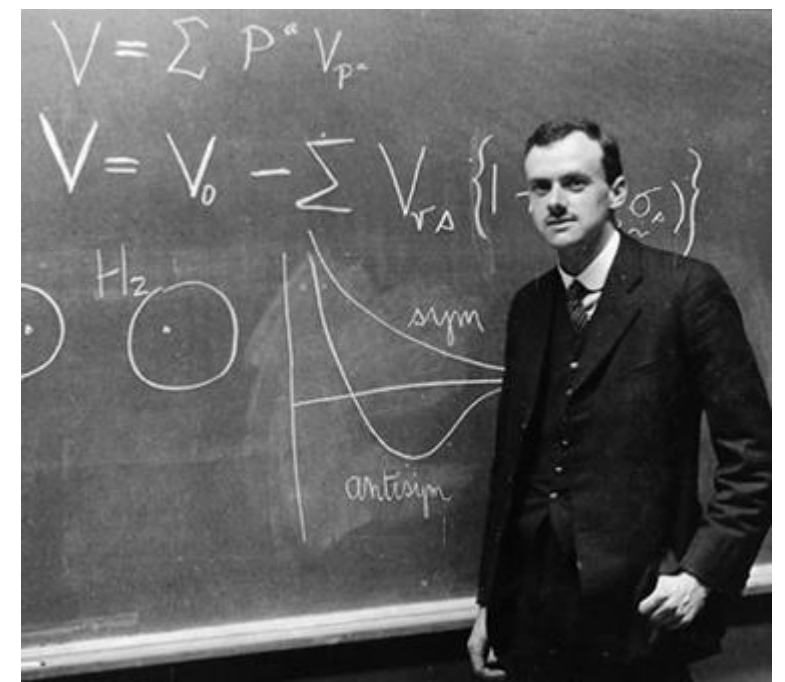
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# Funções de onda

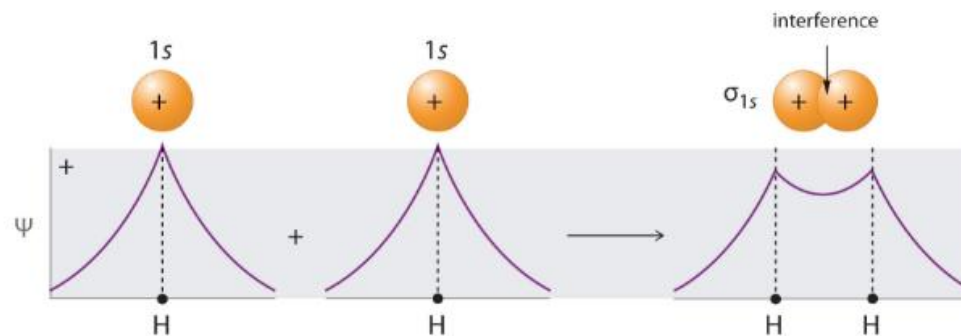
$$|\psi_{bonding}\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$$

$$|\psi_{antibonding}\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$$

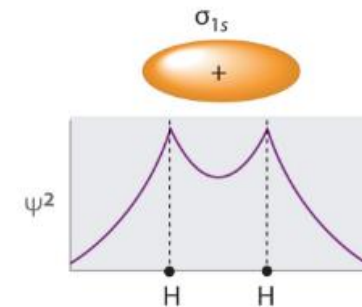
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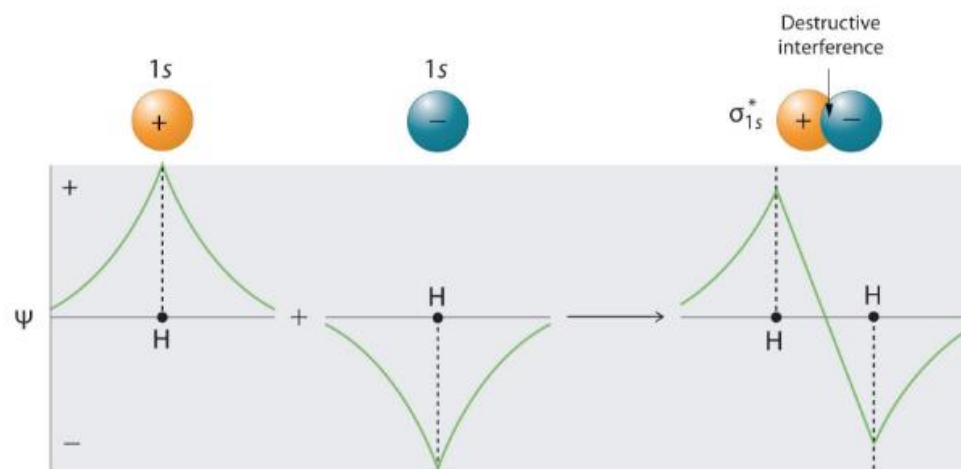
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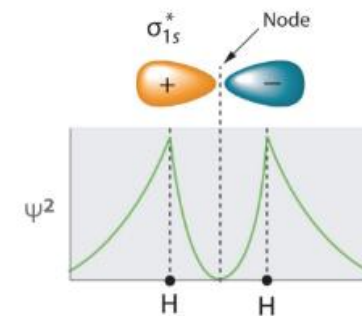
(a) Wave functions combined for  $\sigma_{1s}$



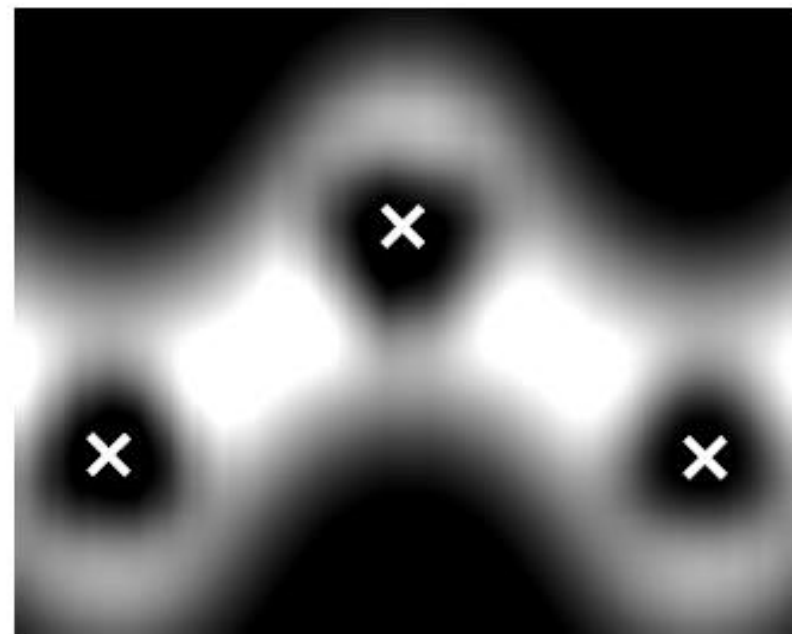
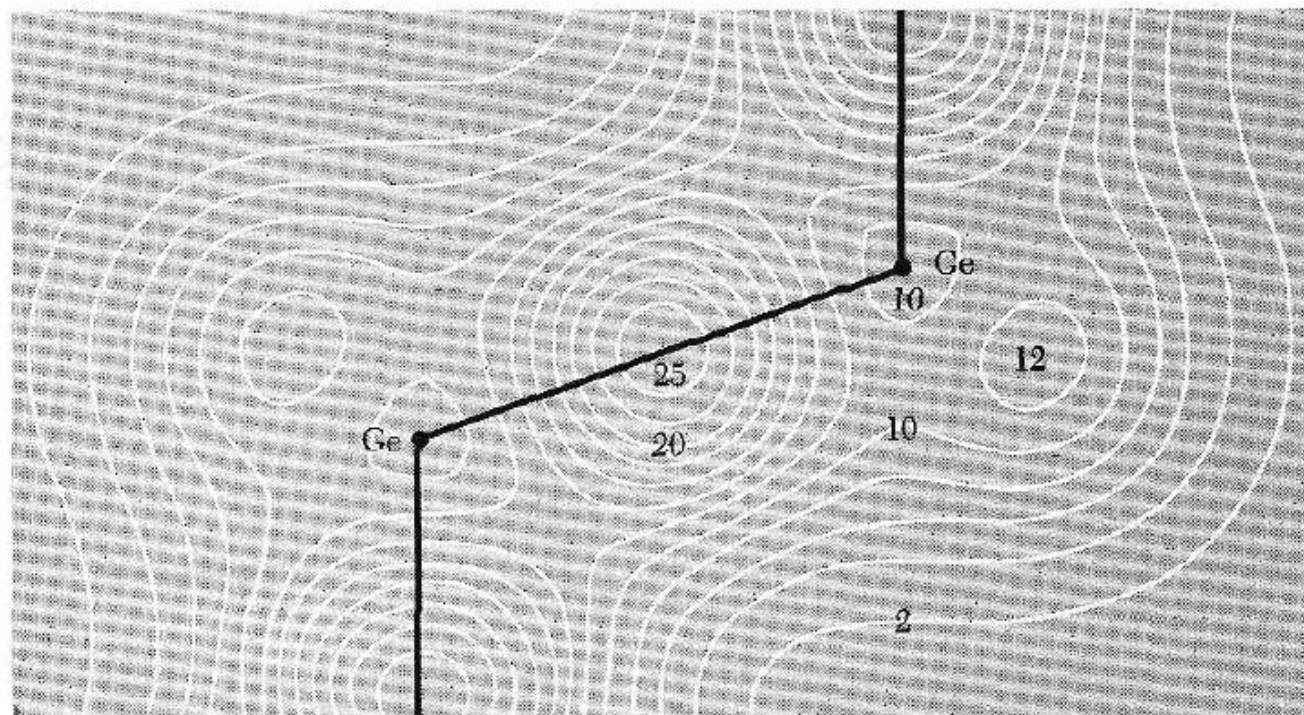
(b) Bonding probability density



(c) Wave functions combined for  $\sigma_{1s}^*$

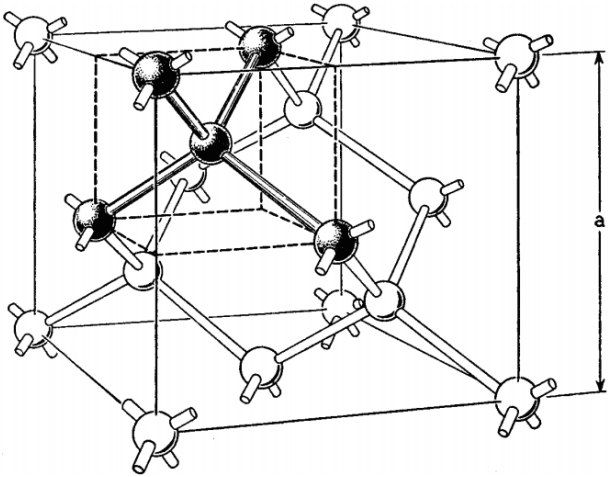


(d) Antibonding probability density

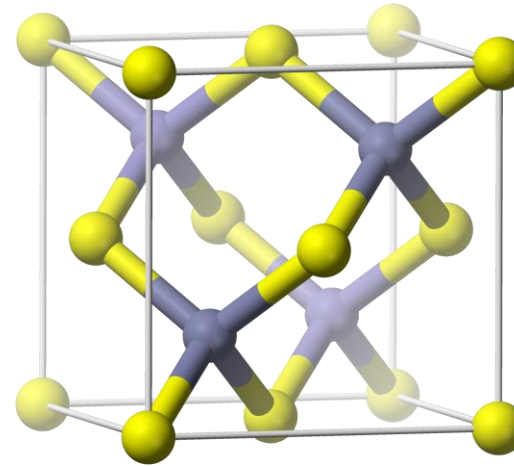


# Sólidos Covalentes

- Ligação típica entre elementos das famílias IIIA-VA, ou sólidos formados por um elemento só.



W. Shockley, Electrons and Holes in semiconductors



GaAs

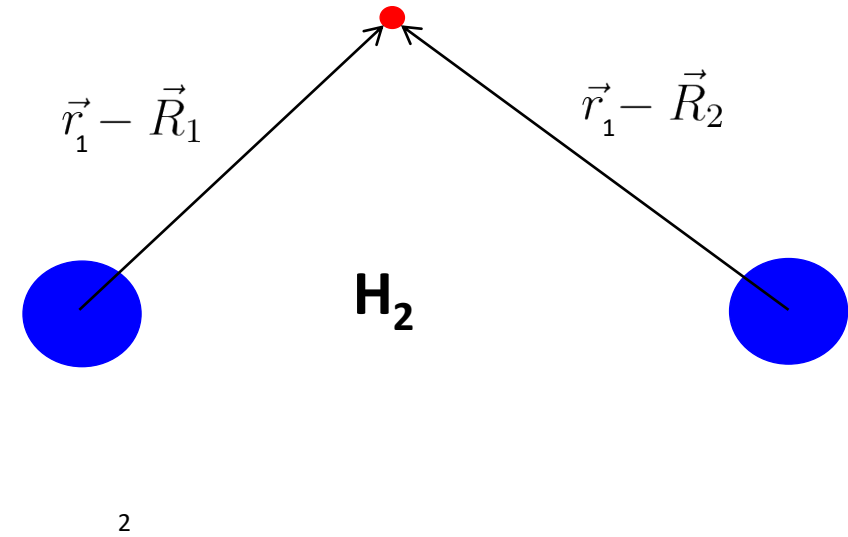
[https://en.wikipedia.org/wiki/Aluminium\\_gallium\\_arsenide](https://en.wikipedia.org/wiki/Aluminium_gallium_arsenide)

Diamante, Ge e Si

- Rígidos
- Ligações são orientadas.
- Pouco densos, devido à orientação da ligação.

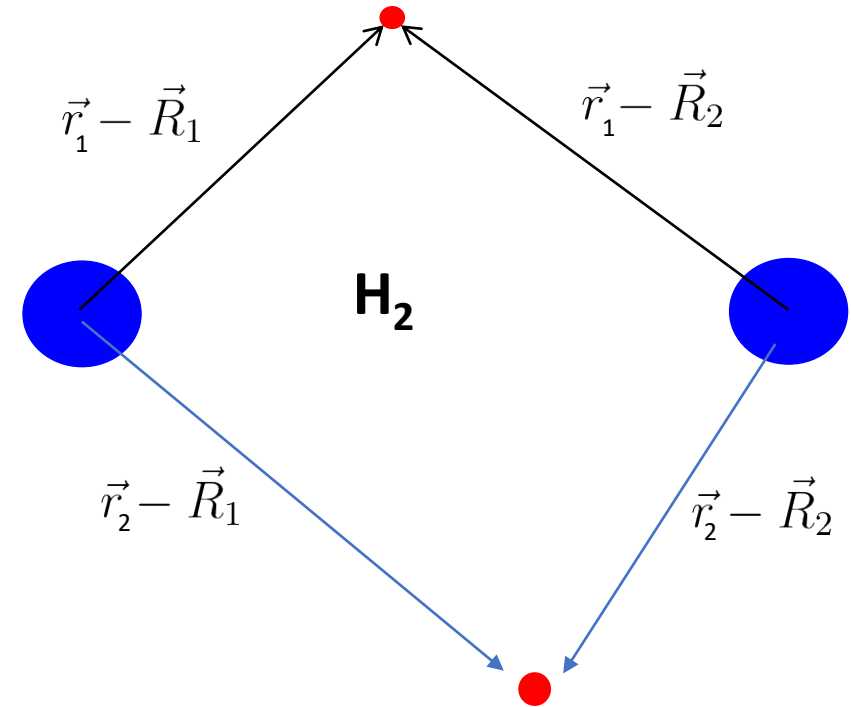
# Teoria do spin-orbital

- Tratamento quântico orbital para  $H_2$ . (Born-Oppenheimer)



# Teoria do spin-orbital

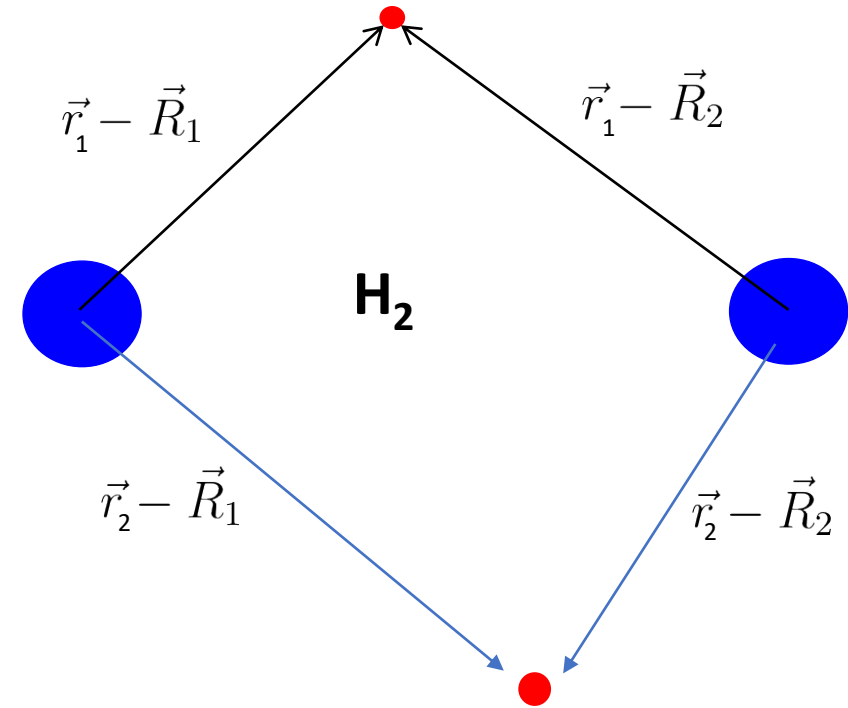
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# Teoria do spin-orbital

- Tratamento quântico orbital para  $H_2$ . (Born-Oppenheimer)

$$\hat{H} = \sum_{i=1}^2 \left( -\frac{\hbar^2}{2m} \Delta_{\mathbf{r}_i} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_a|} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_b|} \right) + \frac{e^2}{R} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$



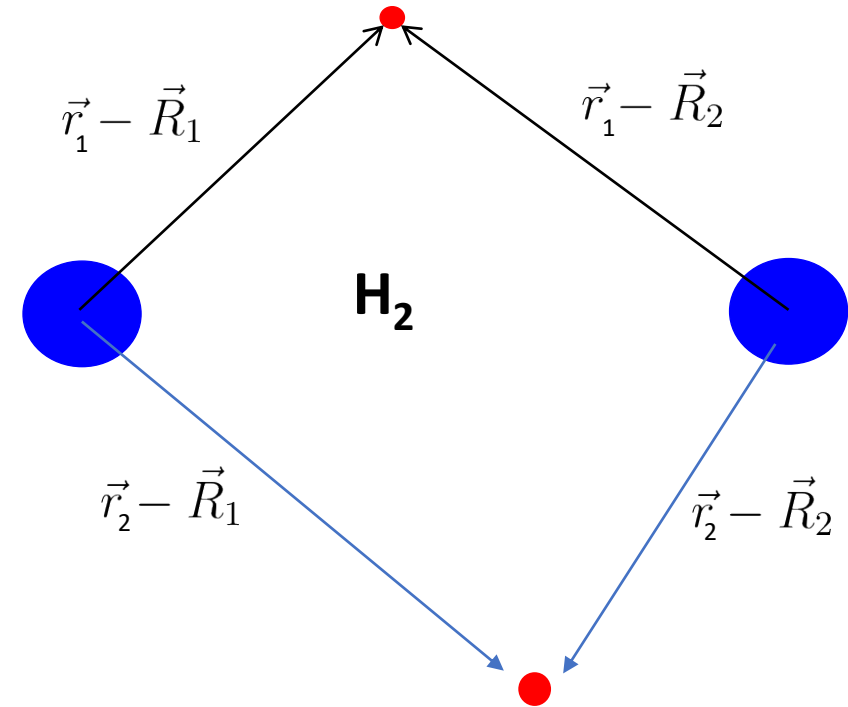
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$$\langle \mathbf{r} | 1 \rangle \equiv a(\mathbf{r})$$

$$\langle \mathbf{r} | 2 \rangle \equiv b(\mathbf{r})$$





# Teoria do spin-orbital

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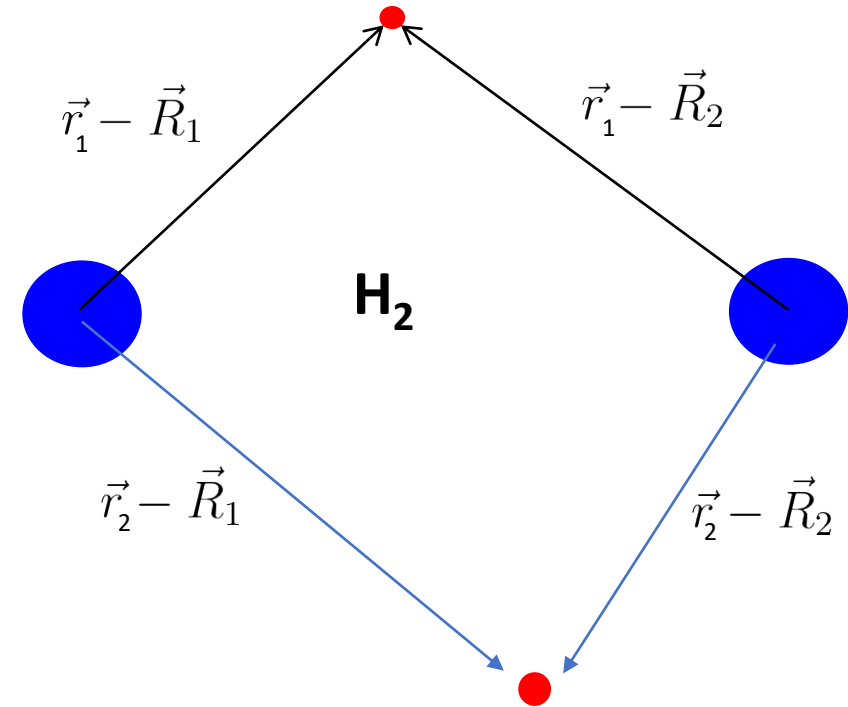
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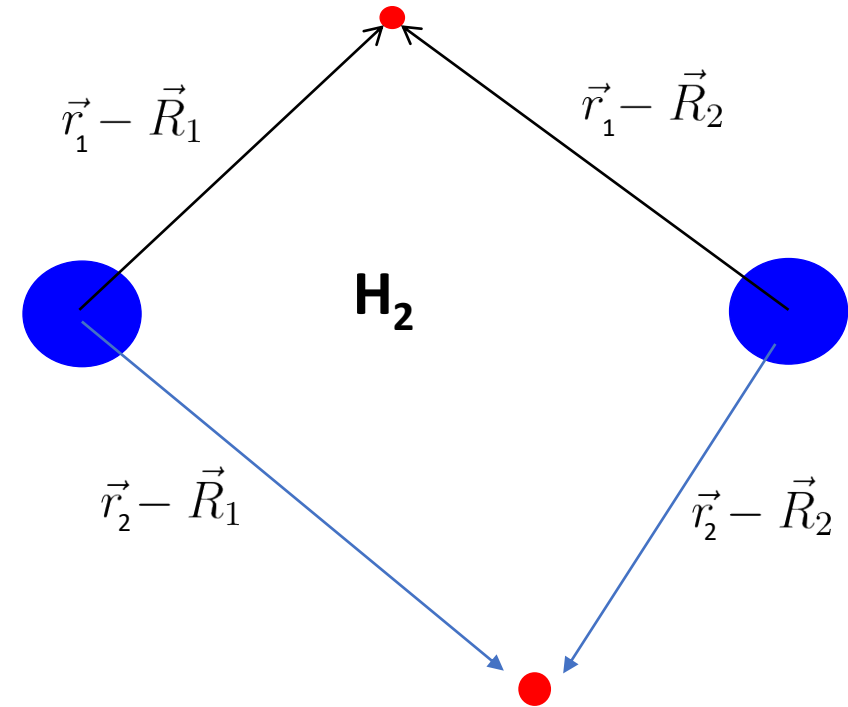
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$$\psi_{\text{Bonding}}(\mathbf{r}) = \frac{1}{\sqrt{2(1+S)}} (a(\mathbf{r}) + b(\mathbf{r})) \equiv B(\mathbf{r})$$

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# Teoria do spin-orbital

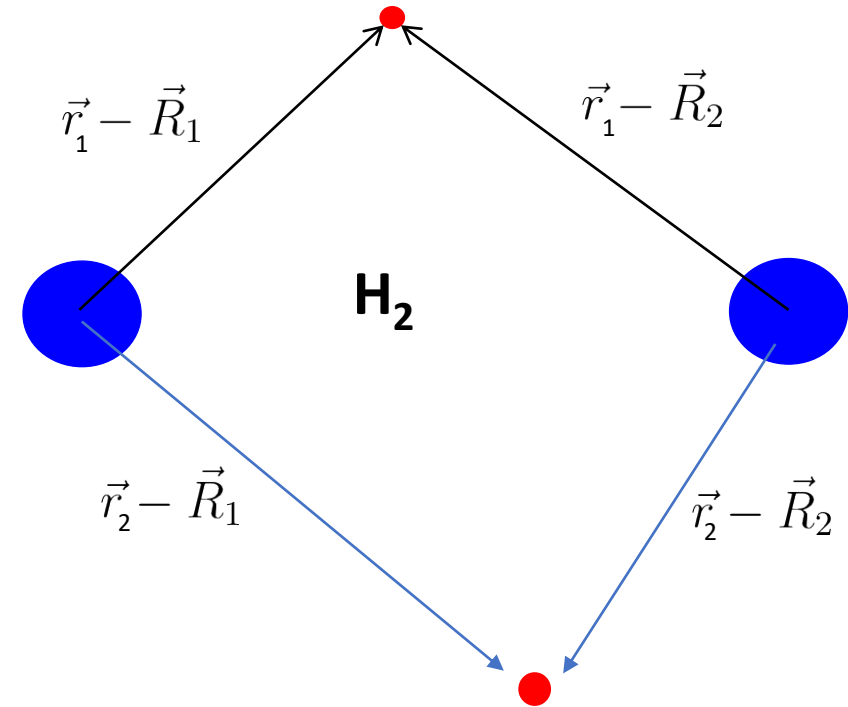
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$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = B(\mathbf{r}_1) B(\mathbf{r}_2) \text{ ???}$$



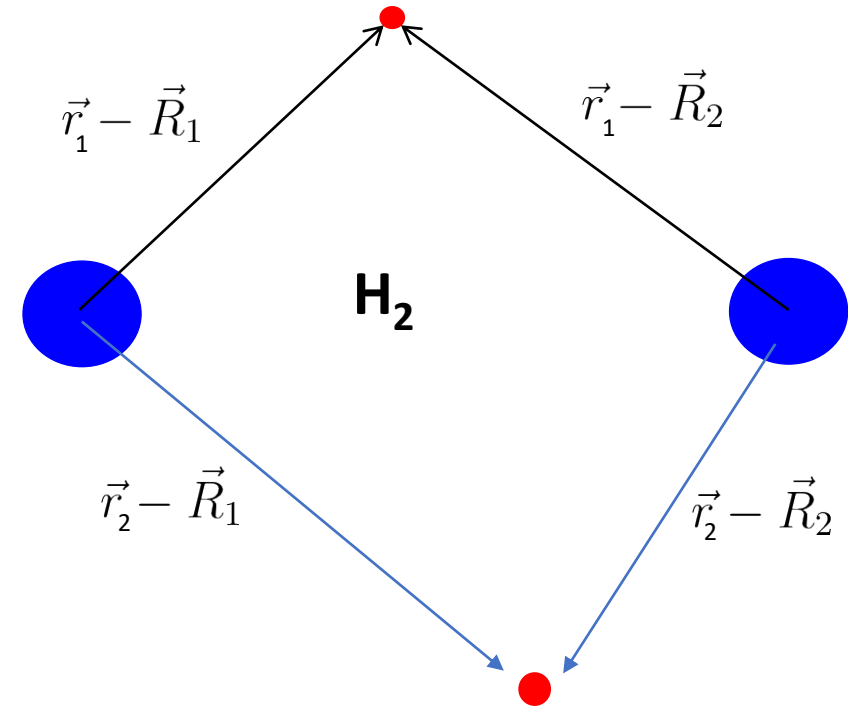
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~~$\Psi(\mathbf{r}_1, \mathbf{r}_2) = B(\mathbf{r}_1)B(\mathbf{r}_2) ???$~~

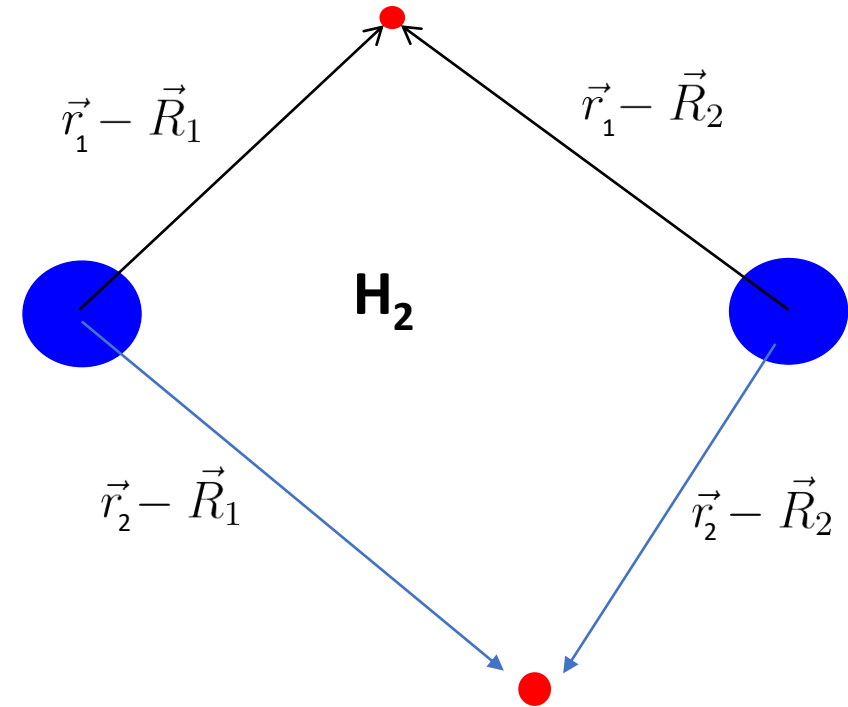
# Teoria do spin-orbital

- Tratamento quântico orbital para  $H_2$ . (Born-Oppenheimer)

$$\hat{H} = \sum_{i=1}^2 \left( -\frac{\hbar^2}{2m} \Delta_{\mathbf{r}_i} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_a|} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_b|} \right) + \frac{e^2}{R} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\psi_{\text{Bonding}}(\mathbf{r}) = \frac{1}{\sqrt{2(1+S)}} (a(\mathbf{r}) + b(\mathbf{r})) \equiv B(\mathbf{r})$$

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Simetrização da  
função de onda:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\mathcal{N}} \begin{vmatrix} A(\mathbf{r}_1) & A(\mathbf{r}_2) \\ B(\mathbf{r}_1) & B(\mathbf{r}_2) \end{vmatrix} \equiv \det |A B|$$

Determinante de Slater

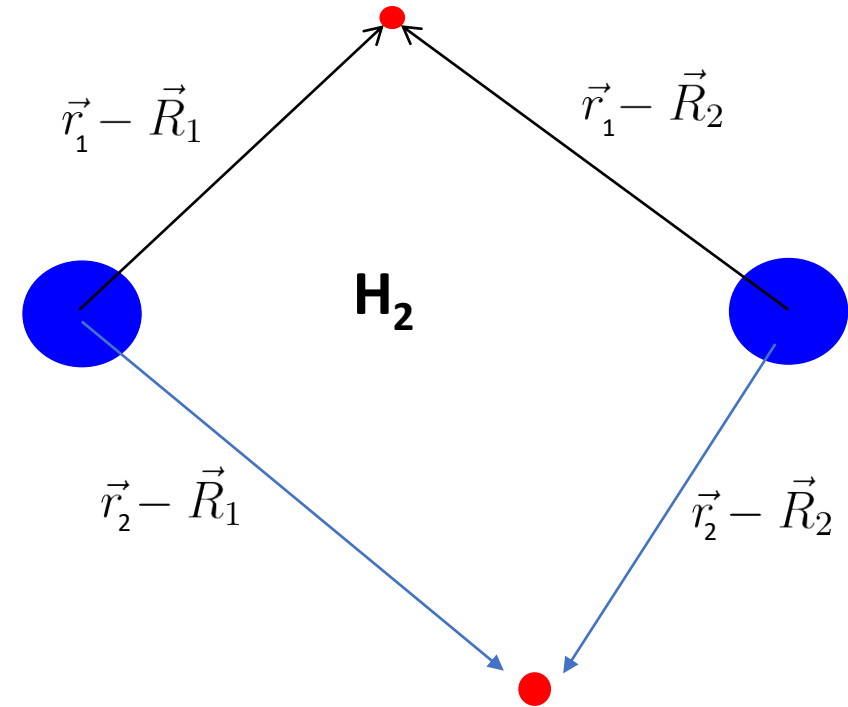
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$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \propto A(\mathbf{r}_1)B(\mathbf{r}_2) - A(\mathbf{r}_2)B(\mathbf{r}_1)$$

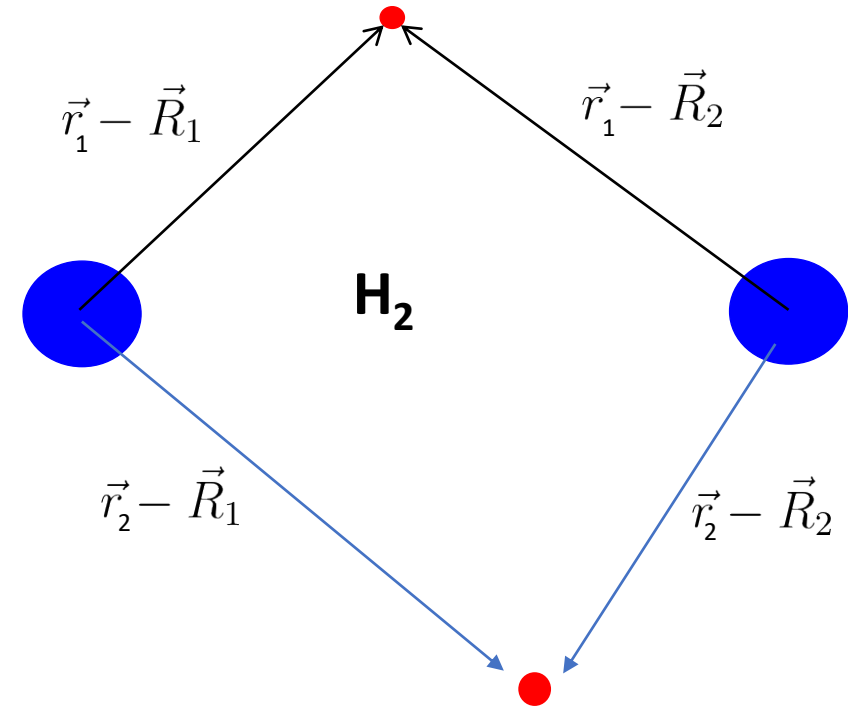
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$|\uparrow\rangle$

$|\downarrow\rangle$

Spin operators!!



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$$\alpha(?) = \langle ? | \uparrow \rangle$$

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Spin operators!!

$$\begin{aligned} \hat{S}_{1+\alpha}(\sigma_1) &= 0, & \hat{S}_{1+\beta}(\sigma_1) &= \hbar\alpha(\sigma_1), \\ \hat{S}_{1-\alpha}(\sigma_1) &= \hbar\beta(\sigma_1), & \hat{S}_{1-\beta}(\sigma_1) &= 0 \end{aligned}$$

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Levando em consideração apenas os spins dos elétrons, temos

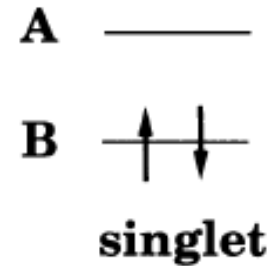
$$\chi_{00}(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}} [\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)] \quad \Rightarrow \quad \text{Singlete}$$

$$\begin{cases} \chi_{1\bar{1}}(\sigma_1, \sigma_2) = \beta(\sigma_1)\beta(\sigma_2) \\ \chi_{10}(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}} [\alpha(\sigma_1)\beta(\sigma_2) + \beta(\sigma_1)\alpha(\sigma_2)] \\ \chi_{11}(\sigma_1, \sigma_2) = \alpha(\sigma_1)\alpha(\sigma_2) \end{cases} \quad \Rightarrow \quad \text{Tripletes}$$

# Teoria do spin-orbital

- Tratamento quântico orbital para  $H_2$ . (Born-Oppenheimer)

$$\Psi_{00}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\mathcal{N}_s} B(\mathbf{r}_1) B(\mathbf{r}_2) \chi_{00}(\sigma_1, \sigma_2) \equiv \det |B\alpha B\beta|$$

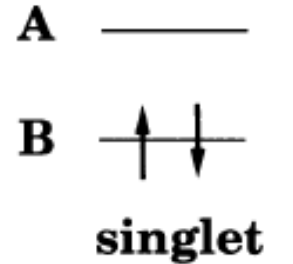


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$$\begin{cases} \Psi_{11}(\mathbf{x}_1, \mathbf{x}_2) \\ \Psi_{10}(\mathbf{x}_1, \mathbf{x}_2) \\ \Psi_{1\bar{1}}(\mathbf{x}_1, \mathbf{x}_2) \end{cases} = R_t(\mathbf{r}_1, \mathbf{r}_2) \begin{cases} \chi_{11}(\sigma_1, \sigma_2) \\ \chi_{10}(\sigma_1, \sigma_2) \\ \chi_{1\bar{1}}(\sigma_1, \sigma_2) \end{cases}$$



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**A** ———  
**B**  $\uparrow \downarrow$   
**singlet**

$$\mathbf{x}_1 = (\mathbf{r}_1 \sigma_1)$$

$$\mathbf{x}_2 = (\mathbf{r}_2 \sigma_2)$$

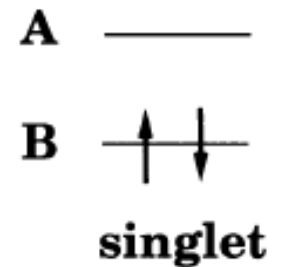
$$R_t(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{N_t} [B(\mathbf{r}_1)A(\mathbf{r}_2) - A(\mathbf{r}_1)B(\mathbf{r}_2)]$$

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$$\mathbf{x}_1 = (\mathbf{r}_1\sigma_1)$$

$$\mathbf{x}_2 = (\mathbf{r}_2\sigma_2)$$

$$R_t(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{N_t} [B(\mathbf{r}_1)A(\mathbf{r}_2) - A(\mathbf{r}_1)B(\mathbf{r}_2)]$$

É sempre possível escrever a função de onda total de um problema de  $N$  elétrons como um produto da função de uma função puramente orbital com outra puramente de spin?

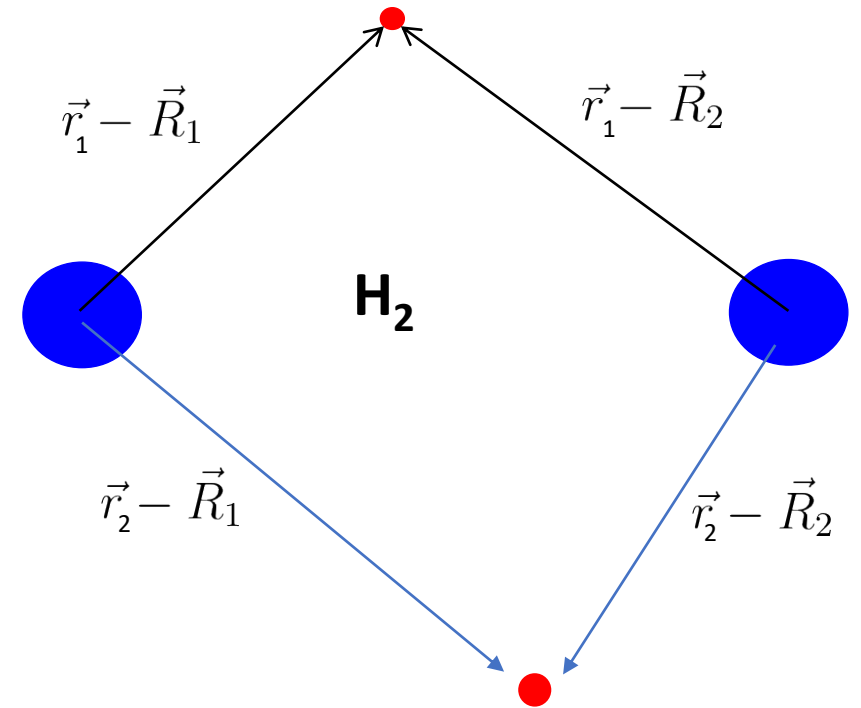


# Teoria do spin-orbital de ligação de valência para H<sub>2</sub>

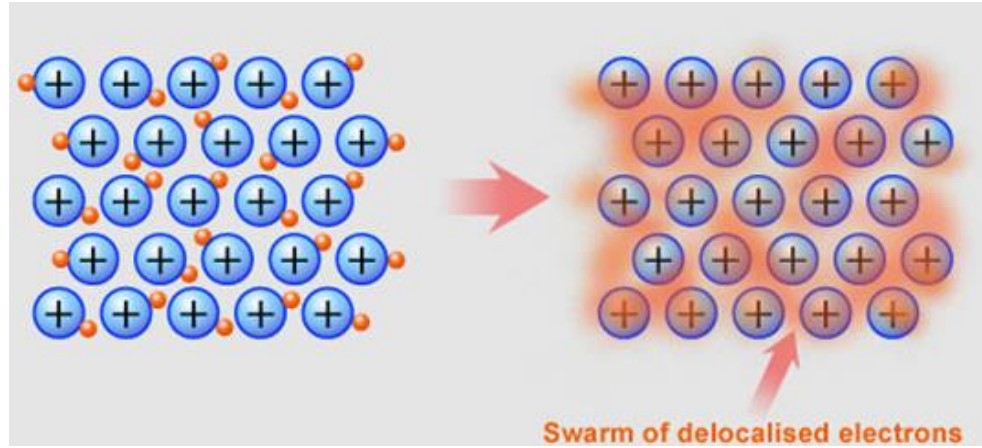
$$\Psi_{00}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{1+S^2}} [a(\mathbf{r}_1)b(\mathbf{r}_2) + b(\mathbf{r}_1)a(\mathbf{r}_2)] \chi_{00}(\sigma_1, \sigma_2)$$

$$\Psi_{1M}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{1+S^2}} [a(\mathbf{r}_1)b(\mathbf{r}_2) - b(\mathbf{r}_1)a(\mathbf{r}_2)] \chi_{1M}(\sigma_1, \sigma_2)$$

Lista!



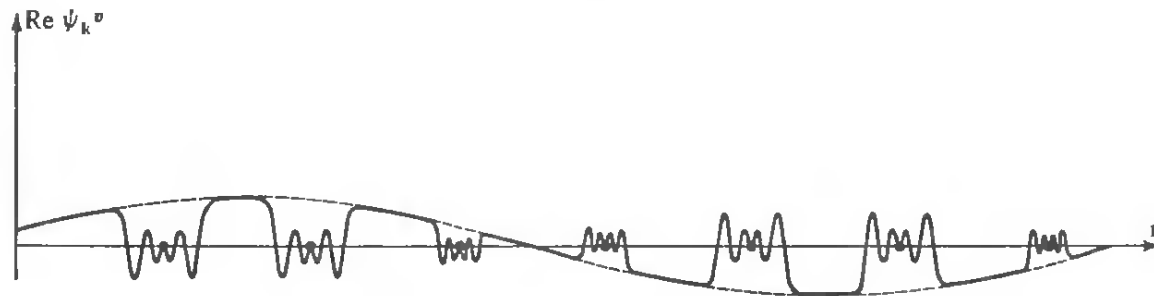
# Coesão Metálica



| Group | 1     | 2     | 3     | 4       | 5      | 6      | 7      | 8      | 9      | 10     | 11     | 12     | 13     | 14     | 15     | 16     | 17     | 18     |
|-------|-------|-------|-------|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1     | 1 H   |       |       |         |        |        |        |        |        |        |        |        |        |        |        |        |        | 2 He   |
| 2     | 3 Li  | 4 Be  |       |         |        |        |        |        |        |        |        |        | 5 B    | 6 C    | 7 N    | 8 O    | 9 F    | 10 Ne  |
| 3     | 11 Na | 12 Mg |       |         |        |        |        |        |        |        |        |        | 13 Al  | 14 Si  | 15 P   | 16 S   | 17 Cl  | 18 Ar  |
| 4     | 19 K  | 20 Ca | 21 Sc | 22 Ti   | 23 V   | 24 Cr  | 25 Mn  | 26 Fe  | 27 Co  | 28 Ni  | 29 Cu  | 30 Zn  | 31 Ga  | 32 Ge  | 33 As  | 34 Se  | 35 Br  | 36 Kr  |
| 5     | 37 Rb | 38 Sr | 39 Y  | 40 Zr   | 41 Nb  | 42 Mo  | 43 Tc  | 44 Ru  | 45 Rh  | 46 Pd  | 47 Ag  | 48 Cd  | 49 In  | 50 Sn  | 51 Sb  | 52 Te  | 53 I   | 54 Xe  |
| 6     | 55 Cs | 56 Ba | 57 La | 72 Hf   | 73 Ta  | 74 W   | 75 Re  | 76 Os  | 77 Ir  | 78 Pt  | 79 Au  | 80 Hg  | 81 Tl  | 82 Pb  | 83 Bi  | 84 Po  | 85 At  | 86 Rn  |
| 7     | 87 Fr | 88 Ra | 89 Ac | 104 Rf  | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 Ds | 111 Rg | 112 Cn | 113 Nh | 114 Fl | 115 Mc | 116 Lv | 117 Ts | 118 Og |
|       |       |       |       | * 58 Ce | 59 Pr  | 60 Nd  | 61 Pm  | 62 Sm  | 63 Eu  | 64 Gd  | 65 Tb  | 66 Dy  | 67 Ho  | 68 Er  | 69 Tm  | 70 Yb  | 71 Lu  |        |
|       |       |       |       | * 90 Th | 91 Pa  | 92 U   | 93 Np  | 94 Pu  | 95 Am  | 96 Cm  | 97 Bk  | 98 Cf  | 99 Es  | 100 Fm | 101 Md | 102 No | 103 Lr |        |

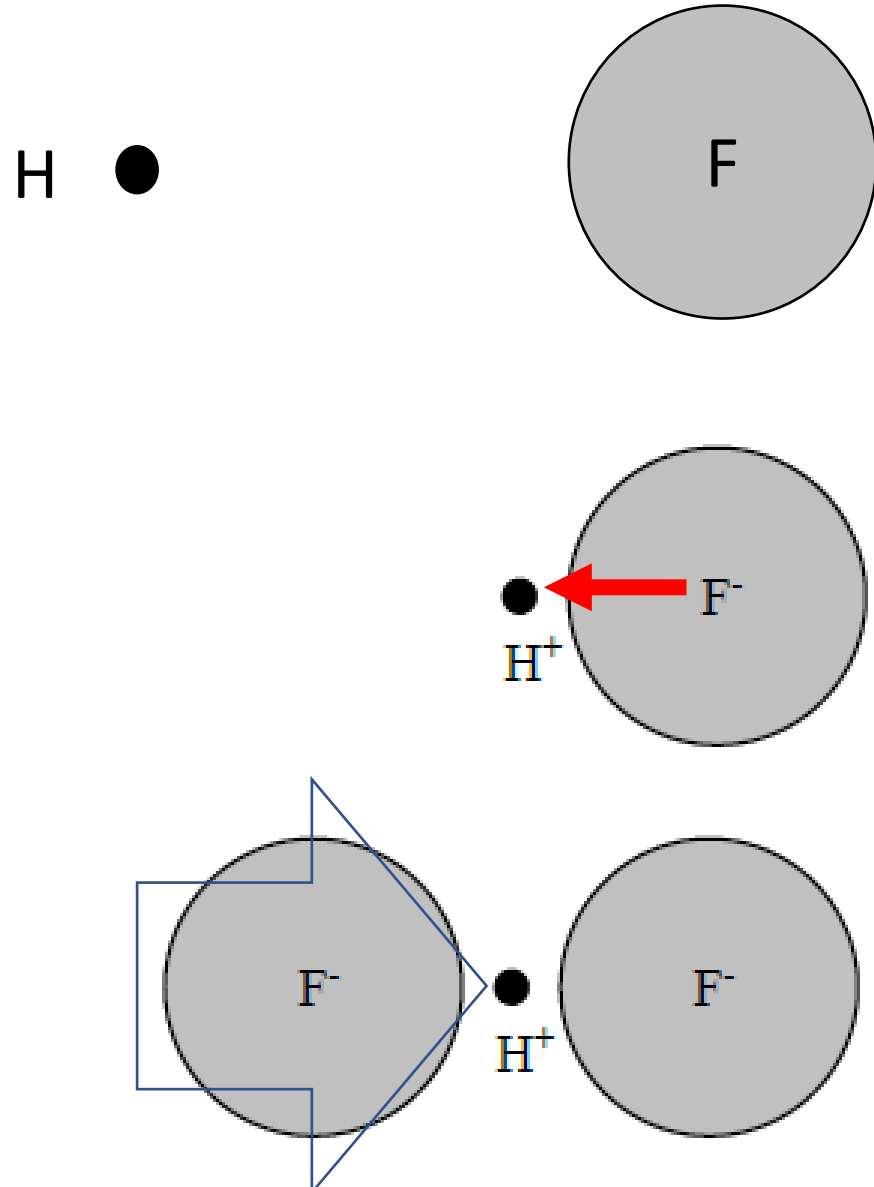
[https://en.wikipedia.org/wiki/Periodic\\_table](https://en.wikipedia.org/wiki/Periodic_table)

<http://www.abc.net.au/science/articles/2010/04/14/2872429.htm>

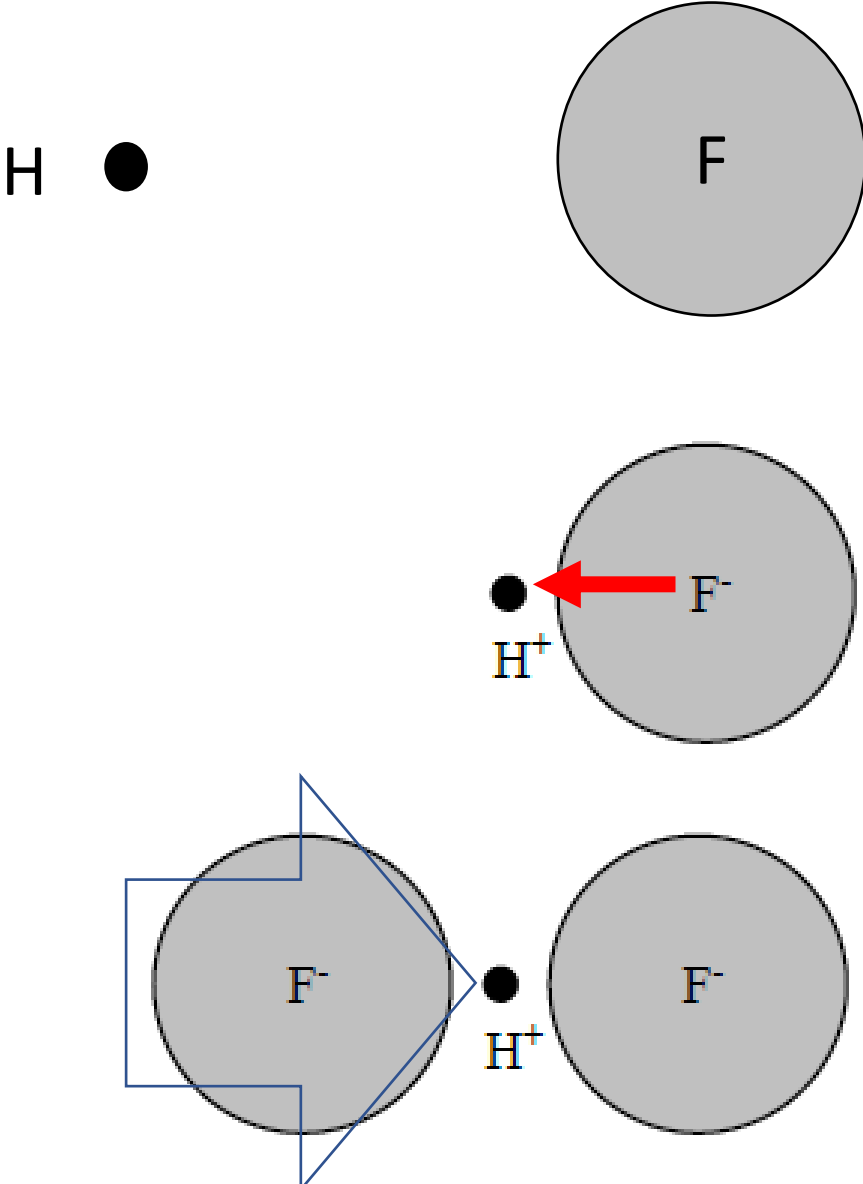


Ashcroft/Mermin

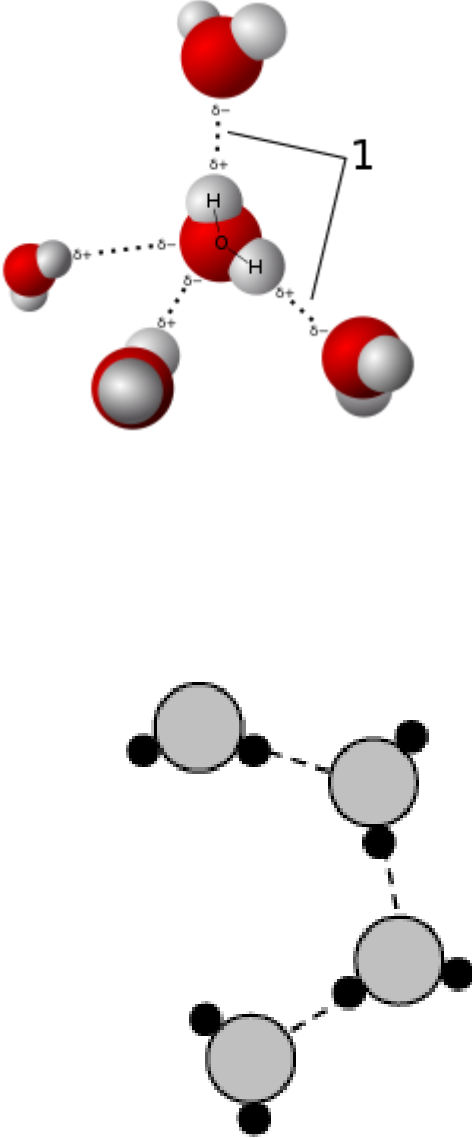
# Pontes de Hidrogênio



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## Exemplo: gelo





Voltando ao van der Waals ...

# Interação de van der Waals

- Onde entra a Mecânica Quântica?

Vamos supor um átomo no nível 1s:

$$\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

Note que o momento de dipolo elétrico é nulo:

$$\langle p \rangle = -e \langle r \rangle = -\frac{e}{\pi a_0^3} 4\pi \int_0^\infty r^3 e^{-2r/a_0} dr = 0$$

Mas, o quadrado do momento de dipolo é não nulo:

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**O dipolo flutua!!!**

- Como resolver esse problema via MQ?

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Sendo o campo de um dipolo

$$\mathbf{E} = -\nabla_{\mathbf{R}} U(\mathbf{R}) = \frac{e}{4\pi\epsilon_0} \frac{1}{R^3} [\mathbf{r}_A - 3(\mathbf{r}_A \cdot \mathbf{n})\mathbf{n}]$$



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Então, na presença de outro dipolo, temos

$$U_{dd} = -\mathbf{E} \cdot \mathbf{p}_B = \frac{q^2}{R^3} [\mathbf{r}_A \cdot \mathbf{r}_B - 3(\mathbf{r}_A \cdot \mathbf{n})(\mathbf{r}_B \cdot \mathbf{n})]$$

com  $q^2 \equiv e^2 / 4\pi\epsilon_0$ . Logo,

$$U_{dd} = \frac{q^2}{R^3} (x_A x_B + y_A y_B - 2z_A z_B)$$

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Quantização canônica:

$$U_{dd} = \frac{q^2}{R^3} (X_A X_B + Y_A Y_B - 2Z_A Z_B)$$

## Interação de van der Waals

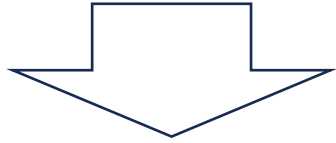
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$$(\mathcal{H}_A + \mathcal{H}_B)|\varphi_{n,l,m}^A \varphi_{n',l',m'}^B\rangle = (E_n + E_{n'})|\varphi_{n,l,m}^A \varphi_{n',l',m'}^B\rangle$$

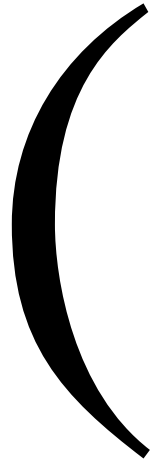
# Interação de van der Waals

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$$\mathcal{H} = \underbrace{\mathcal{H}_A + \mathcal{H}_B}_{\text{Hamiltoniano não perturbado}} + \underbrace{U_{dd}}_{\text{Interação}} \Rightarrow \text{Correções perturbativas!}$$



$$(\mathcal{H}_A + \mathcal{H}_B)|\varphi_{n,l,m}^A, \varphi_{n',l',m'}^B\rangle = (E_n + E_{n'})|\varphi_{n,l,m}^A, \varphi_{n',l',m'}^B\rangle$$



# Teoria de Perturbação Independente do Tempo: caso não degenerado

# Teoria de Perturbação Independente do Tempo: caso não degenerado

Suponha

$$\left\{ \begin{array}{l} H^0 \psi_n^0 = E_n^0 \psi_n^0 \\ \langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \end{array} \right.$$



## Teoria de Perturbação Independente do Tempo: caso não degenerado

Suponha

$$\left\{ \begin{array}{l} H^0 \psi_n^0 = E_n^0 \psi_n^0 \\ \langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \end{array} \right.$$

Como corrigir os autoestados e autovalores se uma perturbação é feita?

$$H = H^0 + \lambda H' \quad (\lambda \ll 1)$$

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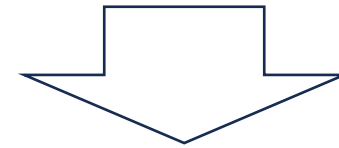
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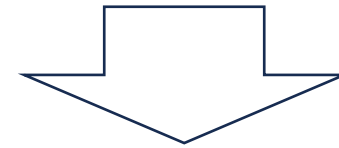
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$$\left\{ \begin{array}{l} \psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots \\ E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \end{array} \right.$$

# Teoria de Perturbação Independente do Tempo: caso não degenerado

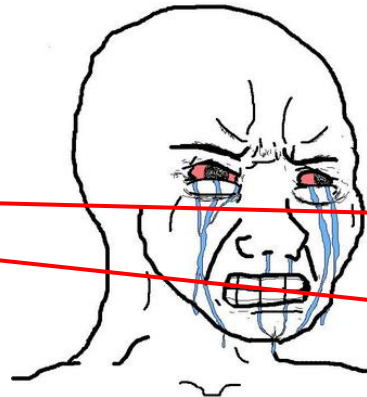
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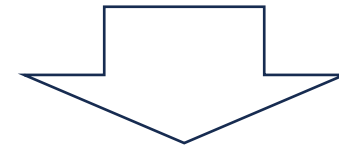
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$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots$$

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## Teoria de Perturbação Independente do Tempo: caso não degenerado

$$(H^0 + \lambda H')[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots],$$

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- *0th* order:



## Teoria de Perturbação Independente do Tempo: caso não degenerado

$$\overbrace{(H^0 + \lambda H')}^{0th \text{ order}} [\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots) [\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots],$$

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1st order

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The equation is annotated with red brackets and labels indicating the order of terms:

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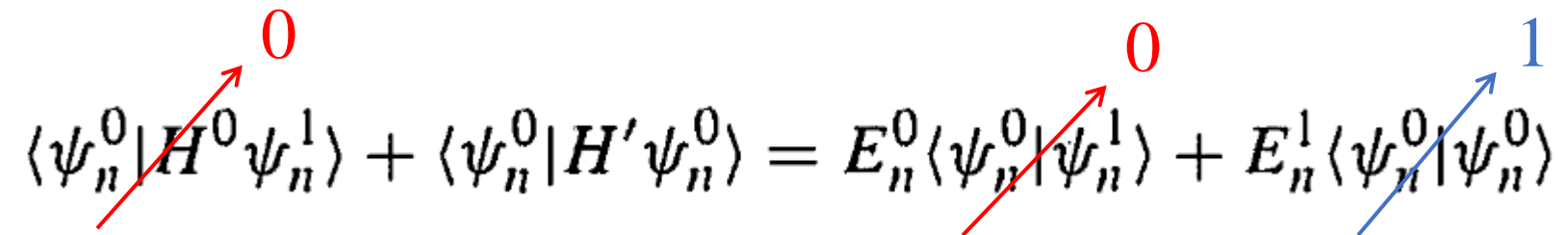
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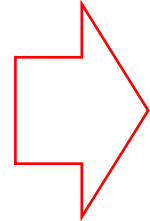
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$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle.$



- 1st order:  $H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$

$$\langle \cancel{\psi_n^0} | H^0 \cancel{\psi_n^1} \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \cancel{\psi_n^0} | \cancel{\psi_n^1} \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle$$

$$\Rightarrow \boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle} \Leftarrow$$

$$\boxed{\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0}$$

- 2nd order:  $H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0$

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Diagrammatic annotations: Red arrows point from the  $\psi_n^0$  in the bra to the  $\psi_n^2$  in the ket for the first three terms. A blue arrow points from the  $\psi_n^0$  in the bra to the  $\psi_n^0$  in the ket for the last term. Red '0' labels are placed above the first three terms, and a blue '1' label is placed above the last term.

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$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle$$

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$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0.$$

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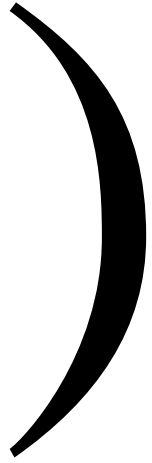
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# Interação de van der Waals

Daí, o Hamiltoniano do sistema é

$$\mathcal{H} = \underbrace{\mathcal{H}_A + \mathcal{H}_B}_{\text{unperturbed}} + \underbrace{U_{dd}}_{\text{perturbation}} \Rightarrow \text{Correções perturbativas!}$$



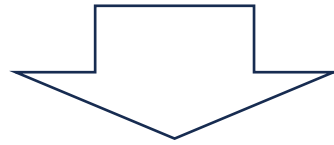
$$(\mathcal{H}_A + \mathcal{H}_B)|\varphi_{n,l,m}^A, \varphi_{n',l',m'}^B\rangle = (E_n + E_{n'})|\varphi_{n,l,m}^A, \varphi_{n',l',m'}^B\rangle$$

- 1st order:

# Interação de van der Waals

Daí, o Hamiltoniano do sistema é

$$\mathcal{H} = \underbrace{\mathcal{H}_A + \mathcal{H}_B}_{\text{Hamiltoniano não perturbado}} + \underbrace{U_{dd}}_{\text{Correções perturbativas!}}$$



$$(\mathcal{H}_A + \mathcal{H}_B)|\varphi_{n,l,m}^A, \varphi_{n',l',m'}^B\rangle = (E_n + E_{n'})|\varphi_{n,l,m}^A, \varphi_{n',l',m'}^B\rangle$$

Por simplicidade, vamos adotar o estado fundamental não perturbado como sendo o 1s nos dois átomos

$$|\varphi_{1,0,0}^A, \varphi_{1,0,0}^B\rangle$$

cuja energia é  $-2E_0$

- 1st order:

# Interação de van der Waals

Daí, o Hamiltoniano do sistema é

$$\mathcal{H} = \underbrace{\mathcal{H}_A + \mathcal{H}_B}_{\text{Hamiltoniano não perturbado}} + \underbrace{U_{dd}}_{\text{Interação}} \Rightarrow \text{Correções perturbativas!}$$



$$(\mathcal{H}_A + \mathcal{H}_B)|\varphi_{n,l,m}^A, \varphi_{n',l',m'}^B\rangle = (E_n + E_{n'})|\varphi_{n,l,m}^A, \varphi_{n',l',m'}^B\rangle$$

- 1st order:  $-2E_0 + E_0^{(1)} + O(2) = -2E_0 + \langle \varphi_{1,0,0}^A, \varphi_{1,0,0}^B | U_{dd} | \varphi_{1,0,0}^A, \varphi_{1,0,0}^B \rangle + O(2)$

Por simplicidade, vamos adotar o estado fundamental não perturbado como sendo o 1s nos dois átomos

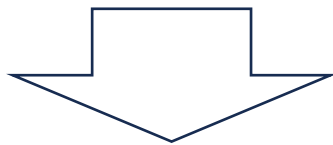
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# Interação de van der Waals

Daí, o Hamiltoniano do sistema é

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + U_{dd} \Rightarrow \text{Correções perturbativas!}$$



$$(\mathcal{H}_A + \mathcal{H}_B)|\varphi_{n,l,m}^A, \varphi_{n',l',m'}^B\rangle = (E_n + E_{n'})|\varphi_{n,l,m}^A, \varphi_{n',l',m'}^B\rangle$$

Por simplicidade, vamos adotar o estado fundamental não perturbado como sendo o 1s nos dois átomos

$$|\varphi_{1,0,0}^A, \varphi_{1,0,0}^B\rangle$$

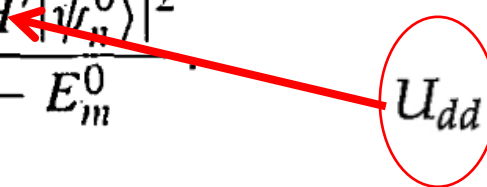
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$$\langle \varphi_{1,0,0}^A, \varphi_{1,0,0}^B | X_A X_B | \varphi_{1,0,0}^A, \varphi_{1,0,0}^B \rangle = \langle \varphi_{1,0,0}^A | X_A | \varphi_{1,0,0}^A \rangle \langle \varphi_{1,0,0}^B | X_B | \varphi_{1,0,0}^B \rangle = 0$$

- 2nd order: 
$$E_0^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}.$$

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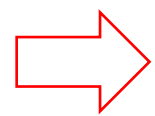
$E_0^{(2)} \approx -6 \frac{e^2}{4\pi\epsilon_0 R} \left(\frac{a_0}{R}\right)^5 = -2 \frac{\langle p^2 \rangle}{4\pi\epsilon_0} \left(\frac{a_0}{R^2}\right)^3$

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Ashcroft Cap 19, Questão 1  
Lista ou prova!!!