Règles LCAO

- 2 règles fondamentales: 2 OA ne se combinent (n'interagissent) fortement que si
  - elles sont proches en énergie (règle 2)

$$\varepsilon(\varphi_A) \cong \varepsilon(\varphi_B)$$

  - elles se recouvrent effectivement (règle 1)

$$S_{AB} = \int \varphi_A \varphi_B dV \neq 0$$

Règles LCAO

- Règle 3: dans le mélange de 2 OA d'énergies différentes, chacune des 2 OM est dominée par (ressemble le plus à) l'OA qui lui est le plus proche en énergie.

Règles LCAO

- Règle 4: conservation du nombre d'orbitales

À partir de N OA, on peut (et doit) obtenir N OM

- Règle 5: transitivité des interactions d'OA

si l'OA ϕ_a interagit fortement avec ϕ_b et ϕ_b avec ϕ_c , alors ϕ_a interagit aussi avec ϕ_c

$$\{\varphi_A \leftrightarrow \varphi_B, \varphi_B \leftrightarrow \varphi_C\} \Leftrightarrow \varphi_A \leftrightarrow \varphi_C$$

Règles LCAO

- Règle 6: propriétés nodales

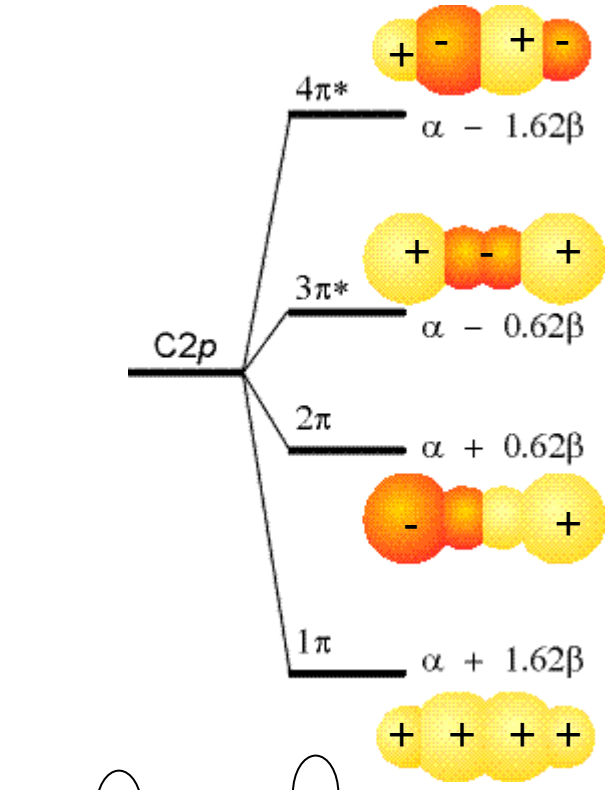
Le nombre de surfaces nodales dans une OM augmente avec l'énergie (le niveau) de l'OM

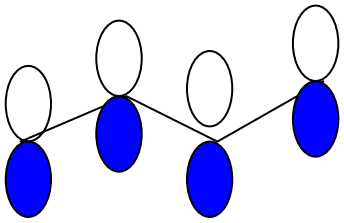
Donc: 1ère OM sera sans nœud, la 2e OM aura 1 nœud, la 3e OM, 2 nœuds

- Règle 7: respect de la symétrie

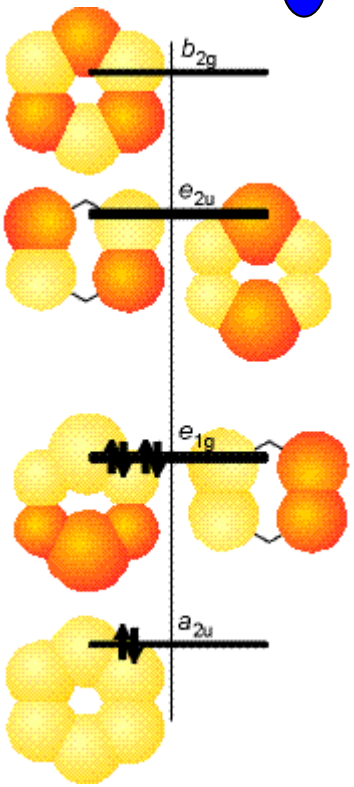
Les OM doivent avoir un caractère de symétrie bien déterminée par rapport à toute symétrie moléculaire

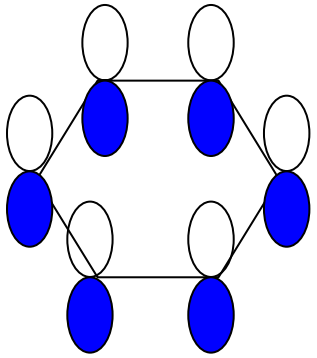
Exemple 2





Butadiène





Benzène

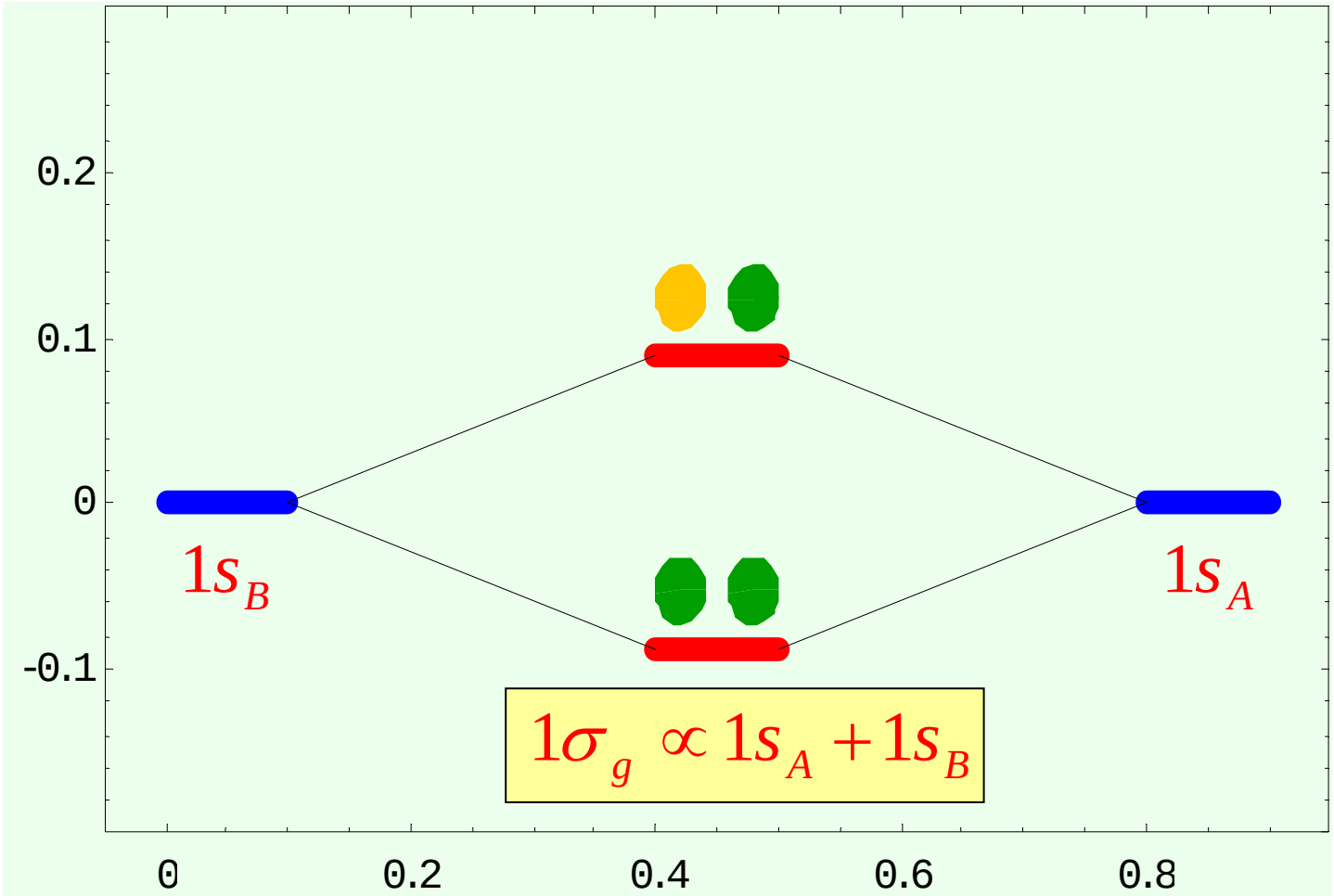
Molécules X_2

OM formées à partir de 1s

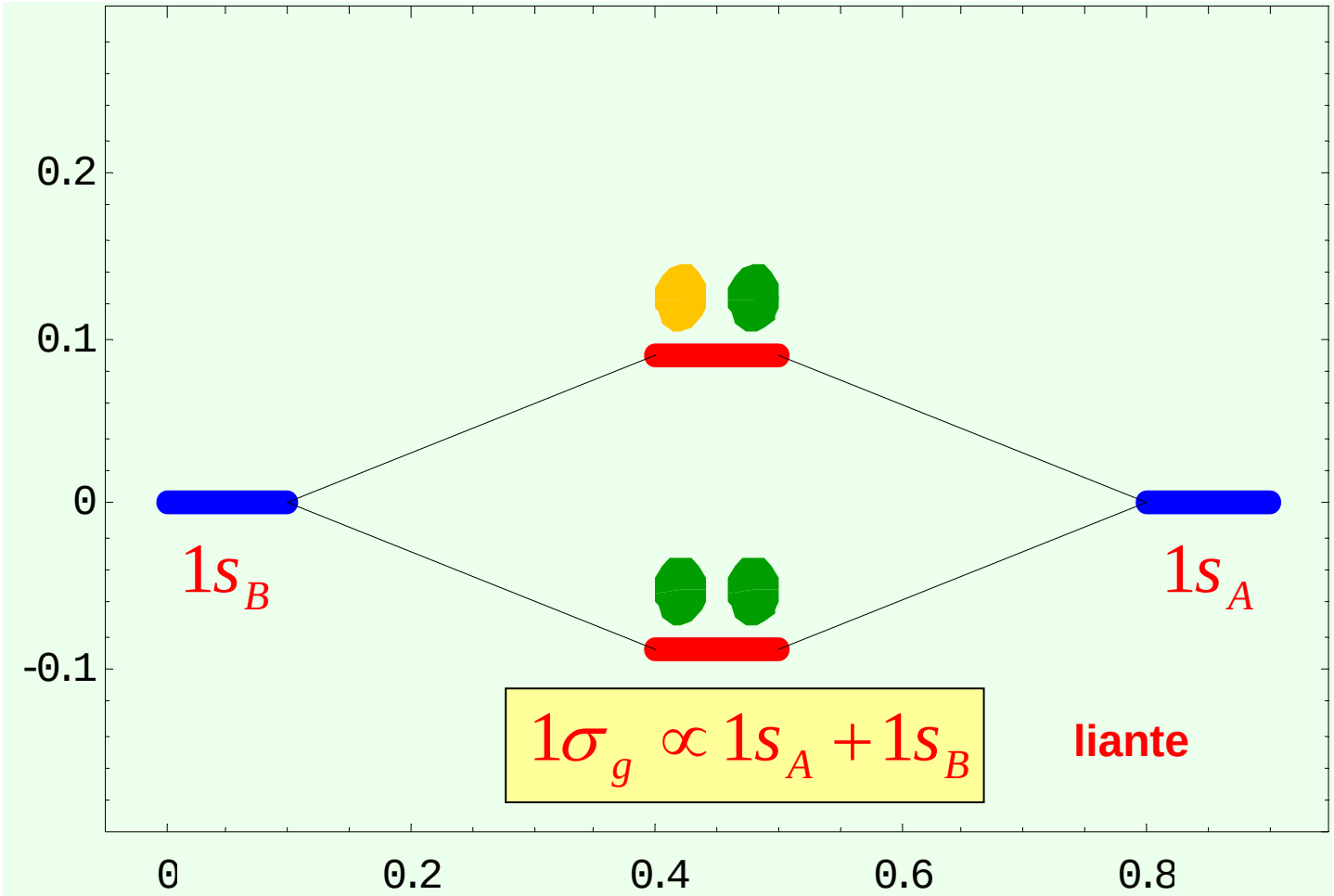
Ex:

$$H_2^+ \xrightarrow[R\to\infty]{} H(1s) + H^+$$

Molécules X_2
$(X_A\text{-}X_B)$



Molécules X_2
$(X_A\text{-}X_B)$



Molécules X_2
$(X_A\text{-}X_B)$

$1\sigma_g \propto 1s_A + 1s_B$ **(ou** $\sigma_g\, 1s$ **)**

g=gerade=pair (par rapport à inversion)

$(\vec{r} \rightarrow -\vec{r})$

Molécules X_2

$$1\sigma_g \propto 1s_A + 1s_B$$

g=gerade=pair (par rapport à inversion)

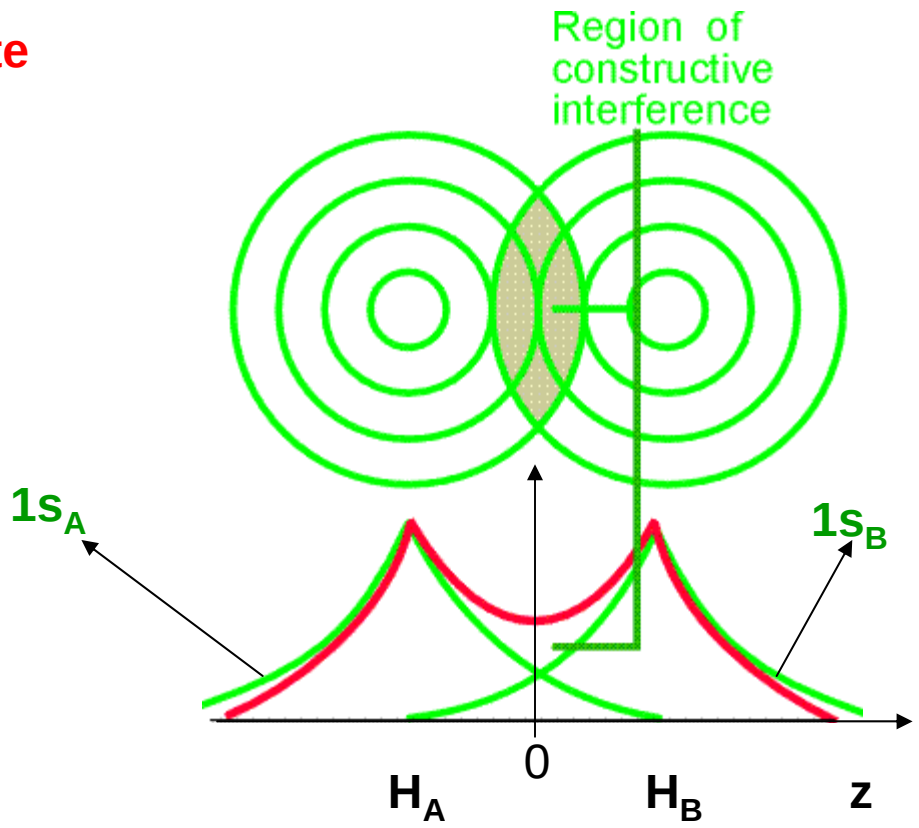
$$(\vec{r} \rightarrow -\vec{r})$$

$$1\sigma_g(-\vec{r}) = 1\sigma_g(\vec{r})$$

Molécules X_2

$$1\sigma_g \propto 1s_A + 1s_B$$

liante



Molécules X_2

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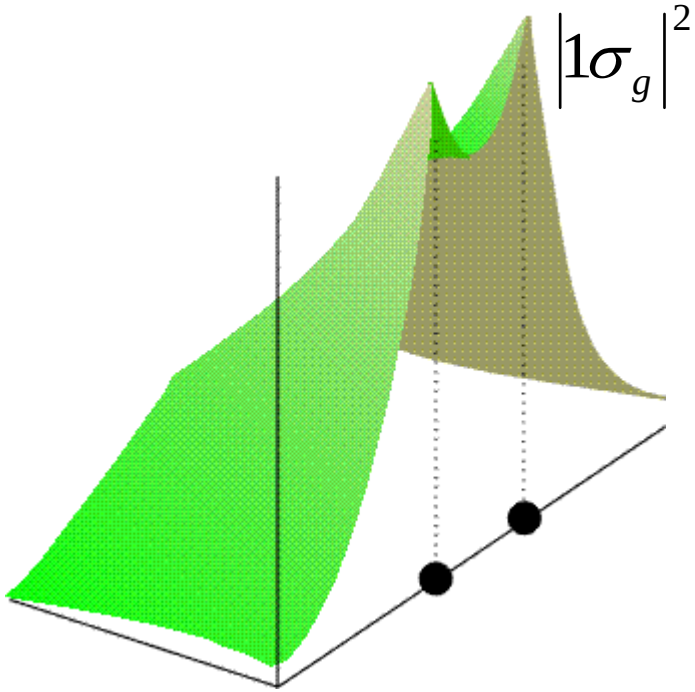

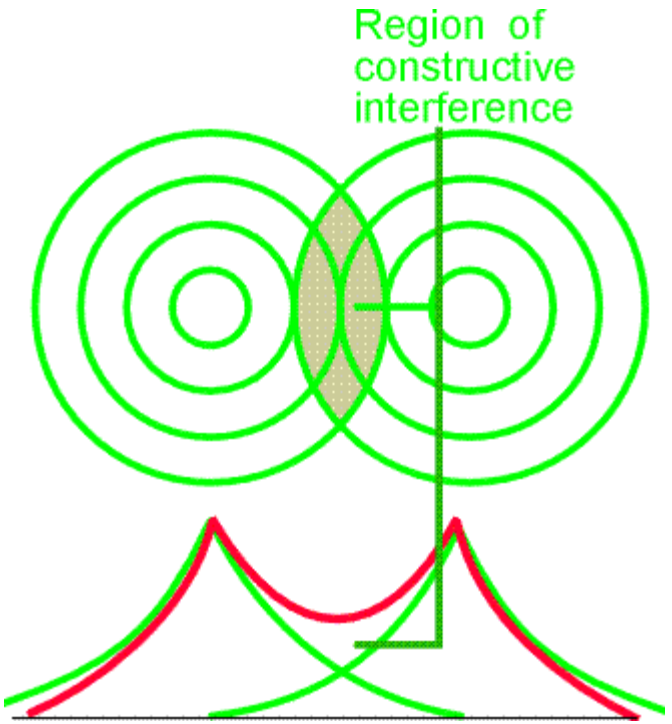

Molécules X_2

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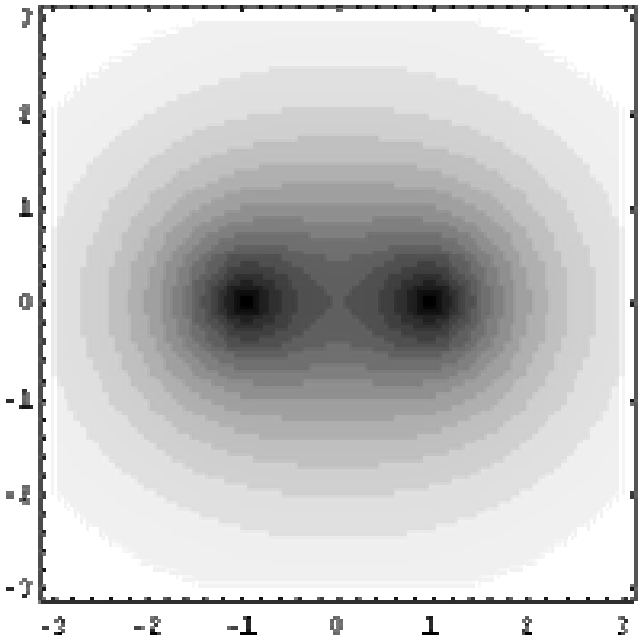
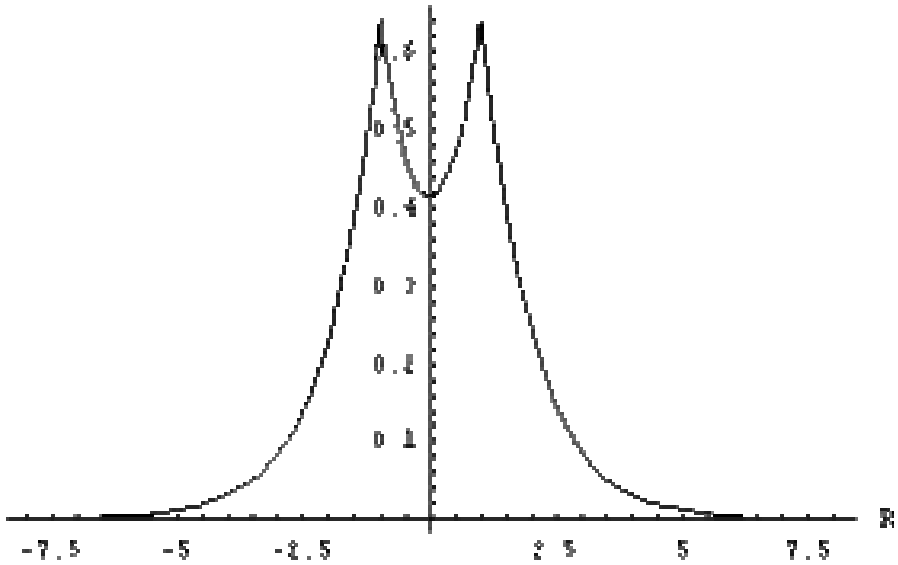
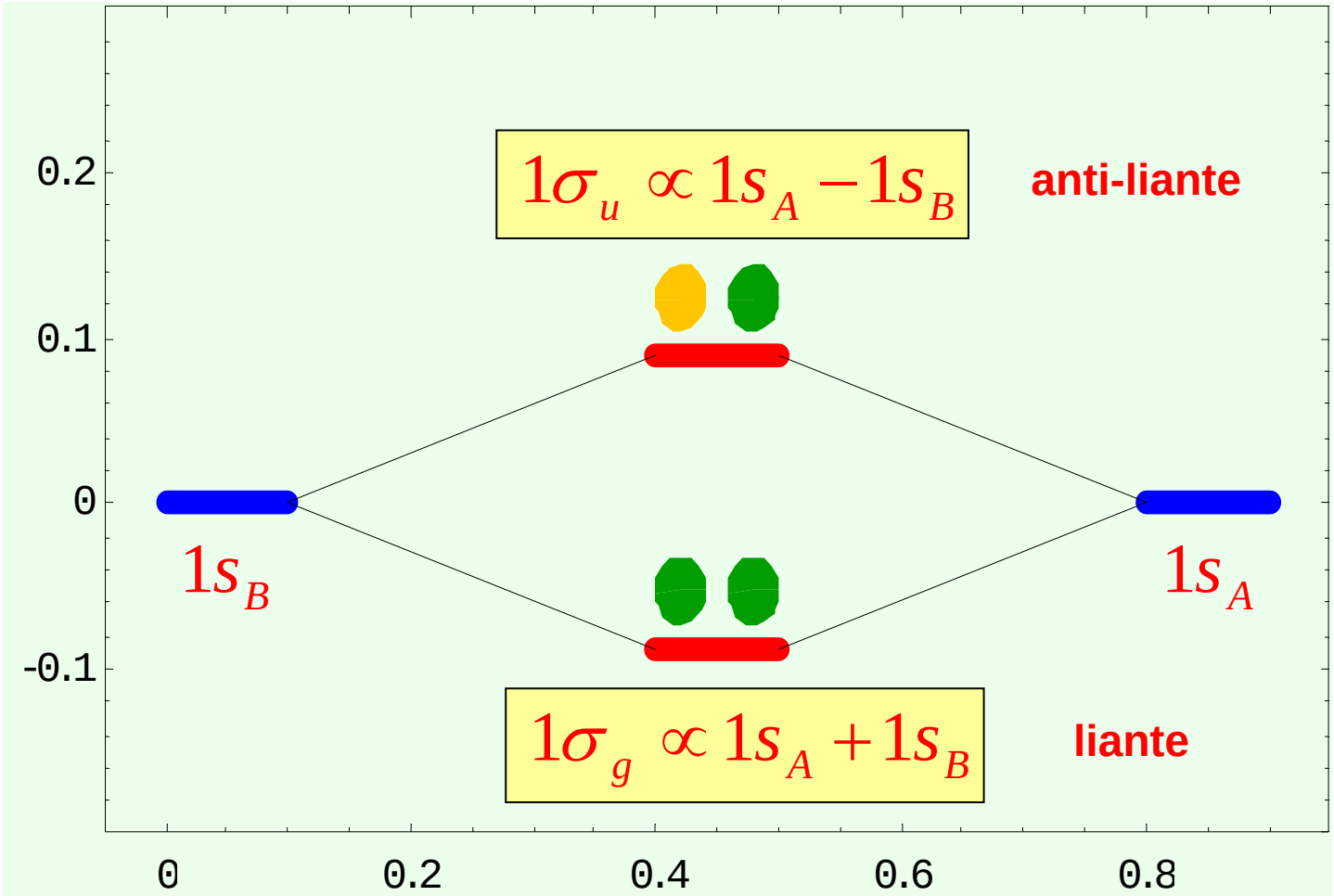




Molécules X_2



Molécules X_2

$1\sigma_u \propto 1s_A - 1s_B$ **(ou** $\sigma_u\, 1s$ **)**

u=ungerade=impair (par rapport à inversion)

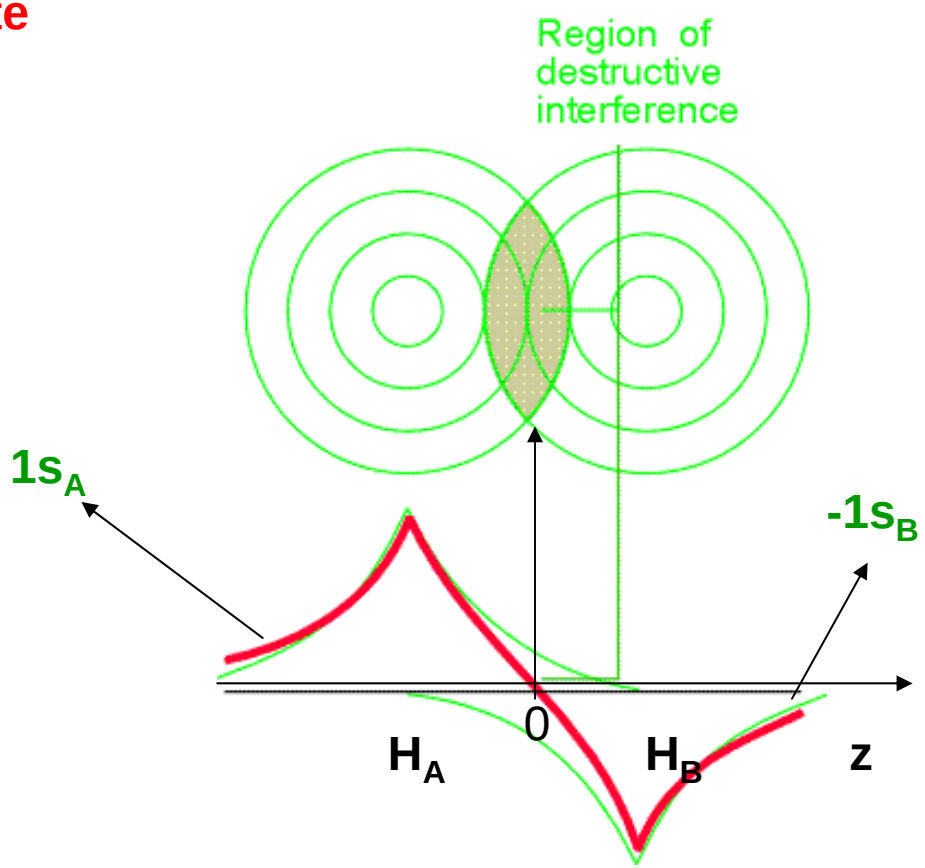
$$(\vec{r} \rightarrow -\vec{r})$$

$$1\sigma_u(-\vec{r}) = -1\sigma_u(\vec{r})$$

Molécules X_2

$$1\sigma_u \propto 1s_A - 1s_B$$

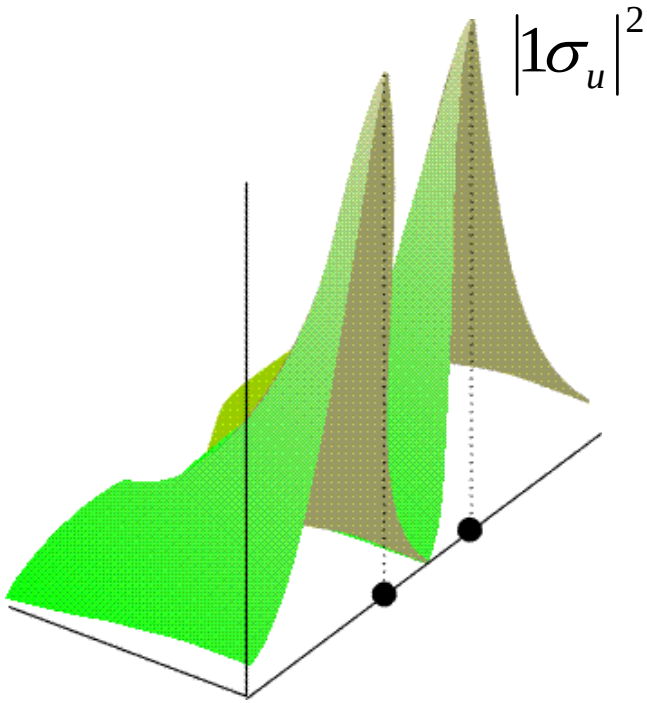
liante

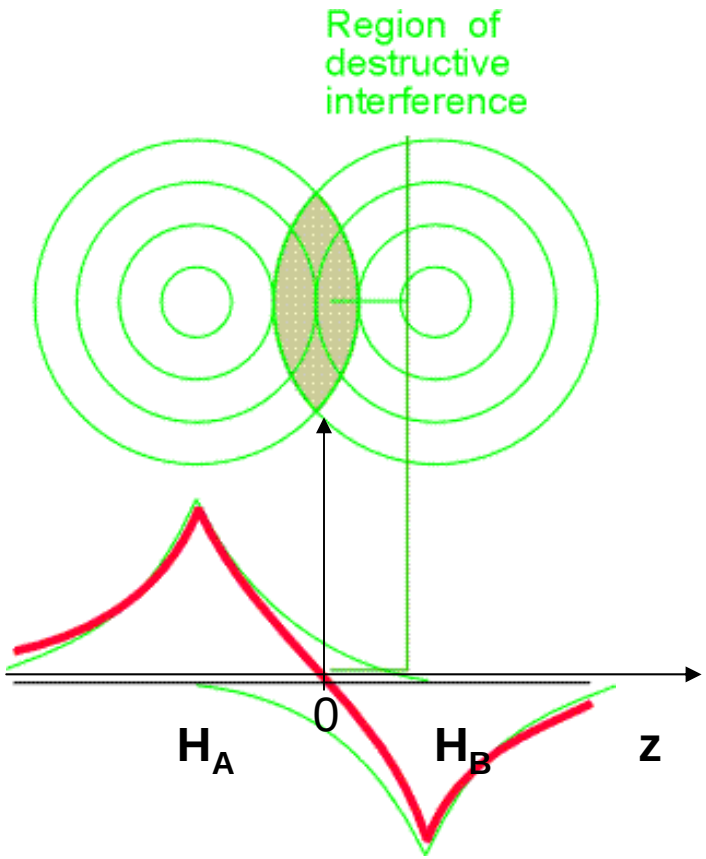


Molécules X_2

$$1\sigma_u \propto 1s_A - 1s_B$$

liante





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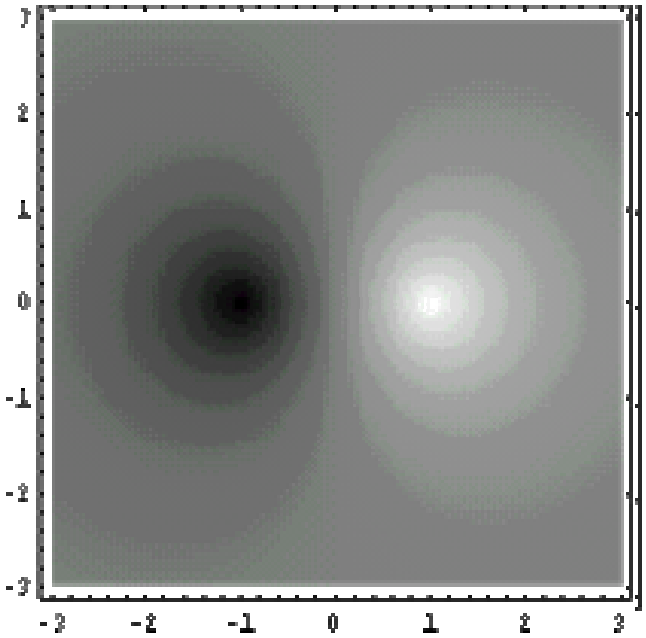
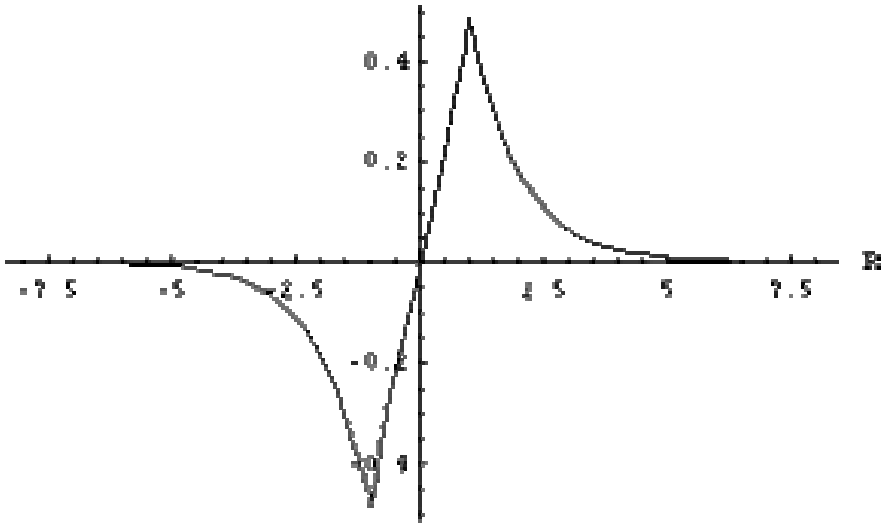
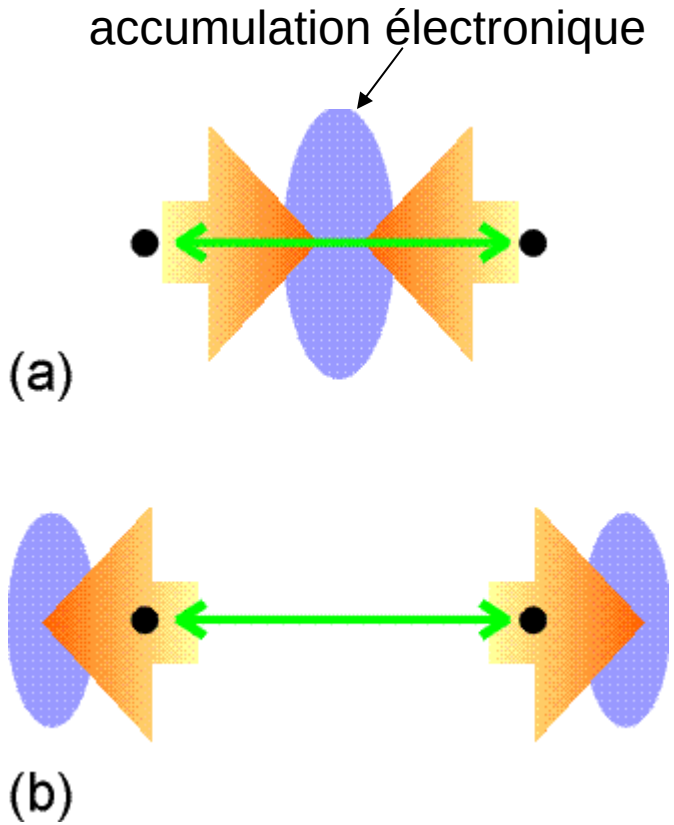
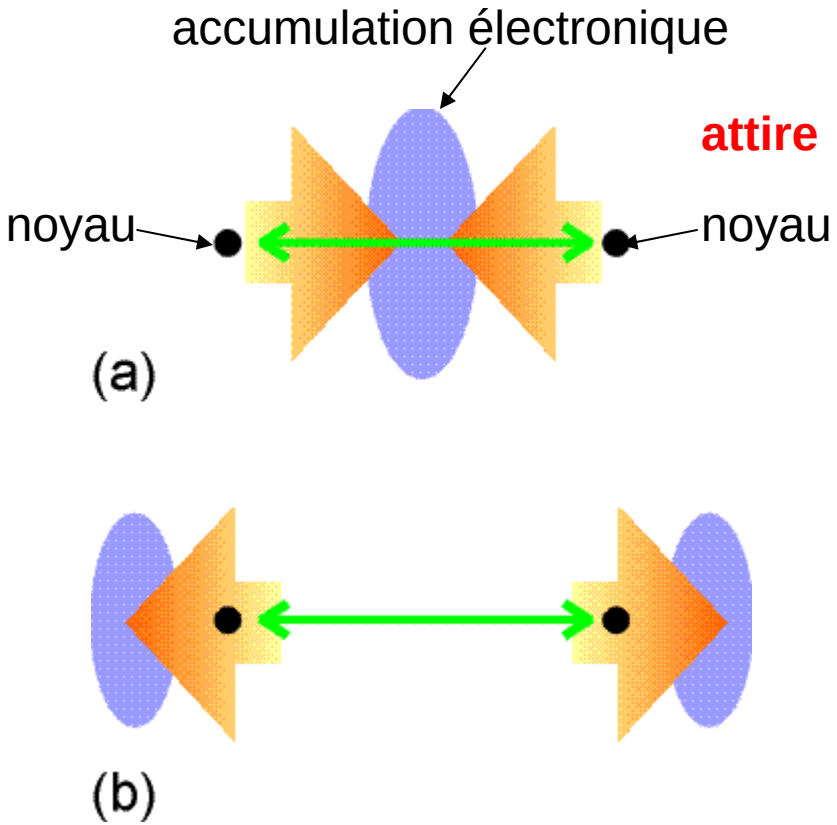




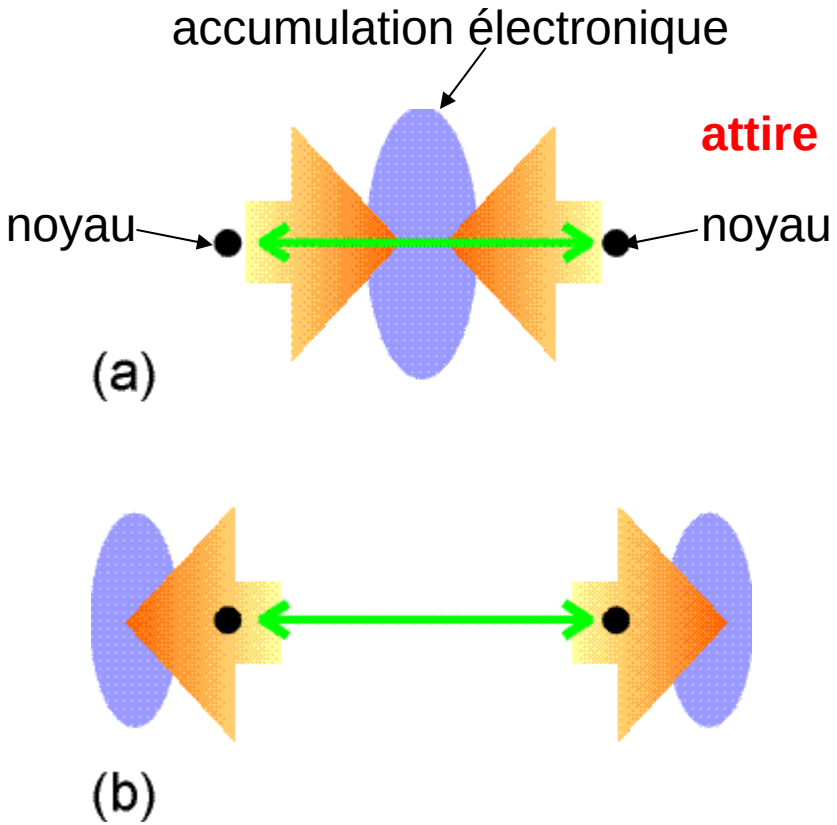
OM liantes vs. antiliantes



OM liantes vs. antiliantes



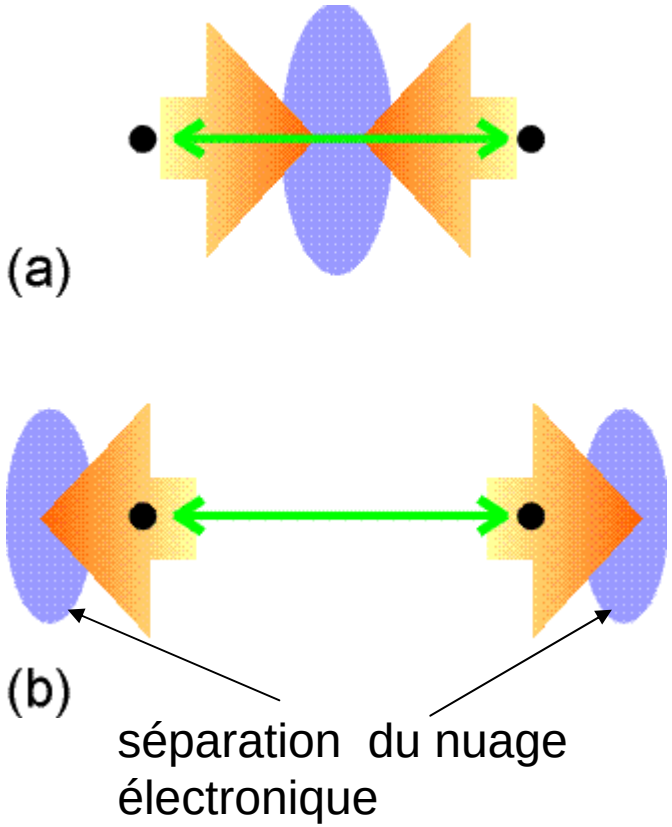
OM liantes vs. antiliantes



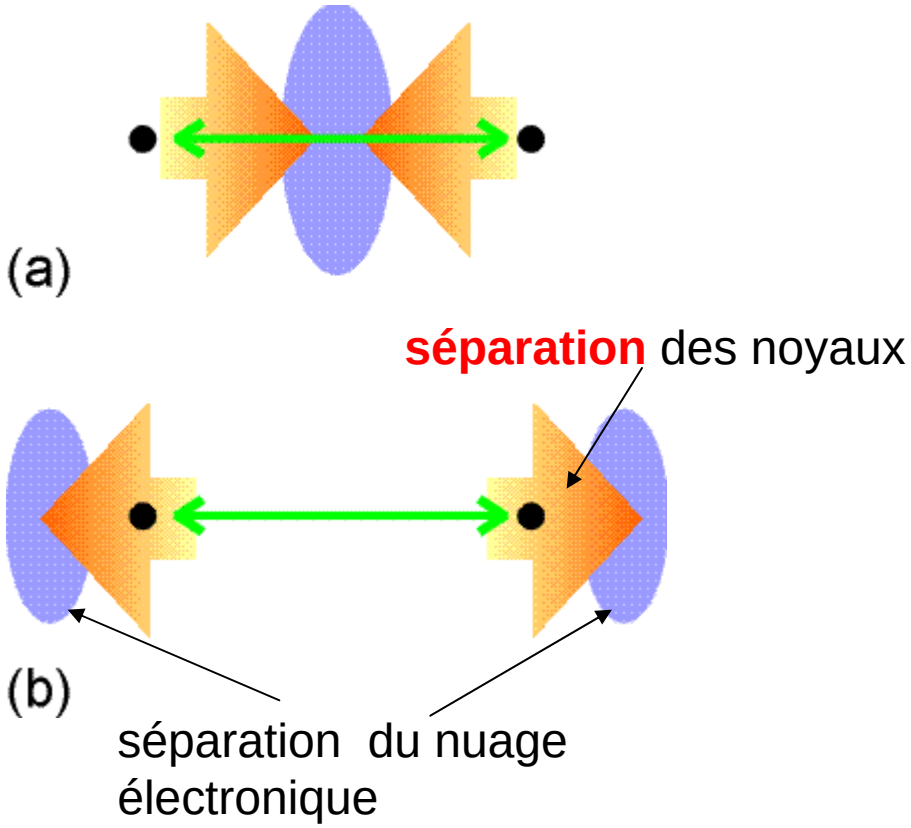
situation

LIANTE

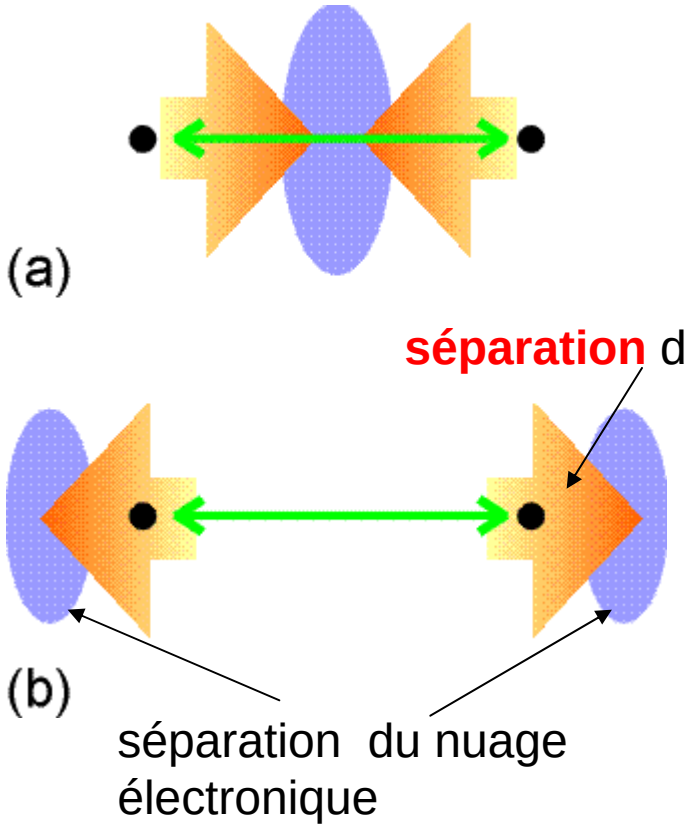
OM liantes vs. antiliantes



OM liantes vs. antiliantes



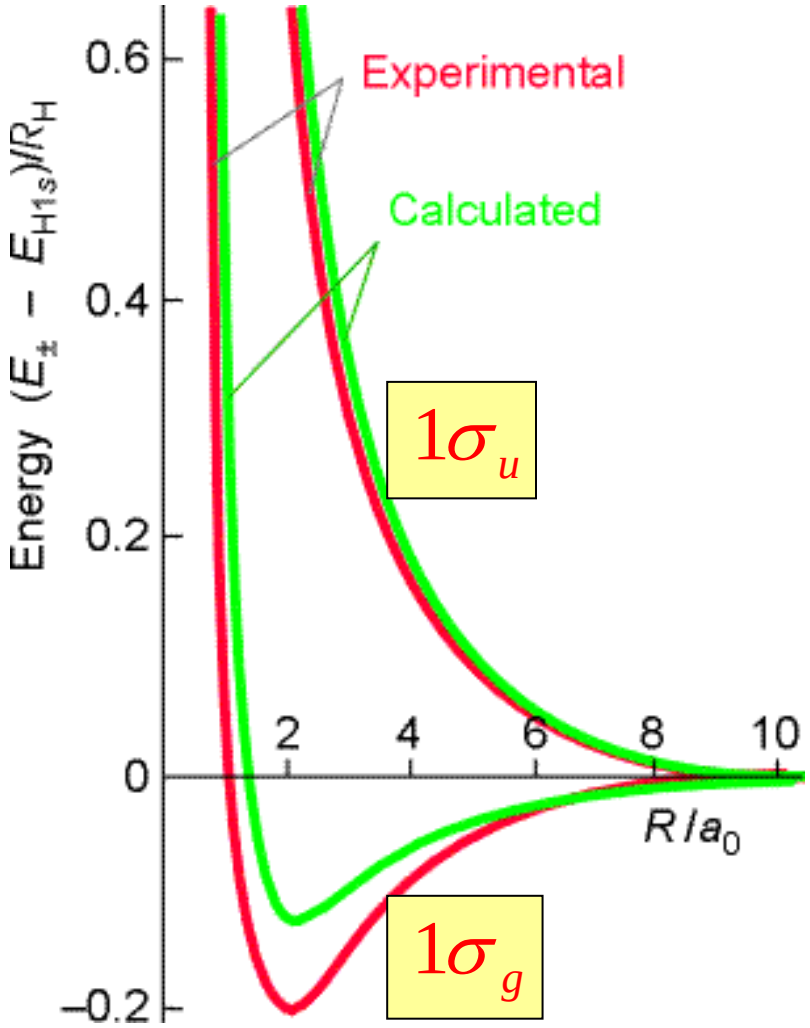
OM liantes vs. antiliantes



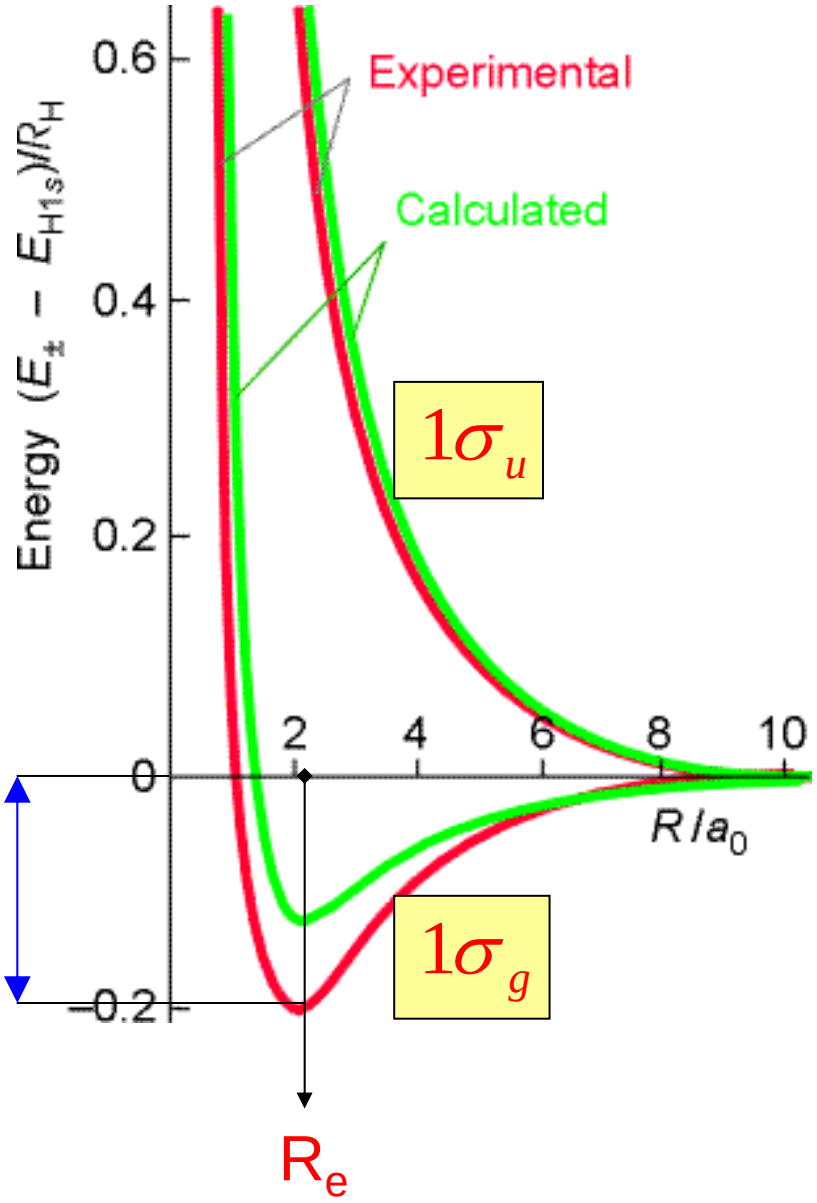
situation

ANTI-LIANTE

H_2^+


Experimental
Calculated
$1\sigma_u$
$1\sigma_g$
Energy $(E_\pm - E_{H1s})/R_H$
0.6
0.4
0.2
0
–0.2
2
4
6
8
10
R/a_0

H_2^+



(Énergie de dissociation)

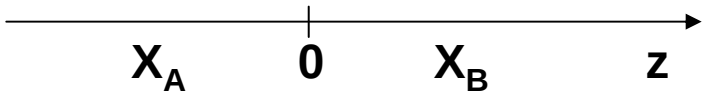
Molécules X_2

- Autres OM σ (symétrie cylindrique)

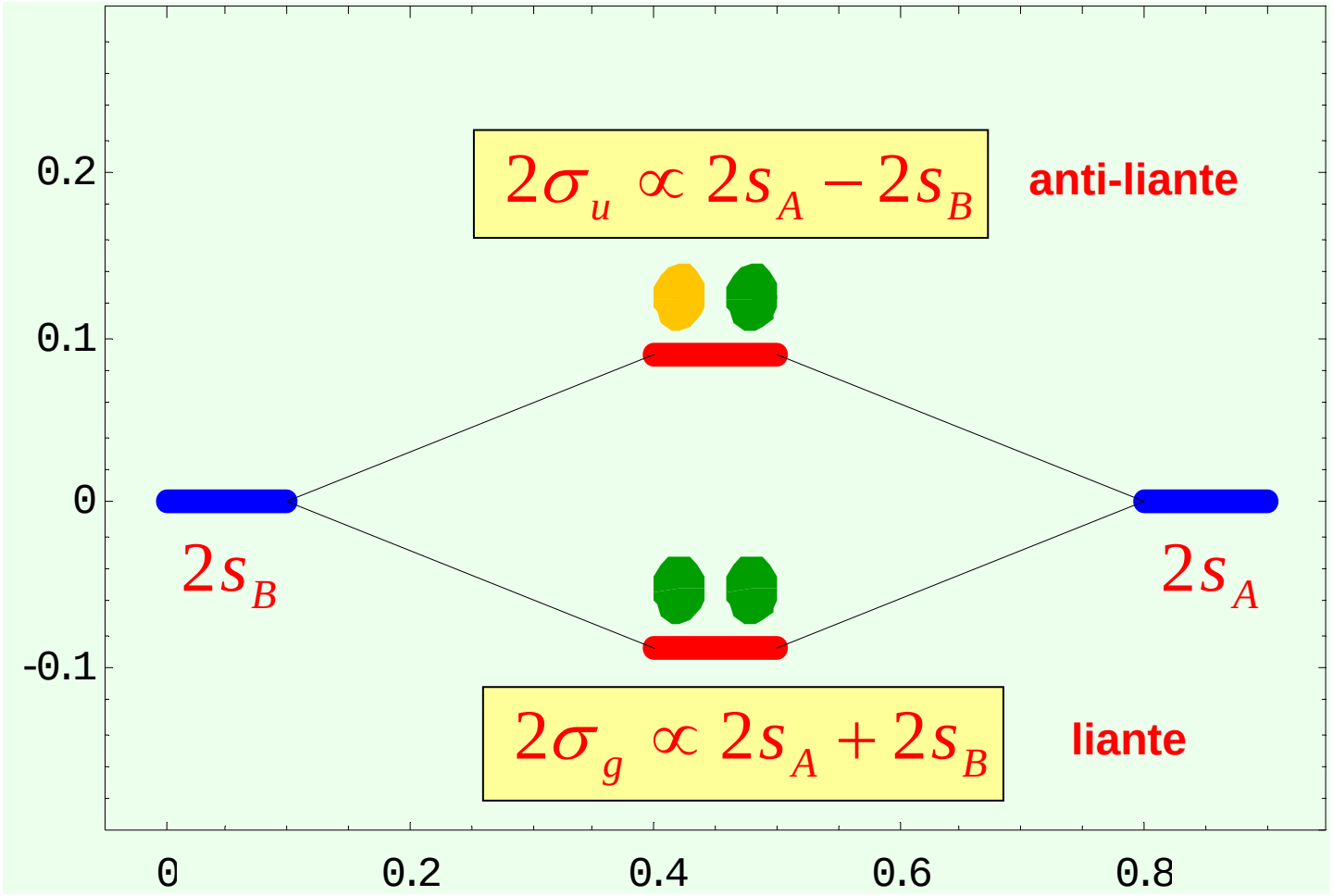
$$2\sigma_{g(u)} \propto 2s_A \pm 2s_B$$ **(ou** $\sigma_{g(u)}\ 2s$ **)**

$$3\sigma_{g(u)} \propto 2p_{z,A} \mp 2p_{z,B}$$ **(ou** $\sigma_{g(u)}\ 2p$ **)**

Convention:



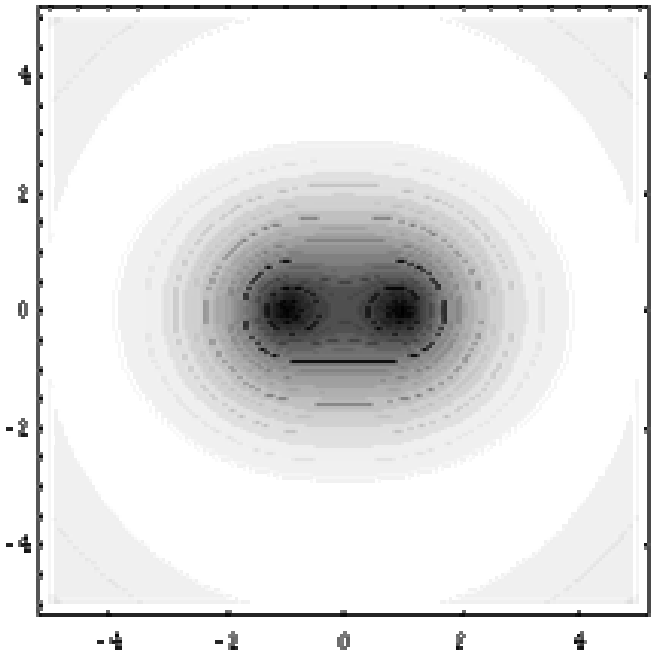
Molécules X_2

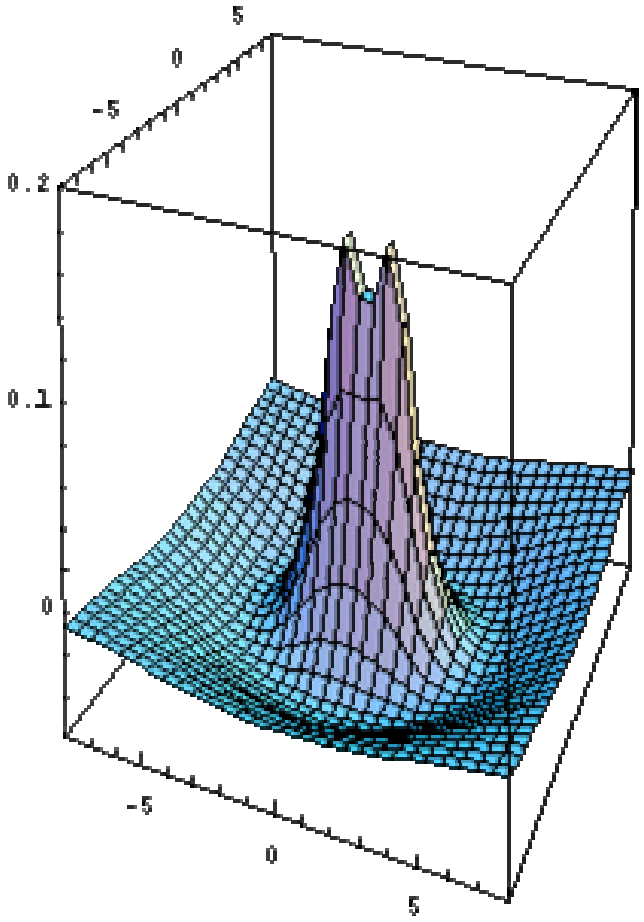


Molécules X_2

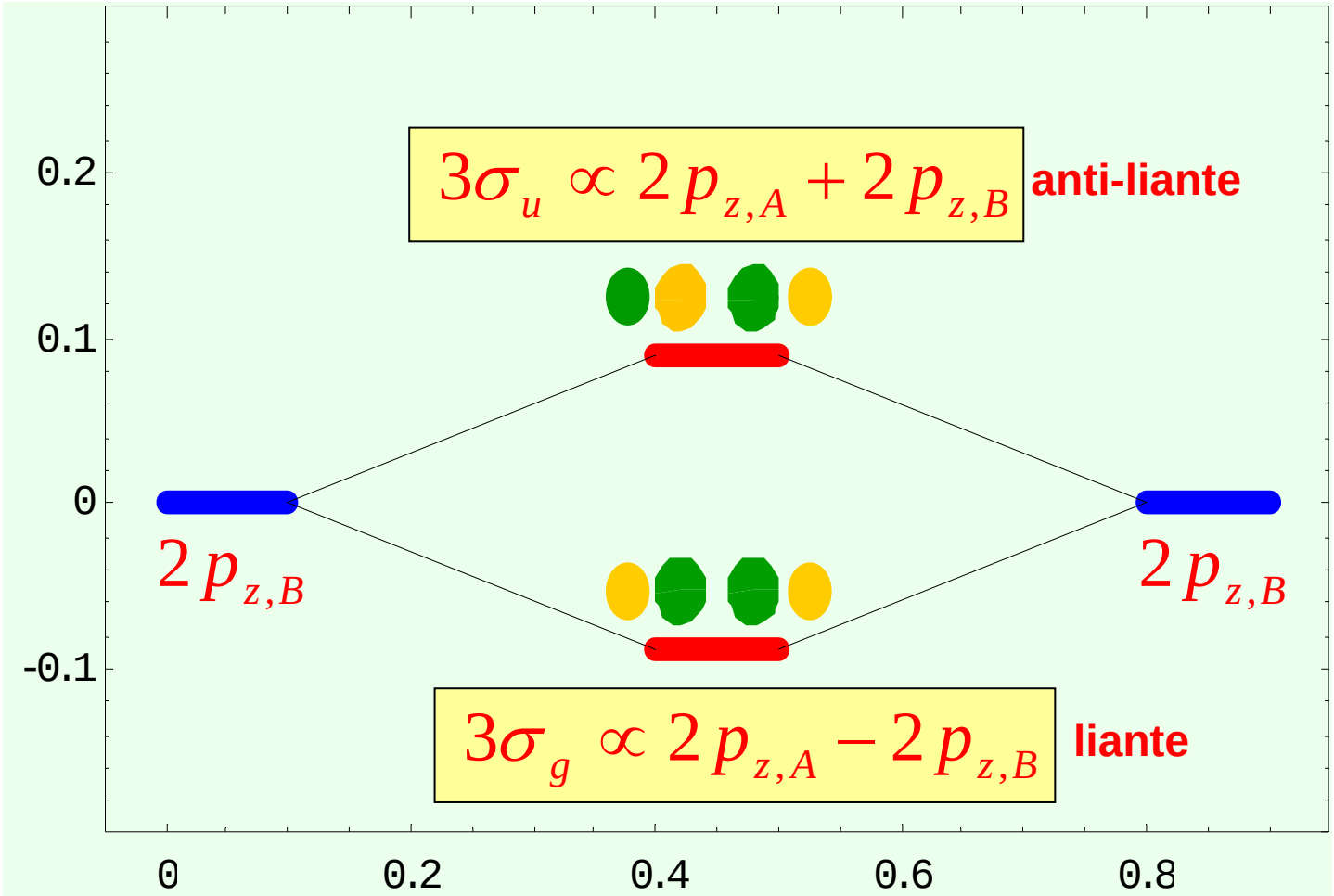
$$2\sigma_g \propto 2s_A + 2s_B$$

liante



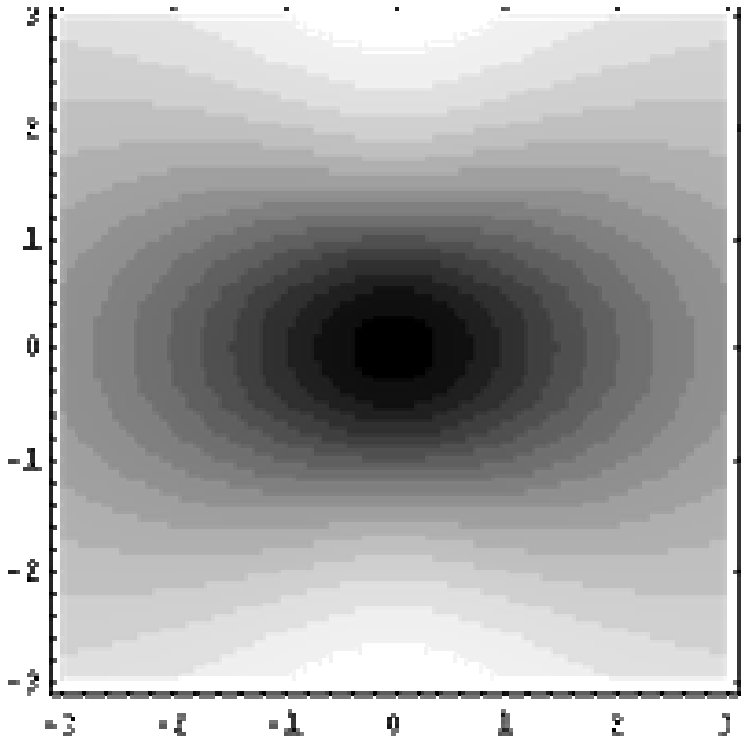


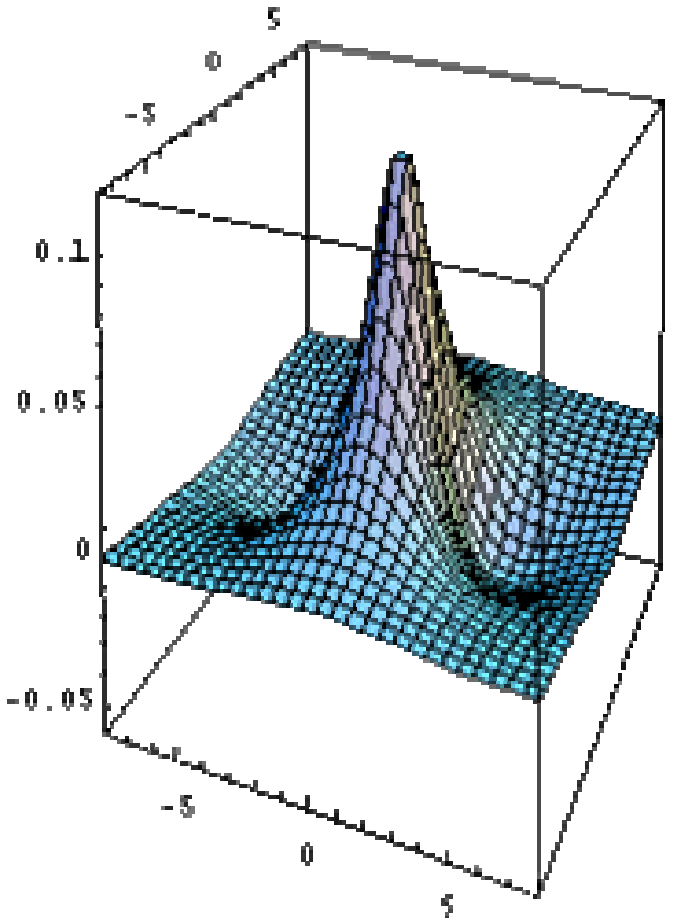
Molécules X_2



Molécules X_2

$3\sigma_g \propto 2p_{z,A} - 2p_{z,B}$ **liante**





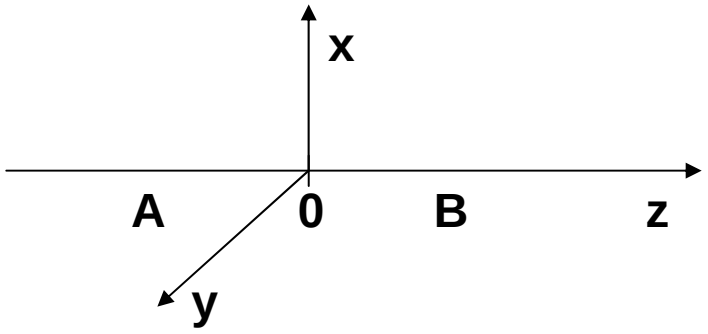
Molécules X_2

- OM π (symétrie latérale, ou de réflexion)

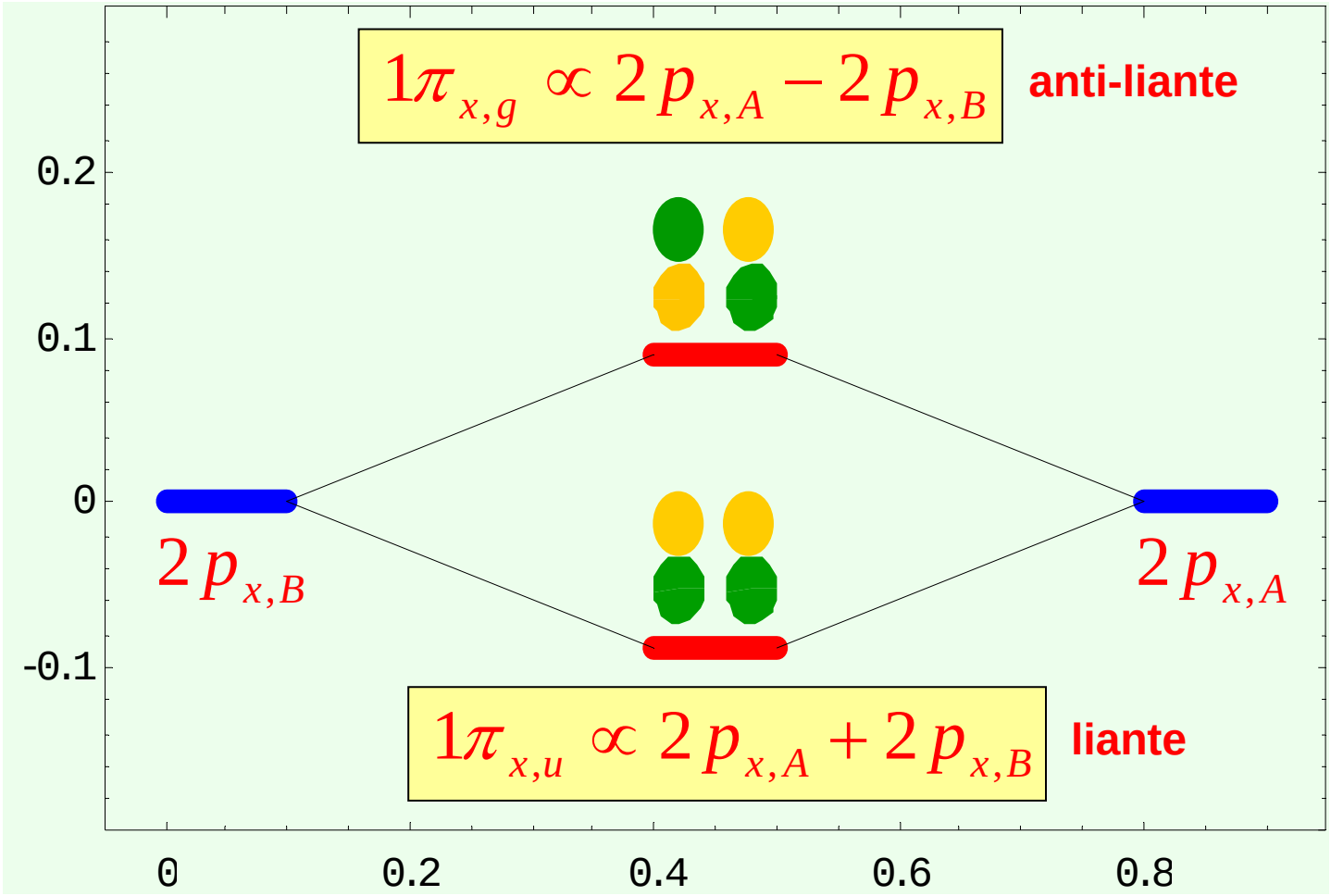
$$1\pi_{x,u(g)} \propto 2p_{x,A} \pm 2p_{x,B}$$ **(ou** $\pi_{u(g)} 2p_x$ **)**

$$1\pi_{y,u(g)} \propto 2p_{y,A} \pm 2p_{y,B}$$ **(ou** $\pi_{u(g)} 2p_y$ **)**

Convention:



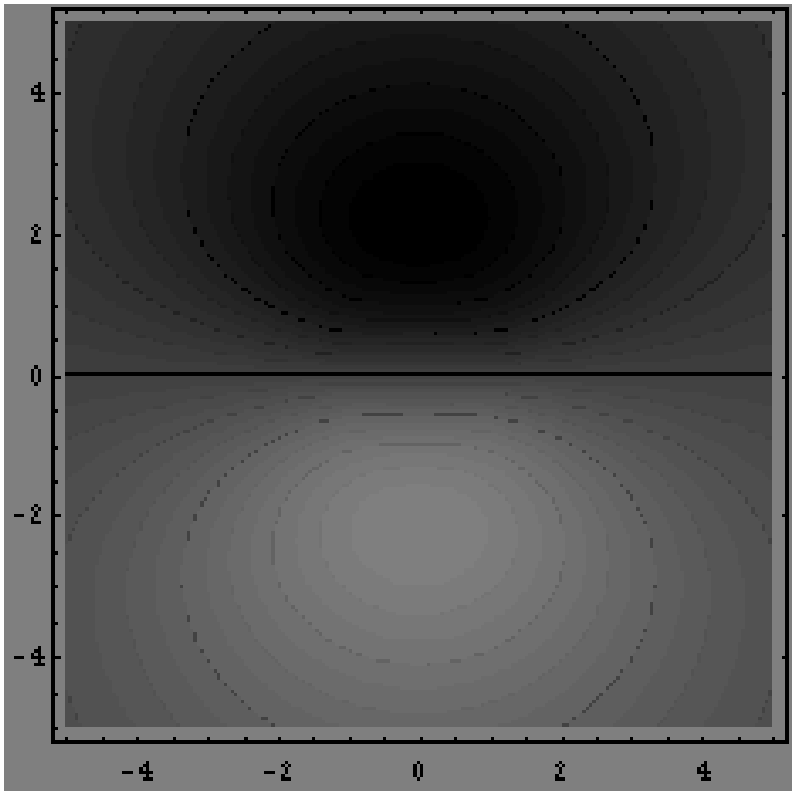
Molécules X_2



Molécules X_2

$$1\pi_{x,u} \propto 2p_{x,A} + 2p_{x,B}$$

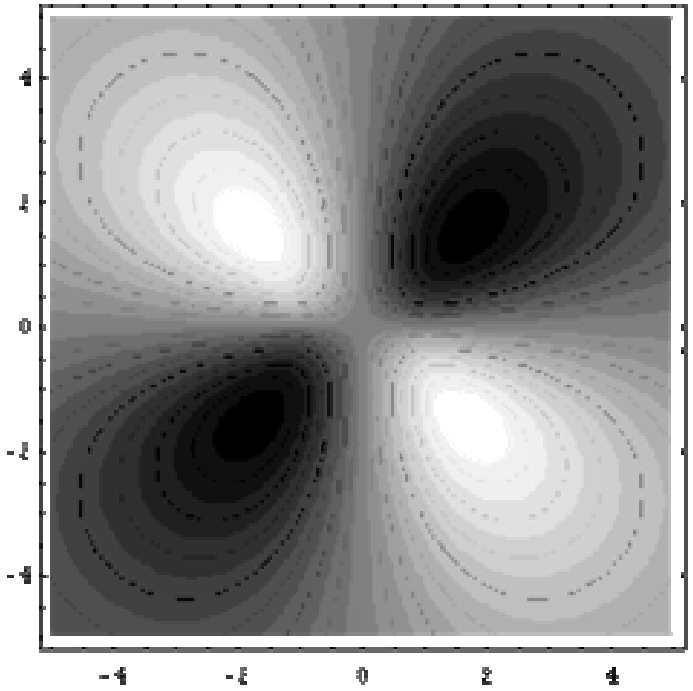
liante

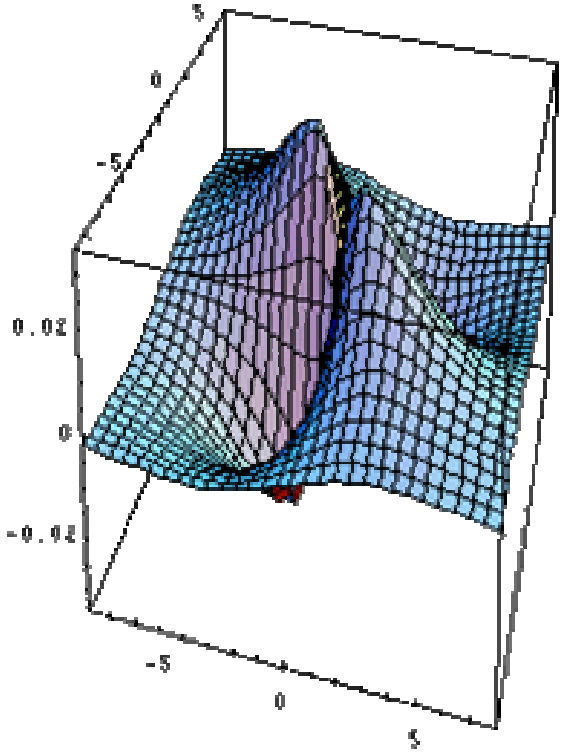


Molécules X_2

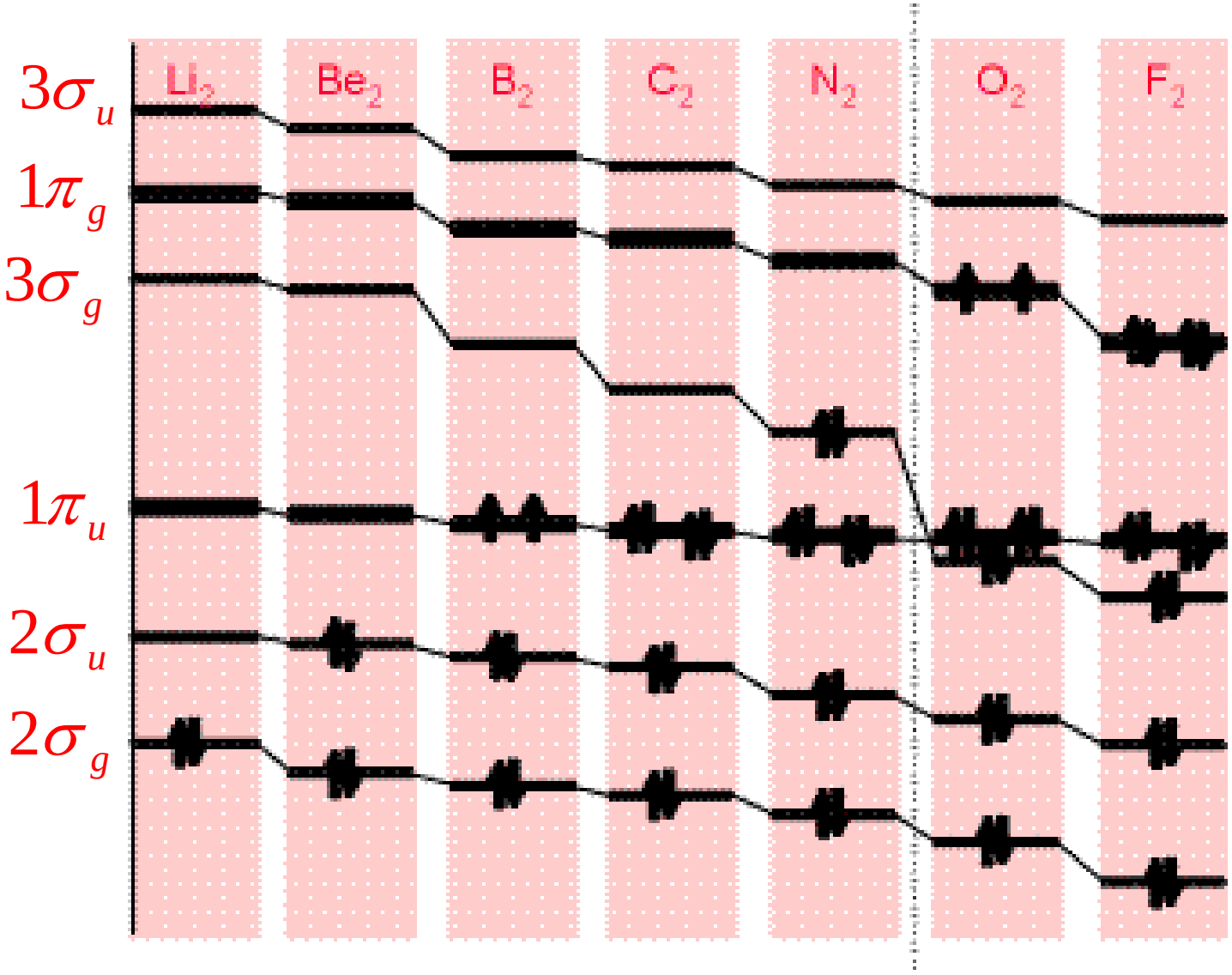
$$1\pi_{x,g} \propto 2p_{x,A} - 2p_{x,B}$$

anti-liante





Molécules X_2



Molécules X_2

- Ordre de liaison: (ou indice de liaison)

$$n = \frac{1}{2}(n_{liant} - n_{antiliant})$$

Molécules X_2

- Ordre de liaison: (ou indice de liaison)

$$n = \frac{1}{2}(n_{liant} - n_{antiliant})$$

nombre d'électrons dans des OM liantes

nombre d'électrons dans des OM anti-liantes

Molécules X_2

- Ordre de liaison: (ou indice de liaison)

$$n = \frac{1}{2}(n_{liant} - n_{antiliant})$$

Exemples:

$Li_2 \quad 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$

Molécules X_2

- Ordre de liaison: (ou indice de liaison)

$$n = \frac{1}{2}(n_{liant} - n_{antiliant})$$

Exemples:

$Li_2 \quad 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 \qquad \{n_{liant} = 4, n_{antiliant} = 2\} \Rightarrow n = 1$

Molécules X_2

- Ordre de liaison: (ou indice de liaison)

$$n = \frac{1}{2}(n_{liant} - n_{antiliant})$$

Exemples:

$Li_2 \quad 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 \qquad \{n_{liant} = 4, n_{antiliant} = 2\} \Rightarrow n = 1$

$N_2 \quad 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_{x,u}^2 1\pi_{y,u}^2 3\sigma_g^2$

Molécules X_2

- Ordre de liaison: (ou indice de liaison)

$$n = \frac{1}{2}(n_{liant} - n_{antiliant})$$

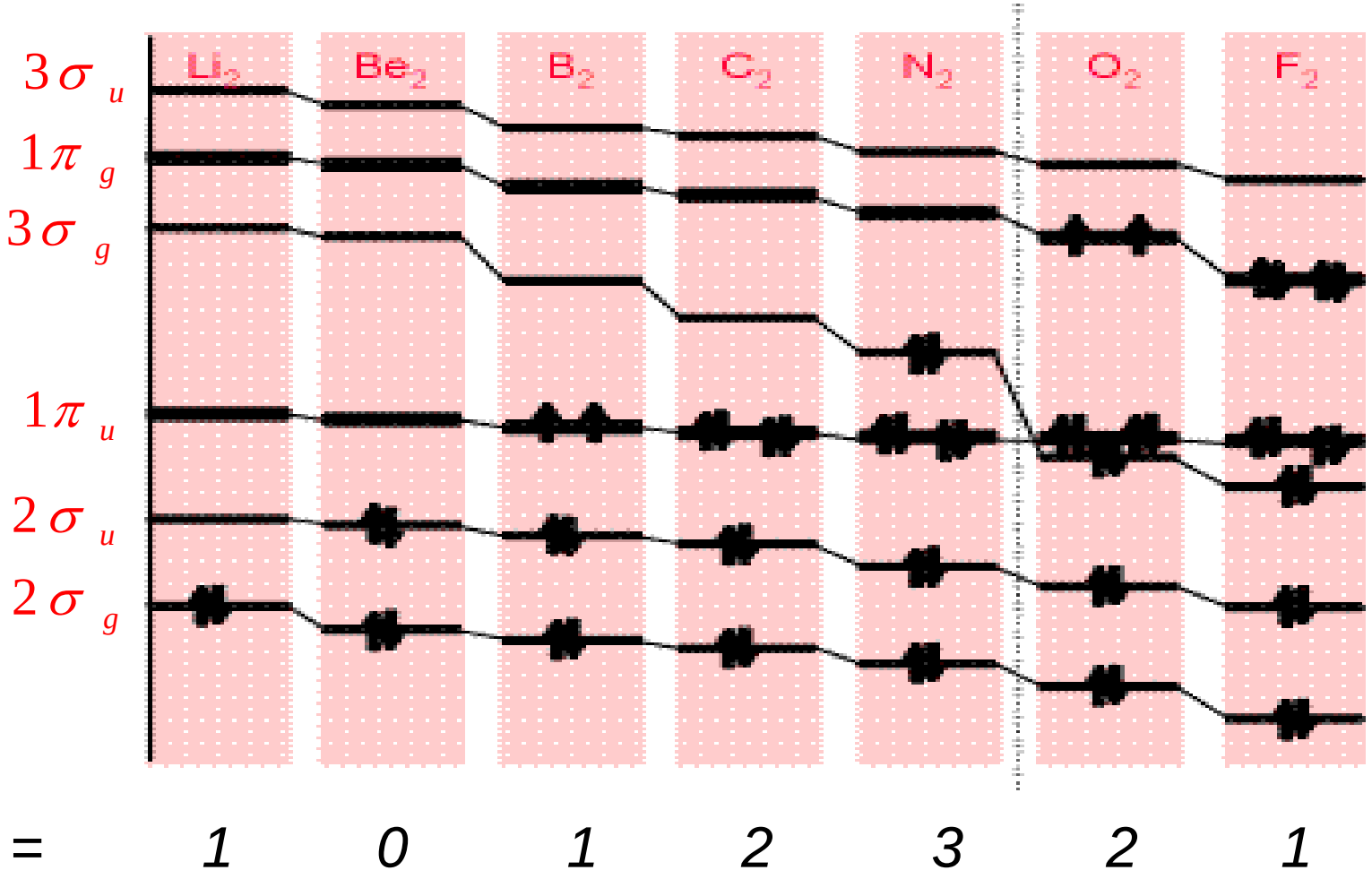
Exemples:

$Li_2 \quad 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 \qquad \{n_{liant} = 4, n_{antiliant} = 2\} \Rightarrow n = 1$

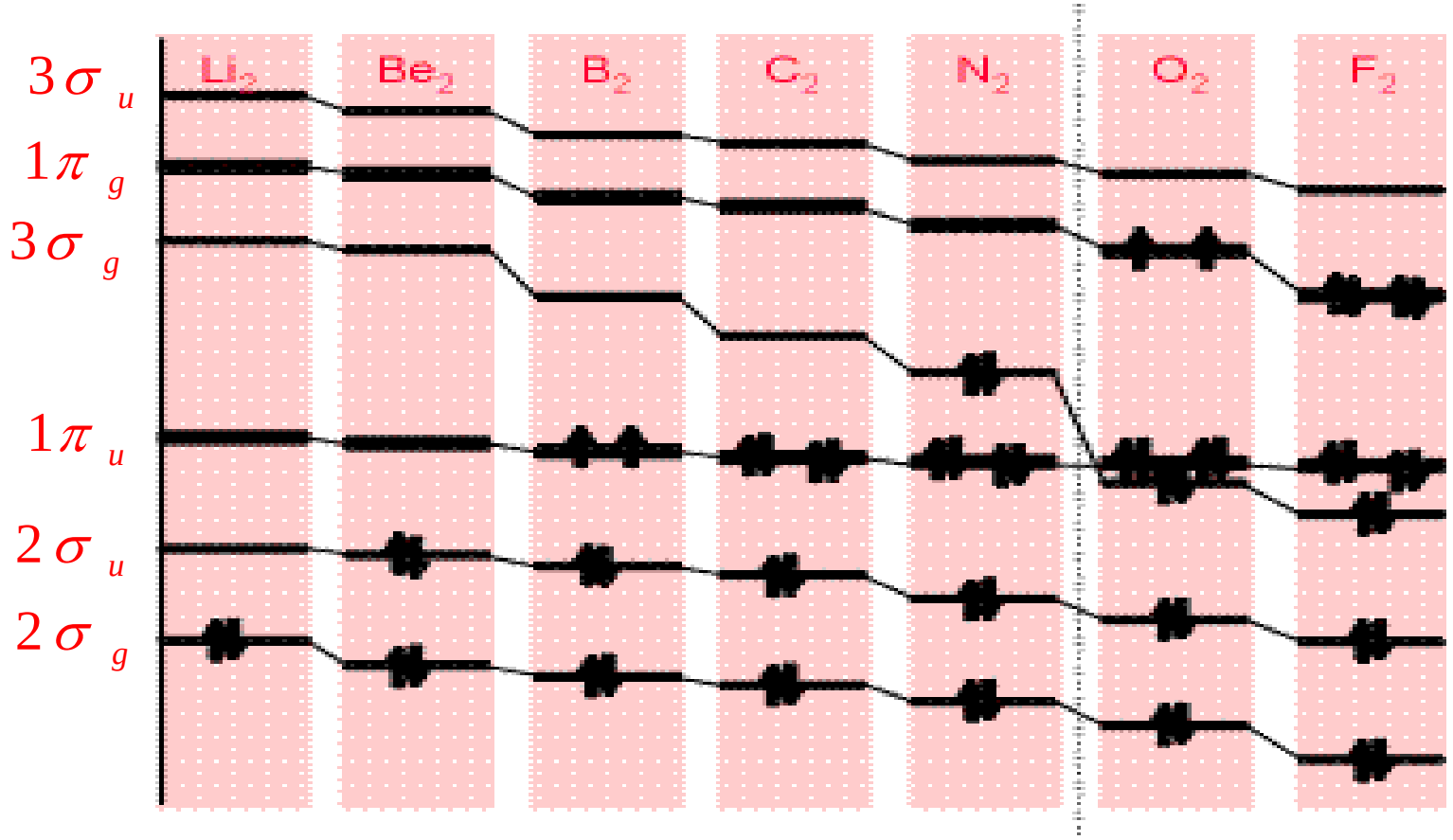
$N_2 \quad 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_{x,u}^2 1\pi_{y,u}^2 3\sigma_g^2$

$\{n_{liant} = 10, n_{antiliant} = 4\} \Rightarrow n = 3$

Molécules X_2

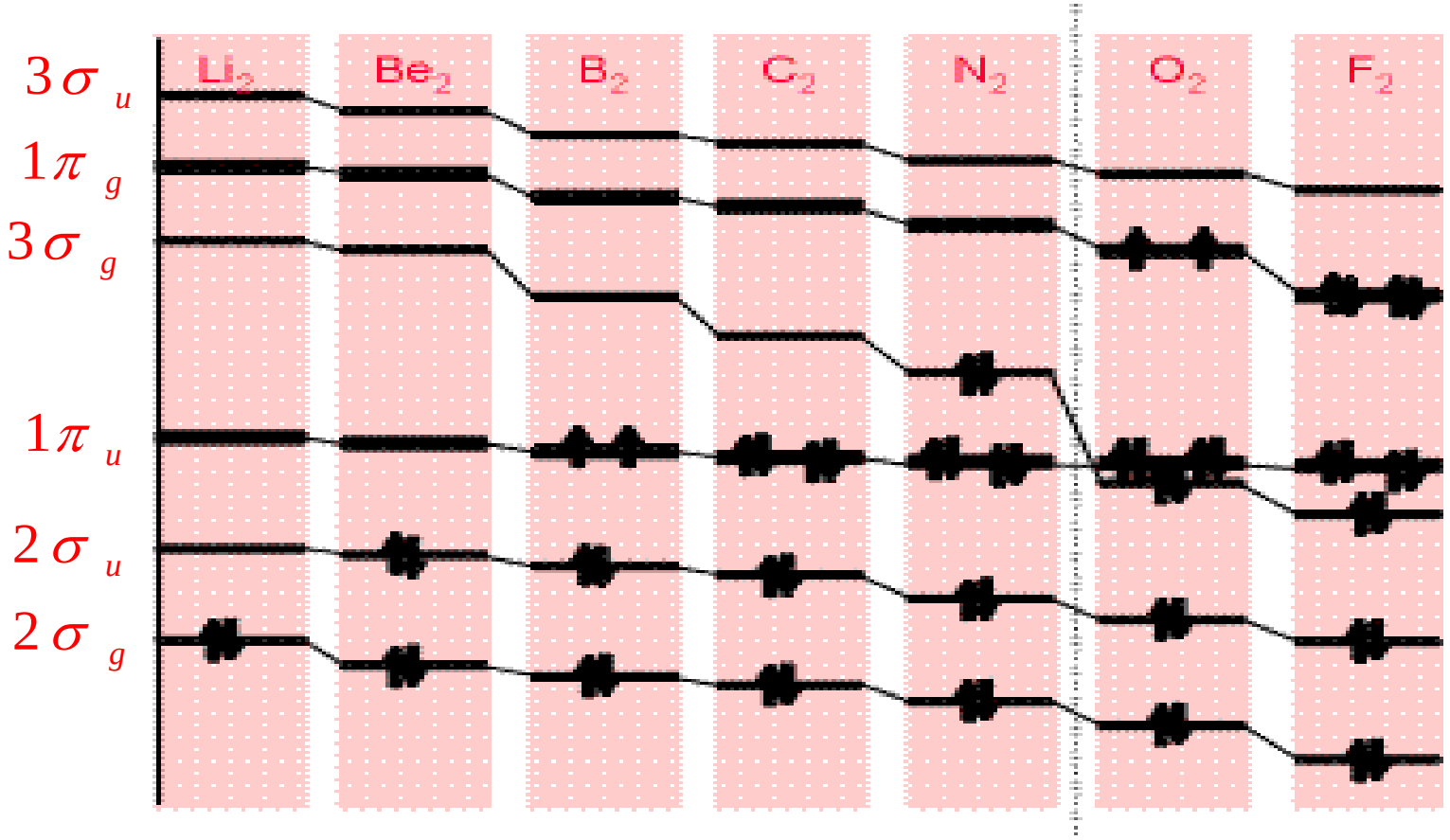


Molécules X_2



n =	*1*	*0*	*1*	*2*	*3*	*2*	*1*
R_e (*pm*) =	*267*	*245*	*159*	*124*	*110*	*121*	*141*

Molécules X_2



n =	*1*	*0*	*1*	*2*	*3*	*2*	*1*
D_e =	*105*	*9*	*289*	*599*	*942*	*494*	*154*

(kJ/mol)