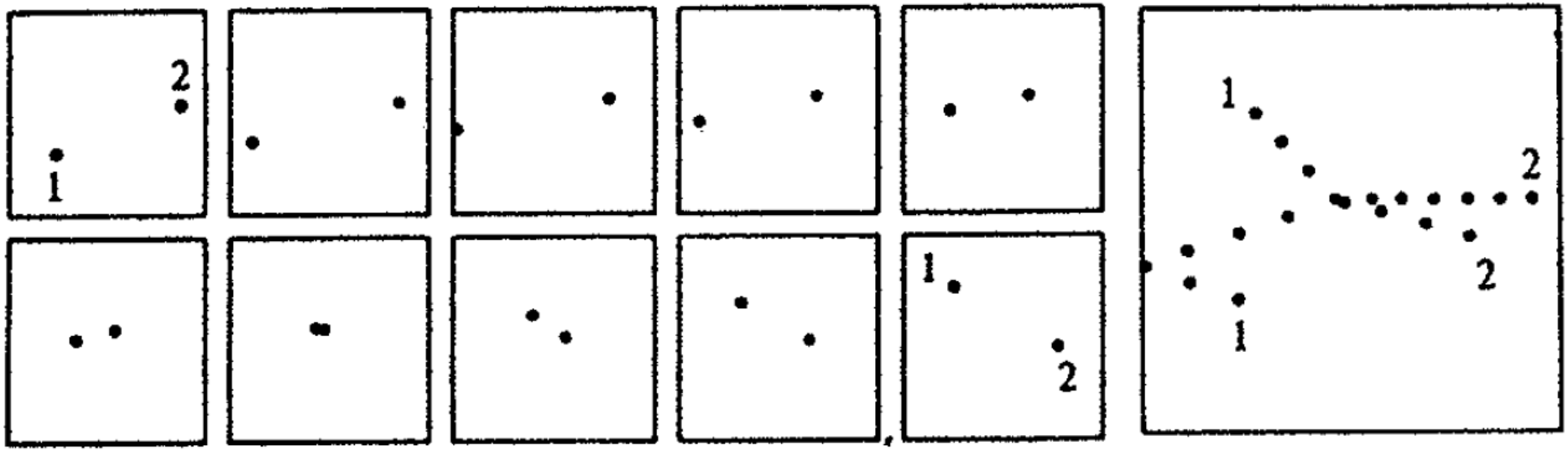
# Átomos Polieletrônicos

## Partículas idênticas




*Em cima*: Uma seqüência de dez quadros de um filme de dois elétrons se movendo em uma caixa, segundo a física clássica. Se rotulássemos suas imagens no primeiro quadro, não haveria ambigüidade na atribuição dos mesmos rótulos às imagens em qualquer quadro subseqüente, embora seja necessário usar grande ampliação e "câmera lenta". *Embaixo*: Uma superposição ampliada de todos os dez quadros, mostrando as trajetórias dos elétrons.

$$\Psi_{total} = \psi(\mathbf{r}_1).\psi(\mathbf{r}_2)$$

**Partículas quânticas idênticas tem que ser indistinguíveis.**

orbital-spin: $\psi(\mathbf{r}_1)\alpha$ e $\psi(\mathbf{r}_2)\beta$

função de onda de spin, $m_s = +½$ e $m_s = -½$

$$\Psi_{total} = \psi_\alpha(\mathbf{r}_1).\psi_\beta(\mathbf{r}_2) + \psi_\beta(\mathbf{r}_1).\psi_\alpha(\mathbf{r}_2)$$

ou

$$\Psi_{total} = \psi_\alpha(\mathbf{r}_1).\psi_\beta(\mathbf{r}_2) - \psi_\beta(\mathbf{r}_1).\psi_\alpha(\mathbf{r}_2)$$

# Funções de onda simétrica e anti-simétrica sob permutação.

$$\Psi_S = \psi_\alpha(\mathbf{r}_1).\psi_\beta(\mathbf{r}_2) + \psi_\beta(\mathbf{r}_1).\psi_\alpha(\mathbf{r}_2)$$

$$\psi_\alpha(\mathbf{r}_2).\psi_\beta(\mathbf{r}_1) + \psi_\beta(\mathbf{r}_2).\psi_\alpha(\mathbf{r}_1)$$

$$\Psi_{AS} = \psi_\alpha(\mathbf{r}_1).\psi_\beta(\mathbf{r}_2) - \psi_\beta(\mathbf{r}_1).\psi_\alpha(\mathbf{r}_2)$$

$$\psi_\alpha(\mathbf{r}_2).\psi_\beta(\mathbf{r}_1) - \psi_\beta(\mathbf{r}_2).\psi_\alpha(\mathbf{r}_1)$$

TABELA 9-1 Característica de Simetria de Várias Partículas.

| Partícula | Simetria | Nome Genérico | Spin ($s$) |
|---|---|---|---|
| Elétron | Anti-simétrica | Férmion | 1/2 |
| Pósitron | Anti-simétrica | Férmion | 1/2 |
| Próton | Anti-simétrica | Férmion | 1/2 |
| Nêutron | Anti-simétrica | Férmion | 1/2 |
| Muon | Anti-simétrica | Férmion | 1/2 |
| Partícula $\alpha$ | Simétrica | Bóson | 0 |
| Átomo de hélio (estado fundamental) | Simétrica | Bóson | 0 |
| Méson $\pi$ | Simétrica | Bóson | 0 |
| Fóton | Simétrica | Bóson | 1 |
| Dêuteron | Simétrica | Bóson | 1 |

## Pauli principle:

When the labels of any two identical fermions are exchanged, the total wavefunction changes sign; when the labels of any two identical bosons are exchanged, the total wavefunction retains the same sign.

Portanto, no caso de funções de muitos elétrons:

$$\Psi_{AS} = \psi_\alpha(\mathbf{r}_1).\psi_\beta(\mathbf{r}_2) - \psi_\beta(\mathbf{r}_1).\psi_\alpha(\mathbf{r}_2)$$

$$\Psi_{AS} = \psi_\alpha(\mathbf{r}_1).\psi_\beta(\mathbf{r}_2) - \psi_\beta(\mathbf{r}_1).\psi_\alpha(\mathbf{r}_2)$$

estado fundamental do He, $1s^2$

$$\Psi_{AS} = 1s_\alpha(\mathbf{r}_1).1s_\beta(\mathbf{r}_2) - 1s_\beta(\mathbf{r}_1).1s_\alpha(\mathbf{r}_2)$$

Se colocarmos os dois elétrons no mesmo orbital-spin?

$$\Psi_{AS} = 1s_\alpha(\mathbf{r}_1).1s_\alpha(\mathbf{r}_2) - 1s_\alpha(\mathbf{r}_1).1s_\alpha(\mathbf{r}_2) = 0$$

**Pauli exclusion principle:**

No more than two electrons may occupy any given orbital, and if two do occupy one orbital, then their spins must be paired.

# Postulados da Mecânica Quântica

**Postulate 6**

*All electronic wave functions must be antisymmetric under the interchange of any two electrons.*

$$\psi(1,2) = 1s\alpha(1)1s\beta(2) \qquad \psi(2,1) = 1s\alpha(2)1s\beta(1)$$

$$\psi(1,2) - \psi(2,1) = 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1)$$

átomo de lítio, $1s^2 2s^1$ : $1s_\alpha(\boldsymbol{r}_1).1s_\beta(\boldsymbol{r}_2).2s_\alpha(\boldsymbol{r}_3)$

É preciso uma função anti-simétrica sob permutação de pares de elétrons.

# Determinante de Slater

Por exemplo, He:

$$1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1)$$

$$\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} = 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1)$$

átomo de lítio, $1s^2 2s^1$:

$$\Psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

# Cálculo da Energia

aproximação orbital: $\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$

$$E = \int\int d\mathbf{r}_1 d\mathbf{r}_2 \phi^*(\mathbf{r}_1)\phi^*(\mathbf{r}_2)\hat{H}\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$$

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right]$$

$$E = \int\int d\mathbf{r}_1 d\mathbf{r}_2 \phi^*(\mathbf{r}_1)\phi^*(\mathbf{r}_2)\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right]\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$$

$$E = \int\int d\mathbf{r}_1 d\mathbf{r}_2 \phi^*(\mathbf{r}_1)\phi^*(\mathbf{r}_2)\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right]\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$$

$$= \int d\mathbf{r}_1 \phi^*(\mathbf{r}_1)\left[-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}\right]\phi(\mathbf{r}_1)\int d\mathbf{r}_2 \phi^*(\mathbf{r}_2)\phi(\mathbf{r}_2)$$

$$+ \int d\mathbf{r}_2 \phi^*(\mathbf{r}_2)\left[-\frac{1}{2}\nabla_2^2 - \frac{Z}{r_2}\right]\phi(\mathbf{r}_2)\int d\mathbf{r}_1 \phi^*(\mathbf{r}_1)\phi(\mathbf{r}_1)$$

$$+ \int\int d\mathbf{r}_1 d\mathbf{r}_2 \phi^*(\mathbf{r}_1)\phi^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$$

1

1

$$E = \int d\mathbf{r}_1 \phi^*(\mathbf{r}_1) \left[ -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} \right] \phi(\mathbf{r}_1)$$

$I_1$
energia de $He^+$

$$+ \int d\mathbf{r}_2 \phi^*(\mathbf{r}_2) \left[ -\frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} \right] \phi(\mathbf{r}_2)$$

$I_2$

$$+ \int \int d\mathbf{r}_1 d\mathbf{r}_2 \phi^*(\mathbf{r}_1)\phi^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$$

$J_{12}$
integral de Coulomb

$$E = I_1 + I_2 + J_{12}$$

$$\hat{H}_1^{\text{eff}}(\mathbf{r}_1)\phi(\mathbf{r}_1) = \epsilon_1 \phi(\mathbf{r}_1)$$

energia orbital: $\varepsilon_1 = I_1 + J_{12} \approx$ energia de ionização

Determinante de Slater:

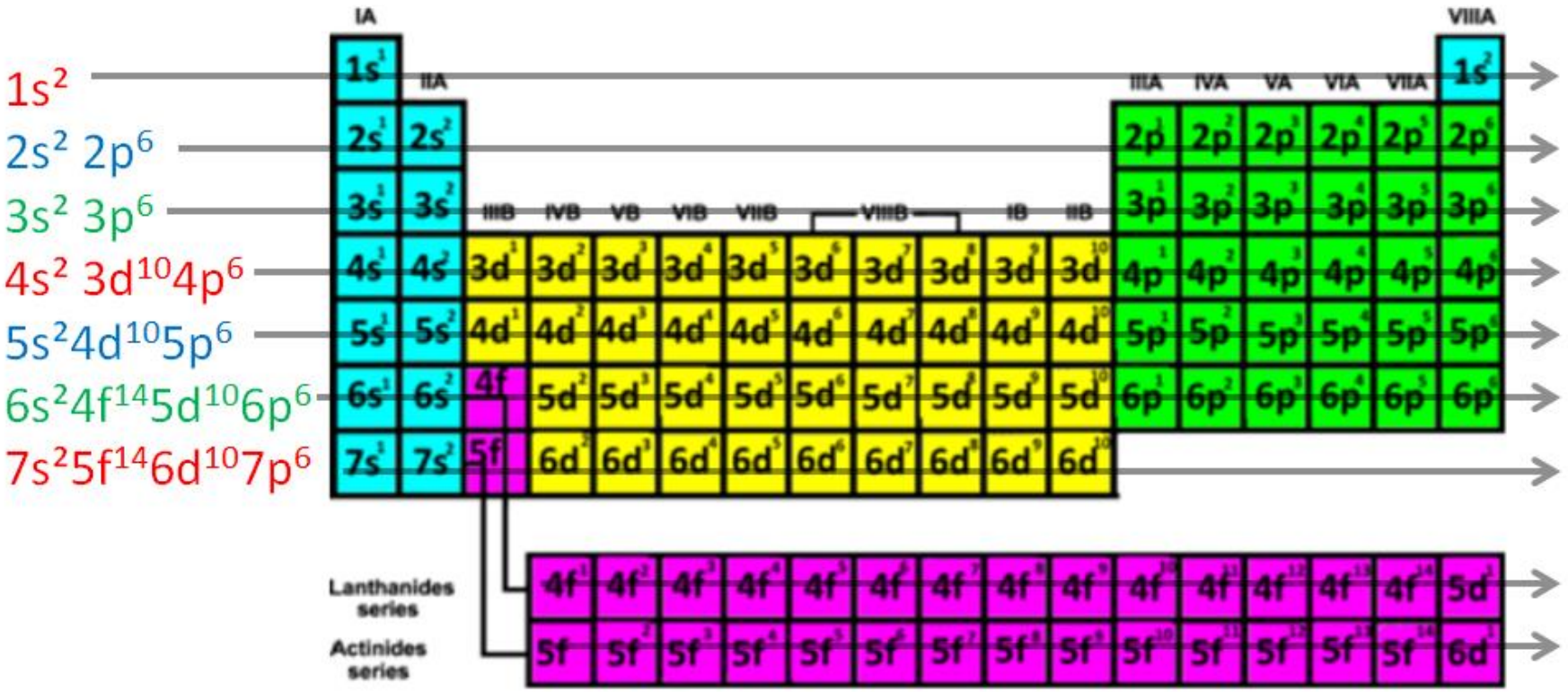
$$\Psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

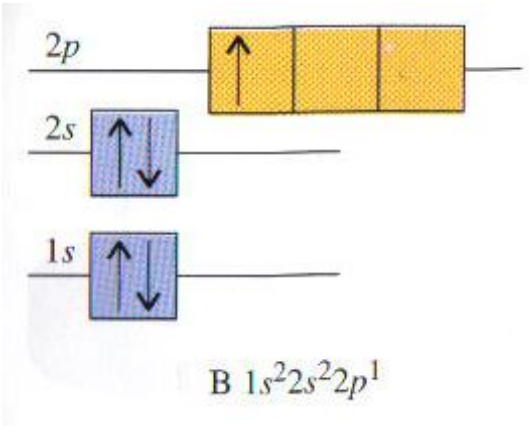
$$E = \int d\mathbf{r}_1 d\sigma_1 \cdots d\mathbf{r}_{2N} d\sigma_{2N} \Psi^*(1, 2, \ldots, 2N) \hat{H} \Psi(1, 2, \ldots, 2N)$$

*N* orbitais ocupados

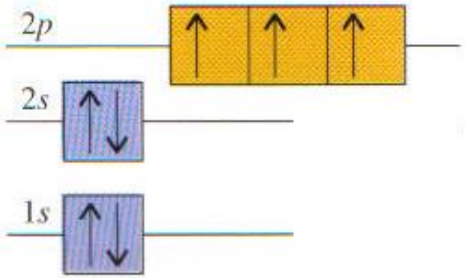
$$E = 2\sum_{j=1}^{N} I_j + \sum_{i=1}^{N}\sum_{j=1}^{N}(2J_{ij} - K_{ij})$$

integral de troca: $$K_{ij} = \int\int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\frac{1}{r_{12}}\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_1)$$




B $1s^2 2s^2 2p^1$




N $1s^2 2s^2 2p^3$, $[He]2s^2 2p^3$