Eletrônica e Fotônica molecular Parte 2

Orbitais Atômicos

Introdução

- Átomos Hidrogeniodes
- Estados Atômicos de um elétron
- Acoplamento spin-orbita
- Estados multi-elétrons
- Metodo de Hartree-Fock

Átomos Hidrogenoides

Potencial de energia: $U(r) = \frac{-Ze^2}{r}$

Equação de Schrodinger: $\left[\frac{-h}{2m}\nabla^2 + U(r)\right]\psi = E\,\psi$

$$\left[\frac{-h}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{sen\theta}\frac{\partial}{\partial\theta}\left(sen\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{sen^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\right\} + U(r)\right]\psi = E\,\psi$$

$$L^2Y(\theta,\varphi) = \lambda Y(\theta,\varphi)$$

$$L_Z Y^{\,m}_l = mhY^m_l \qquad m = 0, \pm1, \pm2, \ldots . \pm l$$

$$L^2 Y^{\,m}_l = l(l+1)h^2 Y^m_l \qquad l = 0, 1, 2, \ldots . (n-1)$$

$$Y^m_l(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}(-1)^m e^{im\emptyset} P^m_l(cos\theta)$$

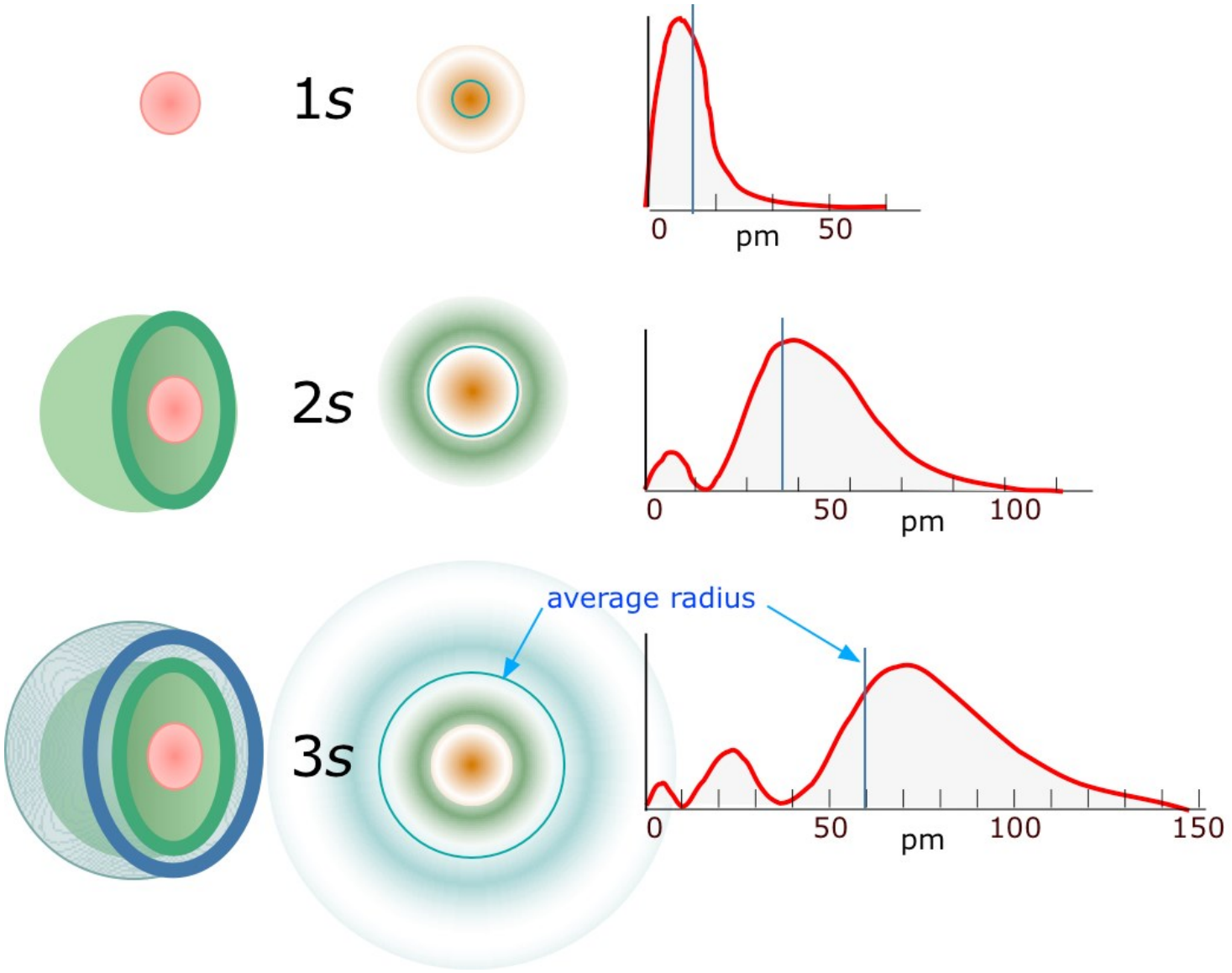
→ Harmônicos esféricos

$$\left[\frac{-h}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{l(l+1)h^2}{2mr^2} + U(r)\right]R(r) = E\,R(r) \longrightarrow E_n = -\frac{Z^2e^2}{2n^2a} \qquad n = 1, 2, 3, \ldots .$$

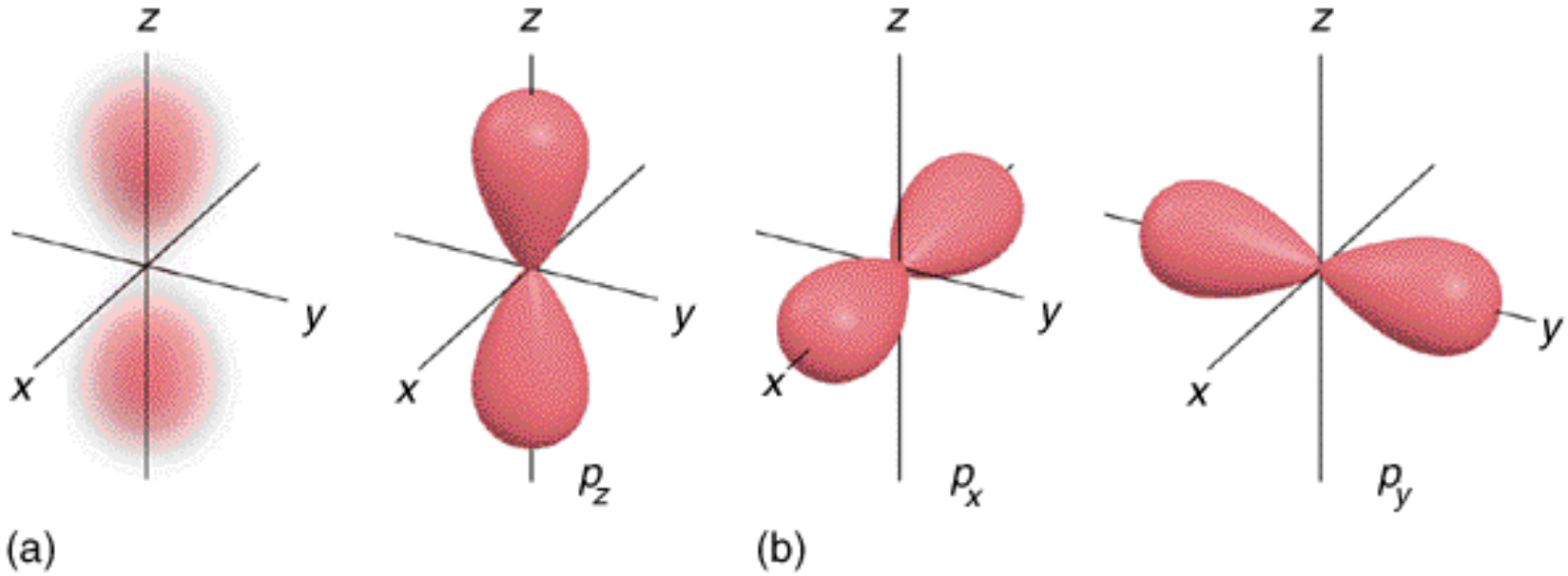
$$R_{n,l}(r) = \left[\frac{(n-l-1)!}{(n+l)!^3}\right]^{\frac{1}{2}}\left(\frac{2Z}{na}\right)^{l+\frac{3}{2}} exp\left(-\frac{Zr}{na}\right) r^l L^{2l+1}_{n+1}\left(\frac{2Zr}{na}\right)$$

→ $L^l_n(x)$: *Polinomios da Laguer associados*

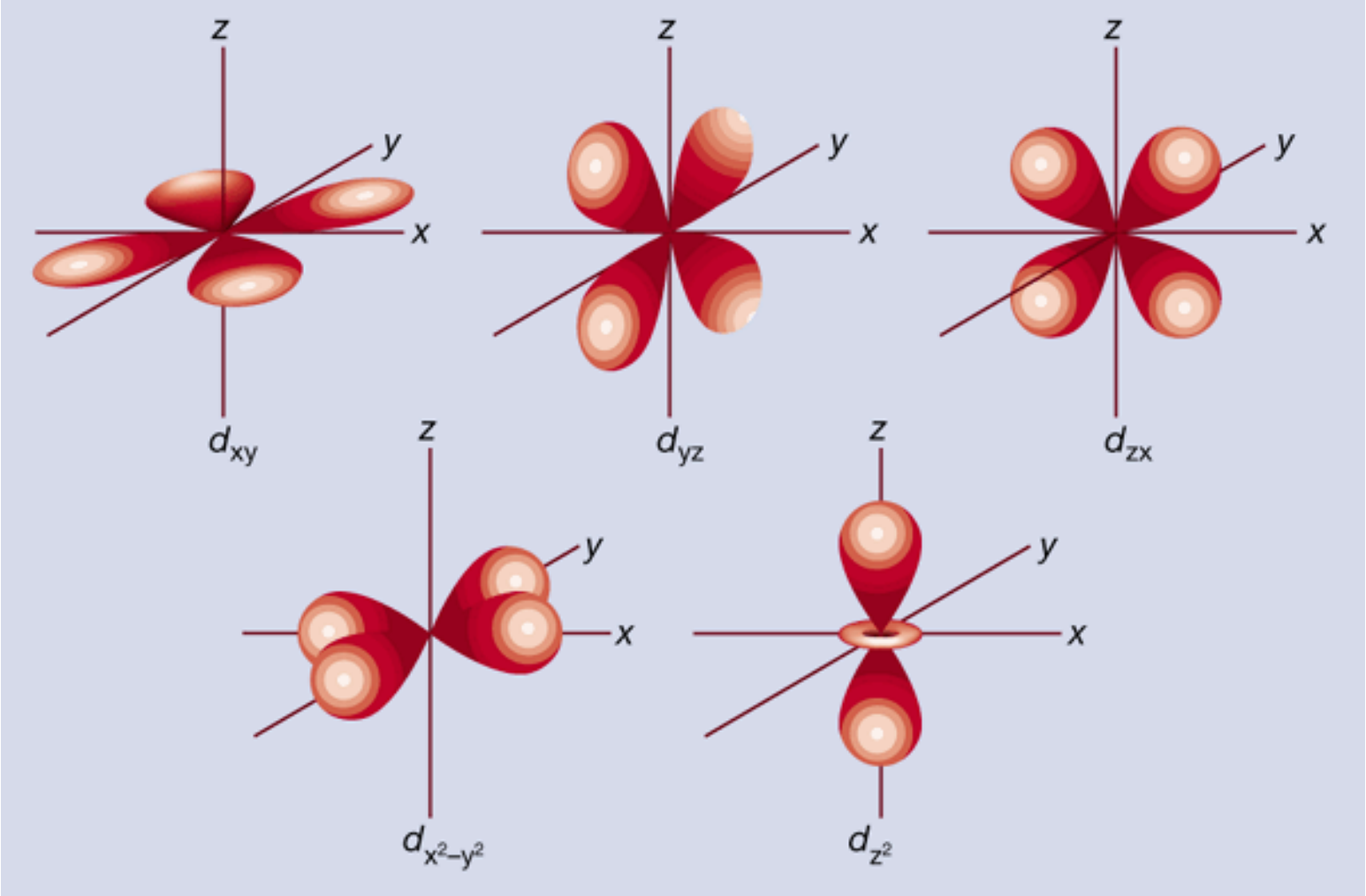
Orbitais S



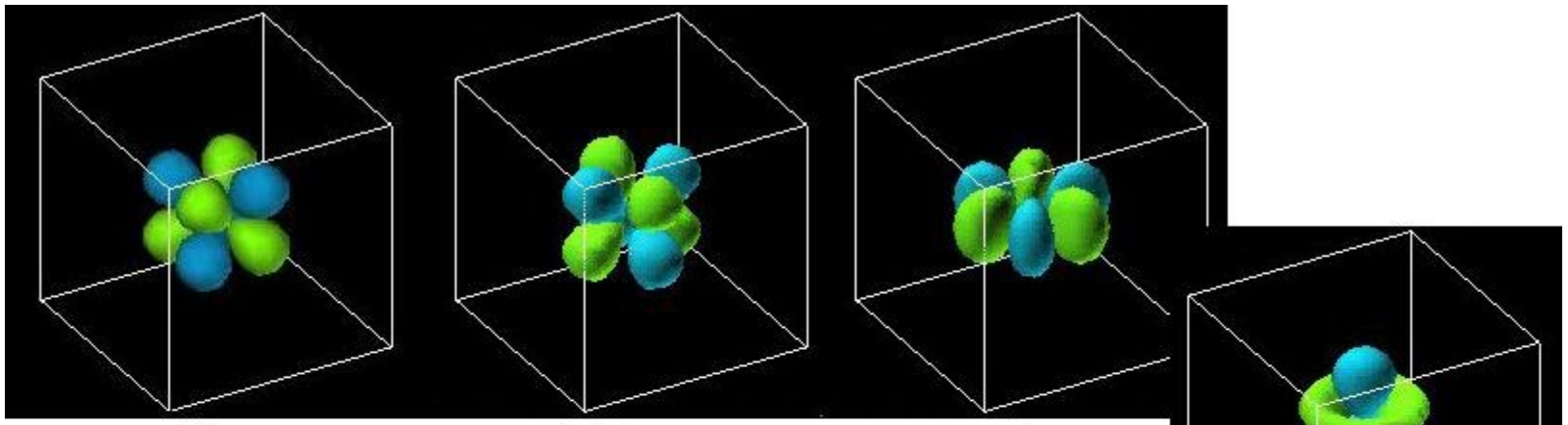
Orbitais P



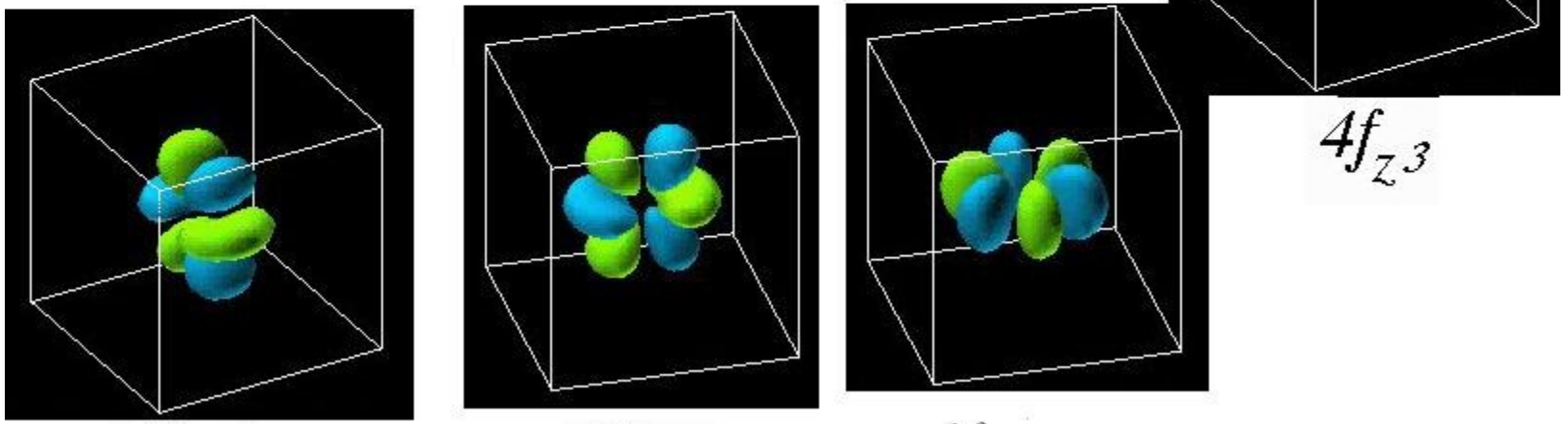
Orbitais d



Orbitais f



$4f_{xyz}$ $4f_{z(x^2-y^2)}$ $4f_{y(3x^2-y^2)}$



$4f_{z^3}$

$4f_{yz^2}$ $4f_{xz^2}$ $4f_{x(3y^2-x^2)}$

Estados Multi-elétrons e Termos de Energia

Pequena interação spin-órbita: J = L +S
Acoplamento LS

$$L = \sum_i l_i \qquad S = \sum_i s_i$$

L= 0, 1, 2, 3, 4, 5, ...
S, P, D, F, G, H

Multiplicidade: (2L+1)(2S+1)

Termo: $^{2S+1}$P

[A](nd)^2 : ^{3}F, ^{1}D, ^{3}P, ^{1}G, ^{1}S ⟵ **Regra de Hunt**

Interação significativa Spin-Órbita:

$$j_i = l_i + s_i \qquad J = \sum_i j_i$$

Termo: $^{2s+1}$P$_J$

Funções de Onda Multi-Elétrons

Quantização de Fermi-Dirac

$$\Phi(1,2,.....,n) = (n!)^{-1/2} \begin{vmatrix} \psi_1(1)\psi_2(2).....\psi_1(n) \\ \psi_2(1)\psi_2(2).....\psi_2(n) \\ ..... \\ ..... \\ \psi_n(1)\psi_n(2).....\psi_n(n) \end{vmatrix}$$

Método de Hartree-Fock (HF)

$$F^k \phi_k(r) = E_k \phi_k(r)$$

$$F^k = H^0 + \sum_i \frac{e^2 \int \phi_i^*(r)(2 - P_{ik})\varphi_i(r')}{|r - r'|} dr'$$

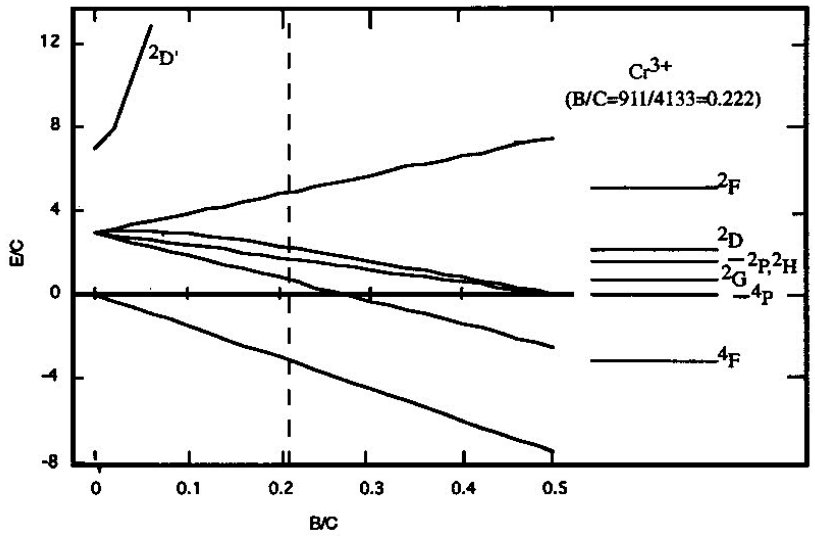
Teoria do funcional de densidade:

$$E(\psi) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$E(\rho) = T(\rho) + V_{ne}(\rho) + V_{ee}(\rho)$$

Estados Multi-elétrons: Cr^{3+}

Termos de Íon livre de Cr^{3+} ($3d^3$)



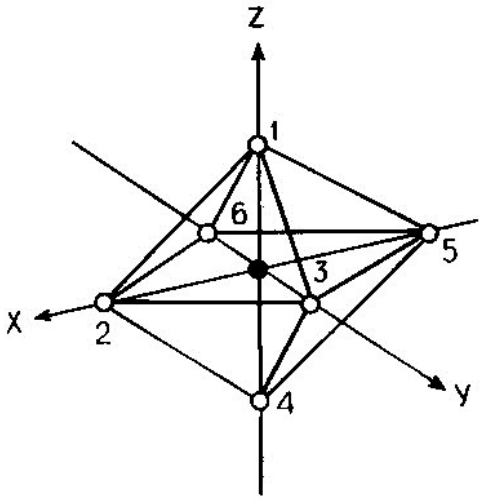


Diagrama de Tanabe-Sugano para um íons $3d^{3+}$