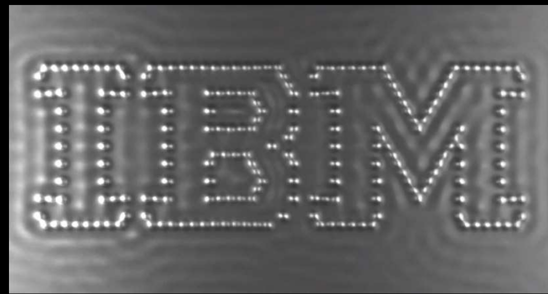
Fluorescência

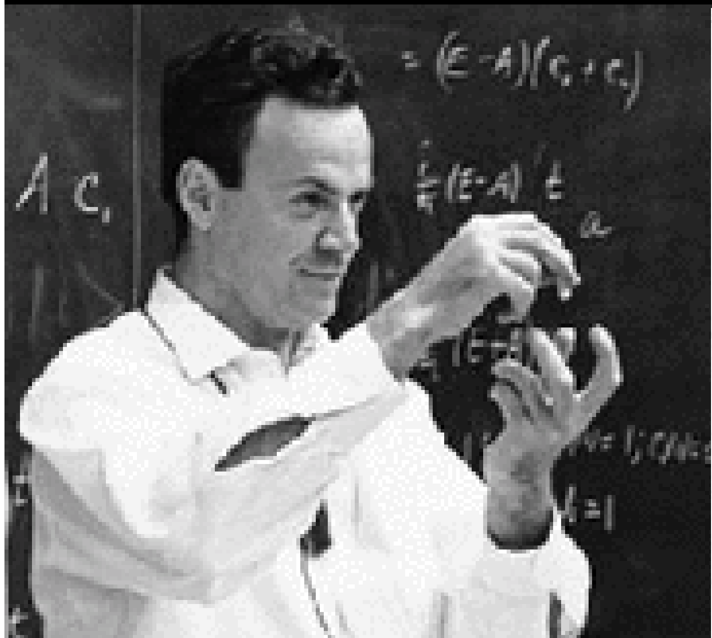
Carlos Lenz Cesar – IFGW - UNICAMP

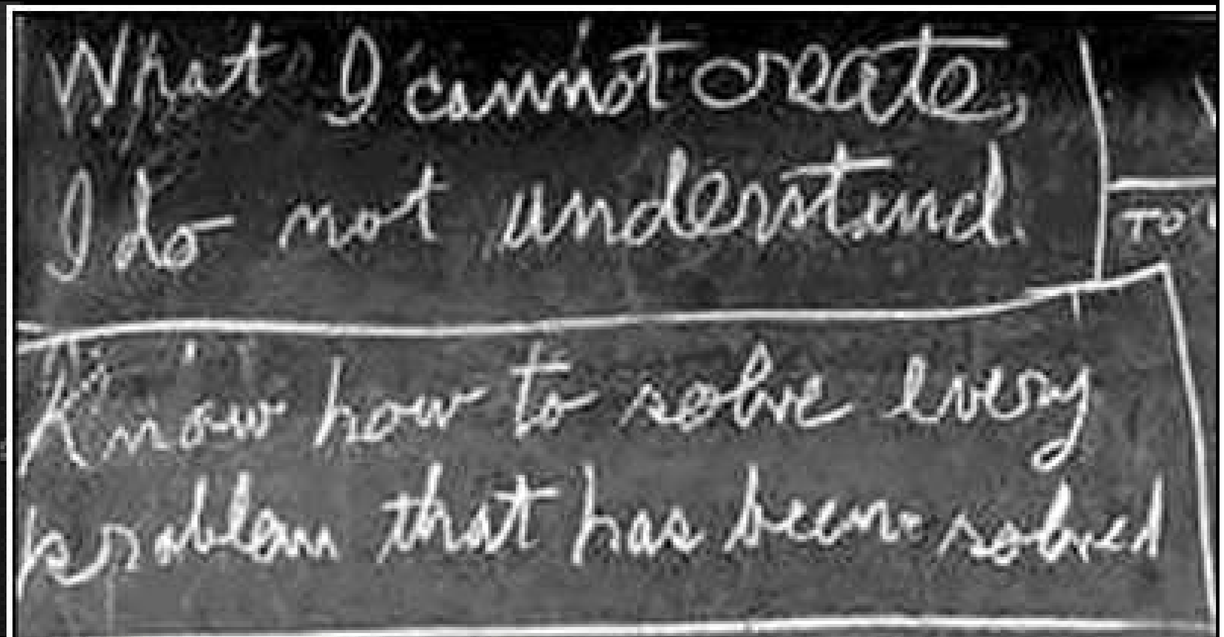
There's plenty of room at the bottom

1953: Feynman proposed manipulation of individual atoms



**What I cannot create,
I do not understand!**





Mecânica Quântica Hard

Mecânica Quântica

Schroendinger e as funções de onda $\Psi(x,t)$

$$E_{cin} + U_{pot} = E_{mec}$$

$$E_{mec} = \hbar\omega \qquad E_{cin} = \frac{p^2}{2m} \qquad p = \hbar k$$

Equação de onda de Schroendinger

$$\hbar\omega\,\Psi = \left[\frac{\hbar^2 k^2}{2m} + U_{pot}\right]\Psi$$

Interpretação de Copenhagen da função de Onda

$\Psi(x,t) = \Psi'(x,t) + i\Psi''(x,t)$ **é complexa** $i = \sqrt{-1}$

Se $z = x + iy$ **então** $z^* = x - iy$ **e** $z\,z^* = x^2 + y^2$

Notamos que $z\,z^*$ **é real e positivo**

$\Psi\Psi^* =$ **probabilidade de encontrar partícula em x e t**

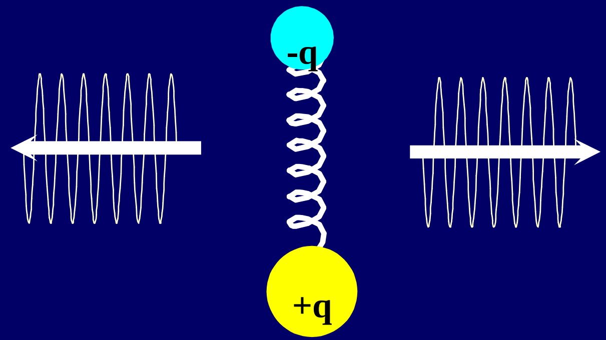
Interpretação de Copenhagen da função de Onda

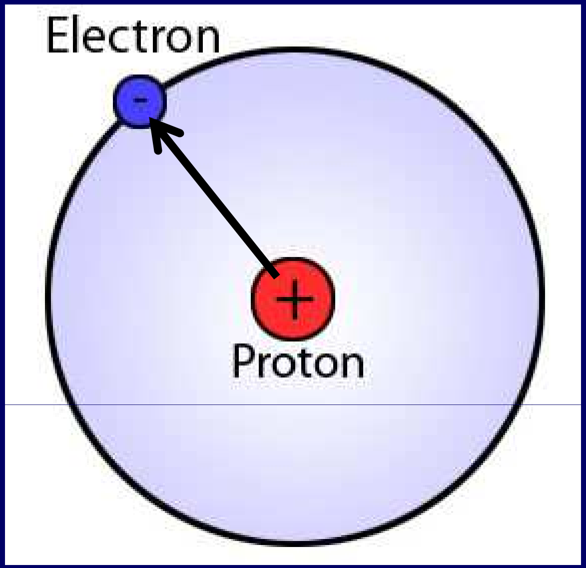
$\Psi\Psi^* =$ probabilidade de encontrar partícula em x e t

Einstein não gostou: Deus não joga dados com o universo

Turma do heavy metal: Joga! E ainda rouba!

Problema: átomo instável





Dipolo que oscila:
irradia – perde energia – colapsa no núcleo

Estados estacionários

Suponha que $\Psi(x,t) = \varphi(x)\left[\cos(\omega t) + i\,sen(\omega t)\right]$

Nesse caso:

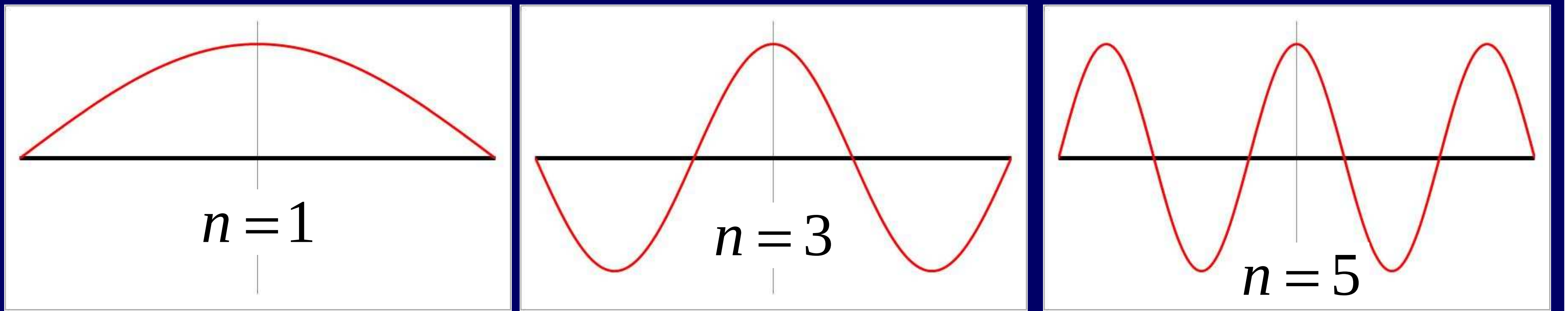
$$\Psi\Psi^* = \varphi(x)\varphi^*(x)\left[\cos^2(\omega t) + sen^2(\omega t)\right] = \varphi(x)\varphi^*(x)$$

Não depende do tempo, só do espaço!
Logo não oscila – não irradia!

Estados estacionários são ESTÁVEIS

Partícula em uma caixa: ondas estacionárias simétricas

$$\varphi(x) = \cos(kx) \qquad \cos\left(\frac{kL}{2}\right) = 0 \qquad \frac{kL}{2} = n_{impar}\frac{\pi}{2} \qquad k = n_{impar}\frac{\pi}{L}$$



$$E = \frac{\hbar^2 k^2}{2m} = n_{impar}^2 \frac{h^2}{8mL^2}$$

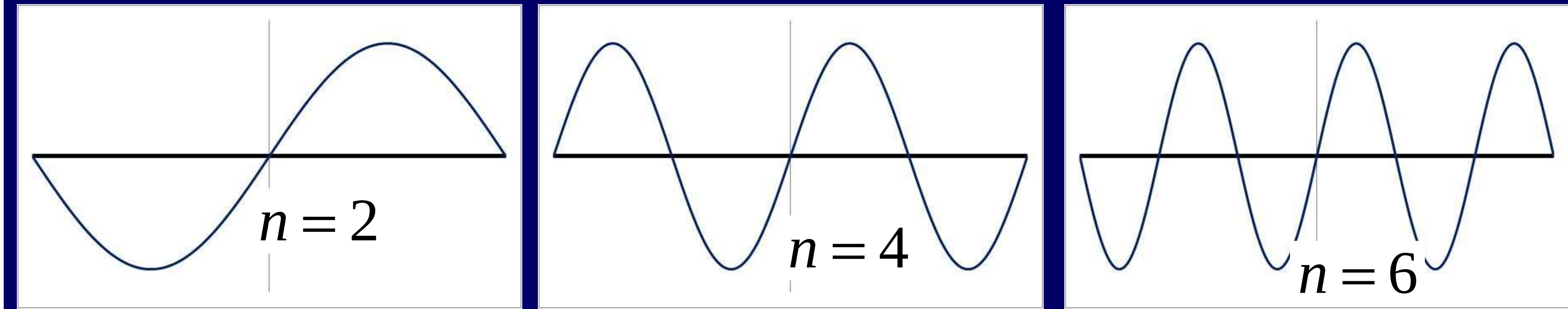
Partícula em uma caixa:
ondas estacionárias anti-simétricas

$$\varphi(x) = sen(kx)$$

$$sen\left(\frac{kL}{2}\right) = 0$$

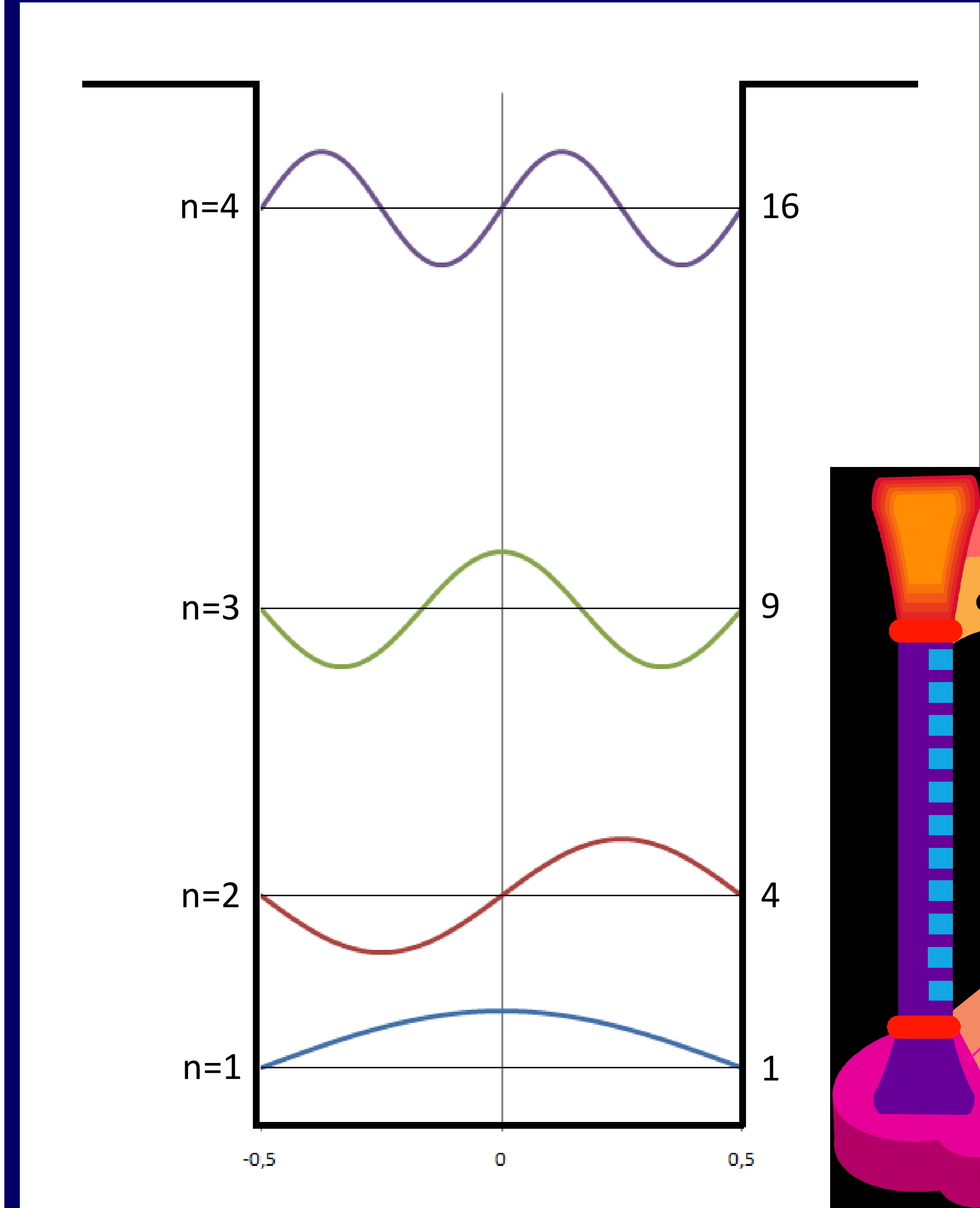
$$\frac{kL}{2} = n_{par}\frac{\pi}{2}$$

$$k = n_{par}\frac{\pi}{L}$$

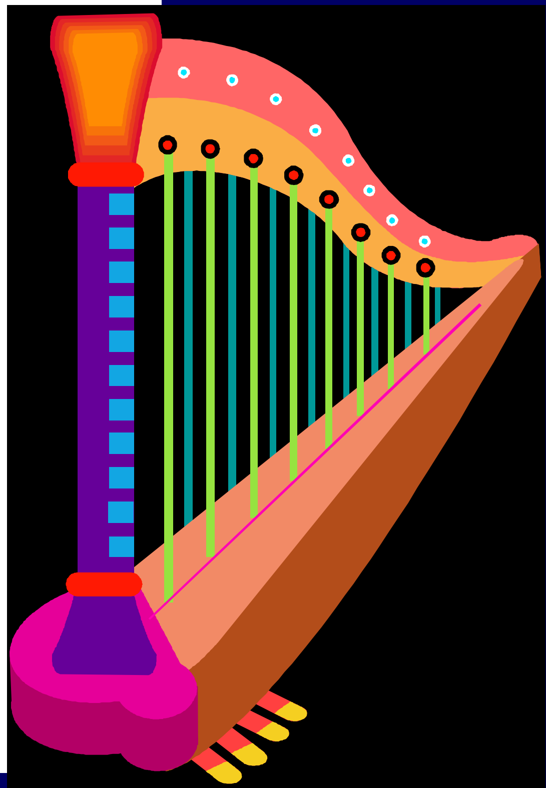


$$E = \frac{\hbar^2 k^2}{2m} = n_{par}^2 \frac{h^2}{8mL^2}$$

Partícula em uma caixa:



$$E_n = n^2 \frac{h^2}{8mL^2}$$



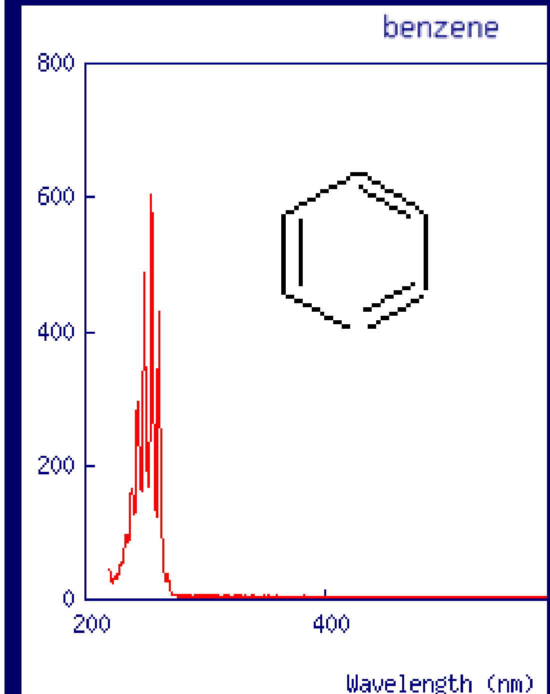
Menor corda
maior freqüência
maior E
menor λ

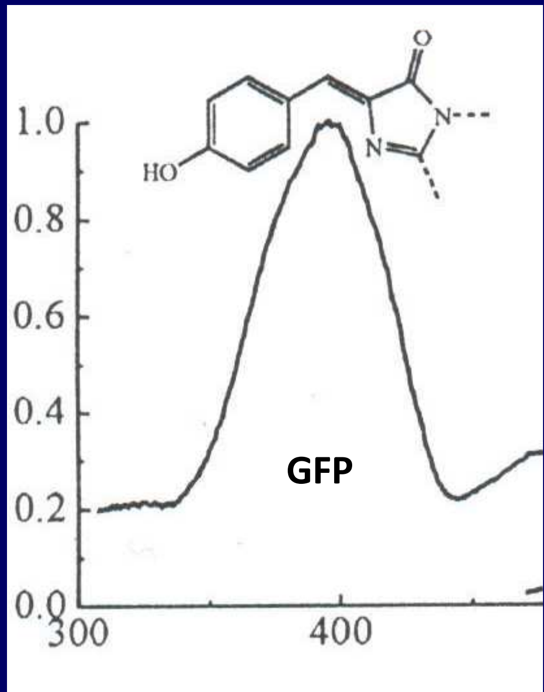
Moléculas orgânicas: conjugações

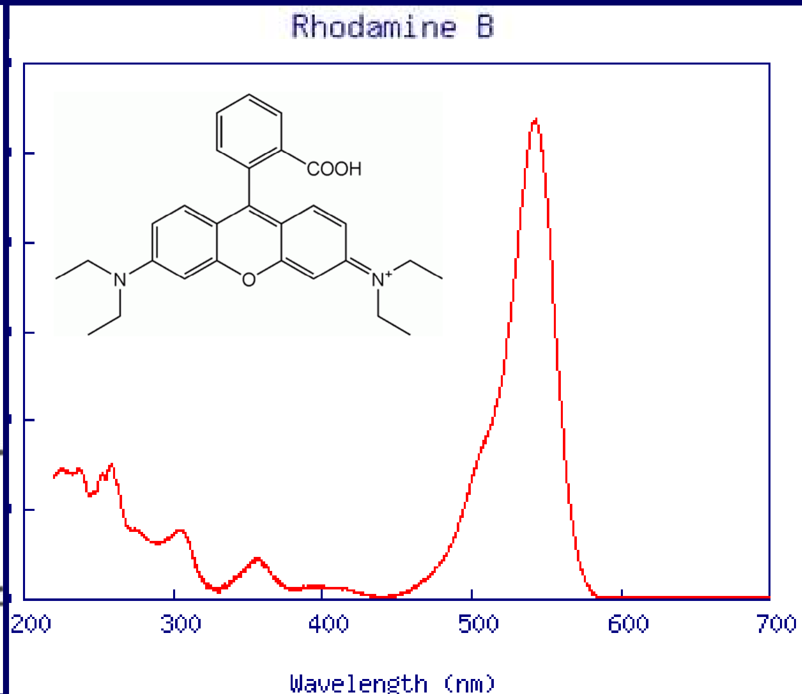
1 elétron solto por conjugação

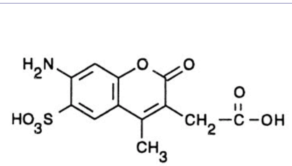
$$\cdots C - C = C - \cdots$$

Partícula em uma caixa:
maior tamanho mais vermelho

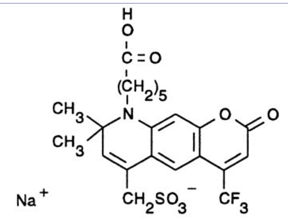








Alexa 350



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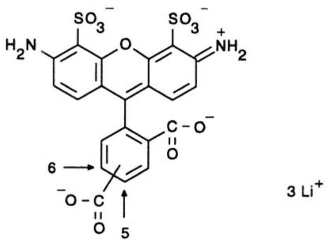

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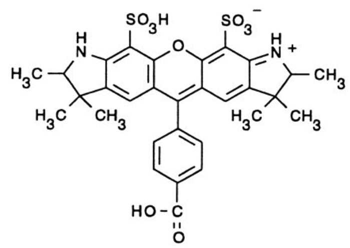
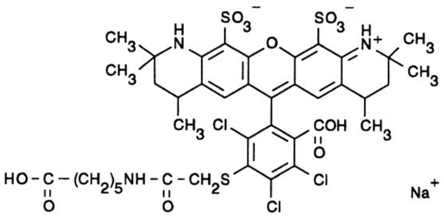


Alexa 532



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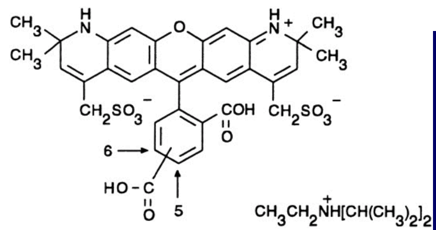
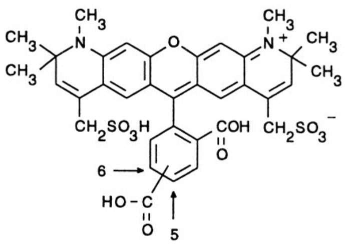
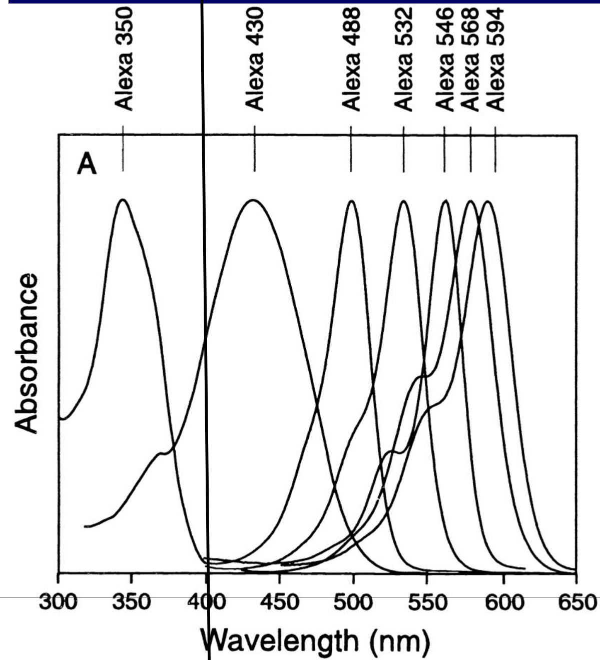


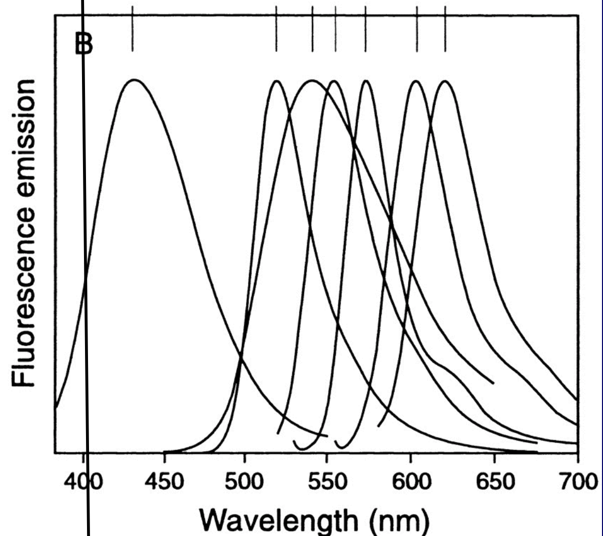
Alexa 568



Alexa 594

Excitação

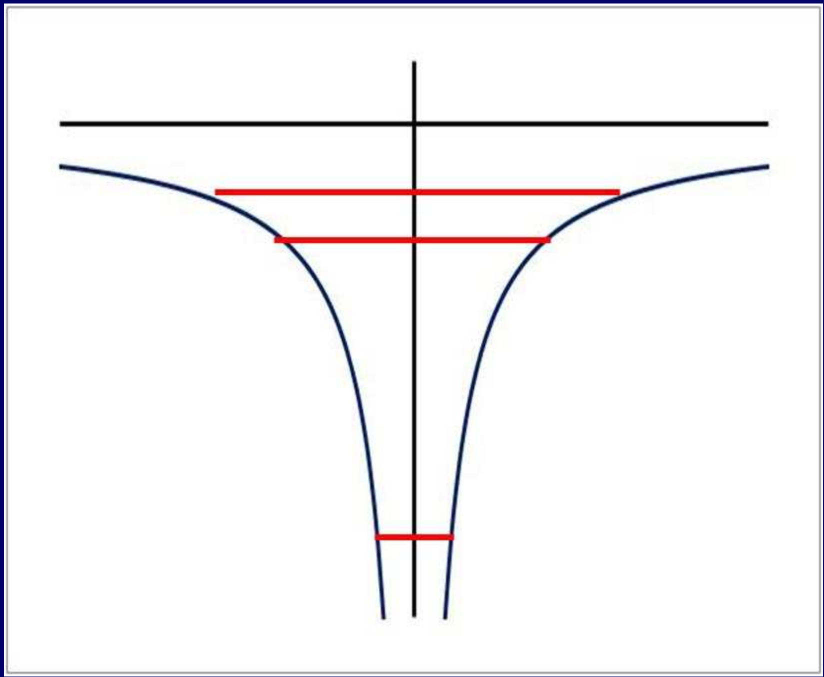




Emissão

Poço Coulombiano:

$$U_{pot} = -k\frac{e^2}{r}$$



$$E_n = n^2 \frac{h^2}{8mL_n^2}$$

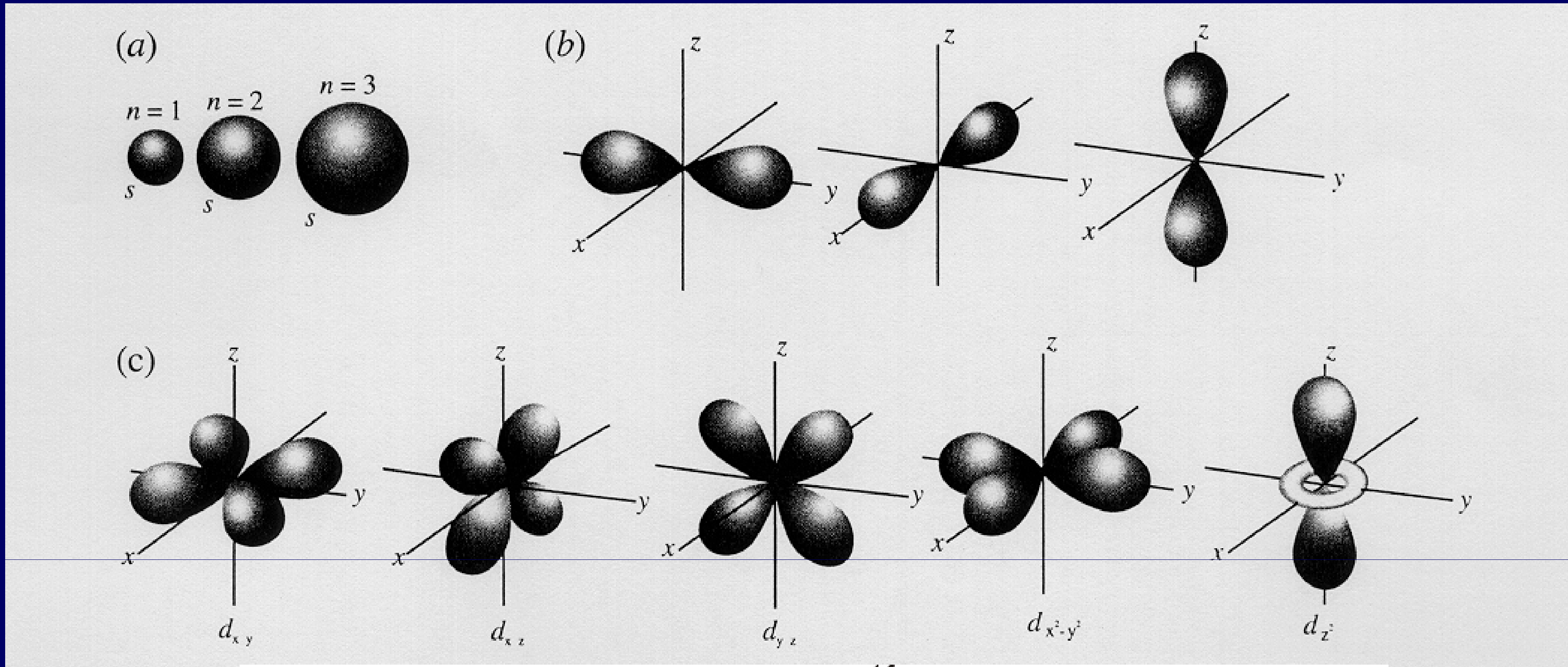
$$E_n = k\frac{e^2}{L_n} \qquad L_n = k\frac{e^2}{E_n}$$

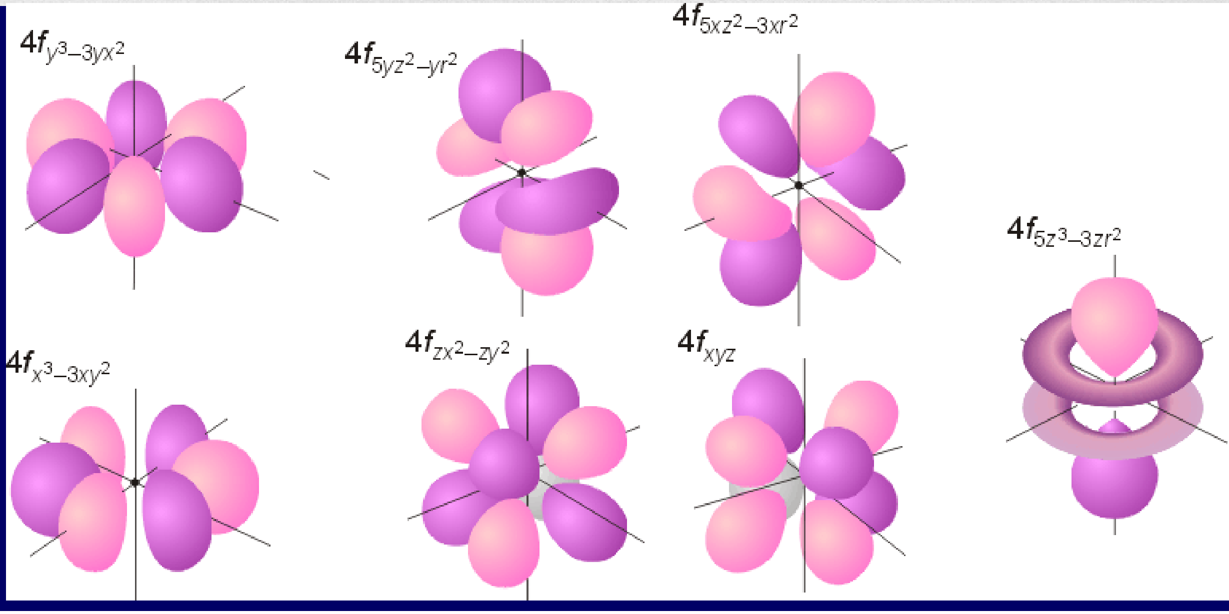
$$E_n = n^2 \frac{h^2 E_n^2}{8mk^2 e^4}$$

$$E_n = \frac{1}{n^2}\frac{8mk^2e^4}{h^2}$$

energia vai com $E_n \propto \frac{1}{n^2}$

Orbitais atômicos





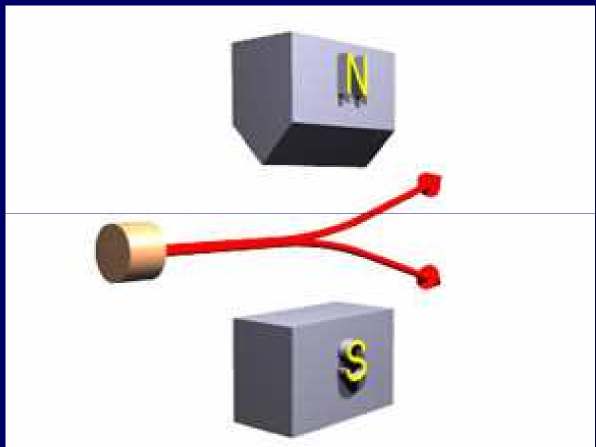
Momento angular orbital

$$2\pi R = n\lambda$$

$$mV = \frac{h}{\lambda}$$

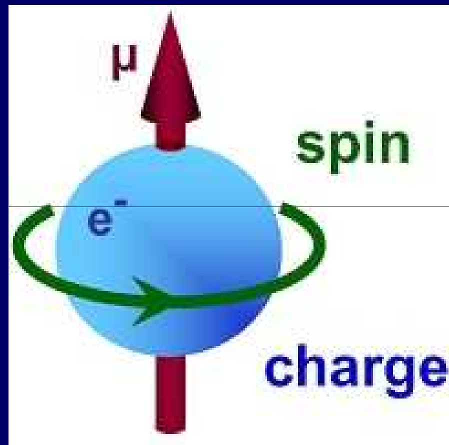
$$L = mVR = n\frac{h}{2\pi} = n\hbar$$

Momento angular de spin

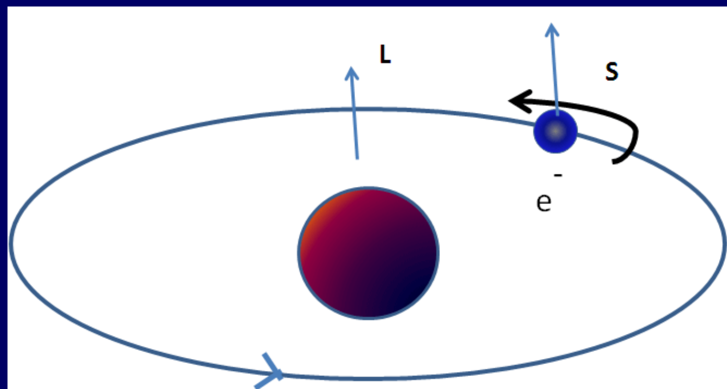


$$S = \uparrow$$

$$S = \downarrow$$



$$S = \pm\frac{\hbar}{2}$$



Partículas idênticas:
Na quântica é impossível notar permutação!

$$\Psi\Psi^*\left(x_1, x_2\right) = \Psi\Psi^*\left(x_2, x_1\right)$$

funções simétricas:

$$\Psi_s = \varphi_1\left(x_1\right)\varphi_2\left(x_2\right) + \varphi_1\left(x_2\right)\varphi_2\left(x_1\right)$$

ou funções anti-simétricas:

$$\Psi_{as} = \varphi_1\left(x_1\right)\varphi_2\left(x_2\right) - \varphi_1\left(x_2\right)\varphi_2\left(x_1\right)$$

Spins: funções simétricas e anti-simétrica

Singleto

$$S = \uparrow\downarrow - \downarrow\uparrow$$

Tripleto

$$T_{+1} = \uparrow\uparrow \quad T_0 = \uparrow\downarrow + \downarrow\uparrow \quad T_{-1} = \downarrow\downarrow$$

Pauli: função total [espaço+spin] anti-simétrica

$$\Psi_s S_{as} \qquad \Psi_{as} S_s$$

Se $\varphi_1(x) = \varphi_2(x) = \varphi(x)$

então $\Psi_{as} = \varphi_1(x_1)\varphi_2(x_2) - \varphi_1(x_2)\varphi_2(x_1) = 0$

Logo só spin pareados no mesmo estado: $S = \uparrow\downarrow$

Repulsão e spin:

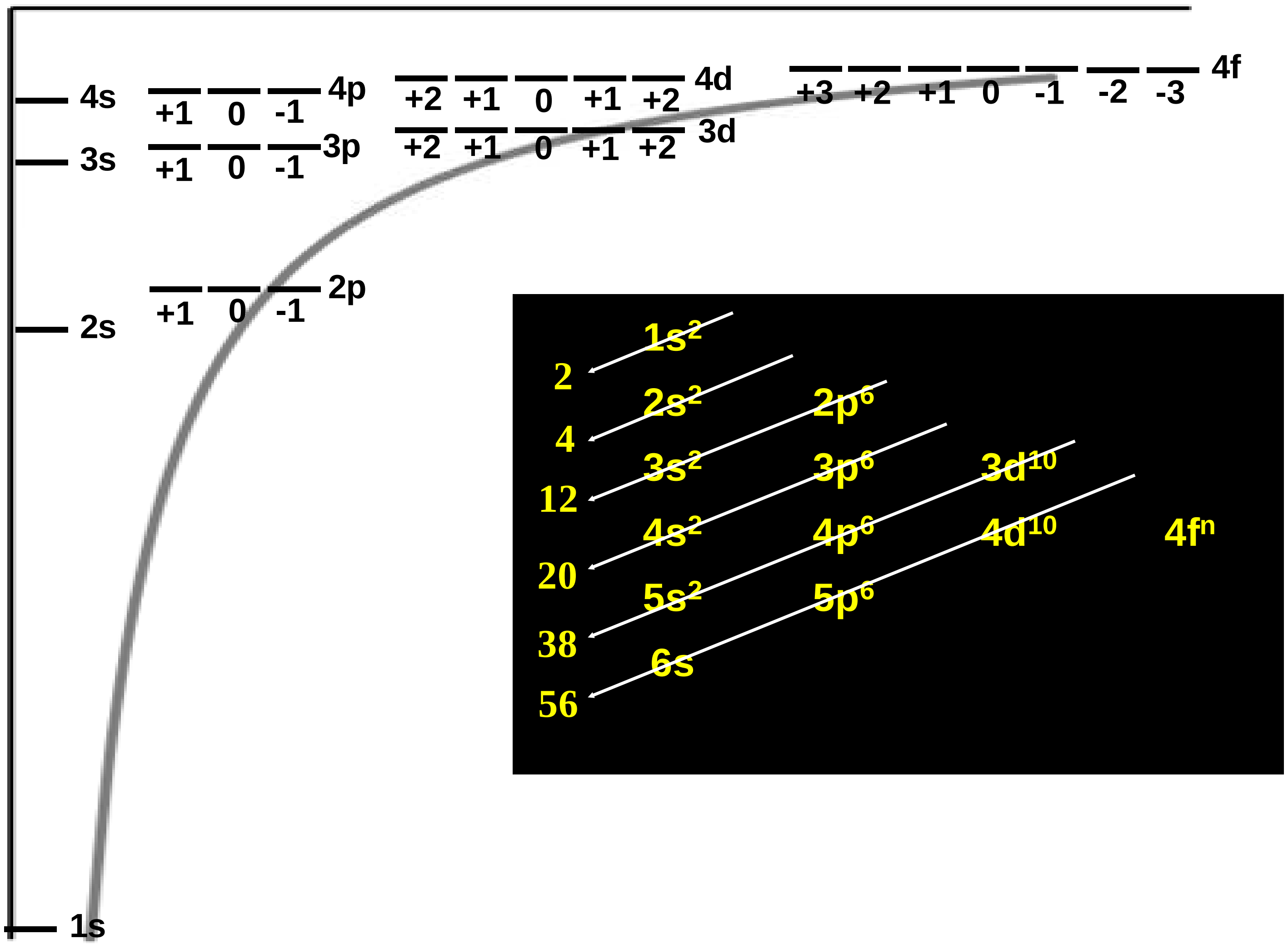
Se $x_1 = x_2$

então $\Psi_s = \varphi_1(x_1)\varphi_2(x_1) + \varphi_1(x_1)\varphi_2(x_1) \neq 0$ singleto

$\Psi_{as} = \varphi_1(x_1)\varphi_2(x_1) - \varphi_1(x_1)\varphi_2(x_1) = 0$ tripleto

Tripleto afasta um elétron do outro, singleto não:
Conclusão: $E_{trip} < E_{sing}$

Níveis de energia dos orbitais atômicos



Regras de seleção:
Transições permitidas se existe dipolo médio entre estados

$$\langle p \rangle = \langle \varphi_2(x) | qx | \varphi_1(x) \rangle \langle S_2 | S_1 \rangle \neq 0$$

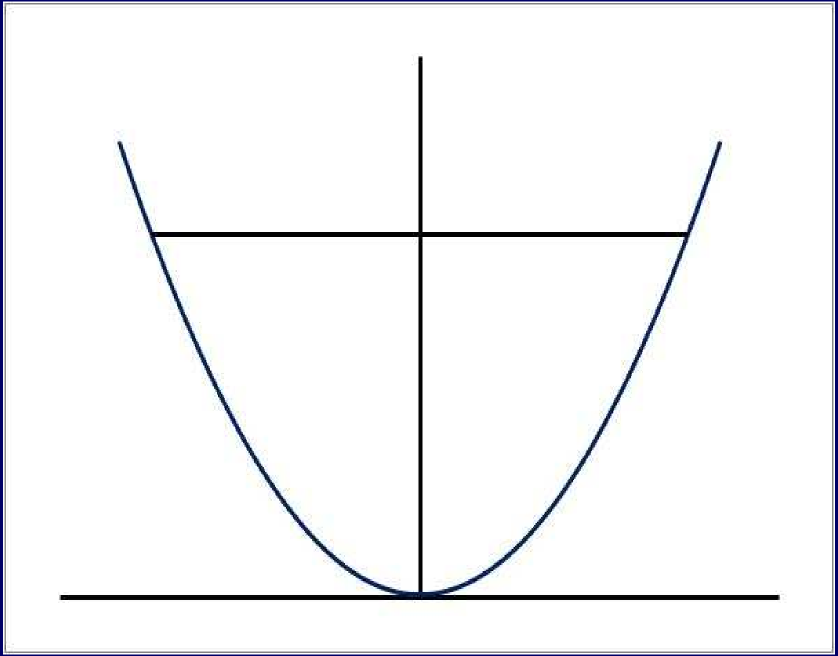
Estados de paridades diferentes

Transições singleto - tripleto são proibidas

Fluorescência: transição permitida por spin
singleto-singleto em orgânicos ou tripleto-tripleto
Tempos de vida < 10 ns

Fosforescência: transição proibida por spin
Tripleto-singleto
Tempos de vida > μs

Molécula tem vibração dos núcleos



$$E_n = n^2 \frac{h^2}{8mL_n^2}$$

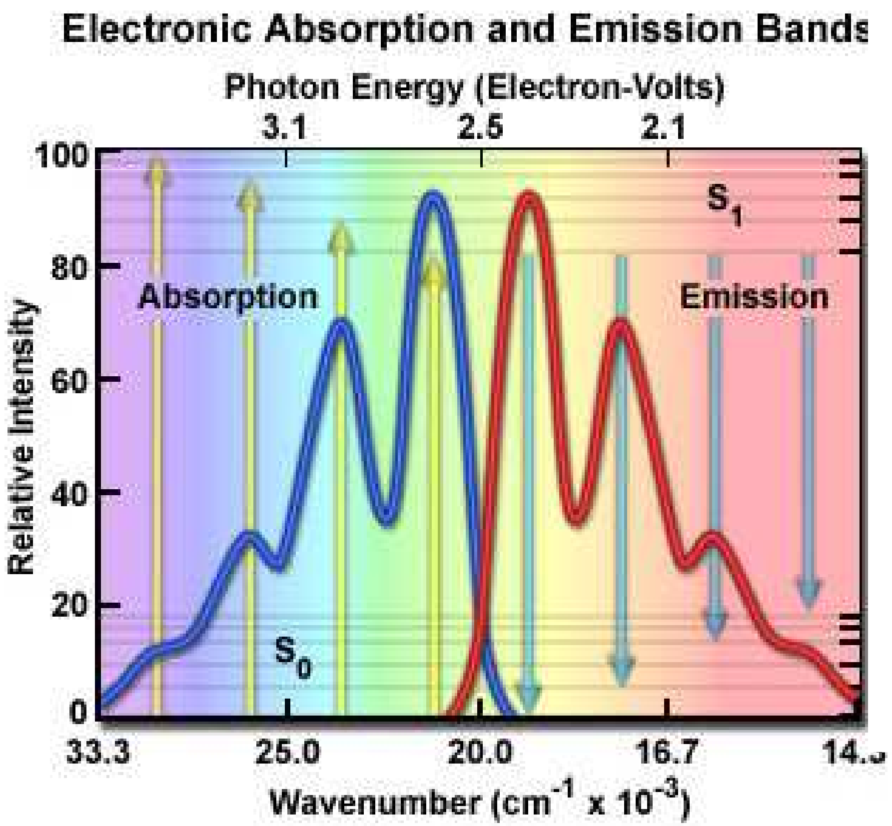
$$E_n = \frac{1}{2}kL_n^2 \qquad L_n^2 = \frac{2E_n}{k}$$

$$E_n = n^2 \frac{kh^2}{16mE_n}$$

$$E_n = n\sqrt{\frac{h^2k}{16m}}$$ **energia igualmente espaçada** $E_n \propto n$

Fluorescência: conceitos importantes

Banda de excitação **Banda de emissão** **Stokes Shift**



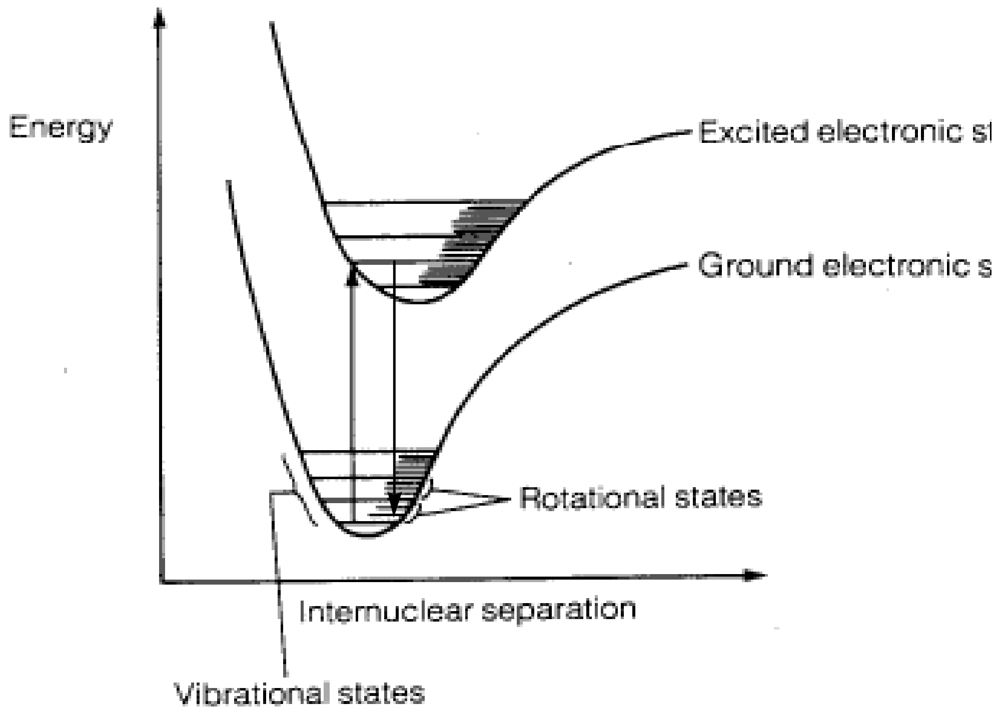
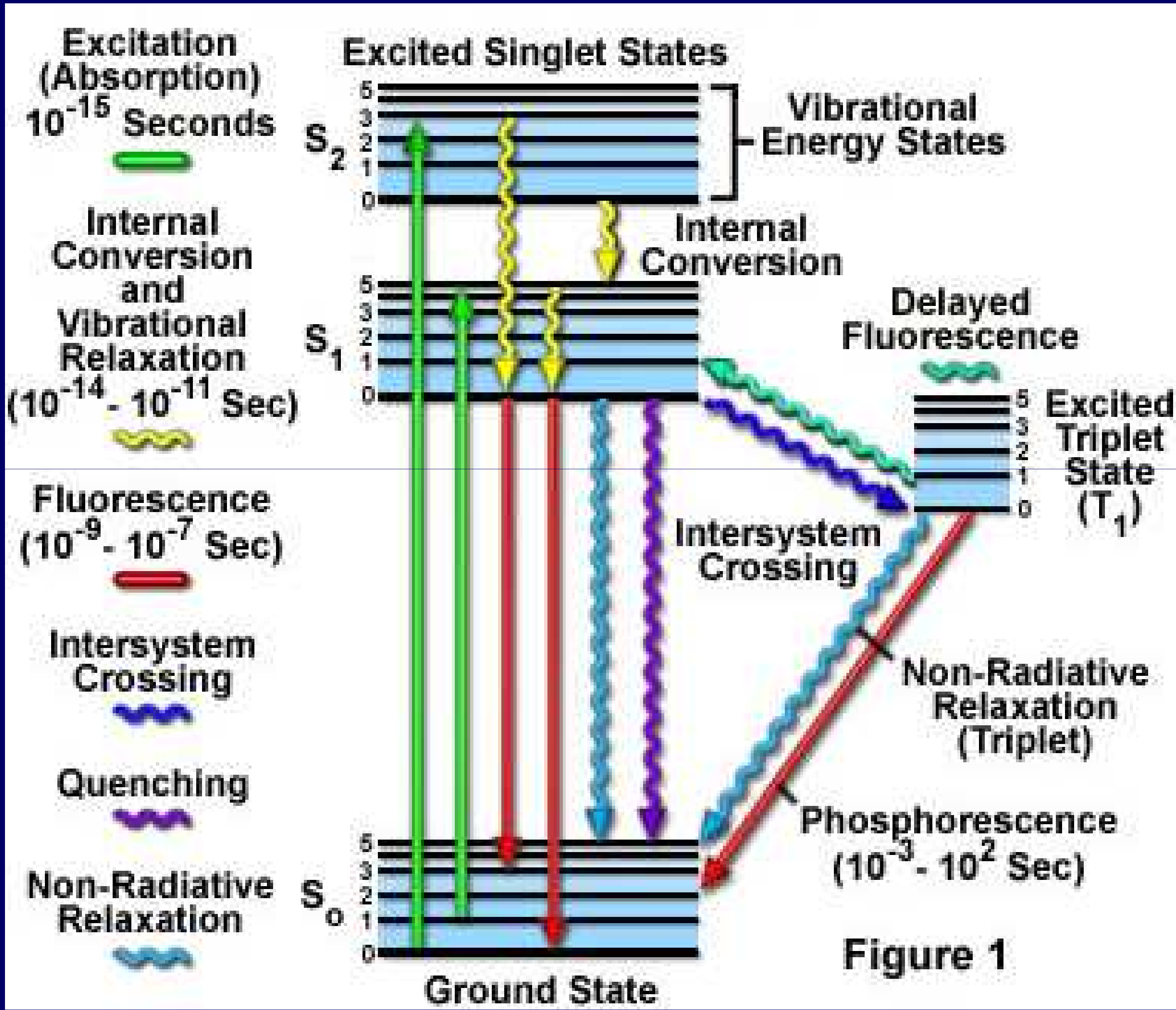


Figure 3

Diagrama de Jablonski



Future is always dark: if it bleeds, it leads

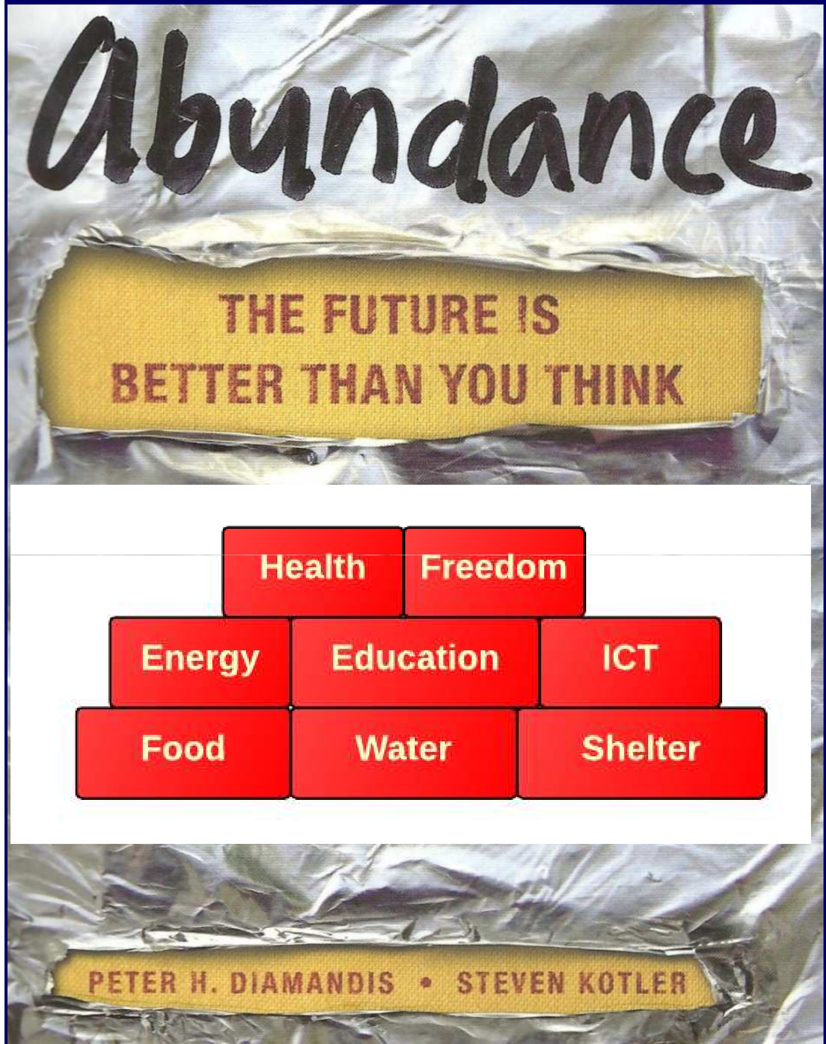
planet of the apes

Mad Max

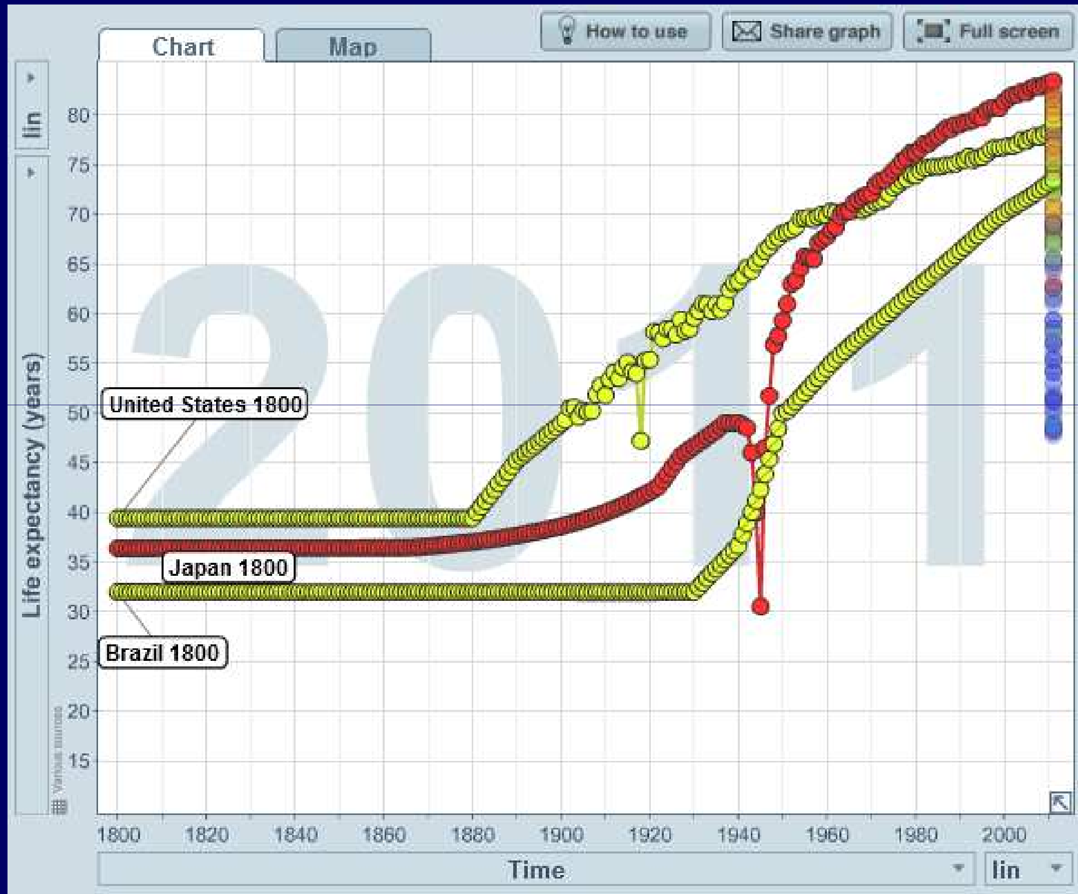
Water world

NY subway

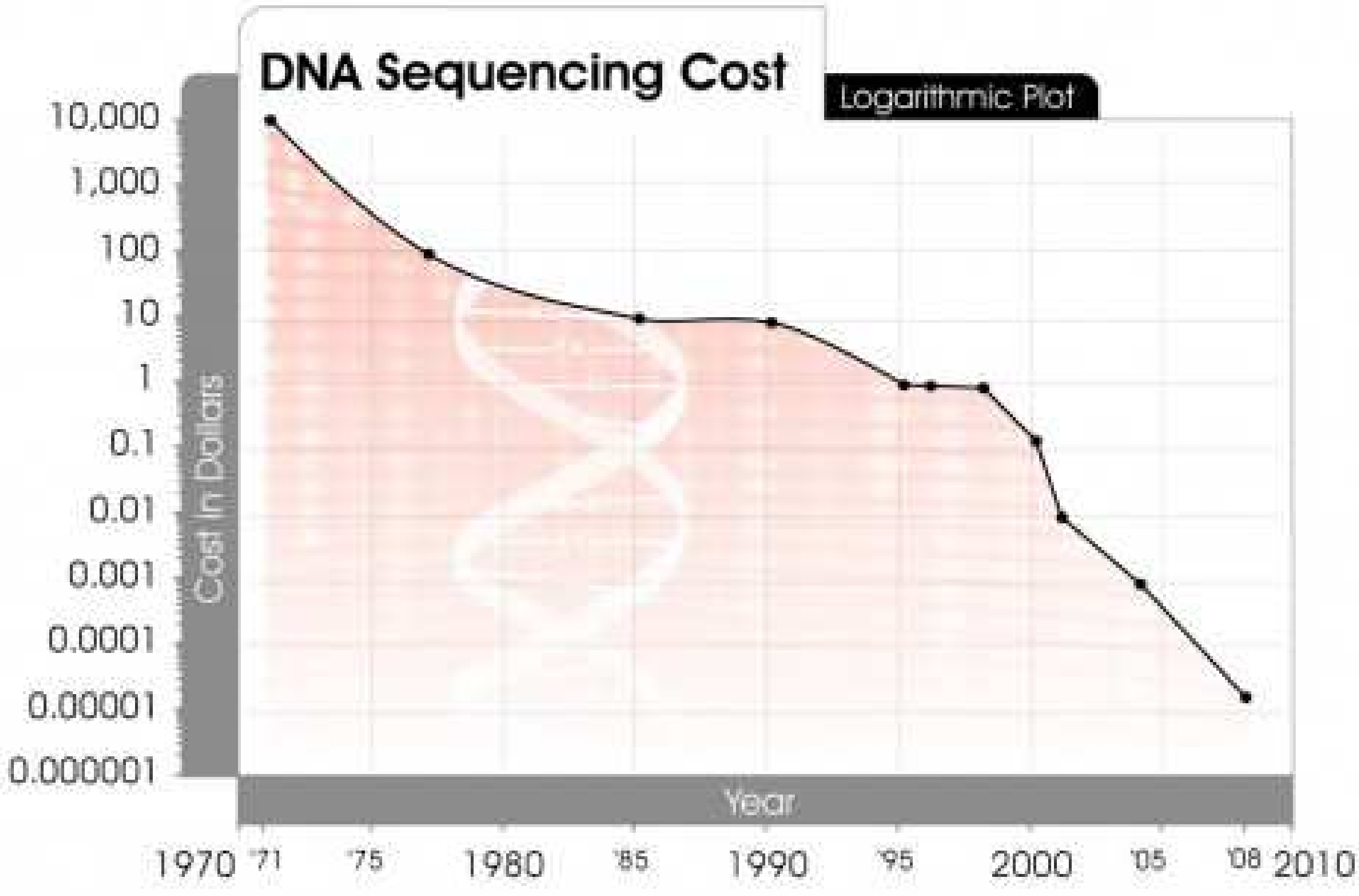
But the future can be the best ever seeing



Life expectancy from 1800 to 2010
www.gapminder.com



Faster than you think:
DNA sequencing cost – similar to microelectronics

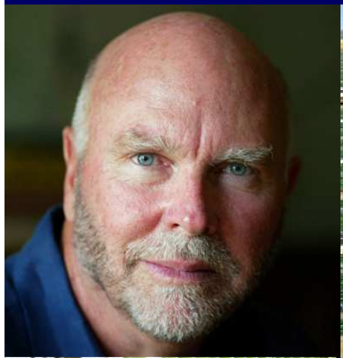


It is coming faster than we think:

Craig Venter and Synthetic Genomics – San Diego

http://www.syntheticgenomics.com/

Scientists Build First Man-Made Genome; Synthetic Life Comes Next



With the new ability to sequence a genome, scientists can begin to custom-design organisms, essentially creating biological robots that can produce from scratch chemicals humans can use. Biofuels like ethanol, for example.

The burger is on the table!

Mark Post – Maastricht - Netherlands

Obrigado pela atenção!

Thanks for the attention