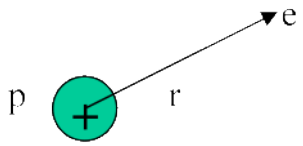
H-Atom



$$V(r) = -\frac{q^2}{4\pi\varepsilon_0 r} \quad \textit{Coulombpotential}$$

$$\hat{H}(r,\theta,\varphi) = -\frac{\hbar^2}{2m}\Delta_{r\theta\varphi} + V(r)$$

$$\Psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\cdot Y_{lm}(\theta,\varphi)$$

mit $Y_{lm}(\theta,\varphi)$ *Kugelwellenfunktionen*

und $R_{nl}(r)$ *Radialwellenfunktion*

q: Elementarladung

μ: reduzierte Masse ($\approx m_e$)

$R_\infty = \frac{q^4\mu}{32\pi^2\varepsilon_0^2\hbar^2}$ Rydberg-Konst.

$$E_n = -\frac{q^4\cdot\mu}{2(4\pi\varepsilon_0)^2\hbar^2}\cdot\frac{1}{n^2}$$

$$n = 1,2,3.....\infty; \quad l = 0,1,...n-1; \quad m = -l,-l+1,....,l-1,l$$

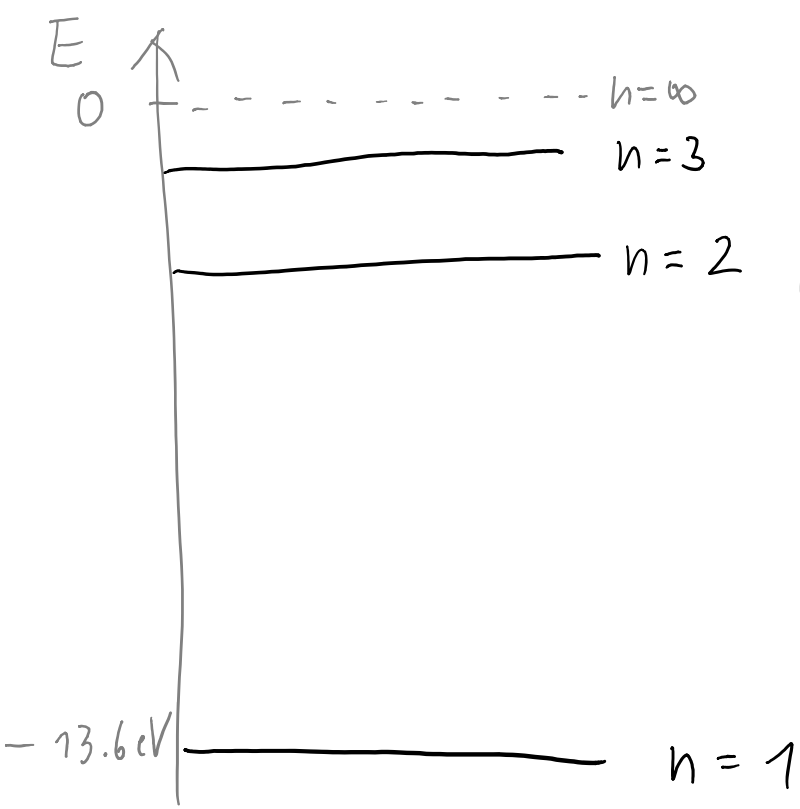
n: Hauptquantenzahl

l: Nebenquantenzahl (Bahndrehimpuls-QZ) {s,p,d,f....}

m: magnetische QZ (z-Komponente des Bahndrehimpulses)

Entartungsgrad (l, m_l)

$\{n, 2l+1\}\ n^2$

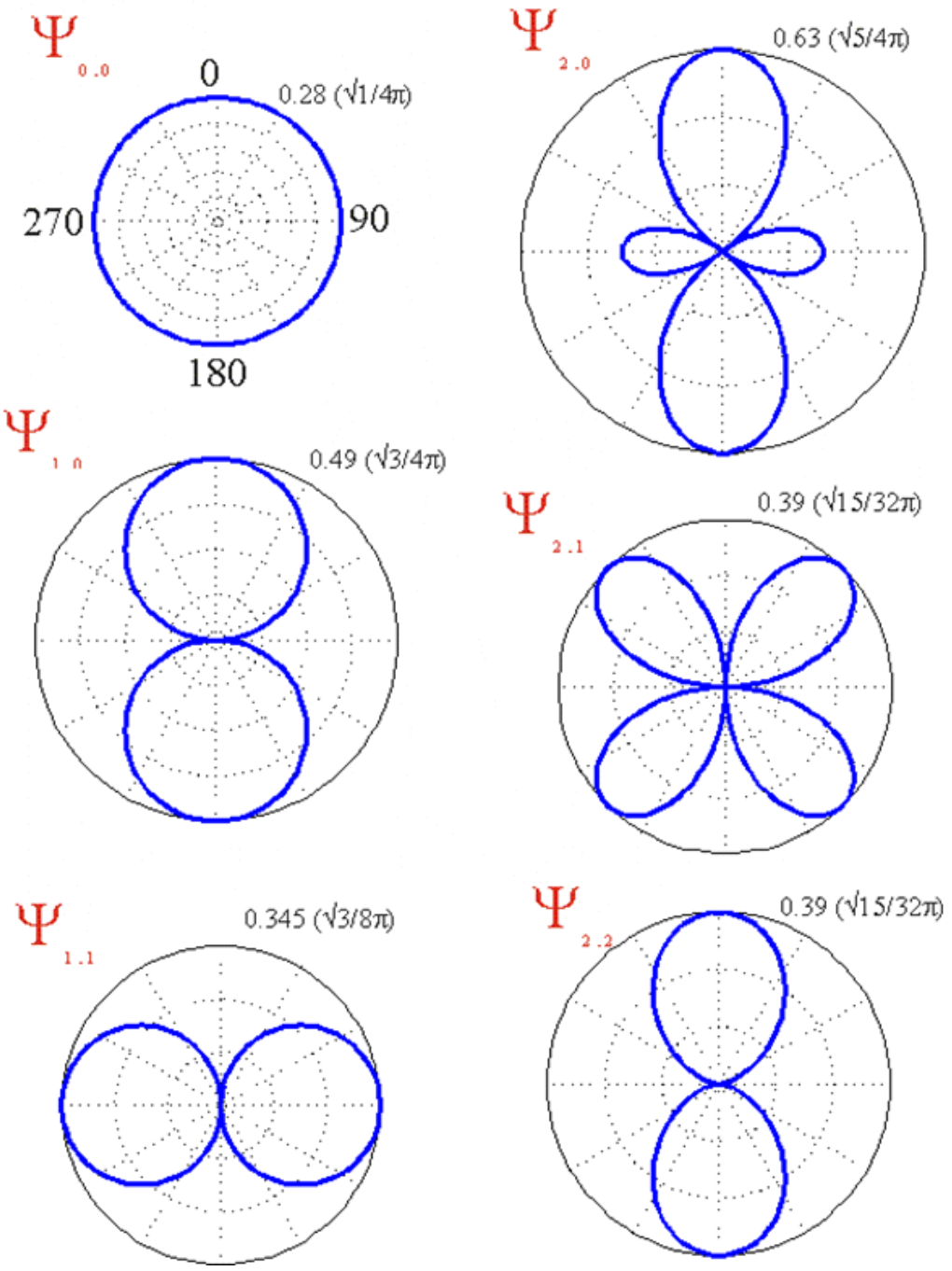


$l=2$ (d) 5 Linien
$l=1$ (p) 3 Linien
$l=0$ (s) 1 Linie
} 9

$l=1$ (p) 3 Linien
$l=0$ (s) 1 Linie
} 4

$l=0$ (s) 1 Linie

Kugelwellenfunktionen $Y_{l,m_l}(\theta,\varphi)$

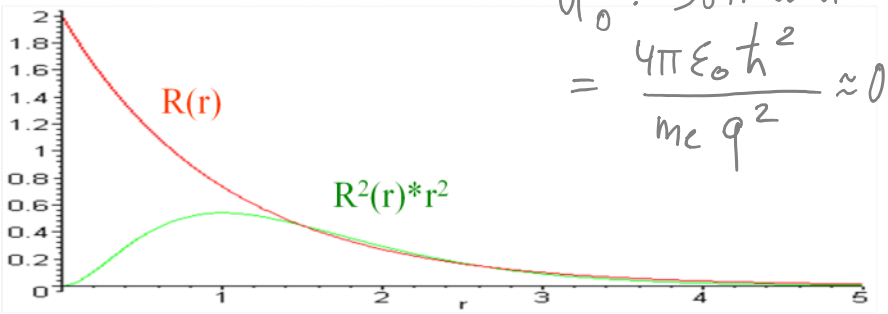


Radialwellenfunktionen

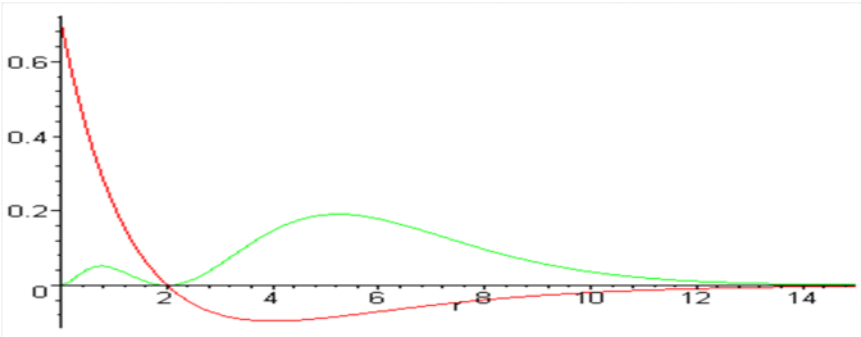
$R_{n,l}(r)$

$R_{10} = 2\,e^{-r/a_0}$

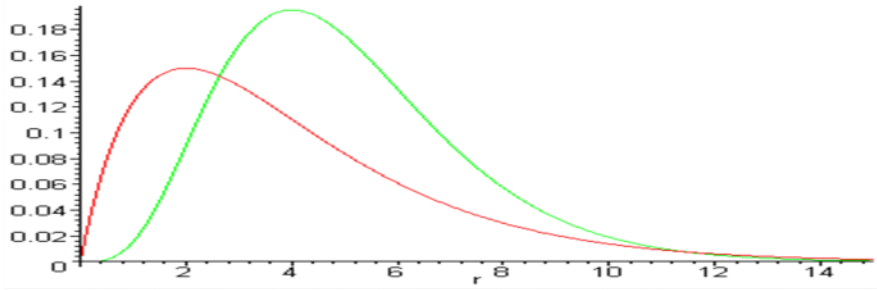
a_0: Bohr'scher Radius $= \frac{4\pi\varepsilon_0\hbar^2}{m_e q^2} \approx 0.5\,\text{Å}$



$R_{20} := \frac{1}{2\sqrt{2}}(2 - r/a_0)\,e^{-r/2a_0}$

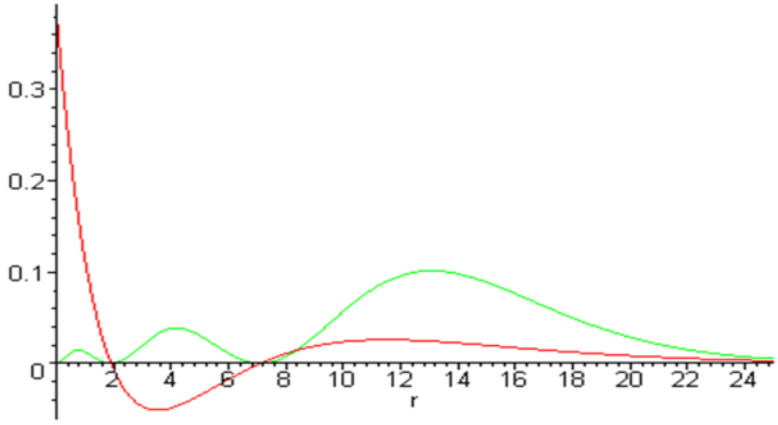


$R_{21} := \frac{1}{2\sqrt{6}}\,r/a_0\,e^{-r/2a_0}$

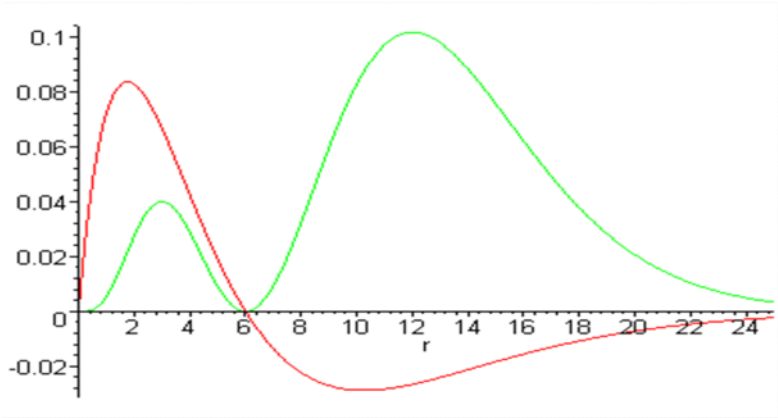


Radialwellenfunktionen

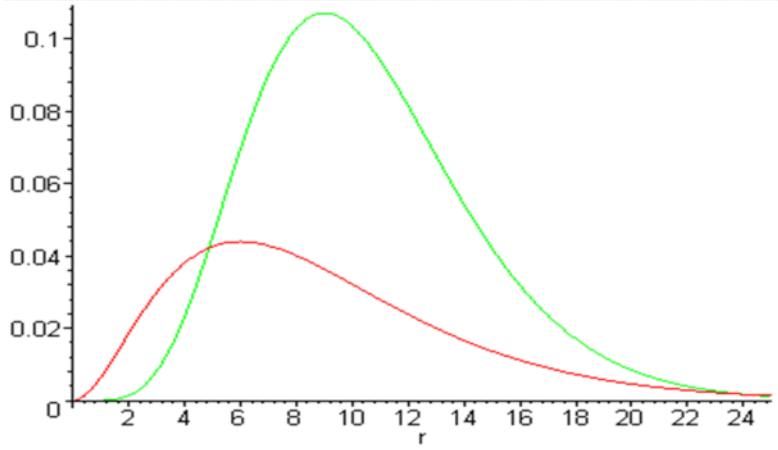
$$R_{30} := \frac{1}{9\sqrt{3}} (6 - 4r/a_0 + (2r/a_0)^2)\, e^{-r/3a_0}$$



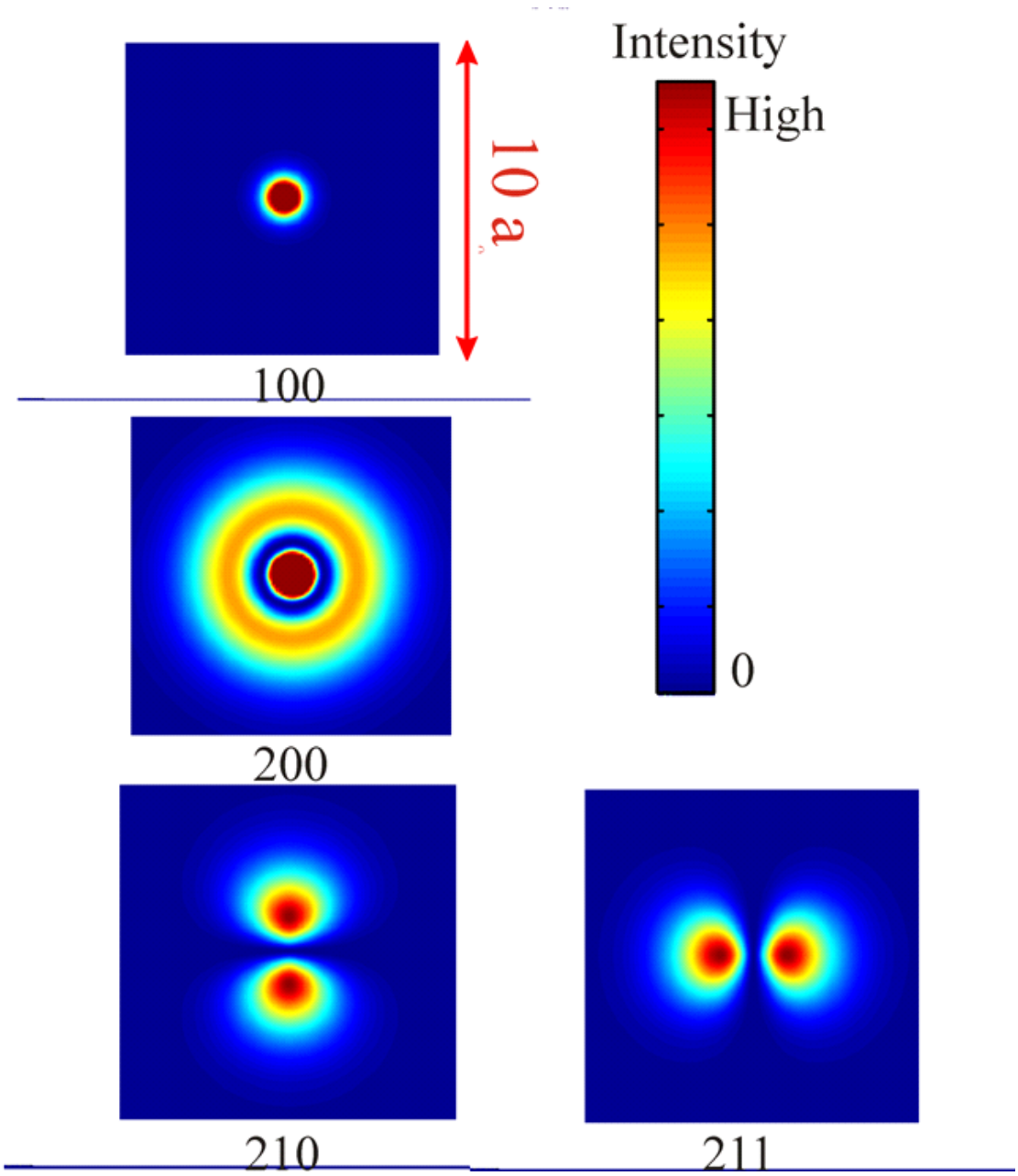
$$R_{31} := \frac{1}{9\sqrt{6}} (4 - 2r/3a_0) 2r/3a_0\, e^{-r/3a_0}$$



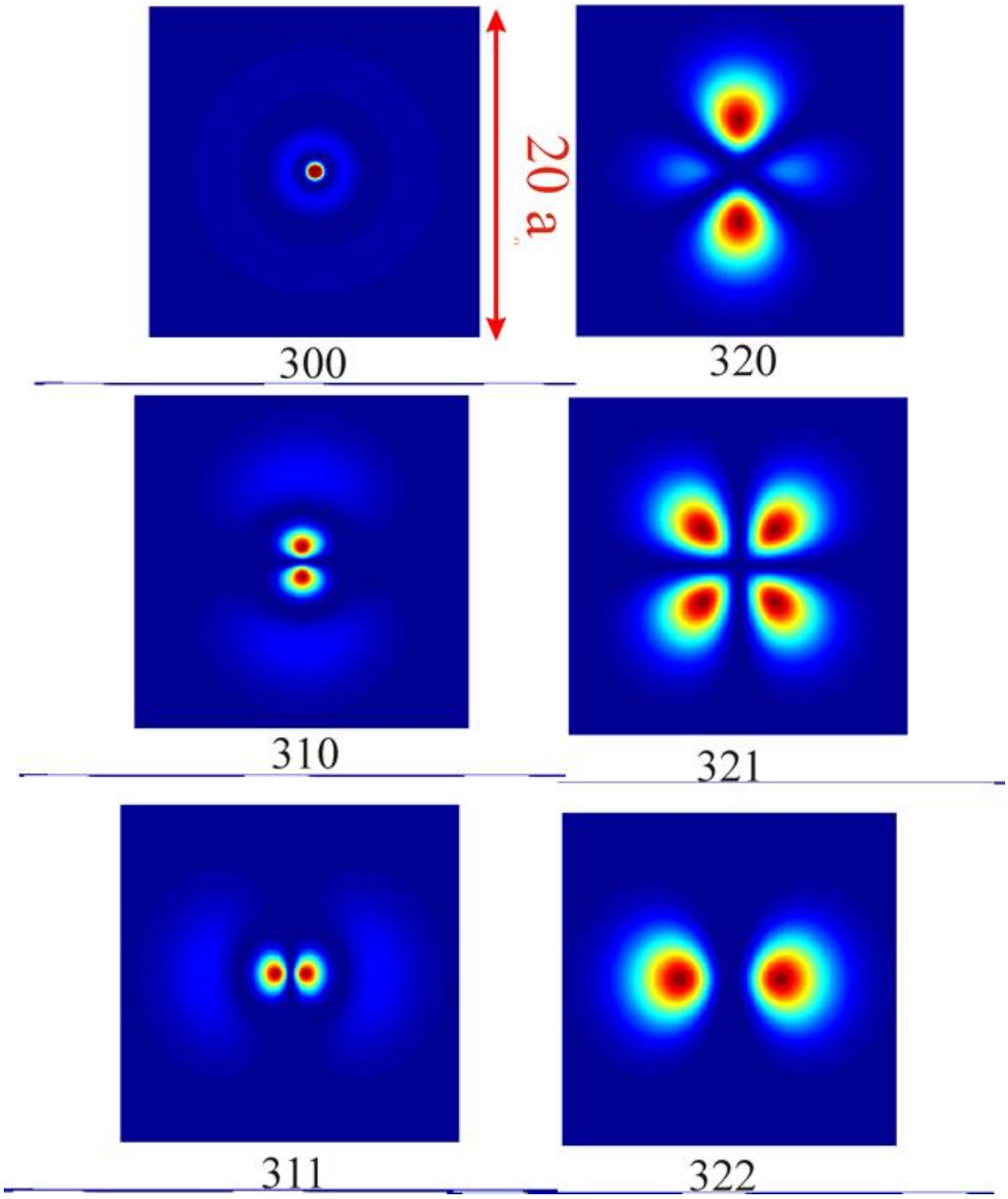
$$R_{32} := \frac{1}{9\sqrt{30}} (2r/3a_0)^2\, e^{-r/3a_0}$$



Gesamtwellenfunktionen



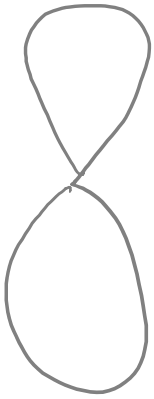
Gesamtwellenfunktionen II



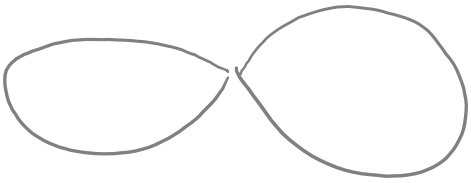
3D Darstellungen

Hülle bei 90% Intensität

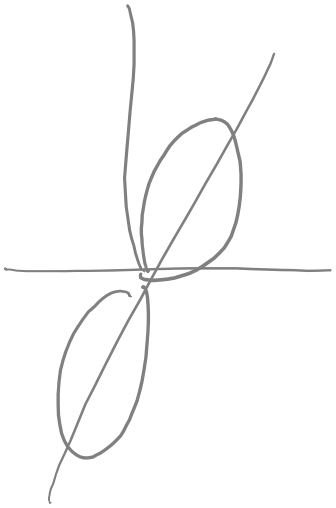
Orbitale und Auswahlregeln



p_z - Orbital $\quad Y_{1,0}$



p_x - Orbital $\quad Y_{1,+1} + Y_{1,-1}$



p_y - Orbital $\quad Y_{1,+1} - Y_{1,-1}$

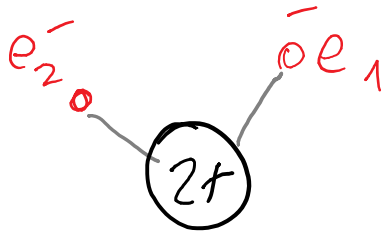
Linearkombination möglich da gleiche E

Auswahlregeln (von Y_{l,m_l}): $\boxed{\Delta l = \pm 1}$

$$\boxed{\Delta m_s = 0}$$

Spinzustand bleibt erhalten

He Atom



$$\Psi = \Psi_{1s}(A) \cdot \Psi_{1s}(B)$$

$$\Psi_{1s}(A) = C \cdot e^{-\frac{Z' r_A}{2 a_0}}$$

$Z' = Z - \sigma$ $\qquad$ σ : Abschirmkonstante

minimiere E bei variablem σ

Pauli-Prinzip

1e $m_s = +1/2$

1e $m_s = -1/2$

$(S = 0)$

$\hookrightarrow$ σ=5/16

E= -77.5 eV (exp. –79 eV)

Variations-Prinzip

Ansatz von Wellenfunktion als Summe von Linearkombination :

$$\Psi = \sum_i c_i \cdot \Psi_i \quad mit \quad \sum_i c_i^* c_i = 1$$

$$E = \int \Psi^* \hat{H} \Psi \, dv$$

Der Grundzustand hat minimale Energie !

$$\frac{\partial E}{\partial c_i} = 0$$

$$\Rightarrow optimiere \quad c_i$$

Termschema

mehrere e^-

$\hat{\vec{L}} = \sum_i \hat{\vec{l}}_i$ Gesamtbahndrehimpuls

$\hat{\vec{S}} = \sum_i \hat{\vec{s}}_i$ Gesamtspin

$\hat{\vec{J}} = \hat{\vec{S}} + \hat{\vec{L}}$ Gesamtdrehimpuls

$$\left.\begin{aligned} \hat{L}_z &= \sum_i \hat{l}_{zi} \\ \hat{S}_z &= \sum_i \hat{s}_{zi} \\ \hat{J}_z &= \hat{S}_z + \hat{L}_z \end{aligned}\right\}$$ entsprechende z-Komponenten

$$\boxed{{}^{2S+1}L_J}$$ $L = S, P, D....$

Termschema

Es gilt: für abgeschlossene Schale: $L=0, S=0, J=0$

Energieentartung für unterschiedliche L ist aufgehoben

Hund'sche Regeln: minimale Energie bei

gleichem n: max. S

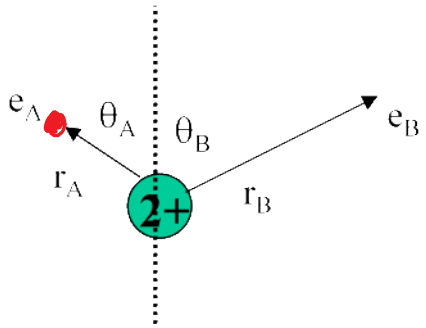
gleichem S: max. L

gleichem L: max. J (falls $< \frac{1}{2}$ gefüllt)

Auswahlregeln: $\Delta L = \pm 1, \Delta S = 0, \Delta J = 0, \pm 1$

(außer $J=0 \to J=0$)

H2+ Molekül



$$\hat{H} \cdot \Psi = E \cdot \Psi$$

mit $\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_{AB}$

$$\hat{H}_A(r_A, \theta_A, \varphi_A) = -\frac{\hbar^2}{2m} \Delta_{r_A \theta_A \varphi_A} + V(r_A)$$

$$\hat{H}_B(r_B, \theta_B, \varphi_B) = -\frac{\hbar^2}{2m} \Delta_{r_B \theta_B \varphi_B} + V(r_B)$$

$$\hat{H}_{AB}(r_A, \theta_A, \varphi_A, r_B, \theta_B, \varphi_B) = \frac{e^2}{r_{AB}}$$

Näherung 1: (ohne $e_A - e_B$ Abstoßung)

$$\hat{H} = \hat{H}_A + \hat{H}_B$$

$$\Psi(r_A, \theta_A, \varphi_A, r_B, \theta_B, \varphi_B) = \Psi_{n_A, l_A, m_A}(r_A, \theta_A, \varphi_A) \cdot \Psi_{n_B, l_B, m_B}(r_B, \theta_B, \varphi_B)$$

$$E = E_{n_A} + E_{n_B}$$

E= -108.8 eV (exp. –79 eV)

Näherung 2: (gleiche Ψ mit $e_A - e_B$ Abstoßung)

$$\Psi(r_A, \theta_A, \varphi_A, r_B, \theta_B, \varphi_B) = \Psi_{n_A, l_A, m_A}(r_A, \theta_A, \varphi_A) \cdot \Psi_{n_B, l_B, m_B}(r_B, \theta_B, \varphi_B)$$

$$\langle E \rangle = E_{n_A} + E_{n_B} + \iint \Psi^* \hat{H}_{AB} \Psi \, dv_A \, dv_B$$

E= -71.2 eV (exp. –79 eV)

H2 Molekül

Ansatz für die Wellenfunktion des Elektrons:

$$\Phi = c_A \Phi_{1s}(A) + c_B \Phi_{1s}(B)$$

$$\frac{\partial E}{\partial c_A} = 0 \qquad \frac{\partial E}{\partial c_A} = 0$$

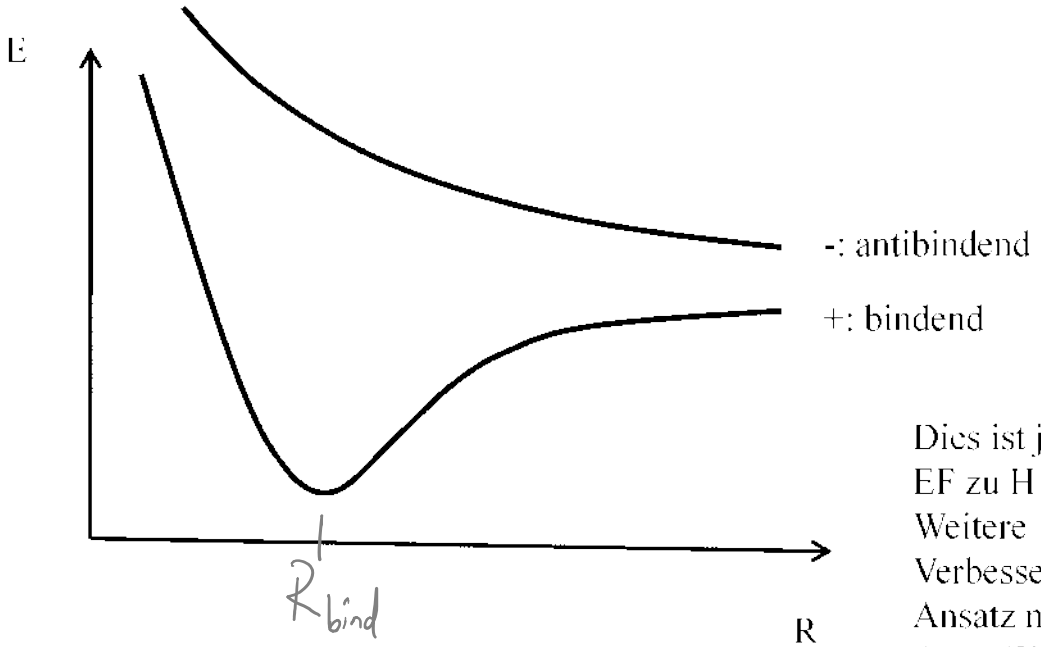
$$\Rightarrow E_+ = \frac{\alpha \pm \beta}{1 \pm S} \qquad (+ : c_B = +c_A \quad - : c_B = -c_A)$$

$$\alpha = \int \Phi^*_{1s}(A)\hat{H}\Phi_{1s}(A)dv = \int \Phi^*_{1s}(B)\hat{H}\Phi_{1s}(B)dv \quad \text{Coulomb-Integral}$$

$$\beta = \int \Phi^*_{1s}(A)\hat{H}\Phi_{1s}(B)dv = \int \Phi^*_{1s}(B)\hat{H}\Phi_{1s}(A)dv \quad \text{Bindungs-Integral}$$

$$S = \int \Phi^*_{1s}(A)\Phi_{1s}(B)dv = \int \Phi^*_{1s}(B)\Phi_{1s}(A)dv \quad \text{Überlapp-Integral}$$

Die Integrale S, α,β, können numerisch oder analytisch mit elliptisch Koordinaten für feste Werte vom Kernabstand R berechnet werden



Dies ist jedoch nicht EF zu H ! Weitere Verbesserung durch Ansatz mit mehr H-Atom Ψ's

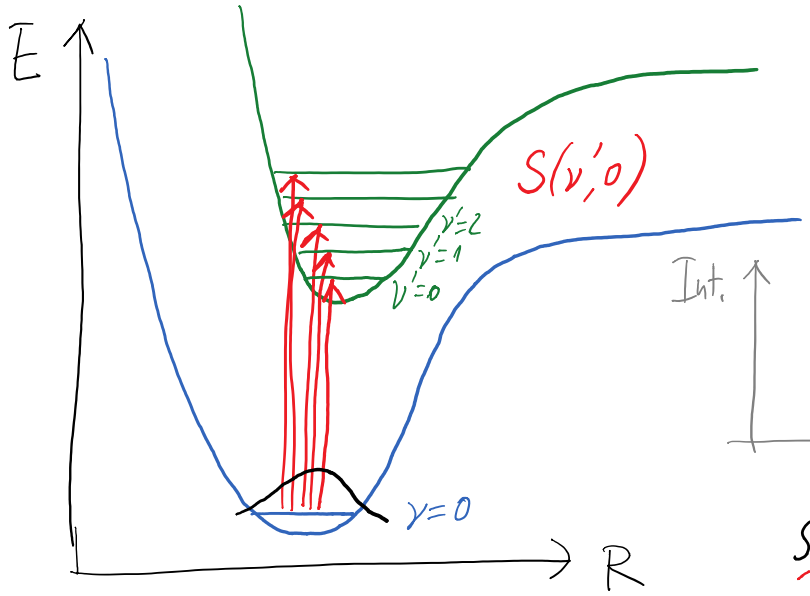
Symmetrische Ortswellenfkt durch

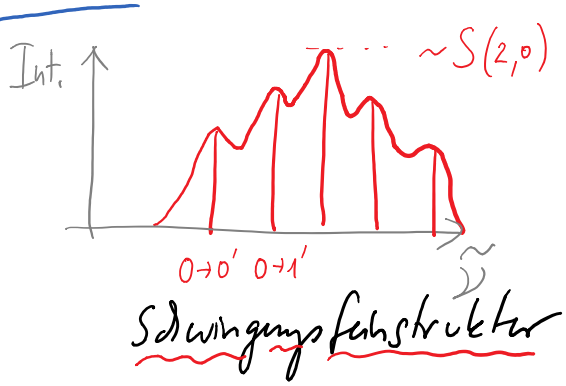
$$\phi(1,2) = \frac{1}{\sqrt{2}}\{\phi(1,A)\phi(2,B) + \phi(1,B)\phi(2,A)\}$$

Antisymmetrische Spinwellenfkt $\chi(1,2) = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$

Frank-Condon Prinzip

Elektronische Anregung + Vibrations-Anregung

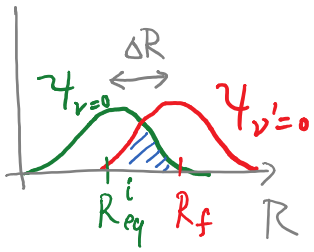




$$\mu_{fi} = \underbrace{\mu_{fi}^{e}}_{\text{elektron. Übergangs-Matrixelement}} \cdot \underbrace{\int_R \psi_{\nu'}^{*}(R)\,\psi_{\nu}(R)\,dv_R}_{\text{Frank-Condon Faktor } S_{\nu\nu'}}$$

(Überlapp der Vibr. ψs)

Einfaches Beispiel:

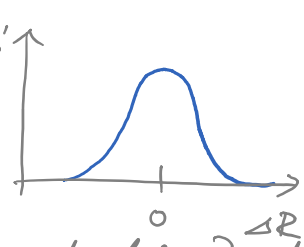


falls $\boxed{k = k'}$ gleiche Kraftkonstante

$$\psi_{\nu=0} = \sqrt{\frac{\alpha}{\pi}}\, e^{-\frac{\alpha^2 x^2}{2}} \qquad \alpha = \sqrt[4]{\frac{\mu k}{\hbar^2}}$$

$$\psi_{\nu'=0} = \sqrt{\frac{\alpha}{\pi}}\, e^{-\frac{\alpha^2 (x-\Delta R)^2}{4}}$$

$$\left(\int_{-\infty}^{+\infty} e^{-ax^2}\,dx = \sqrt{\frac{\pi}{a}}\right) \qquad S_{00'} = e^{-\alpha^2 \left(\frac{\Delta R}{2}\right)^2}$$



falls $\boxed{k = k' \;\&\; R = R'}$ gleiche Kraftkonstante und gleicher Bindungsabstand

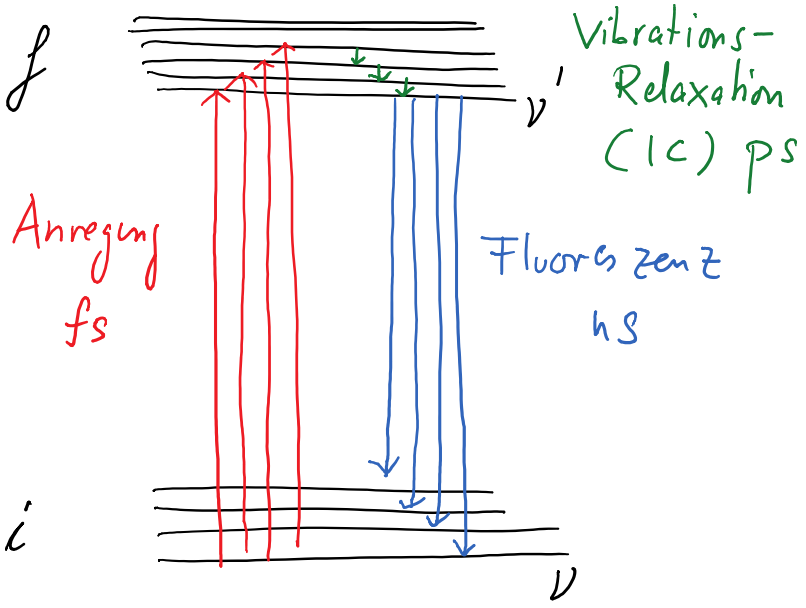
nur $\boxed{\nu = 0 \rightarrow \nu' = 0}$

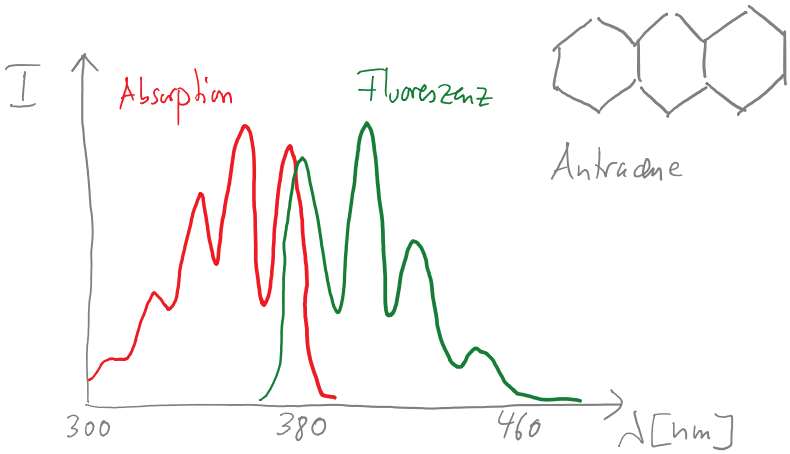
alle anderen verboten, da $\int \psi_{\nu'}^{*} \psi_{\nu}\, dv_R = 0$ falls $\nu' \neq \nu$

im allgemeinen jedoch $k > k'$ und $R < R'$

↳ Integrale $\neq 0$ Intensität durch $S_{\nu\nu'}$ (μ_{fi}^{e})

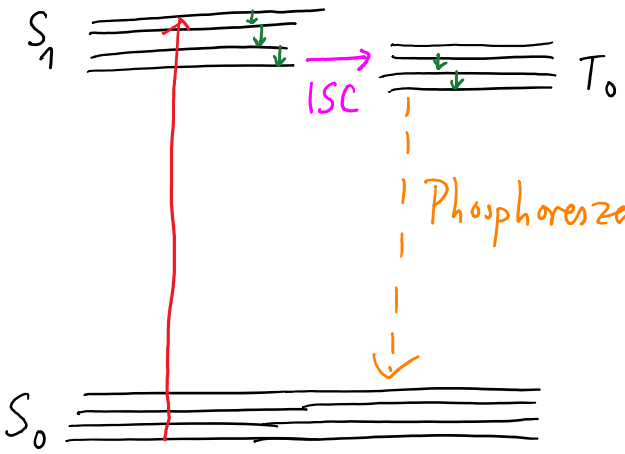
Jablonski Diagramm





Anthracene

N	λ_{abs} [nm]
1	255
2	315
3	380
4	480
5	580



Phosphoreszenz ($\Delta S \neq 0$) verbotener Übergang
langsam (ms – h)