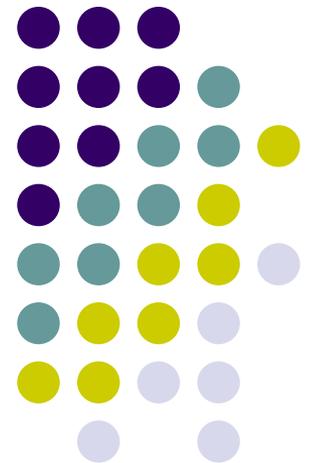
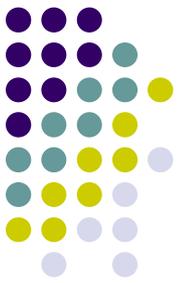


# Energien in der Quantenmechanik

Rotation, Vibration, Feinstruktur



Eliza Târcoveanu



# Einleitung

Born-Oppenheimer:  $E_{tot} = E_{rot} + E_{vib} + E_{el}$

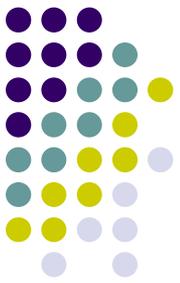
$$h\nu_{rot} \ll h\nu_{vib} \ll h\nu_{el}$$

$\nu_{rot}$  im fernen IR oder Mikrowellen

$\nu_{vib}$  im IR (um 1000 cm<sup>-1</sup>)

$\nu_{el}$  im sichtbaren / UV

Übergangswahrscheinlichkeit:  $\langle m | \mu | n \rangle = \int_{-\infty}^{+\infty} \psi_m^* \mu \psi_n d\tau$



# 1) Energieniveaus der Rotation

## das starre Rotator

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}, J_a = I_a \omega_a$$

- wobei  $I$  – Trägheitsmoment
- $J$  – Drehimpuls

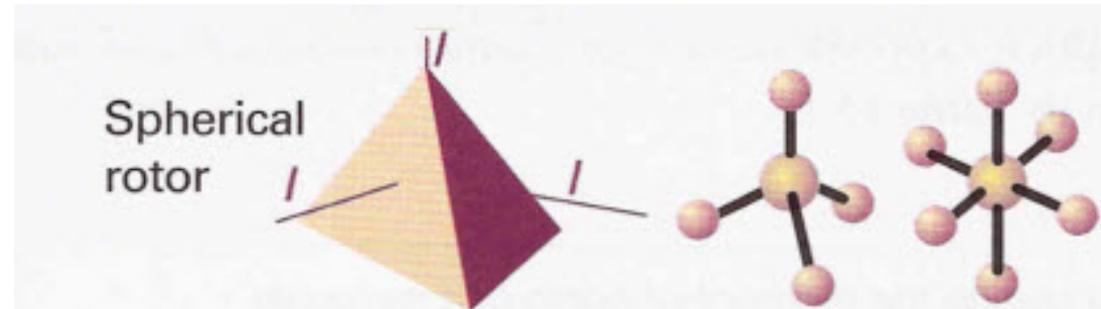
(a) sphärische Kreisel

$$J^2 = J_a^2 + J_b^2 + J_c^2$$

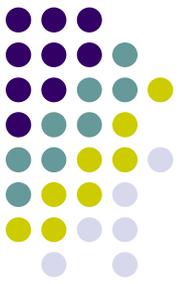
$$J^2 \rightarrow J(J+1)\hbar^2, J = 0,1,2,\dots$$

$$E_J = hcBJ(J+1), B = \frac{\hbar}{4\pi cI}$$

$$F(J) - F(J-1) = 2BJ$$



- wobei  $B$  – Rotationskonstante
- Abstand benachbarter Rotationsterme



(b) symmetrische Kreisel

$$E = \frac{J_b^2 + J_c^2}{2I_{\perp}} + \frac{J_a^2}{2I_{\parallel}}$$

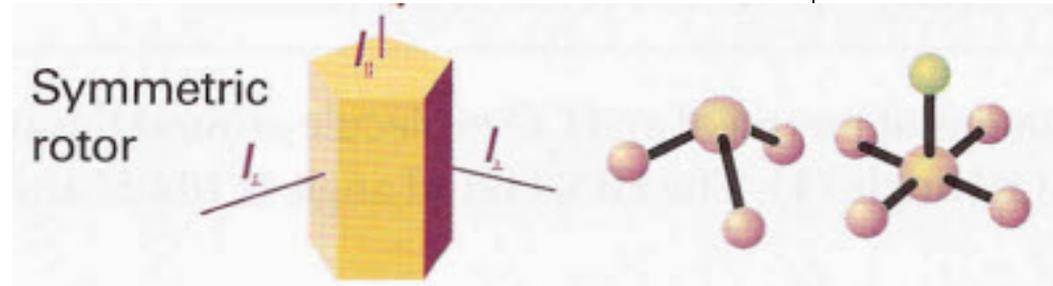
$$E = \frac{J^2}{2I} + \left( \frac{1}{2I_{\parallel}} - \frac{1}{2I_{\perp}} \right) J_a^2$$

$$K = 0, +/_{-}1, \dots, +/_{-}J$$

$$J_a^2 = K^2 \hbar^2$$

$$F(J, K) = BJ(J + 1) + (A - B)K^2$$

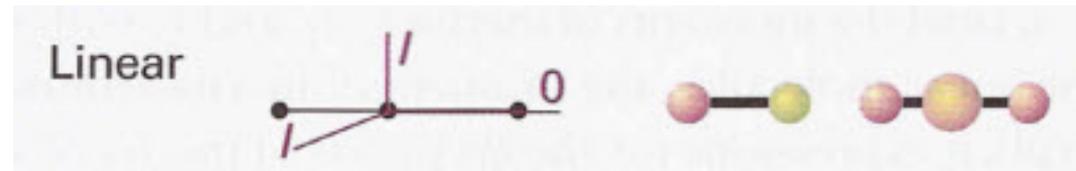
$$A = \frac{\hbar}{4\pi c I_{\parallel}}, B = \frac{\hbar}{4\pi c I_{\perp}}$$

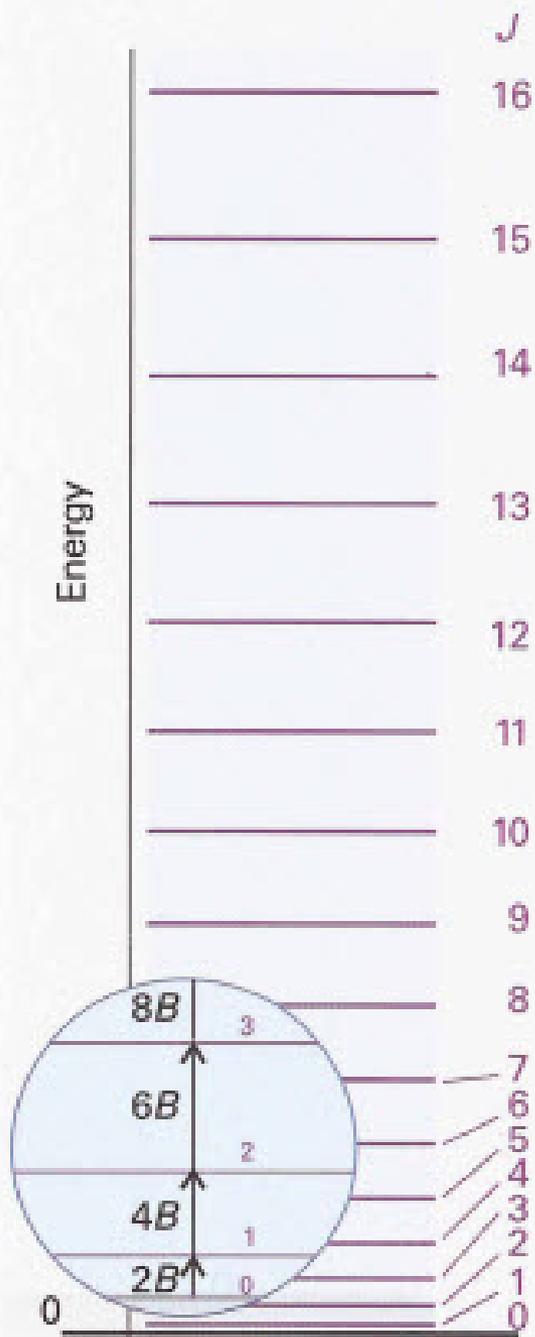


- K – Quantenzahlkomponente des Drehimpulses bezüglich einer Molekülachse

(c) lineare Kreisel

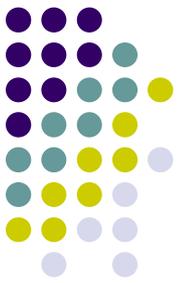
$$F(J) = BJ(J + 1), J = 0, 1, 2, \dots$$





- *Rotationsniveaus* eines linearen od. sphärischen Kreisels mit zunehmende Abstand zw. benachbarten Energieniveaus
- jedes Energieniveau ist  $(2J+1)$  entartet

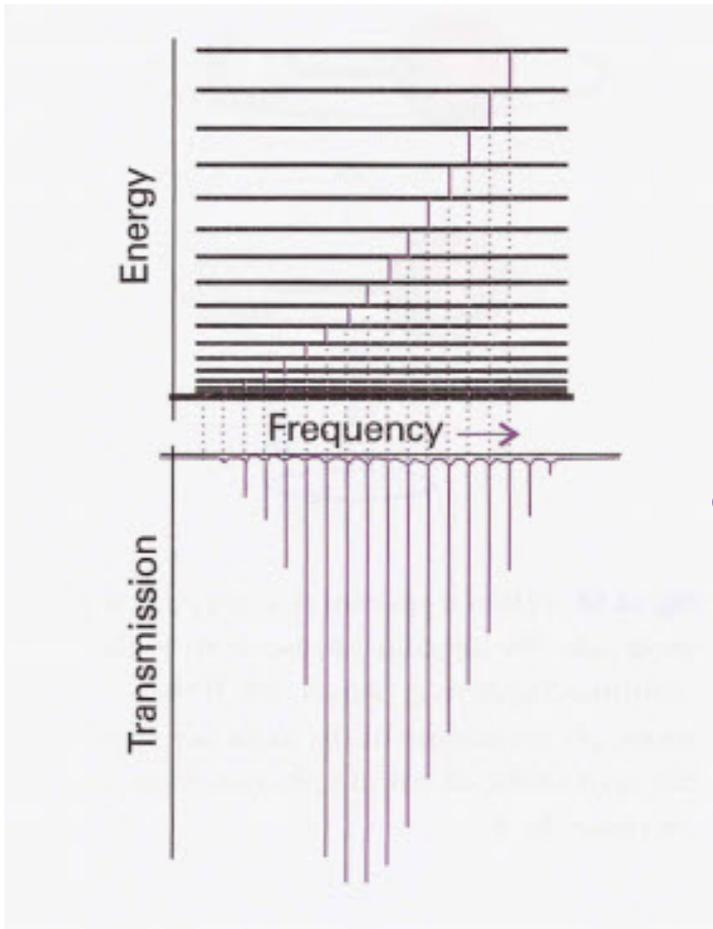




- im Fall des starren, bzw. nicht-starren Rotators, wobei  $D_J$  – Zentrifugaldehnungskt.

$$\tilde{\nu}(J = 1 \leftarrow J) = 2B(J + 1), J = 0, 1, 2, \dots$$

$$\tilde{\nu}(J = 1 \leftarrow J) = 2B(J + 1) - 4D_J (J + 1)^3, J = 0, 1, 2, \dots$$



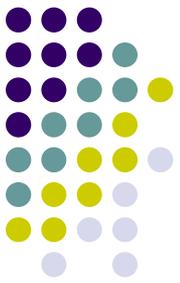
- Besetzungszahl:

$$N_J \propto N g_J e^{-E_J / kT}$$

$$J_{\max} \approx \sqrt{\left(\frac{kT}{2hcB}\right)} - \frac{1}{2}$$

- $g$  - Entartungsgrad des Niveaus  $J$

## 2) Schwingung – Energieniveaus eines harmonischen Oszillators



$$V = \frac{1}{2} kx^2 \quad -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2 \psi = E\psi$$

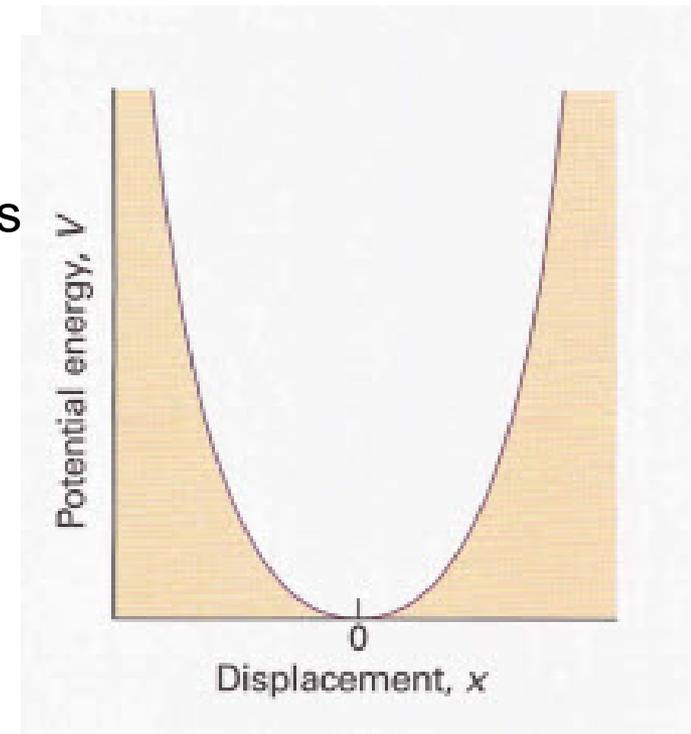
$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \quad \bullet \text{ erlaubte Energieniveaus}$$

$$\omega = \left(\frac{k}{m}\right)^{1/2}$$

$$v = 0, 1, 2, \dots$$

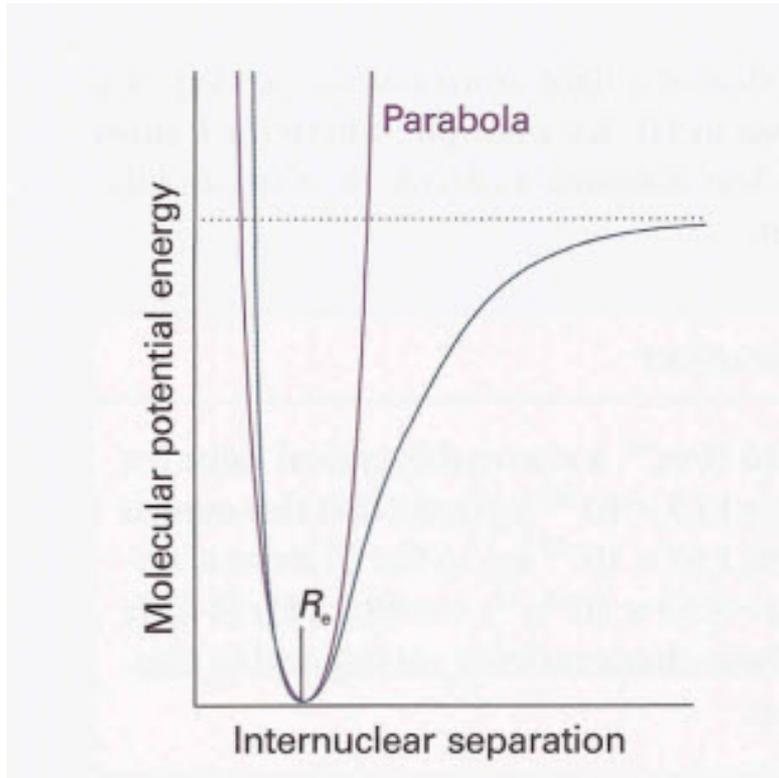
$$E_{v+1} - E_v = \hbar\omega$$

$$E_0 = \frac{1}{2} \hbar\omega \quad \bullet \text{ Nullpunktenergie}$$



# Vibration

## *harmonisch*



- erlaubte Schwingungsniveaus:

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\omega, \omega = \sqrt{\frac{k}{m_{eff}}}, \nu = 0, 1, 2, \dots$$

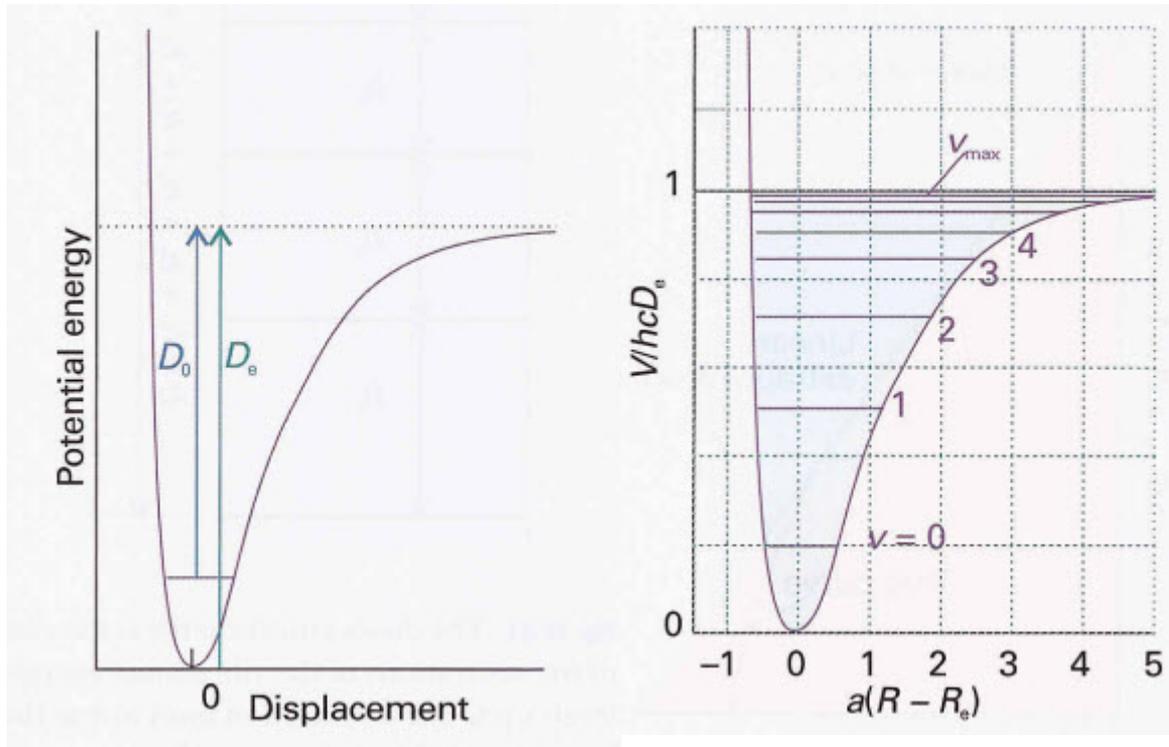
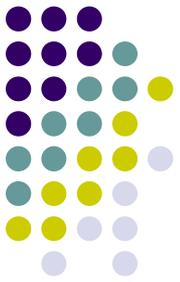
- Schwingungsterme:

$$G(\nu) = \left(\nu + \frac{1}{2}\right)\tilde{\nu}, \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\left(\frac{k}{m_{eff}}\right)}$$

$$E(\nu) = hcG(\nu)$$

# Vibration

## anharmonisch



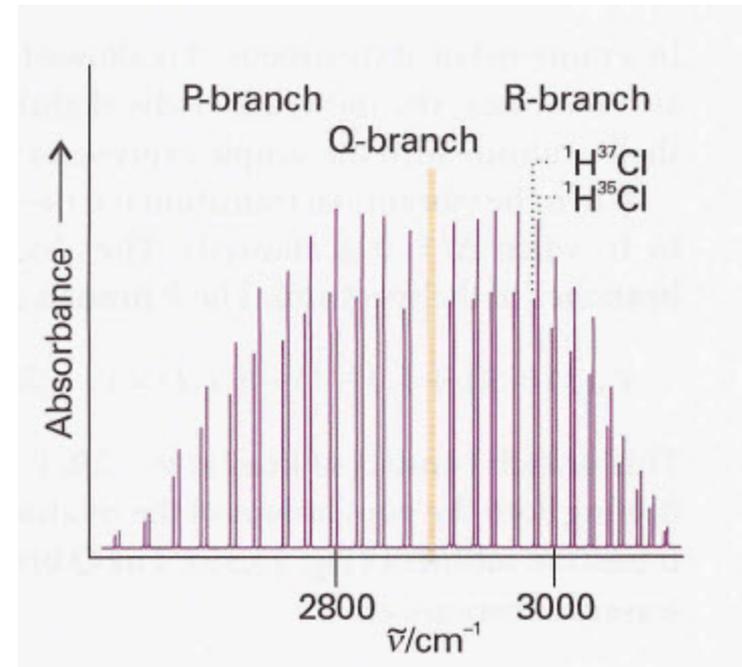
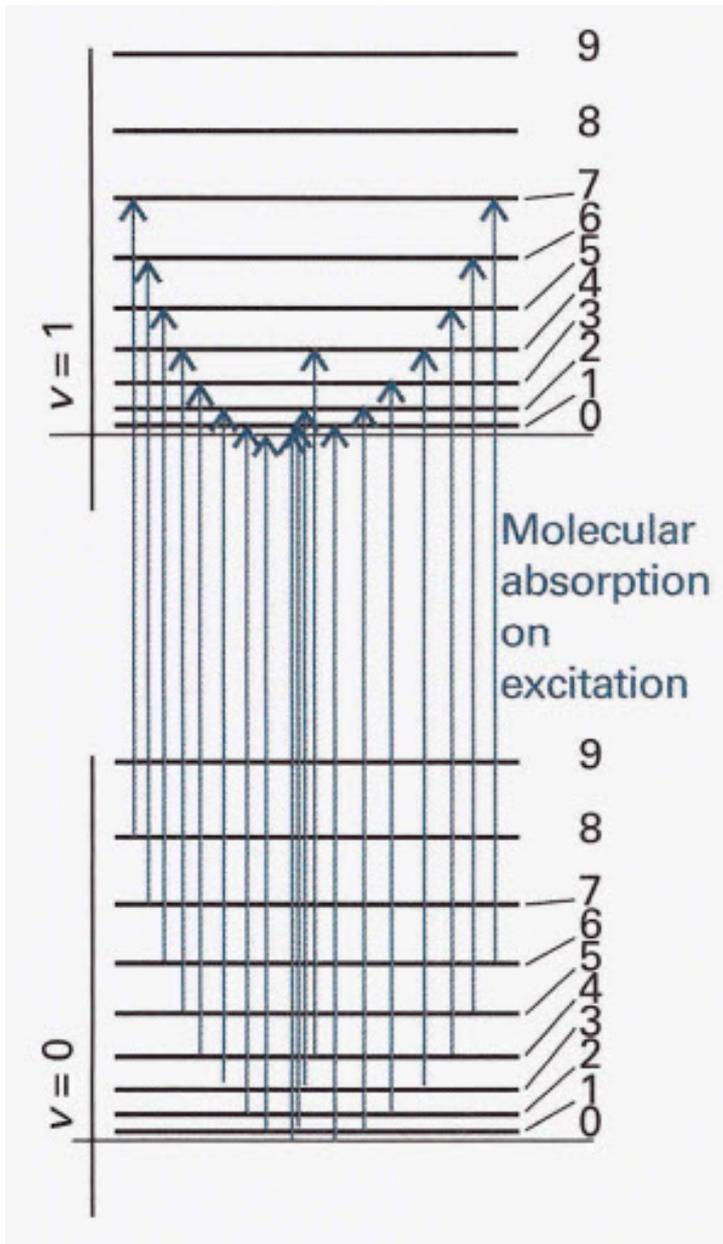
- Morse-Potential:

$$V = hcD_e \{1 - e^{-a(R-R_e)}\}^2, a = \sqrt{\left(\frac{m_{eff} \omega^2}{2hcD_e}\right)}$$

$$G(v) = \left(v + \frac{1}{2}\right)\tilde{\nu} - \left(v + \frac{1}{2}\right)^2 x_e \tilde{\nu}, x_e = \frac{a^2 \hbar}{2m_{eff} \omega} = \frac{\tilde{\nu}}{4D_e}$$

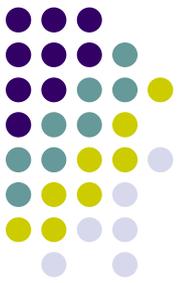


# Rotationsschwingung

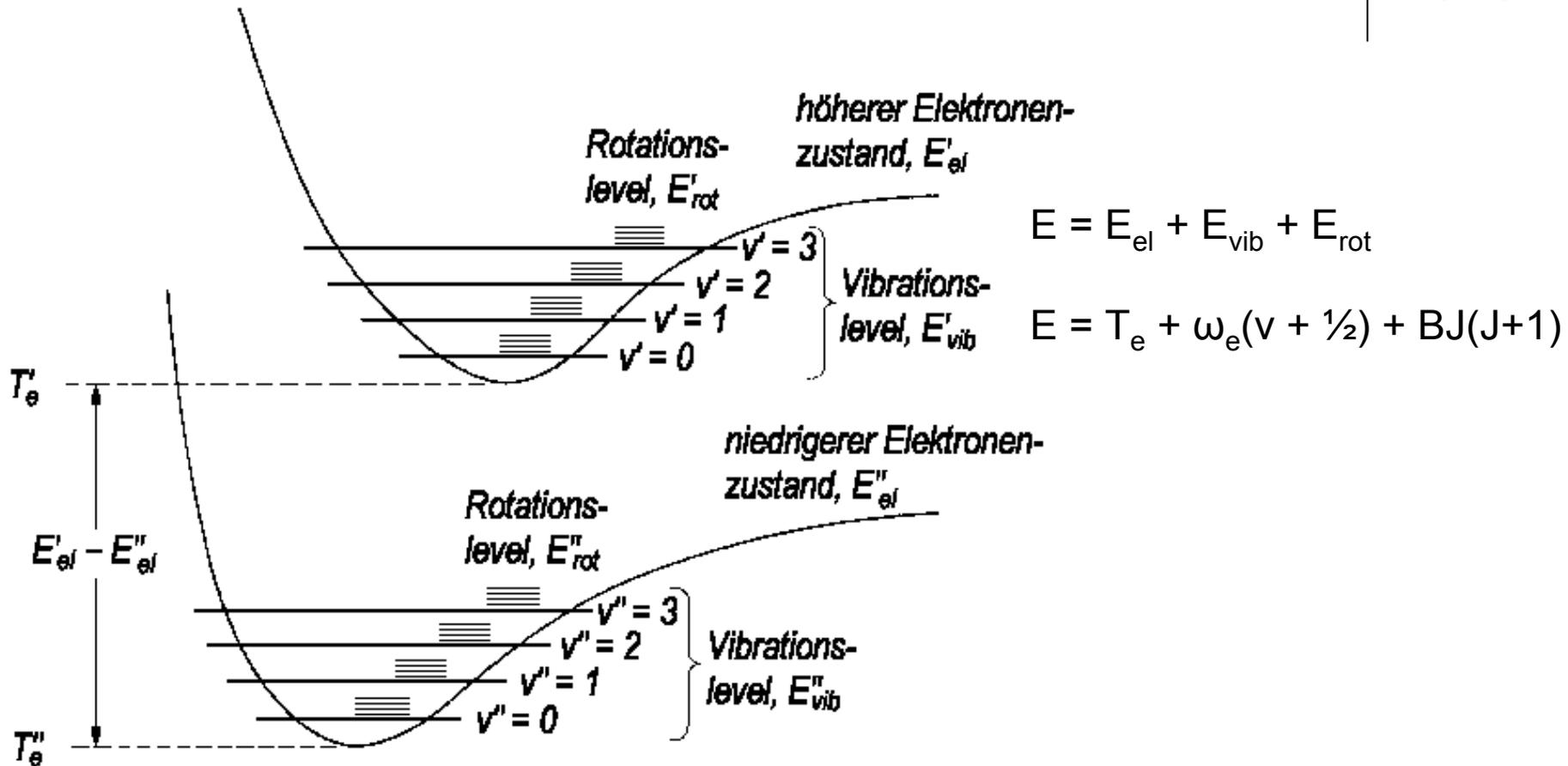


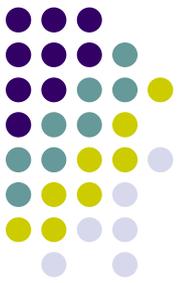
$$S(\nu, J) = G(\nu) + F(J)$$

$$S(\nu, J) = \left(\nu + \frac{1}{2}\right)\tilde{\nu} + BJ(J + 1)$$

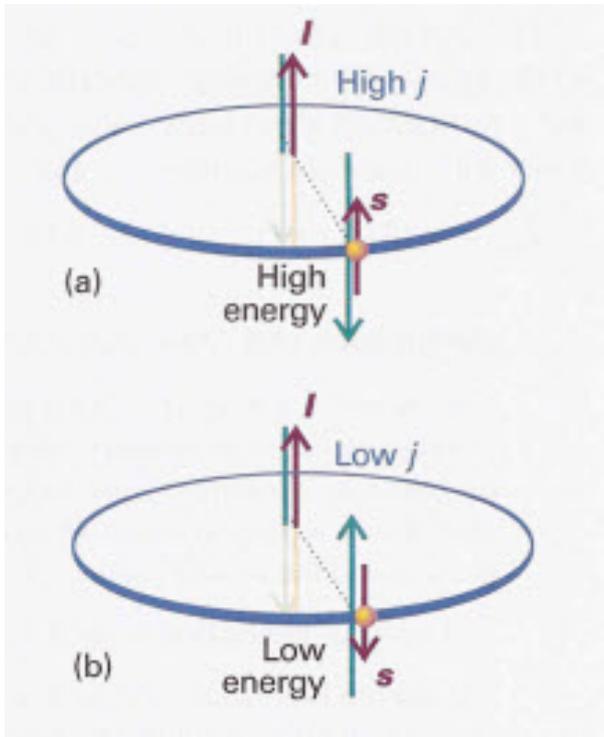


# 3) Elektronische Übergänge

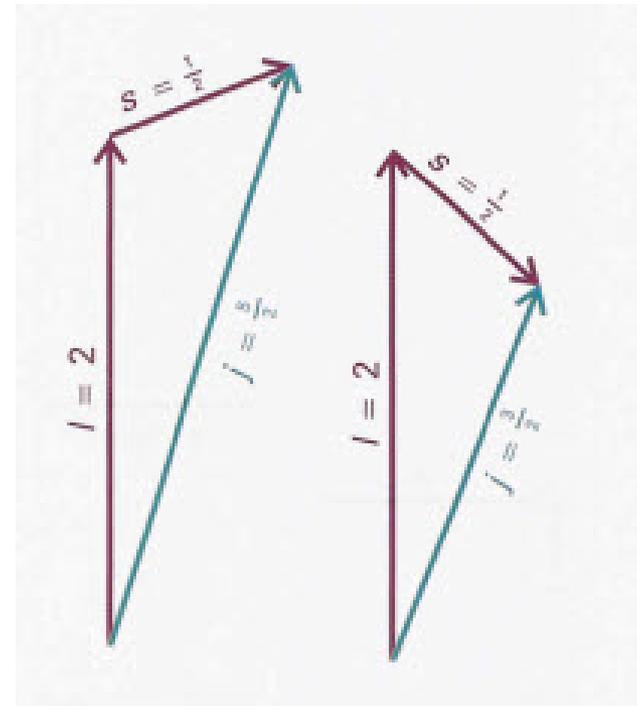




# SB-Kopplung

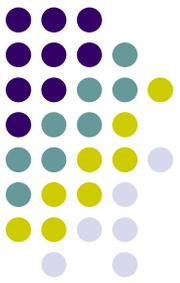


Orientierung der Drehimpulse



SB-Kopplung für ein d-Elektron

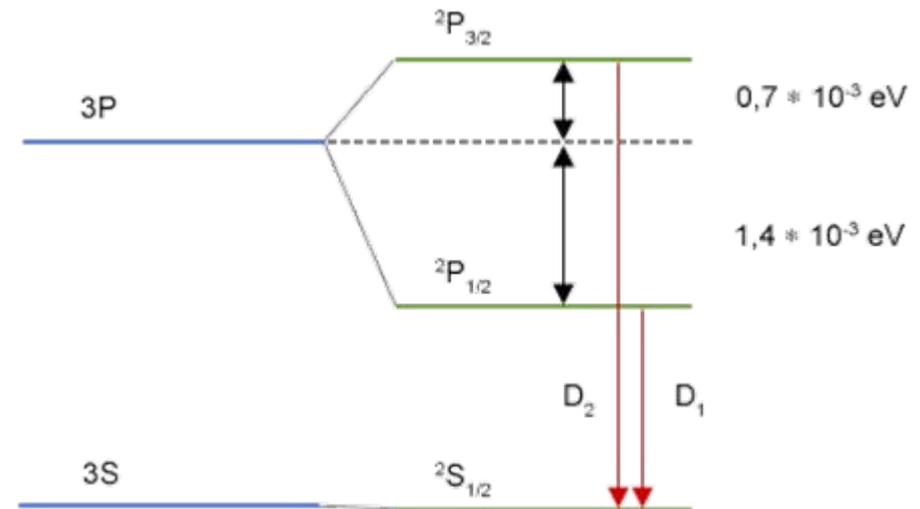
# Rotationsfeinstruktur der Elektron-Schwingungs-Übergänge



Die LS-Kopplung (Russell-Saunders)

$$\Delta E_{SB} = \frac{A}{2} \{ J(J+1) - L(L-1) - S(S-1) \}$$

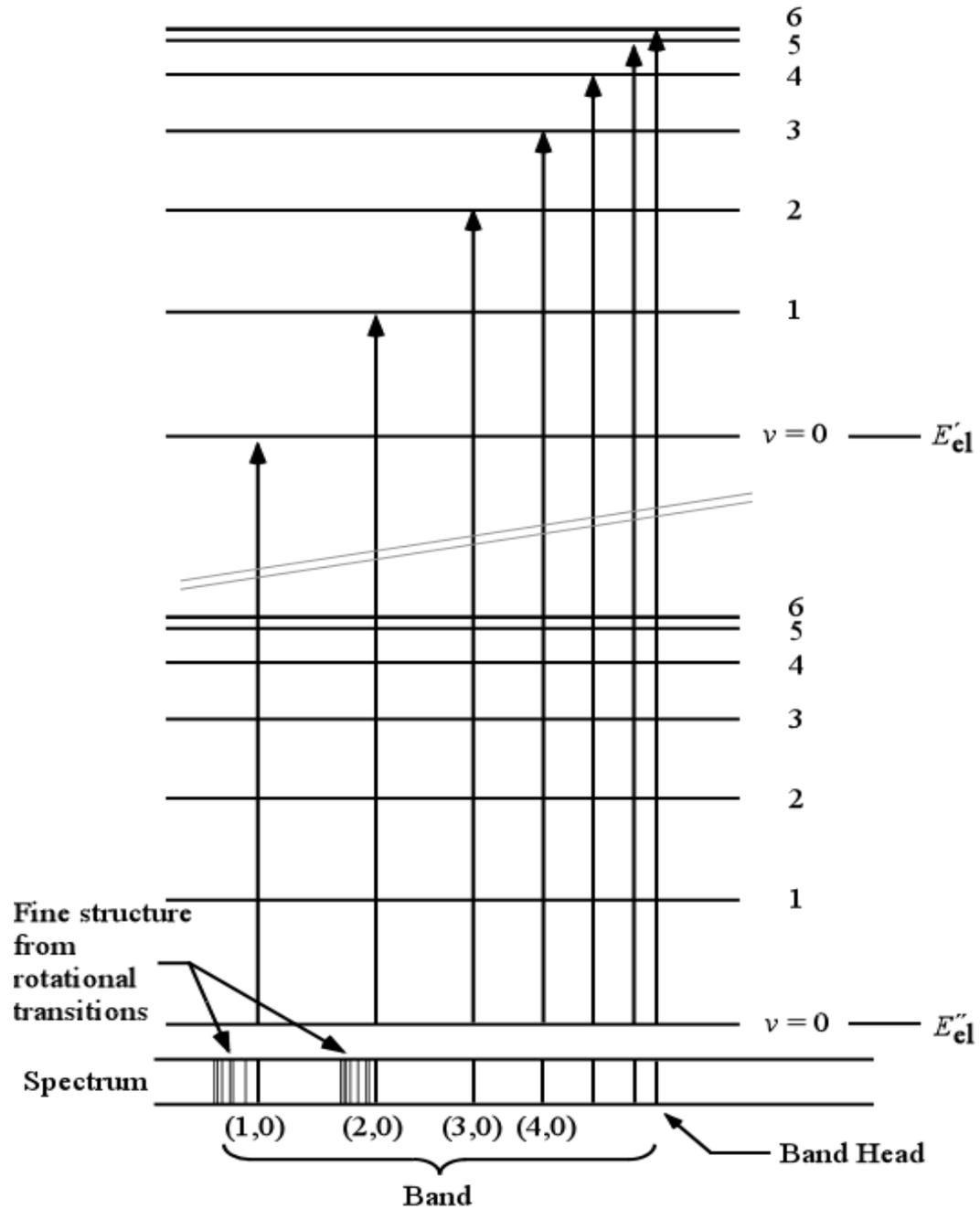
$$\Delta E_{J+1} - \Delta E_J = A(J+1)$$



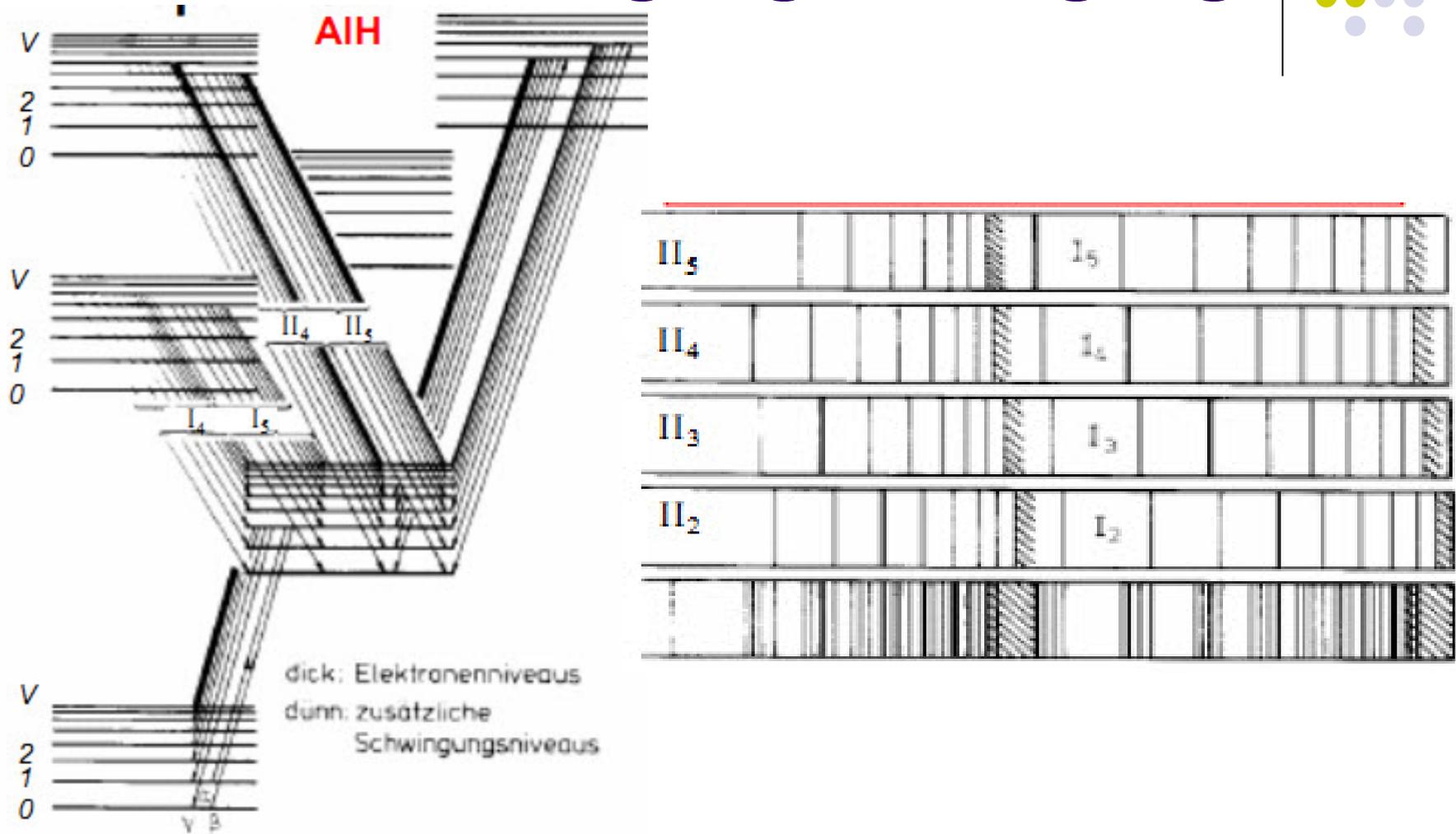
$(2S+1)$ -Entartung, falls  $L \geq S$

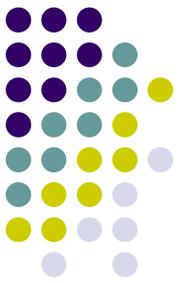
Doppellinie D des Natriums

# ELECTRONIC-VIBRATION-ROTATION SPECTRUM OF A DIATOMIC MOLECULE



# Rotationsfeinstruktur der Elektron-Schwingungs-Übergänge





# Literaturquellen

- Atkins, *Physikalische Chemie*, 4. Auflage; Kap. 13 & 14;
- C. N. Banwell, E. M. McCash, *Molekülspektroskopie*, 1994, Oldenburg-Verlag;
- PC3/PC4-Skripte, *Prof. Dr. Gericke*;
- H. Haken, H.C. Wolf, *Molekülphysik und Quantenchemie*, 2. Auflage, Springer;
- [http://www.tu-chemnitz.de/physik/OHL/vl\\_sc/VL08.pdf](http://www.tu-chemnitz.de/physik/OHL/vl_sc/VL08.pdf)