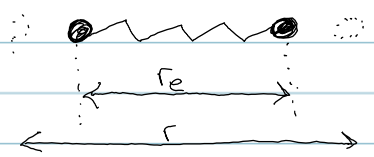
Vorlesung 28.11.2013

Google Molwave – 3D Normal Modes

3. Harmonischer Oszillator

z.B. O_2

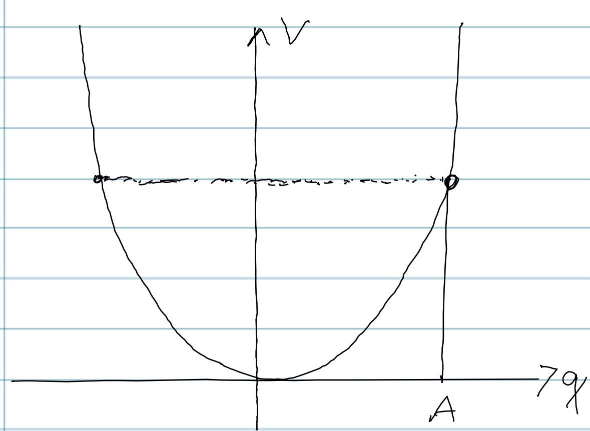


klass. Behandl.

$q = r - r_e$ Auslenkung

$F = -kq$ k = Kraftkonst.

$V = \frac{1}{2} k q^2$



$E_{ges} = \frac{1}{2} k A^2$

$$\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}}$$

q.m. Behandl.

Hamiltonfunktion: $H = \frac{p^2}{2\mu} + \frac{1}{2} k q^2$

– " – operator: $\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2} + \frac{1}{2} k q^2$

Schrödingergl.

$$\boxed{-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dq^2} + \frac{1}{2} k q^2 \psi = E\psi} \quad \Big| \cdot \left(-\frac{2\mu}{\hbar^2}\right)$$

$$\frac{d^2\psi}{dq^2} + \underbrace{\frac{2\mu E}{\hbar^2}}_{\alpha}\psi - \underbrace{\frac{1}{2}k\frac{2\mu}{\hbar^2}}_{\beta^2} q^2\psi = 0$$

$$\frac{d^2\psi}{dq^2} + (\alpha - \beta^2 q^2)\psi = 0$$

<u>Substitution:</u> $\xi = \sqrt{\beta}\cdot q$

$$\frac{d^2\psi}{d\xi^2}\beta + \left(\alpha - \frac{\beta^2}{\beta}\xi^2\right)\psi = 0$$

$$\boxed{\frac{d^2\psi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = 0} \quad (1)$$

für $\xi^2 \gg \frac{\alpha}{\beta}$: $\frac{d^2\psi'}{d\xi^2} = \xi^2\psi'$

Lsg: $\psi' = c\cdot e^{-\xi^2/2}$

allg. Lsg. für (1): $\psi = n(\xi)\cdot e^{-\xi^2/2}$ (2)

(2) in (1) einsetzen:

$$\frac{d^2 n}{d\xi^2} - 2\xi\frac{dn}{d\xi} + \left(\frac{\alpha}{\beta} - 1\right)n = 0$$

$\hat{=}$ Hermitescher DGL für $\left(\frac{\alpha}{\beta} - 1\right) = 2v$ $\quad v = 0, 1, 2, 3 \ldots$

<u>Energieeigenwerte:</u> $\left(\frac{\alpha}{\beta} - 1\right) = 2v$

$$\frac{\alpha}{\beta} = 2v + 1$$

$$\frac{\alpha}{2\beta} = v + \frac{1}{2}$$

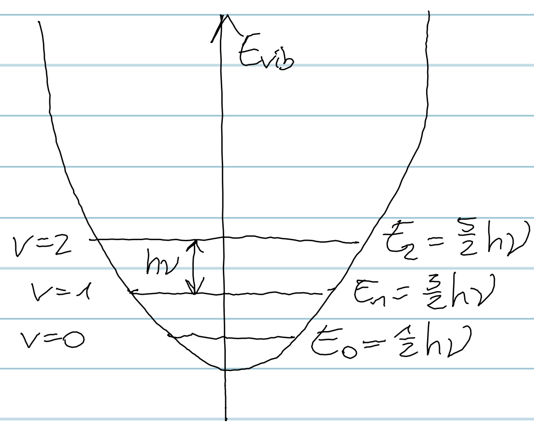
$$\frac{2\mu E \cancel{\hbar}}{\hbar^{\cancel{2}}\cdot 2\sqrt{k\cdot\mu}} = v + \frac{1}{2}$$

$$\frac{E}{\underbrace{h\cdot\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}}_{\nu}} = \frac{E}{\hbar\sqrt{\frac{k}{\mu}}} = v + \frac{1}{2}$$

$\hookrightarrow \boxed{E_{vib} = (v + \frac{1}{2}) h\nu}$ $\quad v = 0, 1, 2, 3, \ldots$

v = Schwingungsquantenzahl

$v = 0: \; E_0 = \frac{1}{2} h\nu$



Wellenfunktionen

aus (1) bzw. hermitesche DGL

$\hookrightarrow$ hermitesche Polynome $H_v(\xi)$ v-ten Grades

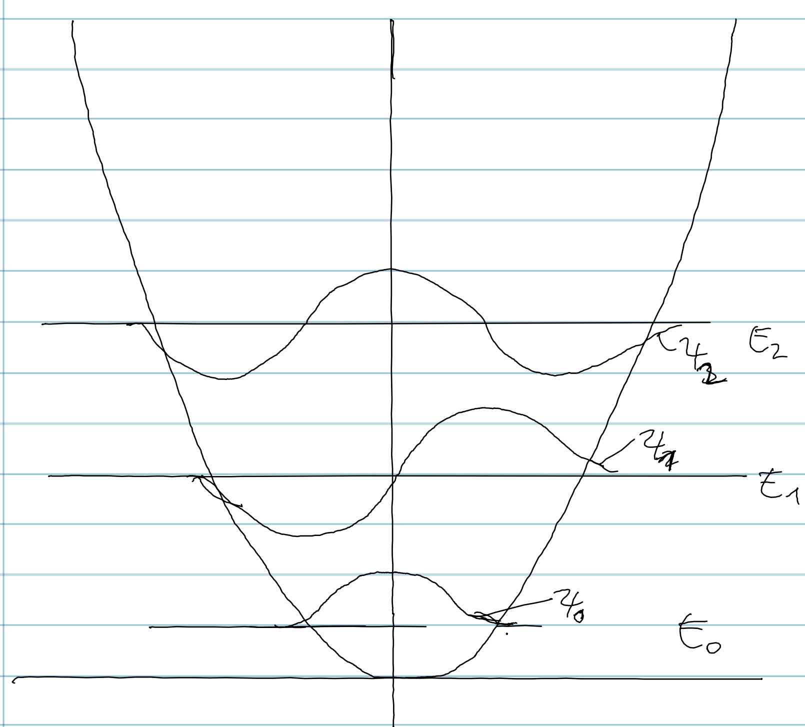
v	$H_v(\xi)$
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$
$\vdots$	$\vdots$

bilden Satz orthogonaler Funktionen

Norm. Gesamtwellenfkt.

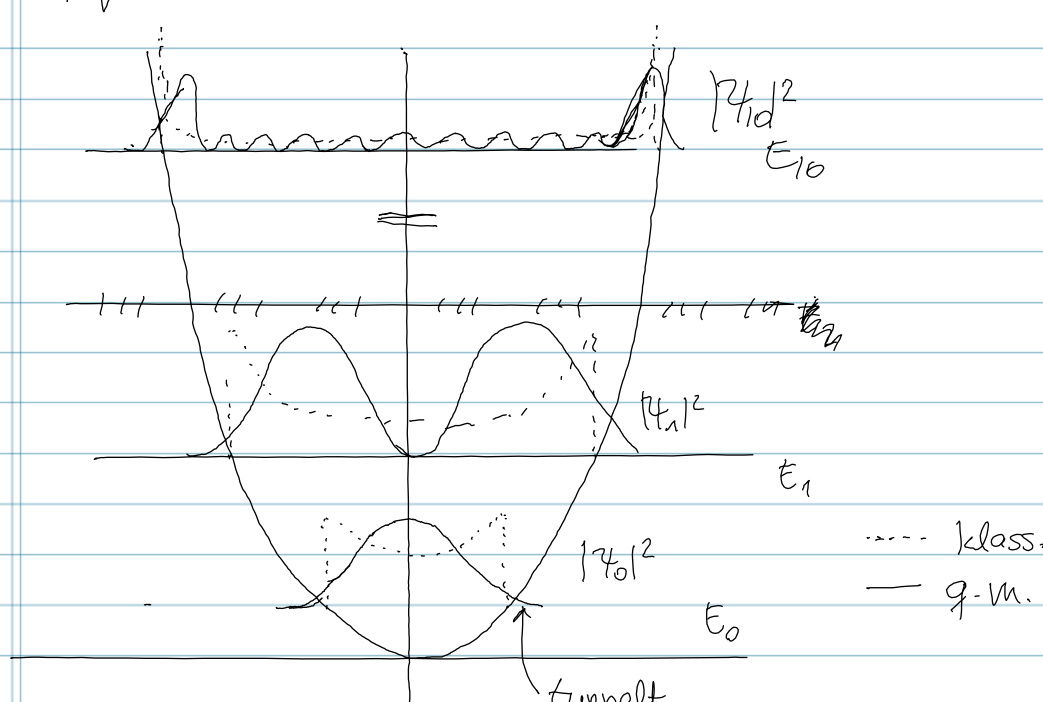
$$\psi_v(q) = \left(\left(\frac{\beta}{\pi} \right)^{1/2} \frac{1}{2^v v!} \right)^{1/2} H_v(\beta^{1/2} q)\, e^{-\beta q^2/2}$$

$v=0$: $\psi_0(q) = \left(\frac{\beta}{\pi}\right)^{1/4} \cdot 1 \cdot e^{-\beta q^2/2}$



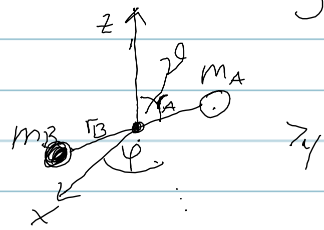
$\psi_v \xrightarrow{\text{hat}} v$ Knoten

$|\psi_v|^2$ Wahrscheinlichkeitsdichte



4. Starrer Rotator

q.m. Behandlung z.B. CO



$r = r_A + r_B$

Trägheitsmoment: $I = \sum_i m_i r_i^2 = m_A r_A^2 + m_B r_B^2$

$m_A r_A = m_B r_B$

$\Rightarrow r_A = \frac{m_B}{m_A + m_B} r \qquad r_B = \frac{m_A}{m_A + m_B} r$

$$\boxed{I = \underbrace{\frac{m_A m_B}{m_A + m_B}}_{\mu} r^2 = \mu r^2}$$

Schrödingergl.

$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2$

$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)_{\vartheta,\varphi} + \frac{1}{r^2 \sin\vartheta} \frac{\partial}{\partial\vartheta}\left(\sin\vartheta \frac{\partial}{\partial\vartheta}\right)_{r,\varphi} + \frac{1}{r^2 \sin^2\vartheta}\left(\frac{\partial^2}{\partial\varphi^2}\right)_{r,\vartheta}$

r = const.

$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\left[\frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta}\left(\sin\vartheta \frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\left(\frac{\partial^2}{\partial\varphi^2}\right)\right]$

$\cancel{\hat{H}}$ $\hat{H}\psi_i = E_i \psi_i$

Ansatz für Ψ-Fkt?

$$\boxed{\Psi(\vartheta,\varphi) = \Theta(\vartheta)\cdot\Phi(\varphi)}$$

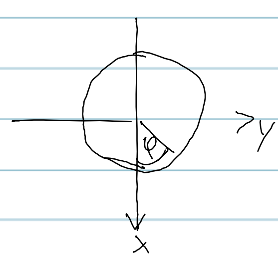
$\hat{H}$ u. Ψ einsetzen $\Rightarrow$

$$\underbrace{\frac{\sin^2\vartheta}{\Theta}\left[\frac{2IE\Theta}{\hbar^2} + \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)\right]}_{\text{const.}} = \underbrace{-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}}_{\text{const.}} = c$$

1. Gl. $\quad -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = c$

Lsg: $\Phi(\varphi) = A\cdot e^{im\varphi} \longrightarrow \Phi''(\varphi) = -Am^2 e^{im\varphi}$

$c = m^2$



Eindeutigkeit: $\Phi(\varphi) = \Phi(\varphi+2\pi)$

$$e^{im\varphi} = e^{im(\varphi+2\pi)}$$

$$1 = e^{im2\pi} = \cos m2\pi + i\sin m2\pi$$

$$1 = A^2\int_0^{2\pi} e^{-im\varphi}\cdot e^{im\varphi}\,d\varphi \qquad m = 0, \pm1, \pm2, \pm3, \ldots$$

$$1 = A^2\cdot 2\pi \Rightarrow A = \sqrt{\frac{1}{2\pi}}$$

2. Gl. $\quad \frac{\sin^2\vartheta}{\Theta}\left[\quad\right] = m^2$

Eindeutigkeit + Stetigkeit von Θ für

$$\frac{2IE}{\hbar^2} = J(J+1) \qquad J = 0, 1, 2, 3, \ldots$$

$J \geq |m|$

↳ Energieeigenwerte $\boxed{E_{rot} = \frac{\hbar^2}{2I} J(J+1)}$ $J = 0, 1, 2, 3, \ldots$

J = Rotationsquantenzahl

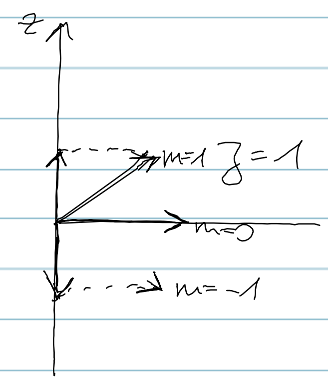
Rotationszustände sind $(2J+1)$fach entartet

$J = 1$: $m = \underbrace{0, \pm 1}_{3fach}$

$J = 2$: $m = \underbrace{0, \pm 1, \pm 2}_{5fach}$

J: Q.Z. des gesamten Drehimpulses

m: seine Komp. in Richtung einer Achse



Wellenfunktionen

$$\psi(\vartheta, \varphi) = \Theta(J, m)\, \Phi(m)$$

↑ zugeordnete Legendre-Polynome
-"- Kugelfkt. 1. Art

J	m	$\Theta(J,m)$
0	0	$\frac{1}{2}\sqrt{2}$
1	0	$\sqrt{\frac{3}{2}} \cdot \cos\vartheta$
1	± 1	$\sqrt{\frac{3}{4}} \cdot \sin\vartheta$
⋮	⋮	⋮

$J=0$: $\psi(\vartheta, \varphi) = \frac{1}{2}\sqrt{2} \cdot \sqrt{\frac{1}{2\pi}} \cdot e^{i0\varphi} = \sqrt{\frac{1}{4\pi}}$

$J=1, m=0$: $\psi(\vartheta, \varphi) = \sqrt{\frac{3}{2}} \cos\vartheta \cdot \sqrt{\frac{1}{2\pi}}\, e^{i0\varphi} = \sqrt{\frac{3}{4\pi}} \cdot \cos\vartheta$