

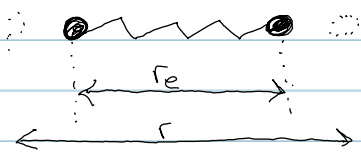
Vorlesung 28.11.2013

Google → Molwave - 3D Normal Modes

3. Harmonischer Oszillator

z.B. O_2

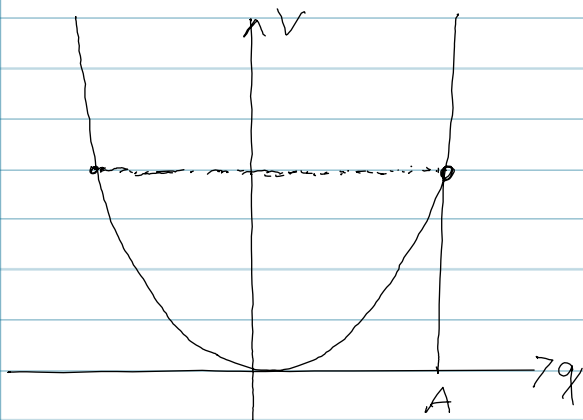
klass. Behandl.



$$q = r - r_e \quad \text{Auslenkung}$$

$$F = -kq \quad k = \text{Kraftkonst.}$$

$$V = \frac{1}{2}kq^2$$



$$E_{ges} = \frac{1}{2}kA^2$$

$$\left[\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \right]$$

q.m. Behandl.

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

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

Schrödinger gl.

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dq^2} + \frac{1}{2}kq^2\psi = E\psi \right] \quad | \cdot \left(-\frac{2\mu}{\hbar^2} \right)$$

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

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

Substitution: $\xi = \sqrt{\beta} \cdot q$

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

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

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

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

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

(2) in (1) einsetzen:

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

⇔ Hermitescher DGL für $\left(\frac{\alpha}{\beta} - 1 \right) = 2\nu$ $\nu = 0, 1, 2, 3, \dots$

Energieeigenwerte $\left(\frac{\alpha}{\beta} - 1 \right) = 2\nu$

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

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

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

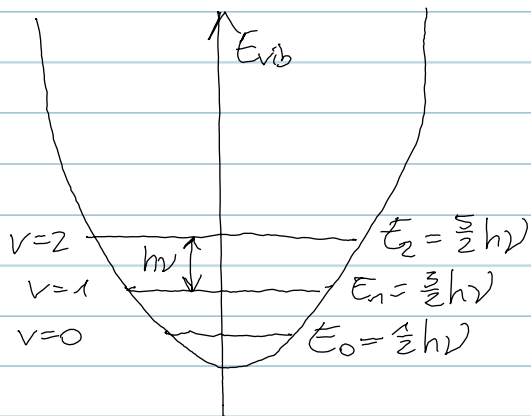
$$\underbrace{\frac{E}{\hbar \frac{1}{2\sqrt{k\mu}}}}_2 = \frac{E}{\hbar \sqrt{k\mu}} = \nu + \frac{1}{2}$$

$$\hookrightarrow \boxed{E_{vib} = (v + \frac{1}{2}) h\nu}$$

$$v = 0, 1, 2, 3, \dots$$

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

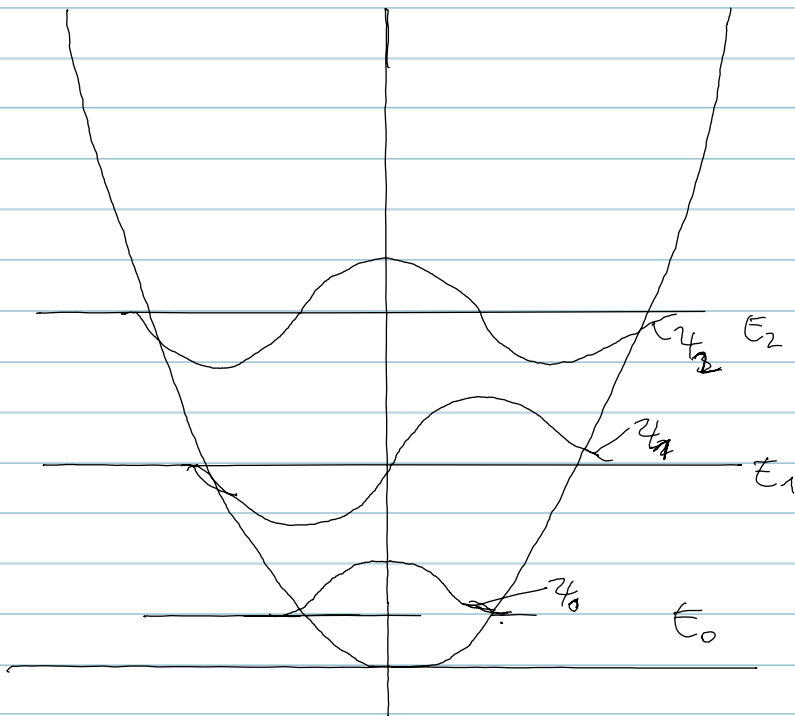
v	$H_v(\xi)$
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$
⋮	⋮
⋮	⋮

bilden Satz orthogonaler Funktionen

Norm. Gesamtwellenfkt.

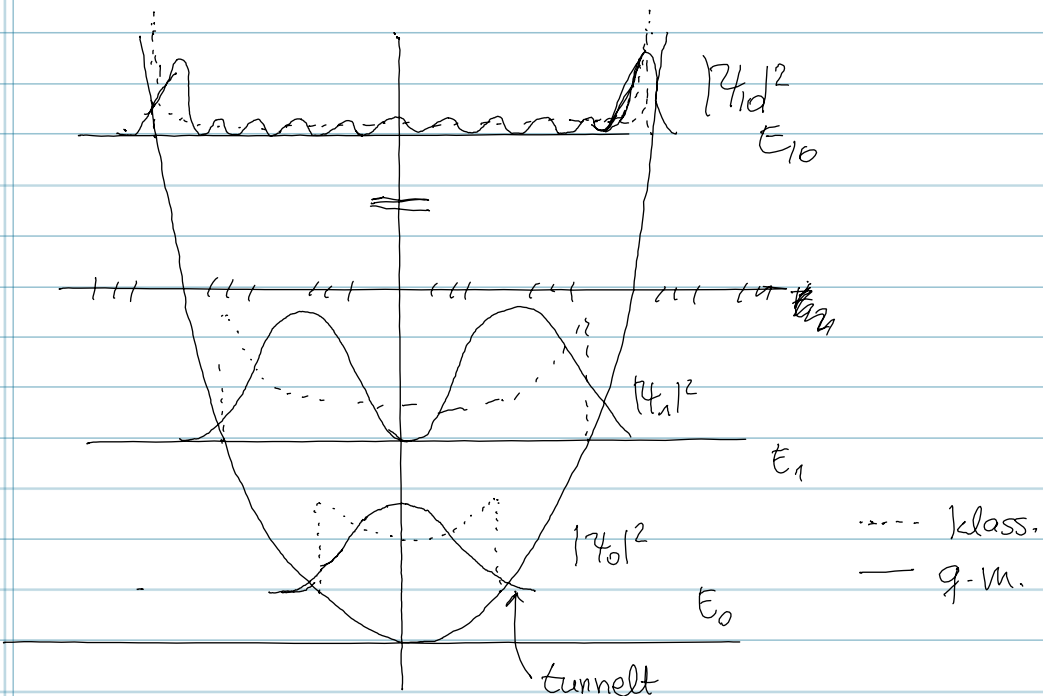
$$\psi_v(q) = \left(\left(\frac{\beta}{\pi} \right)^{1/2} \frac{1}{2^v v!} \right)^{1/2} H_v(\sqrt{\beta} q) e^{-\beta q^2 / 2}$$

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



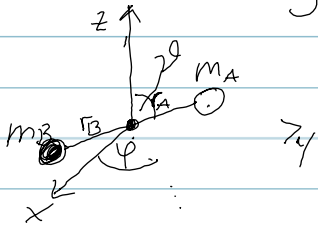
$\psi_v \xrightarrow{\text{hert}} v$ Knoten

$|\psi_v|^2$ Wahrscheinlichkeitsdichte



4. Starrer Rotator

q.m. Behandlung z.B. CO



$$r = r_A + r_B$$

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

$$m_A r_A = m_B r_B$$

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

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

Schrödingergl

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

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

$r = \text{const.}$

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

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

Ansatz für ψ -Fkt?

$$\psi(r, \varphi) = \Theta(r) \cdot \phi(\varphi)$$

Äu. ψ einsetzen \rightarrow

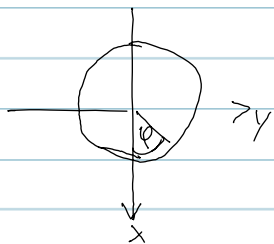
$$\frac{\sin^2 \frac{\varphi}{2}}{\Theta} \left[\frac{2IE\Theta}{\hbar^2} + \frac{1}{\sin^2 \frac{\varphi}{2}} \frac{\partial}{\partial \varphi} \left(\sin^2 \frac{\varphi}{2} \frac{\partial}{\partial \varphi} \right) \right] = - \frac{1}{\phi} \frac{\partial^2 \phi}{\partial \varphi^2} = C$$

Const. const.

1. Gl. $-\frac{1}{\phi} \frac{\partial^2 \phi}{\partial \varphi^2} = C$

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

$C = m^2$



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

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

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

$$1 = A \int_0^{2\pi} e^{-im\varphi} \cdot e^{im\varphi} d\varphi$$

$m = 0, \pm 1, \pm 2, \pm 3, \dots$

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

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

Eindeutigkeit + Stetigkeit von Θ für

$$\frac{2IE}{\hbar^2} = j(j+1) \quad j = 0, 1, 2, 3, \dots$$

$$J \geq |m|$$

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

J = Rotationsquantenzahl

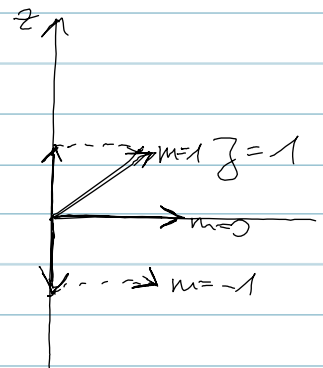
Rotationszustände sind $(2J+1)$ -fach entartet

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

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

J : Q.Z. des gesamten Drehimpulses

m : seine Komp. in Richtung einer Achse



Wellenfunktionen

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

↑
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	$\sqrt{\frac{3}{4}} \cdot \sin \vartheta$

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

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