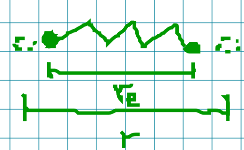
Physikalische Chemie II

29. Nov. 2018
Donnerstag

3 Harmonischer Oszillator

klassische Behandlung

Zwei Massepunkte verbunden über eine Feder

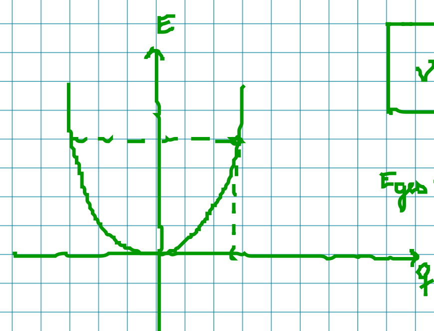


$q = r - r_e$ Auslenkung

$F = -kq$ k - Kraftkonstante

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

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



$E_{ges} = \frac{1}{2}kA^2$ → VL 2

→ Quantenmechanische Behandlung

Hamilton-Fkt: $H = \frac{p^2}{2\mu} + \frac{1}{2}kq^2$

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

Schrödingergleichung

$$\boxed{-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dq^2} + \frac{1}{2}kq^2\psi = E\psi}$$

mit: $\alpha = \frac{2\mu E}{\hbar^2}$

$\beta^2 = \frac{\mu k}{\hbar^2}$

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

Subst: $\xi = \sqrt{\beta}\, q$

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

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Klassische Behandlung

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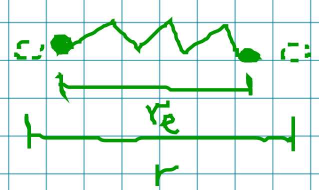

$q = r - r_e$ Auslenkung

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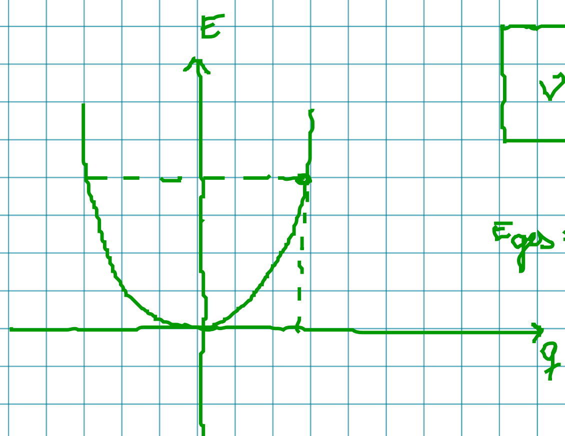

$E_{ges} = \frac{1}{2}kA^2 \quad \rightarrow VL2$

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allgemeine Lösung (1): $\Psi = n(\xi)\, e^{-\xi^2/2}$ (2)

(2) ist LSG für (1), wenn $n(\xi)$ die hermitische DGL erfüllt!

$$\frac{d^2 n}{d\xi^2} - 2\xi\frac{dn}{d\xi} + \left(\frac{\alpha}{\beta} - 1\right) n = 0 \quad \text{mit} \quad \left(\frac{\alpha}{\beta} - 1\right) = 2\nu \quad \nu = 0, 1, 2, 3 \ldots$$

Energieeigenwerte:

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

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

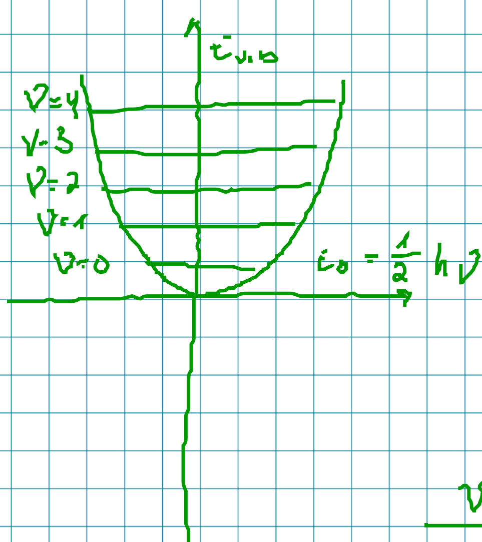
$$= \frac{\cancel{2}\mu E}{\hbar^{\cancel{2}}} \cdot \frac{1}{\cancel{2}} \frac{1 \cdot \cancel{\hbar}}{\sqrt{\mu k}} = \sqrt{\frac{\mu}{k}} \cdot \frac{E}{\hbar}$$

$$= \frac{1}{2\pi\nu}\frac{E}{\hbar} = \frac{E}{h\nu} = \nu + \frac{1}{2}$$

$$\boxed{E_{vib} = \left(\nu + \frac{1}{2}\right) h\nu} \qquad \nu = 0, 1, 2, 3$$

↑ Schwingungs-QZ

z.B. $\nu = 0$: $E_0 = \frac{1}{2} h\nu$ Nullpunktschwingungsenergie



E_{vib}: Schwingungsenergie

→ Wellenfunktion

LSG der hermitischen DGL $(n(\xi))$

↳ Hermit-Polynome $H_\nu(\xi)$

ν	$H_\nu(\xi)$
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$

Satz orthog. Funktionen.

Norm Gesamtwellenfunktion

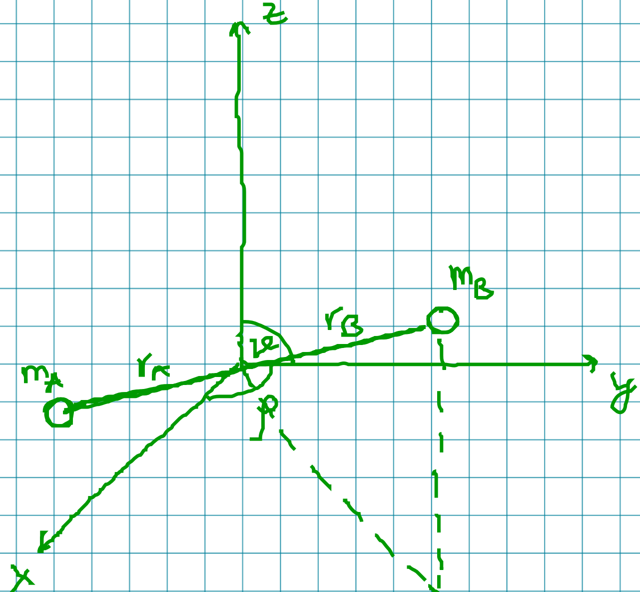
$$\Psi_\nu(q) = N_\nu \, H_\nu(\sqrt{\beta}\, q)\, e^{-\beta q^2/2}$$

$$\Psi_\nu(q) = \sqrt{\frac{\beta}{\pi} \frac{1}{2^\nu \cdot \nu!}} \; H_\nu(\sqrt{\beta}\, q)\, e^{-\beta q^2/2}$$

z. B.: $\nu = 0$ $\qquad \Psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} \cdot e^{-\beta q^2/2}$

4. Starrer Rotator

Quantenmechanische Behandlung



Trägheitsmoment

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

Schwerpunkt: $m_A r_A = m_B r_B$

$r = r_A + r_B$

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

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

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

Hamilton-Funktion: $H = \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2)$

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

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

für $r = \text{const.}$

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

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

Ansatz für ψ

$\psi(\vartheta, \varphi) = \Theta(\vartheta)\,\phi(\varphi)$

$\hat{H}\,\Theta(\vartheta)\,\phi(\varphi) = E\,\Theta(\vartheta)\,\phi(\varphi)$

mathematische Lösung:

$$-\frac{\hbar^2}{2I}\left[\phi(\varphi)\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,\frac{\partial\Theta}{\partial\vartheta}\right)\right.$$

$$\left.+\,\Theta(\vartheta)\,\frac{1}{\sin^2\vartheta}\left(\frac{\partial^2\phi}{\partial\varphi^2}\right)\right] = E\,\phi(\varphi)\,\Theta(\vartheta)$$

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\Theta(\vartheta)}\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,\frac{\partial\Theta}{\partial\vartheta}\right)\right.$$

$$\left.+\,\frac{1}{\phi(\varphi)}\frac{1}{\sin^2\vartheta}\left(\frac{\partial^2\phi}{\partial\varphi^2}\right)\right] = E$$

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

$$\cdots\cdots\cdots + \frac{2IE}{\hbar^2} = -\frac{1}{\phi(\varphi)}\frac{1}{\sin^2\vartheta}\left(\frac{\partial^2\phi}{\partial\varphi^2}\right)$$

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