30.1

30.1.2008

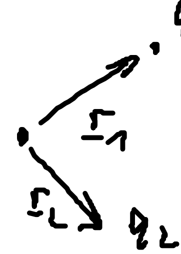
$$\varepsilon_{\alpha K v} = \frac{K(K+1)}{2\mu r_\alpha^2} + U_\alpha(r_\alpha) + \omega_\alpha\left(v + \frac{1}{2}\right)$$

$$|K\ m_K\ v\ \alpha\rangle$$

rot vib elektr.

WW Licht – Materie

$$\mathcal{H}_{dip}(t) = -\underline{d}\,\underline{E}(t);$$



$$\underline{d} \equiv \sum_n q_n \underline{r}_n$$

Übergangsamplituden $|K m_K v \alpha\rangle \rightarrow |K' m_{K'} v' \alpha'\rangle$

Matrixelemente $\langle K m_K v \alpha | \underline{d} | K' m_{K'} v' \alpha' \rangle$

Zerlegung nach Kugelflächenfkts $Y_{Km}(\theta,\varphi)$

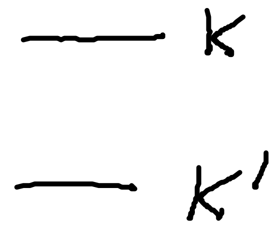
Integrales liefern Auswahlregeln

$$\Delta K = K - K' = \pm 1$$

$$\Delta m_K = 0, \pm 1 .$$

$$\varepsilon_{rot}(K) = B \cdot K(K+1)$$

$\uparrow$ Konstante

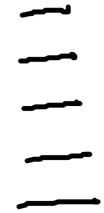


$$\Rightarrow \Delta \varepsilon_{rot}(K) \equiv B(K+1)(K+2) - BK(K+1)$$

$$= 2B(K+1) = \hbar\omega^{(Bohr)}_{K+1 \rightarrow K}$$

$$\Delta \varepsilon_{rot}(K+1) - \Delta \varepsilon_{rot}(K) = 2B$$

= konstant



Vibrations-Übergängen

Harmonischer-Oszillator

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}}\,\hat{x} + \frac{i}{\sqrt{2m\hbar\omega}}\,\hat{p}$$

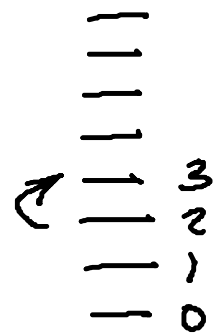
Vernichter

$$\hat{a}^\dagger \equiv \sqrt{\frac{m\omega}{2\hbar}}\,\hat{x} - \frac{i}{\sqrt{2m\hbar\omega}}\,\hat{p}$$

Erzeuger

Erzeugen/Vernichten von Phononen:

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right)$$

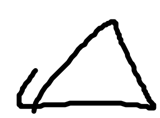


$$[a, a^\dagger] = 1$$

$$[\hat{x}, \hat{p}] = i\hbar$$

$|n\rangle$: Fock-Zustände
Besetzungszahl-Zustände
n-Phononen (n-Bosonen)-Zustände

$$a^\dagger |n\rangle = \sqrt{n+1}\,|n+1\rangle$$



$$a\,|n\rangle = \sqrt{n}\,|n-1\rangle$$

$$\langle x|n\rangle \equiv \psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{n!\,2^n}}\cdot$$

$$\cdot\, H_n\left(\sqrt{\frac{m\omega}{\hbar}}\,x\right) e^{-\frac{m\omega}{2\hbar}x^2}$$

$1/$ Längenskala des Problems

Dipolübergänge

$$|v\rangle \longrightarrow |v'\rangle$$

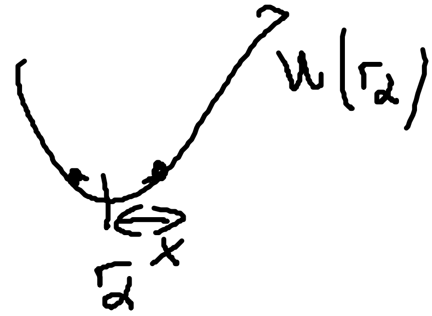
v entspricht jetzt der Quantenzahl n

$$\langle v|\underline{d}_\alpha|v'\rangle, \quad \underline{d}_\alpha \equiv \langle\alpha|\underline{d}|\alpha\rangle$$

Taylor-Entwicklung des Dipolmoments

$$d_\alpha(x) = d_\alpha(0) + d'_\alpha(0)\,x + O(x^2)$$

$x \equiv r - r_\alpha$ Auslenkung aus der Ruhelage



$E_\alpha(r)$

Damit

$\langle v | \underline{d}_\alpha | v' \rangle =$

$\langle v | \underline{d}_\alpha(0) | v' \rangle +$

$\langle v | d_\alpha'(0) \cdot x | v' \rangle +$ ... höhere Terme

$\frac{1}{2!} \langle v | d_\alpha''(0) \cdot x^2 | v' \rangle +$

$$= \underbrace{\underline{d}_\alpha(0) \langle v | v' \rangle}_{\delta_{vv'} = 0 \; (v \neq v')} + d_\alpha'(0) \langle v | x | v' \rangle + \dots$$

$$\overset{v \neq v'}{=} 0 + d_\alpha'(0) \sqrt{\frac{\hbar}{2m\omega}} \langle v | a + a^+ | v' \rangle + \dots$$

$$= d_\alpha'(0) \sqrt{\frac{\hbar}{2m\omega}} \left\{ \langle v | \sqrt{v'} \, | v' - 1 \rangle + \langle v | \sqrt{v' + 1} \, | v' + 1 \rangle \right\}$$

$$= d_\alpha'(0) \sqrt{\frac{\hbar}{2m\omega}} \left\{ \delta_{v, v'-1} \sqrt{v+1} + \delta_{v, v'+1} \sqrt{v} \right\}$$

Auswahlregel $\Delta v = \pm 1$

Entsprechend $\Delta \varepsilon_{vib}(v) = \hbar\omega_\alpha$

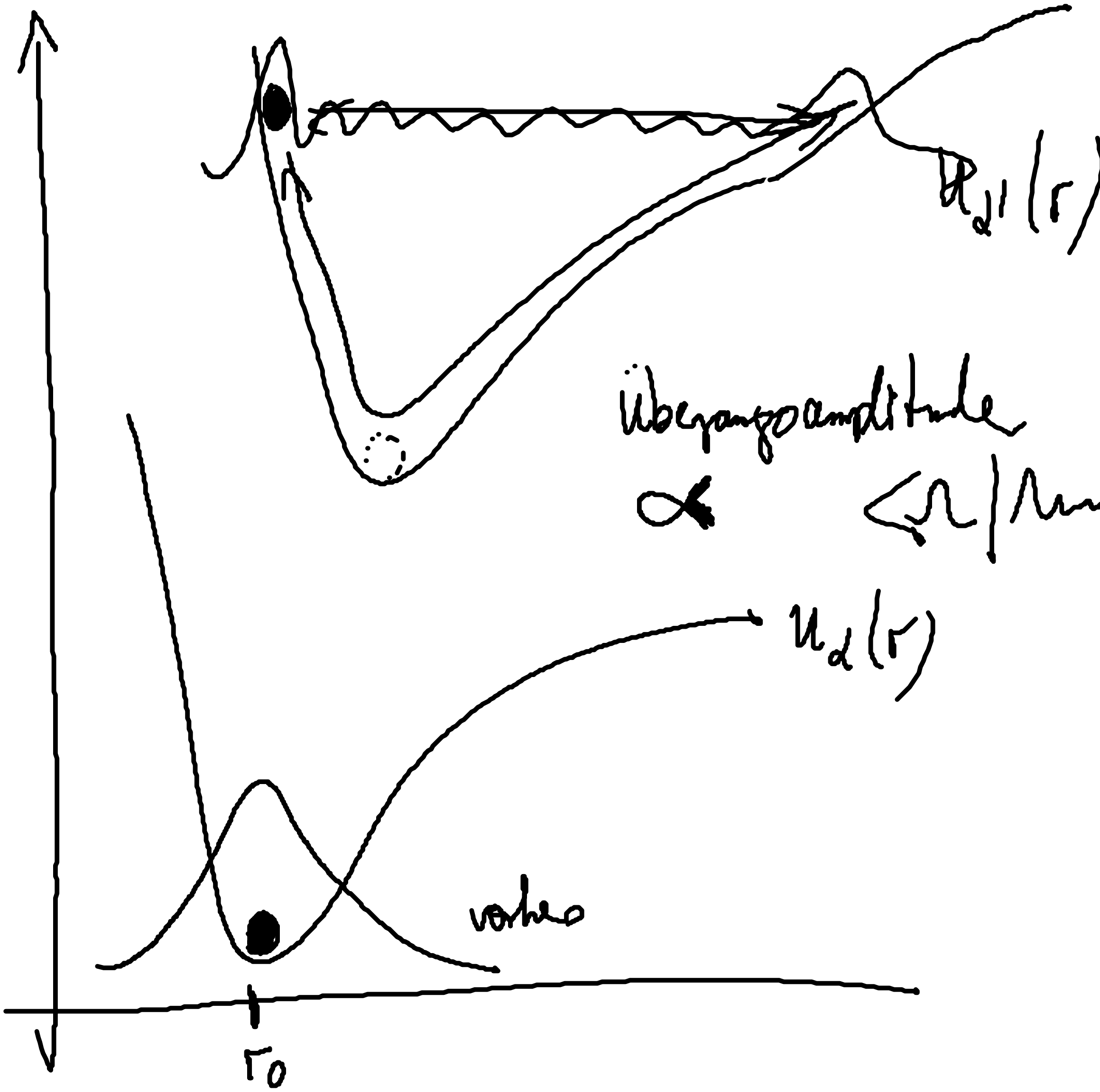
Vibrations-Rotations-Spektren

P-, Q-, R-Zweige für erlaubte Übergänge ; Atkins/Friedman
Weissbluth

Elektronische Übergänge, das Franck-Condon Prinzip

Übergang $\alpha \to \alpha'$,

entsprechend $U_\alpha(r) \longrightarrow U_{\alpha'}(r)$.



Übergangsamplitude /propto

$\propto \langle \chi | \chi_m \rangle$

Gesamt-Dipolmoment

$$\underline{d} = \underbrace{-e \sum_i \underline{r}_i}_{\text{elektr.}} + \underbrace{e \sum_s Z_s \underline{X}_s}_{\text{nukl.}}$$

$$\equiv \underline{d}_e + \underline{d}_n$$

Übergangsamplitude $\alpha \rightarrow \alpha'$

$$\langle \alpha' v' | \underline{d}_e + \underline{d}_n | \alpha v \rangle =$$

$$= \int dq\, dX\, \Psi^*_{\alpha'}(qX) \phi^*_{\alpha' v'}(X) [\underline{d}_e + d_n] \phi_{\alpha v}(X) \Psi_\alpha(qX)$$

$$= \int dX\, \phi^*_{\alpha' v'}(X) \left[\int dq\, \Psi^*_{\alpha'}(q,X)\, \underline{d_e}\, \Psi_\alpha(q,X) \right] \phi_{\alpha, v}(X)$$

$$+ \int dX\, \phi^*_{\alpha' v'}(X) \phi_{\alpha v}(X)\, d_n \cdot \underbrace{\int dq\, \Psi^*_{\alpha'}(qX) \Psi_\alpha(qX)}_{\langle \alpha' | \alpha \rangle = 0 \atop \alpha \neq \alpha'}$$

$$\cong \underbrace{\langle \alpha' | d_e | \alpha \rangle}_{\underbrace{\int dq\, \Psi^*_{\alpha'}(q,X)\, d_e\, \Psi_\alpha(qX)}} \cdot S(v, v'),$$

Annahme: nur schwach von X abhängig, aus dem Integrale herausziehen.

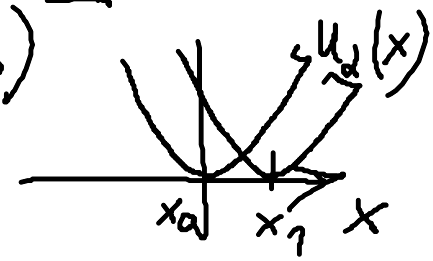
Wobei $$S(v, v') \equiv \underbrace{\langle v | v' \rangle}_{\text{nicht } = \delta_{vv'},}$$

weil die Potentiale verschiedenen

sind

Beispiel:

$$U_\alpha(x) = \frac{1}{2} m\omega^2 (x-x_0)^2$$



$$U_{\alpha'}(x) = \frac{1}{2} m\omega^2 (x-x_1)^2$$

$$|v\rangle = |n=0\rangle_{x_0} \Longleftrightarrow \psi_0(x) \sim e^{-\dots(x-x_0)^2}$$

$$|v'\rangle = |n=0\rangle_{x_1} \Longleftrightarrow \psi_0(x) \sim e^{-\dots(x-x_1)^2}$$

$$\langle v|v'\rangle = \int dx \dots \; e^{-(x-x_0)^2 \dots} \; e^{-(x-x_1)^2 \dots}$$

$$\neq 0$$

$$\neq 1$$

ÜA: ausrechnen!