1.2.2008

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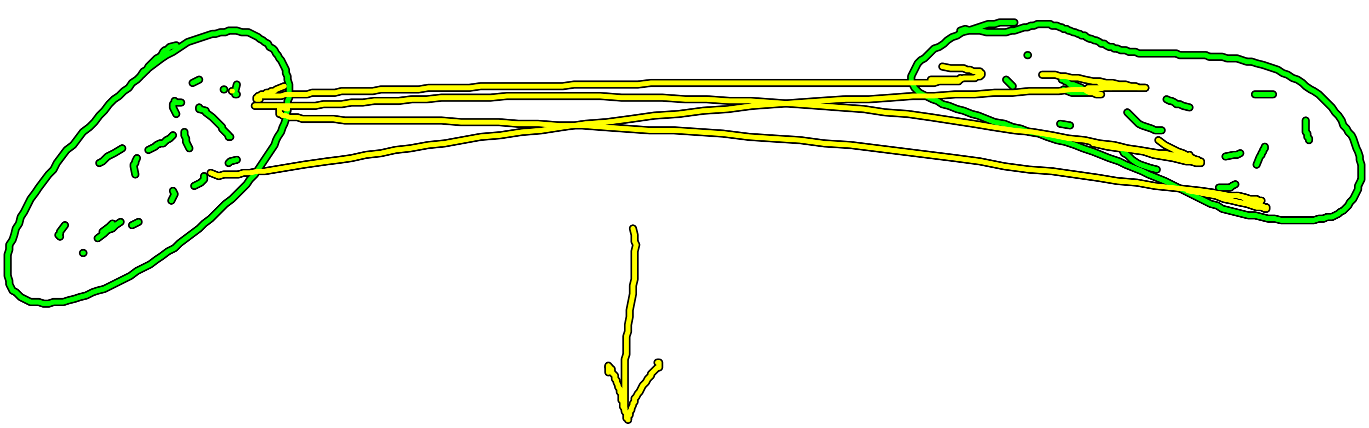
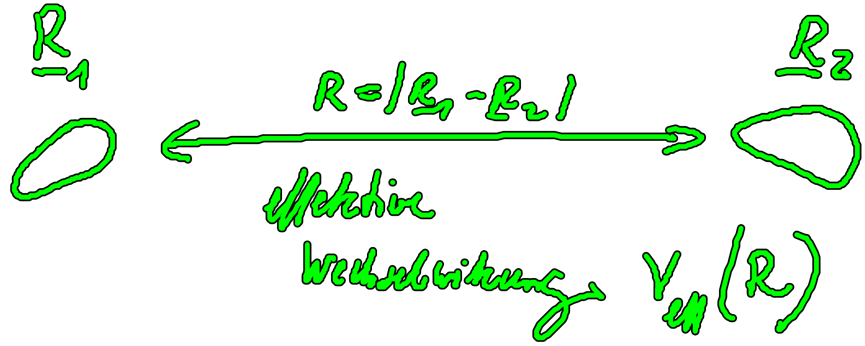
Von mikroskopisch nach makroskopisch





Energie einer Ladungsverteilung

$$E = \frac{1}{2}\sum_{nn'}\int d\underline{x}\, d\underline{x}'\, \frac{\rho_n(\underline{x})\,\rho_{n'}(\underline{x}')}{|\underline{x}-\underline{x}'|}$$

zwei Moleküle bei $\underline{R}_n$, $\underline{R}_{n'}$

$$\underline{x} = \underline{R}_n + \underline{\xi}\,, \qquad \underline{x}' = \underline{R}_{n'} + \underline{\xi}'$$

Entwicklung von $\dfrac{1}{|\underline{x}-\underline{x}'|}$ für jedes Paar n, n',

$\underline{R} = \underline{R}_n - \underline{R}_{n'}$, $\underline{a} = \underline{\xi} - \underline{\xi}'$

Entw. in $\left|\dfrac{a}{R}\right|$

Taylor: $$\frac{1}{|\underline{R}+\underline{a}|} =$$

$$= \frac{1}{R}\left(1 + \frac{\underline{a}^2 + 2\underline{R}\,\underline{a}}{R^2}\right)^{-1/2} =$$

$$= \frac{1}{R}\left(1 - \frac{1}{2R^2}\left(\underline{a}^2 + 2\underline{R}\,\underline{a}\right) + \frac{3}{8R^4}\left(\underline{a}^2 + 2\underline{R}\,\underline{a}\right)^2 + \dots\right)$$

Jetzt Annahme $\int d\underline{x}\, \rho_n(\underline{x}) = 0$

$$\Rightarrow \iint d\underline{x}\, d\underline{x}'\, \frac{\rho_n(\underline{x})\rho_{n'}(\underline{x}')}{|\underline{x} - \underline{x}'|} =$$

$$= \iint d\underline{\xi}\, d\underline{\xi}'\, \rho_n(\underline{\xi})\rho_{n'}(\underline{\xi}')\frac{1}{R}\left\{\cancel{1} - \frac{1}{2R^2}\left(\underbrace{[\underline{\xi}-\underline{\xi}']^2}_{\underset{0}{\xi^2} + \underset{0}{\xi'^2} - 2\xi\xi'} + 2\underline{R}[\underset{0}{\underline{\xi}} - \underset{0}{\underline{\xi}'}]\right)\right.$$

$$\left. + \frac{3}{8R^4}\left([\underline{\xi}-\underline{\xi}']^2 + 2\underline{R}(\underline{\xi}-\underline{\xi}')\right)^2 + \dots\right.$$

$$= \iint d\underline{\xi}\, d\underline{\xi}'\, \rho_n(\underline{\xi})\rho_{n'}(\underline{\xi}')\frac{1}{R}\left\{\frac{\xi\xi'}{R^2} + \frac{3}{8R^4}\left[\overbrace{4\{\underline{R}(\underline{\xi}-\underline{\xi}')\}\{\underline{R}(\underline{\xi}-\underline{\xi}')\}}^{0} + \dots\right.\right.$$

$\neq 0$ $\quad$ 0

$$= \iint d\underline{\xi}\, d\underline{\xi}'\, \rho_n(\underline{\xi})\rho_{n'}(\underline{\xi}')\frac{1}{R}\left\{\frac{\xi'\xi}{R^2}\right.$$

$$- \frac{3}{R^4} (\underline{R}\,\underline{\xi})(\underline{R}\,\underline{\xi}') + \ldots \Big\}$$

$$= \left[\underline{d}_n = \int d\xi\, \underline{\xi}\, \rho_n(\xi) \right]$$

$$= \frac{1}{R^3} \underline{d}_n \cdot \underline{d}_{n'} - \frac{3}{R^5} (\underline{R}\,\underline{d}_n)(\underline{R} \cdot \underline{d}_{n'}) + \ldots$$

Damit hat die Energie E die Form

$$E = \frac{1}{2} \sum_n E_n^{\text{self}} + \frac{1}{2} \sum_{\substack{n n' \\ n \neq n'}} \Big(E_{nn'}^{d\text{-}d} + E_{nn'}^{\text{höhere Multipole}} \Big)$$

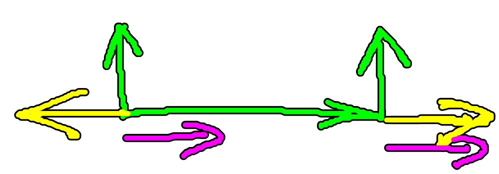
$$E_n^{\text{self}} = \iint d\underline{x}\, d\underline{x}' \frac{\rho_n(\underline{x}) \rho_n(\underline{x}')}{|\underline{x} - \underline{x}'|}$$

Multipol-Entwicklung

Dipol-Dipol-Wechselwirkung

$\underline{d}_1$ $\underline{d}_2$

$$E^{dd}(\underline{R}) = \frac{\underline{d}_1 \underline{d}_2}{R^3} - 3 \frac{(\underline{R}\,\underline{d}_1)(\underline{R}\,\underline{d}_2)}{R^5}$$



läßt sich schreiben als

$$E^{dd}(\underline{R}) = -\underline{d}_1 \underline{E}_2^{dip} - \underline{d}_2 \underline{E}_1^{dip}$$

$\underline{E}_2^{dip}$: elektr. Feld am Ort des Dipols 1, erzeugt durch Dipol 2.

klassisch $\longrightarrow$ quantenmechanisch

$$\mathcal{H}_{eff} = \mathcal{H}_0 + V, \quad V = \frac{1}{2} \sum_{n \neq n'} E^{d-d}_{nn'}$$

gewünscht: Beschreibung im Phasenraum der Moleküle $(\hat{P}_n, \hat{R}_n)$ mit effektiver WW

$$V^{eff}(\{\underline{R}_n\}).$$

Zeitentwicklung in der QM

$$i \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle$$

$$|\Psi(t)\rangle = \underbrace{e^{-i\hat{H}t}}_{\text{Zeitentw.-Operator (Propagator)}} |\Psi(0)\rangle, \quad t \geq 0$$

Laplace-trafo einer Funktion $f(t)$

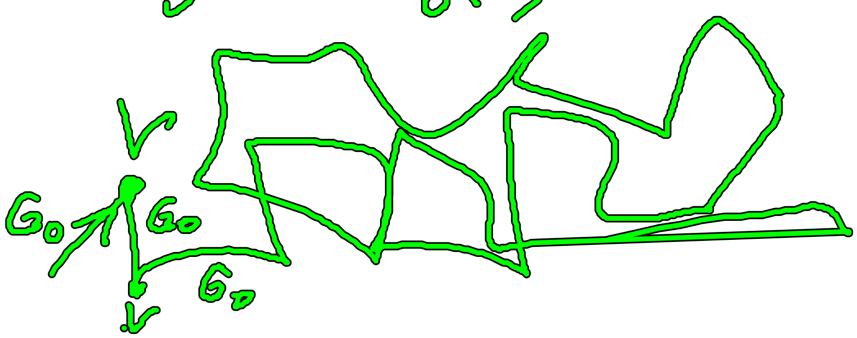
$$\hat{f}(z) = \int_0^\infty dt\, e^{-zt} f(t) .$$

$$\int_0^\infty dt\; e^{-zt - iHt} = \frac{1}{z + i\hat{H}}$$

<u>Definition</u>: Resolvente (Greensfunktion)

$$G(z) = \frac{1}{z - \hat{H}} = (z - \hat{H})^{-1} .$$

$H = H_0 + V$; $\quad G_0(z) = (z - H_0)^{-1}$

$G =$ 

$$G(z) = (\underbrace{z - H_0}_{G_0^{-1}} - V)^{-1} = (G_0^{-1} - V)^{-1}$$

$$= (1 - G_0 V)^{-1} G_0$$

$$= G_0 + G_0 V \{ G_0 + G_0 V G_0 \quad + G_0 V G_0 V G_0$$

$$+ \dots \} =$$

$$= G_0 + \underline{G_0 V G}$$

$$\boxed{G(z) = G_0(z) + G_0(z) V G(z)}$$

<u>Dyson</u>

Reihe $G = G_0 + G_0 \{ V + V \underbrace{G_0}_{} V + V G_0 V G_0 V + \dots \}.$

G_0

„nackte Wechselwirkung"

T-Matrix (effektive Wechselwirkung)

$$= G_0 + G_0 T G_0$$

Zwei Moleküle im Zustand $|k\rangle \otimes |k'\rangle$

Erwartungswert von V^{eff} in diesem Zustand.

1. Term ist der EW

$$\langle kk' | V | kk' \rangle \quad \text{mit}$$

$$V = \frac{\underline{d}_n \cdot \underline{d}_{n'}}{R^3} - 3 \frac{(\underline{R}\,\underline{d})(\underline{R}\,\underline{d}')}{R^5}$$

$$\rightarrow \quad V_{eff}^{(1)}(\underline{R}) = \frac{\langle \underline{d} \rangle \langle \underline{d}' \rangle}{R^3} - 3\,\frac{\left(\underline{R}\langle \underline{d}\rangle\right)\left(\underline{R}\langle \underline{d}'\rangle\right)}{R^5}$$

daraus Kraft $F_{eff}^{(1)}(\underline{R}) = -\underline{\nabla} V_{eff}^{(1)}(\underline{R})$

wie klassische Dipol-Dipol WW

Aber: Null falls $\langle \underline{d} \rangle = 0$.

QM $\quad \langle \underline{d} \rangle = 0 \not\Rightarrow \langle \underline{d}^2 \rangle = 0$

2. Term

$$z = E_k + E_{k'}$$

$$V_{eff}^{(2)}(R) = \langle kk'|V G_0 V|kk'\rangle$$

$$= \sum_{nn'} \frac{\langle kk'|V|nn'\rangle \langle nn'|V|kk'\rangle}{E_k + E_{k'} - E_n - E_{n'}}$$

$$\langle nn'|G_0(z)|mm'\rangle = \langle nn'|\frac{1}{z - H_0}|mm'\rangle$$

$$= \delta_{nm}\,\delta_{n'm'}\,\frac{1}{z - (E_n + E_{n'})}.$$

1.

$$H_0|nn'\rangle \equiv H_0\underset{\uparrow\ 1.}{|n\rangle} \otimes \underset{\uparrow\ 2.\ \text{Molekül}}{|n'\rangle}$$

$$= (E_n + E_{n'})|nn'\rangle$$

1. Schritt : $$E^{dd}(\underline{R}) = \frac{\underline{d}\,\underline{D}}{R^3} - 3\frac{(\underline{R}\,\underline{d})(\underline{R}\,\underline{D})}{R^5}$$

$\underline{R} = R\,\underline{e}_z$

$$= \underline{d}\,\underline{\underline{M}}\,\underline{D}$$

$$\underline{\underline{M}} = \frac{1}{R^3}\begin{pmatrix} 1 & & 0 \\ & 1 & \\ 0 & & -2 \end{pmatrix} ;$$

$$\langle k|\underline{d}_\alpha|n\rangle \equiv d_\alpha^{kn}, \qquad \alpha = x, y, z$$

$$\langle k|\underline{D}_\alpha|n\rangle = D_\alpha^{kn}$$

$$|\langle kk'|V|nn'\rangle|^2 = \sum_{\alpha\gamma} d_\alpha^{kn}\, d_\gamma^{nk}\, D_\alpha^{k'n'}\, D_\gamma^{n'k'}\, M_{\alpha\alpha} M_{\gamma\gamma} .$$

$$d_\alpha^{kn} d_\beta^{nk} = \frac{1}{3} \delta_{\alpha\beta} \underline{d}^{kn} \underline{d}^{nk}$$

$\Rightarrow$ Damit $\quad |kk'\rangle = |GS\rangle$ Grundzustand

$$V^{(2),GS}_{eff}(R) = \frac{2}{3}\frac{1}{R^6} \sum_{\substack{nn' \\ \neq 0}} \frac{\underline{d}^{kn}\underline{d}^{nk}\underline{D}^{k'n'}\underline{D}^{n'k'}}{E_0 + E_{0'} - E_n - E_{n'}}$$

positiv

< 0

- attraktive Wechselwirkung
- fällt ab mit $1/R^6$

van-der-Waals-Wechselwirkung

Kräfte: van-der-Waals-Kräfte (Dispersionskräfte).