Effect of static electric field

polarizability

Recall Quadratic stark shift

$$E^{(2)}_{100} = e^2 E_z^2 \sum_{\substack{n \neq 1 \\ lm}} \frac{|\langle \psi_{nlm} | z | \psi_{100} \rangle|^2}{(E_1 - E_n)} < 0$$

$\vec{E} \parallel \hat{z}$

$H' = -q z E_z = e z E_z$

More generally, $H' = -\sum_i q_i z_i E_z$

$$= -\sum q_i \hat{r}_i \cdot \vec{E}$$

$$= -\vec{E} \cdot \hat{\mu} = -E_z \mu_z$$

$$\therefore \frac{dU}{dE_z} = \left\langle \frac{dH}{dE_z} \right\rangle \equiv \left\langle \frac{dH'}{dE_z} \right\rangle = \left\langle \frac{d(-\mu_z E_z)}{dE_z} \right\rangle$$

$$= -\langle \mu_z \rangle$$

$$U = U(E_z = 0) + \left.\frac{dU}{dE_z}\right|_{E_z=0} E_z + \frac{1}{2!} \left.\frac{d^2U}{dE_z^2}\right|_{E_z=0} E_z^2 + \frac{1}{3!} \left.\frac{d^3U}{dE_z^3}\right|_{E=0} E_z^3 + \cdots$$

$$\frac{dU}{dE_z} = 0 + \left.\frac{dU}{dE_z}\right|_{E_z=0} + \left.\frac{d^2U}{dE_z^2}\right|_{E_z=0} E_z + \frac{1}{2} \left.\frac{d^3U}{dE_z^3}\right|_{E_z=0} E_z^2 + \cdots$$

$$\langle \mu \rangle = 0 + \langle \mu \rangle_{E_z=0} - \left.\frac{d^2U}{dE_z^2}\right|_{E_z=0} E_z - \frac{1}{2} \left.\frac{d^3U}{dE_z^3}\right|_{E_z=0} E_z^2 + \cdots$$

$$\langle \mu \rangle = \langle \mu \rangle_{E_z=0} + \alpha_{zz} E_z + \frac{1}{2} \beta_{zzz} E_z^2 + \cdots$$

$$\therefore \alpha_{zz} = -\left.\frac{d^2U}{dE_z^2}\right|_{E_z=0} \rightarrow \text{polarizability tensor}$$

$$\alpha_{ij} = -\left.\frac{d^2U}{dE_i dE_j}\right|_{E_z=0}$$

$\beta_{zzz} \rightarrow$ hyper polarizability

Recall,

$$U = U^0 + U^{(1)} + U^{(2)} + \cdots$$

$$= U^0 + \left.\frac{dU}{dE_z}\right|_{E_z=0} E_z + \frac{1}{2} \left.\frac{d^2U}{dE_z^2}\right|_{E_z=0} E_z^2 + \cdots$$

$$= U^0 + U^{(1)} + \frac{1}{2}\left(-\alpha_{zz}\right) E_z^2 + \cdots$$

$$\therefore \quad U^{(2)} = -\frac{1}{2}\alpha_{zz} E_z^2$$

$$\therefore \alpha_{zz} = -\frac{2U^{(2)}}{E_z^2} = \frac{-2E^{(2)}_{100}}{E_z^2}$$

$$= -2e^2 \sum_{\substack{n\neq 1 \\ lm}} \frac{|\langle \psi_{nlm}|z|\psi_{100}\rangle|^2}{(E_1 - E_n)}$$

$$= 2e^2 \sum_{\substack{n\neq 1 \\ lm}} \frac{|z_{nlm,100}|^2}{\hbar\omega_{n1}} \rightarrow \text{for given } \theta \text{ ie, } \Omega$$

$$\therefore \underbrace{\frac{1}{4\pi}\int \alpha_{zz}(\Omega)\, d\Omega}_{\bar{\alpha}_{zz}} = \frac{2}{3}e^2 \sum_{\substack{n\neq 1 \\ lm}} \frac{|r_{nlm,100}|^2}{\hbar\omega_{n1}} \quad \because \int \cos^2\theta\, d\Omega = \frac{4\pi}{3}$$

Note $\bar{\alpha}$ is static polarisability which is the $\omega \to 0$ limit of a more elaborate derivation of dynamic $\alpha(\omega)$ from Green Kubo relation.

$\vec{P} = \varepsilon_0 \chi \vec{E}$; $\chi \rightarrow$ Susceptibility.

Recall, $\vec{P}$: polarization $= N \underset{\text{Dipole moment}}{\vec{\mu}}$, $N \rightarrow$ # of atom/mol per unit volume

Since $\vec{P} = \underline{\underline{\bar{\alpha}}} \cdot \vec{E}$, $\underline{\underline{\chi}} = N \underline{\underline{\bar{\alpha}}}$ $\rightarrow$ tensor

Also $\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon\vec{E} = \varepsilon_r \varepsilon_0 \vec{E}$ (Recall from EM class)

$\vec{D}$: Electric displacement

$\Rightarrow \underline{\underline{\varepsilon_r}} = 1 + \underline{\underline{\chi}} = 1 + N\underline{\underline{\bar{\alpha}}}$

Recall, $\bar{\alpha}_{zz} = \frac{2}{3} e^2 \sum_{\substack{n\neq 1 \\ lm}} \frac{|r_{nlm,100}|^2}{\hbar \omega_{n1}}$

$= \frac{2}{3} \sum_{\substack{n\neq 1 \\ lm}} \frac{|\mu_{nlm,100}|^2}{\hbar \omega_{n1}}$

$\bar{\alpha}_{zz} > \frac{2}{3} \frac{1}{\hbar\omega_{21}} \sum_{\substack{n\neq 1 \\ lm}} |\mu_{nlm,100}|^2$

(lower limit)

$= \frac{2}{3} \frac{1}{\hbar\omega_{21}} \left[\sum_{nlm} \langle 100|\hat{\mu}|nlm\rangle\langle nlm|\hat{\mu}|100\rangle - \langle 100|\hat{\mu}|100\rangle\langle 100|\hat{\mu}|100\rangle \right]$

$= \frac{2}{3} \frac{1}{\hbar\omega_{21}} \left[\langle 100|\hat{\mu}^2|100\rangle - (\langle 100|\hat{\mu}|100\rangle)^2 \right]$

$\bar{\alpha}_{zz} > \frac{2}{3\hbar\omega_{21}} (\langle\hat{\mu}^2\rangle - \langle\hat{\mu}\rangle^2)$

$\bar{\alpha}_{zz} \simeq \frac{2}{3\bar{\omega}} (\langle\hat{\mu}^2\rangle - \langle\hat{\mu}\rangle^2) \rightarrow$ fluctuation of $\hat{\mu}$ in ground state (100)

$\bar{\omega} \rightarrow$ little less than ω_{21}

$\bar{\alpha}_{zz} \downarrow$

response fn to external electric field.

Note that this kind of relation between response functions and fluctuation of the related variable quantity. For example specific heat and energy. Recall, $C_v = \frac{1}{kT^2}\left[\langle E^2\rangle - \langle E\rangle^2\right]$

Infact as you see, $\frac{1}{\omega_{n1}}$ converges to 0. So one can define a $\frac{1}{\bar{\omega}}$ quite easily. $\bar{\omega}$ being mean excitation frequency. Note: $\frac{1}{\bar{\omega}} < \frac{1}{\omega_{21}}$ but close.

Also, recall, $f_{ab} = \frac{2m}{3\hbar} \omega_{ba} |r_{ba}|^2$ dimensionless oscillator strength.

$\therefore \bar{\alpha}_{zz} = \frac{e^2}{m} \sum_{\substack{n\neq 0 \\ lm}} \frac{f_{nlm,100}}{\omega^2_{nlm,100}} \simeq \frac{e^2}{m\bar{\omega}^2} \sum_{lm} f_{nlm,100}$

$\Rightarrow \bar{\alpha}_{zz} = \frac{e^2}{m\bar{\omega}^2} N_e \left[\because \sum_{nlm} f_{nlm,100} = N_e \text{ \# of electron}\right] \Rightarrow \bar{\alpha}\uparrow$ as $N_e\uparrow$, $\bar{\alpha}\uparrow$ as $\bar{\omega}\downarrow$

Note: $\bar{\omega}$ will be lower for  than  because sharper the confining potential larger the energy separations.