Jahn-Teller Physics

The spontaneous Jahn-Teller effect is the spontaneous distortion of geometry in an electronically excited state which results when levels are split to reduce the energy of the overall system.

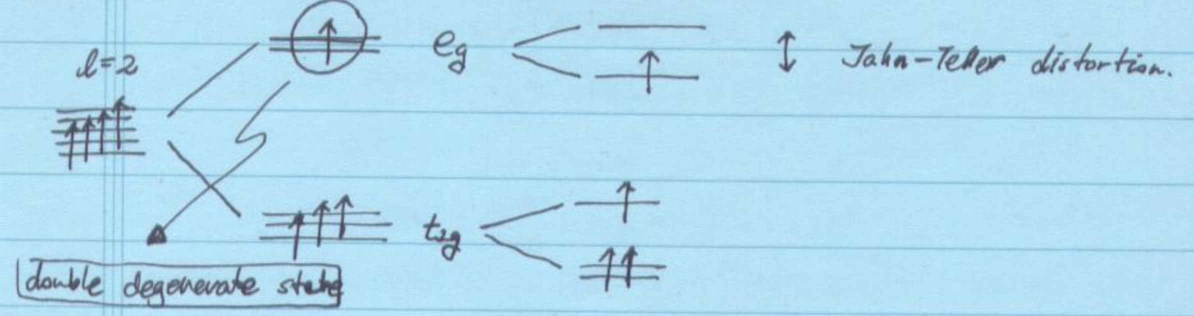
The static Jahn-Teller effect occurs if the lowest energy level of a molecule is degenerate, in which case it will distort spontaneously so as to remove the degeneracy and make one energy level more stable. The proof is technical and difficult, and requires a rather sophisticated application of group theory to quantum mechanics. However, without a complete calculation, the geometric nature and amplitude of the effect cannot be computed.

The following pages are a summary note of this talk.

- Jahn-Teller effect -

* Introduction.

Mn^{3+} $(3d^4)$ under cubic environment.



* Hamiltonian.

$$\mathcal{H}\Psi(r,Q) = E\,\Psi(r,Q) \qquad \text{where } \mathcal{H} = \underbrace{\mathcal{H}_r}_{\text{electronic part}} + \underbrace{\mathcal{H}_Q}_{\text{nuclei kinetic energy}} + V(r,Q)$$

interaction between el & nuclei plus internuclei repulsion.

$$\cancel{\Psi(r,Q) = \sum_k \chi_k(Q)\,\varphi_k(r)}$$

$$V(r,Q) = V(r,0) + \sum_\alpha \left(\frac{\partial V}{\partial Q_\alpha}\right)_0 Q_\alpha + \frac{1}{2}\sum_{\alpha,\beta}\left(\frac{\partial^2 V}{\partial Q_\alpha \partial Q_\beta}\right) Q_\alpha Q_\beta + \cdots$$

→ electronic equation : $[\mathcal{H}_r + V(r,0) - \varepsilon_k'\,]\,\varphi_k(r) = 0.$

→ total wavefunction : $\Psi(r,Q) = \sum_k \chi_k(Q)\,\varphi_k(r)$

→ nuclei equation : $[\mathcal{H}_Q + \varepsilon_k(Q) - E\,]\,\chi_k(Q) + \sum_m{}' W_{km}(Q)\,\chi_m(Q) = 0.$

$$\begin{cases} W(r,Q) = V(r,Q) - V(r,0) = \sum_\alpha \left(\frac{\partial V}{\partial Q_\alpha}\right) Q_\alpha + \frac{1}{2}\sum_{\alpha,\beta}\left(\frac{\partial^2 V}{\partial Q_\alpha \partial Q_\beta}\right) Q_\alpha Q_\beta + \cdots \\ \text{and} \quad \varepsilon_k(Q) = \varepsilon_k' + W_{kk}(Q). \end{cases}$$

→ $[\mathcal{H}_Q + \varepsilon_k(Q) - E\,]\,\chi_k(Q) = 0$: ignore $W_{km}(Q)$ for $k \neq m$.

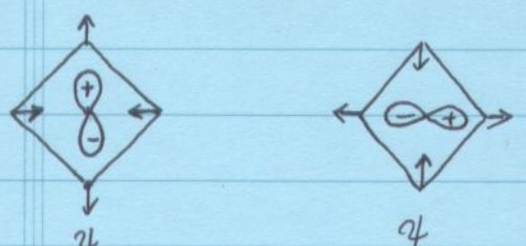
Denoting the symmetrized coordinates by $Q_{\Gamma\gamma}$,

$$W(r,Q) = \sum_{\Gamma\gamma}\left(\frac{\partial V}{\partial Q_{\Gamma\gamma}}\right)_0 Q_{\Gamma\gamma} + \frac{1}{2}\sum_{\Gamma\gamma}\sum_{\Gamma'\gamma'}\left(\frac{\partial^2 V}{\partial Q_{\Gamma\gamma}\partial Q_{\Gamma'\gamma'}}\right)_0 Q_{\Gamma\gamma}Q_{\Gamma'\gamma'} + \cdots.$$

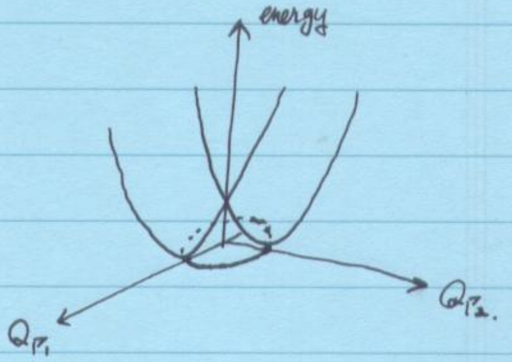
→ Hamiltonian (Γ mode) : $\hat{\mathcal{H}} = \frac{1}{2}(P_{\Gamma\gamma}^2 + \omega_\Gamma^2 Q_{\Gamma\gamma}^2)\,\hat{C}_{A_1} + V_\Gamma Q_{\Gamma\gamma}\,\hat{C}_{\Gamma\gamma}$ up to the 1st order

where $\hat{C}_{A_1} = \begin{pmatrix} 1 & & 0 \\ & \ddots & \\ 0 & & 1 \end{pmatrix}.$

- Jahn-Teller effect in a two fold-degenerate state.



ψ_y $\qquad\qquad$ ψ_x.



$\boxed{E\otimes e}$ — electron (E), lattice (e).

$\psi_\pm \sim e^{\pm i\theta}$ $\qquad Q_\pm \sim e^{\pm 2i\theta}$: coupled mode.

$V(r,Q) \sim V_+(r)\,Q_- + V_-(r)\,Q_+ \implies \sqrt{2}V_E\,(Q_+\hat{\sigma}_- + Q_-\hat{\sigma}_+)$ where $\underbrace{\hat{\sigma}_+ = \begin{pmatrix}0&0\\1&0\end{pmatrix},\ \hat{\sigma}_- = \begin{pmatrix}0&1\\0&0\end{pmatrix}}_{\text{pseudo spin}}$.

→ $E\otimes e$ Jahn-Teller Hamiltonian.

$$* \ \hat{\mathcal{H}} = \underbrace{E_0\hat{\sigma}_0}_{\text{electronic Hamiltonian } \mathcal{H}_e} + \underbrace{\tfrac{1}{2}\left[P_\theta^2 + P_\varepsilon^2 + \omega_\varepsilon^2(Q_\theta^2 + Q_\varepsilon^2)\right]\hat{\sigma}_0}_{\text{ionic vibration } \mathcal{H}_v} + \underbrace{V_E\,(Q_\theta\hat{\sigma}_x + Q_\varepsilon\hat{\sigma}_y)}_{\text{interaction}}$$

$\Psi = \varphi_\pm(r)\,\chi(Q)$. $\longrightarrow$
$$\left|\begin{array}{l} \hat{\mathcal{H}}_e\,\varphi_\pm = E_0\varphi_\pm. \\ \hat{\mathcal{H}}_v\,\chi_n(Q) = \omega_\varepsilon(b_\theta^+ b_\theta + b_\varepsilon^+ b_\varepsilon + 1)\,\hat{\sigma}_0\,\chi_n(Q) = (n+1)\,\omega_E\,\chi_n(Q). \end{array}\right.$$

$\Rightarrow SU(2)\otimes SU(2)$.

transform to the operator form

$Q_\theta = \frac{1}{\sqrt{2\omega_E}}(b_\theta^+ + b_\theta)$, $Q_\varepsilon = \frac{1}{\sqrt{2\omega_\theta}}(b_\varepsilon^+ + b_\varepsilon)$ $\qquad \hat{\sigma}_- = \hat{c}_l^+\hat{c}_r$, $\hat{\sigma}_+ = \hat{c}_r^+\hat{c}_l$.

$$\rightarrow \left\{\begin{array}{l} \hat{\mathcal{H}}_v = \omega_0\,(\hat{n}_\theta + \hat{n}_\varepsilon + 1) \\ \hat{\mathcal{H}}_e = E_0\,(\hat{c}_r^+\hat{c}_r + \hat{c}_l^+\hat{c}_l) = E_0(\hat{n}_r + \hat{n}_l) \\ \hat{V} = \frac{g\omega}{\sqrt{2}}\left[(b_\theta^+ + b_\theta)(\hat{c}_l^+\hat{c}_r + \hat{c}_r^+\hat{c}_l) + i\,(b_\varepsilon^+ + b_\varepsilon)(\hat{c}_l^+\hat{c}_r - \hat{c}_r^+\hat{c}_l)\right] \end{array}\right.$$

where $V_E = g\sqrt{\omega^3 m}$.

$b_r^+ \equiv \frac{1}{\sqrt{2}}(b_\theta^+ + i b_\varepsilon^+)$, $b_l^+ \equiv \frac{1}{\sqrt{2}}(b_\theta^+ - i b_\varepsilon^+)$

$$\rightarrow \bar{\mathcal{H}} = \omega_0\,(\hat{n}_r + \hat{n}_l + 1)_b + E_0(\hat{n}_r + \hat{n}_l)_c - g^2\omega_0\,(n_{cr} - n_{cl})^2 - g^2\omega_0\,\sigma_z L_z$$

where $\sigma_z = n_{cr} - n_{cl}$ $\quad L_z = n_{br} - n_{bl}$.

$$[\mathcal{H}, J_z] = 0 \rightsquigarrow |\psi\rangle = \alpha \underbrace{c_r^+}_{+1/2} |0\rangle + \beta \underbrace{c_\ell^+}_{-1/2} \underbrace{b_r^+}_{+1} |0\rangle \quad = 1/2$$

$$\Rightarrow \psi(r, \theta) = e^{ix} \left(|n_{c_r} = 1\rangle + \underbrace{e^{-i\theta}}_{\text{phonon}} |n_{c_\ell} = 1\rangle \right)$$

$$\left((b_\ell^+)^m |0\rangle = e^{-i\theta m} \right)$$