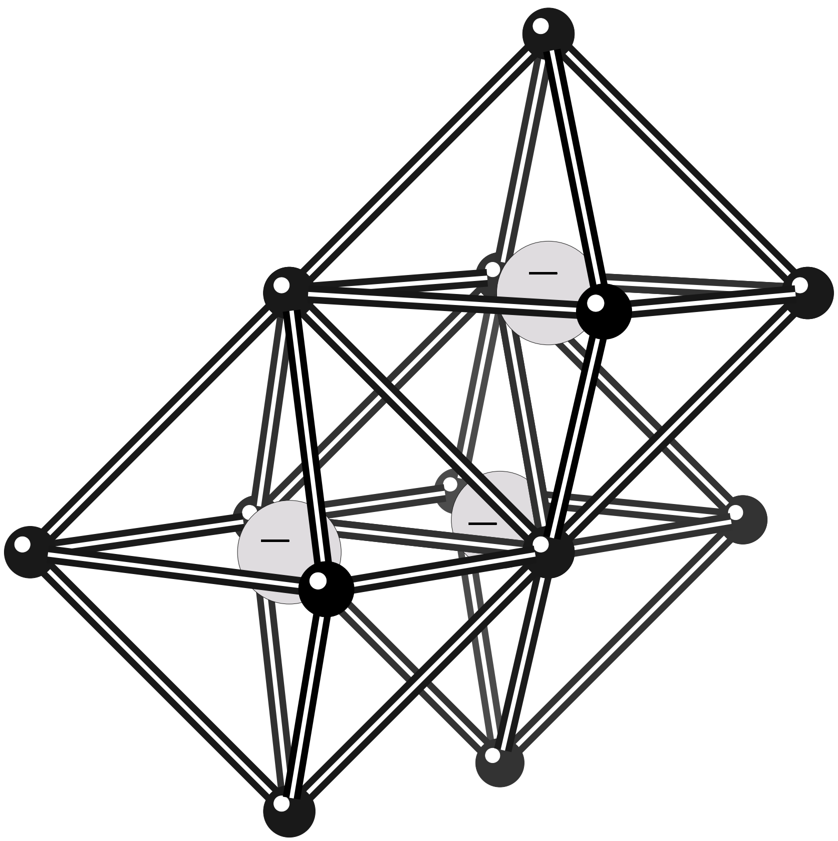
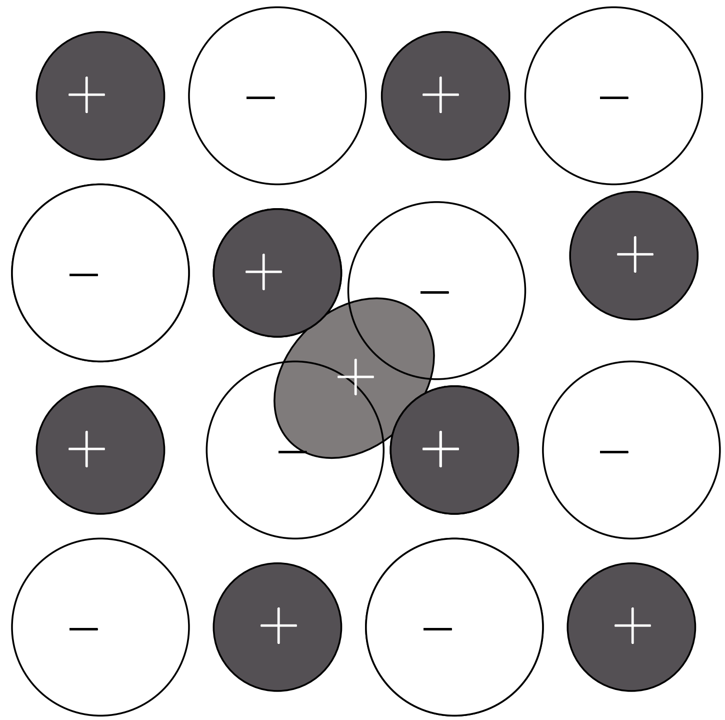
Optical Properties of Insulators

F$_3$ or R center

V$_K$ center



(A)



(B)

Definitions

- ☞ Polarization
- ☞ Optical Modes
- ☞ Polaritons
- ☞ Polarons
- ☞ Point Defects
- ☞ Color Centers
- ☞ Electron Spin Resonance
- ☞ Franck–Condon Effect
- ☞ Urbach Tails

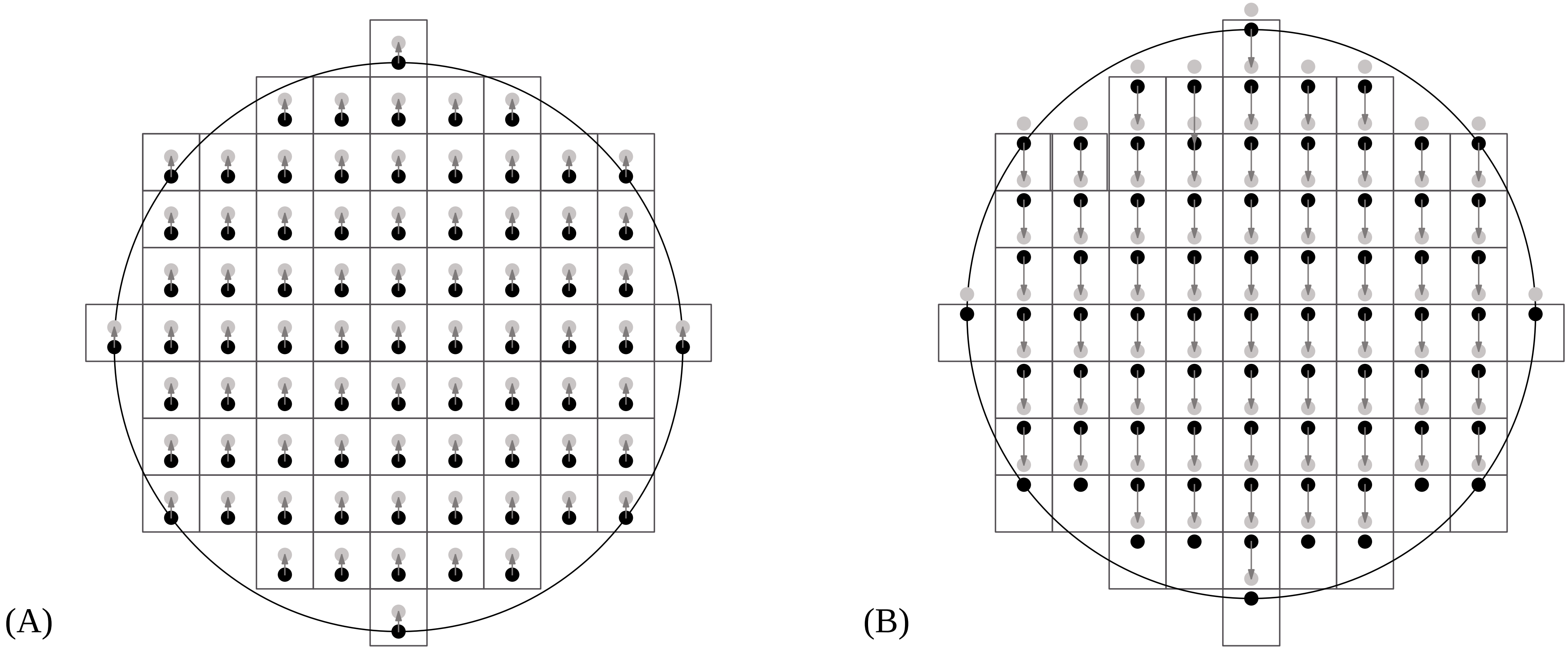


Figure 1: Ambiguity of dielectric

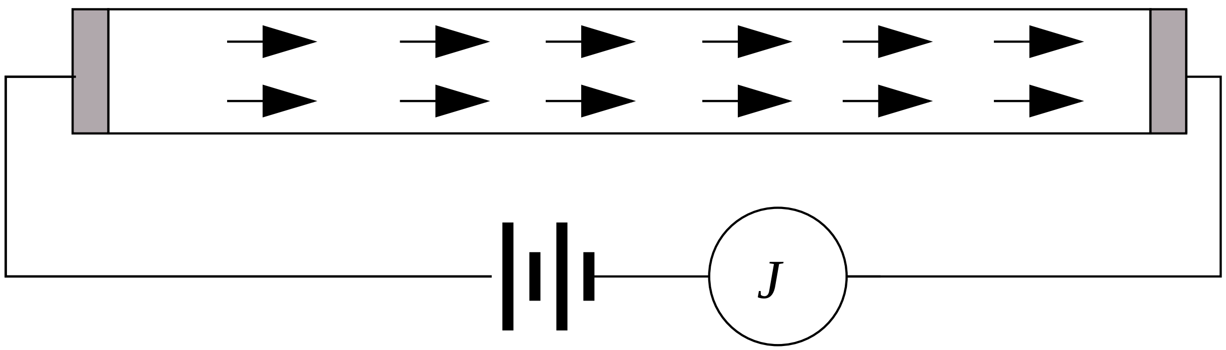


Figure 2: Measuring the spontaneous electric polarization of a sample.

$$\vec{E} = \vec{E}_0 - \frac{4\pi}{3}\vec{P}. \quad \text{(L1)}$$

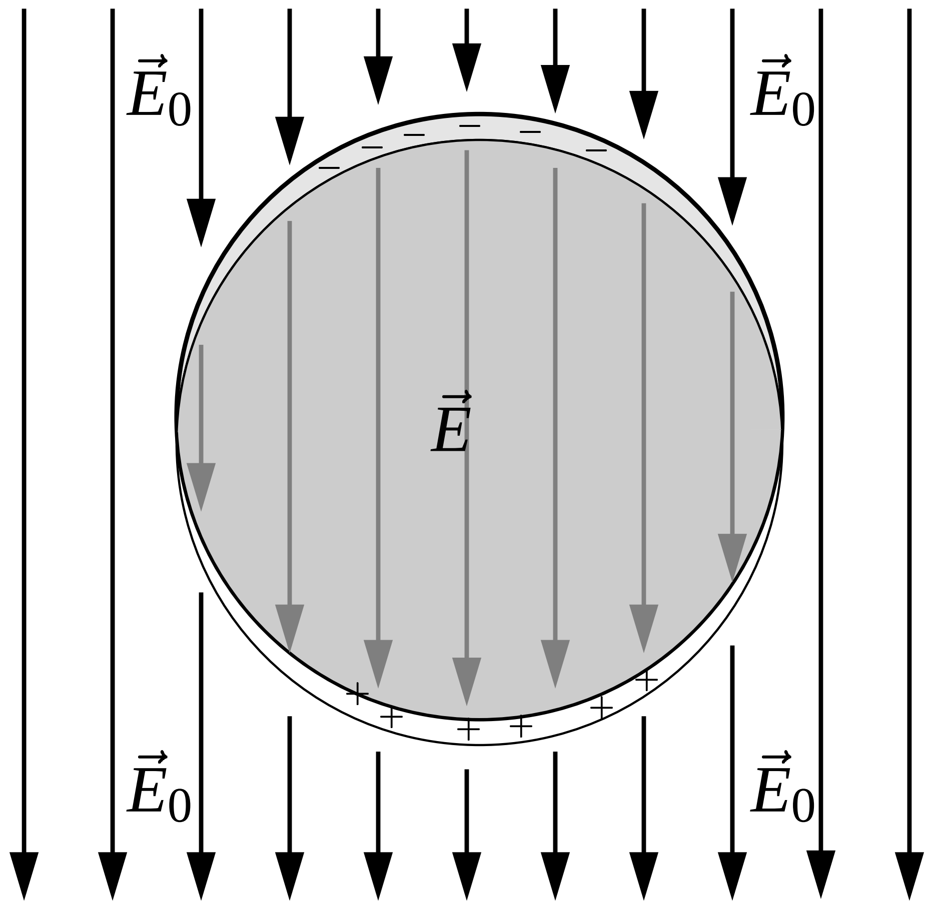


Figure 3: A dielectric sphere placed in a uniform electric field $\vec{E}_0$.

Clausius–Mossotti Relation

$$\vec{E}_1 = -\sum_{\vec{R}\neq 0} \vec{\nabla}_{\vec{R}} \frac{\vec{p}\cdot\vec{R}}{R^3} = \sum_{\vec{R}\neq 0} 3\frac{\vec{R}(\vec{R}\cdot\vec{p})}{R^5} - \frac{\vec{p}}{R^3} \quad \text{(L2)}$$

$$\vec{p} = \alpha\vec{E}_{\text{cell}} \Rightarrow \vec{p} = \alpha\vec{E}_0. \quad \text{(L3)}$$

$$\vec{P} = n\alpha\vec{E}_0. \quad \text{(L4)}$$

$$\frac{E+4\pi P}{E} = \quad ? \qquad ? \quad \text{(L5)}$$

$$\Rightarrow \epsilon = \quad ? \qquad ?. \quad \text{(L6)}$$

$$\vec{E} = \vec{E}_0 - \mathcal{N}\vec{P}, \quad \text{(L7)}$$

Clausius–Mossotti Relation

$$\vec{E}_{\text{cell}} = \vec{E}_0 - \mathcal{N}\vec{P} + \frac{4\pi}{3}\vec{P} = \vec{E} + \frac{4\pi}{3}\vec{P} \tag{L8}$$

$$\Rightarrow \vec{E}_{\text{cell}} = \frac{4\pi}{3}\frac{\epsilon+2}{\epsilon-1}\vec{P} \tag{L9}$$

$$= \frac{4\pi}{3}\frac{\epsilon+2}{\epsilon-1}n\alpha\vec{E}_{\text{cell}} \tag{L10}$$

$$\Rightarrow \alpha = \frac{3}{4\pi n}\left(\frac{\epsilon-1}{\epsilon+2}\right) \tag{L11}$$

$$\Rightarrow \epsilon = \frac{3+8\pi n\alpha}{3-4\pi n\alpha}. \tag{L12}$$

$$\vec{u} = \vec{u}_1 - \vec{u}_2 \tag{L13}$$

$$\bar{\omega} \equiv \sqrt{\frac{2\mathcal{K}}{M}}, \text{ where } M = \frac{M_1 M_2}{(M_1 + M_2)}. \tag{L14}$$

$$M\ddot{\vec{u}} = -M\bar{\omega}^2\vec{u} - M\dot{\vec{u}}/\tau + e^\star \vec{E}_{\text{cell}}. \tag{L15}$$

$$\Rightarrow \vec{u} = -\frac{e^\star}{M(\omega^2 - \bar{\omega}^2 + i\omega/\tau)}\vec{E}_{\text{cell}}. \tag{L16}$$

$$\vec{p} = e^\star \vec{u} + \alpha^\infty \vec{E}_{\text{cell}}. \tag{L17}$$

$$\vec{P} = n\left[\frac{(e^\star)^2}{M(\bar{\omega}^2 - \omega^2 - i\omega/\tau)} + \alpha^\infty\right]\vec{E}_{\text{cell}} \tag{L18}$$

$$\Rightarrow \quad \frac{3}{4\pi}\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = n\left[\frac{(e^\star)^2}{M(\bar{\omega}^2 - \omega^2 - i\omega/\tau)} + \alpha^\infty\right]. \tag{L19}$$

$$\alpha^{\infty} = \frac{3}{4\pi n}\left(\frac{\epsilon^{\infty}-1}{\epsilon^{\infty}+2}\right). \tag{L20}$$

$$\vec{u} = \frac{e^{\star}\vec{E}_{\rm cell}}{M\bar{\omega}^2} \tag{L21}$$

$$(e^{\star})^2 = \frac{9M\bar{\omega}^2}{4\pi n}\left(\frac{\epsilon^0-\epsilon^{\infty}}{(\epsilon^0+2)(\epsilon^{\infty}+2)}\right). \tag{L22}$$

$$\epsilon(\omega) = \epsilon^{\infty} + \frac{\epsilon^{\infty}-\epsilon^0}{\left(\frac{\omega^2}{\bar{\omega}^2}+i\frac{\omega}{\tau\bar{\omega}^2}\right)\left(\frac{\epsilon^0+2}{\epsilon^{\infty}+2}\right)-1}. \tag{L23}$$

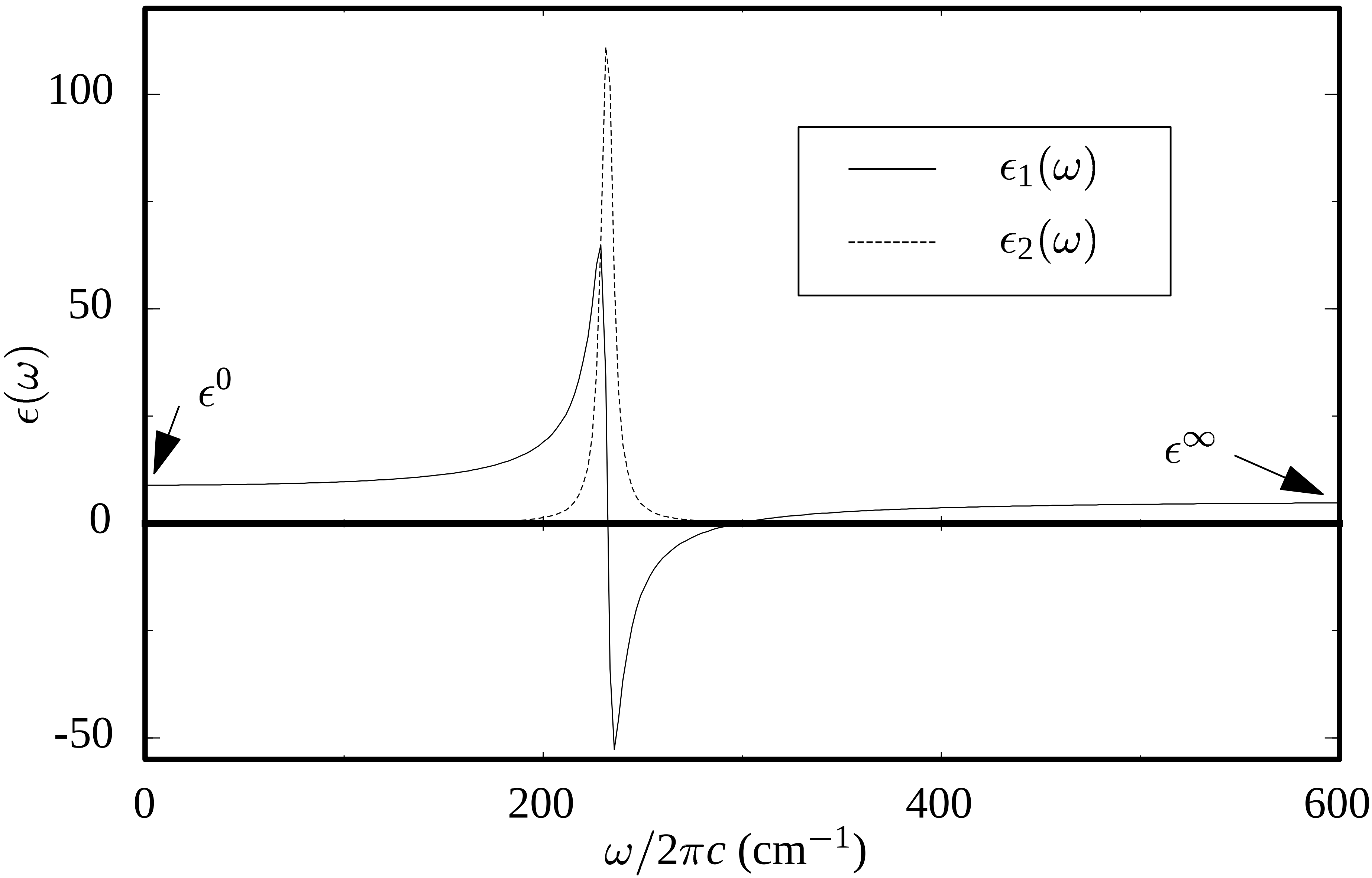


Figure 4: Dielectric function for CdS, deduced from reflection data by Balkanski (1972).

$$\omega_T^2 = \bar{\omega}^2 \left(\frac{\epsilon^\infty + 2}{\epsilon^0 + 2} \right) \tag{L24}$$

$$\omega_{\rm L}^2 = \omega_{\rm T}^2 \left[\frac{\epsilon^0}{\epsilon^\infty} \right] \tag{L25}$$

$$\Rightarrow \epsilon(\omega) = \epsilon^\infty \left[\frac{\omega^2 + i\omega/\tau - \omega_{\rm L}^2}{\omega^2 + i\omega/\tau - \omega_{\rm T}^2} \right]. \tag{L26}$$

$$\frac{\omega^2 \epsilon(\omega)}{c^2} = q^2, \tag{L27}$$

$$\epsilon(\omega) = 0. \tag{L28}$$

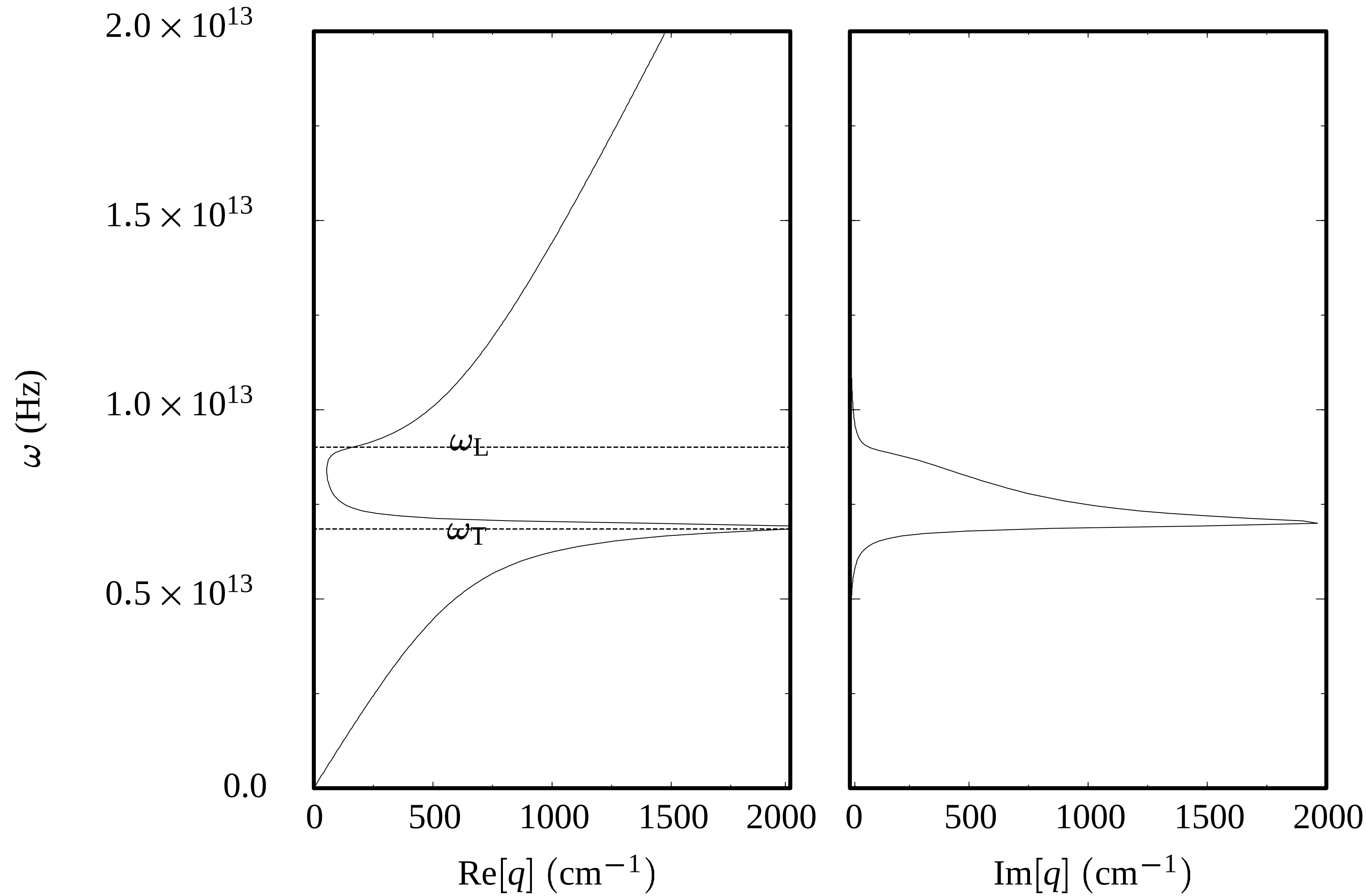


Figure 5: Frequency ω of transverse waves as a function of complex wave vector q.

Compound	ϵ^{∞}	ϵ^{0}	$\frac{\omega_T}{2\pi c}$ (cm^{-1})	$\frac{\omega_L}{2\pi c}$ (cm^{-1})	$\frac{m^\star}{m}$	α_p	$\frac{m^\star}{m}(1+\frac{\alpha_p}{6})$	$\frac{m^\star_{pol}}{m}$
LiF	1.93	8.50	318	667				
LiH	3.60	12.90	590	1116				
NaF	1.75	4.73	262	431				
NaI	3.08	6.60	124	182				
KF	1.86	5.11	202	334				
KI	2.68	4.68	102	144	0.325	2.51	0.461	0.540
RbF	1.94	5.99	163	286				
RbI	2.61	4.55	76	108	0.368	3.16	0.562	0.720
CsF	2.17	7.27	134	245				
CsCl	2.67	6.68	107	168				
CsBr	2.83	6.38	78	118				
CsI	3.09	6.32	66	94	0.420	3.67	0.677	0.960
GaAs	10.90	12.83	273	296	0.066	0.07	0.067	0.066
GaSb	14.40	15.69	231	240	0.047	0.03	0.047	0.047
GaP	8.46	10.28	365	403	0.338	0.20	0.349	0.350
InAs	11.80	14.61	219	243	0.023	0.05	0.023	0.023
InSb	15.68	17.88	185	197	0.014	0.02	0.014	0.013
CdS	5.27	8.42	244	308	0.155	0.53	0.169	0.170
CdSe	6.10	9.30	174	214	0.130	0.46	0.140	0.140
CdTe	7.21	10.23	141	168	0.091	0.32	0.096	0.096
ZnS	5.14	8	282	352	0.280	0.65	0.310	0.313
ZnSe	5.90	8.33	207	246	0.171	0.43	0.183	0.184
ZnTe	7.28	9.86	177	205	0.160	0.33	0.169	0.169
ZnO	4	8.15	414	591	0.240	0.85	0.274	0.279
PbS	18.50	190	67	214	0.082	0.32	0.086	0.087
PbSe	25.20	280	44	147	0.047	0.21	0.049	0.049
PbTe	36.90	450	32	110	0.034	0.15	0.035	0.035

$$\vec{P} = n[e^\star \vec{u} + \alpha^\infty \vec{E}_{\rm cell}]. \tag{L29}$$

$$\vec{E} = -4\pi \vec{P}, \tag{L30}$$

$$\vec{E}_{\rm cell} = \frac{2}{3}\vec{E} = -\frac{8\pi}{3}\vec{P} \tag{L31}$$

$$\Rightarrow \vec{P} = \frac{ne^\star}{1 + n\alpha^\infty 8\pi/3}\vec{u}. \tag{L32}$$

$$\frac{ne^\star}{1 + n\alpha^\infty 8\pi/3} = n\frac{\sqrt{\frac{9M\bar{\omega}^2}{4\pi n}\frac{\epsilon^0 - \epsilon^\infty}{(\epsilon^0 + 2)(\epsilon^\infty + 2)}}}{1 + 2(\epsilon^\infty - 1)/(\epsilon^\infty + 2)} \tag{L33}$$

$$= \sqrt{\frac{M\omega_{\rm L}^2 n}{4\pi}\left(\frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0}\right)}. \tag{L34}$$

$$\vec{P} = \beta\vec{u}, \tag{L35}$$

$$\beta = \sqrt{\frac{M\omega_L^2 n}{4\pi}\left(\frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0}\right)}. \tag{L36}$$

$$\hat{U}_{\text{el-phon}} = e\int d\vec{r}'\,\vec{P}(\vec{r}')\cdot\nabla_{\vec{r}'}\frac{1}{|\hat{R}-\vec{r}'|}. \tag{L37}$$

$$\hat{U}_{\text{el-phon}} = e\beta\int d\vec{r}'\sqrt{\frac{\hbar}{2M\omega_L N}}\sum_{\vec{k}}\frac{\vec{k}}{k}\cdot\left[\nabla_{\vec{r}'}\frac{1}{|\vec{r}'-\hat{R}|}\right][e^{i\vec{k}\cdot\vec{r}'}\hat{a}_{\vec{k}} + e^{-i\vec{k}\cdot\vec{r}'}\hat{a}^\dagger_{\vec{k}}] \tag{L38}$$

$$= -e\beta\int d\vec{r}'\sqrt{\frac{\hbar}{2M\omega_L N}}\sum_{\vec{k}}\frac{i\vec{k}\cdot\vec{k}}{k}\frac{1}{|\vec{r}'-\hat{R}|}[e^{i\vec{k}\cdot\vec{r}'}\hat{a}_{\vec{k}} - e^{-i\vec{k}\cdot\vec{r}'}\hat{a}^\dagger_{\vec{k}}]. \tag{L39}$$

$$\hat{U}_{\text{el-phon}} = e\beta 4\pi i\sum_{\vec{k}}\sqrt{\frac{\hbar}{2M\omega_L N}}\frac{1}{k}[e^{-i\vec{k}\cdot\hat{R}}\hat{a}^\dagger_{\vec{k}} - e^{i\vec{k}\cdot\hat{R}}\hat{a}_{\vec{k}}]. \tag{L40}$$

Polarons

$$\alpha_{\rm p} \equiv \frac{e^2}{2}\sqrt{\frac{2m^\star\omega_L}{\hbar}}\frac{1}{\hbar\omega_L}\left(\frac{1}{\epsilon^\infty}-\frac{1}{\epsilon^0}\right) = 1.44\cdot 10^8\left(\frac{1}{\epsilon^\infty}-\frac{1}{\epsilon^0}\right)\sqrt{\frac{m^\star/m}{\omega_{\rm L}\cdot{\rm s}}}. \tag{L41}$$

$$\hat{U}_{\rm el-phon} = i\sqrt{4\pi\alpha_{\rm p}}\frac{1}{\sqrt{\mathcal{V}}}\left(\frac{\hbar^5\omega_L^3}{2m^\star}\right)^{1/4}\sum_{\vec{k}}\frac{1}{k}[e^{-i\vec{k}\cdot\hat{R}}\hat{a}^\dagger_{\vec{k}} - e^{i\vec{k}\cdot\hat{R}}\hat{a}_{\vec{k}}]. \tag{L42}$$

$$\hat{U}_{\rm el-phon} = \sum_{\vec{q}\vec{q}'}\hat{c}^\dagger_{\vec{q}'}\langle\vec{q}'|\hat{U}_{\rm el-phon}|\vec{q}\rangle\hat{c}_{\vec{q}} \tag{L43}$$

$$\hat{U}_{\rm el-phon} = i\sqrt{4\pi\alpha_{\rm p}}\frac{1}{\sqrt{\mathcal{V}}}\left(\frac{\hbar^5\omega_L^3}{2m^\star}\right)^{1/4}\sum_{\vec{q}''\vec{k}}\frac{1}{k}[\hat{c}^\dagger_{\vec{q}''-\vec{k}}\hat{c}_{\vec{q}''}\hat{a}^\dagger_{\vec{k}} - \hat{c}^\dagger_{\vec{q}''+\vec{k}}\hat{c}_{\vec{q}''}\hat{a}_{\vec{k}}]. \tag{L44}$$

$$\Delta\mathcal{E}^{(2)} = \sum_{\Phi'\vec{q}'}\frac{|\langle\vec{q}|\langle\Phi_0|\hat{U}_{\rm el-phon}|\Phi'\rangle|\vec{q}'\rangle|^2}{\mathcal{E}(\vec{q},\Phi_0)-\mathcal{E}(\vec{q}',\Phi')}. \tag{L45}$$

$$\Delta\mathcal{E}^{(2)} = 4\pi\alpha_p \frac{1}{\mathcal{V}}\sqrt{\frac{\hbar^5\omega_L^3}{2m^\star}} \sum_{\vec{q}'} \frac{1}{|\vec{q}-\vec{q}'|^2}\left[\frac{1}{\frac{\hbar^2 q^2}{2m^\star} - \left(\frac{\hbar^2 q'^2}{2m^\star} + \hbar\omega_L\right)}\right] \tag{L46}$$

$$= 4\pi\alpha_p \frac{1}{\mathcal{V}}\sqrt{\frac{\hbar^5\omega_L^3}{2m^\star}} \int dq' \frac{d(\cos\theta)}{(2\pi)^3} \frac{2\pi\mathcal{V}}{\frac{\hbar^2 q^2}{2m^\star} - \left(\frac{\hbar^2|\vec{q}'+\vec{q}|^2}{2m^\star} + \hbar\omega_L\right)} \tag{L47}$$

$$= \frac{\alpha_p}{\pi}\sqrt{\frac{\hbar^5\omega_L^3}{2m^\star}} \int_{-1}^{1} ds \int_0^\infty dq' \frac{1}{\frac{\hbar^2 q^2}{2m^\star} - \left(\frac{\hbar^2(q'^2+q^2+2qq's)}{2m^\star} + \hbar\omega_L\right)} \tag{L48}$$

$$= -\alpha_p\sqrt{m^\star\hbar\omega_L^3}\frac{\sqrt{2}}{q}\sin^{-1}\sqrt{\frac{\hbar^2 q^2}{2m^\star\hbar\omega_L}}. \tag{L49}$$

$$\Delta\mathcal{E}^{(2)} = -\alpha_p\hbar\omega_L - \alpha_p\frac{\hbar^2 q^2}{12m^\star}. \tag{L50}$$

Polarons

$\frac{m^\star_{\rm pol}}{m^\star} = 1 + \frac{\alpha_{\rm p}}{6}$. Table of data.

$$\Delta\mathcal{E}^{(2)} = -\alpha_{\rm p}\sqrt{m^\star\hbar\omega_{\rm L}^3}\frac{\sqrt{2}}{q}\left[\pi/2 + i\cosh^{-1}\sqrt{\frac{\hbar^2q^2}{2m^\star\hbar\omega_{\rm L}}}\right]. \tag{L51}$$

$$\exp\left[-\frac{i}{\hbar}(\mathcal{E}^{(0)} + \Delta\mathcal{E}^{(2)})t\right], \tag{L52}$$

$$\exp\left[\frac{2}{\hbar}\mathrm{Im}(\Delta\mathcal{E}^{(2)})t\right]. \tag{L53}$$

$$2\alpha_{\rm p}\sqrt{m^\star\hbar\omega_{\rm L}^3}\frac{\sqrt{2}}{\hbar q}\cosh^{-1}\sqrt{\frac{\hbar^2q^2}{2m^\star\hbar\omega_{\rm L}}}. \tag{L54}$$

Vacancies

Crystal	Cohesive Energy $\mathcal{E}/N$ (eV)	Vacancy Energy (eV)
Na	1.16	0.42
Au	3.8	0.97
Al	3.4	0.76
Pt	5.3	1.4
Ne	0.021	0.020
Kr	0.11	0.077
Ge	3.9	2.0

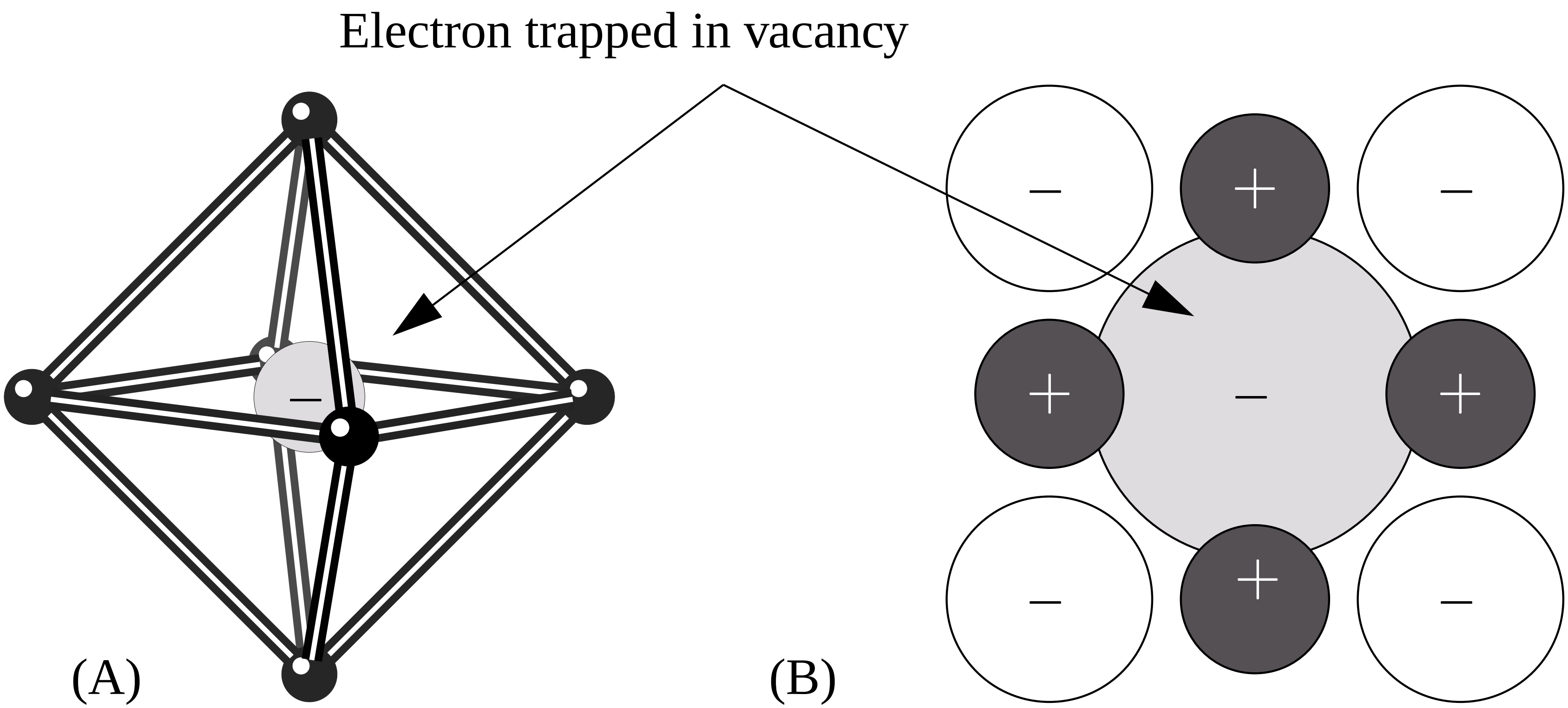


Figure 6: The F center is a halogen ion vacancy that has trapped an electron.

F Centers

Compound	$\mathcal{E}_{abs}$ (eV)	$\mathcal{E}_{em}$ (eV)	Compound	$\mathcal{E}_{abs}$ (eV)	$\mathcal{E}_{em}$ (eV)
NaF	3.72	1.67	RbCl	2.05	1.09
NaCl	2.77	0.98	RbBr	1.86	0.87
KF	2.85	1.66	RbI	1.71	0.81
KCl	2.31	1.22	CsF	1.89	1.42
KBr	2.06	0.92	CsCl	2.17	1.26
KI	1.87	0.83	CsBr	1.96	0.91
RbF	2.43	1.33	CsI	1.68	0.74

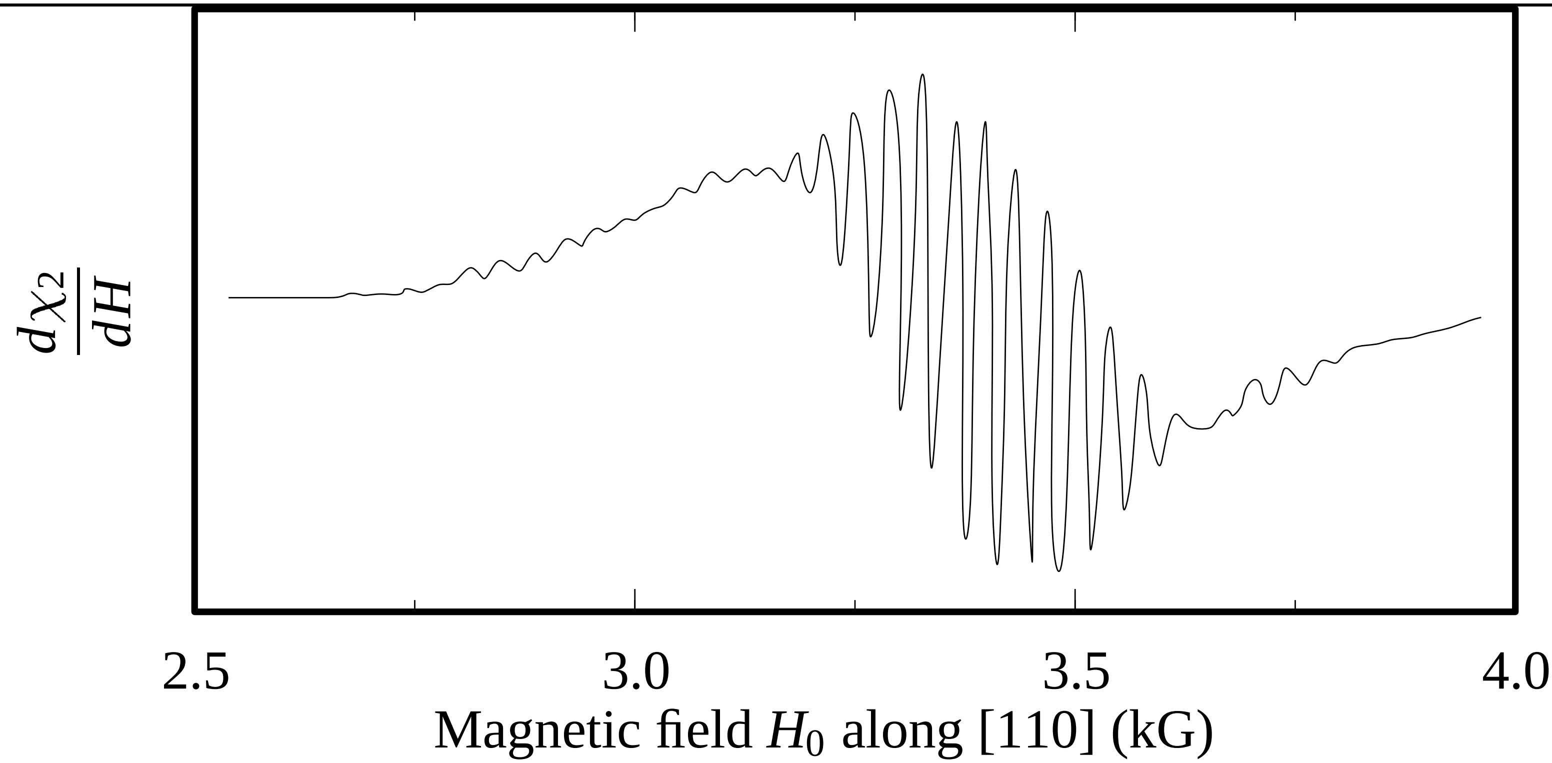


Figure 7: Electron spin resonance in RbCl F centers at a temperature of 90 K. [Source: Pick (1972)]

$$\vec{B} = \vec{B}_0 + \sum_l \vec{B}_l, \tag{L55}$$

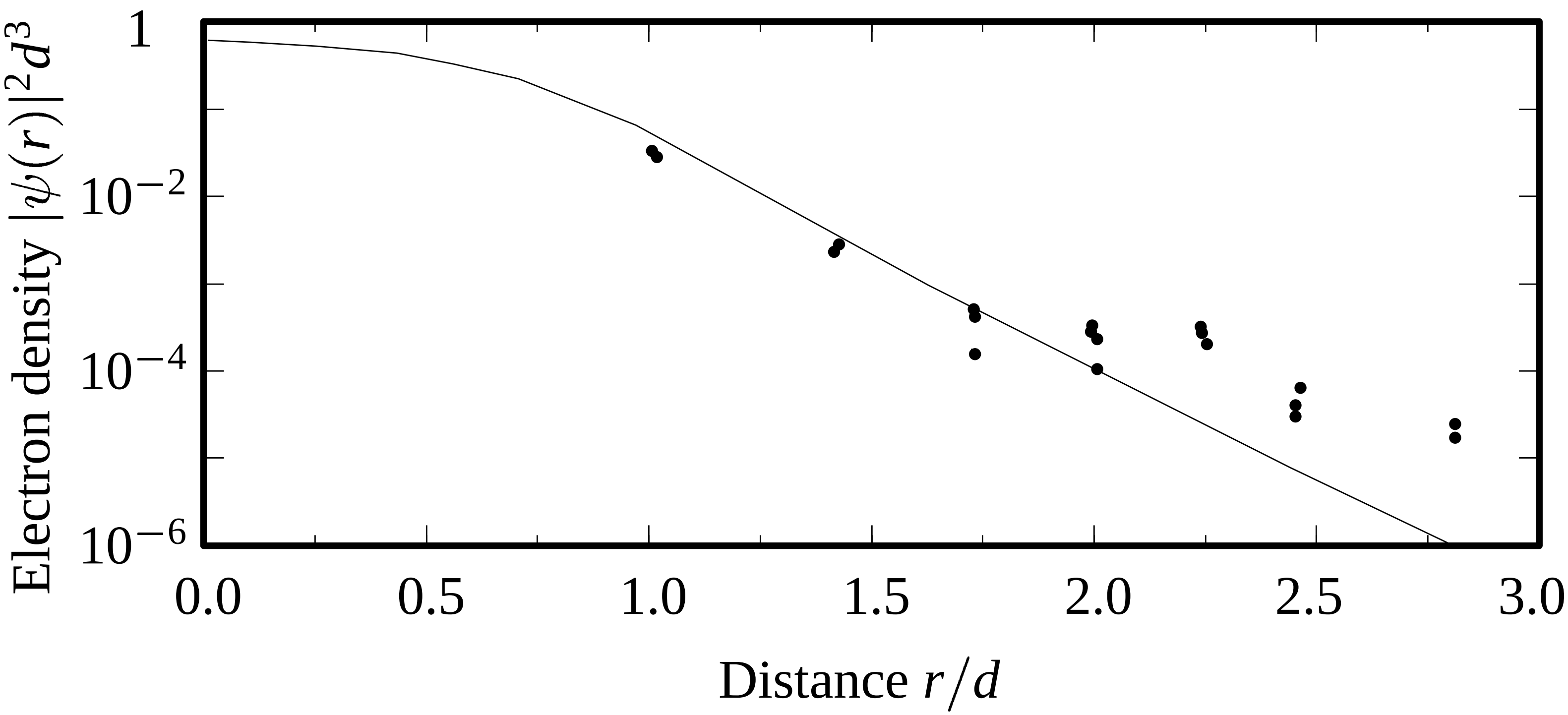


Figure 8: Electron density versus distance from vacancy center [Seidel and Wolf (1968)]

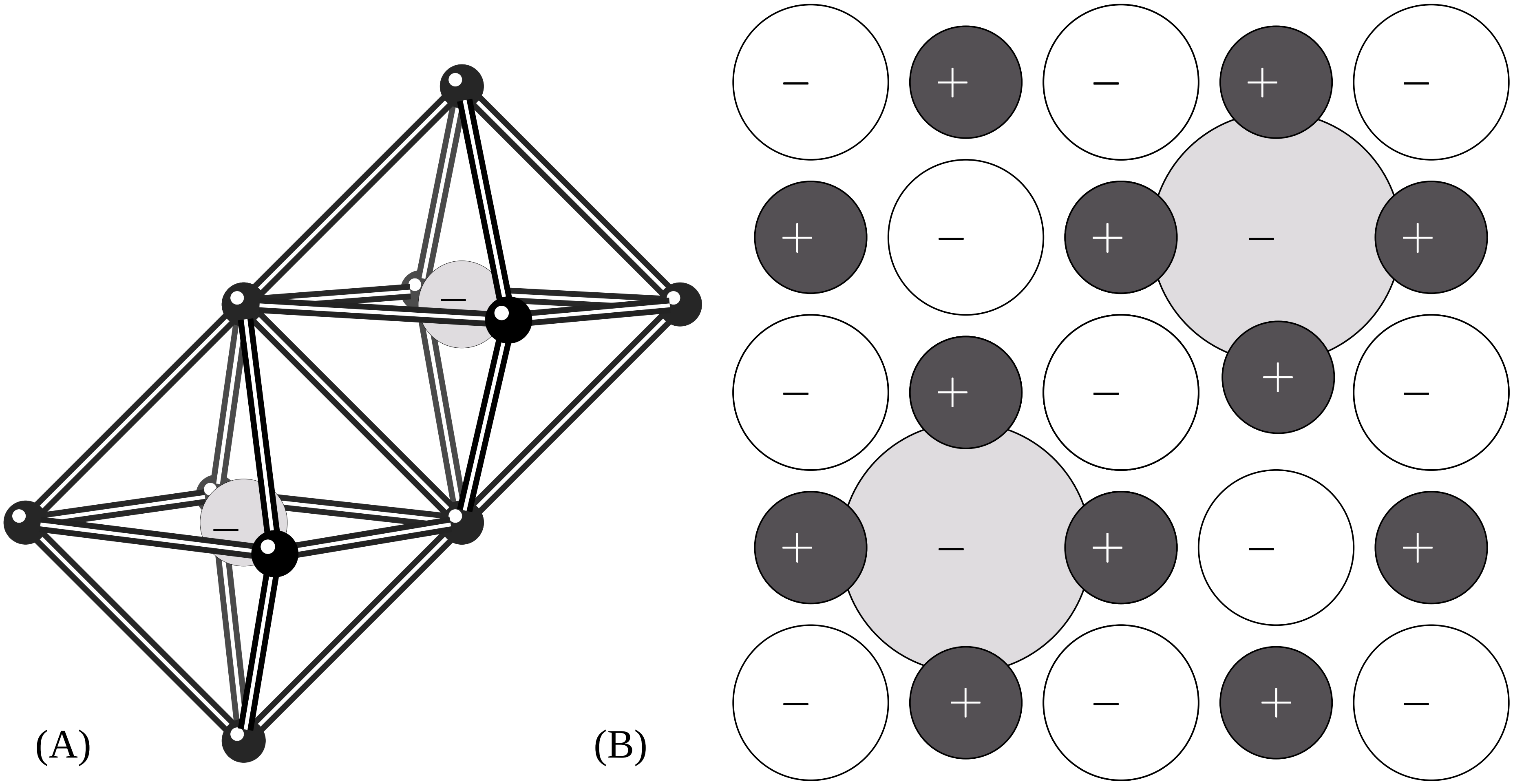


Figure 9: The F_2 or M center.

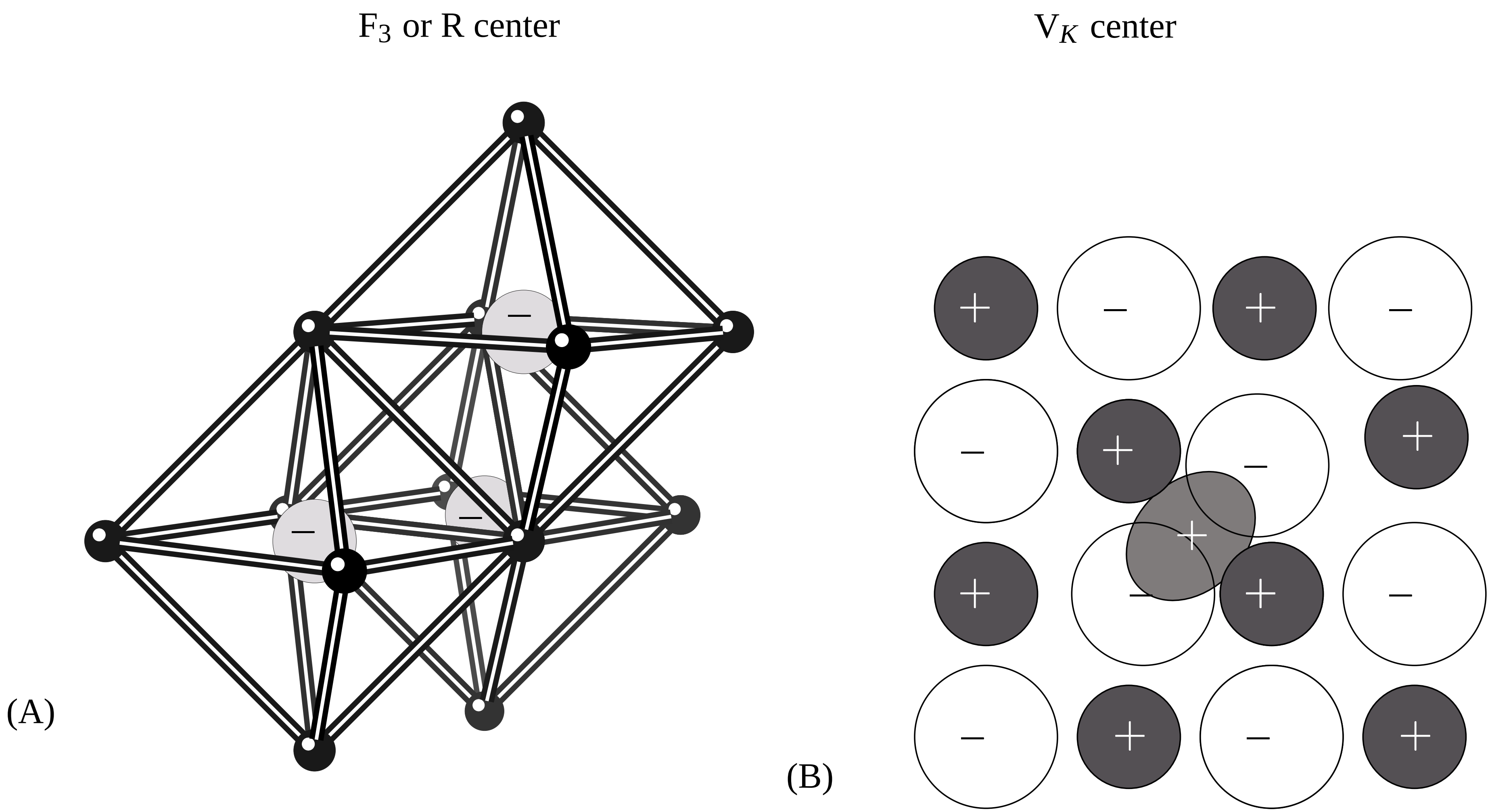


Figure 10: F_3 center [Lüty (1961)]

Franck–Condon Effect

$$\hat{\mathcal{H}}_{\rm F}|F_0\rangle = \mathcal{E}_0|F_0\rangle = 0 \quad \text{(L56a)}$$

$$\hat{\mathcal{H}}_{\rm F}|F_1\rangle = \mathcal{E}_1|F_1\rangle. \quad \text{(L56b)}$$

$$\hat{\mathcal{H}}_{\rm ion} = \frac{\hat{P}^2}{2M} + \frac{M\omega_{\rm i}^2}{2}\hat{x}^2. \quad \text{(L57)}$$

$$\hat{\mathcal{H}}_{\rm int} = g\hat{x}\hat{\mathcal{H}}_{\rm F}, \quad \text{(L58)}$$

$$\left\{\hat{\mathcal{H}}_{\rm F}(1+g\hat{x}) + \hat{\mathcal{H}}_{\rm ion}\right\}|\psi\rangle = \mathcal{E}_{\rm tot}|\psi\rangle. \quad \text{(L59)}$$

$$\phi_l(x) \equiv \langle x, \mathcal{E}_l|\psi\rangle. \quad \text{(L60)}$$

$$\left\{\mathcal{E}_l(1+gx) + \frac{-\hbar^2\nabla^2}{2M} + \frac{M\omega_{\rm i}^2}{2}x^2\right\}\phi_l(x) = \mathcal{E}_{\rm tot}\phi_l(x). \quad \text{(L61)}$$

Franck–Condon Effect

$$\mathcal{D}_l = \frac{\mathcal{E}_l g}{M\omega_\mathrm{i}^2}. \tag{L62}$$

$$\left\{\mathcal{E}_l + \frac{-\hbar^2\nabla^2}{2M} + \frac{M\omega_\mathrm{i}^2}{2}\left[(x+\mathcal{D}_l)^2 - \mathcal{D}_l^2\right]\right\}\phi_l(x) = \mathcal{E}_\mathrm{tot}\phi_l(x). \tag{L63}$$

$$\mathcal{E}_{l,n} = \mathcal{E}_l + \hbar\omega_\mathrm{i}(n+\tfrac{1}{2}) - \tfrac{1}{2}\mathcal{D}_l^2 M\omega_\mathrm{i}^2. \tag{L64}$$

Franck–Condon Effect

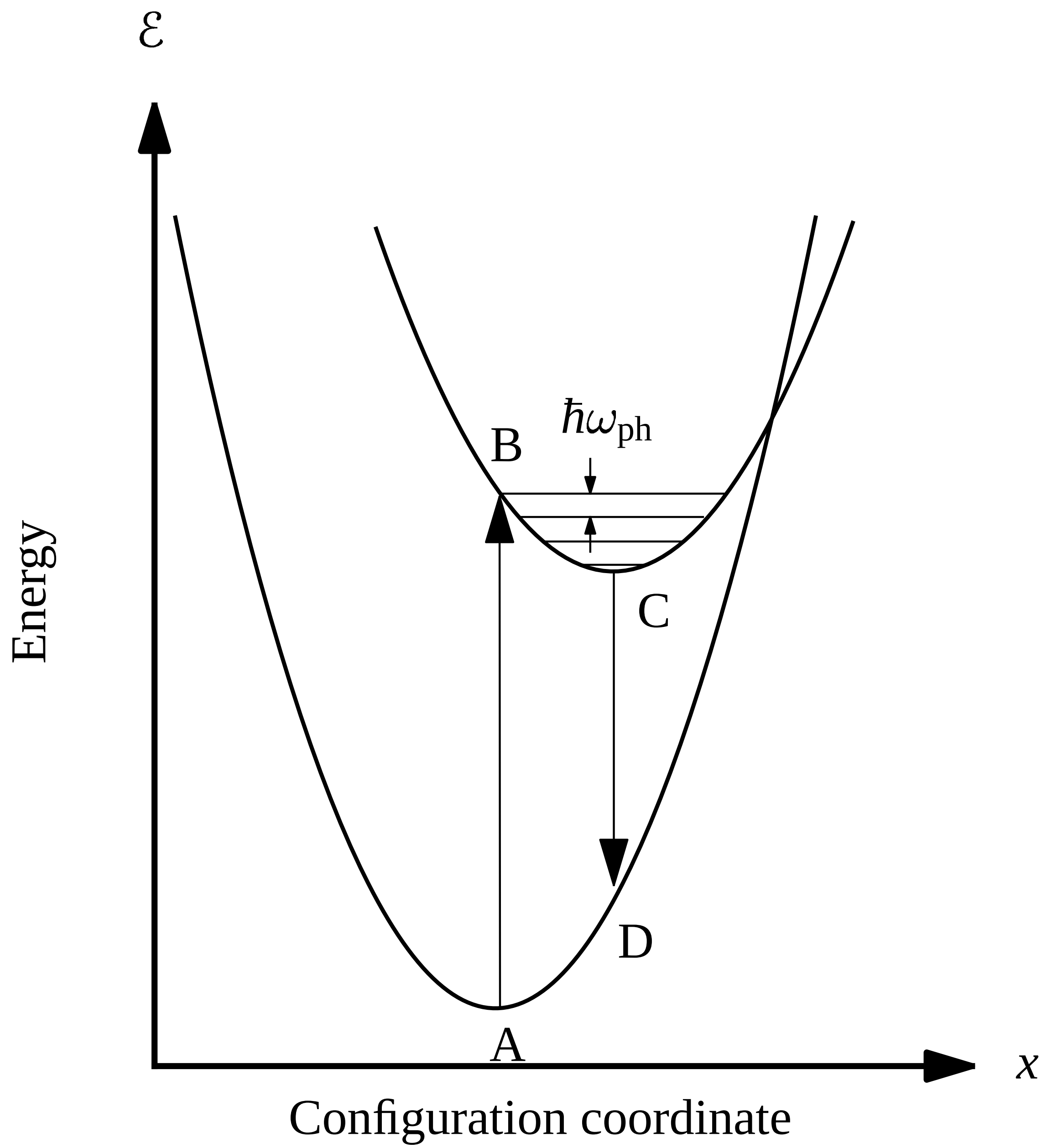


Figure 11: Franck–Condon effect

$$\sum_{\text{final}} \delta(\mathcal{E}_{\text{tot,final}} - \mathcal{E}_{\text{tot},0} - \hbar\omega) |\langle\psi_0|\hat{U}_{\text{int}}|\psi_{\text{final}}\rangle|^2, \tag{L65}$$

$$\hbar\omega = \mathcal{E}_1 + n\hbar\omega_{\text{i}} - \tfrac{1}{2}\mathcal{D}_1^2 M\omega_{\text{i}}^2, \tag{L66}$$

$$|\int dx\, \phi_0(x)\phi_n(x+\mathcal{D}_1)|^2. \tag{L67}$$

$$x_0 = \sqrt{\frac{\hbar}{M\omega_{\text{i}}}} \gg \mathcal{D}_1 \tag{L68}$$

$$\Rightarrow 1 \gg \frac{\mathcal{E}_1 g}{\sqrt{\hbar M\omega_{\text{i}}^3}}. \tag{L69}$$

$$\mathcal{D}_1 \gg x_0, \tag{L70}$$

Franck–Condon Effect

$$\int dx\, \phi_0(x)\phi_n(x+\mathcal{D}_1) \tag{L71}$$

$$= \int d\chi \sqrt{\frac{1}{\pi 2^n n!}} e^{\chi \mathcal{D}_1/x_0 - (\mathcal{D}_1/x_0)^2/2} (-1)^n \frac{d^n}{d\chi^n} e^{-\chi^2} \tag{L72}$$

$$= \int d\chi \sqrt{\frac{1}{\pi 2^n n!}} \left(\frac{\mathcal{D}_1}{x_0}\right)^n e^{\chi \mathcal{D}_1/x_0 - (\mathcal{D}_1/x_0)^2/2} e^{-\chi^2} \tag{L73}$$

$$= \sqrt{\frac{1}{2^n n!}} \left(\frac{\mathcal{D}_1}{x_0}\right)^n e^{-(\mathcal{D}_1/x_0)^2/4}. \tag{L74}$$

$$n = \tfrac{1}{2}(\mathcal{D}_1/x_0)^2. \tag{L75}$$

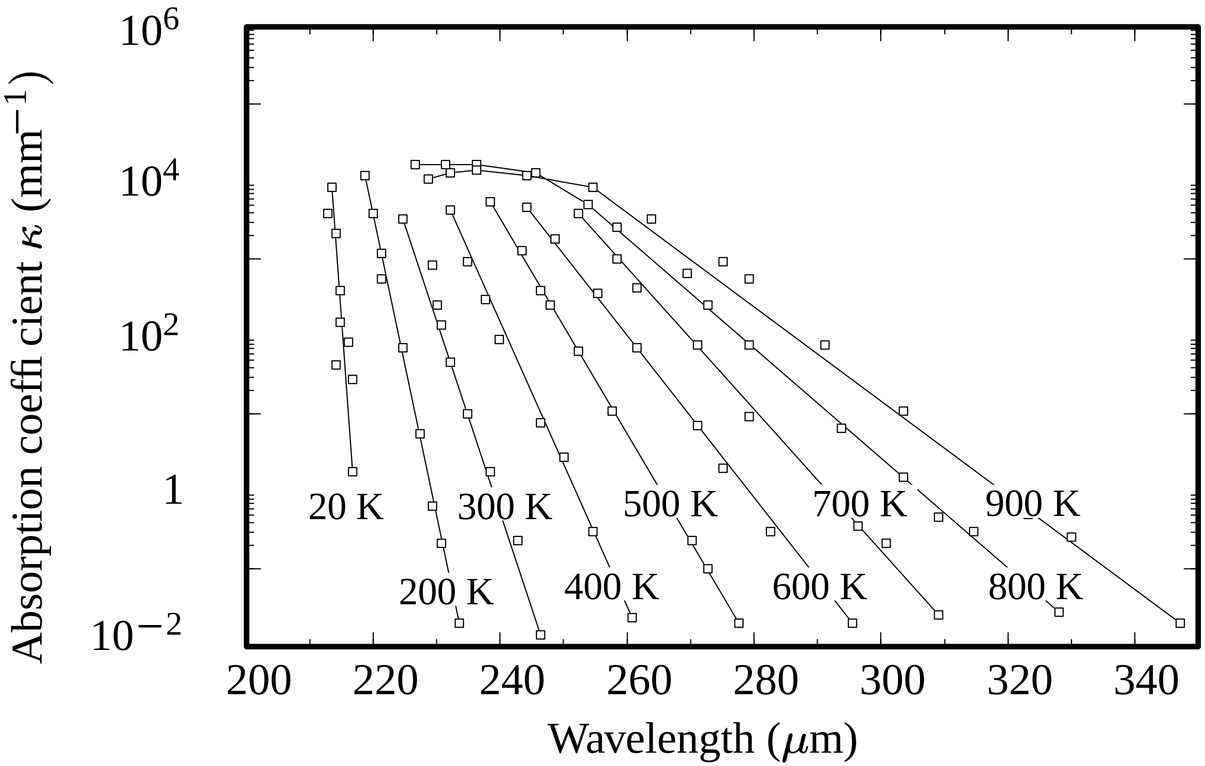


Figure 12: Urbach tails [Haupt (1959)]

$$\alpha \propto \exp\left[-\frac{(\mathcal{E}_g - \hbar\omega)}{k_B T}\right]. \qquad \text{(L76)}$$