Electron-phonon coupling: a tutorial

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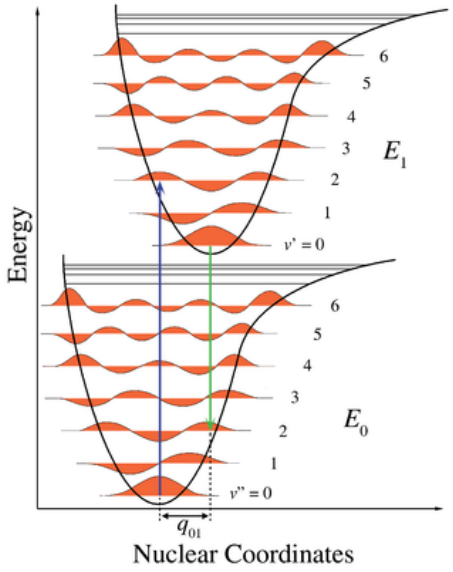

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TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

OPTIMAS

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   - real space
   - energy basis

2. 1D lattice vibrations
   - one atom per primitive cell
   - two atoms per primitive cells

3. Electron-phonon interactions
   - localized electrons
   - small-polaron theory
   - phonons in metals

4. Superconductivity

5. A numerical example: CO

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3) Electron-phonon interaction: Hamiltonian

The basic interaction Hamiltonian is $H = H_p + H_e + H_{ei}$

$$H_p = \sum_{q\lambda} \omega_{q\lambda} \left(a^+_{q\lambda} a_{q\lambda} + 1/2 \right) \qquad H_e = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} e^2 \sum_{ij} \frac{1}{r_{ij}} \qquad H_{ei} = \sum_i \tilde{V}(\vec{r}_i) = \sum_{ij} V_{ei}(\vec{r}_i - \vec{R}_j)$$

Taylor series expansion for the displacements

$$V_{ei}(\vec{r}_i - \vec{R}_j^{(0)} - Q_j) = V_{ei}(\vec{r}_i - \vec{R}_j^{(0)}) - \vec{Q}_j \bullet \nabla V_{ei}(\vec{r}_i - \vec{R}_j^{(0)}) + O(Q^2)$$

the electron-phonon interaction reads $\tilde{V}(\vec{r}) = \sum_j \vec{Q}_j \bullet \nabla V_{ei}(\vec{r}_i - \vec{R}_j^{(0)})$

and the Fourier transform of the potential

$$V_{ei}(\vec{r}) = \frac{1}{N} \sum_q V_{ei}(\vec{q}) e^{i\vec{q}\cdot\vec{r}} \qquad \Rightarrow \qquad \nabla V_{ei}(\vec{r}) = i \frac{1}{N} \sum_q \vec{q} V_{ei}(\vec{q}) e^{i\vec{q}\cdot\vec{r}}$$

3) Electron-phonon interaction: Hamiltonian

we need to calculate

$$\tilde{V}(\vec{r}) = \frac{i}{N}\sum_{q}\vec{q}V_{ei}(\vec{q})e^{i\vec{q}\cdot\vec{r}}\left(\sum_{j}\vec{Q}_j e^{i\vec{q}\cdot\vec{R}_j^{(0)}}\right)$$

by using

$$\frac{i}{N}\sum_{j}\vec{Q}_j e^{i\vec{q}\cdot\vec{R}_j^{(0)}} = \frac{i}{N^{1/2}}\sum_{G}\vec{Q}_{\vec{q}+\vec{G}} = -\sum_{G}\left(\frac{\hbar}{2MN\omega_{\vec{q}+\vec{G}}}\right)^{1/2}\xi_{q+G}\left(a_{\vec{q}+\vec{G}} + a^{+}_{-\vec{q}-\vec{G}}\right)$$

and

$$MN = \rho\nu$$

we can write the Hamiltonian in the form

$$\tilde{V}(\vec{r}) = -\sum_{q,G}e^{i\vec{r}\cdot(\vec{q}+\vec{G})}V_{ei}(\vec{q}+\vec{G})(\vec{q}+\vec{G})\cdot\xi_{\vec{q}}\left(\frac{\hbar}{2\rho\omega_q\nu}\right)^{1/2}\left(a_{\vec{q}} + a^{+}_{-\vec{q}}\right)$$

3) Electron-phonon interaction: Hamiltonian

by integrating the potential over the charge density of the solid

$$H_{ep} = \int d^3 r \rho(\vec{r}) \tilde{V}(\vec{r}) = -\sum_{q,G} \rho(\vec{q}+\vec{G}) V_{ei}(\vec{q}+\vec{G})(\vec{q}+\vec{G}) \cdot \xi_{\vec{q}} \left(\frac{\hbar}{2\rho\omega_q \nu}\right)^{1/2} \left(a_{\vec{q}} + a^{+}_{-\vec{q}}\right)$$

or in an abbreviated form

$$H_{ep} = \frac{1}{\nu^{1/2}} \sum_{q,G} \rho(\vec{q}+\vec{G}) M_{\vec{q}+\vec{G}} \left(a_{\vec{q}} + a^{+}_{-\vec{q}}\right)$$

with

$$M_{\vec{q}+\vec{G}} = -V_{ei}(\vec{q}+\vec{G})(\vec{q}+\vec{G}) \cdot \xi_{\vec{q}} \left(\frac{\hbar}{2\rho\omega_q}\right)^{1/2}$$

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3) Electron-phonon interaction:
localized electrons

If the electrons are localized the Hamiltonian becomes

$$H = H_p + H_{ep} = \sum_{\vec{q}} \left[\omega_q \left(a_q^+ a_q + 1/2 \right) + \sum_i \frac{e^{i\vec{q}\cdot\vec{r}_i}}{v^{1/2}} \left(a_{\vec{q}} + a_{-\vec{q}}^+ \right) \sum_G \rho_0(\vec{q}+\vec{G}) M_{\vec{q}+\vec{G}} e^{i\vec{G}\cdot\vec{r}_i} \right]$$

here the electron density operator is the Fourier transform the localized charge density

$$\rho(\vec{q}+\vec{G}) = \int d^3 r e^{i\vec{r}\cdot(\vec{q}+\vec{G})} \sum_i \left| \phi_0(\vec{r}-\vec{r}_0) \right|^2 = \int d^3 r e^{i\vec{r}\cdot(\vec{q}+\vec{G})} \rho_0(\vec{q}+\vec{G})$$

$$\rho_0(\vec{q}+\vec{G}) = \int d^3 r e^{i\vec{r}\cdot(\vec{q}+\vec{G})} \sum_i \left| \phi_0(r) \right|^2$$

rearranging terms

$$H = \sum_{\vec{q}} \left[\omega_{\vec{q}} \left(a_{\vec{q}}^+ a_{\vec{q}} + 1/2 \right) + \frac{1}{v^{1/2}} \left(a_{\vec{q}} + a_{-\vec{q}}^+ \right) \sum_i e^{i\vec{q}\cdot\vec{r}_i} F_{\vec{q}}(\vec{r}_i) \right]$$

with the periodic function

$$F_{\vec{q}}(\vec{r}) = \sum_G \rho_0(\vec{q}+\vec{G}) M_{\vec{q}+\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

3) Electron-phonon interaction:
localized electrons

we now transform the creation and annhiliation operators

$$A_{\vec{q}} = a_{\vec{q}} + \frac{1}{v^{1/2}} \frac{F_{\vec{q}}(\vec{r})}{\omega_{\vec{q}}} \sum_i e^{i\vec{q}\cdot\vec{r}_i} \qquad \text{and} \qquad A^+_{\vec{q}} = a^+_{\vec{q}} + \frac{1}{v^{1/2}} \frac{F^*_{\vec{q}}(\vec{r})}{\omega_{\vec{q}}} \sum_i e^{-i\vec{q}\cdot\vec{r}_i}$$

and rewrite the Hamiltonian

$$H = \sum_{\vec{q}} \left[\omega_{\vec{q}} \left(A^+_{\vec{q}} A_{\vec{q}} + 1/2 \right) \right] - \frac{1}{v} \sum_{\vec{q}} \left| \sum_i e^{i\vec{q}\cdot\vec{r}_i} \right|^2 \frac{\left| F_{\vec{q}} \right|^2}{\omega_{\vec{q}}}$$

which has the eigenstates and eigenvalues

$$\frac{\left(A^+_{\vec{q}} \right)^{n_{\vec{q}}}}{\left(n_{\vec{q}} ! \right)^{1/2}} |0\rangle \qquad \text{and} \qquad E = \sum_{\vec{q}} \left[\omega_{\vec{q}} \left(n_{\vec{q}} + 1/2 \right) \right] - \frac{1}{v} \sum_{\vec{q}} \left| \sum_i e^{i\vec{q}\cdot\vec{r}_i} \right|^2 \frac{\left| F_{\vec{q}} \right|^2}{\omega_{\vec{q}}}$$

3) Electron-phonon interaction:
deformation potential

Traditionally in semiconductors one parametrizes electron-phonon interactions (long wavelengths)

- deformation-potential coupling to acoustic phonons
- piezoelectric coupling to acoustic phonons
- polar coupling to optical phonons

the deformation-potential coupling takes the form

$$H_{ep} = D\sum_{\vec{q}} \left(\frac{\hbar}{2\rho\omega_q \nu}\right)^{1/2} |\vec{q}|\, \rho(\vec{q}) \left(a_{\vec{q}} + a^{+}_{-\vec{q}}\right)$$

3) Electron-phonon interaction:
piezoelectric interaction

The electric field is proportional the the stress

$$E_k = \sum_{ij} M_{ijk} S_{ij}$$

Stress is the symmetric derivative of the displacement field

$$S_{ij} = \frac{1}{2}\left(\frac{\partial Q_i}{\partial x_j} + \frac{\partial Q_j}{\partial x_i}\right) = \frac{1}{2}\sum_{\vec{q}} \left(\frac{\hbar}{2\rho\omega_{\vec{q}}\nu}\right)^{1/2} \left(\xi_i q_j + \xi_j q_i\right)\left(a_{\vec{q}} + a^{+}_{-\vec{q}}\right) e^{i\vec{q}\cdot\vec{r}_i}$$

The field is longitudinal and can hence be written as the gradient of a potential

$$E_k = -\frac{\partial}{\partial x_k}\phi(\vec{r}) = -\frac{1}{\nu^{1/2}}\sum_{\vec{q}} i q_k \phi_{\vec{q}} e^{i\vec{q}\cdot\vec{r}}$$

This potential is proportional to the displacement

$$\phi(\vec{r}) \propto Q(\vec{r})$$

$$\phi(\vec{r}) = i\sum_{\vec{q}\lambda} \left(\frac{\hbar}{2\rho\omega_{\vec{q}\lambda}\nu}\right)^{1/2} M_\lambda(\hat{q}) e^{i\vec{q}\cdot\vec{r}} \left(a_{\vec{q}\lambda} + a^{+}_{-\vec{q}\lambda}\right)$$

leading to

$$H_{ep} = i\sum_{\vec{q}\lambda} \left(\frac{\hbar}{2\rho\omega_{\vec{q}\lambda}\nu}\right)^{1/2} M_\lambda(\hat{q})\rho(\vec{q})\left(a_{\vec{q}\lambda} + a^{+}_{-\vec{q}\lambda}\right)$$

3) Electron-phonon interaction:
polar coupling

The coupling is only to LO (TO do not set up strong electric fields)

$$\nabla \cdot \vec{D} = 0 = \sum_{\vec{q}} \vec{q}(\vec{E}_{\vec{q}} + 4\pi \vec{P}_{\vec{q}}) e^{i\vec{q}\cdot\vec{r}}$$

induced field

$$\vec{E}_{\vec{q}} = -4\pi \vec{P}_{\vec{q}}$$

The polarization is proportional to the displacement

$$\vec{P}_{\vec{q}} = Ue\vec{Q}_{\vec{q}} \qquad \text{and} \qquad \vec{E}_{\vec{q}} = -4\pi Ue\vec{Q}_{\vec{q}} = -4\pi Ue\left(\frac{\hbar}{2\rho\omega_{LO}\nu}\right)^{1/2} i\hat{q}\left(a_{\vec{q}} + a^{+}_{-\vec{q}}\right)$$

The field points to the direction of q, thus

$$\vec{E} = -\nabla\phi = -i\sum_{\vec{q}} i\vec{q}\phi_{\vec{q}} e^{i\vec{q}\cdot\vec{r}}$$

$$\phi(\vec{r}) = \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} \frac{4\pi Ue}{q}\left(\frac{\hbar}{2\rho\omega_{LO}\nu}\right)^{1/2}\left(a_{\vec{q}} + a^{+}_{-\vec{q}}\right)$$

3) Electron-phonon interaction:
polar coupling

The interaction of two fixed electrons is

$$V_R(r) = -\frac{2}{\hbar\omega_{LO}}(4\pi U e)^2 \left(\frac{\hbar}{2\rho\omega_{LO}}\right)\int \frac{d^3q}{(2\pi)^3}\frac{e^{i\vec{q}\cdot\vec{r}}}{q^2}$$

Fourier transforming

$$V_R(r) = -\Gamma\frac{e^2}{r} \qquad \text{with} \qquad \Gamma = \frac{4\pi U^2}{\rho\omega^2{}_{LO}} \qquad \text{and} \qquad \frac{e^2}{r\varepsilon_0} = \frac{e^2}{r}\left(\frac{1}{\varepsilon_\infty} - \Gamma\right)$$

The coefficient U becomes

$$U^2 = \frac{\rho\omega^2{}_{LO}}{4\pi}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)$$

and the interaction Hamiltonian

$$H_{ep} = \sum_q \frac{M}{qv^{1/2}}\rho(\vec{q})\left(a_{\vec{q}} + a^+_{-\vec{q}}\right) \qquad \text{with} \qquad M^2 = 2\pi e^2\hbar\omega_{LO}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)$$

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3) Electron-phonon interaction:
Fröhlich Hamiltonian

describes the interaction between a single electron in a solid and LO phonons

$$H = \sum_{\vec{p}} \frac{p^2}{2m} c^+_{\vec{p}} c_{\vec{p}} + \omega_0 \sum_q a^+_{\vec{q}} a_{\vec{q}} + \sum_{q\nu} \frac{M_0}{\nu^{1/2}} \frac{1}{|q|} c^+_{\vec{p}+\vec{q}} c_{\vec{p}} \left(a_{\vec{q}} + a^+_{-\vec{q}} \right)$$

where

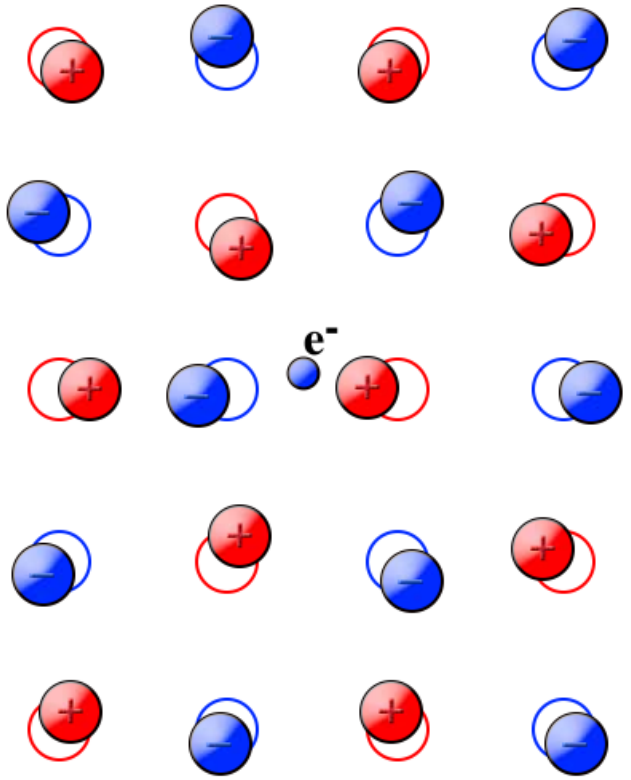
$$M_0^2 = \frac{4\pi\alpha\hbar(\hbar\omega_0)^{3/2}}{(2m)^{1/2}}$$

and

$$\alpha = \frac{e^2}{\hbar} \left(\frac{m}{2\hbar\omega_0} \right)^{1/2} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right)$$

For a single electron it can be rewritten as

$$H = \frac{p^2}{2m} + \omega_0 \sum_q a^+_{\vec{q}} a_{\vec{q}} + \sum_{q\nu} \frac{M_0}{\nu^{1/2}} \frac{e^{i\vec{q}\cdot\vec{r}}}{|q|} \left(a_{\vec{q}} + a^+_{-\vec{q}} \right)$$



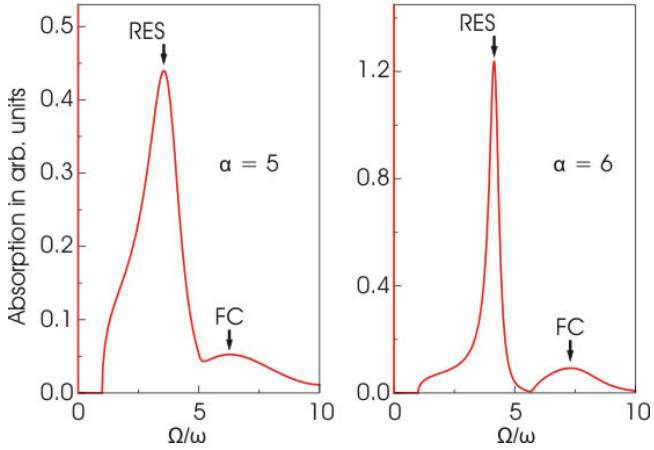
3) Electron-phonon interaction:
small polaron theory – large polarons

Transform to collective coordinates

$$C_{\vec{k}} = \frac{1}{N^{1/2}} \sum_j C_j e^{i\vec{k}\vec{R}_j}$$

$$H = zJ \sum_{\vec{k}} \gamma_{\vec{k}} C^+_{\vec{k}} C_{\vec{k}} + \sum_{\vec{q}} \omega_0 a^+_{\vec{q}} a_{\vec{q}} + \sum_{\vec{k}\vec{q}} C^+_{\vec{k}+\vec{q}} C_{\vec{k}} M_q \left(a_{\vec{q}} + a^+_{-\vec{q}} \right)$$

$$\gamma_{\vec{k}} = \frac{1}{z} \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}$$



optical absorption

the polaron self-energy in first-order Rayleigh-Schrödinger perturbation theory becomes

$$\sum\nolimits^{(1)}_{RS}(k) = \sum_{\vec{q}} M^2_{\vec{q}} \left[\frac{N_{\vec{q}} + 1 - n_F(\varepsilon_{\vec{k}})}{\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}+\vec{q}} - \omega_{\vec{q}}} + \frac{N_{\vec{q}} + n_F(\varepsilon_{\vec{k}})}{\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}+\vec{q}} + \omega_{\vec{q}}} \right]$$

3) Electron-phonon interaction:
small polaron theory – small polarons

Canonical transformation

$$\bar{H} = e^{S} H e^{-S} \qquad \text{with} \qquad S = -\sum_{j\vec{q}} n_j e^{i\vec{q}\vec{R}_j} \frac{M_q}{\omega_q}\left(a_{\vec{q}} - a^{+}_{-\vec{q}}\right)$$

leads to

$$H = J\sum_{j\delta} C^{+}_{j+\delta} C_j X^{+}_{j+\delta} X_j + \sum_q \omega_0 a^{+}_{\vec{q}} a_{\vec{q}} + \sum_j n_j \Delta$$

with polaron self-energy $\Delta = \sum_{\vec{q}} \frac{M^2_{\vec{q}}}{\omega_q}$ and $X_j = \exp\left[\sum_{\vec{q}} e^{i\vec{q}\vec{R}_j} \frac{M_q}{\omega_q}\left(a_{\vec{q}} - a^{+}_{-\vec{q}}\right)\right]$

finally we write

$$\bar{H} = H_0 + V$$

with $H_0 = \sum_q \omega_0 a^{+}_{\vec{q}} a_{\vec{q}} + \sum_j n_j \Delta$ and $V = J\sum_{j\delta} C^{+}_{j+\delta} C_j X^{+}_{j+\delta} X_j$

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3) Electron-phonon interaction:
phonons in metals

The Hamiltonian is

$$H = \sum_i \frac{p_i^2}{2m} + \sum_i \frac{P_j^2}{2M_j} + \frac{1}{2} e^2 \sum_{ij} \frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} + \sum_{i\alpha} V_{ei}\left(\vec{r}_i - \vec{R}_\alpha^{(0)}\right) + \sum_{\alpha\beta} V_{ii}\left(\vec{R}_\alpha - \vec{R}_\beta\right)$$

first we neglect phonons

$$H_{0e} = \sum_i \frac{p_i^2}{2m} + \sum_{i\alpha} V_{ei}\left(\vec{r}_i - \vec{R}_\alpha^{(0)}\right) + \frac{1}{2}\sum_{ij} \frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|} + \frac{1}{2}\sum_{\alpha\beta} V_{ii}\left(\vec{R}_\alpha^{(0)} - \vec{R}_\beta^{(0)}\right)$$

within the harmonic approximation for the phonons

$$\vec{R}_\alpha = \vec{R}_\alpha^{(0)} - \vec{Q}_\alpha \qquad H = H_{0e} + H_{0p} + H_{ep}$$

$$\Phi_{\mu\nu}\left(\vec{R}\right) = \nabla_\mu \nabla_\nu V_{ii}\left(\vec{R}\right) \qquad H_{ep} = \sum_{j\alpha} \vec{Q}_\alpha \cdot \nabla V_{ei}\left(\vec{r}_i - \vec{R}_\alpha^{(0)}\right)$$

with the bare-phonon Hamiltonian

$$H_{0p} = \sum_\alpha \frac{P_\alpha^2}{2M_\alpha} + \frac{1}{4}\sum_{\alpha\beta}\left(\vec{Q}_\alpha - \vec{Q}_\beta\right)_\mu \left(\vec{Q}_\alpha - \vec{Q}_\beta\right)_\nu \Phi_{\mu\nu}\left(\vec{R}_\alpha^{(0)} - \vec{R}_\beta^{(0)}\right)$$

3) Electron-phonon interaction:
phonons in metals

expand displacements and conjugate momenta in a set of normal modes

$$\vec{Q}_\alpha = \frac{1}{(N_i)^{1/2}} \sum_{\vec{k}} \vec{Q}_{\vec{k}} e^{i\vec{k}\cdot\vec{R}_\alpha^{(0)}} \qquad \vec{P}_\alpha = \frac{1}{(N_i)^{1/2}} \sum_{\vec{k}} \vec{P}_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}_\alpha^{(0)}}$$

thus

$$H_{0p} = \sum_{\vec{k}} \left[\frac{1}{2m} \vec{P}_{\vec{k}} \cdot \vec{P}_{-\vec{k}} + \frac{1}{2} \vec{Q}_{\vec{k}\mu} \vec{Q}_{\vec{k}\nu} \phi_{\mu\nu}\left(\vec{k}\right) \right]$$

where

$$\phi_{\mu\nu}\left(\vec{k}\right) = \frac{1}{2} \sum_{\alpha\beta} \left(e^{i\vec{k}\cdot\vec{R}_\alpha^{(0)}} - e^{-i\vec{k}\cdot\vec{R}_\beta^{(0)}} \right) \left(e^{-i\vec{k}\cdot\vec{R}_\alpha^{(0)}} - e^{i\vec{k}\cdot\vec{R}_\beta^{(0)}} \right) \times \Phi_{\mu\nu}\left(\vec{R}_\alpha^{(0)} - \vec{R}_\beta^{(0)}\right) = -\frac{1}{\nu_0} \sum_G \left[\Phi_{\mu\nu}\left(\vec{G}+\vec{k}\right) - \Phi_{\mu\nu}\left(\vec{G}\right) \right]$$

and

$$\Phi_{\mu\nu}\left(\vec{q}\right) = \int d^3R \Phi_{\mu\nu}\left(\vec{R}\right) e^{i\vec{q}\cdot\vec{R}}$$

3) Electron-phonon interaction:
phonons in metals

if the ions were point charges we would have

$$V_{ii}\left(\vec{R}\right)=\frac{Z^2e^2}{\varepsilon_i\vec{R}} \qquad \Phi_{\mu\nu}=-\frac{Z^2e^2}{\varepsilon_i}\left(\frac{\delta_{\mu\nu}}{R^3}-\frac{3R_\mu R_\nu}{R^5}\right) \qquad \Phi_{\mu\nu}\left(q\right)=\frac{-4\pi Z^2e^2q_\mu q_\nu}{\varepsilon_i q^2}$$

find the normal modes of the bare-phonon system through

$$\det\left[M\Omega^2_{\vec{k}\lambda}\delta_{\mu\nu}-\phi_{\mu\nu}\left(\vec{k}\right)\right]=0$$

and use the frequencies and eigenstates to define a set of creation and annihilation operators

$$\vec{Q}_{\vec{k}}=\sum_\lambda\left(\frac{\hbar}{2\rho v\Omega_{\vec{k}\lambda}}\right)^{1/2}\xi_{\vec{k}\lambda}\left(a_{\vec{k}\lambda}+a^+_{-\vec{k}\lambda}\right)$$

$$H_{0p}=\sum_{\vec{k}\lambda}\Omega_{\vec{k}\lambda}\left(a^+_{\vec{k}\lambda}a_{\vec{k}\lambda}+\frac{1}{2}\right)$$

3) Electron-phonon interaction:
phonons in metals

the same set can be used as a basis for the electron-ion interaction

$$H_{ep} = \frac{1}{\nu^{1/2}} \sum_{\vec{q}\lambda,\vec{G}} M_\lambda\left(\vec{G}+\vec{q}\right) e^{i\left(\vec{G}+\vec{q}\right)\cdot\vec{r}} \left(a_{\vec{q}\lambda} + a^{+}_{-\vec{q}\lambda}\right)$$

where

$$M_\lambda\left(\vec{G}+\vec{q}\right) = \left(\frac{\hbar}{2\rho\nu\Omega_{\vec{k}\lambda}}\right)^{1/2} \xi_{\vec{q}\lambda}\left(\vec{G}+\vec{q}\right) V_{ei}\left(\vec{G}+\vec{q}\right)$$

in second quantization

$$H = \sum_{\vec{k}} \xi_{\vec{k}} C^{+}_{\vec{k}} C_{\vec{k}} + \frac{1}{2} \sum_{\vec{q}\vec{k}\vec{p}\sigma\sigma'} \nu_q C^{+}_{\vec{k}+\vec{q}_\sigma} C^{+}_{\vec{p}-\vec{q}_{\sigma'}} C_{\vec{p}_{\sigma'}} C_{\vec{k}_\sigma} + \sum_{\vec{q}\lambda} \Omega_{\vec{q}\lambda} a^{+}_{\vec{q}\lambda} a_{\vec{q}\lambda} + \sum_{n\vec{q}\lambda\vec{k}\sigma} \frac{M_\lambda(q)}{\nu^{1/2}} C^{+}_{\vec{k}+\vec{q}_\sigma} C_{\vec{k}_\sigma} \left(a_{\vec{q}\lambda} + a^{+}_{-\vec{q}\lambda}\right)$$

Note: the phonon-states basis is unrealistic and serves only as starting point for a Green´s function calculation

3) Electron-phonon interaction:
phonons in metals

If the electron-plasma frequency is much larger than the phonon frequency we write the interaction between to electrons as a screened Coulomb interaction and screened phonon interaction

$$V_{eff}\left(q,i\omega\right)=\frac{v_q}{\varepsilon_i\varepsilon\left(\vec{q},i\omega\right)}+\sum_{\lambda}\frac{M_{\lambda}^{2}\left(\vec{q}\right)}{\varepsilon\left(\vec{q},i\omega\right)^{2}}D_{\lambda}\left(\vec{q},i\omega\right)$$

where

$$\varepsilon\left(\vec{q},i\omega\right)=1-\frac{v_q}{\varepsilon_i}P\left(\vec{q},i\omega\right)$$

and the phonon Green´s function

$$D_{\lambda}\left(\vec{q},i\omega\right)=\frac{D_{\lambda}^{(0)}}{1-M_{\lambda}^{2}D_{\lambda}^{(0)}P\left(\vec{q},i\omega\right)/\varepsilon\left(\vec{q},i\omega\right)}$$

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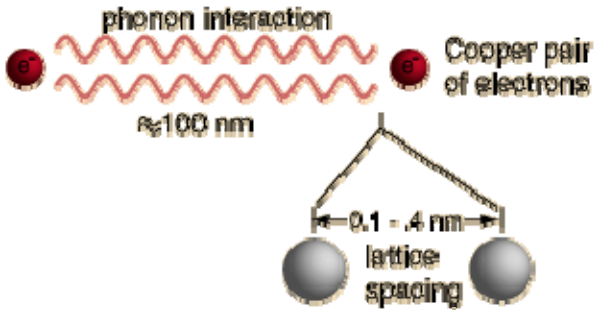
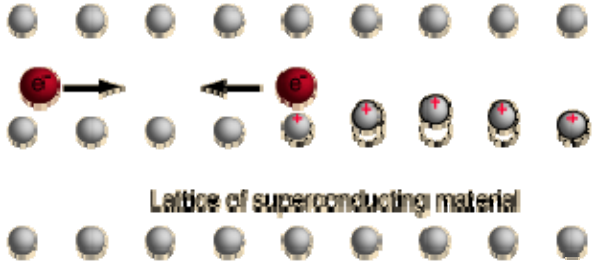
4) Superconductivity
BCS (Bardeen, Cooper, and Schrieffer) theory

Screened interaction of two scattering electrons

$$V_s(q,w) = \frac{v_q}{\varepsilon(q,w)} + \frac{M_q^2(2\Omega_{q\lambda})}{\varepsilon(q)^2\left(\omega^2 - \omega_{q\lambda}^2\right)}$$



$$V_s(q,w) = \begin{cases} -V_0 & |\xi_q| \le \omega_D \\ 0 & |\xi_q| \ge \omega_D \end{cases}$$



The Hamiltonian takes the form

$$H = \sum_{\vec{p}} \xi_{\vec{p}} C^+_{\vec{p}\sigma} C_{\vec{p}\sigma} + \frac{1}{2v} \sum_{\vec{q}\vec{p}'\vec{p}\sigma\sigma'} V(q) C^+_{\vec{p}+\vec{q},\sigma} C^+_{\vec{p}'-\vec{q},\sigma'} C_{\vec{p}',\sigma'} C_{\vec{p},\sigma}$$

4) Superconductivity
BCS (Bardeen, Cooper, and Schrieffer) theory

consider the EOMs

$$\frac{\partial}{\partial\tau}C_{\vec{p},\sigma}(\tau)=\left[H,C_{\vec{p},\sigma}\right]=-\xi_{\vec{p}}C_{\vec{p},\sigma}-\frac{1}{\nu}\sum_{\vec{q}\vec{p}'\sigma'}V(q)C^{+}_{\vec{p}'-\vec{q},\sigma'}C_{\vec{p}',\sigma'}C_{\vec{p},\sigma}$$

first derivative of the equation for the Green´s function

$$\frac{\partial}{\partial\tau}G\left(\vec{p},\tau-\tau'\right)=-\frac{\partial}{\partial\tau}[\theta\left(\tau-\tau'\right)\left\langle C_{\vec{p},\sigma}\left(\tau\right)C^{+}_{\vec{p},\sigma}\left(\tau'\right)\right\rangle-\theta\left(\tau'-\tau\right)\left\langle C^{+}_{\vec{p},\sigma}\left(\tau'\right)C_{\vec{p},\sigma}\left(\tau\right)\right\rangle]=$$

$$=-\delta\left(\tau-\tau'\right)\left\langle\left\{C^{+}_{\vec{p},\sigma},C_{\vec{p},\sigma}\right\}\right\rangle-\left\langle T_{\tau}\left[\frac{\partial}{\partial\tau}C_{\vec{p},\sigma}(\tau)\right]C^{+}_{\vec{p},\sigma}\left(\tau'\right)\right\rangle$$

$$\frac{\partial}{\partial\tau}G\left(\vec{p},\tau-\tau'\right)=-\delta\left(\tau-\tau'\right)-\left\langle T_{\tau}\left[\frac{\partial}{\partial\tau}C_{\vec{p},\sigma}(\tau)\right]C^{+}_{\vec{p},\sigma}\left(\tau'\right)\right\rangle$$

leads after some math to

$$\left(-\frac{\partial}{\partial\tau}-\xi_{\vec{p}}\right)G\left(\vec{p},\tau-\tau'\right)+\frac{1}{\nu}\sum_{\vec{q}\vec{p}'\sigma'}V(q)\times\left\langle T_{\tau}C^{+}_{\vec{p}'-\vec{q},\sigma'}(\tau)C_{\vec{p}',\sigma'}(\tau)C_{\vec{p}-\vec{q},\sigma}(\tau)C^{+}_{\vec{p},\sigma}(\tau')\right\rangle=\delta\left(\tau-\tau'\right)$$

4) Superconductivity
BCS (Bardeen, Cooper, and Schrieffer) theory

Neglecting electron pairing at $q = 0$ (long-wavelength phonons) leads for up and down spins to

$$-\left\langle T_\tau C_{\vec{p}',\downarrow}(\tau) C_{\vec{p}-\vec{q},\uparrow}(\tau)\right\rangle \left\langle T_\tau C^+_{\vec{p}',\uparrow}(\tau') C^+_{\vec{p}'-\vec{q},\downarrow}(\tau)\right\rangle = -\delta_{\sigma,-\sigma'}\delta_{\vec{p}'=-\vec{p}+\vec{q}} F\left(\vec{p}-\vec{q},0\right) F^+\left(\vec{p},\tau'-\tau\right)$$

and

$$-\left\langle T_\tau C_{\vec{p}-\vec{q},\downarrow}(\tau) C_{\vec{p}',\uparrow}(\tau)\right\rangle \left\langle T_\tau C^+_{\vec{p}'-\vec{q},\uparrow}(\tau) C^+_{\vec{p}',\downarrow}(\tau')\right\rangle = -\delta_{\sigma,-\sigma'}\delta_{\vec{p}'=-\vec{p}+\vec{q}} F\left(-\vec{p}+\vec{q},0\right) F^+\left(-\vec{p},\tau-\tau'\right)$$

thus we get

$$\frac{1}{\nu}\sum_{\vec{q}\vec{p}'\sigma'} V(q)\times\left\langle T_\tau C^+_{\vec{p}'-\vec{q},\sigma'}(\tau) C_{\vec{p}',\sigma'}(\tau) C_{\vec{p}-\vec{q},\sigma}(\tau) C^+_{\vec{p},\sigma}(\tau')\right\rangle = \frac{1}{\nu}\sum_{\vec{q}} V(q)\left[G\left(\vec{p},\tau-\tau'\right) n_{\vec{p}-\vec{q}} - F\left(\vec{p}-\vec{q},0\right) F^+\left(\vec{p},\tau'-\tau\right)\right]$$

defining $\Delta\left(\vec{p}\right) = -\frac{1}{\nu}\sum_{\vec{q}} V(q) F\left(\vec{p}-\vec{q},\tau=0\right)$ with $F\left(\vec{p},\tau=0\right) = \frac{1}{\beta}\sum_{ip}\frac{\Delta}{p_n^2+E_p^2}$

gives the EOM for the Green´s function

4) Superconductivity
BCS (Bardeen, Cooper, and Schrieffer) theory

we sum over frequencies by the contour integral

$$0 = \oint \frac{dZ}{2\pi i} n_F(Z) \frac{\Delta}{Z^2 - E_p^2}$$

and get

$$F\left(\vec{p}, \tau = 0\right) = \frac{\Delta}{2E_p} \tanh\left(\frac{\beta E_p}{2}\right)$$

which, in turn, gives the equation for the gap function

$$\Delta\left(\vec{p}\right) = -\frac{1}{v}\sum_{\vec{q}} V(q) \frac{\Delta\left(\vec{p}-\vec{q}\right)}{2E_{\vec{p}-\vec{q}}} \tanh\left(\frac{\beta E_{\vec{p}-\vec{q}}}{2}\right)$$

where $\Delta = \frac{\Delta}{2} N_F V_0 \int_{-\omega_D}^{\omega_D} d\xi \frac{\tanh\left(\beta E_{\vec{p}-\vec{q}}/2\right)^2}{E}$ and $E = \left(\xi^2 + \Delta^2\right)^{1/2}$

4) Superconductivity
BCS (Bardeen, Cooper, and Schrieffer) theory

factoring out the constant Δ and considering zero temperature leads to

$$1 = N_F V_0 \ln\left[\xi + \left(\xi^2 + \Delta^2\right)^{1/2}\right]_0^{\omega_D} \approx N_F V_0 \ln\left(\frac{2\omega_D}{\Delta}\right)$$

which, solved, produces the energy gap

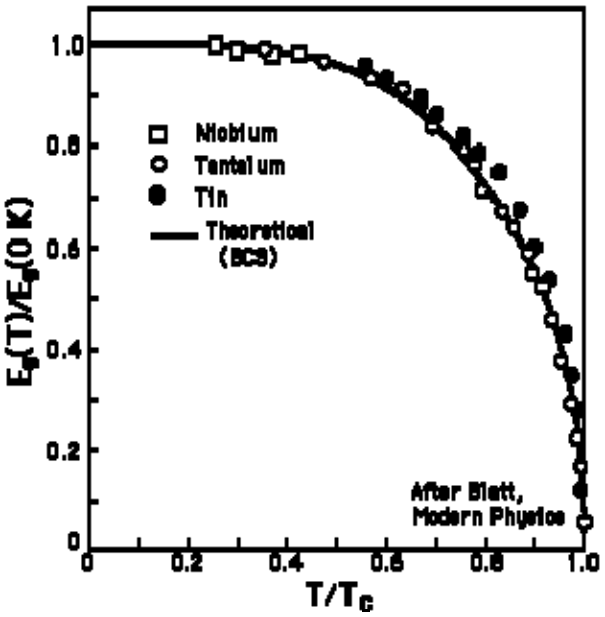
$$E_g = 2\Delta = 4\omega_D e^{-1/N_F V_0}$$

The energy gap decreases as the temperature increases.
The critical temperature is

$$kT_c = 1.14\omega_D e^{-1/N_F V_0}$$

BCS predicts

$$\frac{E_g}{kT_c} = \frac{4.0}{1.14} = 3.52$$



Outline

1. The harmonic oscillator
   - real space
   - energy basis

2. 1D lattice vibrations
   - one atom per primitive cell
   - two atoms per primitive cells

3. Electron-phonon interactions
   - localized electrons
   - small-polaron theory
   - phonons in metals

4. Superconductivity

5. A numerical example: CO

6. Literature

A numerical example: CO

Static nonrelativistic Hamiltonian

$$\hat{H}^{(0)} = -\frac{1}{2}\sum_{i=1}^{N_{el}}\nabla^2 - \sum_{i=1}^{N_{el}}\sum_{a=1}^{N_{at}}\frac{Z_a}{\left|\mathbf{R}_a(\mathbf{q}) - \mathbf{r}_i\right|} +$$

$$\sum_{i=1}^{N_{el}}\sum_{j=1}^{N_{el}}\frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} + \sum_{a=1}^{N_{at}}\sum_{b=1}^{N_{at}}\frac{Z_a}{\left|\mathbf{R}_a(\mathbf{q}) - \mathbf{R}_b(\mathbf{q})\right|}$$

SOC, external magnetic field, and eletron-phonon coupling involved

$$\hat{H}^{(1)} = \sum_{i=1}^{N_{el}}\frac{Z_a^{eff}}{2c^2R_i^3}\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} + \sum_{i=1}^{N_{el}}\mu_L\hat{\mathbf{L}}\cdot\mathbf{B}_{\mathbf{stat}} +$$

$$\sum_{i=1}^{N_{el}}\mu_S\hat{\mathbf{S}}\cdot\mathbf{B}_{\mathbf{stat}} + \sum_{i=1}\sum_{\mathbf{q}}\lambda_a^{\mathbf{q}}\langle\mathbf{q}\rangle$$

5) A numerical example: CO
The Hellmann-Feynman theorem

In quantum mechanics, the Hellmann–Feynman theorem relates the derivative of the total energy with respect to a parameter, to the expectation value of the derivative of the Hamiltonian with respect to that same parameter.

$$\frac{\partial E}{\partial \lambda} = \int \psi^*(\lambda) \frac{\partial \hat{H}_\lambda}{\partial \lambda} \psi(\lambda) d\tau$$

where

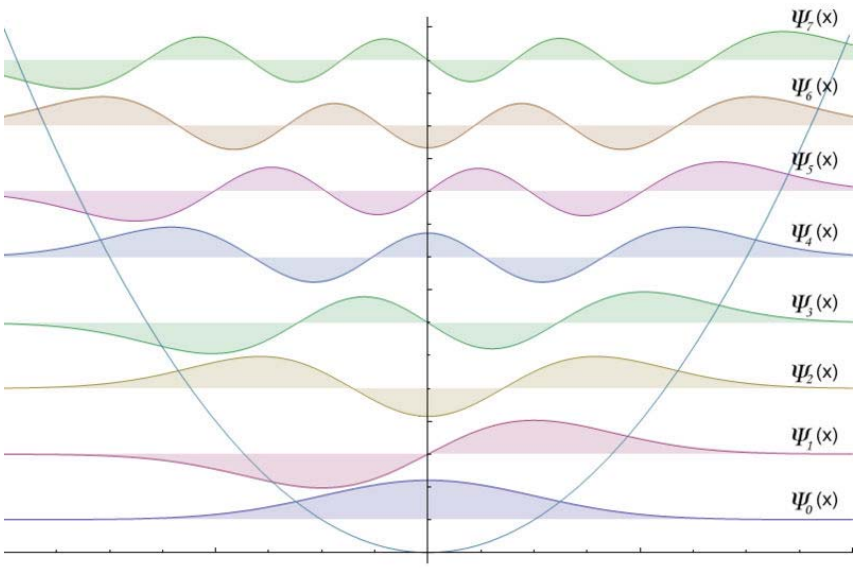
- $\hat{H}_\lambda$ is a Hamiltonian operator depending upon a continuous parameter λ,
- $\psi(\lambda)$ is a wavefunction (eigenfunction) of the Hamiltonian, depending implicitly upon λ,
- E is the energy (eigenvalue) of the wavefunction,
- $d\tau$ implies an integration over the domain of the wavefunction.

5) A numerical example: CO
calculating the electron-phonon coupling

$$\lambda^i_{a,b} = \left\langle a,\mathbf{0}_i \left| \frac{\partial \hat{H}}{\partial q} \right| b,\mathbf{1}_i \right\rangle$$

$$\lambda^i_{a,b} = \delta_{a,b} E_b - E^0_b = \Delta E_b \equiv \lambda^i_a$$

Wavefunctions of the harmonic oscillator



$$E_n = \hbar\omega(n + \frac{1}{2})$$

$$\psi_0(x) = (\frac{m\omega}{\pi\hbar})^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}$$

$$\psi_1(x) = (\frac{m\omega}{\pi\hbar})^{1/4} \sqrt{\frac{2m\omega}{\hbar}} x e^{-\frac{m\omega}{2\hbar}x^2}$$

5) A numerical example: CO
calculating the electron-phonon coupling

When $\lambda_a^i = 0$

$$\hat{H}_e^0 = \begin{pmatrix} E_e & 0 \\ 0 & E_e + E_{ph} \end{pmatrix}$$

With coupling

$$\hat{H}_e = \begin{pmatrix} E_e & \lambda_a^i \\ \lambda_a^i & E_e + E_{ph} \end{pmatrix}$$

Diagonalizing

$$\hat{H}_{ab-initio} = \begin{pmatrix} E_e & 0 \\ 0 & E_e + E_{ph} + \Delta E_a^i \end{pmatrix}$$

Result in

$$\lambda_a^i = \pm\sqrt{\frac{(\Delta E_a^i)^2 + 2E_{ph}\Delta E_a^i}{4}}$$

5) A numerical example: CO
calculating the electron-phonon coupling

1st step: geometry optimization

2nd step: CI calculation at the equilibrium position

3rd step: Normal modes calculation and quantization

4th step: CI calculation at the phononic position and obtain the EP coupling coefficient

(GAUSSIAN 03)

```
                         ---------------------------
                         !   Optimized Parameters   !
                         ! (Angstroms and Degrees)  !
--------------------------                           ---------------------------
! Name  Definition              Value          Derivative Info.                !
--------------------------------------------------------------------------------
! R1    R(1,2)                  1.1307         -DE/DX =    0.0                 !
--------------------------------------------------------------------------------
     Excited State   1:   Triplet-?Sym    5.6305 eV  220.20 nm  f=0.0000
           7 ->  9         0.69474
           7 -> 12        -0.12308
```

$E_e = 5.6305\mathbf{eV}$

```
                      SG
 Frequencies --   2286.0338
 Red. masses --     13.4388
 Frc consts  --     41.3785
 IR Inten    --    145.6415
 Raman Activ --     12.3068
 Depolar (P) --      0.2937
 Depolar (U) --      0.4541
 Atom AN      X      Y      Z
    1   6     0.00   0.00   0.80
    2   8     0.00   0.00  -0.60
```

According to $E_n = \hbar\omega(n+\frac{1}{2})$

$E_{ph0} = 0$

$E_{ph1} = \hbar\omega = 0.2834\mathbf{eV}$

```
Excited State   1:   Triplet-?Sym    5.3361 eV  232.35 nm  f=0.0000
      7 ->  9         0.69473
      7 -> 11        -0.12040
```

$E_{ph+} = 5.3361\mathbf{eV}$

$E_e + E_{ph} + \Delta E_a^i = 5.3361\mathbf{eV}$ $\quad \lambda_a^i = \pm\sqrt{\frac{(\Delta E_a^i)^2 + 2E_{ph}\Delta E_a^i}{4}} = 0.04\mathbf{eV}$

```
Excited State   1:   Triplet-?Sym    5.9382 eV  208.79 nm  f=0.0000
      7 ->  9         0.69461
      7 -> 12        -0.12560
```

$E_{ph-} = 5.9382\mathbf{eV}$

$E_e + E_{ph} + \Delta E_a^i = 5.9382\mathbf{eV}$ $\quad \lambda_a^i = \pm\sqrt{\frac{(\Delta E_a^i)^2 + 2E_{ph}\Delta E_a^i}{4}} = 0.06\mathbf{eV}$

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