Vibrational effects in electronic structure: temperature dependence and zero-point motion

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T-dependence of electronic/optical properties

- peaks shift in energy
- peaks broaden with increasing temperature: decreased electron lifetime

- even at 0K, vibrational effects are important, due to Zero-Point Motion

Usually, not included in first-principles (DFT or beyond) calculations!


Overview

1. Thermal expansion and phonon population effects
2. First-principles Allen-Heine-Cardona (AHC) theory
3. Breakdown of the adiabatic quadratic approximation for infra-red active materials
4. Zero-point renormalization (ZPR) : theory vs experiment
5. The physics of the ZPR in infra-red active materials

References :


Thermal expansion and phonon population effects
Divide and conquer …

Constant-pressure temperature dependence of the electronic eigenenergies: two contributions

\[
\left( \frac{\partial \varepsilon_{nk}}{\partial T} \right)_p = \left( \frac{\partial \varepsilon_{nk}}{\partial T} \right)_V + \left( \frac{\partial \varepsilon_{nk}}{\partial \ln V} \right)_T \left( \frac{\partial \ln V}{\partial T} \right)_p
\]

Constant volume  Constant temperature

= \alpha_p(T)

Thermal expansion coefficient

Contribution of the phonon population, i.e. the vibrations of the atomic nuclei, at constant volume

+ 

Contribution of the thermal expansion, i.e. the change in volume of the sample, at constant temperature
Ab initio thermal expansion

\[ \alpha(T) = \frac{V}{3B} \sum_{q,m} \frac{1}{\omega_{q,m}} \gamma_{q,m} \left( \frac{\partial n(\omega_{q,m})}{\partial T} \right) \]

Mode-Grüneisen parameters

\[ \gamma_{m,q} = -\left( \frac{\partial (\ln \omega_{m,q})}{\partial (\ln V)} \right) \]

Alternative path: minimisation of free energy
Ab initio thermal expansion

Linear thermal expansion coefficient of bulk silicon

Thermal expansion contribution to the gap of Si

- Calculation
  * Exp (thermal exp. only)

But total exp. change between 0K and 300K = 0.06 eV!

...Thermal expansion contribution is negligible (for Si)...

NOT always the case, can be of same size: black phosphorus (Villegas, et al, Nanolett. 16, 5095 (2016)), Bi$_2$Se$_3$ family (Monserrat & Vanderbilt, PRL117, 226801 (2016)).
Phonon population effects

Different levels of approximation:
- dynamics of the nuclei … classical … quantum?
- harmonic treatment of vibrations or anharmonicities?
- adiabatic decoupling of nuclei and electronic dynamic, or non-adiabatic corrections?
- independent electronic quasi-particles (DFT or GW), or many-body approach with spectral functions?

… At least 5 first-principles methodologies:
(1) Time-average
(2) Thermal average
(3) Harmonic approximation + thermal average
(4) Diagrammatic approach (Allen-Heine-Cardona)
(5) Exact factorization (H. Gross and co-workers)
Phonon population effects in solids

Concepts ...
... can be explained with diatomic molecules

Simple:
- discrete levels, simple molecular orbitals
- only one relevant vibration mode.

(6 modes decouple as 3 translations, 2 rotations + the stretch.)
Average eigenenergies in the BO approx.

Electronic eigenenergies, function of the bond length $\epsilon_n(\Delta R)$ =>
=> broadening and shift!

(1) Time-average of eigenenergies from Molecular Dynamics trajectories, $\Delta R(t)$ at average T, with

$$\epsilon_n(T) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau \epsilon_n(\Delta R(t)) \, dt$$

Pros: well-defined procedure ; compatible with current implementations and computing capabilities ; $\epsilon_n(\Delta R(t))$ from DFT or GW ; anharmonicities

Cons: if classical dynamics => no zero-point motion ; adiabatic (vibrations, but no exchange of energy !) ; hard for solids (supercell) also supercell mix eigenstates, need unfolding
Average eigenenergies in the BO approx.

Electronic eigenenergies function of the bond length $\varepsilon_n(\Delta R)$

(2) Thermal average with accurate quantum vibrational states,

$$
\varepsilon_n(T) = \frac{1}{Z} \sum_m e^{-\frac{E_{ph}(m)}{k_B T}} \left( \int \chi_m^*(\Delta R) \varepsilon_n(\Delta R) \chi_m(\Delta R) d\Delta R \right)
$$

$$
Z = \sum_m e^{-\frac{E_{ph}(m)}{k_B T}}
$$

Pros: zero-point motion; $\varepsilon_n(\Delta R(t))$ from DFT or GW; anharmonicities

Cons: hard to sample more than a few vibrational degrees of freedom; adiabatic (vibrations, but no exchange of energy!); hard for solids (supercell), also supercell mix eigenstates, need unfolding

Alternative: one very large supercell with prepared atomic displacements

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Average eigenenergies: BO and harmonic approx.

(3) Thermal average with quantum vibrational states in the harmonic approximation, and expansion of $\epsilon_n(\Delta R)$ to second order

$$E_{ph}(m) = \hbar \omega (m + \frac{1}{2})$$

$$n_{vib}(T) = \frac{1}{\hbar \omega} e^{\frac{\epsilon_n}{k_B T}} - 1$$

T-dependent phonon occupation number (Bose-Einstein)

$$\epsilon_n = \epsilon_n^0 + \frac{\partial \epsilon_n}{\partial R} \Delta R + \frac{1}{2} \frac{\partial^2 \epsilon_n}{\partial R^2} \Delta R^2$$

$$\delta \epsilon_n(T) = \frac{\partial \epsilon_n}{\partial n_{vib}} \left( n_{vib}(T) + \frac{1}{2} \right)$$

Pros: zero-point motion; $\epsilon_n(\Delta R)$ from DFT or GW; tractable … for molecules …

Cons: hard for solids (supercells); no anharmonicities; adiabatic (vibrations, but no exchange of energy!); supercell mix eigenstates, need unfolding
First-principles Allen-Heine-Cardona theory
Long history of the theory of T-dependent effects

In a semi-empirical context (empirical pseudopotential, tight-binding) …

Work from the ’50:
H. Y. Fan. Phys. Rev. 78, 808 (1950); 82, 900 (1951)

Within 2nd order perturbation theory treatment of electron-phonon effect, both contributions are needed (of course!).

Unification by:

=> the Allen-Heine-Cardona (AHC) theory.

Used for semi-empirical calculations in the ‘80s
Allen-Heine-Cardona (AHC) formalism


Second-order (time-dependent) perturbation theory
(no average contribution from first order)
* Formulas for solids (phonons have crystalline momentum)
* If adiabatic approximation ... neglect the phonon frequencies with respect to the electronic gap, no transfer of energy:

\[
\delta \varepsilon_{kn}(T, V = \text{const}) = \frac{1}{N_{\bar{q}}} \sum_{\bar{q}j} \frac{\partial \varepsilon_{kn}}{\partial n_{\bar{q}j}} \left( n_{\bar{q}j}(T) + \frac{1}{2} \right)
\]

occupation number from Bose-Einstein statistics

\[
\frac{\partial \varepsilon_{kn}}{\partial n_{\bar{q}j}} = \frac{1}{2\omega_{\bar{q}j}} \sum_{\kappa\kappa'b} \frac{\partial^2 \varepsilon_{kn}}{\partial R_{\kappa a} \partial R_{\kappa'b}} \frac{\xi_{\kappa a}(\bar{q}j) \xi_{\kappa'b}(-\bar{q}j)}{\sqrt{M_\kappa M_{\kappa'}}} e^{iq \cdot (R_{\kappa'b} - R_{\kappa a})}
\]

Electron-phonon coupling energy (EPCE)

“Phonon mode factor”

\[
\xi_{\kappa a}(\bar{q}j) \text{ phonon eigenmodes} \quad \kappa = \text{atom label} \quad a=x, y, or z
\]
Eigenvalue changes

\[ \left( \frac{\partial^2 \varepsilon_{kn}}{\partial R_{\kappa a} \partial R_{\kappa' b}} \right) \]

\[ \varepsilon_{kn} = \langle \phi_{\tilde{k} n} | \hat{H}_k | \phi_{\tilde{k} n} \rangle \]

\[ \hat{H} = \hat{T} + \hat{V}_{\text{nucl}} + \int \frac{\rho(r')}{|r-r'|} dr' + \frac{dE_{xc}}{d\rho(r)} \]

Hellman-Feynman theorem:

\[ \varepsilon_{kn}^{(1)} = \langle \phi_{\tilde{k} n}^{(0)} | \hat{H}_k^{(1)} | \phi_{\tilde{k} n}^{(0)} \rangle \]

One more derivative:

\[ \varepsilon_{kn}^{(2)} = \langle \phi_{\tilde{k} n}^{(0)} | \hat{H}_k^{(2)} | \phi_{\tilde{k} n}^{(0)} \rangle + \frac{1}{2} \left( \langle \phi_{\tilde{k} n}^{(0)} | \hat{H}_{\tilde{k} + \tilde{q}}^{(1)} | \phi_{\tilde{k} q n} \rangle + (c.c.) \right) \]

Debye-Waller
Antoncik

Fan
“self-energy”

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First-principles implementation

- Density-Functional Theory (later, GW results will be shown as well)
- Implementation in ABINIT ([www.abinit.org](http://www.abinit.org))
- Plane wave + pseudopotential methodology
- Converged number of plane waves (for diamond 30 ... 40 Hartree)
- $k$ point sampling (for diamond 6x6x6 sufficient for first-order Hamiltonian)
- Density Functional Perturbation Theory for phonons => no sum on conduction bands, no supercell

Technology used in the Materials project ([http://materialsproject.org](http://materialsproject.org))
>1500 phonon band structures from ABINIT freely available
ABINIT phonons uploaded in Materials Project

Warning! These calculations were performed using a PBEsol exchange correlation functional in the framework of DFPT using the Abinit code. Please see the wiki for more info.
DFT T-dependent band structure

Diamond 0 Kelvin (incl. Zero-point motion)

Note the widening of the bands = lifetime

DFT T-dependent band structure

Diamond 300 Kelvin

Note the widening of the bands = lifetime

DFT T-dependent band structure

Diamond 900 Kelvin

Note the widening of the bands = lifetime

DFT T-dependent band structure

Diamond 1500 Kelvin

Note the widening of the bands = lifetime

First-principles implementation

- Density-Functional Theory (later, GW results will be shown as well)
- Implementation in ABINIT (www.abinit.org)
- Plane wave + pseudopotential methodology
- Converged number of plane waves (for diamond 30 ... 40 Hartree)
- k point sampling (for diamond 6x6x6 sufficient for first-order Hamiltonian)
- Density Functional Perturbation Theory for phonons => no sum on conduction bands, no supercell need; reformulation of the Debye-Waller term thanks to the rigid-ion approximation
- Sampling on the q phonon wavevectors for the Fan term is a big issue!

\[
\delta \varepsilon_{\Gamma n}^{ZPM} = \frac{1}{N_q} \sum_{\bar{q} j} \frac{\partial \varepsilon_{\Gamma n}}{\partial n_{\bar{q} j}} \frac{1}{2} 
\]

\[
\frac{\partial \varepsilon_{\Gamma n} (Fan)}{\partial n_{\bar{q} j}} = \frac{1}{\omega_{\bar{q} j}} \Re \sum_{\kappa \kappa' b n'} \langle \phi_{\Gamma n} | \nabla_{\kappa a} H_k | \phi_{\bar{q} n'} \rangle \langle \phi_{\bar{q} n'} | \nabla_{\kappa' b} H_{k'} | \phi_{\Gamma n} \rangle \frac{\xi_{\kappa a} (\bar{q} j) \xi_{\kappa' b} (-\bar{q} j)}{\sqrt{M_{\kappa} M_{\kappa'}}} e^{i q j (R_{\kappa' b} - R_{\kappa a})}
\]

Indeed intraband contributions diverge due to the denominator!

Still, can be integrated out ... for diamond ...

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Intraband divergence for small $q$

Can be integrated in 3D!

Optic modes:

$$\lim_{\tilde{q} \to 0} \frac{\partial \varepsilon_{\Gamma_n}(Fan)}{\partial n_{\tilde{q}j}} = \lim_{\tilde{q} \to 0} \frac{1}{\omega_{\tilde{q}j}} \frac{f(\tilde{q}jn)}{\varepsilon_{\Gamma_n} - \varepsilon_{\tilde{q}n}}$$

$$\lim_{\tilde{q} \to 0} \frac{\partial \varepsilon_{\Gamma_n}(Fan)}{\partial n_{\tilde{q}j}} \propto \frac{1}{q^2}$$

+ For acoustic modes, Fan/DDW contribs cancel each other
Divergences on isoenergetic surface

\[
\lim_{\bar{q} \to \bar{q}_{iso}} \frac{\partial \epsilon_{\Gamma n} (Fan)}{\partial n_{\bar{q}_{ij}}} = \lim_{\bar{q} \to \bar{q}_{iso}} \frac{1}{\omega_{\bar{q}_{ij}}} \frac{f(\bar{q}_{jn})}{\epsilon_{\Gamma n} - \epsilon_{\bar{q}_{jn}}} \propto \frac{1}{\nabla_q \epsilon_{\bar{q}_{jn}} \bigg|_{\bar{q}_{iso}} \cdot (\bar{q} - \bar{q}_{iso})}
\]

Can be integrated!
Such problem occurs only off the extrema
Smoothing the denominator

Standard recipe in AHC works in the 80s: C, but also Si, III-V compounds ...

\[
\frac{\partial \epsilon_{\Gamma_n}(Fan)}{\partial n_{\bar{q}j}} = \frac{1}{\omega_{\bar{q}j}} \Re \sum_{\kappa\kappa'bn'} \langle \phi_{\Gamma_n} \big| \nabla_{\kappa a} H_{\kappa} \big| \phi_{\bar{q}n'} \rangle \langle \phi_{\bar{q}n'} \big| \nabla_{\kappa' b} H_{\kappa'} \big| \phi_{\Gamma_n} \rangle \frac{\xi_{\kappa a}(\bar{q}j)\xi_{\kappa' b}(-\bar{q}j)}{\sqrt{M_{\kappa}M_{\kappa'}}} e^{i q \cdot (R_{\kappa' b} - R_{\kappa a})} (\epsilon_{\Gamma_n} - \epsilon_{\bar{q}n'} + i\delta)
\]

... dramatically helps the convergence ... to a (slightly) different value ...

If imaginary part = 100 meV (considering direct gap at Gamma):

<table>
<thead>
<tr>
<th>q grid</th>
<th>#q in IBZ</th>
<th>ZPR VBM (meV)</th>
<th>ZPR CBM (meV)</th>
<th>ZPR gap (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8x8x8 x4s</td>
<td>60</td>
<td>140.5</td>
<td>-181.9</td>
<td>-322.4</td>
</tr>
<tr>
<td>12x12x12 x4s</td>
<td>182</td>
<td>141.7</td>
<td>-293.1</td>
<td>-434.8</td>
</tr>
<tr>
<td>16x16x16 x4s</td>
<td>408</td>
<td>141.7</td>
<td>-273.9</td>
<td>-415.6</td>
</tr>
<tr>
<td>20x20x20 x4s</td>
<td>770</td>
<td>141.7</td>
<td>-260.1</td>
<td>-401.8</td>
</tr>
<tr>
<td>24x24x24 x4s</td>
<td>1300</td>
<td>141.7</td>
<td>-257.5</td>
<td>-399.2</td>
</tr>
<tr>
<td>28x28x28 x4s</td>
<td>2030</td>
<td>141.7</td>
<td>-269.1</td>
<td>-410.8</td>
</tr>
<tr>
<td>32x32x32 x4s</td>
<td>2992</td>
<td>141.7</td>
<td>-271.8</td>
<td>-413.5</td>
</tr>
</tbody>
</table>
Changing the imaginary delta

$$f(\bar{q}jn) \over \epsilon_{\Gamma n} - \epsilon_{\bar{q}n} + i\delta$$

For very large q-wavevector sampling, rate of convergence understood, + correspond to expectations!
Breakdown of the adiabatic quadratic approximation for infra-red active materials
Boron nitride renormalization of gap

when the imaginary delta tends to zero, the ZPR diverges!

… such a divergence is confirmed by a « post-mortem » analysis …
Electric field with IR-active optic modes

Collective displacement with wavevector \( |q| \to 0 \quad \mathbf{G} = 0 \)

\[
H_{q}^{(1)} = \bar{V}_{\text{ext.,}q}^{(1)} + \bar{V}_{H,q}^{(1)} + \bar{V}_{\text{xc.,}q}^{(1)}
\]

\[
\bar{V}_{\text{ext.,}q}^{(1)}(\mathbf{G}) = \frac{-i}{\Omega_0} (\mathbf{G} + \mathbf{q})_\alpha e^{-i(\mathbf{G} + \mathbf{q}) \cdot \tau} v_\kappa(\mathbf{G} + \mathbf{q})
\]

\[
\bar{V}_{H,q}^{(1)}(\mathbf{G}) = 4\pi \frac{\bar{n}_{q}^{(1)}(\mathbf{G})}{|\mathbf{G} + \mathbf{q}|^2}
\]

Both the “external” and Hartree potentials can diverge like \( 1/|q| \).

Definition of the polarization of a phonon mode : \( P_{\alpha}^{(1)}(\mathbf{q}j) = \sum_{\kappa \beta} Z_{\kappa,\alpha \beta}^{*} \xi_{\kappa \beta}(\mathbf{q}j) \)

\[
Z_{\kappa,\alpha \beta}^{*} = \Omega_0 \left. \frac{\partial P_\alpha}{\partial u_{\kappa, \beta}} \right|_{\delta \mathbf{E} = 0}
\]

Born effective charge tensor for atom \( \kappa \)

Associated electric field \( E_\alpha = -\frac{4\pi}{\Omega_0} \sum_{\delta} P_{\delta}^{(1)}(\mathbf{q}j) q_\delta \)

\[
E_\alpha = -\frac{4\pi}{\Omega_0} \sum_{\gamma \delta} q_\gamma \varepsilon_{\gamma \delta} q_\delta = iH_{q}^{(1)}(\mathbf{G} = 0)
\]
Quadratic approx. with IR-active optic modes

\[
\frac{\partial \varepsilon_{\Gamma_n}(Fan)}{\partial n_{\bar{q}j}} = \frac{1}{\omega_{\bar{q}j}} \Re \sum_{\kappa\kappa' n' b' n} \left< \phi_{\Gamma_n} | \nabla_{\kappa a} H_{\kappa} | \phi_{\bar{q}n'} \right> \left< \phi_{\bar{q}n'} | \nabla_{\kappa' b} H_{\kappa'} | \phi_{\Gamma_n} \right> \frac{\xi_{\kappa a}(\bar{q}j) \xi_{\kappa' b}(-\bar{q}j)}{\sqrt{M_{\kappa} M_{\kappa'}}} (e^{iq(R_{\kappa' b} - R_{\kappa a})} - \varepsilon_{\Gamma_n} - \varepsilon_{\bar{q}n'})
\]

Twice \( H^{(1)}_{\bar{q}} = \sum_{\kappa a} \nabla_{\kappa a} H_{\kappa} \xi_{\kappa a}(\bar{q}j) \), each diverges like \( 1/q \), for polar optic modes.

At band extrema, the denominator induces a \( 1/q^2 \) divergence.

For polar optic modes: total divergence is like \( 1/q^4 \), cannot be integrated!

The adiabatic quadratic approximation breaks down for materials with IR-active optic modes.

[Note: In gapped systems, only elemental solids do not have IR-active modes]
Dynamical AHC theory

Beyond adiabatic perturbation theory … Many-body perturbation theory!

Fan self-energy (also called Migdal self-energy):

$$\sum_{\lambda,\lambda'} F_{\lambda,\lambda'}(\omega) = \sum_{\nu} \frac{1}{2\omega_{\nu}} \sum_{\lambda''} \langle \psi_{\lambda} | H^{(1)}_{\nu} | \psi_{\lambda''} \rangle \langle \psi_{\lambda''} | H^{(1)*}_{\nu} | \psi_{\lambda} \rangle$$

$$\left[ \frac{n_{\nu}(T) + f_{\lambda''}(T)}{\omega - \varepsilon_{\lambda''}^0 + \omega_{\nu} + i\eta \text{sgn}(\omega)} + \frac{n_{\nu}(T) + 1 - f_{\lambda''}(T)}{\omega - \varepsilon_{\lambda''}^0 - \omega_{\nu} + i\eta \text{sgn}(\omega)} \right]$$

→ integrable divergences!

Different levels:

On-the-mass shell approximation

$$\varepsilon_{\lambda} = \varepsilon_{\lambda}^0 + \Sigma_{\lambda}^{ep}(\varepsilon_{\lambda}^0)$$

Quasi-particle approximation

$$\varepsilon_{\lambda} = \varepsilon_{\lambda}^0 + \Sigma_{\lambda}^{ep}(\varepsilon_{\lambda})$$

$$Z_{\lambda} = \left( 1 - \text{Re} \left. \frac{\partial \Sigma_{\lambda}^{ep}(\omega)}{\partial \omega} \right|_{\omega = \varepsilon_{\lambda}^0} \right)^{-1}$$

Or even spectral functions

Zero-point renormalization: theory vs experiment
Non-adiabatic AHC theory vs experiment

Theoretical ZPR (meV)

Experimental ZPR (meV)

ZPR of the band gap
Two different exp techniques

\[ E_M = E_\infty + B M^{-1/2} \]
What about other theories?

ASC = Adiabatic SuperCell, based on DFT (PBE) or on GW - in principle more accurate than DFT.

For both ASC types, less than one third of points fall inside 15% zone

The DFT bandgap problem

Comparison of DFT/LDA and Many-Body Perturbation Theory GW band structures with photoemission and inverse photoemission experiments for Silicon.

E_{g}^{(exp)}=1.17 \ eV
E_{g}^{(GW)}=1.2 \ eV
E_{g}^{(DFT/LDA)}=0.6 \ eV

From "Quasiparticle calculations in solids", by Aulbur WG, Jonsson L, Wilkins JW,

**Motivation**

$G_0W_0$ + self-consistency + vertex (+e-h)...?

<table>
<thead>
<tr>
<th>Material</th>
<th>scGW RPA</th>
<th>scGW $e-h$</th>
<th>EXP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.95</td>
<td>0.81</td>
<td>0.74</td>
</tr>
<tr>
<td>Si</td>
<td>1.41</td>
<td>1.24</td>
<td>1.17</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.85</td>
<td>1.62</td>
<td>1.52</td>
</tr>
<tr>
<td>SiC</td>
<td>2.88</td>
<td>2.53</td>
<td>2.40</td>
</tr>
<tr>
<td>CdS</td>
<td>2.87</td>
<td>2.39</td>
<td>2.42</td>
</tr>
<tr>
<td>AlP</td>
<td>2.90</td>
<td>2.57</td>
<td>2.45</td>
</tr>
<tr>
<td>GaN</td>
<td>3.82</td>
<td>3.27</td>
<td>3.20</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.8</td>
<td>3.2</td>
<td>3.44</td>
</tr>
<tr>
<td>ZnS</td>
<td>4.15</td>
<td>3.60</td>
<td>3.91</td>
</tr>
<tr>
<td>C</td>
<td>6.18</td>
<td>5.79</td>
<td>5.48</td>
</tr>
<tr>
<td>BN</td>
<td>7.14</td>
<td>6.59</td>
<td>$\approx$ 6.25</td>
</tr>
<tr>
<td>MgO</td>
<td>9.16</td>
<td>8.12</td>
<td>7.83</td>
</tr>
<tr>
<td>LiF</td>
<td>15.9</td>
<td>14.5</td>
<td>14.20</td>
</tr>
<tr>
<td>Ar</td>
<td>14.9</td>
<td>13.9</td>
<td>14.20</td>
</tr>
<tr>
<td>Ne</td>
<td>22.1</td>
<td>21.4</td>
<td>21.70</td>
</tr>
</tbody>
</table>

scGW RPA vs EXP

Diff. 0.1 eV ... 1.4 eV

scGW + e-h is even better ...

Remaining discrepancy

0.1 eV ... 0.4 eV

Due to phonons, at least partly!

From Shishkin, Marsman, Kresse, PRL 99, 246403 (2007)
Band gap: theory vs experiment

$E_{g,\text{exp}}$: 0.7, 1.2, 1.5, 2.4, 2.4, 2.5, 3.2, 3.4, 3.9, 5.5, 6.3, 7.7, 14.2 (eV)

Ratio theory/experiment

- GWheh
- $G_0W_0$
- +ZPR

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The physics of the zero-point renormalization in IR-active materials
Try Fröhlich Hamiltonian ...

One (c or v) electronic band with only one LO phonon branch. Moreover :

(1) el-ph coupling = macroscopically screened Coulomb;
(2) parabolic (c or v) band with effective mass ;
(3) only intraband electronic contributions;
(4) phonon energy constant with respect to wavevector q.

Hypotheses (1-4) CORRECT for $q \neq 0$, but extended to full BZ and beyond.
NO Debye-Waller, no TO, no acoustic branches ! Long history (large polarons) …

For non-degenerate isotropic c or v band extrema + isotropic material :

$$\alpha = \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right) \left( \frac{m^*}{2\omega_{LO}} \right)^{1/2}$$

Lowest-order perturbation theory

$$ZPR^{Fr}_p = -\alpha \omega_{LO}$$
Fröhlich Hamiltonian


One (c or v) electronic band with only one LO phonon branch...

\[
\hat{H}^{Fr} = \hat{H}^{Fr}_{el} + \hat{H}^{Fr}_{ph} + \hat{H}^{Fr}_{EPI}
\]

\[
\hat{H}^{Fr}_{el} = \sum_{k} \frac{k^2}{2m^*} \hat{c}_k^+ \hat{c}_k
\]

\[
\hat{H}^{Fr}_{ph} = \sum_{q} \omega_{LO} \hat{a}_q^+ \hat{a}_q
\]

\[
\hat{H}^{Fr}_{EPI} = \sum_{q,k} g^{Fr}(q) \hat{c}_{k+q}^+ \hat{c}_k (\hat{a}_q + \hat{a}_q^+)
\]

\[
g^{Fr}(q) = \frac{i}{q} \left[ \frac{2\pi \omega_{LO}}{V_B \nu K} \left( \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right) \right]^{1/2}
\]

Lowest-order perturbation theory

\[
ZPR^{Fr} = -\alpha \omega_{LO}
\]

\[
\alpha = \left( \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right) \left( \frac{m^*}{2\omega_{LO}} \right)^{1/2}
\]
Generalisation of Fröhlich Hamiltonian

Here, lowest-order PT generalized to degenerate & anisotropic extrema + anisotropic materials + multiple phonon branches, still with hypotheses (1-4) \((Z^*, m^*, \text{dynamical matrix at } \Gamma \ldots \text{from 1st-principles})\)

\[
\hat{H}^{gFr}_{el} = \sum_{kn} \frac{k^2}{2m^*_n(k)} \hat{c}^+_k \hat{c}_k
\]

\[
\hat{H}^{gFr}_{ph} = \sum_{\mathbf{q}j} \omega_{j0}(\mathbf{q}) \hat{a}^+_q \hat{a}_q
\]

\[
\hat{H}^{gFr}_{EPI} = \sum_{\mathbf{q}j, kn'} g^{gFr}(\mathbf{q}j, kn') \hat{c}^+_k \hat{c}_{kn} (\hat{a}_q + \hat{a}^+_{-q})
\]

\[
g^{gFr}(\mathbf{q}j, kn') = \frac{i 4\pi}{q} \frac{1}{\Omega_0} \left( \frac{1}{2\omega_{j0}(\mathbf{q})} \right)^{1/2} \frac{\mathbf{q} \cdot \mathbf{p}_j(\mathbf{q})}{\epsilon(\mathbf{q})} \sum_m s_{n'm}(\mathbf{k}') (s_{nm}(\mathbf{k}))^*
\]

Lowest-order perturbation theory

\[
ZPR^{gFr}_{c} = -\sum_{jn} \frac{1}{\sqrt{2\Omega_0 n_d}} \int_{4\pi} d\mathbf{q} (m^*_n(\mathbf{q}))^{1/2} (\omega_{j0}(\mathbf{q}))^{-3/2} \left( \frac{\mathbf{q} \cdot \mathbf{p}_j(\mathbf{q})}{\epsilon(\mathbf{q})} \right)^2
\]
### Strongly IR active materials: oxides

<table>
<thead>
<tr>
<th>Material</th>
<th>AHC (meV)</th>
<th>gFr (meV)</th>
<th>gFr/AHC</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaO</td>
<td>-271</td>
<td>-358</td>
<td>1.32</td>
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<tr>
<td>SrO</td>
<td>-326</td>
<td>-370</td>
<td>1.13</td>
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<tr>
<td>CaO</td>
<td>-371</td>
<td>-377</td>
<td>1.11</td>
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<tr>
<td>TiO₂</td>
<td>-337</td>
<td>-371</td>
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<tr>
<td>Li₂O</td>
<td>-573</td>
<td>-536</td>
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<tr>
<td>ZnO</td>
<td>-157</td>
<td>-144</td>
<td>0.92</td>
</tr>
<tr>
<td>MgO</td>
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<td>-464</td>
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<tr>
<td>SnO₂</td>
<td>-215</td>
<td>-191</td>
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<tr>
<td>SrTiO₃</td>
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<td>-255</td>
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<tr>
<td>SiO₂</td>
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<td>-459</td>
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<tr>
<td>BeO</td>
<td>-699</td>
<td>-480</td>
<td>0.69</td>
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</table>
Weakly IR active materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Delta$E (meV)</th>
<th>$g_Fr$ (meV)</th>
<th>$g_Fr/\Delta$E</th>
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</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>-20</td>
<td>-16</td>
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<tr>
<td>CdS</td>
<td>-70</td>
<td>-54</td>
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<tr>
<td>CdSe</td>
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<tr>
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<td>-30</td>
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<tr>
<td>ZnTe</td>
<td>-22</td>
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<td>0.68</td>
</tr>
<tr>
<td>ZnS</td>
<td>-88</td>
<td>-59</td>
<td>0.67</td>
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<tr>
<td>GaN-zb</td>
<td>-176</td>
<td>-107</td>
<td>0.61</td>
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<tr>
<td>GaN-w</td>
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<tr>
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<td>SiC</td>
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<tr>
<td>GaAs</td>
<td>-24</td>
<td>-5</td>
<td>0.21</td>
</tr>
</tbody>
</table>
Why are LO phonon frequencies so important?

\[ ZPR^{Fr} = -\alpha \omega_{LO} \]

\[ \alpha = \left( \frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right) \left( \frac{m^*}{2\omega_{LO}} \right)^{1/2} \]

Crucial dynamical effects!

“Slow electrons + fast phonons” = “polarons”
Adiabatic approximation: fast electrons

$$\Sigma_{qV} \propto \frac{1}{\epsilon_{kn}^0 - \epsilon_{k+q}^0 \pm \omega_{qV}}, \quad \text{where} \quad \epsilon_{kn}^0 - \epsilon_{k+q}^0 = \Delta \epsilon^0 \sim \frac{q^2}{2m^*}$$

Combine states $|kn\rangle$ and $|k + qn\rangle$:

**Static (adiabatic) case**

LO phonon potential

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Skoltech, April 16, 2019
Are electrons always fast?

\[ \Sigma_{qV} \propto \frac{1}{\varepsilon_{kn}^0 - \varepsilon_{k+qn}^0 \pm \omega_{qV}}, \quad \text{where} \quad \varepsilon_{kn}^0 - \varepsilon_{k+qn}^0 = \Delta \varepsilon^0 \sim \frac{q^2}{2m^*} \]

Combine states \(|kn\rangle\) and \(|k+qn\rangle\):

**Dynamical (non-adiabatic) case**

\[ \tau \sim \frac{\hbar}{\Delta \varepsilon^0} \]

LO phonon potential

\[ \tau_{ph} \sim \frac{1}{\omega_{LO}} \]
Are electrons always fast?

\[ \Sigma_{qV} \propto \frac{1}{\varepsilon_{kn}^0 - \varepsilon_{k+q_n}^0 \pm \omega_{qV}} , \quad \text{where} \quad \varepsilon_{kn}^0 - \varepsilon_{k+q_n}^0 = \Delta \varepsilon^0 \sim \frac{q^2}{2m^*} \]

Combine states \(|kn\rangle\) and \(|k+qn\rangle\):

Dynamical (non-adiabatic) case

At variance with adiabatic hypothesis, in IR-active materials, LO phonons are faster than the added electron (or the hole) \(\Rightarrow\) polarons

When \(\tau > \tau_{ph}\) : electron has no time to adjust
Summary

- Many effects: Fan, Debye-Waller, dynamical self-energy, accurate starting electronic structure (GW) and el-phon coupling (GW) … but also thermal expansion, anharmonicities, non-rigid ion behaviour … (not presented here)
- Sampling phonon wavevector (= supercell size) is a serious issue
- Adiabatic quadratic approximation breaks down for infra-red active solids (both for AHC and supercell case), while inclusion of dynamical effects remove divergences
- Fröhlich Hamiltonian captures well the main features of first-principle results for IR-active materials!
- Crucial dynamical effects!
  “Slow electrons + fast phonons” = “polarons”