

Ab initio methods in solid state physics

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Density-functional perturbation theory (DFPT)

S. Baroni, S. de Gironcoli, A. D. Corso, and P. Giannozzi,
Rev. Mod. Phys. **73**, 515 (2001)

We assume that the external potential acting on the electrons is a differentiable function of a set of parameters, $\lambda = \{\lambda_i\}$ ($\lambda_i = \mathbf{R}_I$ in the case of atomic displacements), and the total energy is given by

$$E = T + V_{\text{el}} + \int d\mathbf{r} V_{\lambda}(\mathbf{r}) n(\mathbf{r}). \quad (1)$$

According to the Hellmann-Feynman theorem, the first and second derivatives of the ground-state energy read

$$\frac{\partial E}{\partial \lambda_i} = \int d\mathbf{r} \frac{\partial V_{\lambda}(\mathbf{r})}{\partial \lambda_i} n_{\lambda}(\mathbf{r}), \quad (2)$$

$$\frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j} = \int d\mathbf{r} \frac{\partial^2 V_{\lambda}(\mathbf{r})}{\partial \lambda_i \partial \lambda_j} n_{\lambda}(\mathbf{r}) + \int d\mathbf{r} \frac{\partial V_{\lambda}(\mathbf{r})}{\partial \lambda_i} \frac{\partial n_{\lambda}(\mathbf{r})}{\partial \lambda_j}. \quad (3)$$

Linear response

The variation of the Kohn-Sham orbitals $\Delta\psi_m(\mathbf{r})$ is obtained by standard first-order perturbation theory

$$(H - \varepsilon_m)|\Delta\psi_m(\mathbf{r})\rangle = -(\Delta V(\mathbf{r}) - \Delta\varepsilon_m)|\psi_m(\mathbf{r})\rangle, \quad (4)$$

where the first-order correction to the self-consistent potential is

$$\Delta V(\mathbf{r}) = \Delta V_{ion}(\mathbf{r}) + \int d\mathbf{r}' \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{dv_{xc}}{dn} \Delta n(\mathbf{r}), \quad (5)$$

the linear change of electron density $n(\mathbf{r}) = \sum_m |\psi_m(\mathbf{r})|^2$ is given by

$$\Delta n(\mathbf{r}) = 4 \sum_m \psi_m^*(\mathbf{r}) \Delta\psi_m(\mathbf{r}) = 4 \sum_m \psi_m^*(\mathbf{r}) \sum_i \frac{\partial \psi_m(\mathbf{r})}{\partial \lambda_i} \Delta\lambda_i, \quad (6)$$

and the first-order variation of the Kohn-Sham eigenvalue ε_m

$$\Delta\varepsilon_m = \langle \psi_m | \Delta V | \psi_m \rangle. \quad (7)$$

Linear response – reciprocal space

One of the greatest advantages of the method is that the responses to perturbations of different wavelengths (wave vectors \mathbf{k}) are decoupled.

For the Bloch functions

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \quad (8)$$

the Fourier component of the charge-density response at wave vector \mathbf{q} is obtained from

$$\Delta n_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{k}} u_{\mathbf{k}}^*(\mathbf{r}) \Delta u_{\mathbf{k}+\mathbf{q}}(\mathbf{r}). \quad (9)$$

The Fourier component of the self-consistent potential response reads

$$\Delta v_{\mathbf{q}}(\mathbf{r}) = \Delta v_{\mathbf{q}}^{ion}(\mathbf{r}) + \int d\mathbf{r}' \frac{\Delta n_{\mathbf{q}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{dv_{xc}}{dn} \Delta n_{\mathbf{q}}(\mathbf{r}). \quad (10)$$

Linear response – phonon calculations

The position of the l th atom is given by

$$\mathbf{R}_l = \mathbf{R}_n + \boldsymbol{\tau}_i + \mathbf{u}_i(n) = \mathbf{R}_n + \boldsymbol{\tau}_i + \mathbf{u}_i(\mathbf{q})e^{i\mathbf{q}\mathbf{R}_n}, \quad (11)$$

where \mathbf{R}_n is the position of the n th unit cell in the Bravais lattice, $\boldsymbol{\tau}_i$ is the equilibrium position of the atom in the unit cell, and $\mathbf{u}_i(n)$ indicates the deviation from equilibrium of the nuclear position. The force constants matrix depends on the distance between two unit cells, $\mathbf{R} = \mathbf{R}_n - \mathbf{R}_m$

$$\Phi_{ij}^{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m) = \frac{\partial^2 V}{\partial u_i^\alpha(n) \partial u_j^\beta(m)}. \quad (12)$$

The Fourier transform of the force constants matrix gives the dynamical matrix

$$\sqrt{m_i m_j} D_{ij}^{\alpha\beta}(\mathbf{q}) = \sum_{\mathbf{R}} \Phi_{ij}^{\alpha\beta}(\mathbf{R}) e^{-i\mathbf{q}\mathbf{R}} = \frac{1}{N} \frac{\partial^2 V}{\partial u_i^\alpha(\mathbf{q}) \partial u_j^\beta(\mathbf{q})}. \quad (13)$$

Dynamical matrix

Dynamical matrix consists of the electronic and ionic part

$$D_{ij}^{\alpha\beta}(\mathbf{q}) = D_{ij}^{\alpha\beta}(\mathbf{q})_{\text{el}} + D_{ij}^{\alpha\beta}(\mathbf{q})_{\text{ion}} \quad (14)$$

The electronic part includes changes in charge density

$$D_{ij}^{\alpha\beta}(\mathbf{q})_{\text{el}} = \frac{1}{N\sqrt{m_i m_j}} \int d\mathbf{r} \left[\frac{\partial n(\mathbf{r})}{\partial u_i^\alpha(\mathbf{q})} \frac{\partial V_{\text{ion}}(\mathbf{r})}{\partial u_j^\beta(\mathbf{q})} + n(\mathbf{r}) \frac{\partial^2 V_{\text{ion}}(\mathbf{r})}{\partial u_i^\alpha(\mathbf{q}) \partial u_j^\beta(\mathbf{q})} \right]. \quad (15)$$

The phonon frequencies $\omega(\mathbf{q})$ and polarization vectors $e_{i\alpha}(\mathbf{q})$ are obtained from the eigenequation

$$\sum_{j\beta} D_{ij}^{\alpha\beta}(\mathbf{q}) e_{j\beta}(\mathbf{q}) = \omega^2(\mathbf{q}) e_{i\alpha}(\mathbf{q}). \quad (16)$$

Phonons in polar materials

In the long-wavelength limit ($\mathbf{q} \rightarrow 0$), the dynamical matrix can be split into the sum of an analytic and a nonanalytic contribution (Born and Huang, 1954)

$$D_{ij}^{\alpha\beta} = D_{ij,\text{an}}^{\alpha\beta} + D_{ij,\text{na}}^{\alpha\beta}, \quad (17)$$

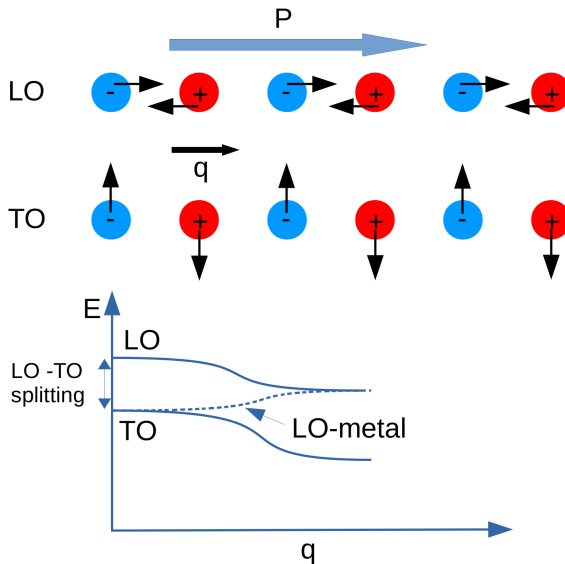
where analytic part is the matrix obtained from the response to a zone-center phonon ($\mathbf{q} = 0$), calculated at zero macroscopic electric field. The nonanalytic part describes the longitudinal vibrations of the infrared modes, and can be obtained from the equation

$$D_{ij,\text{na}}^{\alpha\beta} = \frac{4\pi e^2}{\Omega} \frac{\sum_{\gamma} Z_i^{*\gamma\alpha} q_{\gamma} \sum_{\nu} Z_j^{*\nu\beta} q_{\nu}}{\sum_{\gamma\nu} q_{\gamma} \epsilon_{\infty}^{\gamma\nu} q_{\nu}}, \quad (18)$$

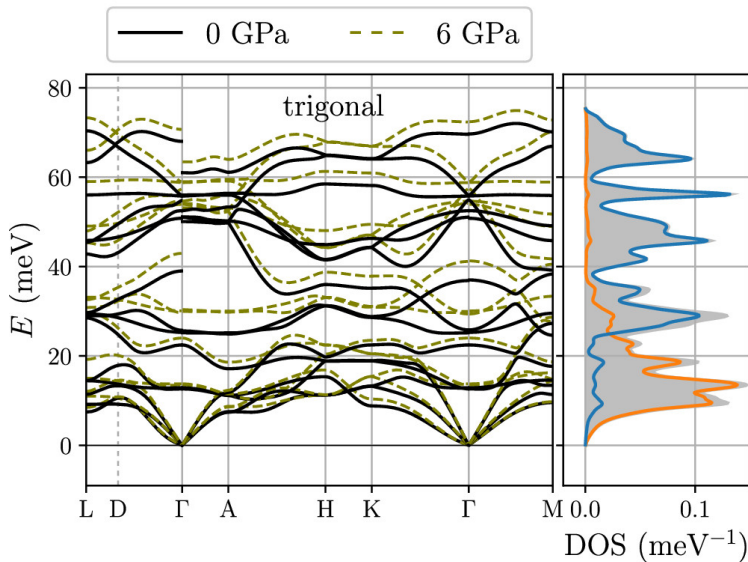
where $\epsilon_{\infty}^{\gamma\nu}$ is the electronic dielectric-constant tensor and $Z_i^{*\gamma\alpha}$ is the Born effective charge tensor

$$Z_i^{*\gamma\alpha} = \frac{\Omega}{e} \frac{\partial P_{\alpha}}{\partial u_i^{\beta}(\mathbf{q} = 0)}. \quad (19)$$

Longitudinal optic - transverse optic (LO-TO) splitting



Example: LO-TO splitting in Eu_2O_3



Electron-phonon interaction

F. Giustino, Rev. Mod. Phys. **89**, 015003 (2017)

Electron-phonon interaction is important for transport properties – electric and heat conductivity. Interaction of phonons with electrons leads to reduction of phonon lifetime $\tau_{i\mathbf{q}}$

$$\frac{1}{\tau_{i\mathbf{q}}} = \frac{4\pi}{\hbar} \sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} |g_{mni}(\mathbf{k}, \mathbf{q})|^2 (f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}) \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{i\mathbf{q}}). \quad (20)$$

Electron-phonon matrix elements are given by

$$g_{mni}(\mathbf{k}, \mathbf{q}) = \langle u_{m\mathbf{k}+\mathbf{q}} | \Delta_{i\mathbf{q}} V | u_{n\mathbf{k}} \rangle = \int d\mathbf{r} u_{m\mathbf{k}+\mathbf{q}}^* \Delta_{i\mathbf{q}} V u_{n\mathbf{k}}, \quad (21)$$

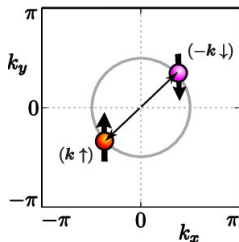
where

$$\Delta_{i\mathbf{q}} V = \sum_{j\alpha} e_{j\alpha,i}(\mathbf{q}) \sum_{\mathbf{R}} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{R})} \frac{\partial V}{\partial u_j^\alpha}. \quad (22)$$

Phonon mediated superconductivity

In the Bardeen-Cooper-Schrieffer (BCS) theory, the superconducting current is carried by the Cooper pairs, created by to attraction between electrons due to electron-phonon coupling. The strength of electron-phonon interaction is described by the coupling constant

$$\lambda = 2 \int d\omega \frac{\alpha^2 F(\omega)}{\omega}. \quad (23)$$



$\alpha^2 F(\omega)$ is the Eliashberg function

$$\alpha^2 F(\omega) = \frac{1}{N_F} \int \frac{d\mathbf{k} d\mathbf{q}}{\Omega_{\text{BZ}}^2} \sum_{mni} |g_{mni}(\mathbf{k}, \mathbf{q})|^2 \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_F) \delta(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_F) \delta(\omega - \omega_{i\mathbf{q}}). \quad (24)$$

Phonon mediated superconductivity

The superconducting critical temperature can be estimated using on a semiempirical expression first introduced by McMillan and then refined by Allen and Dynes

$$T_c = \frac{\hbar\omega_{\log}}{1.2} \exp \left[- \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right], \quad (25)$$

where ω_{\log} is obtained using the Eliashberg function

$$\omega_{\log} = \exp \left[\frac{2}{\lambda} \int d\omega \frac{\alpha^2 F(\omega)}{\omega} \log \omega \right]. \quad (26)$$

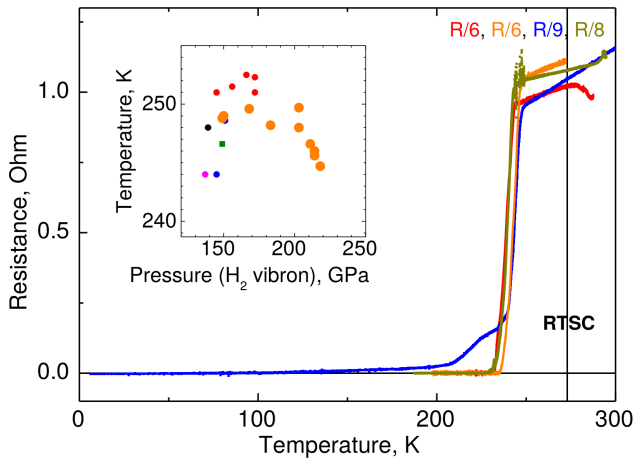
The parameter μ^* is obtained as

$$\frac{1}{\mu^*} = \frac{1}{\mu} - \log \frac{\omega_p}{\omega_{ph}}, \quad (27)$$

where μ is the average electron-electron Coulomb repulsion, ω_p is the characteristic plasma frequency, and ω_{ph} is the largest phonon frequency.

Superconductivity of LaH_{10}

A. P. Drozdov *et al.*, Nature **569**, 528 (2019)



Superconductivity of LaH_{10}

I. A. Kruglov *et al.*, Phys. Rev. B **101**, 024508 (2020)

The calculations of the electron-phonon coupling (EPC) constant and critical temperature were carried out using the Quantum Espresso package within DFPT.

