Ab initio methods in solid state physics
Density-functional perturbation theory (DFPT)

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Linear response

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, $\lambda = \{\lambda_i\}$ ($\lambda_i = \boldsymbol{R}_I$ in the case of atomic displacements), and the total energy is given by

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

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

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

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

Linear response

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

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

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

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

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

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

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

$$\Delta\varepsilon_m = \langle\psi_m|\Delta V|\psi_m\rangle. \tag{7}$$

Linear response – reciprocal space

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

For the Bloch functions

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

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

$$\Delta n_{\boldsymbol{q}}(\boldsymbol{r}) = \sum_{\boldsymbol{k}} u^*_{\boldsymbol{k}}(\boldsymbol{r}) \Delta u_{\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{r}). \tag{9}$$

The Fourier component of the self-consistent potential response reads

$$\Delta v_{\boldsymbol{q}}(\boldsymbol{r}) = \Delta v^{ion}_{\boldsymbol{q}}(\boldsymbol{r}) + \int d\boldsymbol{r} \frac{\Delta n_{\boldsymbol{q}}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} + \frac{dv_{\mathrm{xc}}}{dn} \Delta n_{\boldsymbol{q}}(\boldsymbol{r}). \tag{10}$$

Linear response – phonon calculations

The position of the lth atom is given by

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

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

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

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

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

Dynamical matrix

Dynamical matrix consists of the electronic and ionic part

$$D_{ij}^{\alpha\beta}(\boldsymbol{q}) = D_{ij}^{\alpha\beta}(\boldsymbol{q})_{\mathrm{el}} + D_{ij}^{\alpha\beta}(\boldsymbol{q})_{\mathrm{ion}} \tag{14}$$

The electronic part includes changes in charge density

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

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

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

Phonons in polar materials

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

$$D_{ij}^{\alpha\beta} = D_{ij,\mathrm{an}}^{\alpha\beta} + D_{ij,\mathrm{na}}^{\alpha\beta}, \tag{17}$$

where analytic part is the matrix obtained from the response to a zone-center phonon ($\boldsymbol{q} = 0$), calculated at zero macroscopic electric field. The nonanalytic part describes the longitudinal optic/transverse optic (LO/TO) splitting of the infrared modes, and has the general form

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

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

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

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 $\tau_{i\boldsymbol{q}}$

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

Electron-phonon matrix elements are given by

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

where

$$\Delta_{i\boldsymbol{q}}V = \sum_{j\alpha} e_{j\alpha,i}(\boldsymbol{q})\sum_{\boldsymbol{R}} e^{-i\boldsymbol{q}(\boldsymbol{r}-\boldsymbol{R})}\frac{\partial V}{\partial u^{\alpha}_{j}}. \tag{22}$$

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

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

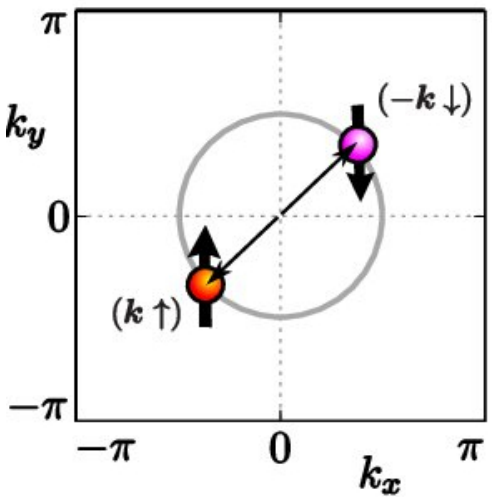


Figure made by Andrzej Ptok

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

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

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

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

where $\omega_{\log}$ is obtained using the Eliashberg function

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

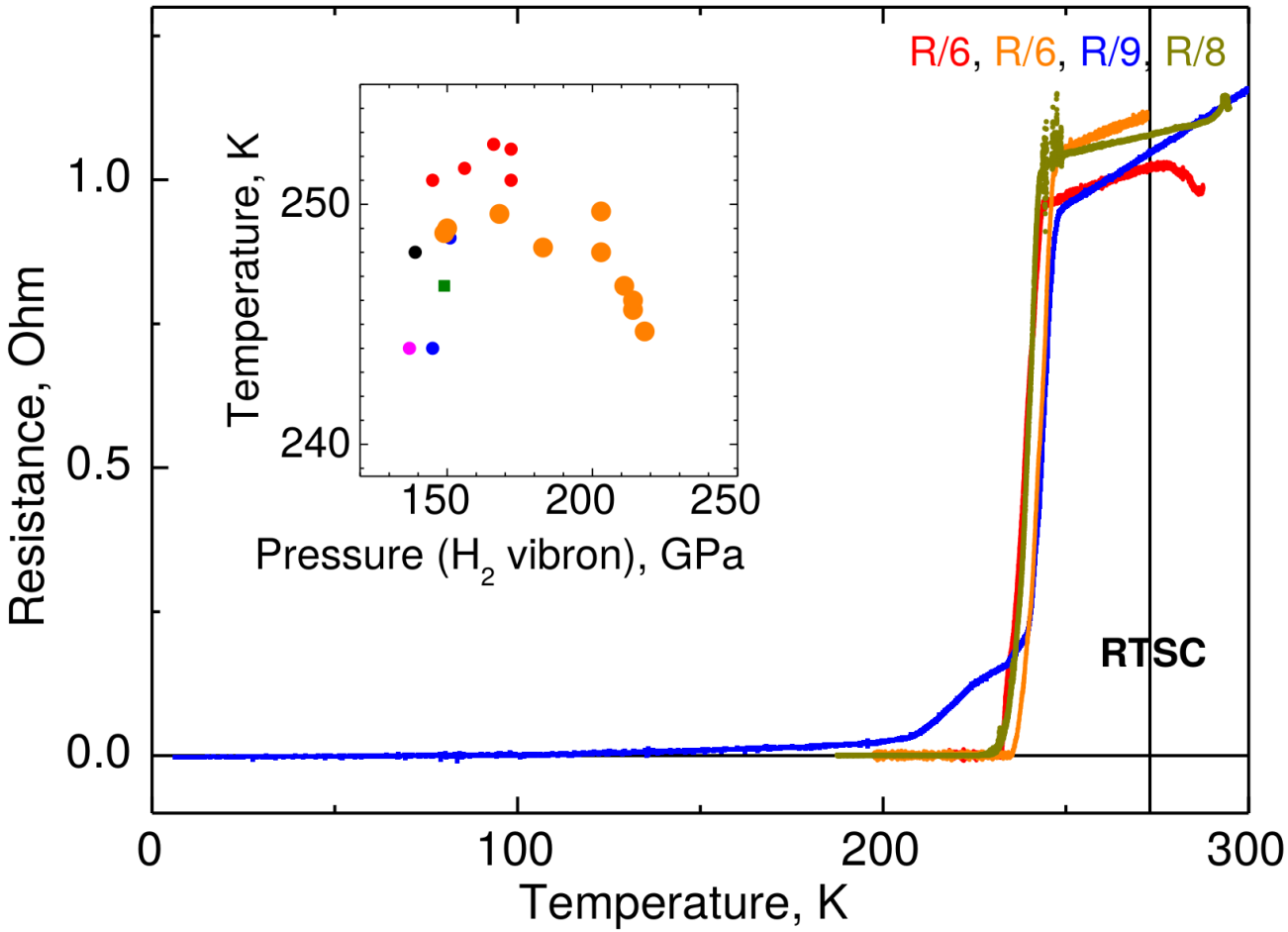
The parameter μ^* is obtained as

$$\frac{1}{\mu*} = \frac{1}{\mu} - \log\frac{\omega_p}{\omega_{ph}}, \tag{27}$$

where μ is 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 critical temperature and electron-phonon coupling (EPC) parameters were carried out using the QUANTUM ESPRESSO package within density functional perturbation theory, employing the plane-wave pseudopotential method and PBE exchange-correlation functional.