VASP: Dielectric response
Perturbation theory, linear response, and finite electric fields

University of Vienna,
Faculty of Physics and Center for Computational Materials Science,
Vienna, Austria

Outline

- Dielectric response

- Frequency dependent dielectric properties

- The static dielectric response

- Response to electric fields from DFPT

- The macroscopic polarization

- SCF response to finite electric fields

- Ionic contributions to dielectric properties

Experiment: Static and frequency dependent dielectric functions: measurement of absorption, reflectance and energy loss spectra. (Optical properties of semiconductors and metals.)

- The long-wavelength limit of the frequency dependent microscopic polarizability and dielectric matrices determine the optical properties in the regime accessible to optical and electronic probes.

Theory: The frequency dependent polarizability matrix is needed in many post-DFT schemes, e.g.:

- GW
) frequency dependent microscopic dielectric response needed to compute W.
) frequency dependent macroscopic dielectric tensor required for the
    analytical integration of the Coulomb singularity in the self-energy.
- Exact-exchange optimized-effective-potential method (EXX-OEP).
- Bethe-Salpeter-Equation (BSE)
) dielectric screening of the interaction potential needed to properly include
    excitonic effects.

Frequency dependent

- Frequency dependent microscopic dielectric matrix
) In the RPA, and including changes in the DFT xc-potential.

- Frequency dependent macroscopic dielectric tensor
) Imaginary and real part of the dielectric function.
) In- or excluding local field effects.
) In the RPA, and including changes in the DFT xc-potential:

Static

- Static dielectric tensor, Born effective charges, and Piezo-electric tensor,
  in- or excluding local field effects.
) From density-functional-perturbation-theory (DFPT).
    Local field effects in RPA and DFT xc-potential.
) From the self-consistent response to a finite electric field (PEAD).
    Local field effects from changes in a HF/DFT hybrid xc-potential, as well.

Macroscopic continuum considerations

- The macroscopic dielectric tensor couples the electric field in a material to an applied external electric field:

$$\mathbf{E} = \epsilon^{-1}\mathbf{E}_{\text{ext}}$$ where ϵ is a 3✕3 tensor

- For a longitudinal field, i.e., a field caused by stationary external charges, this can be reformulated as (in momentum space, in the long-wavelength limit):

$$v_{\text{tot}} = \epsilon^{-1}v_{\text{ext}}$$ with $v_{\text{tot}} = v_{\text{ext}} + v_{\text{ind}}$

- The induced potential is generated by the induced change in the charge density ρ_{ind}. In the linear response regime (weak external fields):

$$\rho_{\text{ind}} = \chi v_{\text{ext}}$$ where χ is the reducible polarizability

$$\rho_{\text{ind}} = P v_{\text{tot}}$$ where P is the irreducible polarizability

- It may be straightforwardly shown that:

$$\epsilon^{-1} = 1 + \nu\chi \qquad \epsilon = 1 - \nu P \qquad \chi = P + P\nu\chi$$ (a Dyson eq.)

where ν is the Coulomb kernel. In momentum space: $\nu = 4\pi e^2/q^2$

Macroscopic and microscopic quantities

The macroscopic dielectric function can be formally written as

$$\mathbf{E}(\mathbf{r}, \omega) = \int d\mathbf{r}' \epsilon_{\mathrm{mac}}^{-1}(\mathbf{r} - \mathbf{r}', \omega) \mathbf{E}_{\mathrm{ext}}(\mathbf{r}', \omega)$$

or in momentum space

$$\mathbf{E}(\mathbf{q}, \omega) = \epsilon_{\mathrm{mac}}^{-1}(\mathbf{q}, \omega) \mathbf{E}_{\mathrm{ext}}(\mathbf{q}, \omega)$$

The microscopic dielectric function enters as

$$\mathbf{e}(\mathbf{r}, \omega) = \int d\mathbf{r}' \epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) \mathbf{E}_{\mathrm{ext}}(\mathbf{r}', \omega)$$

and in momentum space

$$\mathbf{e}(\mathbf{q} + \mathbf{G}, \omega) = \sum_{\mathbf{G}'} \epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q}, \omega) \mathbf{E}_{\mathrm{ext}}(\mathbf{q} + \mathbf{G}', \omega)$$

The microscopic dielectric function is accessible through ab-initio calculations. Macroscopic and microscopic quantities are linked through:

$$\mathbf{E}(\mathbf{R}, \omega) = \frac{1}{\Omega} \int_{\Omega(\mathbf{R})} \mathbf{e}(\mathbf{r}, \omega) d\mathbf{r}$$

Macroscopic and microscopic quantities

Assuming the external field varies on a length scale much larger that the atomic distances, one may show that

$$\mathbf{E}(\mathbf{q}, \omega) = \epsilon_{0,0}^{-1}(\mathbf{q}, \omega) \mathbf{E}_{\text{ext}}(\mathbf{q}, \omega)$$

and

$$\epsilon_{\text{mac}}^{-1}(\mathbf{q}, \omega) = \epsilon_{0,0}^{-1}(\mathbf{q}, \omega)$$

$$\epsilon_{\text{mac}}(\mathbf{q}, \omega) = \left(\epsilon_{0,0}^{-1}(\mathbf{q}, \omega) \right)^{-1}$$

For materials that are homogeneous on the microscopic scale, the off-diagonal elements of $\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q}, \omega)$, (i.e., for $\mathbf{G} \neq \mathbf{G}'$) are zero, and

$$\epsilon_{\text{mac}}(\mathbf{q}, \omega) = \epsilon_{0,0}(\mathbf{q}, \omega)$$

This called the "neglect of local field effects"

The longitudinal microscopic dielectric function

The microscopic (symmetric) dielectric function that links the longitudinal component of an external field (i.e., the part polarized along the propagation wave vector $\mathbf{q}$) to the longitudinal component of the total electric field, is given by

$$\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \delta_{\mathbf{G},\mathbf{G}'} + \frac{4\pi e^2}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|} \frac{\partial \rho_{\text{ind}}(\mathbf{q}+\mathbf{G},\omega)}{\partial v_{\text{ext}}(\mathbf{q}+\mathbf{G}',\omega)}$$

$$\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \delta_{\mathbf{G},\mathbf{G}'} - \frac{4\pi e^2}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|} \frac{\partial \rho_{\text{ind}}(\mathbf{q}+\mathbf{G},\omega)}{\partial v_{\text{tot}}(\mathbf{q}+\mathbf{G}',\omega)}$$

and with $\quad \chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \dfrac{\partial \rho_{\text{ind}}(\mathbf{q}+\mathbf{G},\omega)}{\partial v_{\text{ext}}(\mathbf{q}+\mathbf{G}',\omega)} \qquad P_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \dfrac{\partial \rho_{\text{ind}}(\mathbf{q}+\mathbf{G},\omega)}{\partial v_{\text{tot}}(\mathbf{q}+\mathbf{G}',\omega)}$

and $\quad \nu^s_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) := \dfrac{4\pi e^2}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}$

one obtains the Dyson equation linking *P* and χ

$$\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = P_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) + \sum_{\mathbf{G}_1,\mathbf{G}_2} P_{\mathbf{G},\mathbf{G}_1}(\mathbf{q},\omega) \nu^s_{\mathbf{G}_1,\mathbf{G}_2}(\mathbf{q}) \chi_{\mathbf{G}_2,\mathbf{G}'}(\mathbf{q},\omega)$$

Approximations

Problem: We know neither P and χ

Problem: The quantity we can easily access in Kohn-Sham DFT is the: "irreducible polarizability in the independent particle picture" χ^0 (or χ^{KS})

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \frac{\partial \rho_{\mathrm{ind}}(\mathbf{q}+\mathbf{G},\omega)}{\partial v_{\mathrm{eff}}(\mathbf{q}+\mathbf{G}',\omega)}$$

Adler and Wiser derived expressions for χ^0 which, in terms of Bloch functions, can be written as (in reciprocal space):

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{1}{\Omega} \sum_{nn'\mathbf{k}} 2w_{\mathbf{k}}(f_{n'\mathbf{k}+\mathbf{q}} - f_{n'\mathbf{k}})$$

$$\times \frac{\langle\psi_{n'\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\psi_{n\mathbf{k}}\rangle \langle\psi_{n\mathbf{k}}|e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}|\psi_{n'\mathbf{k}+\mathbf{q}}\rangle}{\epsilon_{n'\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}} - \omega - i\eta}$$

Approximations (cont.)

For the Kohn-Sham system, the following relations can be shown to hold

$$\chi = \chi^0 + \chi^0(\nu + f_{\mathrm{xc}})\chi$$
$$P = \chi^0 + \chi^0 f_{xc} P$$
$$\chi = P + P\nu\chi$$

where ν is the Coulomb kernel and $f_{\mathbf{xc}}$ is the DFT xc-kernel: $f_{\mathrm{xc}} = \partial v_{xc}/\partial\rho \mid_{\rho=\rho_0}$

$$\epsilon^{-1} = 1 + \nu\chi \qquad\qquad \epsilon = 1 - \nu P$$

Random-Phase-Approximation (RPA): $\quad P = \chi^0$

$$\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \delta_{\mathbf{G},\mathbf{G}'} - \frac{4\pi e^2}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$$

Including changes in the DFT xc-potential: $\quad P = \chi^0 + \chi^0 f_{xc} P$

Calculation of optical properties

The long-wavelength limit ($\mathbf{q} \longrightarrow \mathbf{0}$) of the dielectric matrix determines the optical properties in the regime accessible to optical probes.

The macroscopic dielectric tensor $\epsilon_\infty(\omega)$

$$\frac{1}{\hat{\mathbf{q}} \cdot \epsilon_\infty(\omega) \cdot \hat{\mathbf{q}}} = \lim_{\mathbf{q} \to 0} \epsilon_{0,0}^{-1}(\mathbf{q}, \omega)$$

can be obtained at various levels of approximation:

- LOPTICS = .TRUE.
) $\epsilon_{0,0}(\mathbf{q}, \omega)$ in the independent-particle (IP) picture.
) neglect of local field effects:

$$\hat{\mathbf{q}} \cdot \epsilon_\infty(\omega) \cdot \hat{\mathbf{q}} \approx \lim_{\mathbf{q} \to 0} \epsilon_{0,0}(\mathbf{q}, \omega)$$

- ALGO = CHI
) Including local field effects: in RPA and due to changes in the DFT xc-potential
    LRPA = .TRUE. | .FALSE., default: .TRUE.

Frequency dependent (neglecting local field effects)

LOPTICS = .TRUE.

$$\hat{\mathbf{q}} \cdot \epsilon_\infty(\omega) \cdot \hat{\mathbf{q}} \approx \lim_{\mathbf{q} \to 0} \epsilon_{0,0}(\mathbf{q}, \omega)$$

The imaginary part of $\epsilon_\infty(\omega)$ (3✕3 tensor) of which is given by

$$\epsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{v,c,\mathbf{k}} 2w_\mathbf{k} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega)$$

$$\times \langle u_{c\mathbf{k}+q\mathbf{e}_\alpha} | u_{v\mathbf{k}} \rangle \langle u_{v\mathbf{k}} | u_{c\mathbf{k}+q\mathbf{e}_\beta} \rangle$$

and the real part is obtained by a Kramers-Kronig transformation

$$\epsilon_{\alpha\beta}^{(1)}(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\epsilon_{\alpha\beta}^{(2)}(\omega')\omega'}{\omega'^2 - \omega^2} d\omega'$$

The difficulty lies in the computation of the quantities

$$\left| u_{n\mathbf{k}+q\mathbf{e}_\alpha} \right\rangle$$

the first-order change in the cell periodic part of $|\psi_{n\mathbf{k}}\rangle$ w.r.t. the Block vector $\mathbf{k}$.

First-order change in the orbitals

Expanding up to first order in **q**

$$|u_{n\mathbf{k}+\mathbf{q}}\rangle = |u_{n\mathbf{k}}\rangle + \mathbf{q} \cdot |\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle + \dots$$
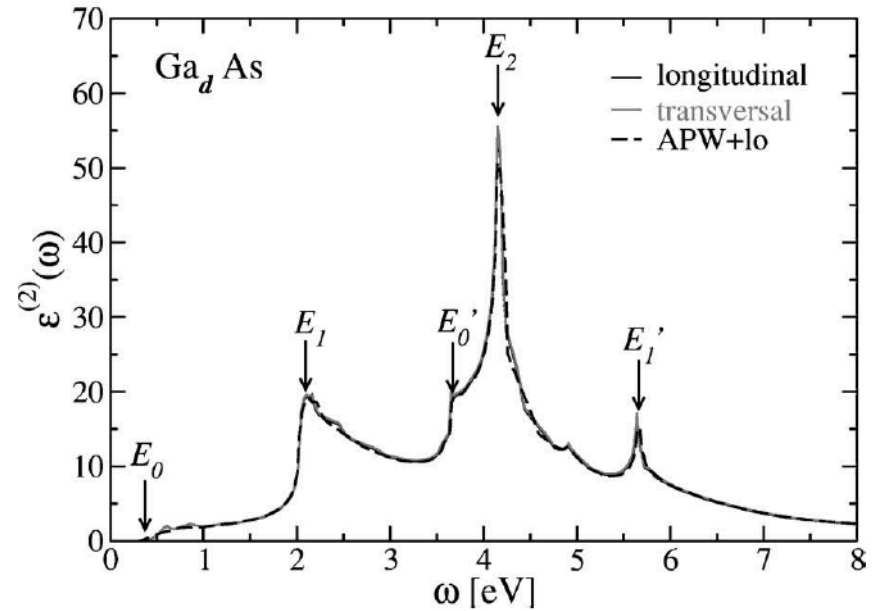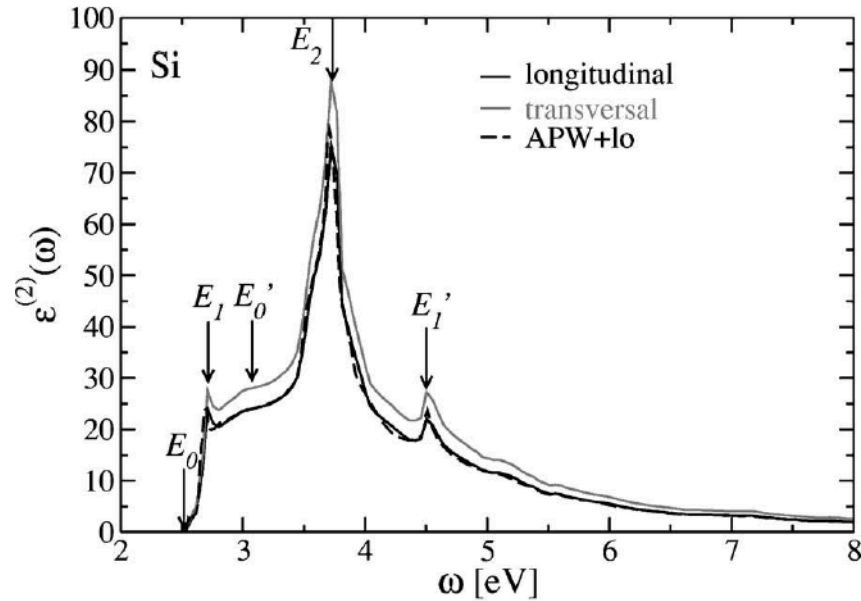
and using perturbation theory we have

$$|\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle = \sum_{n \neq n'} \frac{|u_{n'\mathbf{k}}\rangle \langle u_{n'\mathbf{k}}| \frac{\partial [H(\mathbf{k}) - \epsilon_{n\mathbf{k}} S(\mathbf{k})]}{\partial \mathbf{k}} |u_{n\mathbf{k}}\rangle}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}}$$

where *H*(**k**) and *S*(**k**) are the Hamiltonian and overlap operator for the cell-periodic part of the orbitals.

Examples

Gajdoš *et al.*, Phys. Rev. B 73, 045112 (2006).

The frequency dependent dielectric function is written to the OUTCAR file.
Search for

```
frequency dependent IMAGINARY DIELECTRIC FUNCTION (independent particle, no local field effects)
```

and

```
frequency dependent     REAL DIELECTRIC FUNCTION (independent particle, no local field effects)
```

Frequency dependent (including local field effects)

For the Kohn-Sham system, the following relations can be shown to hold

$$\chi = \chi^0 + \chi^0(\nu + f_{\mathrm{xc}})\chi$$
$$P = \chi^0 + \chi^0 f_{xc} P$$
$$\chi = P + P\nu\chi$$

where ν is the Coulomb kernel and $f_{\mathbf{xc}}$ is the DFT xc-kernel: $f_{\mathrm{xc}} = \partial v_{xc}/\partial\rho \mid_{\rho=\rho_0}$

$$\epsilon^{-1} = 1 + \nu\chi \qquad\qquad \epsilon = 1 - \nu P$$

Random-Phase-Approximation (RPA): $P = \chi^0$

$$\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \delta_{\mathbf{G},\mathbf{G}'} - \frac{4\pi e^2}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$$

Including changes in the DFT xc-potential: $P = \chi^0 + \chi^0 f_{xc} P$

Irreducible polarizability in the IP picture: χ^0

The quantity we can easily access in Kohn-Sham DFT is the:
"irreducible polarizability in the independent particle picture" χ^0 (or χ^{KS})

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \frac{\partial \rho_{\text{ind}}(\mathbf{q}+\mathbf{G},\omega)}{\partial v_{\text{eff}}(\mathbf{q}+\mathbf{G}',\omega)}$$

Adler and Wiser derived expressions for χ^0 which, in terms of Block functions, can be written as

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{1}{\Omega} \sum_{nn'\mathbf{k}} 2w_{\mathbf{k}}(f_{n'\mathbf{k}+\mathbf{q}} - f_{n'\mathbf{k}})$$

$$\times \frac{\langle\psi_{n'\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\psi_{n\mathbf{k}}\rangle\langle\psi_{n\mathbf{k}}|e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}|\psi_{n'\mathbf{k}+\mathbf{q}}\rangle}{\epsilon_{n'\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}} - \omega - i\eta}$$

The IP-polarizability: χ^0

And in terms of Block functions χ^0 can be written as

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{1}{\Omega} \sum_{nn'\mathbf{k}} 2w_{\mathbf{k}}(f_{n'\mathbf{k}+\mathbf{q}} - f_{n'\mathbf{k}})$$

$$\times \frac{\langle \psi_{n'\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\psi_{n\mathbf{k}}\rangle \langle \psi_{n\mathbf{k}}|e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}|\psi_{n'\mathbf{k}+\mathbf{q}}\rangle}{\epsilon_{n'\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}} - \omega - i\eta}$$

Expensive: computing the IP-polarizability scales as N^4

Once we have χ^0 the screened Coulomb interaction (in the RPA) is computed as:

$$W = \nu + \nu\chi_0\nu + \nu\chi_0\nu\chi_0\nu + \nu\chi_0\nu\chi_0\nu\chi_0\nu + \ldots = \nu \underbrace{(1-\chi_0\nu)^{-1}}_{\epsilon^{-1}}$$

geometrical series

1. The bare Coulomb interaction between two particles

2. The electronic environment reacts to the field generated by a particle: induced change in the density $\chi_0\nu$, that gives rise to a change in the Hartree potential: $\nu\chi_0\nu$.

3. The electrons react to the induced change in the potential: additional change in the density, $\chi_0\nu\chi_0\nu$, and corresponding change in the Hartree potential: $\nu\chi_0\nu\chi_0\nu$.

and so on, and so on …

The OUTPUT

- Information concerning the dielectric function in the independent-particle picture is written in the OUTCAR file, after the line

  `HEAD OF MICROSCOPIC DIELECTRIC TENSOR (INDEPENDENT PARTICLE)`

- Per default, for ALGO=CHI, local field effects are included at the level of the RPA (LRPA=.TRUE.), i.e., limited to Hartree contributions only. See the information in the OUTCAR file, after

  `INVERSE MACROSCOPIC DIELECTRIC TENSOR (including local field effects in RPA (Hartree))`

- To include local field effects beyond the RPA, i.e., contributions from DFT exchange and correlation, on has to specify LRPA=.FALSE. in the INCAR file. In this case look at the output in the OUTCAR file, after

  `INVERSE MACROSCOPIC DIELECTRIC TENSOR (test charge-test charge, local field effects in DFT)`

Virtual orbitals/empty states

Problem: the iterative matrix diagonalization techniques converge rapidly for the lowest eigenstates of the Hamiltonian. High lying (virtual/empty states) tend to converge much slower.

- Do a groundstate calculation (i.e., DFT or hybrid functional).
  By default VASP will include only a very limited number of empty states (look for NBANDS and NELECT in the OUTCAR file).

- To obtain virtual orbitals (empty states) of sufficient quality, we diagonalize the groundstate Hamilton matrix (in the plane wave basis: $\langle \mathbf{G}|H|\mathbf{G}'\rangle$) exactly. From the N_{FFT} eigenstates of this Hamiltonian, we then keep the NBANDS lowest.

  Your INCAR file should look something like:

```
..
ALGO = Exact
NBANDS = .. #set to include a larger number of empty states
..
```

Typical jobs: 3 steps

1. Standard groundstate calculation

2. Restart from the WAVECAR file of step 1, and to obtain a certain number of virtual orbitals specify:

```
..
ALGO = Exact
NBANDS = .. #set to include a larger number of empty states
..
```
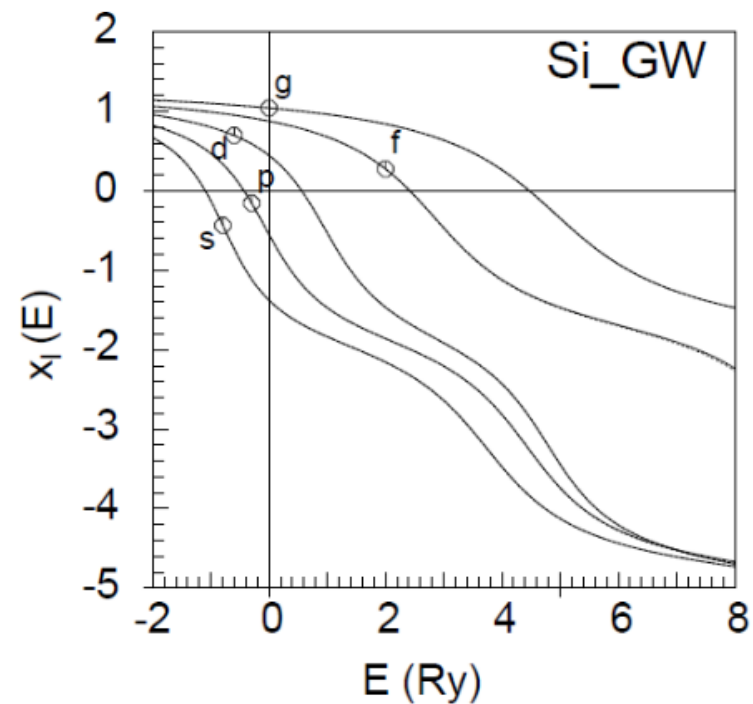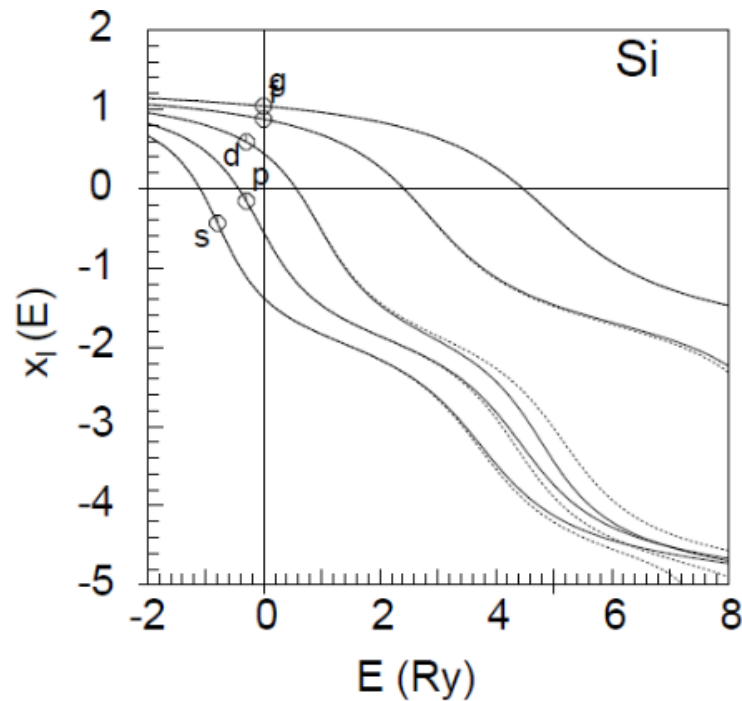
in your INCAR file.

3. Compute frequency dependent dielectric properties: restart from the WAVECAR of step 2, with the following in your INCAR file:

```
ALGO = CHI      or      LOPTICS = .TRUE.
```

N.B.: In the case of LOPTICS=.TRUE. step 2 and 3 can be done in the same run (simply add LOPTICS=.TRUE. to INCAR of step 2).

The GW potentials: *_GW POTCAR files

$\Delta(PAW)_{(VASP)} = 0.4$ meV/atom

H																	He
0,0																	0,0
Li	Be											B	C	N	O	F	Ne
0,1	0,5											0,2	0,2	0,7	0,1	0,1	0,1
Na	Mg											Al	Si	P	S	Cl	Ar
0,4	0,0											0,3	0,1	0,0	0,2	0,0	0,1
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0,1	0,4	0,3	0,3	0,1	0,8	0,1	0,1	0,2	0,8	0,5	0,6	0,8	0,7	0,8	0,4	0,2	0,1
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0,1	0,2	0,5	0,4	0,2	0,9	0,1	0,2	0,3	0,4	0,3	2,5	0,2	0,2	0,5	0,9	0,9	0,1
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0,1	0,3	3,5	1,7	0,8	1,2	0,9	0,5	0,8	0,3	0,1	1,0	0,2	0,1	0,5	0,6		0,0

The static dielectric response

The following quantities:

- The ion-clamped static macroscopic dielectric tensor $\epsilon_\infty(\omega = 0)$ (or simply ϵ_∞).

- Born effective charge tensors Z^*:

$$Z_{ij}^* = \frac{\Omega}{e} \frac{\partial P_i}{\partial u_j} = \frac{1}{e} \frac{\partial F_i}{\partial E_j}$$

- Electronic contribution to piezo-electric tensors:

$$e_{ij}^{(0)} = -\frac{\partial \sigma_i}{\partial E_j}, \qquad i = xx, yy, zz, xy, yz, zx$$

May be calculated using density functional perturbation theory (DFPT):
`LEPSILON=.TRUE.`
or from SC response of the orbitals to a finite electric field (PEAD):
`LCALCEPS=.TRUE.`   (only for insulating systems!)

(Useful in case one works with hybrid functionals, where LEPSILON=.TRUE. does not work.)

Response to electric field from DFPT

LEPSILON=.TRUE.
Instead of using a sum over states (perturbation theory) to compute $|\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle$,
one can solve the linear Sternheimer equation:

$$[H(\mathbf{k}) - \epsilon_{n\mathbf{k}} S(\mathbf{k})] |\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle = -\frac{\partial [H(\mathbf{k}) - \epsilon_{n\mathbf{k}} S(\mathbf{k})]}{\partial \mathbf{k}} |u_{n\mathbf{k}}\rangle$$

for $|\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle$.

The linear response of the orbitals to an externally applied electric field $|\xi_{n\mathbf{k}}\rangle$,
can be found solving

$$[H(\mathbf{k}) - \epsilon_{n\mathbf{k}} S(\mathbf{k})] |\xi_{n\mathbf{k}}\rangle = -\Delta H_{\mathrm{SCF}}(\mathbf{k}) |u_{n\mathbf{k}}\rangle - \hat{\mathbf{q}} \cdot |\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle$$

where $\Delta H_{\mathrm{SCF}}(\mathbf{k})$ is the microscopic cell periodic change in the Hamiltonian,
due to changes in the orbitals, i.e., local field effects (!): these may be included at
the RPA level only (LRPA=.TRUE.) or may include changes in the DFT xc-potential
as well

Response to electric fields from DFPT (cont.)

- The static macroscopic dielectric matrix is then given by

$$\hat{\mathbf{q}} \cdot \epsilon_{\infty} \cdot \hat{\mathbf{q}} = 1 - \frac{8\pi e^2}{\Omega} \sum_{v\mathbf{k}} 2w_{\mathbf{k}} \langle \hat{\mathbf{q}} \cdot \nabla_{\mathbf{k}} u_{n\mathbf{k}} | \xi_{n\mathbf{k}} \rangle$$

where the sum over *v* runs over occupied states only.

- The Born effective charges and piezo-electric tensor may be conveniently computed from the change in the Hellmann-Feynman forces and the mechanical stress tensor, due to a change in the wave functions in a finite difference manner:

$$|u_{n\mathbf{k}}^{(1)}\rangle = |u_{n\mathbf{k}}\rangle + \Delta s |\xi_{n\mathbf{k}}\rangle$$

The OUTPUT

- The dielectric tensor in the independent-particle picture is found in the `OUTCAR` file, after the line

`HEAD OF MICROSCOPIC STATIC DIELECTRIC TENSOR (INDEPENDENT PARTICLE, excluding Hartree and local field effects)`

Its counterpart including local field effects in the RPA (`LRPA=.TRUE.`) after:

`MACROSCOPIC STATIC DIELECTRIC TENSOR (including local field effects in RPA (Hartree))`

and including local field effects in DFT (`LRPA=.FALSE.`) after:

`MACROSCOPIC STATIC DIELECTRIC TENSOR (including local field effects in DFT)`

- The piezoelectric tensors are written to the `OUTCAR` immediately following:

`PIEZOELECTRIC TENSOR  for field in x, y, z        (e  Angst)`

c.q.,

`PIEZOELECTRIC TENSOR  for field in x, y, z        (C/m^2)`

- The Born effective charge tensors are printed after:

`BORN EFFECTIVE CHARGES (in e, cummulative output)`

(but only for LRPA=.FALSE.).

Examples

TABLE III. The ion clamped static macroscopic dielectric constants ε_∞ calculated using the PAW method and various approximations. ε_{mic} reports values neglecting local field effects, ε_{RPA} includes local field effects in the Hartree approximation, and ε_{DFT} includes local field effects on the DFT level. ε^{cond} are values obtained by summation over conduction band states, whereas ε^{LR} are values obtained using linear response theory (density functional perturbation theory).

Method	C	Si	SiC	AlP	GaAs	Ga_dAs
Longitudinal						
ε_{mic}^{LR}	5.98	14.08	7.29	9.12	14.77	15.18
ε_{mic}^{cond}	5.98	14.04	7.29	9.10	14.75	15.16
ε_{RPA}^{LR}	5.54	12.66	6.66	7.88	13.31	13.77
ε_{RPA}^{cond}	5.55	12.68	6.66	7.88	13.28	13.73
ε_{DFT}^{LR}	5.80	13.29	6.97	8.33	13.98	14.42
ε_{DFT}^{cond}	5.82	13.31	6.97	8.33	13.98	14.37
Transversal						
ε_{mic}^{cond}	5.68	16.50	8.00	10.63	14.72	15.33
ε_{mic}^{cond} incl. d projectors	5.99	14.09	7.28	9.11		
ε_{mic}^{cond} APW+LO		13.99				15.36
Experiment (Ref. 33)	5.70	11.90	6.52	7.54		11.10

Gajdoš *et al.*, Phys. Rev. B 73, 045112 (2006).

The change in the polarization induced by an adiabatic change in the crystalline potential is given by

$$\Delta \mathbf{P} = \int_{\lambda_1}^{\lambda_2} \frac{\partial \mathbf{P}}{\partial \lambda} d\lambda = \mathbf{P}(\lambda_2) - \mathbf{P}(\lambda_1)$$

where

$$\mathbf{P}(\lambda) = -\frac{fie}{(2\pi)^3} \int_{\Omega_{\mathbf{k}}} d\mathbf{k} \langle u_{n\mathbf{k}}^{(\lambda)} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}}^{(\lambda)} \rangle$$

To illustrate this, consider a Wannier function

$$|w\rangle = \frac{V}{(2\pi)^3} \int_{\Omega_{\mathbf{k}}} d\mathbf{k} |\psi_{\mathbf{k}}\rangle \qquad\qquad \psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

with well-defined dipole moment

$$e\langle \mathbf{r} \rangle = e \int d\mathbf{r} \langle w | \mathbf{r} | w \rangle$$

$$= \frac{eV^2}{(2\pi)^6} \int_{\Omega_{\mathbf{k}}} d\mathbf{k} \int_{\Omega_{\mathbf{k}'}} d\mathbf{k}' \sum_{\mathbf{R}} \int_V d\mathbf{r} u_{\mathbf{k}}^*(\mathbf{r})(\mathbf{R}+\mathbf{r}) u_{\mathbf{k}'}(\mathbf{r}) e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}+\mathbf{r})}$$

$$= \frac{eV^2}{(2\pi)^6} \int_{\Omega_{\mathbf{k}}} d\mathbf{k} \int_{\Omega_{\mathbf{k}'}} d\mathbf{k}' \sum_{\mathbf{R}} \int_V d\mathbf{r} u_{\mathbf{k}}^*(\mathbf{r}) u_{\mathbf{k}'}(\mathbf{r}) (-i\nabla_{\mathbf{k}'}) e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}+\mathbf{r})}$$

$$= -i\frac{eV}{(2\pi)^3} \int_{\Omega_{\mathbf{k}}} d\mathbf{k} \langle u_{\mathbf{k}} | \nabla_{\mathbf{k}} | u_{\mathbf{k}} \rangle$$

where we used integration by parts to let $\nabla_{\mathbf{k}'}$ work on $u_{\mathbf{k}'}$ instead of on the exponent, and the following relation

$$\sum_{\mathbf{R}} e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} = \frac{(2\pi)^3}{V} \delta(\mathbf{k}-\mathbf{k}')$$
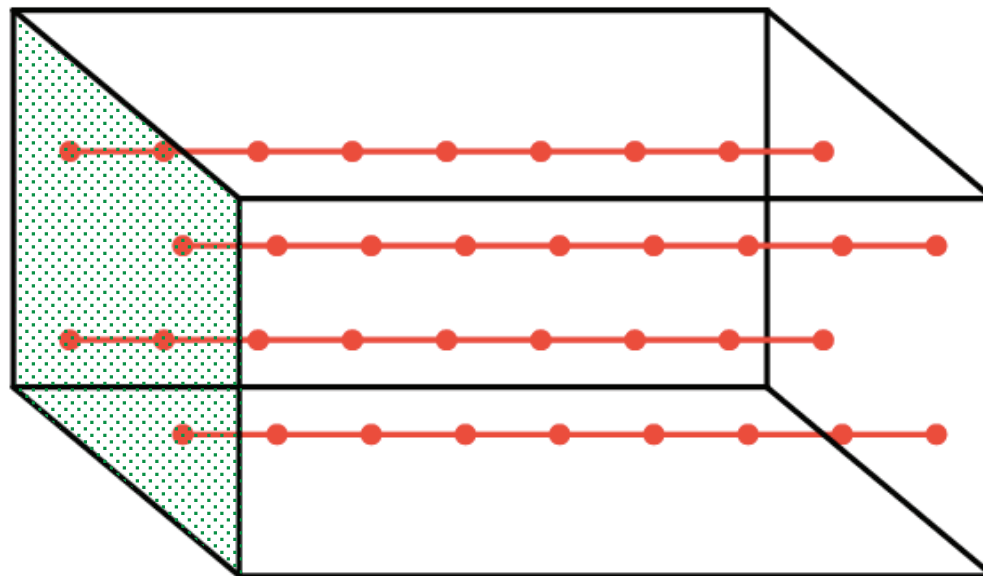
The final expression, proposed by King-Smith and Vanderbilt, to evaluate the polarization on a discrete mesh of **k**-points, reads:

$$\mathbf{B}_i \cdot \mathbf{P}(\lambda) = \frac{f|e|}{V} \frac{\mathbf{A}_i}{N_{\mathbf{k}_\perp}} \sum_{N_{\mathbf{k}_\perp}} \Im\{\ln \prod_{j=0}^{J-1} \det|\langle u_{n\mathbf{k}_j}^{(\lambda)} | u_{m\mathbf{k}_{j+1}}^{(\lambda)} \rangle|\}$$

where

$$\mathbf{k}_j = \mathbf{k}_\perp + j\frac{\mathbf{B}_i}{J}, \quad j = 1, ..., J \qquad \text{and} \qquad u_{n\mathbf{k}_\perp + \mathbf{B}_i}^{(\lambda)}(\mathbf{r}) = e^{-i\mathbf{B}_i\cdot\mathbf{r}} u_{n\mathbf{k}_\perp}^{(\lambda)}(\mathbf{r})$$

$$\mathbf{k}_j = \mathbf{k}_\perp + j\frac{\mathbf{B}_i}{J}, \quad j = 1, ..., J \qquad \text{and} \qquad u_{n\mathbf{k}_\perp+\mathbf{B}_i}^{(\lambda)}(\mathbf{r}) = e^{-i\mathbf{B}_i\cdot\mathbf{r}} u_{n\mathbf{k}_\perp}^{(\lambda)}(\mathbf{r})$$

Self-consistent response to finite electric fields (PEAD)†

Add the interaction with a small but finite electric field $\mathcal{E}$ to the expression for the total energy

$$E[\{\psi^{(\mathcal{E})}\}, \mathcal{E}] = E_0[\{\psi^{(\mathcal{E})}\}] - \Omega\mathcal{E} \cdot \mathbf{P}[\{\psi^{(\mathcal{E})}\}]$$

where $P[\{\psi^{(\mathcal{E})}\}]$ is the macroscopic polarization as defined in the "modern theory of polarization"‡

$$\mathbf{P}[\{\psi^{(\mathcal{E})}\}] = -\frac{2ie}{(2\pi)^3}\sum_n \int_{\mathrm{BZ}} d\mathbf{k} \langle u_{n\mathbf{k}}^{(\mathcal{E})} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}}^{(\mathcal{E})} \rangle$$

Adding a corresponding term to Hamiltonian

$$H|\psi_{n\mathbf{k}}^{(\mathcal{E})}\rangle = H_0|\psi_{n\mathbf{k}}^{(\mathcal{E})}\rangle - \Omega\mathcal{E} \cdot \frac{\delta\mathbf{P}[\{\psi^{(\mathcal{E})}\}]}{\delta\langle\psi_{n\mathbf{k}}^{(\mathcal{E})}|}$$

allows one to solve for $\{\psi^{(\mathcal{E})}\}$ by means of a direct optimization method (iterate intil self-consistency is achieved).

† R. W. Nunes and X. Gonze, Phys. Rev. B 63, 155107 (2001).
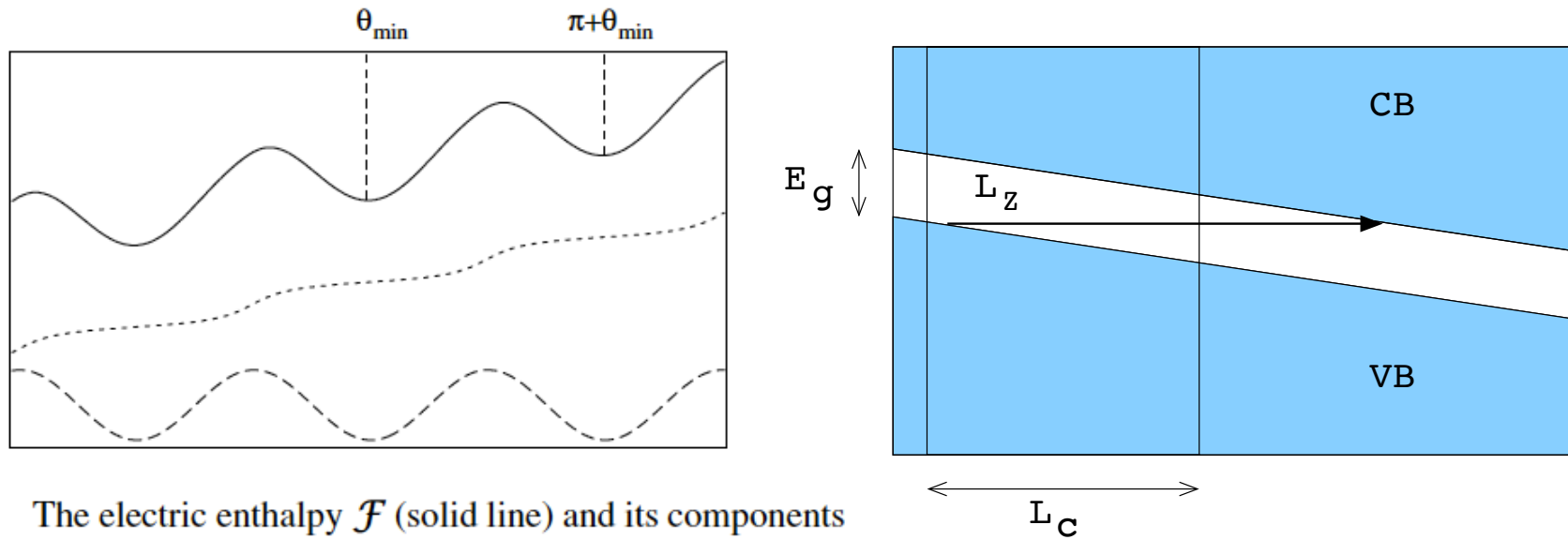‡ R. D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993).

PEAD (cont.)

θ_{min} $\quad\quad$ $\pi+\theta_{min}$

E_g

FIG. 1. The electric enthalpy $\mathcal{F}$ (solid line) and its components E_{KS} (dashed line) and $-\Omega \mathbf{P}_{mac} \cdot \mathcal{E}$ (dotted line), plotted as a function of the parameter θ that controls the update of a polarized Bloch state in a conjugate-gradients step.

CB

L_Z

VB

L_C

$$e|\mathcal{E}_c \cdot \mathbf{A}_i| \approx E_g/N_i$$

$$N_i A_i < L_Z$$

Souza *et al.*, Phys. Rev. Lett. 89, 117602 (2002).

PEAD (cont.)

Once the self-consistent solution $\{\psi^{(\mathcal{E})}\}$ has been obtained:

- the static macroscopic dielectric matrix is given by

$$(\epsilon_\infty)_{ij} = \delta_{ij} + 4\pi \frac{(\mathbf{P}[\{\psi^{(\mathcal{E})}\}] - \mathbf{P}[\{\psi^{(0)}\}])_i}{\mathcal{E}_j}$$

- and the Born effective charges and ion-clamped piezo-electric tensor may again be conveniently computed from the change in the Hellman-Feynman forces and the mechanical stress tensor.

The PEAD method is able to include local field effects in a natural manner (the self-consistency).

```
INCAR-tags

LCALPOL =.TRUE.            Compute macroscopic polarization.
LCALCEPS=.TRUE.           Compute static macroscopic dielectric-, Born effective charge-,
                          and ion-clamped piezo-electrictensors, including local field effects.
EFIELD_PEAD = E_x E_y E_z  Electric field used by the PEAD routines.
                          (Default if LCALCEPS=.TRUE.: EFIELD_PEAD= 0.01 0.01 0.01 [eV/Å].)
LRPA=.FALSE.              Skip the calculations without local field effects (Default).
LSKIP_NSCF=.TRUE.         idem.
LSKIP_SCF=.TRUE.          Skip the calculations with local field effects.
```

Example: ion-clamped ϵ_∞ using the HSE hybrid

TABLE I. Ion clamped (high frequency) macroscopic dielectric constants ϵ^∞ from TD-DFT using the LDA and the HSE ($\mu=0.3$ Å^{-1}) hybrid functional in the independent-particle approximation (ϵ_{IP}^∞) and including all electron-electron interactions. The HSE results have been obtained either by solving the Dyson equation or by applying a finite field and extracting the response from the change in the polarization (Refs. 30 and 31). For ZnO the dielectric constants are reported for the wurtzite structure along the a and c axes. All data are calculated at the experimental volumes.

	LDA		HSE		HSE fin. field		
	ϵ_{IP}^∞	ϵ^∞	ϵ_{IP}^∞	ϵ^∞	ϵ_{IP}^∞	ϵ^∞	Expt.
Si	14.1	13.35	10.94	11.31	10.87	11.37	11.9[a]
GaAs	14.81	13.98	10.64	10.95	10.54	11.02	11.1[a]
AlP	9.12	8.30	7.27	7.35	7.32	7.35	7.54[a]
SiC	7.29	6.96	6.17	6.43	6.15	6.44	6.52[a]
C	5.94	5.80	5.21	5.56	5.25	5.59	5.7[a]
ZnO c	5.31	5.15	3.50	3.71	3.57	3.77	3.78[b]
ZnO a	5.28	5.11	3.48	3.67	3.54	3.72	3.70[b]
LiF	2.06	2.02	1.85	1.90	1.86	1.91	1.9[c]

J. Paier, M. Marsman, and G. Kresse, Phys. Rev. B 78, 121201(R) (2008).

PEAD: Hamiltonian terms

The additional terms in the Hamiltonian, arising from the $\Omega\mathcal{E} \cdot \mathbf{P}\big[\{\psi^{(\mathcal{E})}\}\big]$ term in the enthalpy are of the from

$$\frac{\delta \sum_j \Im\{\ln \det |S(\mathbf{k}_j, \mathbf{k}_{j+1})|\}}{\delta u^*_{n\mathbf{k}_j}} =$$

$$-\frac{i}{2} \sum_{m=1}^{N} \big[|u_{n\mathbf{k}_{j+1}}\rangle S^{-1}_{mn}(\mathbf{k}_j, \mathbf{k}_{j+1}) - |u_{n\mathbf{k}_{j-1}}\rangle S^{-1}_{mn}(\mathbf{k}_j, \mathbf{k}_{j-1})\big]$$

where $S_{nm}(\mathbf{k}_j, \mathbf{k}_{j+1}) = \langle u_{n\mathbf{k}_j}|u_{m\mathbf{k}_{j+1}}\rangle$

By analogy we have

$$\frac{\partial|u_{n\mathbf{k}_j}\rangle}{\partial k} \approx \frac{1}{2\Delta k} \sum_{m=1}^{N} \big[|u_{n\mathbf{k}_{j+1}}\rangle S^{-1}_{mn}(\mathbf{k}_j, \mathbf{k}_{j+1}) - |u_{n\mathbf{k}_{j-1}}\rangle S^{-1}_{mn}(\mathbf{k}_j, \mathbf{k}_{j-1})\big]$$

i.e., a finite difference expression for $|\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle$.

The OUTPUT

- The dielectric tensor including local field effects is written to the OUTCAR file, after the line

  `MACROSCOPIC STATIC DIELECTRIC TENSOR (including local field effects)`

- The piezoelectric tensors are written to the OUTCAR immediately following:

  `PIEZOELECTRIC TENSOR (including local field effects) (e Angst)`

  c.q.,

  `PIEZOELECTRIC TENSOR (including local field effects) (C/m^2)`

- The Born effective charge tensors are found after:

  `BORN EFFECTIVE CHARGES (including local field effects)`

For LSKIP_NSCF=.FALSE. one will additionally finf the counterparts of the above:

  `... (excluding local field effects)`

Ionic contributions

From finite difference expressions w.r.t. the ionic positions (`IBRION=5 or 6`) or from perturbation theory (`IBRION=7 or 8`) we obtain

$$\Phi_{ij}^{ss'} = -\frac{\partial F_i^s}{\partial u_j^{s'}} \qquad \Xi_{il}^s = -\frac{\partial \sigma_l}{\partial u_i^s}$$

the force-constant matrices and internal strain tensors, respectively.

Together with the Born effective charge tensors, these quantities allow for the computation of the ionic contribution to the dielectric tensor

$$\epsilon_{ij}^{\mathrm{ion}} = \frac{4\pi e^2}{\Omega} \sum_{ss'} \sum_{kl} Z_{ik}^{*s} (\Phi^{ss'})_{kl}^{-1} Z_{lj}^{*s'}$$

and to the piezo-electric tensor

$$e_{il}^{\mathrm{ion}} = e \sum_{ss'} \sum_{jk} Z_{ij}^{*s} (\Phi^{ss'})_{jk}^{-1} \Xi_{kl}^{s'}$$

The End

Thank you!