VASP Workshop: Day 2

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1. Dielectric response
2. Frequency dependent dielectric properties
3. The static dielectric response
4. The GW approximation

Experiment: Static and frequency dependent dielectric response 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: Frequency dependent polarizability matrix needed in many post-DFT schemes, e.g.:

- GW
) frequency dependent microscopic dielectric response
) 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 matrix
) Imaginary and real part of the dielectric function.
) In the RPA, and including changes in the DFT xc-potential.
) In- or excluding local field effects

Static

- Static dielectric tensor, Born effective charges, and Piezo-electric tensor, in- or exluding 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.)

Macroscopic continuum consideration

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

$$\mathbf{E} = \epsilon^{-1}\mathbf{E}_{\text{ext}}, \qquad \text{where } \epsilon \text{ is } 3 \times 3 \text{ tensor}$$

- 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):

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

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

$$\rho_{\text{ind}} = \chi v_{\text{ext}}, \qquad \text{where } \chi \text{ is the reducible polarizability}$$
$$\rho_{\text{ind}} = P v_{\text{tot}}, \qquad \text{where } P \text{ is the irreducible polarizability}$$

- It may be straightforwardly shown that:

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

where $\nu = 4\pi e^3/q^2$ is the Coulomb kernel in momentum space.

Macroscopic and microscopic quantities

The macroscopic dielectric function can be formally written as

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

or in momentum space

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

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 momemtum space

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

The microscopic dielectric functions 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 (cont.)

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

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

and

$$\begin{aligned} \epsilon^{-1}_{\text{mac}}(\mathbf{q},\omega) &= \epsilon^{-1}_{0,0}(\mathbf{q},\omega) \\ \epsilon_{\text{mac}}(\mathbf{q},\omega) &= \left(\epsilon^{-1}_{0,0}(\mathbf{q},\omega)\right)^{-1} \end{aligned}$$

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

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

This is 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

$$\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \frac{\partial \rho_{\text{ind}}(\mathbf{q}+\mathbf{G},\omega)}{\partial v_{\text{ext}}(\mathbf{q}+\mathbf{G}',\omega)} \qquad P_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \frac{\partial \rho_{\text{ind}}(\mathbf{q}+\mathbf{G},\omega)}{\partial v_{\text{tot}}(\mathbf{q}+\mathbf{G}',\omega)} \qquad \nu^s_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) := \frac{4\pi e^2}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}$$

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 χ nor P.

Solution: 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

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{1}{\Omega}\sum_{nn'\mathbf{k}} 2w_{\mathbf{k}}(f_{n'\mathbf{k}+\mathbf{q}} - f_{n'\mathbf{k}}) \times \frac{\langle\psi_{n'\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\psi_{n\mathbf{k}}\rangle\langle\psi_{n\mathbf{k}}|e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}|\psi_{n'\mathbf{k}+\mathbf{q}}\rangle}{\epsilon_{n'\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}} - \omega - i\eta}$$

Approximations cont.

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

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

where ν is the Coulomb kernel and $f_{\text{xc}} = \partial v_{xc}/\partial\rho\,|_{\rho=\rho_0}$ is the DFT xc-kernel.

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

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: $P = \chi^0 + \chi^0 f_{xc} P$

Calculation of optical properties

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

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

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

can be obtained at various levels of approximation:

- LOPTICS = .TRUE.
) $\epsilon_{0,0}(\mathbf{q},\omega)$ in the RPA
) neglect of local field effects: $\hat{\mathbf{q}} \cdot \epsilon_\infty(\omega) \cdot \hat{\mathbf{q}} \approx \lim_{\mathbf{q}\rightarrow 0} \epsilon_{0,0}(\mathbf{q},\omega)$
- ALGO = CHI
) Including local field effects: in RPA and due to changes in the DFT xc-potential (LRPA = .TRUE. | .FALSE.).

Calculation of optical properties (cont.)

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

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

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

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

The difficulty lies in the computation of the quantities

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

the first order change in the cell periodic part of $|\psi_{n\mathbf{k}}\rangle$ with respect to the Bloch vector $\mathbf{k}$.

Expanding up to first order in $\mathbf{q}$

$$|u_{n\mathbf{k}+\mathbf{q}}\rangle = |u_{n\mathbf{k}}\rangle + \mathbf{q} \cdot |\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle + ...$$

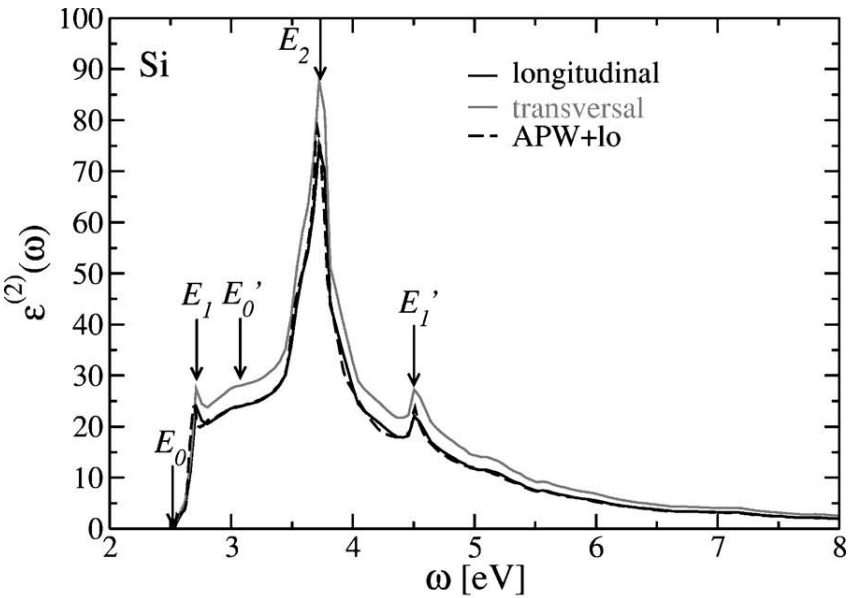
and using perturbation theory to write

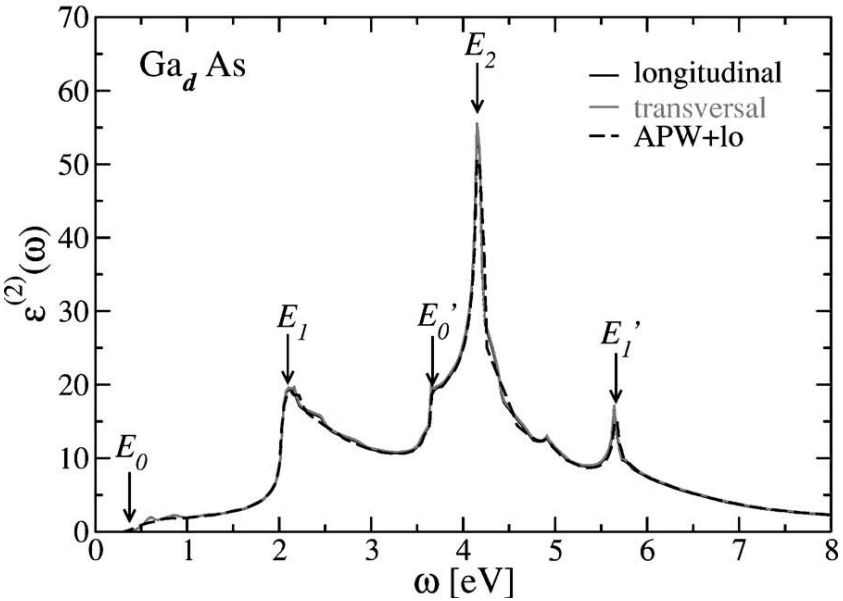
$$|\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle = \sum_{n \neq n'} \frac{|u_{n'\mathbf{k}}\rangle\langle u_{n'\mathbf{k}}| \frac{\partial [H(\mathbf{k}) - \epsilon_{n\mathbf{k}} S(\mathbf{k})]}{\partial \mathbf{k}} |u_{n\mathbf{k}}\rangle}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}}$$

where $H(\mathbf{k})$ and $S(\mathbf{k})$ are the Hamiltonian and overlap operator for the cell-periodic part of the wave functions.

Examples

GAJDOŠ *et al.* PHYSICAL REVIEW B **73**, 045112 (2006)





The GW potentials: ∗_GW POTCARs

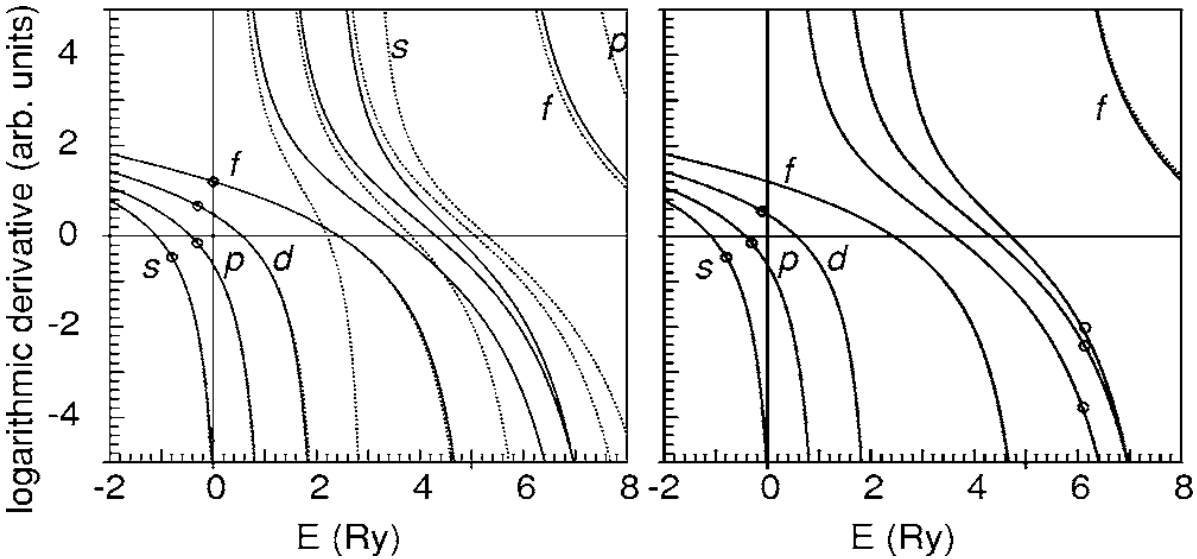


FIG. 2. Atomic scattering properties of the Si TM (left) and PAW (right) potentials used in the present work for QP calculations (Tables I and II). Shown are the logarithmic derivatives of the radial wave functions for different angular momenta for a spherical Si atom, evaluated at a distance of r=1.3 Å from the nucleus. Solid lines correspond to the all-electron full-potential, and dotted lines to the TM pseudopotential or PAW potential. The energy zero corresponds to the vacuum level. Circles indicate linearization energies for projectors.

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:

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

may be calculated using density functional perturbation theory (DFPT):
LEPSILON=.TRUE.
or from the SC response of the wave functions 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 fields from DFPT

LEPSILON=.TRUE.

Instead of using perturbation theory to compute $|\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle$, one can solve the linear Sternheimer equation:

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

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

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

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

where $\Delta H_{\mathrm{SCF}}(\mathbf{k})$ is the microscopic cell periodic change in the Hamiltonian, due to changes in the wave functions, 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:

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

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

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

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

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

Adding a corresponding term to the Hamiltonian

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

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

[†] 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.

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

- the static macroscopic dielectric matrix is given by

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

- and the Born effective charges and ion-clamped piezo-electric tensor may again be conveniently computed from the change in the Hellmann-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

LCALCPOL = .TRUE. Compute macroscopic polarization.

LCALCEPS = .TRUE. Compute static macroscopic dielectric-, Born effect charge-, and ion-clamped piezo-electric tensors, both with as well as without local field effects.

EFIELD_PEAD = E_x E_y E_z Electric field used by 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).

SKIP_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 (μ=0.3 Å^{-1}) hybrid functional in the independent-particle approximation ($\epsilon^\infty_{\rm IP}$) 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		
	$\epsilon^\infty_{\rm IP}$	ϵ^∞	$\epsilon^\infty_{\rm IP}$	ϵ^∞	$\epsilon^\infty_{\rm IP}$	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]

Why go beyond DFT and HF-DFT hybrid functionals?

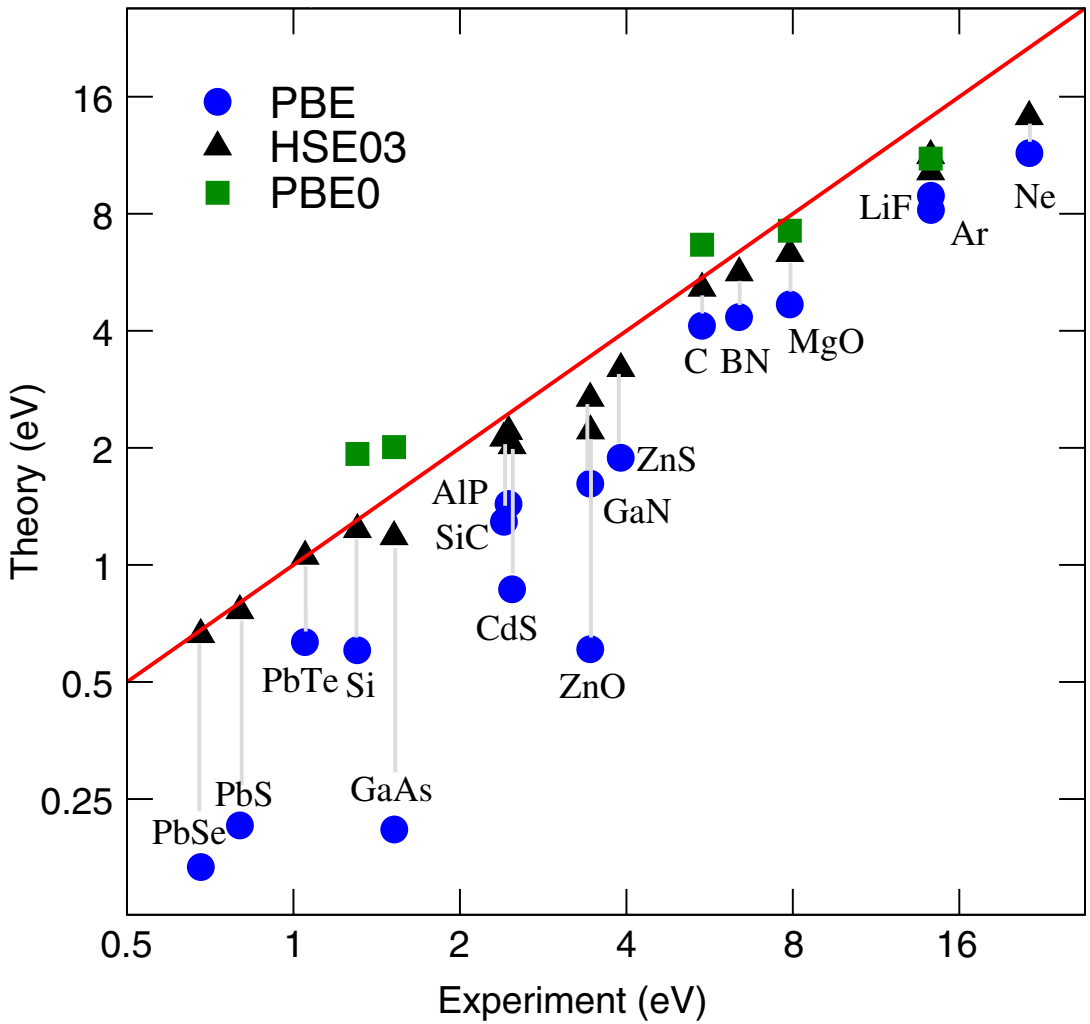


Figure 8. Band gaps from PBE, PBE0, and HSE03 calculations, plotted against data from experiment.

One-electron energies

- DFT

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

- HF-DFT hybrid functionals

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int V_{\text{X}}(\mathbf{r},\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

- Quasiparticle equations

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

The GW approximation to Σ [L. Hedin, Phys. Rev. 139, A796 (1965)]

In the GW approximation the self-energy is given by

$$\Sigma = iGW$$

Where G is the Green's function

$$G(\mathbf{r}, \mathbf{r}', \omega) = \sum_n \frac{\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')}{\omega - \epsilon_n + i\eta\,\mathrm{sgn}(\epsilon_n - \mu)}$$

and W is the screened Coulomb kernel $W = \epsilon^{-1}\nu$

$$W_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, \omega) = \frac{4\pi e^2}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, \omega)$$

In reciprocal space $\langle\psi_{n\mathbf{k}}|\Sigma(\omega)|\psi_{n\mathbf{k}}\rangle$ is given by

$$\langle\psi_{n\mathbf{k}}|\Sigma(\omega)|\psi_{n\mathbf{k}}\rangle = \frac{i}{2\pi\Omega}\sum_{\mathbf{q}}\sum_{\mathbf{G}\mathbf{G}'}\sum_{n'}\int_{-\infty}^{\infty} d\omega' W_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, \omega')\times$$
$$\times \frac{\langle\psi_{n\mathbf{k}}|e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\psi_{n'\mathbf{k}-\mathbf{q}}\rangle\langle\psi_{n'\mathbf{k}-\mathbf{q}}|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\psi_{n\mathbf{k}}\rangle}{\omega - \omega' - \epsilon_{n'\mathbf{k}-\mathbf{q}} + i\eta\,\mathrm{sgn}(\epsilon_n - \mu)}$$

GW Quasiparticle equations

The GW quasiparticle equation

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

The quasiparticle energies are given by

$$E_{n\mathbf{k}} = \Re\left[\langle\psi_{n\mathbf{k}}| - \frac{1}{2}\Delta + V_{\text{ext}} + V_{\text{H}} + \Sigma(E_{n\mathbf{k}})|\psi_{n\mathbf{k}}\rangle\right]$$

which may be solved by iteration

$$\begin{aligned}
E^{N+1}_{n\mathbf{k}} &= \Re\left[\langle\psi_{n\mathbf{k}}| - \frac{1}{2}\Delta + V_{\text{ext}} + V_{\text{H}} + \Sigma(E^{N}_{n\mathbf{k}})|\psi_{n\mathbf{k}}\rangle\right] \\
&\quad + (E^{N+1}_{n\mathbf{k}} - E^{N}_{n\mathbf{k}})\Re\left[\langle\psi_{n\mathbf{k}}|\frac{\partial\Sigma(\omega)}{\partial\omega}\Big|_{\omega=E^{N}_{n\mathbf{k}}}|\psi_{n\mathbf{k}}\rangle\right] \\
&= E^{N}_{n\mathbf{k}} + Z^{N}_{n\mathbf{k}}\Re\left[\langle\psi_{n\mathbf{k}}| - \frac{1}{2}\Delta + V_{\text{ext}} + V_{\text{H}} + \Sigma(E^{N}_{n\mathbf{k}})|\psi_{n\mathbf{k}}\rangle - E^{N}_{n\mathbf{k}}\right]
\end{aligned}$$

where

$$Z^{N}_{n\mathbf{k}} = \left(1 - \langle\psi_{n\mathbf{k}}|\frac{\partial\Sigma(\omega)}{\partial\omega}\Big|_{\omega=E^{N}_{n\mathbf{k}}}|\psi_{n\mathbf{k}}\rangle\right)^{-1}$$

G_0W_0 and GW_0

- Single shot GW: G_0W_0

$$E_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}} \Re \left[\langle \psi_{n\mathbf{k}} | -\frac{1}{2}\Delta + V_{\text{ext}} + V_{\text{H}} + \Sigma(\epsilon_{n\mathbf{k}}) | \psi_{n\mathbf{k}} \rangle - \epsilon_{n\mathbf{k}} \right]$$

and

$$Z_{n\mathbf{k}} = \left(1 - \langle \psi_{n\mathbf{k}} | \frac{\partial \Sigma(\omega)}{\partial \omega} \Big|_{\omega=\epsilon_{n\mathbf{k}}} | \psi_{n\mathbf{k}} \rangle \right)^{-1}$$

Recipe for G_0W_0 calculations.

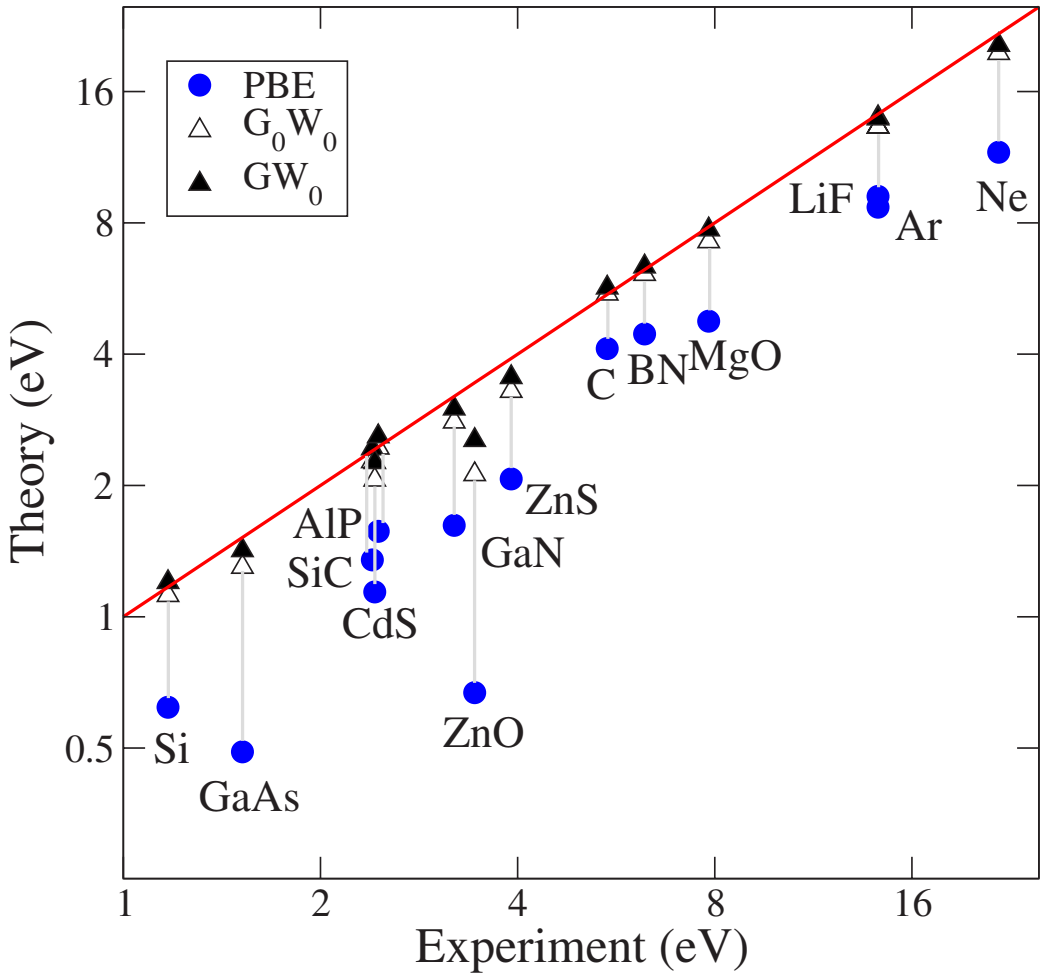
- Partially self-consistent GW: GW_0

Iteration of the quasiparticle energies in G only

$$G^N(\mathbf{r}, \mathbf{r}', \omega) = \sum_n \frac{\psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}')}{\omega - E_n^N + i\eta \, \text{sgn}(\epsilon_n - \mu)}$$

Recipe for GW_0 calculations.

G_0W_0(PBE) and GW_0 quasiparticle gaps



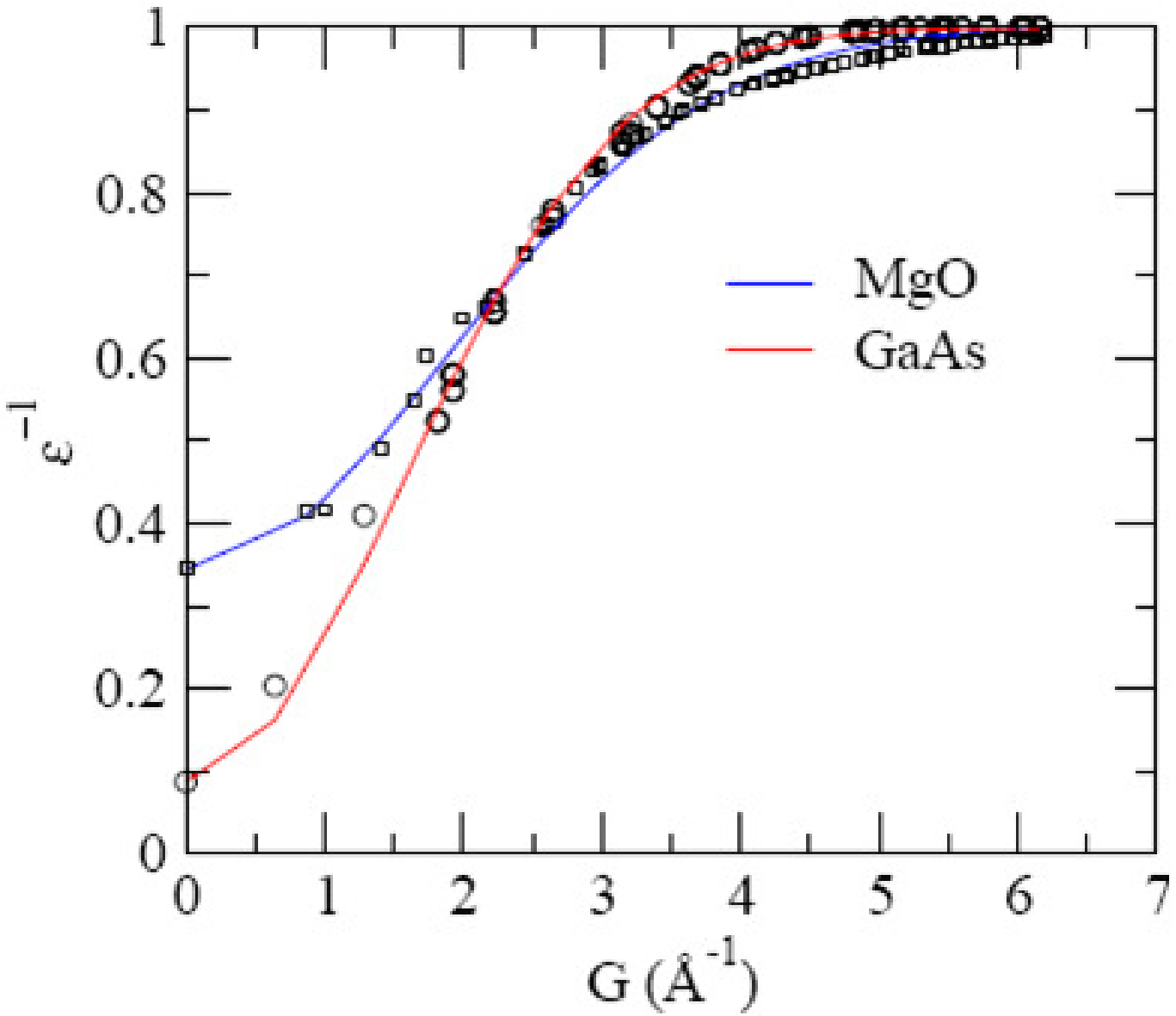
G_0W_0: MARE=8.5% and GW_0: MARE=4.5%

G_0W_0(PBE) and GW_0 quasiparticle gaps cont.

TABLE I. Results of DFT-PBE and quasiparticle (G_0W_0, GW_0, and GW) calculations. An $8\times8\times8$ k-point mesh is used for all calculations except for the GW case (see text). Experimental values for gaps (Expt.), lattice constants (a), and the calculated values for spin-orbit coupling (SO) are also provided. Underlined values correspond to zero-temperature values. The mean absolute relative error (MARE) and the mean relative error (MRE) are also reported; lead chalcogenides are excluded in the MARE and MRE.

	PBE	G_0W_0	GW_0	GW	Expt.	a	SO
PbSe	−0.17	0.10	0.15	0.19	0.15[a]	6.098[b]	0.40
PbTe	−0.05	0.20	0.24	0.26	0.19[c]	6.428[b]	0.73
PbS	−0.06	0.28	0.35	0.39	0.29[d]	5.909[b]	0.36
Si	0.62	1.12	1.20	1.28	1.17[e]	5.430[f]	
GaAs	0.49	1.30	1.42	1.52	1.52[e]	5.648[f]	0.10
SiC	1.35	2.27	2.43	2.64	2.40[g]	4.350[g]	
CdS	1.14	2.06	2.26	2.55	2.42[h]	5.832[h]	0.02
AlP	1.57	2.44	2.59	2.77	2.45[h]	5.451[h]	
GaN	1.62	2.80	3.00	3.32	3.20[i]	4.520[i]	0.00
ZnO	0.67	2.12	2.54	3.20	3.44[e]	4.580[h]	0.01
ZnS	2.07	3.29	3.54	3.86	3.91[e]	5.420[h]	0.02
C	4.12	5.50	5.68	5.99	5.48[g]	3.567[g]	
BN	4.45	6.10	6.35	6.73	6.1–6.4[j]	3.615[h]	
MgO	4.76	7.25	7.72	8.47	7.83[k]	4.213[l]	
LiF	9.20	13.27	13.96	15.10	14.20[m]	4.010[n]	
Ar	8.69	13.28	13.87	14.65	14.20[o]	5.260[p]	
Ne	11.61	19.59	20.45	21.44	21.70[o]	4.430[p]	
MARE	45%	9.9%	5.7%	6.1%			
MRE	45%	−9.8%	−3.6%	4.7%			

An analogy between GW and hybrid functionals



Spectral representation of the polarizability

It is cheaper to calculate the polarizability in its spectral representation

$$\chi^S_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega') = \frac{1}{\Omega}\sum_{nn'\mathbf{k}} 2w_{\mathbf{k}}\,\mathrm{sgn}(\omega')\delta(\omega' + \epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}-\mathbf{q}})(f_{n\mathbf{k}} - f_{n'\mathbf{k}-\mathbf{q}})\times$$
$$\times\langle\psi_{n\mathbf{k}}|e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\psi_{n'\mathbf{k}-\mathbf{q}}\rangle\langle\psi_{n'\mathbf{k}-\mathbf{q}}|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\psi_{n\mathbf{k}}\rangle$$

which is related to the imaginary part of χ^0 through

$$\chi^S_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega') = \frac{1}{\pi}\Im\left[\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)\right]$$

The polarizability χ^0 is then obtained from its spectral representation through the following Hilbert transform

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \int_0^\infty d\omega'\chi^S_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega')\times\left(\frac{1}{\omega-\omega'-i\eta} - \frac{1}{\omega+\omega'+i\eta}\right)$$

LSPECTRAL=.TRUE. NOMEGA = [integer]
(Default for ALGO = CHI | GW0 | GW | scGW | scGW0, when NOMEGA $>$ 2).

Links and literature

Manual sections

Optical properties and DFPT

Frequency dependent GW calculations

Some literature

"Linear optical properties in the projector-augmented wave methodology", M. Gajdoš, K. Hummer, and G. Kresse, Phys. Rev. B 73, 045112 (2006).

"Implementation and performance of the frequency-dependent GW method within the PAW framework", M. Shishkin and G. Kresse, Phys. Rev. B 74, 035101 (2006).

"Self-consistent GW calculations for semiconductors and insulators", M. Shishkin and G. Kresse, Phys. Rev. B 75, 235102 (2007).

"Accurate quasiparticle spectra from self-consistent GW calculations with vertex corrections", M. Shishkin, M. Marsman, and G. Kresse, Phys. rev. Lett. 99, 246403 (2007).

Some nice derivations of equations in this presentation may be found in: Chapter 2 and Chapter 4 of the Ph.D thesis of Judith Harl.