Meta-GGA-based adiabatic time-dependent density-functional theory

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Outline of this talk: LDA $\rightarrow$ GGA $\rightarrow$ MGGA

- Short reminder of the static DFT:

  From *Local density approximation* (LDA) ...
  through *Generalized gradient approximation* (GGA) ...
  to *meta-GGA* (MGGA);

- Time-dependent density functional theory (TDDFT);

- Adiabatic TDDFT (ATDDFT) of optical response:
  LDA and GGA fail, MGGA succeeds;

- Results and discussion.

Short reminder of static DFT

Universal functional

$$E = \int v_{ext}(\mathbf{r}) n_0(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n_0(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n_0(\mathbf{r})] \ , \quad (1)$$

Kohn-Sham equations:

$$\left[-\frac{1}{2}\Delta + v_{eff}(\mathbf{r}) \right] \psi_\alpha(\mathbf{r}) = \epsilon_\alpha \psi_\alpha(\mathbf{r}). \quad (2)$$

External potential

Hartree potential

$$v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int \frac{n_0(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \ .$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n_0(\mathbf{r})} \ : \ \textit{Exchange-correlation potential}$$

Hierarchy of approximations in static DFT

Electron density

$$n_0(\mathbf{r}) = \sum_{\alpha \in occ} |\psi_\alpha(\mathbf{r})|^2.$$

- LDA : $E_{xc} = \int \varepsilon_{xc}[n_0(\mathbf{r})]d\mathbf{r}$: local;
- GGA : $E_{xc} = \int \varepsilon_{xc}[n_0(\mathbf{r}), \nabla n_0(\mathbf{r})]d\mathbf{r}$: semi-local;
- MGGA: $E_{xc} = \int \varepsilon_{xc}[n_0(\mathbf{r}), \nabla n_0(\mathbf{r}), \tau(\mathbf{r})]d\mathbf{r}$: non-local.

where

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_{\alpha \in occ} |\nabla \psi_\alpha(\mathbf{r})|^2$$

is the density of *kinetic energy*.

Time-dependent linear response (RPA)

$$n(\mathbf{r},t) = n_0(\mathbf{r}) + n_1(\mathbf{r},t) + ... \tag{3}$$

$$n_1(\mathbf{r},t) = \int \chi_s(\mathbf{r},\mathbf{r}',t-t')v_{eff}(\mathbf{r}',t')d\mathbf{r}'dt', \tag{4}$$

RPA:
$$v_{eff}(\mathbf{r},t) = v_{ext}(\mathbf{r},t) + \int \frac{n_0(\mathbf{r}',t)}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}'. \tag{5}$$

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) = \sum_{\alpha\beta} \frac{f_\alpha - f_\beta}{\omega - \epsilon_\beta + \epsilon_\alpha + i\eta} \psi^*_\alpha(\mathbf{r})\psi_\beta(\mathbf{r})\psi^*_\beta(\mathbf{r}')\psi_\alpha(\mathbf{r}') \tag{6}$$

- Lindhard's independent-particles response function.

DF of semiconductors from static DFT (LDA RPA)

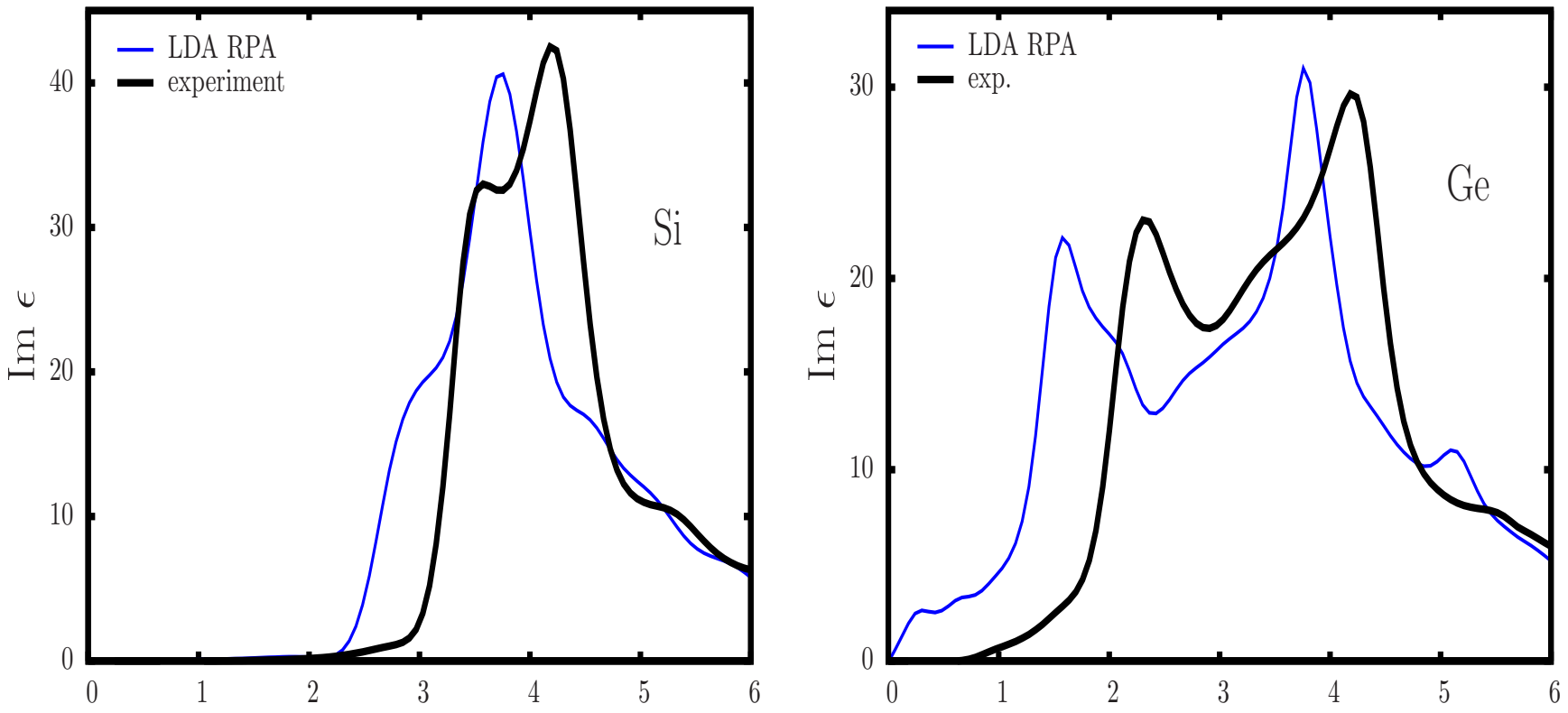


Fig.1: Dielectric function of crystalline Si and Ge (LDA RPA).

DF of semiconductors from static DFT (MGGA RPA)

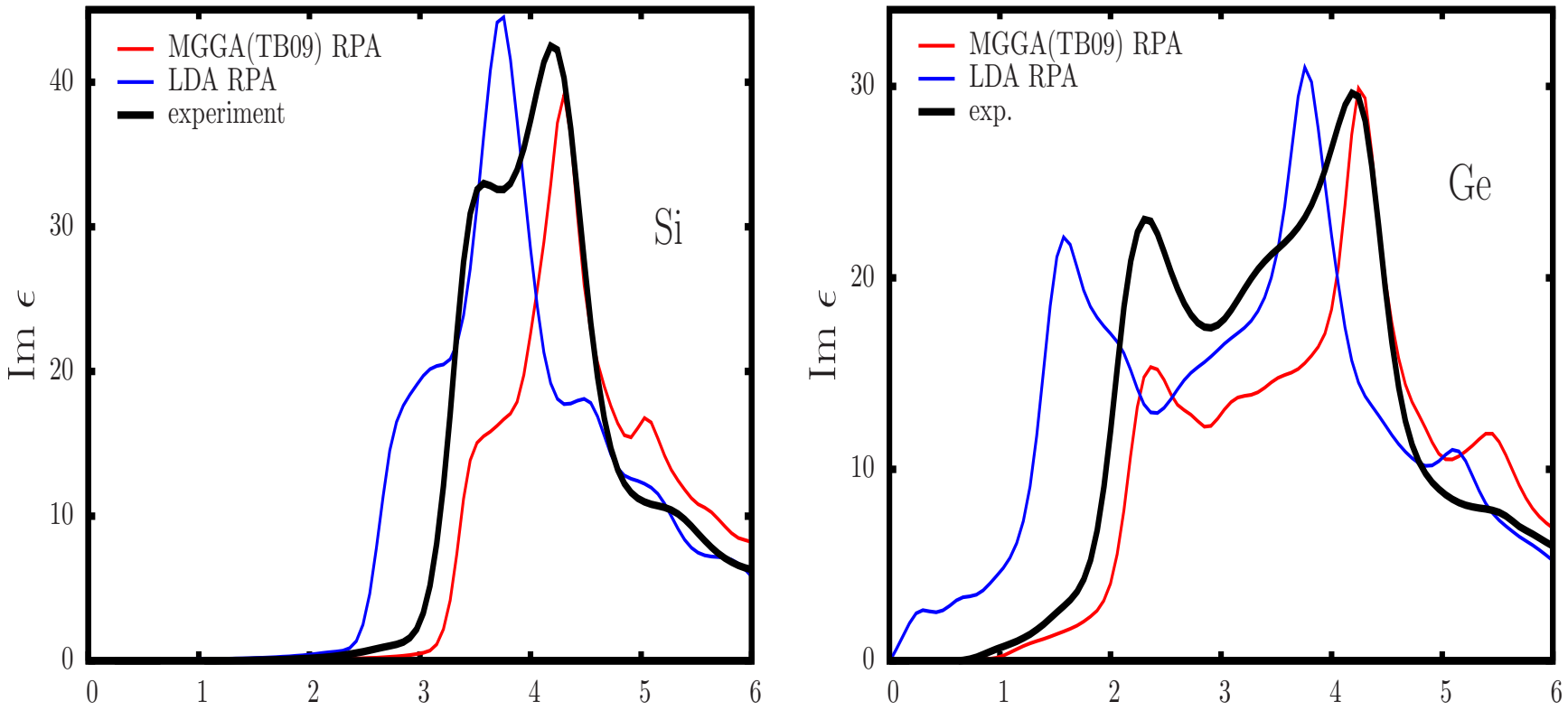


Fig.2: Dielectric function of crystalline Si and Ge (MGGA RPA).

The best what can be achieved with RPA ($f_{xc} = 0$)!

Time-dependent density functional theory (TDDFT)

TD Kohn-Sham equations:

$$i\frac{\partial}{\partial t}\psi_\alpha(\mathbf{r},t) = \left[-\frac{1}{2}\Delta + v_{eff}(\mathbf{r},t)\right]\psi_\alpha(\mathbf{r},t), \tag{7}$$

$$v_{eff}(\mathbf{r},t) = v_{ext}(\mathbf{r},t) + \int \frac{n_0(\mathbf{r}',t)}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}' + v_{xc}(\mathbf{r},t). \tag{8}$$

In varience with RPA .

Time-dependent linear response (TDDFT)

$$n(\mathbf{r},t) = n_0(\mathbf{r}) + n_1(\mathbf{r},t) + ..., \tag{9}$$

$$n_1(\mathbf{r},t) = \int \chi(\mathbf{r},\mathbf{r}',t-t')v_{ext}(\mathbf{r}',t')d\mathbf{r}'dt'. \tag{10}$$

Interacting particles response function (unknown).

$$n_1(\mathbf{r},t) = \int \chi_s(\mathbf{r},\mathbf{r}',t-t')v_{eff}(\mathbf{r}',t')d\mathbf{r}'dt', \tag{11}$$

Lindhard's independent particles response function of Eq. (6).

The concept of the exchange-correlation kernel f_{xc}

$$\boxed{f_{xc}(\mathbf{r},\mathbf{r}',\omega)=\frac{\delta v_{xc}(\mathbf{r},\omega)}{\delta n_1(\mathbf{r}',\omega)}},$$

(12)

$$\chi^{-1}(\mathbf{r},\mathbf{r}',\omega)=\chi_s^{-1}(\mathbf{r},\mathbf{r}',\omega)-\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}-f_{xc}(\mathbf{r},\mathbf{r}',\omega).$$

- $f_{xc}(\mathbf{r},\mathbf{r}',\omega)=0$: RPA;
- $f_{xc}(\mathbf{r},\mathbf{r}',\omega)=f_{xc}(\mathbf{r},\mathbf{r}',\omega=0)$: Adiabatic TDDFT:
  - Adiabatic LDA: $f_{xc}(\mathbf{r},\mathbf{r}')=\frac{\delta^2 E_{xc}^{LDA}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}=\frac{d^2E_{xc}^h(n)}{dn^2}\Big|_{n=n_0(\mathbf{r})}\delta(\mathbf{r}-\mathbf{r}')$;
  - Adiabatic MGGA: $f_{xc}(\mathbf{r},\mathbf{r}')=\frac{\delta^2 E_{xc}^{MGGA}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}$.

$$E_{xc} = \int \varepsilon_{xc}[n_0(\mathbf{r}), \nabla n_0(\mathbf{r}), \tau(\mathbf{r})] d\mathbf{r}, \tag{13}$$

$$\begin{aligned} v_{xc}(\mathbf{r}) &= \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \\ &= \frac{\partial \varepsilon_{xc}}{\partial n}(\mathbf{r}) - \nabla \frac{\partial \varepsilon_{xc}}{\partial \nabla n}(\mathbf{r}) + \int \frac{\partial \varepsilon_{xc}}{\partial \tau}(\mathbf{r}') \frac{\delta \tau(\mathbf{r}')}{\delta n(\mathbf{r})} d\mathbf{r}'. \end{aligned} \tag{14}$$

And sorry for the upcoming Eq. (15) ...

$$f_{xc}(\mathbf{r},\mathbf{r}') = \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}$$

$$= \frac{\partial^2 \varepsilon_{xc}}{\partial n^2}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') - \left[\nabla \frac{\partial^2 \varepsilon_{xc}}{\partial n \partial \nabla n}(\mathbf{r})\right]\delta(\mathbf{r}-\mathbf{r}') - \nabla_i \frac{\partial^2 \varepsilon_{xc}}{\partial \nabla_i n \partial \nabla_j n}(\mathbf{r})\nabla_j \delta(\mathbf{r}-\mathbf{r}')$$

$$+ \frac{\partial^2 \varepsilon_{xc}}{\partial n \partial \tau}(\mathbf{r})\frac{\delta\tau(\mathbf{r})}{\delta n(\mathbf{r}')} + \frac{\partial^2 \varepsilon_{xc}}{\partial n \partial \tau}(\mathbf{r}')\frac{\delta\tau(\mathbf{r}')}{\delta n(\mathbf{r})}$$

$$-\nabla \frac{\partial^2 \varepsilon_{xc}}{\partial \nabla n \partial \tau}(\mathbf{r})\frac{\delta\tau(\mathbf{r})}{\delta n(\mathbf{r}')} - \nabla' \frac{\partial^2 \varepsilon_{xc}}{\partial \nabla' n \partial \tau}(\mathbf{r}')\frac{\delta\tau(\mathbf{r}')}{\delta n(\mathbf{r})} + \int \frac{\partial^2 \varepsilon_{xc}}{\partial \tau^2}(\mathbf{r}'')\frac{\delta\tau(\mathbf{r}'')}{\delta n(\mathbf{r})}\frac{\delta\tau(\mathbf{r}'')}{\delta n(\mathbf{r}')}d\mathbf{r}''$$

$$+ \int \frac{\partial \varepsilon_{xc}}{\partial \tau}(\mathbf{r}'')\frac{\delta^2\tau(\mathbf{r}'')}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\, d\mathbf{r}'', \qquad (15)$$

which is the ‘exact‘ adiabatic MGGA f_{xc}.

Ultra-nonlocality of f_{xc} in optical limit

Since

$$\epsilon(\mathbf{q},\omega) = 1 - \frac{4\pi}{q^2}\frac{\chi_s(\mathbf{q},\omega)}{1-\chi_s(\mathbf{q},\omega)f_{xc}(\mathbf{q},\omega)}, \quad \text{and} \quad \chi_s(\mathbf{q},\omega) \underset{\mathbf{q}\to\mathbf{0}}{\longrightarrow} const\times q^2, \tag{16}$$

we need

$$f_{xc}(\mathbf{q},\omega) \underset{\mathbf{q}\to\mathbf{0}}{\longrightarrow} \frac{\alpha}{q^2}, \quad \text{with} \quad \alpha \neq 0. \tag{17}$$

True for MGGA!

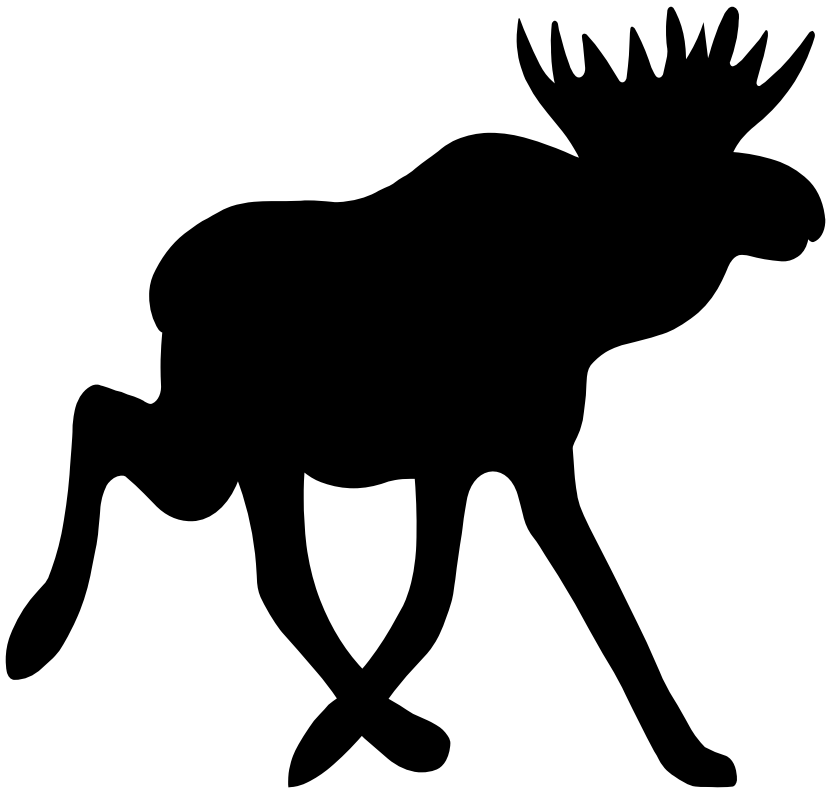
Wrong for LDA & GGA

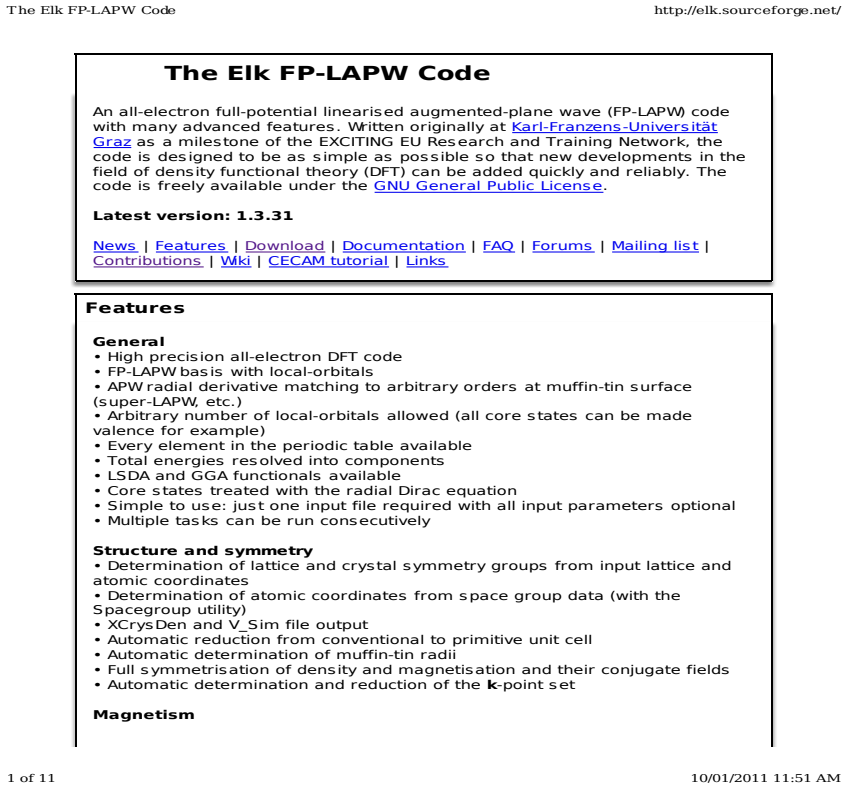
Main approximation to Eq. (15)

$$\boxed{f_{xc}(\mathbf{q}) \approx -\overline{\frac{\partial\epsilon_{xc}}{\partial\tau}}\,\chi_s^{-1}(\mathbf{q})}, \tag{18}$$

$$\alpha = -\overline{\frac{\partial\varepsilon_{xc}}{\partial\tau}}\lim_{\mathbf{q}\to\mathbf{0}} q^2\chi_s^{-1}(\mathbf{q}). \tag{19}$$

Details of calculations





The Elk FP-LAPW Code http://elk.sourceforge.net/

The Elk FP-LAPW Code

An all-electron full-potential linearised augmented-plane wave (FP-LAPW) code with many advanced features. Written originally at Karl-Franzens-Universität Graz as a milestone of the EXCITING EU Research and Training Network, the code is designed to be as simple as possible so that new developments in the field of density functional theory (DFT) can be added quickly and reliably. The code is freely available under the GNU General Public License.

Latest version: 1.3.31

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Features

General
- High precision all-electron DFT code
- FP-LAPW basis with local-orbitals
- APW radial derivative matching to arbitrary orders at muffin-tin surface (super-LAPW, etc.)
- Arbitrary number of local-orbitals allowed (all core states can be made valence for example)
- Every element in the periodic table available
- Total energies resolved into components
- LSDA and GGA functionals available
- Core states treated with the radial Dirac equation
- Simple to use: just one input file required with all input parameters optional
- Multiple tasks can be run consecutively

Structure and symmetry
- Determination of lattice and crystal symmetry groups from input lattice and atomic coordinates
- Determination of atomic coordinates from space group data (with the Spacegroup utility)
- XCrysDen and V_Sim file output
- Automatic reduction from conventional to primitive unit cell
- Automatic determination of muffin-tin radii
- Full symmetrisation of density and magnetisation and their conjugate fields
- Automatic determination and reduction of the **k**-point set

Magnetism

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Fig.3: The Elk FP-LAPW code (`http://elk.sourceforge.net`) was used with our implementation of meta-GGA.

DF of semiconductors from the MGGA-based TDDFT

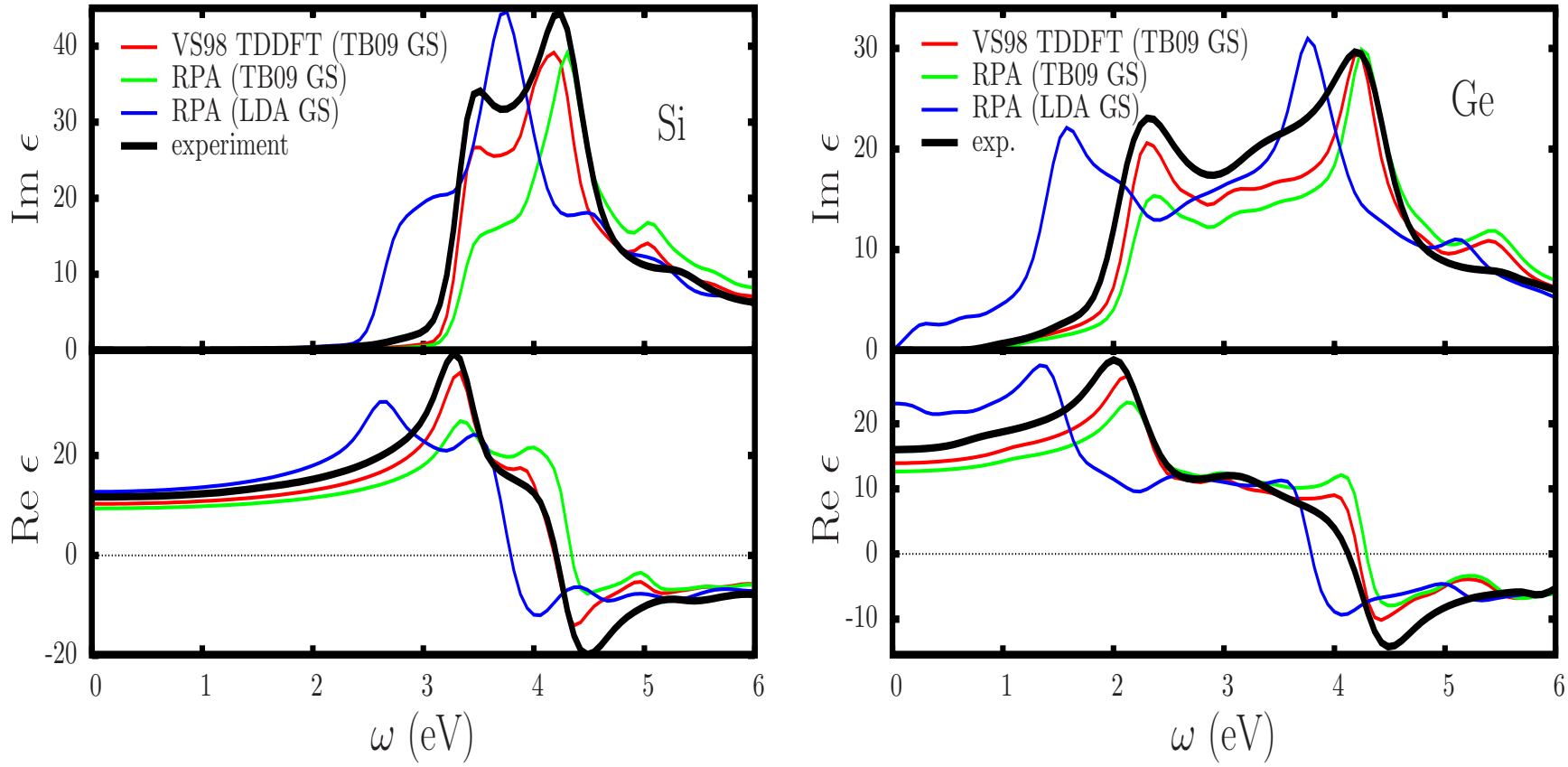

Fig.4: Dielectric function of crystalline silicon and germanium from MGGA TDDFT, (Nazarov & Vignale, 2011).

DF of semiconductors from the MGGA-based TDDFT

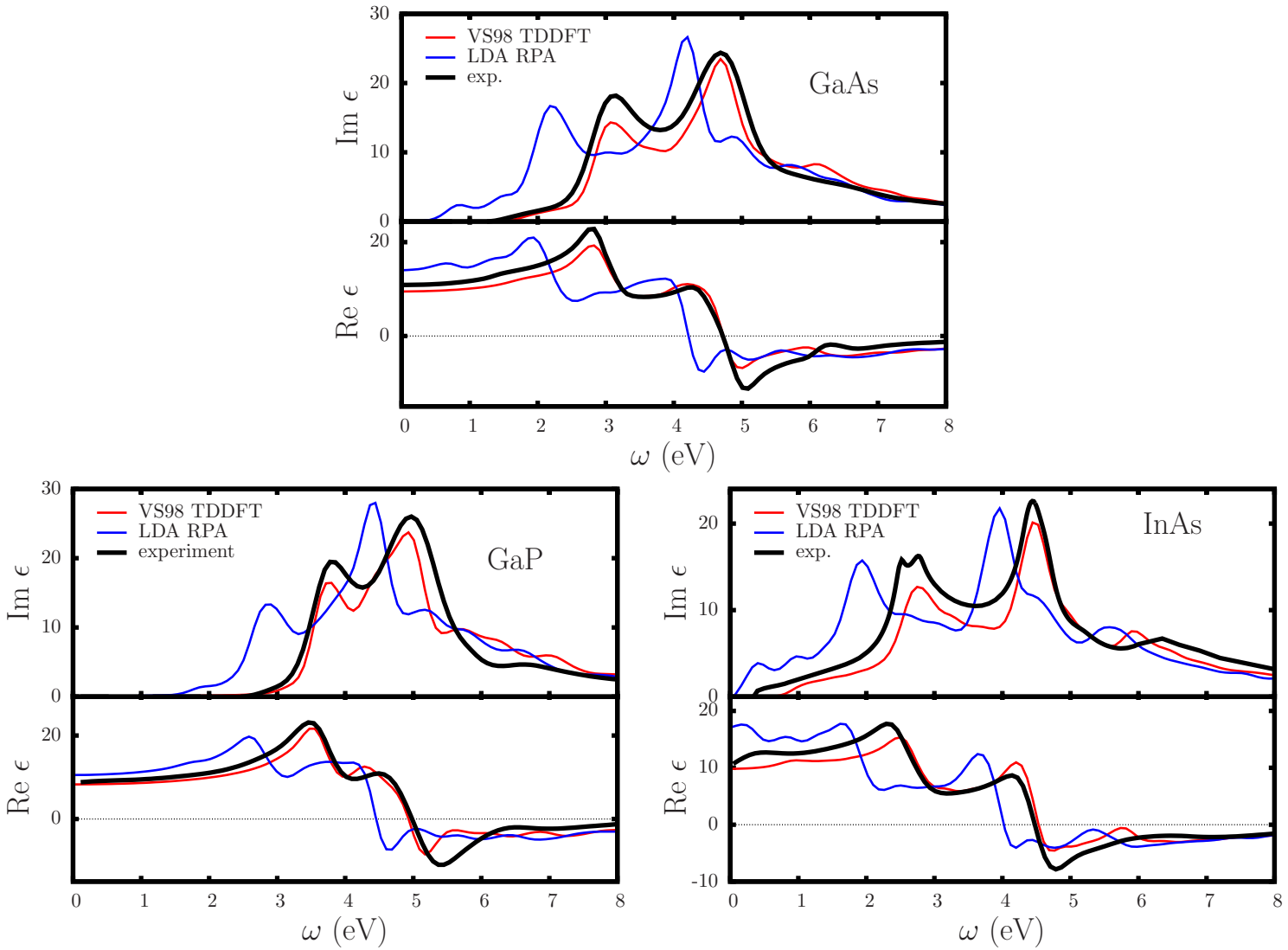

Fig.5: Dielectric function of zincblende semiconductors GaAs, GaP, and InAs, (Nazarov & Vignale, 2011).

Conclusions

- We have developed the adiabatic kinetic energy dependent (MGGA) TDDFT;
- Contrary to LDA and GGA, MGGA xc kernel f_{xc} exhibits the singularity of the type α/q^2, which is important to describe the excitonic effect in crystals;
- Our calculations for a number of the diamond-structure and zincblende semiconductors demonstrate the high promise of the MGGA-based xc functionals as a new tool in the arsenal of TDDFT methods.

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