TDDFT in

exciting

http://www.exciting-code.org

Stephan Sagmeister, University of Leoben, Austria

Outline

- Review TDDFT linear response
- Implementation within LAPW and exciting
  - Elements of the Dyson equation
    - Kohn-Sham response function
    - xc kernel
  - Matrix elements
    - q-dependent
    - Momentum operator
- Parallelization

TDDFT linear response in one slide

$$\chi = \chi_{\mathrm{KS}} + \chi_{\mathrm{KS}}(v + f_{\mathrm{xc}})\chi$$

(G,G') basis

$$\chi^{\mathrm{KS}}_{\mathbf{GG'}}(\mathbf{q},\omega) = \frac{1}{V}\sum_{nm\mathbf{k}} \frac{f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \omega + i\delta} M_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}) M^{*}_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}')$$

$$\langle n\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|n'\mathbf{k}+\mathbf{q}\rangle$$

$$\epsilon^{-1} = 1 + v\chi$$

$$\epsilon_M(\mathbf{q},\omega)$$

Spectroscopic quantities

- Macroscopic dielectric function
- Loss function
- Dynamical structure factor
- Optical conductivity
- Sumrules

Formalism revisited

TDDFT linear response: Dyson equation for response function

$$\delta n(1) = \int \mathrm{d}(2)\, \chi^R_{nn}(1,2)\delta v_{\text{ext}}(2)$$

$$\chi = \chi_{\text{KS}} + \chi_{\text{KS}}(v + f_{\text{xc}})\chi$$

↓ Fourier transform, periodicity ↓

$$\begin{aligned}\tilde{\chi}_{\mathbf{GG}'}(\mathbf{q},\omega) &= \tilde{\chi}^{\text{KS}}_{\mathbf{GG}'}(\mathbf{q},\omega) \\ &+ \sum_{\mathbf{G}_1\mathbf{G}_2} \tilde{\chi}^{\text{KS}}_{\mathbf{GG}_1}(\mathbf{q},\omega)[\tilde{v}_{\mathbf{G}_1}(\mathbf{q})\delta_{\mathbf{G}_1\mathbf{G}_2} + \tilde{f}^{\text{xc}}_{\mathbf{G}_1\mathbf{G}_2}(\mathbf{q},\omega)]\tilde{\chi}_{\mathbf{G}_2\mathbf{G}'}(\mathbf{q},\omega)\end{aligned}$$

Kohn-Sham response function

Starting point for Dyson equation for full response

$$\chi_{\mathrm{KS}}(\mathbf{r},\mathbf{r}';\omega) = \sum_{i,j}(f_i - f_j)\frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j + \omega + i\delta}$$

↓ Fourier transform, periodicity, pick a **q**-vector ↓

$$\chi^{\mathrm{KS}}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \frac{1}{V}\sum_{nm\mathbf{k}}\frac{f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \omega + i\delta} M_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}) M^*_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}')$$

$$M_{nm\mathbf{k}}(\mathbf{q}+\mathbf{G}) = \langle \phi_{n\mathbf{k}} \mid e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}} \mid \phi_{m\mathbf{k}+\mathbf{q}} \rangle$$

Optics: limit q → 0

- Properties of the head (00) and wing (0,G), (G,0) components
  (see also Pick et al. PR 1970)

$$\chi^0_{00}(\mathbf{q}) \sim q^2$$

$$\chi^0_{0\mathbf{G}}(\mathbf{q}),\, \chi^0_{\mathbf{G}0}(\mathbf{q}) \sim q$$

- Leads to non-Hermitian dielectric function (DF) $\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \delta_{\mathbf{G}\mathbf{G}'} - \chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)\, v_{\mathbf{G}'}(\mathbf{q})$

- Take symmetrized DF, Hermitian, analytic everywher

$$\tilde{\epsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \sum_{\mathbf{G}_1\mathbf{G}_2} v^{-\frac{1}{2}}_{\mathbf{G}\mathbf{G}_1}(\mathbf{q})\, \epsilon_{\mathbf{G}_1\mathbf{G}_2}(\mathbf{q})\, v^{\frac{1}{2}}_{\mathbf{G}_2\mathbf{G}'}(\mathbf{q})$$

Optics: limit q → 0

- SQRT of Coulomb potential

$$v^{\frac{1}{2}}_{\mathbf{GG'}}(\mathbf{q}) = \frac{\sqrt{4\pi}}{|\mathbf{q}+\mathbf{G}|}\delta_{\mathbf{GG'}}$$

$$v^{\frac{1}{2}}(\mathbf{r},\mathbf{r}') = \frac{\pi^{-\frac{3}{2}}}{|\mathbf{r}-\mathbf{r}'|^2}$$

- Symmetrize $\tilde{\chi}^{\mathrm{KS}}_{\mathbf{GG'}}$ and xc kernel:

$$\tilde{\chi}_{\mathbf{GG'}}(\mathbf{q},\omega) = v^{\frac{1}{2}}_{\mathbf{G}}(\mathbf{q})\chi_{\mathbf{GG'}}(\mathbf{q},\omega)v^{\frac{1}{2}}_{\mathbf{G'}}(\mathbf{q})$$

$$\tilde{\chi}^{\mathrm{KS}}_{\mathbf{GG'}}(\mathbf{q},\omega) = v^{\frac{1}{2}}_{\mathbf{G}}(\mathbf{q})\chi^{\mathrm{KS}}_{\mathbf{GG'}}(\mathbf{q},\omega)v^{\frac{1}{2}}_{\mathbf{G'}}(\mathbf{q})$$

- Dyson equation for symmetrized quantities

$$\tilde{v}_{\mathbf{G}}(\mathbf{q}) = v^{-\frac{1}{2}}_{\mathbf{G}}(\mathbf{q})v_{\mathbf{G}}(\mathbf{q})v^{-\frac{1}{2}}_{\mathbf{G}}(\mathbf{q}) = 1$$

$$\tilde{f}^{\mathrm{xc}}_{\mathbf{G}}(\mathbf{q}) = v^{-\frac{1}{2}}_{\mathbf{G}}(\mathbf{q})f^{\mathrm{xc}}_{\mathbf{GG'}}(\mathbf{q})v^{-\frac{1}{2}}_{\mathbf{G'}}(\mathbf{q}).$$

Controlling $\tilde{\chi}^{\mathrm{KS}}_{\mathbf{GG}'}$

<qpoint>

$$\chi^{\mathrm{KS}}_{\mathbf{GG}'}(\mathbf{q},\omega) = \frac{1}{V}\sum_{nm\mathbf{k}} \frac{f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \omega + i\delta} M_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}) M^{*}_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}')$$

@gqmax

@nempty

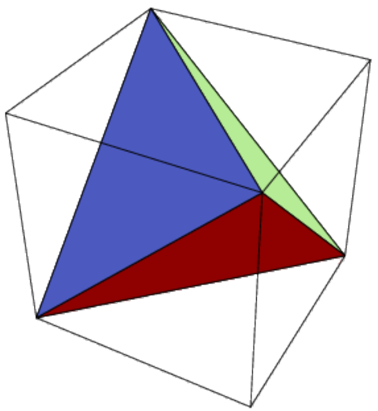
@ngridk

@broad

<energywindow>

Summation in $\tilde{\chi}^{KS}_{\mathbf{GG'}}$

- Direct summation in real frequency interval – Lorentzian broadening
- Linear tetrahedron method – interpolation scheme, no broadening



- Analytic continuation: imaginary frequency interval, Wick rotation to real axis + broadening, N-point Padé approximants
- Anti-resonant parts $N_c \rightarrow N_v$ $(\varepsilon_v < \varepsilon_c)$

Controlling $\tilde{\chi}^{\mathrm{KS}}_{\mathbf{GG}'}$ ...

- **`@acont, <tetra>`** (analytic continuation, tetrahedron method)

$$\chi^{\mathrm{KS}}_{\mathbf{GG}'}(\mathbf{q},\omega) = \frac{1}{V}\sum_{nm\mathbf{k}} \frac{f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \omega + i\delta} M_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}) M^{*}_{nm\mathbf{k}}(\mathbf{q},\mathbf{G}')$$

`@aresdf` (anti-resonant part)

xc kernel

- RPA $$f_{\rm xc} \equiv 0$$

- ALDA independet of **q**
$$f_{\rm xc}^{\rm ALDA}(\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}') \left. \frac{{\rm d}v_{\rm xc}^{\rm LDA}(n)}{{\rm d}n} \right|_{n=n_0(\mathbf{r})}$$
↓ Fourier transform ↓
$$f_{\mathbf{GG}'}^{\rm xc,ALDA}(\mathbf{q}) = \frac{1}{V} \int {\rm d}^3 r\, e^{-i(\mathbf{G}-\mathbf{G}')\mathbf{r}} \left. \frac{{\rm d}v_{\rm xc}^{\rm LDA}(n)}{{\rm d}n} \right|_{n=n_0(\mathbf{r})}$$

- LRC kernels (α kernel)
(Reining PRL 2002,
Botti, PRBs 2003, 2005)
$$f_{\rm xc}(\mathbf{r}, \mathbf{r}'; \omega) = -\frac{\alpha}{4\pi} v(\mathbf{r}, \mathbf{r}')$$
↓ FT ↓
$$f_{\rm xc}(\mathbf{q}, \omega) \sim -\alpha(\omega) \frac{1}{q^2}$$

xc kernel

- MBPT derived kernel, see next talk on Bethe-Salpeter equation

wave function within APW-like basis sets

Atomic like basis functions in muffin-tin: **spherical harmonics** expansion

$$\phi_{n\mathbf{k}}^{\mathrm{MT}}(\mathbf{r}) = \sum_{\alpha lmp} A_{lmp}^{\alpha}(n\mathbf{k}) u_{lp}^{\alpha}(r_{\alpha}) Y_{lm}(\hat{\mathbf{r}}_{\alpha})$$

$$\phi_{n\mathbf{k}}^{\mathrm{I}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}$$

$$A_{lmp}^{\alpha}(n\mathbf{k}) = \sum_{\mathbf{G}} c_{n\mathbf{k}+\mathbf{G}} A_{lmp}^{\alpha}(\mathbf{k}+\mathbf{G})$$

Plane waves for interstitial region, slow changes in wave function

α … atom

n … band index

Matrix elements ($\mathbf{q}$) Interstitial

$$M_{nn'\mathbf{k}}(\mathbf{q}+\mathbf{G}) = \langle n\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|n'\mathbf{k}+\mathbf{q}\rangle$$

↓ interstitial WF ↓

$$\phi^{\mathrm{I}}_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}$$

$$M^{\mathrm{I}}_{nn'\mathbf{k}}(\mathbf{q}+\mathbf{G}) = \sum_{\mathbf{G}'\mathbf{G}''} c^{*}_{n\mathbf{k}+\mathbf{G}'} c_{n'\mathbf{k}+\mathbf{q}+\mathbf{G}''} M^{\mathrm{I}}_{\mathbf{G}'\mathbf{G}''\mathbf{k}}(\mathbf{q}+\mathbf{G})$$

$$M^{\mathrm{I}}_{\mathbf{G}'\mathbf{G}''\mathbf{k}}(\mathbf{q}+\mathbf{G}) = \tilde{\theta}_I(\mathbf{G}'-\mathbf{G}''-\mathbf{G})$$

$$\tilde{\theta}_I(\mathbf{G}) = \begin{cases} 1 - \sum_\alpha \frac{4\pi R_\alpha^3}{3\Omega} & \mathbf{G}=0 \\ -\sum_\alpha \frac{4\pi R_\alpha^3}{3\Omega} \frac{j_1(|\mathbf{G}|R_\alpha)}{|\mathbf{G}|R_\alpha} 3 e^{i\mathbf{G}\mathbf{R}_\alpha} & \mathbf{G}\neq 0. \end{cases}$$

Matrix elements ($\mathbf{q}$) Muffin-Tin

$$M^{\mathrm{MT}}_{nn'\mathbf{k}}(\mathbf{q}+\mathbf{G}) = 4\pi \sum_{\alpha} S^{*}_{\alpha}(\mathbf{q}+\mathbf{G}) \sum_{l'm'p'} A^{\alpha}_{l'm'p'}(n\mathbf{k})^{*}$$

$$\sum_{l''m''p''} A^{\alpha}_{l''m''p''}(n'\mathbf{k}) X^{\alpha}_{l'm'p',l''m''p''}(\mathbf{q}+\mathbf{G})$$

Rayleigh-expansion of exp

$$X^{\alpha}_{l'm'p',l''m''p''}(\mathbf{q}+\mathbf{G}) = \sum_{l} (-i)^{l} R^{\alpha}_{l'p'l''p''l}(\mathbf{q}+\mathbf{G}) \sum_{m} Y_{lm}(\widehat{\mathbf{q}+\mathbf{G}})^{*} C^{l'm'}_{lml''m''}$$

$$R^{\alpha}_{l'p'l''p''l}(\mathbf{q}+\mathbf{G}) = \int_{0}^{R^{\mathrm{MT}}_{\alpha}} \mathrm{d}r\, r^{2} u^{\alpha}_{l'p'}(r) j_{l}(|\mathbf{q}+\mathbf{G}|r) u^{\alpha}_{l''p''}(r),$$

Gaunt coefficients

Spherical Bessel functions

Controlling M(q)

$$M_{nn'\mathbf{k}}(\mathbf{q}+\mathbf{G}) = \langle n\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|n'\mathbf{k}+\mathbf{q}\rangle$$

$$\langle \underbrace{n\mathbf{k}}_{\sum_{\mathbf{G}} + \sum_{\alpha lmp} \cdots} |$$

Rayleigh expansion

$$e^{i\mathbf{gr}} = 4\pi \sum_{lm} i^l j_l(gr) Y_{lm}(\hat{\mathbf{r}}) Y^*_{lm}(\hat{\mathbf{g}})$$

@lmaxapwwf

@lmaxemat

Limit q $\rightarrow$ 0

k.p perturbation theory for KS Hamiltonian H(**k+q**)

$$M_{nm\mathbf{k}}(\mathbf{q} \rightarrow 0, \mathbf{G} = 0) = \delta_{nm} + \frac{q\hat{\mathbf{\Omega}}_q \mathbf{P}_{nm\mathbf{k}}}{\epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}}}(1 - \delta_{nm})$$

- Leads to matrix elements of momentum operator
- Carefully take limit q $\rightarrow$ 0 in all equations

Matrix elements (**p**) Interstitial

$$P^j_{nn'\mathbf{k}} = \langle n\mathbf{k}|-i\nabla_j|n'\mathbf{k}\rangle$$

- Plane wave expansion in interstitial

$$P^{j,\mathrm{I}}_{nn'\mathbf{k}} = \sum_{\mathbf{G}\mathbf{G}'} c^*_{n\mathbf{k}+\mathbf{G}} c_{n'\mathbf{k}+\mathbf{G}'} P^{j,\mathrm{I}}_{\mathbf{G}\mathbf{G}'\mathbf{k}}$$

$$P^{j,\mathrm{I}}_{\mathbf{G}\mathbf{G}'\mathbf{k}} = (\mathbf{k}+\mathbf{G}')\tilde{\theta}_I(\mathbf{G}-\mathbf{G}')$$

Matrix elements (**p**) Muffin-Tin

$$P^{j,\mathrm{MT}}_{nn'\mathbf{k}} = \sum_{\alpha} \sum_{l'm'p'} A^{\alpha}_{l'm'p'}(n\mathbf{k})^{*} \sum_{l''m''p''} A^{\alpha}_{l''m''p''}(n'\mathbf{k}) \zeta^{\alpha,j}_{l'm'p',l''m''p''}$$

$$\zeta^{\alpha,j}_{l'm'p',l''m''p''} = \int_0^{R^{\mathrm{MT}}_{\alpha}} \mathrm{d}r\, r^2 u^{\alpha}_{l'p'}(r) u^{\alpha,j}_{l''m''p'',l'm'}(r).$$

$$u^{\alpha,j}_{l''m''p'',l'm'}(r) = -\left[\frac{l''+1}{2l''+1}\right]^{\frac{1}{2}} \left[\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l''}{r}\right] u^{\alpha}_{l''p''}(r) C^{j}_{l''m'',l'm'} \delta_{l',l''+1} + \left[\frac{l''}{2l''+1}\right]^{\frac{1}{2}} \left[\frac{\mathrm{d}}{\mathrm{d}r} + \frac{l''+1}{r}\right] u^{\alpha}_{l''p''}(r) C^{j}_{l''m'',l'm'} \delta_{l',l''-1}$$

related to Clebsch-Gordon coefficients

Controlling M(p)

$$P^{j}_{nn'\mathbf{k}} = \langle n\mathbf{k}|-i\nabla_j|n'\mathbf{k}\rangle$$

$$\langle \underbrace{n\mathbf{k}}_{\sum_{\mathbf{G}} + \sum_{\alpha lmp} \cdots} |$$

@lmaxapwwf

Important parameters

`(input/xs/)`

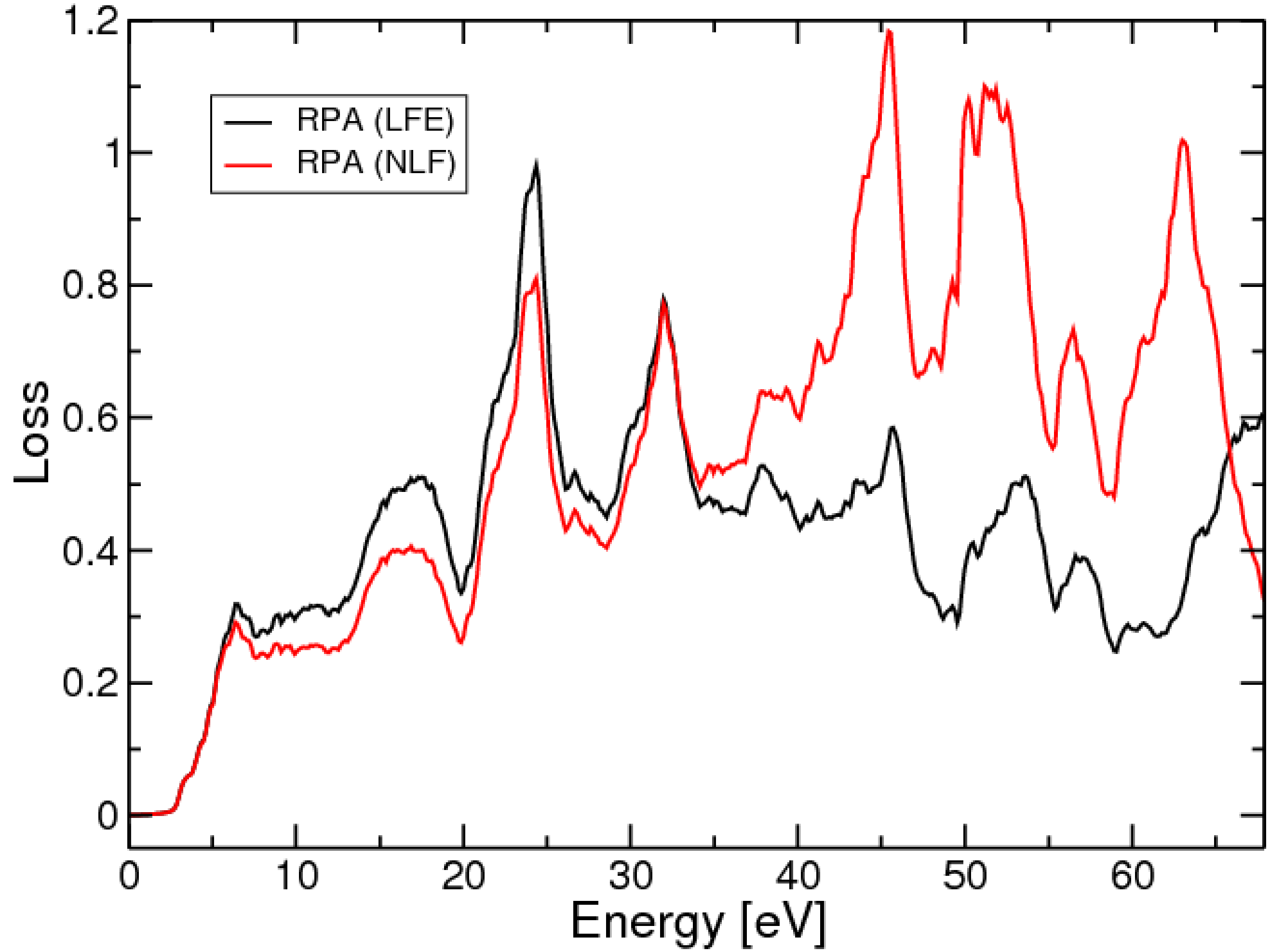
- **`@ngridk`** k-point grid sizes
- **`@rgkmax`** $|G+k|_{max}R_{min}$ basis set size for wavefunction
- **`@nempty`** #conduction states
- **`energywindow`** range of energies for spectrum
- **`@gqmax`** $|G+q|_{max}$ local field effects size
- **`tddft/@fxctype`** type of xc kernel

In practice:

```
<xs xstype="TDDFT"
 ngridq="4 4 4"
 ngridk="4 4 4" vkloff="0.05 0.15 0.25"
 gqmax="3"
 broad="0.0073499">

  <tddft fxctype="ALDA" />

   <energywindow intv="0.0 1.0"
    points="1200" />

   <qpointset>
     <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

</xs>
```

data

templates



Parallelization

MPI parallelization

- Wavefunctions – #k-points
- Matrix elements – #k-points
- Kohn-Sham response – #frequencies
- xc kernel, Dyson equation – #frequencies

Data parallelism throughout – no side effects

Now grab your coffee and we meet at the excercises...