

Time-dependent relativistic density functional theory for complex linear response based on the zeroth order regular approximation

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We develop a time-dependent quasirelativistic density functional theory based on ZORA approximation for computing frequency dependent linear response of molecules. Density fitting was used for the calculation of complex components of frequency dependent dipole-dipole polarizability. CPKS based on 2-component ZORA response were derived. Using damping techniques, excitation energies corresponding to the poles of the polarizability curve were calculated. Results of calculations of 2- and 3-D gold clusters, and absorption spectra of heavy metal oxides are presented.

SO-ZORA Complex Linear Response

The ZORA equation reads:

$$H^{ZORA}\psi^{ZORA} = \left(V + \vec{\sigma} \cdot \mathbf{p} \frac{c^2}{2c^2 - V} \vec{\sigma} \mathbf{p} \right) \psi^{ZORA} \quad (1)$$

where spinor ψ may be complex and has 2-component

$$\psi = \begin{pmatrix} \phi_{\alpha}^R & + & i\phi_{\alpha}^I \\ \phi_{\beta}^R & + & \phi_{\beta}^I \end{pmatrix} \quad (2)$$

and $\vec{\sigma}$ is a vector of Pauli matrices ($\sigma_x, \sigma_y, \sigma_z$).

$$H^{ZORA}\psi^{ZORA} = \left(H_{SR}^{ZORA} + H_{SO}^{ZORA} \right) \psi^{ZORA} \quad (3)$$

$$\left(V + \mathbf{p} \frac{c^2}{(2c^2 - V)} \mathbf{p} + \frac{c^2}{(2c^2 - V)^2} \boldsymbol{\sigma} (\nabla \mathbf{V} \times \mathbf{p}) \right) \psi^{ZORA} \quad (4)$$
$$= \epsilon^{ZORA} \psi^{ZORA}$$

Frequency-dependent dynamic polarizability

$$\alpha_{u,v}(\omega) = - \sum_{\mu,\nu} \hat{h}_{\mu,\nu}^{(u)} P_{\mu,\nu}^{(v)}(\omega) \quad (5)$$

$P_{\mu,\nu}^{(v)}(\omega)$: perturbed density matrix (PDM).

In KS-TDDFT, PDM is computed via perturbed MO coefficients.

Expansion of two-component orbitals φ_i in AO basis χ_μ :

$$\varphi_i = \sum_{\mu} \chi_{\mu} C_{\mu,i} \quad \text{with} \quad C_{\mu i} = \begin{pmatrix} C_{\mu i}^{\alpha} \\ C_{\mu i}^{\beta} \end{pmatrix} \quad (6)$$

Unlike spin-free case:

- ▶ Two spin-components: $\gamma \in \{\alpha, \beta\}$
- ▶ In general $C_{\mu i}^{\gamma}$ are complex numbers.

Spin-free density matrix:

$$\mathbf{P} = \sum_{\gamma} \mathbf{C}^{\gamma*} \mathbf{C}^{\gamma T} \quad (7)$$

Collecting terms to first order in $\exp(\pm i\omega t)$

$$\mathbf{P}^{(+,Re)} = \text{Re}\{\mathbf{C}^{(0)*} \mathbf{C}^{(-)T} + \mathbf{C}^{(+)*} \mathbf{C}^T\} \quad (8)$$

$$\mathbf{P}^{(+,Im)} = \text{Im}\{\mathbf{C}^{(0)*} \mathbf{C}^{(-)T} + \mathbf{C}^{(+)*} \mathbf{C}^T\}$$

$$\mathbf{P}^{(-,Re)} = \text{Re}\{\mathbf{C}^{(0)*} \mathbf{C}^{(+)T} + \mathbf{C}^{(-)*} \mathbf{C}^T\} \quad (9)$$

$$\mathbf{P}^{(-,Im)} = \text{Im}\{\mathbf{C}^{(0)*} \mathbf{C}^{(+)T} + \mathbf{C}^{(-)*} \mathbf{C}^T\}$$

The perturbed coefficients:

$$\mathbf{C}^{(\pm)} = \mathbf{C}^{(0)} \mathbf{A}^{(\pm)} \quad (10)$$

For an occupied-virtual or virtual-occupied MO index pair (ij):

$$A_{ij}^{(\pm)} = \frac{F_{ij}^{(\pm)}}{\varepsilon_j^{(0)} - \varepsilon_i^{(0)} \mp \omega} \quad (11)$$

Damping is introduced to avoid singularity at resonance:

$$A_{ij}^{(a)}(\pm\omega) = \frac{F_{ij}^{(a)}(\pm\omega)}{\omega_{ij} \mp \omega \pm i\gamma} \quad (12)$$

For a given frequency, the real and imaginary part of the MO mixing matrix are then computed as

$$\text{Re}[A_{ij}^{(\pm)}] = \frac{(\omega_{ij} \mp \omega) \text{Re}[F_{ij}^{(\pm)}] \pm \gamma \text{Im}[F_{ij}^{(\pm)}]}{(\omega_{ij} \mp \omega)^2 + \gamma^2} \quad (13)$$

$$\text{Im}[A_{ij}^{(\pm)}] = \frac{(\omega_{ij} \mp \omega) \text{Im}[F_{ij}^{(\pm)}] \mp \gamma \text{Re}[F_{ij}^{(\pm)}]}{(\omega_{ij} \mp \omega)^2 + \gamma^2} \quad (14)$$

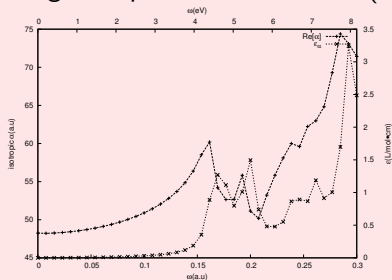
we obtain $\varepsilon(\omega)$ as

$$\varepsilon_{\text{isotropic}}(\omega) = \frac{2 \cdot 10^5}{3.48 \cdot \pi \cdot b} \omega \text{Im}[\alpha_{\text{isotropic}}(\omega)] \quad (15)$$

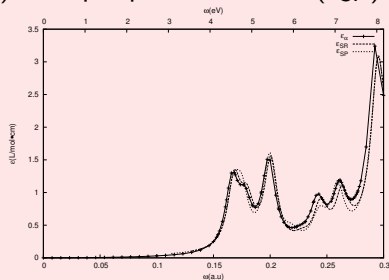
where $b = 27.211$ eV/hartree.

Absorption spectra of RuO₄ from Imaginary polarizability

Real dynamic polarizability ($\text{Re}[\alpha]$) and molar extinction coefficients of RuO₄ calculated from imaginary dynamic polarizability (ϵ_{α}) and from spin-orbit TDDFT oscillator strengths: spin-restricted value (ϵ_{SR}) and spin-polarized value (ϵ_{SP})



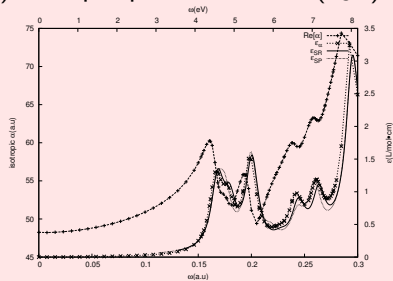
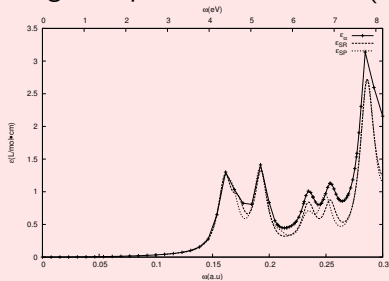
$\text{Re}[\alpha]$ and $\epsilon(\text{Im}[\alpha])$








Simul. absorption spectra from $\alpha(\omega)$ and TDDFT exc. energies

Absorption spectra of OsO₄







Absorption spectra calculated from imaginary dynamic polarizability (ϵ_{α}) and from spin-orbit TDDFT oscillator strengths: spin-restricted value (ϵ_{SR}) and spin-polarized value (ϵ_{SP})



Polarizability of 2D Gold Cluster $(Au)_n$

2D Models	N_{Au}	α_x	α_y	α_z	α_{iso}	α_{iso}/N_{Au}
	2	45	45	101	63.7	31.8
	4	122	229	76	142.3	35.6
	6	274	274	104	217.3	36.2
	8	383	398	132	304.3	38.0
	10	621	433	155	403.0	40.3

Polarizability of 3D Gold Cluster $(Au)_n$

3DModels	N_{Au}	α_x	α_y	α_z	α_{iso}	α_{iso}/N_{Au}
	16	514	514	514	514.0	32.1
	18	616	613	616	615.0	34.2
	20	716	716	716	716.0	35.8
	22	774	774	804	784	35.6
	24	765	867	739	787	32.8
	26	876	763	1007	882	33.9

SO-ZORA LR

- ▶ Implemented as module in ADF package:
Features include:
 - ▶ Pulay convergence acceleration.
 - ▶ Parallel implementation.
 - ▶ LDA and SAOP functionals can be used at present.
- ▶ ZORA $\bar{\alpha}(\omega)$ agrees well with 4-component DFT results.
- ▶ $\text{Im}[\alpha(\omega)]$ absorption spectra agrees with TDDFT-simulated.
- ▶ TDDFT: all lower-lying roots have to be calculated,
SO-ZORA-LR: only region of interest can be scanned.
- ▶ Easy to extend to other response properties.

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Thank You!