

Optical and X-ray absorption spectra with ADF

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Optical and X-ray absorption spectra with ADF

1. Optical: A New TDDFT Algorithm for Large Systems and Plasmons in Metal Clusters

2. X-ray absorption spectra: Core electron excitations (NEXAFS).

A New TDDFT Algorithm for Large Systems and Plasmons in Metal Clusters

- 1. Conventional (Casida like) TDDFT for large systems (bottleneck: diagonalization of large matrix with Davidson algorithm)
- 2. New TDDFT algorithm: inspired by previous work on photoionization to overcome problem 1)
- 3. Some applications to metal clusters
- Just published: O. Baseggio, G. Fronzoni and M. Stener, J. Chem. Phys., 143 (2015) 024106

The new algorithm to solve TDDFT equations

Before to describe the new algorithm, it is worth mentioning other recent TDDFT strategies, which are very promising for applications to large systems:

• the explicit time-propagation technique over real space grids, implemented in the OCTOPUS program [K. Yabana and G. F. Bertsch, Phys. Rev. B 54, 4484 (1996), M. A. L. Marques, A. Castro, G. F. Bertsch and A. Rubio, Comput. Phys. Comm., 151 (2003) 60.]

• the superoperator formulation of the TDDFT, which allows the calculation of the dynamical polarizability by means of a very efficient Lanczos method, implemented with plane waves basis set [B. Walker, A. M. Saitta, R. Gebauer and S. Baroni, Phys. Rev. Lett. 96 (2006) 113001.]

• the very recent simplified sTDA and sTDDFT schemes of S. Grimme [J. Chem. Phys. 138 (2013) 244104, Comput. Theoret. Chem. 1040 (2014) 45]

• the Linear-scaling TDDFT of Zuehlsdorff [T. J. Zuehlsdorff, N. D. M. Hine, J. S. Spencer, N. M.

Harrison, D. J. Riley, and P. D. Haynes, J. Chem. Phys. 139 (2013) 064104]

• TDDFT time-propagation with Transition Contribution Map (TCM) of Hakkinen [Sami Malola, Lauri Lehtovaara, Jussi Enkovaara and Hannu Häkkinen, ACS Nano 7 (2013) 10263]

TDDFT: Linear Response (LR)

In general, the density $\rho^{(1)}$ induced by an external TD perturbative field $V^{(1)}$ is:

$$\rho^{(1)}(\mathbf{r},\omega) = \int \chi(\omega,\mathbf{r},\mathbf{r}') V^{(1)}(\mathbf{r}',\omega) d\mathbf{r}'$$

Where χ is the dielectric susceptibility of the interacting system, not easily accessible

- 1. LR (general): R. McWeeny, "Methods of molecular quantum mechanics", Second Edition, Academic Press, London 1989
- LR-TDDFT: M. E. Casida, in "Recent Advances in Density Functional Theory", World Scientific, Singapore 1995 p. 155.
- 3. TDHF: A. D. McLachlan and M. A. Ball, Rev. Mod. Phys. 36 (1964) 844

TDDFT justifies the use of the χ_{KS} of the non-interacting system:

$$\rho^{(1)}(\mathbf{r},\omega) = \int \chi^{KS}(\omega,\mathbf{r},\mathbf{r}') V_{SCF}^{(1)}(\mathbf{r}',\omega) d\mathbf{r}'$$

Provided:

$$V_{SCF}^{(1)}(\mathbf{r},\omega) = V^{(1)}(\mathbf{r},\omega) + \int \frac{\rho^{(1)}(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \int f_{XC}(\omega,\mathbf{r},\mathbf{r}')\rho^{(1)}(\mathbf{r}',\omega) d\mathbf{r}'$$

 f_{XC} (XC kernel) is unknown, approximated by Adiabatic LDA: $f_{XC}(\omega, \mathbf{r}, \mathbf{r}') = \frac{dV_{XC}^{LDA}(\rho(\mathbf{r}'))}{d\rho(\mathbf{r}')}\delta(\mathbf{r} - \mathbf{r}')$

 $\succ \chi^{\text{KS}}$ is easy to calculate:

 χ_{KS} is known for the non-interacting (KS) system:

$$\chi_{KS}(\vec{r},\vec{r}',\omega) = \sum_{i}^{occ} \sum_{a}^{unocc} \frac{\varphi_{i}^{*}(\vec{r})\varphi_{a}(\vec{r})\varphi_{a}^{*}(\vec{r}')\varphi_{i}(\vec{r}')}{\omega - (\varepsilon_{a} - \varepsilon_{i}) + i\delta} + \sum_{i}^{occ} \sum_{a}^{unocc} \frac{\varphi_{i}(\vec{r})\varphi_{a}^{*}(\vec{r})\varphi_{a}(\vec{r}')\varphi_{i}^{*}(\vec{r}')}{-\omega - (\varepsilon_{a} - \varepsilon_{i}) - i\delta}$$

Infinite summations are involved: not practical for numerical implementation as it is.



Exploit linearity of the problem:



The Response Equation becomes:

$$\left[1 - \chi_{KS} K\right] \rho^{(1)} = \chi_{KS} V_{EXT}$$

To solve : represent the response equation in the **auxiliary density fitting basis functions**, dimension of fitting set (**density-based** formulation), at variance with **density-matrix** Casida formulation (1h1p space)

Extract the spectrum from polarizability:

$$\alpha_{pq}(\omega) = \int \rho_p^{(1)}(\omega, \bar{r}) q d\bar{r}$$
$$\alpha(\omega) = \frac{1}{3} \sum_{q=1}^{3} \alpha_{qq}(\omega)$$
$$\sigma(\omega) = \frac{4\pi\omega}{c} \Im[\alpha(\omega)]$$

The first order density $\rho^{(1)}$ calculated from TDDFT equations, with $\omega = \omega_R + i\omega_I$ basis set: auxiliary density fitting functions!

$$\begin{bmatrix} 1 - \chi_{KS} K \end{bmatrix} \rho^{(1)} = \chi_{KS} V_{EXT} \qquad \begin{bmatrix} \mathbf{S} - \mathbf{M}(\omega) \end{bmatrix} \mathbf{b} = \mathbf{d}(\omega)$$

The "only" problem is to calculate efficiently χ_{KS} !

Change the double sum:



The energy grid consists of P+1 knots: $\{E_k\}_{k=1,...,P+1}$ and are defined P intervals: $I_k = [E_k, E_{k+1}], k = 1,...,P$

Now it is possible to change the double sum of previous equation (13) as follows:

$$\chi_{KS}(\omega,\bar{r},\bar{r}') = \sum_{k=1}^{P} \sum_{\varepsilon_{ia}\in I_{k}} \Theta_{ia}(\bar{r})\lambda_{ia}(\omega)\Theta_{ia}(\bar{r}')$$
$$\chi_{KS}(\omega,\bar{r},\bar{r}') = \sum_{k=1}^{P} \frac{4\overline{E}_{k}}{\omega^{2} - \overline{E}_{k}^{2}} \sum_{\varepsilon_{ia}\in I_{k}} \Theta_{ia}(\bar{r})\Theta_{ia}(\bar{r}')$$

Build the matrix:TDDFT equation:
$$[S - M(\omega)]b = d(\omega)$$

$$M(\omega)_{\mu\nu} = \sum_{k=1}^{P} s_{k}(\omega) \sum_{\varepsilon_{ia} \in I_{k}} \langle f_{\mu} | \Theta_{ia}(\bar{r}) \rangle \langle \Theta_{ia}(\bar{r}') | K | f_{\nu} \rangle = \sum_{k=1}^{P} s_{k}(\omega) G_{\mu\nu}^{k}$$

$$s_k(\omega) = \frac{4E_k}{\omega^2 - \overline{E}_k^2}$$

With this scheme, the M matrix is calculated at each photon energy ω , simply as a linear combination of matrices \mathbf{G}^k with coefficients $s_k(\omega)$.

The calculation of χ_{KS} is fast (just sum of matrices) and small (over the fitting functions)!

Approximations: imaginary broadening and energy discretization.

Technical details:

$$G_{\mu\nu}^{k} = \sum_{\epsilon_{ia} \in I_{k}} \langle f_{\mu} | \Theta_{ia}(\bar{r}) \rangle \langle \Theta_{ia}(\bar{r}') | K | f_{\nu} \rangle = \sum_{\epsilon_{ia} \in I_{k}} A_{\mu,ia}^{k} B_{ia,\nu}^{k}; \mathbf{G}^{k} = \mathbf{A}^{k} \mathbf{B}^{k}$$

$$A_{\mu,ia}^{k} = \langle f_{\mu} | \varphi_{i} \varphi_{a} \rangle = \sum_{\sigma\tau}^{basis} (f_{\mu} | \sigma\tau) c_{\sigma i} c_{\pi i} B_{ia,\nu}^{k} = \langle \varphi_{i} \varphi_{a} | \frac{1}{|\bar{r}' - \bar{r}''|} | f_{\nu} \rangle + \langle \varphi_{i} \varphi_{a} | \frac{\partial V_{XC}}{\partial \rho} | f_{\nu} \rangle$$
Pair fitting (very efficient!)
$$\langle \varphi_{i} \varphi_{a} | \frac{\partial V_{XC}}{\partial \rho} | f_{\nu} \rangle = \sum_{\eta\eta}^{\gamma} \langle \varphi_{i} \varphi_{a} | f_{\gamma} \rangle S_{\eta}^{*} \langle f_{\eta} | \frac{\partial V_{XC}}{\partial \rho} | f_{\nu} \rangle = \langle \mathbf{A}^{k} \mathbf{B}^{k} \mathbf{S}^{-1} \mathbf{Z}$$
New integrals, easily implemented in ADF (numerical integration over grid)

$$\mathbf{G}^{k} = \mathbf{A}^{k} \left(\mathbf{A}^{k} \right)^{+} \mathbf{S}^{-1} \left(\mathbf{F} + \mathbf{Z} \right) = \mathbf{D}^{k} \mathbf{L}$$

Technical details:

$$d_{\mu} = \left\langle f_{\mu} \left| \chi_{KS}(\omega) \right| z \right\rangle = \sum_{k=1}^{P} s_{k}(\omega) \sum_{\varepsilon_{ia} \in I_{k}} \left\langle f_{\mu} \left| \Theta_{ia}(\bar{r}) \right\rangle \left\langle \Theta_{ia}(\bar{r}) \right| z \right\rangle = \sum_{k=1}^{P} s_{k}(\omega) \sum_{\varepsilon_{ia} \in I_{k}} A_{\mu,ia}^{k} \left\langle \varphi_{i} \left| z \right| \varphi_{a} \right\rangle$$

Once matrix **M S** and vector **d** are available, the TDDFT equation is solved (linear system) and the vector **b** is obtained, then polarizability and absorption spectrum are calculated.

$$\begin{bmatrix} \mathbf{S} - \mathbf{M}(\omega) \mathbf{b} = \mathbf{d}(\omega) \\ \mathbf{a}_{zz}(\omega) = \int \rho_{z}^{(1)}(\omega, \bar{r}) z d\bar{r} = \sum_{\mu} b_{\mu} \int f_{\mu} z d\bar{r} = \sum_{\mu} b_{\mu} n_{\mu}$$

Accurate polarizability and analysis

It is useful to employ the Modified Sternheimer Approach (MSA) for the response:

$$\begin{bmatrix} H_{KS}^{0} - \varepsilon_{i} - \omega \end{bmatrix} \varphi_{i}^{(1,-)} = -V_{SCF} \varphi_{i}$$
$$\begin{bmatrix} H_{KS}^{0} - \varepsilon_{i} + \omega \end{bmatrix} \varphi_{i}^{(1,+)*} = -V_{SCF} \varphi_{i}$$
$$\rho^{(1)} = 2 \sum_{i}^{occ} \varphi_{i} \left(\varphi_{i}^{(1,-)} + \varphi_{i}^{(1,+)*} \right)$$

These equations are convenient to be represented in the basis of virtual KS orbitals:

$$\begin{bmatrix} \varepsilon_{a} - \varepsilon_{i} - \omega \end{bmatrix} c_{i}^{a-} = -\langle \varphi_{a} | V_{SCF} | \varphi_{i} \rangle$$
$$\begin{bmatrix} \varepsilon_{a} - \varepsilon_{i} + \omega \end{bmatrix} c_{i}^{a+*} = -\langle \varphi_{a} | V_{SCF} | \varphi_{i} \rangle$$

Accurate polarizability and analysis

So actually the polarizability (and the spectrum) are calculated by:

$$\alpha_{zz}(\omega) = 2\sum_{i}^{occ} \sum_{a}^{virt} \langle \varphi_{i} | z | \varphi_{a} \rangle (c_{i}^{a-} + c_{i}^{a+*}) = \sum_{i}^{occ} \sum_{a}^{virt} \langle \varphi_{i} | z | \varphi_{a} \rangle P_{i}^{a}$$
With:
$$P_{i}^{a} = s_{k} (\omega) \left[\langle \varphi_{i} | z | \varphi_{a} \rangle + \sum_{\mu\tau}^{fit} (A^{k})_{ia,\mu}^{+} L_{\mu\tau} b_{\tau} \right]$$

In practice:

- from the imaginary part of α the absorption spectrum is obtained

- from imaginary part of P_i^a the analysis in terms of one-electron excited configurations and Transition Contribution Map (TCM) is obtained [Sami Malola, Lauri Lehtovaara, Jussi Enkovaara and Hannu Häkkinen, ACS Nano 7 10263 (2013).]

Validation of the method, comparison with ADF

H₂ molecule, electric field polarization along the bond (Z)

DZ basis set, LB94 XC, the discrete lines of ADF convoluted by Lorentzian functions with Half Width Half Maximum (HWHM) $\eta = \omega_i = 0.3$ eV, original fitting: 39 functions!



Validation of the method, Na₂



Na₂ molecule, **E** polarization along (Z) and perpendicular (X) to the bond.

DZP basis set, LB94 XC, Lorentzian (HWHM) $\eta = \omega_i = 0.15$ eV

Fitting: original set (14s 7p 6d 2f 1g) for Na (88 functions), reduced to (7s 5p) only 22 functions!



Validation of the method, Au₂



 Au_2 molecule, **E** polarization along (Z) and perpendicular (X) to the bond.

Scalar Relativistic ZORA, DZ basis set, LB94 XC, Lorentzian (HWHM) $\eta = \omega_i = 0.30$ eV

Fitting: original set (25s 15p 12d 8f 7g) for Au (249 functions), reduced to (5s 4p 4d 1f) only 44 functions! <u>Max. error: 0.2 eV</u>

Transition	E (eV)	f	assignment
$1\Sigma_u$	3.23	0.157	100% 14 $\sigma_{\rm g}$ (86% 6s 14% 5d _z ²) → 14 $\sigma_{\rm u}$ (78% 6s
$3\Sigma_{\rm u}$	6.21	0.165	78% 13σ _g (85% 5d _z ² 14% 6s) → 14σ _u
$7\Sigma_{\rm u}$	8.50	1.299	$62\% \ 8\pi_{g} \ (100\% \ 5d_{xz}) \rightarrow 9\pi_{u} \ (100\% \ 6p_{x,y})$
			17% 13σ _u (99% 5d _z ²) → 15σ _g (95% 6p _z)

Validation of the method, Au₈₆



-14

-13

-12

 ε_{i} (eV)

-11

-10

-9

Fig. 8

Au₈₆ nanowire, **E** longitudinal polarization along (Z).

Scalar Relativistic ZORA, DZ basis set, LB94 XC, energy cutoff at 7 eV, fitting: as in Au₂, intense plasmon at 2.35 eV

TCM analysis at 2.35 eV:

Strong intraband $6s \rightarrow 6s$ 6p transitions, cutoff at 7 eV justified a posteriori

Induced density analysis:

Simple dipolar shape

Validation of the method, [Au₁₄₇]⁻



 $[Au_{147}]^{-} D_{5d}$ cluster, **E** polarization along C₅ axis (Z).

Scalar Relativistic ZORA, DZ basis set, LB94 XC, energy cutoff at 7 eV, fitting: as in Au₂, weak plasmon at 3.45 eV, accurate transition energy, but the intensity is overestimated

TCM analysis at 3.45 eV:

Strong interband $5d \rightarrow 6s$ 6p transitions, Plasmon is quenched by screening!

cutoff at 7 eV justified a posteriori

Induced density analysis: Simple dipolar shape

Plasmon analysis by scaling factor λ



$$V_{SCF}(\vec{r},\omega) = V_{EXT}(\vec{r},\omega) + \int d\vec{r}' \frac{\rho^{(1)}(\vec{r}',\omega)}{|\vec{r}-\vec{r}'|} + \frac{dV_{XC}^{LDA}(\rho(\vec{r}))}{d\rho(\vec{r})}\rho^{(1)}(\vec{r},\omega)$$

$$\lambda K(r,r') \text{ (kernel)}$$

Scaling method: "Plasmons in molecules" S. Bernadotte F. Evers and C. R. Jacob JPCC 117 (2013) 1863.

Applications: plasmon re-birth $Au_{30}(SX)_{18}$ X = t-Butyl, Phenyl and Phenyl-NO₂

Re-birth with TDDFT in Au23/Au25 clusters: L. Sementa, G. Barcaro, A. Dass, M. Stener, and A. Fortunelli Chem. Comm. 51 (2015) 7935 – 7938.



Going from t-But to PhenylNO2:

-) Red shift
- 2) Enhanced absorption
- 3) Rising of a new structure at 3.5 3.1 2.8 eV!

Further analysis is under consideration

Conclusions:

- •The density-matrix Casida approach is not practical to treat plasmons in big metal clusters, since many roots (lowest eigenvalues) are necessary.
- •A complex polarizability TDDFT algorithm is suggested too treat large systems
- •Implementation of the complex polarizability algorithm is completed in ADF code and in published in JCP:
- O. Baseggio, G. Fronzoni and M. Stener, J. Chem. Phys., 143 (2015) 024106
- •Pros: efficiency, low memory, analysis of the transitions
- •Cons: some approximation (imaginary energy, energy grid), density dependent kernel.
- Applications to large and low symmetric systems, higher energy
- Specific applications: re-birth, big clusters (>1000 metal atoms), chiral clusters.

Core electron excitations (NEXAFS).

- 1. TDDFT extensions to treat core electron excitations
- 2. Illustrative example: calculations of XAS Ti2p excitation spectra in TiCl₄ and relativistic effects
- 3. Choice of XC functional
- 4. When TDDFT (L-edge) and when DFT (K-edge)?
- 5. Adsorbed molecules
- 6. Conclusions

NEXAFS (Near Edge X-ray Absorption spectroscopy)

NEXAFS spectroscopy refers to the **absorption fine structure around the absorption edge** of a specific atomic species in the sample



The fine structure corresponds to transitions of core electrons towards unoccupied valence states electric dipole selection rules require p final states for K edge, s and d for $L_{2,3}$ edges

characterization of electronic structure

DFT: the Kohn-Sham (KS) method

The electron density ρ can be extracted from a system of non-interacting electrons:

$$H_{KS} = -\frac{1}{2} \nabla^2 - \sum_{N} \frac{Z_N}{|\bar{r} - \bar{R}_N|} + \int \frac{\rho(\bar{r}')d\bar{r}'}{|\bar{r} - \bar{r}'|} + V_{XC}[\rho(\bar{r})]$$

$$H_{KS} \varphi_i = \varepsilon_i \varphi_i \quad i = 1, ..., n$$

$$\rho = \sum_{i}^{occ} n_i \varphi_i \varphi_i^* \qquad \text{SCF iterative solution}$$

Excited states are beyond the KS validity!

However, from a pragmatic point of view, the Transition State (TS) method has been proposed by Slater:

SCF with TS Configuration: $(i)^{-\frac{1}{2}}(a)^{+\frac{1}{2}}$ difficult to converge for high virtual orbitals

$$\Delta E_{i \to a} = \varepsilon_{a}^{TS} - \varepsilon_{i}^{TS}$$

$$f_{i \to a} = \frac{2}{3} \Delta E_{i \to a} n_{i} |\langle \varphi_{i} | \bar{r} | \varphi_{a} \rangle|^{2}$$

SCF with "ionic" TS Configuration: $(i)^{-\frac{1}{2}}(a)^{0}$ widely employed, no SCF problem, relaxation included

TDDFT: linear response

The problem is recast to the following eigenvalue equation:

$$\Omega \mathbf{F}_{I} = E_{I}^{2} \mathbf{F}_{I}$$

$$\Omega_{ia\sigma,jb\tau} = \delta_{\sigma\tau} \delta_{ij} \delta_{ab} (\varepsilon_{a} - \varepsilon_{i})^{2} + 2\sqrt{(\varepsilon_{a} - \varepsilon_{i})} K_{ia\sigma,jb\tau} \sqrt{(\varepsilon_{b} - \varepsilon_{j})}$$

$$K_{ij\sigma,kl\tau} = \int d\mathbf{r} \int d\mathbf{r}' \varphi_{i\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}^{ALDA}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \right] \varphi_{k\tau}(\mathbf{r}') \varphi_{l\tau}(\mathbf{r}')$$

ε and φ are the KS eigenvalues and eigenfunctions obtained at the GS configuration (unrelaxed) Common V_{XC} choices do not obey to correct asymptotic -1/r behavior, in TDDFT this feature is important to obtain accurate excitation energies and intensities

Correct asymptotics can be implemented by:

- 1. SIC (orbitals no more orthogonal)
- 2. OEP (computationally demanding)
- **3. LB94 Our choice (model GGA)**

(R. van Leeuwen and E. J. Baerends, PRA 49 (1994) 2421)

Such ADF implementation is, in practice, limited to valence electron excitation

Core electron excitations:

 are at high energy in the spectrum, difficult to be extracted by iterative algorithms (Davidson)

2. coupled with the continuum (standard basis sets (STO) are not suitable)

Extension of the TDDFT method to treat core electron excitations (ADF program)

M. Stener, G. Fronzoni and M de Simone, CPL 373 (2003) 115.

 $\Omega_{ia\sigma,jb au}$

- The pairs *ia* e *jb* span the 1h-1p space
- To limit the run of the indeces *i* and *j* to core orbitals
- >Core excitations become the lowest, are no more coupled with the valence, and Ω matrix is reduced:



Case study: Ti2p excitations in TiCl₄

KS TDDFT $\hat{H}_{KS}\varphi_i = \mathcal{E}_i\varphi_i$ $\mathbf{\Omega}\mathbf{F}_{j} = \boldsymbol{\omega}_{j}^{2}\mathbf{F}_{j}$ $\Delta E_{i \to a} = \varepsilon_a - \varepsilon_i$ $\Delta E = \omega_i$ $f_{i \to a} = \frac{2}{3} \Delta E_{i \to a} n_i \left| \left\langle \varphi_i | \bar{r} | \varphi_a \right\rangle \right|^2$

TDDFT vs KS

Inclusion of configuration mixing effects

➤ Mandatory for an accurate description of excitations of degenerate core orbitals (2p) of transition metals

≻Calculation: discrete lines, convoluted with gaussian functions (FWHM=0.6 eV)

> large absolute errors
(~3 eV)



TiCl₄: T_d point group symmetry



At TDDFT level extradiagonal terms introduce mixing of 1h1p configurations



Title TiCl4 TD-DFT non relativistic Units LENGTH BOHR End

ADF input

Atoms Ti 0. 0. 0. Cl 2.36754 2.36754 2.36754 Cl -2.36754 -2.36754 2.36754 Cl 2.36754 -2.36754 -2.36754 Cl -2.36754 2.36754 -2.36754 End SYMMETRY T(D)

XC

GGA LB94 End

ModifyExcitation UseOccupied T2 2 SubEnd END

Excitation

Davidson & T2 12 SubEnd Onlysing End

Basis

Ti \$ADFRESOURCES/TZP/Ti Cl \$ADFRESOURCES/TZP/Cl End

end input

Ti2p excitations in TiCl₄: relativistic effects

2 KINDS OF RELATIVISTIC EFFECTS:

• SCALAR RELATIVISTIC CORRECTIONS (scalar ZORA TDDFT)

 SPIN-ORBIT COUPLING (two components ZORA TDDFT)

TiCl₄ – RELATIVISTIC APPROACH

SCALAR RELATIVISTIC CORRECTIONS

excitation energies increased (better agreement with experiment)
mandatory for heavy atoms
much important as the core hole is deeper

 BUT the effect on energy differences is almost negligible

SPIN-ORBIT COUPLING

• SPLITTING of Ti 2p orbitals



TiCl₄ – RELATIVISTIC APPROACH



high level complexity in the attribution of excited states;
complex distinction between valence and Rydberg transitions: careful choice of basis set functions!

Physics behind the Ti2p spectrum:

3d crystal field splitting
configuration mixing
Spin-orbit coupling

G. Fronzoni, M. Stener, P. Decleva, F. Wang, T. Ziegler, E. van Lenthe and E. J. Baerends

CPL **416**, 56 - 63 (2005).

Fe(Cp)₂ – covalent nature: LB94 deterioration!



•LB94 - scalar relativistic: poor description of L₃, features too close and wrong intensity distribution.

B3LYP - scalar relativistic: good description. Assignment:
A 2p_z → 3d_{xz} 3d_{yz} C2p_z π*
B 2p_x 2p_y → 3d_{xz} 3d_{yz} C2p_z π*
C 2p_x 2p_y → 3d_{x2-y2} C2p_z π*

Fe(Cp)₂ – B3LYP: scalar relativistic vs spin-orbit



Inclusion of SO coupling changes only slightly the spectrum, SR seems already adequate
The choice of XC functional is much more crucial than

relativistic effects!

Fe(Cp)(Cp-R) – B3LYP SR: a stringent test





Limitation of TDDFT: good for Metal 2p, less accurate for C1s and N1s: metal phtalocyanine

R. De Francesco, M. Stener, and G. Fronzoni, JPCA 116 (2012) 2885.



Limitation of TDDFT: good for Metal 2p, less accurate for C1s and N1s: metal phtalocyanine



NEXAFS spectra of molecules adsorbed on surfaces

great asset of NEXAFS : polarization dependence

if the molecule is oriented the peak intensity depends on the scalar product between **E** vector of the X-ray (linearly polarized for SR) and the transition moment vector

 $I_{if} \propto \left| \left\langle f \left| \mathbf{\epsilon} \cdot \mathbf{r} \right| i \right\rangle \right|^2$ ($\mathbf{\epsilon}$ versor along \mathbf{E})

K-shell transitions : the resonance intensity relative to a specific MOfinal state isThe Search Light Effect

largest if E vector points along the direction of that MO
vanishes if E is perpendicular to the direction of the MO



Angle resolved NEXAFS : ideal technique for probing the orientation of molecules adsorbed on a surface

Computational approach to NEXAFS spectra of adsorbed system

PERIODIC CALCULATIONS

- periodic slab methodology to simulate the surface
- surface reconstruction
- optimization of the adsorbate systems

(Quantum ESPRESSO calculations)

from the periodic structure suitable finite cluster is manually cut out

CLUSTER MODEL FOR SOLID SYSTEM

- Molecular Orbital (MO) scheme
- explicit treatment of core orbitals
- drawbacks: **cluster design**, embedding

Finite size cluster model for solid systems : very efficient and accurate to simulate NEXAFS due to the localized nature of core excitation processes.

NEXAFS SIMULATION Total and polarized spectra

- Core excitation energies and oscillator strengths
 DFT-TS approximation (K-edge transitions)
- TDDFT (L-edge or valence transitions)

C₂H₄ on Si(100) case study: C K-edge

NEXAFS spectra of C₂H₄ on Si(100)

model system for the adsorption of unsaturated organic molecules on semiconductor Si surface

➤ the adsorbtion of C₂H₄ is based on the interaction of the π C=C bond with the Si dimers of the surface



stable di-σ Si-C bonds

G. Fronzoni, G. Balducci, R. De Francesco, M. Romeo, M. Stener, J. Phys. Chem. C, 116 (35) 18910-18919 (2012).

C₂H₄ on Si(100) on top



C₂H₄ on Si(100) bridge

angle-resolved C K-edge 24 x polarization 21 **NEXAFS** ${\sigma^{\ast}}_{CH}$ 18 15 fx10³ 12 9 bridge adsorption **E** ||surface 6 3 21 y polarization σ^{*} 18 15 σ^*_{SiC} 5×10³ 12 9 6 **E** ||surface 3 Si141 z polarization 21 TT σ*_{SiC} 18 15 fx10³ 12 calculated NEXAFS for bridge 9 adsorption do not reproduce all 6 3 the trend of the experimental $E \perp surface$ features with the polarization 292 294 296 298 300 290 excitation energy (eV)

•tilted-facing (8 PDB on Au₄₈ surface cluster)



CONCLUSIONS AND PERSPECTIVES

TDDFT applications to XAS

- 1. Metal L_{2,3} edges, large systems: good compromise (efficiency), relativistic effects (formalism).
- 2. XC **functional**: LB94 (ionic systems) B3LYP (covalent systems, but not efficient).

DFT applications to XAS

1. Metal K-edges, computationally very cheap, good description of relaxation.

Perspective:

- 1. Even larger systems: new TDDFT algorithms (avoid diagonalization)
- 2. **Open-shell** systems: TDDFT is not very well suited

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