Optical properties of nanoalloys: Theory

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Summary

1. **THEORY** - Review of DFT and TDDFT basic theory and equations, with the aim to underline what we get useful from theory!

2. **COMPUTATIONAL** - Some numerical aspects of the implementation in the ADF code, most important computational choices, relativistic effects.

3. **APPLICATIONS** – Optical properties of $\text{Ag}_n\text{Au}_m$ nanoalloys: effects of shape, chemical ordering and compositions, spectra analysis.
ADF program: a) DFT Kohn-Sham (KS) Equations

\[ H_{KS} \varphi_i = \varepsilon_i \varphi_i \quad i = 1, \ldots, n \]

1. LCAO formulation (STO basis set) \( \varphi_i(r) = \sum_k \mu_k(r) C_{ki} \)

2. Numerical integrals \( \langle \varphi_i | O | \varphi_a \rangle \approx \sum_k w_k \varphi_i(r_k) O(r_k) \varphi_a(r_k) \)

3. Density fitting \( \rho = \sum_{i=1}^{occ} n_i \varphi_i \varphi_i^* \approx \bar{\rho} = \sum_n a_n f_n(r') \)

\[ a_n : \min \left\{ \int |\rho - \bar{\rho}|^2 d\mathbf{r} \right\} \]

Auxiliary basis functions
ADF program: available STO basis set

STO (Slater Type Orbital): more physical than GTO (Gaussian)

ADF employs STO for both basis set for wavefunction and auxiliary basis set for density fitting

STO (Slater Type Orbital): more physical than GTO (Gaussian)
SZ: Single Zeta (Minimal Basis) 1 function for each shell (1s, 2p ecc.)
DZ: Double Zeta, 2 functions for each shell
DZP: DZ + polarization: higher angular momentum (es. 3d for C)
TZ Triple Zeta, TZP Triple Zeta + polarization
ET: Even Tempered (very large basis set, dangerous for numerical stability)
ZORA: relativistic basis set
ADF program: b) TDDFT Equations

$$\Omega F_I = E_I^2 F_I$$

Diagonalization of $\Omega$ matrix furnishes discrete excitation energies and intensities

$[\text{Au}_{172}]^{4+}$ Cubic TDDFT
optimized geometry at LDA level

Gaussian broadening

TDDFT results, lowest $n$ eigenvalues
TDDFT equations:

\[ \Omega F_I = E_I^2 F_I \quad \Omega_{ia\sigma, jb\tau} \]

i and j run over \( N_{\text{occ}} \)

a and b run over \( N_{\text{virt}} \)

TDDFT results: \( F_I \) eingenvectors give

1) Intensity (Oscillator Strength \( f \))

2) Allow analysis of excited state in terms of 1h1p excited configurations:

\[
|\Phi_I\rangle = \sum_{a}^{\text{VIRT}} \sum_{i}^{\text{OCC}} c_{i,a}^I |\Psi^a_i\rangle, \quad |\Psi^a_i\rangle = |\chi_1\chi_2\ldots\hat{\chi}_a\ldots\chi_N\rangle
\]
1 transition ⇒ many excited config.

<table>
<thead>
<tr>
<th>Excitation</th>
<th>$E_{\text{exc}}$ (eV)</th>
<th>$f$</th>
<th>Excited State Composition$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>162$E_u$ (D)</td>
<td>2.50</td>
<td>0.0289</td>
<td>35% $98b_{1g}$ (5d) $\rightarrow$ 188$e_u$ (6s 41%, 6p 22%, 5d 1%)</td>
</tr>
<tr>
<td></td>
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<td>18% $119a_{1g}$ (6s 33%, 6p 21%, 5d 19%) $\rightarrow$ 191$e_u$ (6s 47%, 6p 19%)</td>
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<td></td>
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<td>9% $156e_g$ (6s 41%, 6p 21%, 5d 6%) $\rightarrow$ 107$a_{2u}$ (6s 47%, 6p 37%, 5d 1%)</td>
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<td></td>
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<td>8% $99b_{1g}$ (6s 26%, 6p 5%, 5d 49%) $\rightarrow$ 189$e_u$ (6s 38%, 6p 24%, 5d 4%)</td>
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<td>5% $71a_{2g}$ (6s 42%, 6p 27%, 5d 17%) $\rightarrow$ 194$e_u$ (6s 43%, 6p 24%)</td>
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<td></td>
<td>4% $100b_{1g}$ (6s 34%, 6p 26%, 5d 20%) $\rightarrow$ 191$e_u$ (6s 47%, 6p 19%)</td>
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<td></td>
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<td></td>
<td>3% $83b_{2u}$ (6s 31%, 6p 13%, 5d 41%) $\rightarrow$ 158$e_g$ (6s 44%, 6p 29%)</td>
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<td></td>
<td>3% $183e_u$ (6s 31%, 6p 5%, 5d 30%) $\rightarrow$ 72$a_{2g}$ (6s 45%, 6p 35%, 5d 10%)</td>
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<td>23% $186e_u$ (6s 40%, 6p 14%, 5d 14%) $\rightarrow$ 89$b_{2g}$ (6s 48%, 6p 35%, 5d 2%)</td>
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<td>21% $121a_{1g}$ (6s 45%, 6p 28%, 5d 7%) $\rightarrow$ 196$e_u$ (6s 14%, 6p 67%)</td>
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<td>18% $84b_{2g}$ (6s 36%, 6p 21%, 5d 28%) $\rightarrow$ 162$e_g$ (6s 47%, 6p 34%)</td>
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<td>4% $185e_u$ (6s 35%, 6p 15%, 5d 10%) $\rightarrow$ 105$b_{1g}$ (6s 50%, 6p 28%, 5d 3%)</td>
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<tr>
<td></td>
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<td></td>
<td>3% $155e_g$ (6s 36%, 6p 19%, 5d 15%) $\rightarrow$ 87$e_u$ (6s 50%, 6p 36%, 5d 3%)</td>
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<td>35% $187e_u$ (6s 33%, 6p 29%, 5d 3%) $\rightarrow$ 128$a_{1g}$ (6s 54%, 6p 33%, 5d 1%)</td>
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<td></td>
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<td></td>
<td>16% $182e_u$ (5d) $\rightarrow$ 72$a_{2g}$ (6s 45%, 6p 35%, 5d 10%)</td>
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<td></td>
<td>7% $95b_{1g}$ (6s 3%, 5d 79%) $\rightarrow$ 189$e_u$ (6s 38%, 6p 24%, 5d 4%)</td>
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<td></td>
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<td></td>
<td>7% $82b_{2u}$ (6s 1%, 5d 90%) $\rightarrow$ 158$e_g$ (6s 44%, 6p 29%)</td>
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<td></td>
<td>6% $115a_{1g}$ (6s 3%, 5d 80%) $\rightarrow$ 189$e_u$ (6s 38%, 6p 24%, 5d 4%)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>3% $154e_g$ (6s 36%, 6p 12%, 5d 20%) $\rightarrow$ 73$b_{1u}$ (6s 48%, 6p 38%, 5d 1%)</td>
</tr>
</tbody>
</table>

$^a$ Excitation energy ($E_{\text{exc}}$), oscillator strength ($f$), and excited-state composition in terms of monoexcited configurations are reported. $^b$ The main contributions to the initial and final orbitals are reported in parenthesis.
Efficient numerical algorithms (ADF) to solve:

$$\Omega F_I = E_I^2 F_I$$

Computational effort: storage $N_{occ}^2 \times N_{virt}^2$  
CPU $N_{occ}^3 \times N_{virt}^3$

$$\Omega \text{ia} \sigma, \text{jb} \tau$$

i and j run over $N_{occ}$

a and b run over $N_{virt}$

- Davidson iterative diagonalization: $n$ lowest eigenvalues
- Efficient management of matrix-vector $P_{out} = K \cdot P_{in}$ product
  - $K$ matrix is not calculated and is not stored!

$$[P_{out}]_{ia} = \sum_{jb} K_{ia,jb} [P_{in}]_{jb}$$

$N^4$ scaling!
\[
[p_{\text{out}}]_{ia} = \int dr \int dr' \phi_{i\sigma}(r) \phi_{a\sigma}(r) \left[ \frac{1}{|r - r'|} + f_{xc}^{\text{ALDA}}(r) \delta(r - r') \right] \sum_{jb} \varphi_{j\tau}(r') \varphi_{b\tau}(r') [p_{\text{in}}]_{jb}
\]

Density fitting procedure:

\[
\rho^{(1)}(1) \equiv \tilde{\rho}^{(1)} = \sum_{n} a_n f_n(r')
\]

\[f_n\] Auxiliary basis functions for the density

\[a_n\]: fitting coefficients such that: \[
\min \left\{ \int |\rho - \tilde{\rho}|^2 \, dr \right\}
\]
$$[p_{\text{out}}]_{ia} = \langle \varphi_i | v_{\text{ind}} | \varphi_a \rangle \cong \sum_k w_k \varphi_i (r_k) v_{\text{ind}} (r_k) \varphi_a (r_k)$$

Numerical integration (Gaussian weights and points)

$$v_{\text{ind}} (r) = \int \left[ \frac{1}{|r - r'|} + f_{xc}^{ALDA} (r) \delta (r - r') \right] \sum_n a_n f_n (r') dr'$$

A favourable N³ scaling is gained, run over three index: i a n
TDDFT spectra and numerical stability issues

- Davidson iterative diagonalization: $n$ roots (lowest eigenvalues)
- Stable up to $n = 350$, for $n = 400$ numerical instability shows up
- Numerical stability: improved by tight SCF convergence criterion: $|\text{FP-PF}| < 10^{-8}$
$Au_6^{4+}$: TEST

(BASIS SET)

Computational details:

- negligible difference
- computational economy

DZ TDDFT with DZ optimized geometry

- 100 roots
- TDDFT LB94 XC potential
- geo opt VWN XC potential
- All Electron basis set
Au_6^{4+}: TEST
(FROZEN CORE)

- negligible differences
- Computational saving around 53% from AE to FC4f

Core orbital frozen up to Au 4f

Computational details:
- 100 roots
- LB94 XC potential
- TZP basis set
\( Au_{6}^{4+} \): TEST

(EXCHANGE CORRELATION POTENTIAL)

- SAOP is usually considered more accurate than LB94
- negligible differences
- LB94 is chosen, since SAOP does not support FC!

**Computational details:**
- 100 roots
- AE TZP basis set
Relativistic effects in Au compounds

Large relativistic contraction of the Au 6s shell

P. Pyykko and J. P. Desclaux, Acc. Chem. Res. 12 (1979) 276

Strong relativistic narrowing of the 5d – 6s gap

Relativistic effects: transformation

- in ADF: ZORA (Zero Order Regular Approximation)

\[ H^{ZORA} = V + \left( \sigma \cdot p \right) \frac{c^2}{2mc^2 - V} (\sigma \cdot p) \]

- ZORA: well behaved over the nuclei
- Two components: Spin-Orbit (SO) coupling included
- If SO is neglected: Scalar Relativistic (SR)
Gold bimetallic clusters: $M@\text{Au}_{12}$

- Icosahedral bimetallic gold clusters: Au cage with encapsulated heteroatom

- First theoretically predicted, then synthesized and characterized by spectroscopy

- Analysis of the spin orbit coupling on optical spectra
WAu$_{12}$: scalar relativistic electronic structure


Spin-orbit interaction in molecules

- Similar to atoms: lower degeneracy
- States classified according to Double Groups
- Example: $I_h$

<table>
<thead>
<tr>
<th>$I_h$</th>
<th>$I_h^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>$E_{1g}(1/2)$</td>
</tr>
<tr>
<td>$T_{1g}$</td>
<td>$E_{1g}(1/2) + G_g(3/2)$</td>
</tr>
<tr>
<td>$T_{2g}$</td>
<td>$I_g(5/2)$</td>
</tr>
<tr>
<td>$G_g$</td>
<td>$E_{2g}(7/2) + I_g(5/2)$</td>
</tr>
<tr>
<td>$H_g$</td>
<td>$G_g(3/2) + I_g(5/2)$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>$E_{1u}(1/2)$</td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td>$E_{1u}(1/2) + G_u(3/2)$</td>
</tr>
<tr>
<td>$T_{2u}$</td>
<td>$I_u(5/2)$</td>
</tr>
<tr>
<td>$G_u$</td>
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</tr>
<tr>
<td>$H_u$</td>
<td>$G_u(3/2) + I_u(5/2)$</td>
</tr>
</tbody>
</table>
**WAu$_{12}$: spin-orbit electronic structure**

**Exp: photodetachment of WAu$_{12}^-$**

TDDFT electronic excitations (valence)

WAu$_{12}$ SR
ZORA TZ2P
LB94

Excitation energy (eV)
WAu$_{12}$: spin-orbit effect over spectrum

- SO low energy
  - red shift
  - intensity reduction

SO above 5 eV: strong configuration remixing
MoAu$_{12}$ vs. WAu$_{12}$

The diagram compares the electronic structures of MoAu$_{12}$ and WAu$_{12}$, focusing on the energy levels and orbitals. The labels $\varepsilon_{KS}$ indicate the Kohn-Sham energy levels, with $5s$, $4d$, $5p$, $5t_2u$, $5a_g$, $6t_{1u}$, $7t_{1u}$, and $7h_g$ orbitals highlighted. The differences between the two structures are emphasized, particularly in the $5a_g$, $5t_{2u}$, and $8h_g$ (LUMO) orbitals.
MoAu$_{12}$: spin-orbit effect over spectrum

SO: low energy:
- more lines
- intensity spread
- not simply red shift

SO:
- strong remixing, the nature of lines change
$\text{WAu}_{12}$: Scalar Relativistic vs Spin-Orbit TDDFT

1. Discrete lines are very sensitive to SO
2. Broadened spectrum is much less sensitive to SO
3. When “density” of lines is high SO can be reasonably neglected
4. SO inclusion is computationally very demanding
Comments:

1. Technical: ADF employs STO, FC DZ is adequate, density fitting is efficient, TDDFT diagonalization is optimized.

2. Computational: ADF code is fully parallelized via standard MPI, very good performance on IBM SP6 supercomputer at CINECA (up to 128 cpu for SCF, 64 cpu for TDDFT)

3. Careful choices: numerical parameters (SCF convergence and number of roots to extract in TDDFT) and proper relativistic scheme for gold or other heavy elements.

4. Outlook: improve the present algorithm to enlarge the energy range without numerical stability problems