Electronic and Optical Excitations in Noble Metal Clusters and Si Nanoshells

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Outline

• Silver and Gold Clusters (Structures, Polarizabilities)
• Optical Properties within TDLDA
• TDLDA vs GWBSE
• Quasiparticle Gaps in Si Nanoshells
• Exciton Coulomb Energies in Si Nanoshells

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Due to their intriguing physical/chemical properties (of particular relevance in catalysis, optoelectronics, and nanophotonics applications), noble metal (Cu, Ag, Au) clusters and nanoparticles, currently a topic of technological and fundamental interest.

Electronic configuration: \( nd^{10}(n+1)s^1p^0 \). Though completely filled, molecular orbitals associated with \( d \) electrons have close energetic proximity to and spatial overlap with \( sp \) states, giving rise to important structural, electronic, and optical properties.

One particular area, posing a computational challenge is related to accurate modeling of optical properties of noble metal clusters.

As an example, measured spectra for Ag\(_n\) \((n < 40)\) embedded in rare-gas matrices have been available since the early 1990s, but direct comparisons with \textit{ab initio} modeling techniques have lagged significantly.

Recent results from extensive searches yielded ground state and low-energy isomers (up to \( n = 20 \)) Use them to compute absorption spectra for comparison with experiment and to investigate the role of \( d \) electrons on the spectra.

Motivation (Computational Challenge)

- Two of the state-of-the-art computational techniques for calculating optical excitations in materials: Time-dependent linear response theory using DFT (TDDFT) and adiabatic LDA (TDLDA), and Green’s function many-body perturbation methods such as GW+Bethe-Salpeter Equation (GWBSE).

- Computational demand for TDLDA (2-point kernel) considerably smaller compared to GWBSE (4-point kernel). GWBSE, however, gives much more accurate excitation energies in extended systems (excitonic effects).

- The two methods mostly applied to $sp$-bonded clusters with considerable success. Systematic application and comparison of TDLDA and GWBSE in finite systems with tightly bound $d$ electrons to investigate the role of $d$ electrons in optical excitations.
Calculated Ground State Structures, $\text{Au}_n$ ($n = 3$-$14,20$)

- For Au clusters, shape transition from 2D to 3D at $n = 14$ (Ag clusters at $n = 7$).
- Significant drop in the static polarizability correlates with this shape transition.
Calculated Ground State Structures, Agₙ (n = 10-20)

- Many low-energy isomers at a given size.
- Close-packed structures, high coordination numbers.
- Shape evolution (from layered prolate to oblate to spherical).
Polarizability:
$$\delta \rho(r, E) = \int \text{d}r' \, \Pi(r, r', E) V_{\text{ext}}(r', E)$$

Expansion in poles:
$$\Pi(r, r', E) = \sum_m \frac{\rho^*_m(r) \rho_m(r')}{E - \omega_m} - \sum_m \frac{\rho_m(r) \rho^*_m(r')}{E + \omega_m}$$

Eigenvalue problem:
$$\sum_{v'c'} \left[ (\varepsilon_c - \varepsilon_{v'})^2 \delta_{cc'} \delta_{vv'} + 2 \sqrt{\varepsilon_c - \varepsilon_{v'}} K_{vc,v'c'}^{\text{LDA}} \sqrt{\varepsilon_{c'} - \varepsilon_{v'}} \right] F_{v'c'}^{m} = \omega_m^2 F_{vc}^{m}$$

$$\rho_m(r) = \sum_{vc} \frac{\varepsilon_c - \varepsilon_{v'}}{\omega_m} F_{vc}^{m} u_v(r) u_c^*(r)$$

$$K_{vc,v'c'}^{\text{LDA}} \equiv \int \text{d}r \text{d}r' u_v(r) u_{v'}^*(r) K^{\text{LDA}}(r, r') u_{v'}(r') u_c(r)$$

$$K^{\text{LDA}} = V_{\text{Coul}} + f_{xc}$$

$$f_{xc} = \frac{\delta V_{xc}}{\delta \rho} \bigg|_{\text{LDA}}$$

Frequency representation: M. Casida (1995)
Comparison with Experiment

**Ag\textsubscript{18}**

Iso3

Iso2

Iso1

Experiment

**Ag\textsubscript{19}**

Iso3

Iso2

Iso1

Experiment

**Ag\textsubscript{20}**

Iso3

Iso2

Iso1

Experiment

Absorption Cross Section (Arb. Units)

Energy (eV)
Integrated Oscillator Strengths

- Screening by $d$ electrons quenches the OS in noble metal clusters.
- Integrated OS (below 6 eV) per $s$ electron significantly below 1.
- Generally good agreement with experimental data.
- $d$ electron screening more enhanced in $Au_n$ clusters.
To understand the effect of $d$ states on the OS more quantitatively, calculated the $%d$ character for transitions below $E_{cut} = 6 \text{ eV}$

$$%d = \frac{\sum_{n} f_n \sum_{vc} |F_{vc}^n|^2 |\langle d | \phi_v \rangle|^2}{\sum_{n} f_n \sum_{\Omega_n < E_{cut}} |F_{vc}^n|^2 |\langle d | \phi_v \rangle|^2}$$

- $d$ contribution below 6 eV increases almost monotonically up to $n \sim 13$ with cluster size.

- For larger clusters, most of the low energy transitions (about 70%) originate from $d$ levels.

- $d$ character in $\text{Au}_n$ larger than in $\text{Ag}_n$ due to enhanced $sd$ hybridization.
Comparison with Mie-Gans Theory

\[ \sigma_{abs}(\omega) = \frac{4 \pi \omega ABC}{9c} \sum_{i=1}^{3} \frac{\varepsilon_2(\omega)}{[G_i(\varepsilon_1(\omega) - \varepsilon_m) + \varepsilon_m]^2 + [G_i\varepsilon_2(\omega)]^2} \]

Prolate

\[ A = B < C \]
\[ G_1 = G_2 > G_3 \]

Sphere

\[ A = B = C \]
\[ G_1 = G_2 = G_3 = 1/3 \]

Oblate

\[ A = B > C \]
\[ G_1 = G_2 < G_3 \]
Calculated normalized moments of inertia

$$\langle I_i \rangle = \frac{3I_i}{I_1 + I_2 + I_3}$$

to determine the shape of clusters

\begin{align*}
(0.45, 0.35, 0.2) & \quad \text{Ag}_{12} \\
(0.6, 0.2, 0.2) & \quad \text{Ag}_{14} \\
(0.4, 0.3, 0.3) & \quad \text{Ag}_{19} \\
(1/3, 1/3, 1/3) & \quad \text{Ag}_{20}
\end{align*}
Electronic Excitations: GW theory

$$\Sigma = i \, GW\Gamma_{\text{LDA}}$$

$$W = V_{\text{coul}} + V_{\text{coul}}PW$$
$$= V_{\text{coul}} + V_{\text{coul}}\Pi_{\text{LDA}}V_{\text{coul}}$$

- Electron screening from time-dependent DFT-LDA.
- Explicit energy integration.
- LDA vertex included in Self-Energy.
- Results directly comparable to photoelectron spectroscopy.

Bethe-Salpeter Equation

Many-body neutral excitations:

$$|S\rangle = \sum_{vc} A_{vc}^S |vc\rangle + \text{corrections}$$

Eigenvalue problem:

$$(\varepsilon_c^{qp} - \varepsilon_v^{qp}) A_{cv}^S + \sum_{c'v'} \langle vc|K^{BSE}|c'v'\rangle A_{c'v'}^S = \Omega^S A_{cv}^S$$

$$K^{BSE} = -i [V + W + V \Pi f_{xc}]$$
Electronic Excitations (IP and EA) Comparison with ΔSCF and Experiment

- Within ΔSCF, \( IP = E(n-1) - E(n) \) and \( EA = E(n) - E(n+1) \).
- Within GW, \( IP = -HOMO \) and \( EA = -LUMO \).
- Generally quite good agreement of GW results with experiment (especially Ag and Ag\(_2\)). Agreement not so good with ΔSCF.
- \( \Sigma \) very sensitive to the number of virtual orbitals. Convergence accelerated by including a static remainder (estimate the numerical error by truncating the sum over virtual orbitals at the level of COHSEX).

<table>
<thead>
<tr>
<th></th>
<th>IP (eV)</th>
<th>EA (eV)</th>
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<tbody>
<tr>
<td></td>
<td>NS</td>
<td>ST</td>
</tr>
<tr>
<td>Ag</td>
<td>7.12</td>
<td>7.53</td>
</tr>
<tr>
<td>Ag(_2)</td>
<td>6.27</td>
<td>7.54</td>
</tr>
</tbody>
</table>

(700 orbitals included in \( \Sigma \))
Electronic Excitations: Case of Ag⁺

- Observed good agreement at this level of theory due to the fact that HOMO and LUMO of Agₙ (n≤8) have almost entirely sp character (little or no d character). For example, in Ag₂, HOMO is 92% sp, 8% d, LUMO is 98% sp, and 2% d.

- Singly ionized Ag atom, Ag⁺, is a good test case for a system with large (entirely) d character in HOMO (and purely s character in LUMO!). IP of Ag⁺ is the double IP of Ag, which is experimentally available. EA of Ag⁺ is the IP of neutral Ag!

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<tr>
<td></td>
<td>NS</td>
<td>ST</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>16.64</td>
<td>18.92</td>
</tr>
</tbody>
</table>

- 2.6 eV underestimate of IP in Ag⁺ (4d level) due to core-valence separation in the pseudopotential construction (standard 4d¹⁰5s¹⁵p⁰ reference). Though 4s and 4p levels are ~80 and 50 eV below the 4d level, due to their strong spatial overlap with 4d levels, exchange and correlation among 4s, 4p, and 4d electrons are not described properly by a Slater type exchange-correlation [Rohlfing et al. PRL 75, (1995)]

- Remedy: Create semi-core pseudopotentials by keeping 4s and 4p levels in the valence. Use the reference 4s²4p⁶4d¹⁰ with sp core radii ~ 1.1 a.u. Very deep pseudopotentials. Use ħ = 0.2 a.u (limited tests)

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<thead>
<tr>
<th></th>
<th>NS</th>
<th>ST</th>
<th>Exp</th>
<th>NS</th>
<th>ST</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺(semicore)</td>
<td>20.67</td>
<td>21.85</td>
<td>21.50</td>
<td>7.04</td>
<td>7.30</td>
<td>7.57</td>
</tr>
</tbody>
</table>
Optical Excitations within GWBSE and TDDFT: Ag and Ag$_2$

### Ag

<table>
<thead>
<tr>
<th>Transition</th>
<th>TDLDA</th>
<th>GWBSE</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>5s → 5p</td>
<td>4.09</td>
<td>3.68</td>
<td>3.74</td>
</tr>
<tr>
<td>5s → 6p</td>
<td>5.44</td>
<td>6.05</td>
<td>6.01</td>
</tr>
</tbody>
</table>

### Ag$_2$

<table>
<thead>
<tr>
<th>Transition</th>
<th>TDLDA</th>
<th>GWBSE</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A - X</td>
<td>3.11</td>
<td>2.54</td>
<td>2.85</td>
</tr>
<tr>
<td>B - X</td>
<td>3.96</td>
<td>3.99</td>
<td>4.44</td>
</tr>
<tr>
<td>C - X</td>
<td>4.75</td>
<td>4.27</td>
<td>4.67</td>
</tr>
</tbody>
</table>

GWBSE clearly performs well for Ag atom. In Ag$_2$, agreement with experiment not as good. TDLDA in slightly better agreement (perhaps).
For $n > 2$, agreement between TDLDA and GWBSE very poor. At low energies, OS from GWBSE quenched significantly, above 5 eV, high OS transitions.

TDLDA has clearly better agreement with experimental data (esp. $n = 5 - 8$).

Exchange-correlation effects involving $4d$ orbitals and strong non-locality of the BSE kernel are the main reasons for this behavior.

Even a small mixture of $d$ character results in significant quenching and red-shifting of the predicted transitions at the GWBSE level, as best illustrated for the case of Ag$_2$. 
The increase in $d$ character of optical excitations at the GWBSE level accompanied by a redshift and quenching of OS compared to TDLDA.
Thought experiment: “Remove” the $d$ electrons

When $d$ electrons are removed, very good agreement between TDLDA and GWBSE.

$d : \nu = 1 - 10 \quad s : \nu = 11$ (HOMO)

Diagonalize this only
How do electronic and optical properties of Si nanostructures evolve in going from quantum dots to “nanoshells”?

Recent interest in optical properties of metallic (typically Au or Ag) shells over a dielectric core.

Dielectric and optical properties of Si nanostructures are, in many ways, reminiscent of metallic nanoparticles, with the added bonus that Si is much easier to work with!

Just got curious about effects of confinement vs geometry in Si nanostructures.
• Single-band effective mass approximation (EMA) for impenetrable nanoshells

\[ V(r) = 0 \quad \text{if} \quad R_1 < r < R_2 \quad \text{and} \quad \infty \quad \text{elsewhere} \]

• The \( l = m = 0 \) eigen-functions are

\[
\psi(\vec{r}) = \frac{1}{\sqrt{2\pi(R_2 - R_1)}} \frac{\sin\left(\frac{\pi(R_2 - r)}{R_2 - R_1}\right)}{r} \quad \text{for} \quad R_1 < r < R_2
\]

• The energy spectrum \( E \) depends only on the thickness \( t = R_2 - R_1 \) implying \( E_{\text{gap}}(R_1, R_2) = E_{\text{gap}}(t) \sim t^{-2} \)

• To investigate the real \( R_1, R_2 \) dependence of Si nanoshells, considered

  - Nanoshells of fixed \( R_1 \) (changing \( R_2 \))
  - Nanoshells of fixed \( R_2 \) (changing \( R_1 \) from 0 to \( R_{1,max} \))

  Both the inner and outer surfaces were passivated by H.
• *Ab initio* real-space calculations (PARSEC) with TM pseudopotentials using a grid spacing $h = 0.6$ a.u. and boundary radii from 36 a.u. to 50 a.u.

• Quasiparticle gaps calculated with $\Delta$SCF method by computing ionization potentials (IP) and electron affinities (EA) of $n$-electron nanoshells:

$$ IP = E(n-1) - E(n) \quad EA = E(n) - E(n+1) \quad E_{\text{gap}} = IP - EA $$

• $GW$ calculations on Si quantum dots suggest that the $\Delta$SCF method is accurate for EA, while IPs should be shifted upward by $\sim 0.5$ eV. [Tiago and Chelikowsky, PRB 73, 205334 (2006)]

• Performed $GW_f$ calculations on the smallest nanoshell $\text{Si}_{156}\text{H}_{184}$ ($R_1 = 5$ Å, $R_2 = 10.3$ Å) with $h = 0.8$ a.u., 750 orbitals (404 occupied). Self-energy computed with a vertex correction using the TDLDA polarizability.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta$SCF</th>
<th>$GW_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP (eV)</td>
<td>6.65</td>
<td>7.10</td>
</tr>
<tr>
<td>EA (eV)</td>
<td>2.62</td>
<td>2.56</td>
</tr>
</tbody>
</table>

Similar trend for Si nanoshells
Size Dependence of Quasiparticle Gaps

\[ \Delta E_{qp}(t) \propto t^{-1} \]

\[ \bar{E}_{qp}(t) \propto t^{-1/4} \]

- \( R_1 = 5 \text{ A} \)
- \( R_1 = 6.9 \text{ A} \)
- \( R_1 = 8.4 \text{ A} \)
- \( R_2 = 14.2 \text{ A} \)
- \( R_2 = 16.2 \text{ A} \)
Exciton Coulomb Energies for Q. Dots

\[ E_{\text{Coul}}(\varepsilon = 1) = \int \int \left| \psi_e(\vec{r}_1) \right|^2 \left| \psi_h(\vec{r}_2) \right|^2 \frac{d^3\vec{r}_1 d^3\vec{r}_2}{|\vec{r}_1 - \vec{r}_2|} \]

\[ E_{\text{Coul}}^{\text{EMA}} = \frac{1.786}{R} \]

\[ E_{\text{Coul}}^{\text{Ab Initio}} \propto R^{-0.7} \]
The unscreened Coulomb energy in the EMA with envelope wavefunctions vanishing at the inner/outer radii can be evaluated.

\[
E_{\text{Coul}} = \frac{2}{\pi t} \int_0^\pi dx \frac{\sin^2 x(2x - \sin 2x)}{x + \frac{\pi R_1}{t}}
\]

Even at the EMA level, \( E_{\text{Coul}} \) depends on both \( R_1 \) and \( R_2 \)

\[
R_1 \to 0 \quad E_{\text{Coul}} = \frac{1.786}{t}
\]
Exciton Coulomb Energies at Fixed $R_1$

- Both EMA and ab initio results find an inverse correlation of $E_{\text{Coul}}$ with nanoshell thickness at fixed $R_1$ (Quantum confinement).
- Ab initio results significantly reduced in magnitude wrt EMA predictions.
Exciton Coulomb Energies at Fixed $R_2$

$E_{\text{Coul}}$ decreases as the nanoshell becomes more confining!
Confinement versus Geometry

In going from the quantum dot to the nanoshell

- The $e$ or $h$ “wavefunction amplitude” increases (confinement)
- The average distance between $e$ and $h$ increases (less Coulomb interaction)

For a spherical shell, the distance “wins” less $E_{Coul}$

Easiest way to see this: Assume a somewhat unrealistic “constant” wavefunction for the $e$ or the $h$. $E_{Coul}$ can be calculated analytically

$$\psi(\vec{r}) = V^{-1/2} \quad \Rightarrow \quad E_{Coul}(R_1 \neq 0, R_2) < E_{Coul}(R_1 = 0, R_2)$$
Topology versus Geometry

The nanoshell is neither convex (geometrical) nor simple-connected (topological).

Which is more important?

How about the case of a nano-star or a nano-crescent-moon?
Simple-connected yet non-convex
Summary

• Time-dependent density functional theory (TDDFT) within the local density approximation (TDLDA) generally yields good agreement with existing experimental studies on absorption spectra of noble Ag$_n$ ($n = 1 - 20$) clusters.

• $d$ electrons affect optical spectra in two distinct ways: (i) quenching the oscillator strengths by screening the $s$ electrons, and (ii) by getting directly involved in low-energy optical excitations. These effects enhance in going from Ag to Au to Cu due to increased $spd$ hybridization.

• Many-body approach based on the solution of the Bethe-Salpeter equation for the two-particle Green’s function (GWBSE method) with standard (non-semicore) pseudopotentials has serious deficiencies (over-screening $s$ electrons, strong non-locality) compared to TDDFT.

• The size dependence of electronic excitations in a Si nanoshell can be explained quite well, to a first approximation, by assuming it to be a metallic macroscopic object (within classical EM). Exciton Coulomb energies, on the other hand, have counter-intuitive (in the “nano” quantum-confinement-sense) size dependencies.

• Nano is not just “small”. Geometry (or topology) is just as important as “small”