Precise Plasmonic Spectra of Gold and Silver Clusters Using the DFT+U Method

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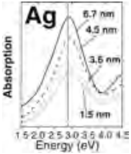
European Theoretical Spectroscopy Facility, www.etsf.eu

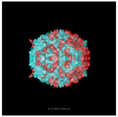
Note: animations disabled

Outline

Plan

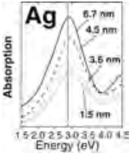
Surface Plasmons in Metal Clusters

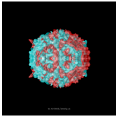


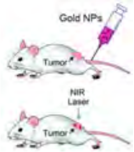


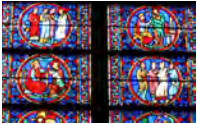
Surface Plasmons in Metal Clusters

Applications









- Manyfold applications
  - Biomolecule labeling and sensing
  - Cancer therapy / Medical imaging
  - Surface-enhanced Raman Scattering
  - Nanoplasmonics
  - Antibacteriel effects
  - Photo-catalysis
  - Solar cells, ... etc. etc.

Surface Plasmons in Metal Clusters

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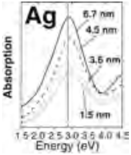

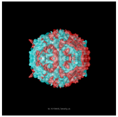

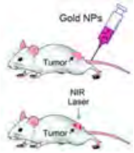

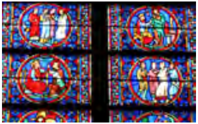

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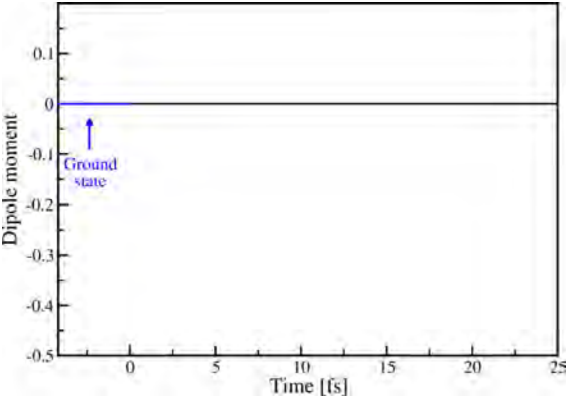
Theoretical understanding?
Tune plasmon energy
Materials ??? (Cost!)

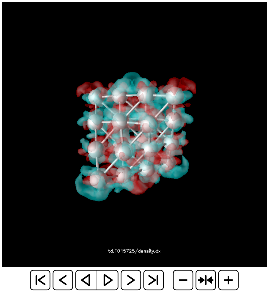
Help understand experiment / engineer desired propt's!

Plan

The Method: Time-Evolution Formalism of TD-DFT



- Octopus code
- Norm-cons. pseudo-pot.
- For optics: PBE, PBE+U, ...



Yabana & Bertsch, PRB **54**, 4484 (1996).

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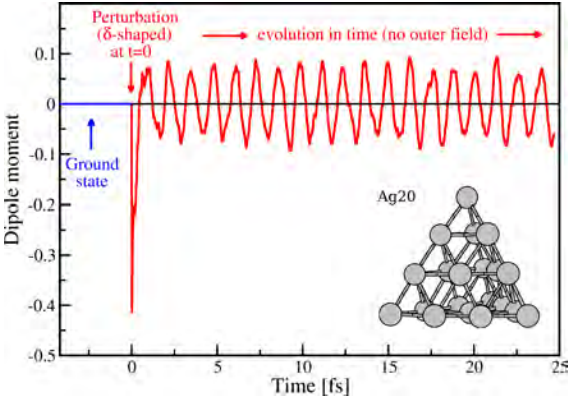

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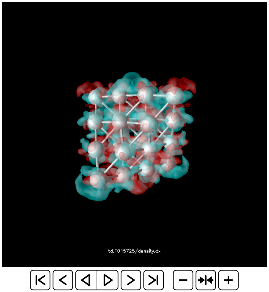

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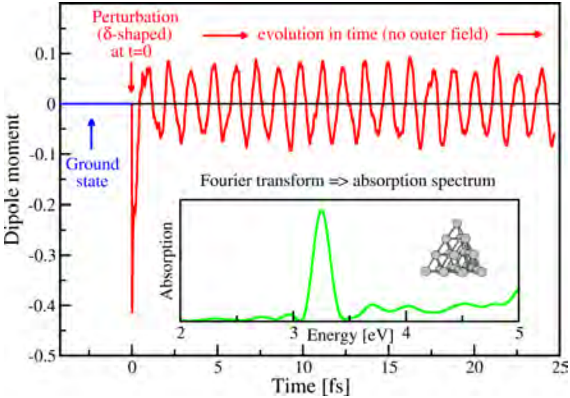

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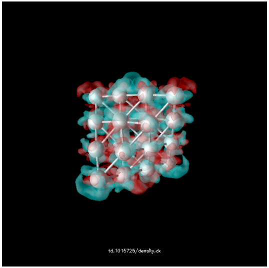

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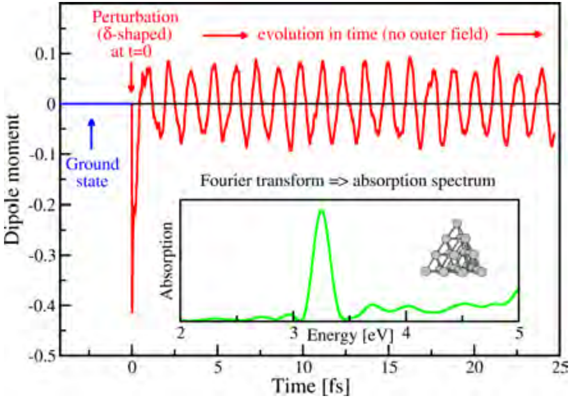

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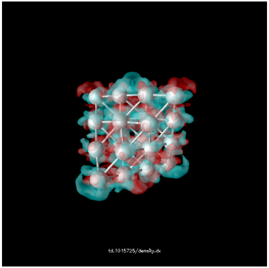

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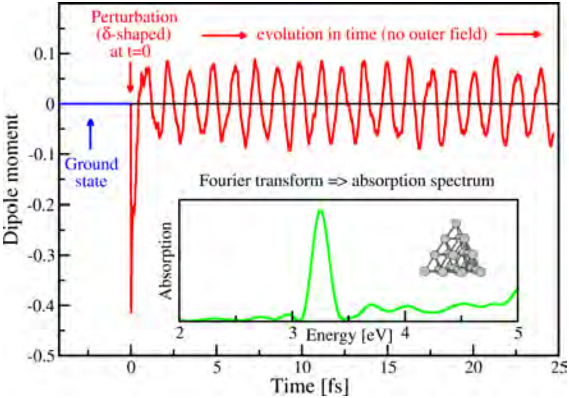

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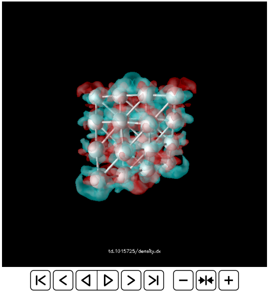

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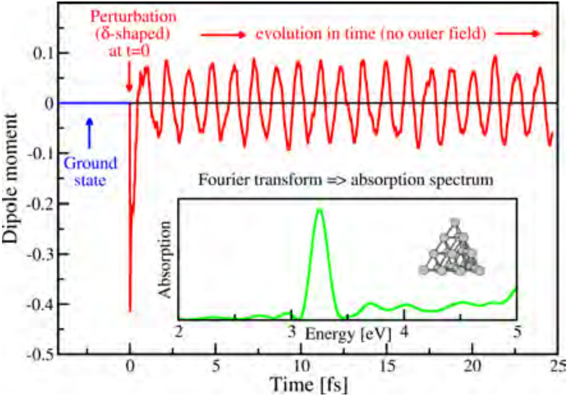

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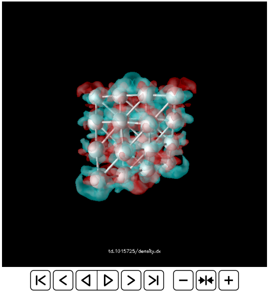

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- ✔ Disadvantage: no direct information about transitions
- ✔ **Advantage: explicit view of charge dynamics**

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Pure and Alloyed Bare Clusters – General Results

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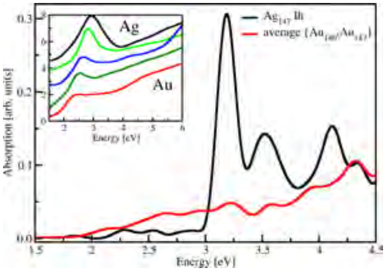

López-Lozano & Weissker, JPCC 117, 3062 (2013).

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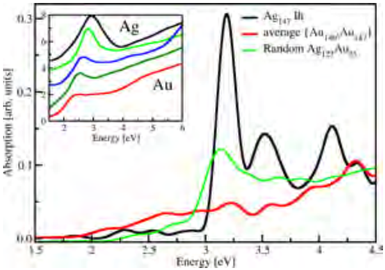

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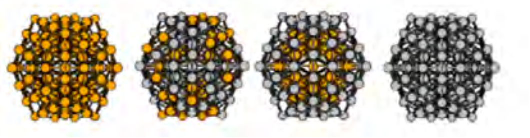

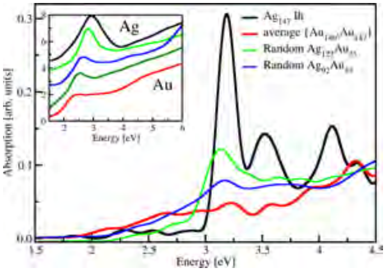

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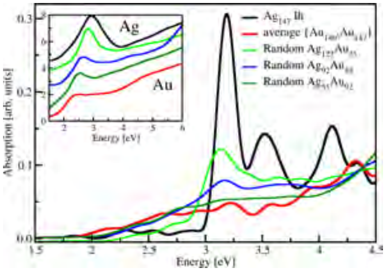

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- ✔ Agreement experiment-theory

  Redshift? Size distribution in experiment? Matrix?
  Temperature? Spin-orbit coupling? Ligands? v_{XC} & f_{XC} ...

- ✔ Ag vs. Au & alloying

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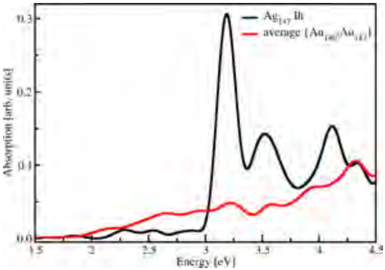

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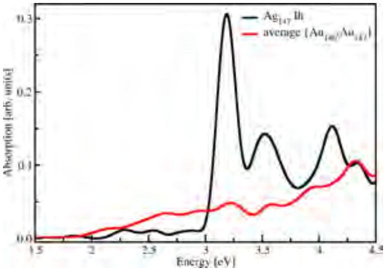

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Redshift? Size distribution in experiment? Matrix?
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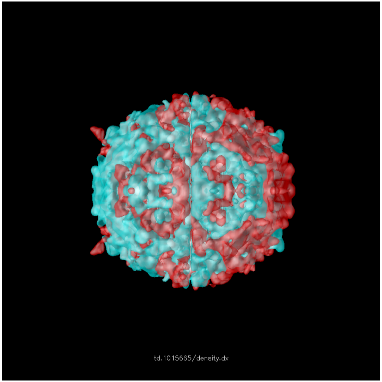
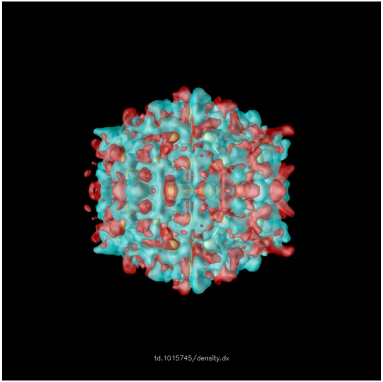
⇒ LSPR as charge oscillation**?**

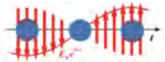
Icosahedra Ag_{147} and Au_{147}

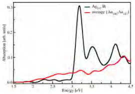
Weissker & López-Lozano, PCCP **17,** 28379 (2015).



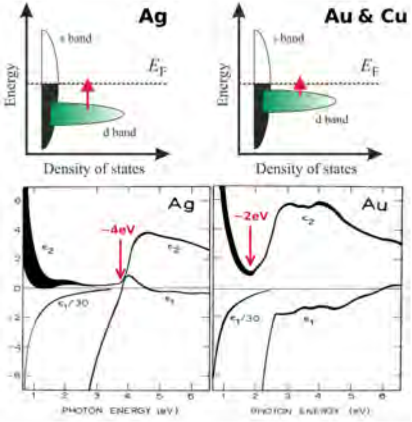


- Density oscillation ↔ classical picture
- $\rho(t, \mathbf{r}) - \rho_{GS}(\mathbf{r})$;   Ag vs. Au





Interband Transitions: Silver vs. Gold



Johnson & Christy, PRB, 1972

- "Interband" transitions from d band
- Interband onset:
  - Ag at ~4 eV
  - Au & Cu at ~2 eV

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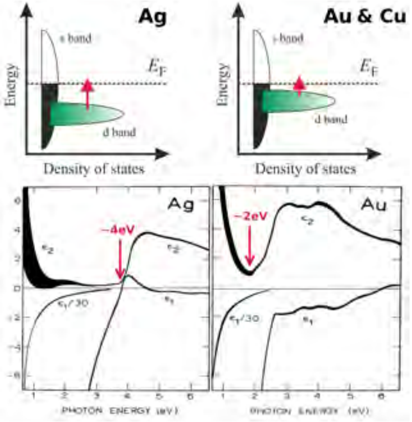
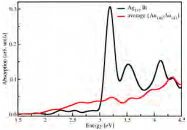


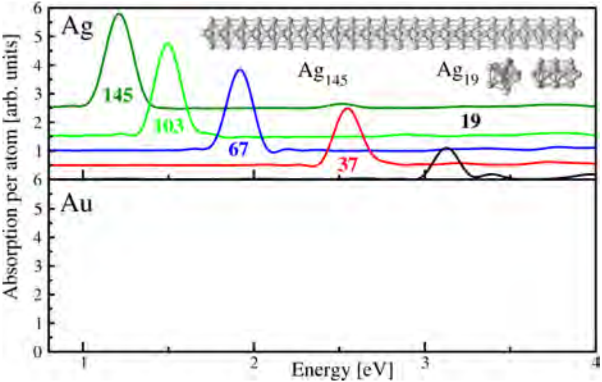
Johnson & Christy, PRB, 1972

- “Interband” transitions from d band
- Interband onset:
  - Ag at ∼4 eV
  - Au & Cu at ∼2 eV
- Size just below ≈2 nm:
  - → Ag shows LSPR,
  - → Au & Cu do not.



Plan

Nanorods: Aspect-Ratio-Dependent Emergence of SPR in Gold



- Aspect-ratio-dependent longitudinal resonance: Mie or TDDFT
- Short Au rods: no strong resonance

López-Lozano, Barron, Mottet & Weissker, PCCP **16**, 1820 (2014).

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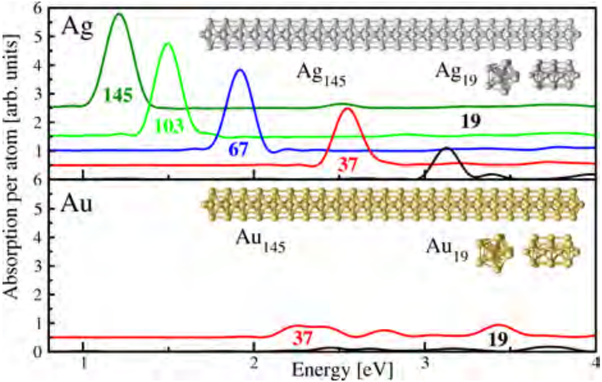

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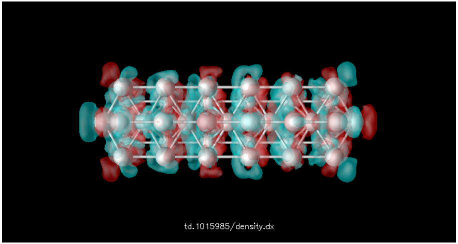
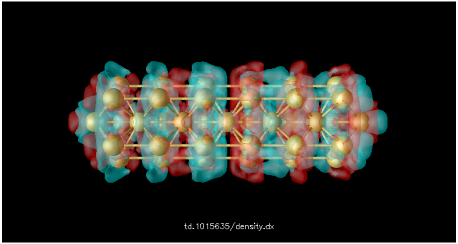
Nanorods Ag_{37} and Au_{37}





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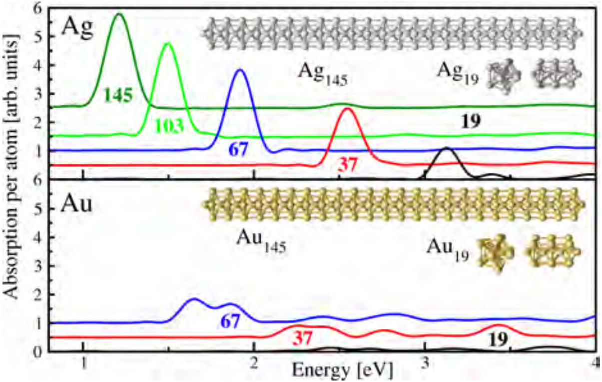

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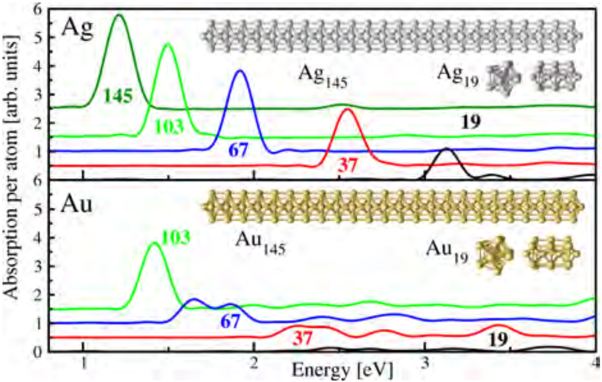

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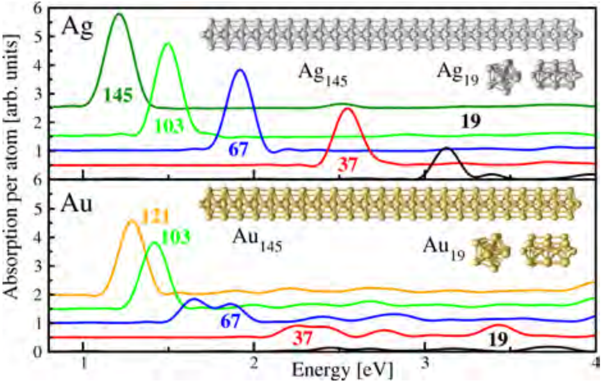

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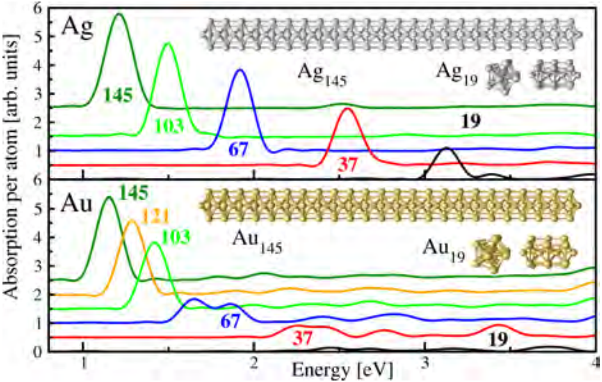

- High aspect-ratio ⇒ strong resonance; gold becomes silver-like

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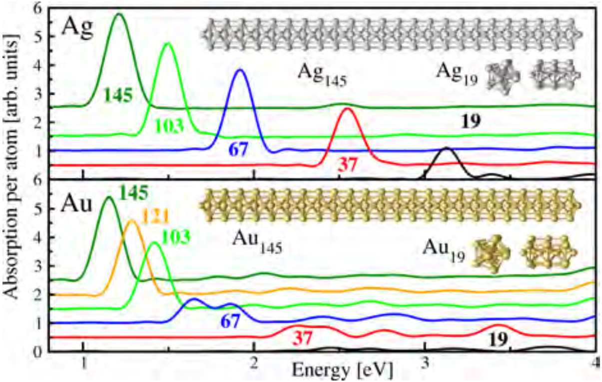

- High aspect-ratio ⇒ strong resonance; gold becomes silver-like
- Decoupling from interband transitions from d electrons

López-Lozano, Barron, Mottet & Weissker, PCCP **16**, 1820 (2014). (M. Stener; Ch. Aikens)

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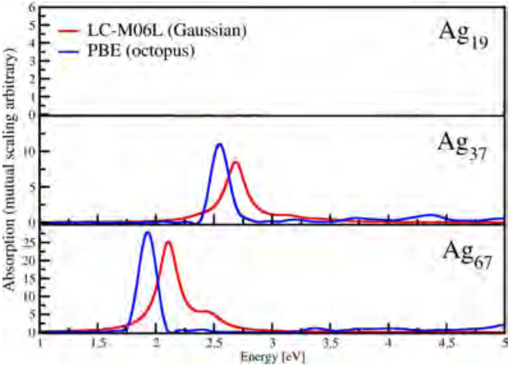
Approximations for exchange and correlation (v_{xc}, f_{xc})

- Absorption in pentagonal silver rods, excitation || axis



Rajarshi Sinha-Roy, [...], H.-Ch. Weissker, F. Rabilloud, A.I. Fernández-Domínguez, ACS Phot., **4,** 1484 (2017)

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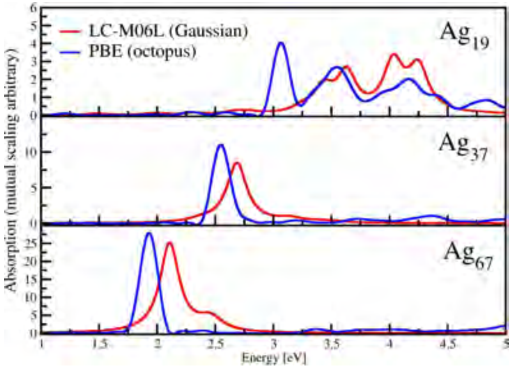

- LDA / GGA fine for LSPR well decoupled from d-electron excitations; fails badly if strong coupling with d excitations

Rajarshi Sinha-Roy, [...], H.-Ch. Weissker, F. Rabilloud, A.I. Fernández-Domínguez, ACS Phot., **4,** 1484 (2017)

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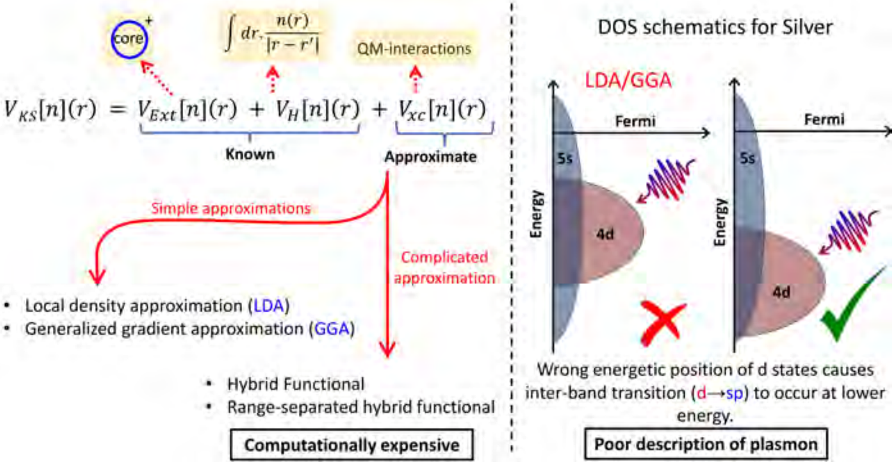
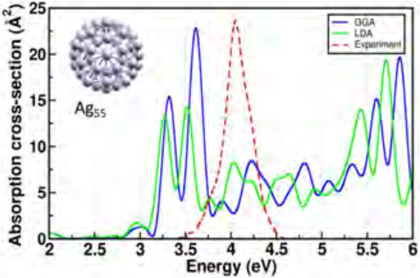
The d band in noble-metals with DFT and DFT+U



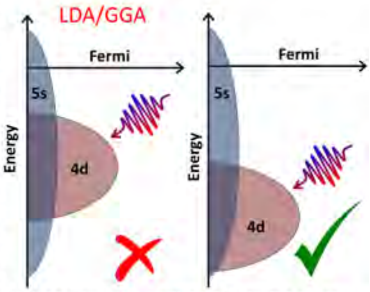
The d band in noble-metals with DFT and DFT+U

core$^+$ $\quad \int dr.\frac{n(r)}{|r-r'|} \quad$ QM-interactions

$$V_{KS}[n](r) = V_{Ext}[n](r) + V_H[n](r) + V_{xc}[n](r)$$



DOS schematics for Silver



Wrong energetic position of d states causes inter-band transition (d→sp) to occur at lower energy.

Poor description of plasmon

The d band in noble-metals with DFT and DFT+U

$$E_{DFT+U}(n,\{n^{I,\sigma}_{mm'}\}) = E_{DFT}(n) + E_{ee}(\{n^{I,\sigma}_{mm'}\}) - E_{dc}(\{n^{I,\sigma}_{mm'}\})$$

Correction term (E_u)

- I : atomic site index
- σ : spin
- m, m' : angular quantum number
- $n^{I,\sigma}_{mm'}$: density matrix in localized atomic basis

$$E_u(\{n^{I,\sigma}_{mm'}\}) = \sum_{I,n,l} \frac{U^{eff}_{I,n,l}}{2} \sum_{m,\sigma} \left[n^{I,n,l,\sigma}_{mm} - \sum_{m'} n^{I,n,l,\sigma}_{mm'} n^{I,n,l,\sigma}_{mm'} \right]$$

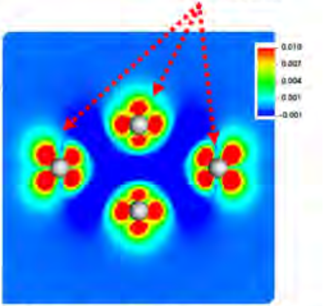
dropping **n** and **l** index

$$E_u(\{n^{I,\sigma}_{mm'}\}) = \sum_{I} \frac{U^{eff}_{I}}{2} \sum_{m,\sigma} \left[n^{I,\sigma}_{mm} - \sum_{m'} n^{I,\sigma}_{mm'} n^{I,\sigma}_{m'm} \right]$$

① Increases Energy

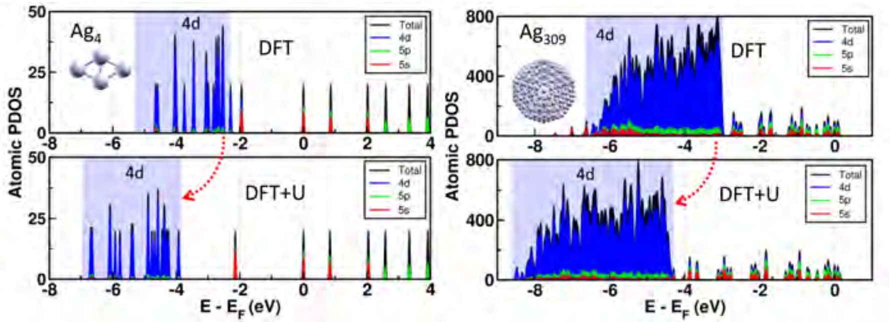
② Decreases Energy

Electron accumulation after U correction



Total charge density difference between DFT+U (4eV) and DFT calculation with GGA

PDOS before and after adding the U correction

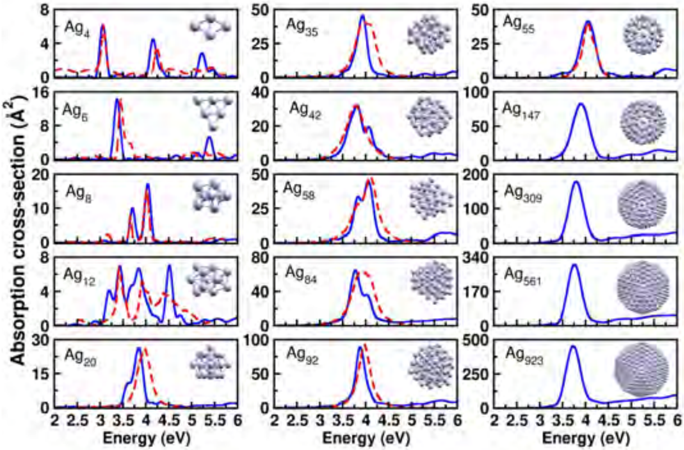


- Use U = 4 eV, shown to give good results for bulk silver

Avakyan *et al.*, Optical Materials, **109,** 110264 ,(2020)

- shifts d edge from ≈3 eV to ≈4 eV after applying the correction; consistent with photoemission spectra in the literature

Spectra of silver clusters using DFT+U



All Clusters in experiments are inside a neon matrix except Ag_{12} which is in argon.

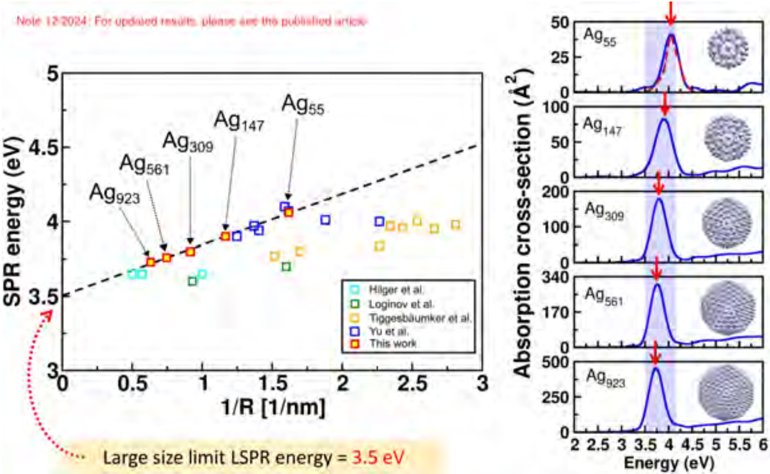
Experimental curves for Ag_{20} to Ag_{92} are blue shifted by 0.17 eV to compensate the neon matrix dielectric effect.

- DFT+U yields excellent spectra very efficiently (size!)
- Transferability: one U value works for all sizes

Mohit Chaudhary

SPR energies of silver clusters using DFT+U

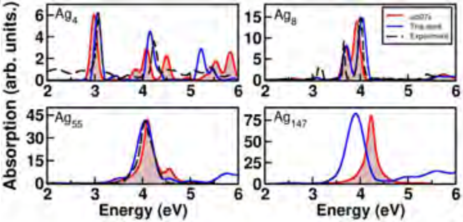
Note 12/2024: For updated results, please see the published article



- SPR energies in agreement with experiment. Size dependence!
- Transferability: one U value works for all sizes ~~to be submitted~~

Now published: Nat. Commun. **15,** 9225 (2024).

Comparison with previous calculations



Comparison with RS-hybrid functional:

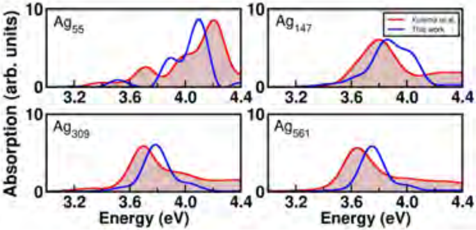
- We obtained better agreement with experiments in our calculations
- Calculation with RS-hybrid limited to Ag_{147}

[1]Schira & Rabilloud, J. Phys. Chem. C, 123(10), 2019
[2]Rabilloud, J. Phys. Chem. A, 117(20), 2013

Comparison with mGGA functional

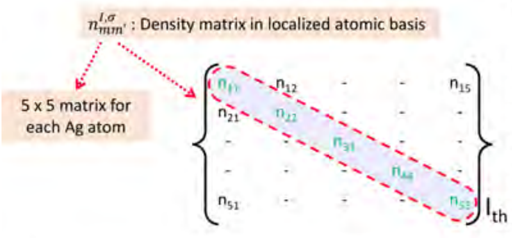
- For smaller cluster (Ag_{55}), overestimation of LSPR.
- For bigger clusters, underestimation of LSPR

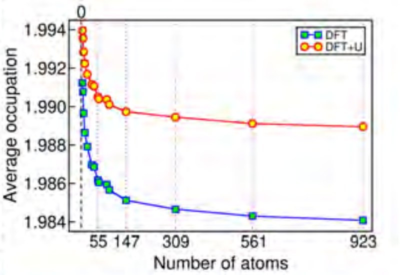
[3]Kuisma et al., PRB, 91(11), 2015



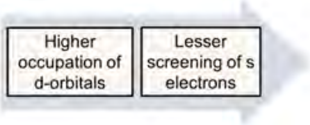
- Range-separated hybrid functions good but *heavy*
- A meta-GGA functional: good for large clusters...

Size dependent localization of 4d electrons



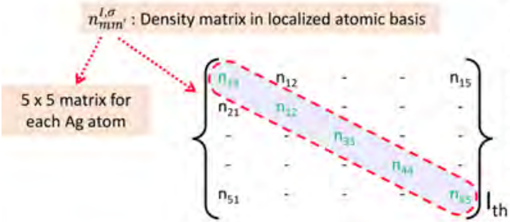


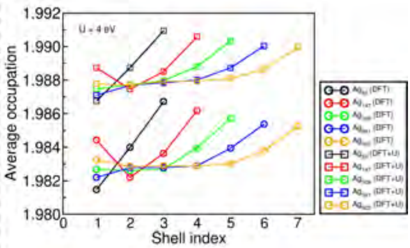
$$Average\ Occupation = \frac{1}{atoms} \sum_{l}^{atoms} \frac{Trace\{n^{l}_{mm'}\}}{5}$$



- With U correction, average d electron localization increases
- With increasing size, average occupation decreases, or screening because of d-electrons increases.
- Higher screening → lower value of LSPR

Size dependent localization of 4d electrons





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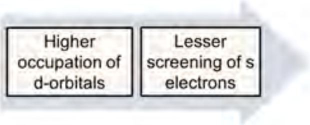
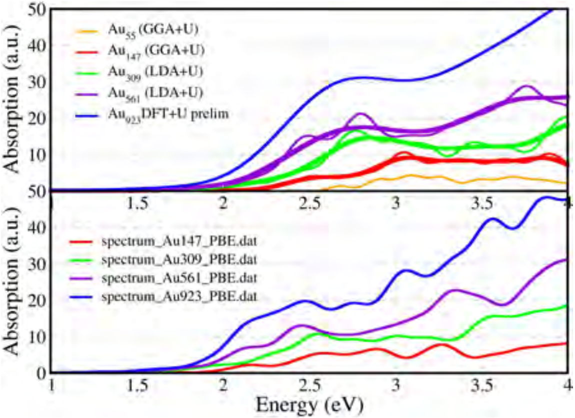


- With U correction, average d electron localization increases.
- Outermost two shells have higher average localization, pointing towards reduced screening of s-electrons on the surface

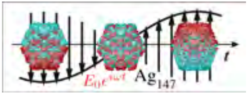
DFT+U for Gold Clusters



- Very preliminary: DFT+U improves description of SPR emergence
- Small clusters: no good agreement

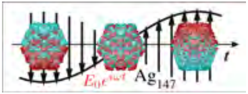
Plan

Conclusions



- TDDFT for "Quantum-sized" Ag and Au clusters: LSPR as charge oscillation
  - Difference Ag vs. Au; d screening
  - Aspect-ratio-dependent red shift may decouple LSPR from interband transitions in rods

Conclusions



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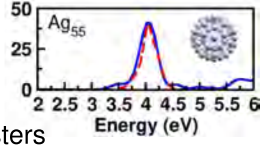
  - Aspect-ratio-dependent red shift may decouple LSPR from interband transitions in rods



- **Excellent silver spectra using DFT+U**
  - Excellent agreement for **small and large** clusters
  - Size dependence of SPR energies: agreement with experiment
  - Using the **same value of U for all sizes up to 1000 atoms (3 nm)**

⇒ Opens the possibility for calculations coupling the clusters to molecules, among each other, etc. — in other words, to describe many of the situations found in experiments and applications.

~~to be submitted~~

Now published: Nat. Commun. **15,** 9225 (2024).