A TDDFT study of the optical absorption spectra of bare and coated Au₅₅ and Au₆₉ clusters

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Abstract

The optical absorption of bare and ligand-coated Au₅₅ and Au₆₉ "Schmid" clusters was calculated using time-dependent density functional theory (TDDFT). Calculations were performed using the explicit time propagation method with the local density approximation (LDA) for the exchange-correlation potential. Both icosahedral and cuboctahedral structures of the Au₅₅ gold core were simulated. The ligand coating was shown to have the effect reducing the features of the optical absorption spectrum of the clusters, giving a profile more similar to experimental results. The difference in the optical absorption between the different geometries and core sizes is also less marked when the clusters are coated. The results suggest that within the 1.4 nm size range, the absorption spectra are dominated by the coating and are not experimentally distinguishable. Binding energies were also calculated for the Au₅₅ cluster, showing that the cuboctahedral structure has lower energy although the energy difference is very small. The effect of the coating on the electron density of the gold cluster is also investigated by subtracting the electron densities of the bare clusters from those of the coated clusters.

Introduction

Metal nanoparticles are currently of great technological interest due to their unique optical properties.^{1,2} They can show high non-linearity, tunable absorption and the potential for the manipulation of light using structures smaller than one wavelength.^{3–5} Gold particles can be fabricated to bridge the middle-ground between individual atoms and bulk materials in a continuous fashion.^{6,7} In small clusters quantum effects become apparent and a classical description of the properties is no longer accurate.^{2,8}

Ligand passivated gold particles are of particular interest because of their stability and that they can be produced in monodisperse solutions.^{9,10} Several such solutions have been synthesised, including $Au_{102}(SR)_{44}$,^{10,11} $Au_{25}(SR)_{18}$,¹² $Au_{38}(RS)_{24}$,^{13,14} and $Au_{144}(RS)$,¹⁵ among others.

One cluster that has attracted significant interest is the Au₅₅(PPh₃)₁₂Cl₆ "Schmid" cluster.^{16,17} A number of experimental studies have been dedicated to the Schmid structure, including optical absorption,^{18–21} XPS,^{22–24} conductivity,²⁵ and Mössbauer spectroscopy measurements.²⁶

Measurements of the optical absorption of the Schmid cluster showed a featureless absorption spectra with decreasing absorption cross-section for increasing wavelength.^{18–20} Another measurement on films of the Schmid cluster showed a peak attributed to plasmon absorption at 2.4 eV, as well as another distinct peak at 6.0 eV.²¹ Also measured was an absorption peak at around 1 eV. This peak disappeared after further heating, leading to the hypothesis that this peak was caused by ellipsoidal particles in the sample.²¹

Initial specification of the stoichiometry was based on preference for a 55 atoms cluster, and supported by Mössbauer spectroscopy measurements.²⁷ A cluster of 55 atoms was preferred because a 55 atom cluster corresponds to a full shell cluster. A full shell cluster comprises of a single atom, surrounded by complete shells of atoms, ending in a perfect external geometry, and can have either icosahedral or cuboctahedral geometries. The number of atoms in each subsequent shell is given by $10n^2 + 2$ where *n* is the shell number. This gives cluster sizes of 13, 55, 147, 309 etc. The stability of clusters containing these numbers of atoms was first observed for Xenon using yields in a mass spectrometer.²⁸Ligand-coated clusters of transmission metals including gold were synthesised having numbers of metal atoms corresponding to full shell clusters¹⁷ and coated clusters with Pt₃₀₉²⁹ and Pd₂₀₅₇³⁰ cores have been observed under high resolution transmission electron microscopy (HRTEM), further supporting full-shell clusters of transmission metals.

However, there is also evidence that the cluster may have a different stoichiometry and it has been proposed that a free-electron shell closing picture is a better predictor of cluster stability.^{31–33} Most recently the results from density functional theory (DFT) have been used to claim that this cluster is better represented as $Au_{69}(PR_3)_{20}Cl_{12}$.³⁴ It should be noted that the computational work

performed so far has neglected kinetic and entropic effects and uses the approximation of replacing the phenyl groups by H. The experimental evidence for the size and stoichiometry is inconclusive and sometimes contradictory.^{35–40} Images obtained in the transmission electron microscope^{17,20} suggest that, although the size distribution is narrow, there is a significant range of particle sizes. The experimental work suggests that more than one stoichiometry for the particles occurs and the material preparation methods may play a role.

Despite the uncertainty about the stoichiometry for the $Au_{55}(PPh_3)_{12}Cl_6$ cluster, there has been significant research to determine its structure. HRTEM images of coated Pt_{309}^{29} and Pd_{2057}^{30} cores indicated a cuboctahedral geometry to the central core. This gave early preference to cuboctahderal arrangements for full shell transmission metal clusters, including Au_{55} . Symmetry considerations of $Au_{55}(PPh_3)_{12}Cl_6$ further support the cuboctahedral structure: a cuboctahedron has 12 vertices and 6 square faces, matching the 12 phosphine groups and 6 Cl atoms of $Au_{55}(PPh_3)_{12}Cl_6$.^{17,18}

This is contradicted by investigations of the bare cluster using density functional theory (DFT), which suggest a distorted icosahedron to be the lowest energy structure.^{7,41} Given the large number of atoms and the large volume involved, DFT simulations of the full coated cluster have not yet been performed. Instead an intermediate $Au_{55}(PH_3)_{12}Cl_6$ cluster was investigated, which again showed a distorted icosahedral geometry to have the lowest energy.^{42,43} These calculations resulted in a structure with a central atom surrounded by an icosahedron of 12 gold atoms 0.29nm from the center and a second icosahedron of 12 atoms at 0.58nm. The remaining 30 gold atoms are arranged roughly on the edges of the outer icosahedron, but at a distance of 0.51nm from the central atom. The PH₃ groups are bonded to the vertices of the outer icosahedron and the chlorine atoms arranged on 6 of the 20 faces (see Figure 1).

Time-dependent DFT (TDDFT) can be viewed as an extension of traditional DFT to the timedependent domain, allowing calculation of properties such as optical absorption spectra.^{44,45} Bare gold clusters of sizes 1-14 atoms^{46–48} and 20 atoms^{48–51} have had their optical absorption spectra calculated by TDDFT. Smaller ligand-coated gold particles have also had their optical absorption calculated, including $Au_{25}(RS)_{18}$ ^{8,52} and $Au_{38}(RS)_{24}$.^{53,54} Bare clusters of other metals have also been analysed using TDDFT, including silver,⁵⁵ sodium,^{56–58} and lithium.^{57,59} Clusters with up to 120 silver atoms have had their optical absorption calculated with TDDFT.⁶⁰ To our knowledge, no TDDFT calculations have been reported for either the Au_{55} cluster or the recently suggested alternative Au_{69} cluster, either coated or bare. Theoretical calculations of the optical properties could help resolve between competing atomic structures, and improved understanding of the optical properties for technological applications.⁴²

This work investigated the optical response of bare and coated Au_{55} and Au_{69} clusters and the effect of the ligand coating to the optical response of the gold cluster. The connections between charged bare Au_{55} clusters and coated clusters is explored, and the calculated optical response is compared to experimental measurements in the literature.^{18–21}

Computational Details

All calculations were performed using the TDDFT package Octopus.⁴⁵ Within Octopus calculations are performed over a discrete grid in real-space and ground-state electron distributions are calculated under DFT. The time propagations for TDDFT are performed over discrete steps in realtime.

The real-space grid used was contained in a volume consisting of a series of overlapping spheres of radius 3.5 Å with a sphere centred on each atom. The spacing between grid points within this volume was 0.2 Å. Testing on smaller gold particles showed that this gave good convergence of

the total energy and electron density. Fully relativistic pseudopotentials were generated under the improved Troullier and Martins method⁶¹ using the Ceperly and Alder LDA exchange-correlation potential.⁶² Ground state calculations were performed using a Fermi-Dirac type electron smearing to simulate an electronic temperature and to ease convergence of open-shell systems.⁶³ In all cases a smearing of 0.01 eV was used.

Six structures were studied; two bare Au₅₅ clusters, two Au₅₅(PH₃)₁₂Cl₆ clusters, a bare Au₆₉ cluster and a Au₆₉(PR₃)₂₀Cl₁₂ cluster (see Figure 1). A bare cuboctahedral structure was cleaved directly from a bulk crystal, a coated icosahedral and bare icosahedral structure were generated following the arrangement of Periyasamy and Remacle.⁴² The coated cuboctahedral structure was generated by placing a PH₃ group bonded onto each of the 12 gold atoms located on a vertex and a chlorine atom bonded onto the 6 gold atoms centred in the middle of each square face. Finally, the Au₆₉(PR₃)₂₀Cl₁₂ used is the same as used in the work of Walter *et al*,³⁴ the bare Au₆₉ is the same cluster but the coating removed. The bare Au₅₅ structures were relaxed then coatings were added to the relaxed bare structure. Relaxation of the coated cluster allowing movement of the gold atoms resulted in negligible movement (<0.05 Å) of the gold atoms. Instead the coated structure was relaxed with the gold atoms held stationary. Holding the gold atoms in place for the relaxation of the coated structures allowed the direct subtraction of densities from coated and uncoated structures. All relaxations were performed using a Fletcher-Reeves conjugate-gradient algorithm.⁶⁴ For comparison with the coated clusters, the bare clusters were also simulated with charges ranging from +9 through to -12 electron charges. This was done to identify the trends of the changes to the electron density of the structure as charge is added or subtracted.

Time propagation calculations were performed using the explicit time-propagation method.⁶⁵ This method was chosen because it scales best with the size of the system being calculated. Testing on smaller systems showed that inclusion of spin-polarization made negligible difference to the optical response, so the calculations presented here do not include spin-polarization. Previous work has demonstrated that spin-orbit coupling effects are significant in gold chains and two-dimensional structures, but are quenched for more compact three-dimensional structures.⁶⁶ Therefore spin orbit coupling was not included. Propagations were performed under the LDA approximation, and used the approximated enforced time-reversal symmetry (AERTS) method.⁶⁵ Approximation of the exponential of the Hamiltonian was made with the Lanczos method.⁶⁵

Time steps were checked for stability before continuing a full propagation. This was done by propagating the unperturbed ground state, with most systems being stable with a time step of $5 - 7 \times 10^{-18}$ s. A delta-kick was then applied to the electron density, and all systems were propagated over a period of 1.97×10^{-14} s ($30\hbar/eV$). The broadening of the absorption peaks when using this method is inversely proportional to the propagation time. The propagation time was therefore selected such that the major features are visible, and the spectral resolution is qualitatively comparable to experimental measurements. This propagation time is similar to that use in previous calculations on gold clusters using Octopus.⁶⁶ The frequency-dependent response was calculated by taking the Fourier transform of the time-dependent dipole moment.

Optical absorption calculations for both of the bare Au_{55} systems were able to use symmetry, as described by Oliveira *et. al.*⁶⁷ to reduce the calculation times. Calculation of the coated clusters and the bare Au_{69} were performed without symmetry considerations.

Results and Discussion

Ground state calculations for the bare icosahedral and cuboctahedral clusters gave a binding energy of 3.40 and 3.53 eV/atom respectively. This is in disagreement with earlier works^{7,41,42} which found that the icosahedron has the lower energy. For more direct comparison, the calculation was extended to include spin polarisation and solved under the GGA approximation for the exchange

correlation potential. New pseudopotentials were also generated using the Perdew, Burke, Ernzerhof GGA exchange-correlation potential⁶⁸ and included full core corrections. The extended calculation gave binding energies of 2.50 and 2.55 eV/atom respectively, very close to previously calculated binding energies of 2.51 and 2.49 eV/atom. The binding energies of the coated icosahedral and cuboctahedral geometries were calculated to be 418 and 428 eV/molecule respectively.

Calculations under the LDA approximation without spin considerations gave binding energies almost 1 eV/atom higher, 3.40 eV/atom and 3.53 eV/atom. The energy differences between the two competing structures are very small and are not necessarily in contradiction to earlier calculations.^{42,43} It is possible that the difference in stability between our work and that given previously is due to slightly different structures resulting from different levels of relaxation.

Figure 2 shows the electron density of the icosahedral $Au_{55}(PH_3)_{12}Cl_6$ structure with the electron density of the bare icosahedral structure subtracted, highlighting the shifts to the electron configuration by the coating. The density has been plotted over a 2-dimensional plane through the middle of the cluster, with 2 chlorine atoms as well as 4 PH₃ groups lying in the plane. By comparison, Figure 3 shows the electron density of the bare icosahedral with various additional charges, with the electron density of the neutral icosahedron subtracted.

Figure 4 similarly shows the electron density of the cuboctahedral $Au_{55}(PH_3)_{12}Cl_6$ structure with the electron density of the bare neutral cuboctahedral Au_{55} cluster subtracted, and Figure 5 shows the electron density of various charged bare cuboctahedral structures with the neutral electron density subtracted. Once again the shift in the density is shown on a 2-dimensional plane passing through the middle of the clusters. In this case the coated structure has 4 PH₃ groups and 4 chlorine atoms lying in this plane.

The extra electron density around the outside of both coated clusters is to be expected for ob-

vious reasons. Examination of the change to the density in the inner areas of the clusters show similarities to the negatively charged bare cluster for both geometries indicating that the coating has the net effect of adding electrons to the inner core. In particular both changes to electron density show concentric areas of lower, then higher electron density around the central atom, and inward-facing lobes of low electron density around the outer atoms. This is in agreement with other calculations which also show a negatively charged core.⁴³

It would seem counter-intuitive that the coating has an effect similar to a net negative charge until the electron energy levels and occupations are investigated. Table 1 shows the electron energy levels and occupations around the Fermi level for the bare Au_{55} clusters. Energy levels are set such that the Fermi level is at 0. Both clusters have a series of energy levels very close to each other which are over half-full, indicating that the clusters would be be likely to attract electrons rather than lose them. This is in agreement with a "super-atom" theory of ligand-coated gold particles, proposing that gold clusters are more stable with numbers of electrons corresponding to the filling of electron shells i.e. 2, 8, 18, 34, 58, ...³² Further examination will show that both bare clusters are 3 electrons short of filling the energy levels around the Fermi level, bringing the number up to the proposed 58 electrons.

Figure 6 shows the optical absorption spectra of the all calculated clusters. The bare cuboctahedron shows a distinct peak at 5 eV, whilst the bare icosahedron shows distinct peaks at 3.5 eV, 7 eV and 7.5 eV. By contrast, all the coated structures and the bare Au₆₉ have fewer distinct features.

The bare clusters display absorption cross-sections that are have fewer features than those calculated for smaller gold particles.^{48,66} The Au₆₉ cluster also has far fewer features than the bare Au₅₅ clusters, this can be attributed to the 69 atom cluster having lower symmetry. The Au₅₅ clusters do however still have a few distinct peaks and all bare clusters have significantly different absorption spectra. The absorption spectra for the coated clusters are more featureless, the Au₆₉ cluster particularly having no peaks. The most recent experimental measurement of the absorption spectra of the Schmid cluster also showed a featureless absorption spectra increasing with frequency and is shown in Figure 6 for comparison.²⁰

These calculations indicate that the coating serves to reduce the features of the absorption spectra of the bare clusters to something more similar to what is measured experimentally. The calculations also indicate that as the coating is added to the cluster the internal geometry of the gold cluster becomes less important to the optical absorption. It would be expected that calculation of the full coated structure with PPh₃ instead of the PH₃ used here would produce a spectra with even fewer features, giving absorption spectra for all structures that are indistuinguishable.

There are a number of possible reasons that could cause or contribute to the loss of features after adding the coating. The high symmetry of the 55 atom bare gold clusters would likely cause degeneracy of electron states, causing absorption peaks. The addition of the coating reduces the symmetry, which could broaden these peaks. This is supported by the absorption spectrum of the lower-symmetry bare 69 atom cluster, which has an absorption spectrum with fewer features than the bare 55 atom clusters. Also the addition of more atoms and therefore more electron states would cause broadening to the absorption cross-section. This is demonstrated by even the bare clusters presented here having absorption cross-sections with less distinct features than the absorption cross-sections of small clusters presented in previous calculations.^{46–48}

Some measurements of the absorption spectra of the Schmid cluster have shown distinct peaks at 2.5 and 6 eV,²¹ but this work also identified elliptical particles as a cause of another absorption peak at approximately 1 eV. This suggests the inhomogeneity of the sample studied, and could be responsible for the other absorption peaks, which would be expected in larger clusters.

Conclusion

The first TDDFT calculations of the optical absorption spectra of the gold clusters of around 1.4 nm have been performed. Results show the addition of the coating produces an absorption spectra very different and with far fewer features than that of the bare cluster. They also show the absorption spectra for the coated clusters are very similar and would be difficult to distinguish between them using experimental methods. Given the large contribution of the coating to the spectrum, it is likely that any gold particle of similar size and the same coating would have a similar optical cross section. It is therefore unlikely that the presence of 55 atom cores or 69 atoms cores, as suggested,³⁴ could be determined using the optical absorption cross section. Differences in the binding energy the between the icosahedral and cuboctahedral structures are small and it is likely that both would exist experimentally, should a 55 atom cluster occur.

Further calculations such as the calculation of the full coated cluster will become feasible as computer powers continue to increase. This work demonstrates that even now TDDFT calculations can be performed on gold clusters that are far larger than those previously investigated, and that calculation of experimentally produced clusters can be done. It highlights the importance of the coating to the spectra of coated metallic nanoparticles; absorption spectra of very different gold cores likely are indistuinguishable after the addition of the ligand coating.

References

- (1) Eustis, S.; El-Sayed, M. Chemical Society Reviews 2006, 35, 209-217.
- (2) Alvarez, M.; Khoury, J.; Schaaff, T.; Shafigullin, M.; Vezmar, I.; Whetten, R. Journal of Physical Chemistry B 1997, 101, 3706–3712.
- (3) Yang, Y.; Matsubara, S.; Nogami, M.; Shi, J.; Huang, W. Nanotechnology 2006, 17, 2821.
- (4) Danckwerts, M.; Novotny, L. Physical Review Letters 2007, 98, 26104.

- (5) Nie, S.; Emory, S. R. Science 1997, 275, 1102–1106.
- (6) Daniel, M.; Astruc, D. Chemical Reviews 2004, 104, 293–346.
- (7) Häberlen, O.; Chung, S.; Stener, M.; Rösch, N. *The Journal of Chemical Physics* 1997, *106*, 5189.
- (8) Aikens, C. The Journal of Physical Chemistry A 2009, 113, 10811–10817.
- (9) Templeton, A.; Wuelfing, W.; Murray, R. Accounts of Chemical Research 2000, 33, 27–36.
- (10) Jadzinsky, P.; Calero, G.; Ackerson, C.; Bushnell, D.; Kornberg, R. Science 2007, 318, 430.
- (11) Li, Y.; Galli, G.; Gygi, F. ACS Nano 2008, 2, 1896–1902.
- (12) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. Journal of the American Chemical Society 2008, 130, 3754–3755.
- (13) Wang, W.; Lee, D.; Murray, R. W. The Journal of Physical Chemistry B 2006, 110, 10258–10265.
- (14) Qian, H.; Zhu, Y.; Jin, R. ACS Nano 2009, 3, 3795–3803.
- (15) Qian, H.; Jin, R. Nano Letters 2009, 9, 4083-4087.
- (16) Schmid, G.; Klein, N.; Korste, L.; Kreibig, U.; Schönauer, D. Polyhedron 1988, 7, 605–608.
- (17) Schmid, G. Chemical Society Reviews 2008, 37, 1909–1930.
- (18) Fauth, K.; Kreibig, U.; Schmid, G. Zeitschrift für Physik D Atoms, Molecules and Clusters 1989, 12, 515–520.
- (19) Fauth, K.; Kreibig, U.; Schmid, G. Zeitschrift für Physik D Atoms, Molecules and Clusters 1991, 20, 297–300.
- (20) Weare, W.; Reed, S.; Warner, M.; Hutchison, J. Journal of the American Chemical Society 2000, 122, 12890–12891.

- (21) Miyauchi, H.; Taketomi, K.; Egami, A.; Hosoi, S.; Fukutani, H. Absorption and Photoemission Studies of Au–55 Metal Clusters. In *Mesoscopic materials and clusters: their physical and chemical properties*; Arai, T., Mihama, K., Yamamoto, K., Sugano, S. E., Eds.; Springer-Verlag, 1999; pp 223–228.
- (22) Marcus, M. A.; Andrews, M. P.; Zegenhagen, J.; Bommannavar, A. S.; Montano, P. *Physical Review B* 1990, 42, 3312–3316.
- (23) Boyen, H.-G.; Kästle, G.; Weigl, F.; Ziemann, P.; Schmid, G.; Garnier, M. G.; Oelhafen, P. *Physical Review Letters* 2001, 87, 276401.
- (24) Van Der Putten, D.; Zanoni, R. *Physics Letters A* **1995**, *208*, 345–350.
- (25) Brom, H.; van Staveren, M.; de Jongh, L. Zeitschrift für Physik D Atoms, Molecules and Clusters 1991, 20, 281–287.
- (26) Mulder, F.; v.d. Zeeuw, E.; Thiel, R.; Schmid, G. Solid State Communications 1993, 85, 93 –
 97.
- (27) Schmid, G.; Pfeil, R.; Boese, R.; Bandermann, F.; Meyer, S.; Calis, G.; van der Velden, J. *Chemische Berichte* 1981, 114, 3634–3642.
- (28) Echt, O.; Sattler, K.; Recknagel, E. Physical Review Letters 1981, 47, 1121–1124.
- (29) Schmid, G.; Morun, B.; Malm, J. Angewandte Chemie International Edition in English 1989, 28, 778–780.
- (30) Schmid, G.; Harms, M.; Malm, J.; Bovin, J.; Van Ruitenbeck, J.; Zandbergen, H.; Fu, W. Journal of the American Chemical Society 1993, 115, 2046–2048.
- (31) de Heer, W. Reviews of Modern Physics 1993, 65, 611–676.

- (32) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P.; Calero, G.; Ackerson, C.; Whetten, R.; Grönbeck, H.; Häkkinen, H. Proceedings of the National Academy of Sciences 2008, 105, 9157.
- (33) Häkkinen, H. Chemical Society Reviews 2008, 37, 1847–1859.
- (34) Walter, M.; Moseler, M.; Whetten, R. L.; Hakkinen, H. Chemical Science 2011, -.
- (35) Sharma, R.; Holland, G.; Solomon, V.; Zimmermann, H.; Schiffenhaus, S.; Amin, S.; Buttry, D.; Yarger, J. *The Journal of Physical Chemistry C* 2009, *113*, 16387–16393.
- (36) Chen, W.; Chen, S. Angewandte Chemie International Edition 2009, 48, 4386–4389.
- (37) Fackler Jr, J.; McNeal, C.; Pignolet, L.; Winpenny, R. Journal of the American Chemical Society 1989, 111, 6434–6435.
- (38) Cluskey, P.; Newport, R.; Benfield, R.; Gurman, S.; Schmid, G. *Chemical Processes in Inor*ganic Materials: Metal and Semiconductor Clusters and Colloids **1992**, 289–294.
- (39) Cluskey, P.; Newport, R.; Benfield, R.; Gurman, S.; Schmid, G. Zeitschrift für Physik D Atoms, Molecules and Clusters 1993, 26, 8–11.
- (40) Fairbanks, M.; Benfield, R.; Newport, R.; Schmid, G. Solid state communications 1990, 73, 431–436.
- (41) Barnard, A.; Curtiss, L. ChemPhysChem 2006, 7, 1544–1553.
- (42) Periyasamy, G.; Remacle, F. Nano Letters 2009, 9, 3007-3011.
- (43) Pei, Y.; Shao, N.; Gao, Y.; Zeng, X. ACS nano 2010, 4, 2009–2020.
- (44) Runge, E.; Gross, E. Physical Review Letters 1984, 52, 997–1000.
- (45) Castro, A.; Marques, M.; Appel, H.; Oliveira, M.; Rozzi, C.; Andrade, X.; Lorenzen, F.;
 Gross, E.; Rubio, A. *Physica Status Solidi. B. Basic Research* 2006, 243, 2465–2488.

- (46) Wang, J.; Wang, G.; Zhao, J. *Physical Review B* 2002, 66, 35418.
- (47) Öğüt, S.; Idrobo, J.; Jellinek, J.; Wang, J. Journal of Cluster Science 2006, 17, 609–626.
- (48) Idrobo, J.; Walkosz, W.; Yip, S.; Ögüt, S.; Wang, J.; Jellinek, J. *Physical Review B* 2007, 76, 20.
- (49) Wu, K.; Li, J.; Lin, C. Chemical Physics Letters 2004, 388, 353–357.
- (50) Xie, R.; Bryant, G.; Zhao, J.; Kar, T.; Smith, V. Physical Review B 2005, 71, 125422-1.
- (51) Aikens, C. M.; Schatz, G. C. The Journal of Physical Chemistry A 2006, 110, 13317–13324.
- (52) Akola, J.; Walter, M.; Whetten, R.; Hakkinen, H.; Gronbeck, H. Journal of the American Chemical Society **2008**, 130, 3756–3757.
- (53) Jiang, D.; Luo, W.; Tiago, M.; Dai, S. The Journal of Physical Chemistry C 2008, 112, 36.
- (54) Hidalgo, F.; Sánchez-Castillo, A.; Garzón, I.; Noguez, C. *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics* 2009, 52, 179–182.
- (55) Idrobo, J.; Ogut, S.; Jellinek, J. Physical Review B 2005, 72, 085445.
- (56) Vasiliev, I.; Öğüt, S.; Chelikowsky, J. R. Physical Review B 2002, 65, 115416.
- (57) Blase, X.; Ordejon, P. Physical Review B 2004, 69, 085111.
- (58) Tsolakidis, A.; Sánchez-Portal, D.; Martin, R. Physical Review B 2002, 66, 235416.
- (59) Rubio, A.; Alonso, J.; Blase, X.; Balbas, L.; Louie, S. *Physical Review Letters* **1996**, 77, 247–250.
- (60) Aikens, C.; Li, S.; Schatz, G. Journal of Physical Chemistry C 2008, 112, 11272–11279.
- (61) Troullier, N.; Martins, J. Solid State Communications 1990, 74, 613-616.
- (62) Ceperley, D. M.; Alder, B. J. Physical Review Letters 1980, 45, 566–569.

- (63) Nogueira, F.; Castro, A.; Marques, M. A tutorial on density functional theory. In *A Primer in Density Functional Theory*; Fiolhais, C., Nogueira, F., Marques, M. A. E., Eds.; Springer: Berlin, 2003; pp 218–256.
- (64) Fletcher, R.; Reeves, C. The Computer Journal 1964, 7, 149–154.
- (65) Castro, A.; Marques, M.; Rubio, A. The Journal of Chemical Physics 2004, 121, 3425.
- (66) Castro, A.; Marques, M.; Romero, A.; Oliveira, M.; Rubio, A. *The Journal of Chemical Physics* **2008**, *129*, 144110.
- (67) Oliveira, M.; Castro, A.; Marques, M.; Rubio, A. *Journal of Nanoscience and Nanotechnol*ogy **2008**, *8*, 3392–3398.
- (68) Perdew, J. P.; Burke, K.; Ernzerhof, M. Physical Review Letters 1996, 77, 3865–3868.



Figure 1: Structures simulated in this work. The left and column shows the bare clusters, whilst the right hand column shows the coated clusters. Starting from the top, the icosahedral Au_{55} , cuboctahedral Au_{55} , Au_{69} clusters. Gold atoms are yellow, the Phosphorous atoms are orange, the Hydrogen atoms are shown as white and the Chlorine atoms are green.



Figure 2: Calculated electron density of the icosahedral $Au_{55}(PH_3)_{12}Cl_6$ with the electron density of the bare Au_{55} subtracted. The scale of the shift in electron density is in electrons per Å³



Figure 3: Calculated electron density of the icosahedral Au₅₅ with various net charges with the electron density of the neutral Au₅₅ subtracted. The scale of the shift in electron density is in electrons per $Å^3$



Figure 4: Calculated electron density of the cuboctahedral $Au_{55}(PH_3)_{12}Cl_6$ with the electron density of the bare Au_{55} subtracted. The scale of the shift in electron density is in electrons per Å³



Figure 5: Calculated electron density of the cuboctahedral Au₅₅ with various net charges with the electron density of the neutral Au₅₅ subtracted. The scale of the shift in electron density is in electrons per $Å^3$

Table 1: Electron energy levels and occupations around the Fermi level of the bare, neutral Au₅₅ structures.

Icosahedron		Cuboctahedron	
Energy (eV)	Occupation	Energy (eV)	Occupation
-0.521937	2.000000	-0.451197	2.000000
-0.521937	2.000000	-0.451197	2.000000
-0.521937	2.000000	-0.451070	2.000000
-0.518341	2.000000	-0.409173	2.000000
-0.518341	2.000000	-0.409173	2.000000
-0.000001	1.274653	-0.000111	1.668730
0.000000	1.274653	0.000000	1.665635
0.000000	1.274653	0.000000	1.665635
0.002079	1.176041	0.218539	0.000000
0.929956	0.000000	0.653891	0.000000
0.929956	0.000000	0.654370	0.000000
0.929956	0.000000	0.654370	0.000000
1.020167	0.000000	1.056086	0.000000



Figure 6: Absorption spectrum of the bare and coated A) cuboctahedral Au_{55} and B) icosahedral Au_{55} and the C) Au_{69} clusters. Absorption cross section is in arbitrary units.