

Validation study of the ability of density functionals to predict the planar-to-three-dimensional structural transition in anionic gold clusters

Manjeera Mantina, Rosendo Valero, and Donald G. Truhlar^{a)}

Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, USA

(Received 20 April 2009; accepted 9 July 2009; published online 13 August 2009)

As gold clusters increase in size, the preferred structure changes from planar to three-dimensional and, for anionic clusters, Au_n^- , the two-dimensional (2D) \rightarrow three-dimensional (3D) transition is found experimentally to occur between $n=11$ and $n=12$. Most density functionals predict that planar structures are preferred up to higher n than is observed experimentally, an exception being the local spin density approximation. Here we test four relatively new functionals for this feature, in particular, M05, M06-L, M06, and SOGGA. We find that M06-L, M06, and SOGGA all predict the 2D \rightarrow 3D transition at the correct value of n . Since the M06-L and M06 functionals have previously been shown to be reasonably accurate for transition metal bond energies, main group atomization energies, barrier heights, and noncovalent interaction energies, and, since they are here shown to perform well for the s - d excitation energy and ionization potential of Au atoms and for the size of Au_n^- clusters at which the 2D \rightarrow 3D transition occurs, they are recommended for simulating processes catalyzed by gold clusters. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3190492]

I. INTRODUCTION

Bulk gold is the most noble metal, but supported gold nanoparticles are reactive and have intriguing catalytic power.¹⁻⁷ For this reason, as well as for potential biological and nanotechnological applications, recent years have seen tremendous interest⁸⁻⁵⁵ in the structure of gold clusters and nanoparticles. Anionic clusters with an even number of electrons seem to have the most catalytic activity.⁵⁶

A particularly fascinating structural characteristic is that ion mobility experiments show Au_n^- clusters up to $n=11$ to be planar, whereas for $n \geq 13$ they have three-dimensional structures; the original experimental results were not definitive for $n=12$, for which there appear two low-lying structures, one planar and one 3D.⁵⁷ Photoelectron spectroscopy⁵⁸ also found evidence for multiple isomers with $n=12$, but concluded that the two-dimensional (2D)-to-3D transition occurs between $n=12$ and $n=13$. Electron diffraction experiments⁵⁹ are consistent with a planar structure for $n=11$, with a 54:46 mix of 2D and 3D structures for $n=12$, with a 20:80 mixture of 2D and 3D structures for $n=13$, and with 3D structures for $n \geq 14$. A subsequent improved electron diffraction study⁵³ with an extended range of electron momentum transfer and a lower temperature yielded a planar structure for Au_{11}^- and 3D structures for Au_{12}^- and Au_{13}^- . This is the most reliable experimental determination available and it was used⁵³ (as discussed below) to judge the quality of six density functionals; it will be used to judge the quality of four more density functionals in the present article. The intrinsic properties of the clusters are important because simu-

lations have shown that for supported clusters, 2D islands are more catalytically active than adsorbed 3D structures.⁶⁰ The 3D transition at $n=12$ is a surprisingly high value of n , e.g., neutral^{21,24} and cationic^{61,62} gold clusters become 3D at $n \approx 8$, cationic Ag clusters are 3D already at $n=5$,⁶³ and neutral Al clusters are 3D already at $n=4$ (Ref. 64) and anionic Ag, Cu, and Na clusters are also 3D at $n=7$.⁶⁵

Several groups^{10,24,25,36,39,57,59,65} speculated that relativistic lowering of the s orbital energies in Au may increase the likelihood of sd^m hybrid orbitals and that this may favor more directional and lower-coordination bonding as in the planar structures, in contrast with highly delocalized high-coordination bonding in more compact structures. Predicting the transition to 3D structures at $n=12$ is a challenge for density functional theory. Häkkinen *et al.*⁶⁵ carried out calculations with the PBE (Ref. 66) functional and found that Au_7^- is calculated to be planar, whereas PBE makes both Cu_7^- and Ag_7^- 3D. Furche *et al.*⁵⁷ employed the BP86^{67,68} functional and found planar structures for Au_n^- up to $n=15$ (the highest n they considered). Another example of density functional theory predicting overly stable planar gold clusters is provided by the calculations of Landon *et al.*¹⁹ and Fa *et al.*²⁵ on neutral Au_n ; they found that the PW91 (Ref. 69) functional predicts the 2D \rightarrow 3D transition between $n=13$ and $n=15$ [recall that for neutral clusters the transition occurs at $n \approx 8$ (Ref. 21)]. Recently Johansson *et al.*⁵³ made a careful study of Au_n^- for $n=11-13$, in which they included a relativistic effective core potential to include scalar relativistic effects, spin-orbital coupling (which is a vector relativistic effect), a correction for correlating the core (the core is not correlated directly when one uses an effective core potential), zero-point vibrational energy, and thermal vibrational-

^{a)}Electronic mail: truhlar@umn.edu.

TABLE I. Relative energies (eV) for various structures of Au_n^- .

| n -SN ^a | dim. ^d | Johansson <i>et al.</i> ^b | | | | | | Present | | | |
|----------------------|-------------------|--------------------------------------|-------|-------|--------|-------|-------|---------|-------|------|-------|
| | | 1 ^c | 2 | 2 | 2 | 3 | 4 | 4 | 3 | 4 | 2 |
| | | LSDA | BP86 | PBE | PBEsol | TPSS | TPSSh | M05 | M06-L | M06 | SOGGA |
| 11-I | 2D | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 11-II | 3D | 0.08 | 0.22 | 0.21 | 0.15 | 0.19 | 0.20 | 0.10 | 0.06 | 0.03 | 0.06 |
| 11-III | 3D | 0.45 | 0.23 | 0.24 | 0.36 | 0.27 | 0.23 | 0.10 | 0.25 | 0.17 | 0.37 |
| 12-I | 3D | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 12-II | 2D | 0.19 | -0.56 | -0.44 | -0.06 | -0.17 | -0.16 | -0.11 | 0.40 | 0.11 | 0.19 |
| 13-II | 3D | 0.06 | 0.04 | 0.00 | 0.02 | 0.01 | 0.00 | 0.00 | 0.11 | 0.01 | 0.05 |
| 13-I | 3D | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 13-III | 2D | 0.59 | -0.17 | -0.06 | 0.32 | 0.23 | 0.26 | 0.34 | 0.93 | 0.57 | 0.54 |

^a n is the number of gold atoms; SN is the structure number assigned by Johansson *et al.* (Ref. 53).

^bReference 53.

^cThe number above each functional denotes the rung on Jacob's ladder of density functionals.

^dDimensionality.

rotational contributions. Including these “corrections,” they showed that the BP86 and PBE functionals predict 2D structures for $n=11-13$; the PBEsol,⁷⁰ TPSS,⁷¹ and TPSSh (Ref. 72) functionals predict 2D is lowest for $n=11$ and 12 but 3D is lowest for $n=13$; LSDA^{73,74} predicts that 2D is lowest for $n=11$ and 3D is lowest for $n=12$ and 13. Thus the LSDA functional leads to the best agreement with experiment and the PBEsol, TPSS, and TPSSh functionals predict the transition value of n to be only one atom higher than experiment ($n=13$ versus $n=12$). The authors did not explain the success of LSDA but they concluded that the good performance of PBEsol may be due to the PBEsol parametrization⁷⁰ to yield nearly exact jellium surface energies. While TPSS and TPSSh were not parametrized to make this model nearly exact, numerical tests⁷⁵ of various functionals show mean unsigned relative errors in the jellium surface exchange-correlation energy of 2.1% for LSDA and 4.9% for PBE but only 1.1% for TPSS and TPSSh. These values are consistent with LSDA, TPSS, and TPSSh performing better than PBE but do not explain why LSDA performs better than PBEsol. In the present article we test the M05,⁷⁶ M06-L,⁷⁷ M06,⁷⁸ and SOGGA (Ref. 79) functionals for Au_n^- with $n=11-13$.

II. CALCULATIONS

We use the same basis set [$7s5p3d1f$ (Ref. 61, 62, and 80)] and relativistic effective core potential [SDD (Ref. 81)] as

Johansson *et al.*⁵³ The effective core potential replaces the shells with principal quantum numbers 1–4 (with 60 electrons) and treats the remaining 19 electrons (11 valence electrons plus the outer-core $5s$ and $5p$ electrons) explicitly. All geometries are optimized consistently (in contrast with Johansson *et al.*⁵³ who used TPSS geometries for all density functionals). All calculations include the correction terms of Ref. 53, which are summarized in the Introduction. [We did recalculate the relative zero point energy with the new functionals considered here in several cases and found only small differences, typically 0.001–0.002 eV, therefore we elected to follow Johansson *et al.* and use the same set of correction

values for all functionals so that the tabulated relative energies directly reflect electronic energy differences (including nuclear repulsion as usual).] All calculations were carried out with an ultrafine grid using a locally modified version⁸² of the GAUSSIAN03 (Ref. 83) program. A spin multiplicity of 1 is used for Au_{11}^- and Au_{13}^- clusters and 2 is used for Au_{12}^- clusters.

III. RESULTS AND PRELIMINARY DISCUSSION

We label the structures as in Ref. 53. Table I gives the relative energies, referenced for each n to the structure that best fits the experimental data and that best-fit structure is listed first. A functional that predicts the dimensionality in agreement with experiment for every n would therefore give positive values for structures 11-II, 11-III, 12-II, and 13-III with zero for 11-I and 12-I and zero or either sign for structures 13-II and 13-I. The table shows that the LSDA, M06-L, M06, and SOGGA functionals predict the correct dimensionality in all three cases, PBEsol, TPSS, TPSSh, and M05 predict it correctly for two cases ($n=11$ and either $n=12$ or 13), and BP86 and PBE predict it correctly for only one case ($n=11$).

Accurate prediction of atomic $s \rightarrow d$ excitation energies (ΔE) is an important factor in the reliability of a density functional for a transition metal. In particular, the $s \rightarrow d$ excitation energy may be very important for predicting the right 2D \rightarrow 3D transition size of highly relativistic Au clusters because the magnitude of this orbital energy gap is directly related to the tendency to form sd^m hybrid orbitals and the tendency to form such orbitals may be directly related to the geometrical preferences for the coordination geometry of a Au atom.⁶⁵ Table II compares the $s \rightarrow d$ excitation energies of a single gold atom as predicted by the various density functionals we considered (the table also shows results for the popular B3LYP functional). Time-dependent DFT within the linear response approximation^{84–86} was used for the excitation energies. Table II shows that LSDA, the generalized gradient approximations (GGAs) (BP86, PBE, PBEsol, and SOGGA), the popular B3LYP, the metafunctional TPSS, and

TABLE II. Atomic $s \rightarrow d$ excitation energies ($d^{10}s^1 \rightarrow d^9s^2$, ΔE) and first IP ($d^{10}s^1 \rightarrow d^{10}$, IP) for Au atoms (in eV) with the SDD relativistic effective core potential and the $7s5p3d1f$ valence basis set.

| Functional | ΔE | IP |
|-------------------------|------------|-------|
| LSDA | 1.37 | 10.30 |
| BP86 | 1.39 | 9.67 |
| PBE | 1.44 | 9.48 |
| PBEsol | 1.42 | 9.55 |
| B3LYP | 1.59 | 9.38 |
| TPSS | 1.50 | 9.31 |
| TPSSh | 1.62 | 9.19 |
| M05 | 1.75 | 8.64 |
| M06-L | 1.73 | 8.95 |
| M06 | 1.80 | 9.02 |
| SOGGA | 1.45 | 9.43 |
| Experiment ^a | 1.74 | 9.22 |

^aTaken from Ref. 98. The $s \rightarrow d$ excitation energy is a degeneracy-weighted average of the experimental excitation energies to the $^2D_{3/2}$ and $^2D_{5/2}$ levels, which are split by spin-orbit coupling.

the hybrid meta functional TPSSh all seriously underestimate the $s \rightarrow d$ excitation energy, but the hybrid metafunctionals M05, M06-L, and M06 predict it reasonably accurately. Unfortunately, $s \rightarrow d$ excitation energy alone does not correlate well with the success or failure of the various density functionals to predict the n value of the 2D \rightarrow 3D transition; for example, M05 predicts the excitation energy more accurately than SOGGA, but SOGGA predicts the transition n value more accurately. Nevertheless, we can have more confidence in a functional that predicts both correctly.

The ionization potential (IP) is another important quantity that should be predicted correctly if one is to obtain reliable predictions of other properties for the right reason (rather than by cancellation of errors) and it is also a good check because it is sensitive to the relativistic effects that have a large effect on the properties of gold.^{87,88} (Relativistic effects increase the d orbital energy and decrease the s orbital energy;⁸⁸ this makes it easier to form hybrid orbitals.) Table II shows that several functionals (PBE, SOGGA, B3LYP, TPSS, TPSSh, M06-L, and M06) predict the IP within 0.3 eV (it was checked separately than the spin-orbit effect on the IP is negligible). Only M06-L and M06, however, are able to predict ΔE within 0.1 eV and the IP within 0.3 eV. Note that there is an anticorrelation between the values of ΔE and IP in that when the predicted ΔE increases, the predicted IP tends to decrease. This seems to indicate that most functionals situate the d orbitals at roughly the same energy, but the energy of the s orbital (equal to minus the IP) varies significantly depending on the functional.

IV. FURTHER DISCUSSION

Table I also gives the classification of the functionals according to the rungs of Jacob's ladder. The rungs of the ladder indicate the variables upon which the exchange-correlation functional F depends.⁸⁹ On rung 1, F depends on local spin densities. On rung 2, F also depends on the reduced gradients, s_σ , of these spin densities; such functionals are called GGAs. In the rung-3 functionals considered here,

one adds dependence on the local spin kinetic energy densities; functionals on this rung will be called metafunctionals. On rung 4, one adds some nonlocal exchange. The three functionals considered here that are on rung 4 are TPSSh, M05, and M06, and since they depend on spin kinetic energy density as well as Hartree-Fock exchange, we call them hybrid metafunctionals. To put the new results in perspective, we next discuss the performance of the functionals in the order in which they appear in Table I.

The LSDA performs remarkably well, considering its antiquity and simplicity. It has long been known though that the LSDA is more accurate for geometries than for energies⁹⁰ and that the LSDA is not a satisfactory functional for considering the energetics of transition metal systems.⁹¹⁻⁹⁴

BP86 and PBE are GGAs that are widely used for organometallic chemistry and solid-state physics, respectively. These functionals improve on the energetics of bond energies as compared to LSDA. For example, with a triple-zeta quality basis set the mean error averaged over databases of bond energies for transition metal dimers and bonds of transition metals to nonmetallic ligands are 1.25 eV for LSDA and 0.43 eV for BP86 and PBE.⁹³ However, as pointed out previously,⁵³ BP86 and PBE predict planar structures for all three cases and therefore miss the 2D \rightarrow 3D transition. The PBEsol functional was obtained by empirically changing two parameters in the PBE functional, one to fit jellium surface energies and the other to enforce the correct second-order dependence of exchange energy on s_σ (but not the correct second-order behavior of the whole exchange-correlation energy). Table I shows that PBEsol correctly predicts that Au₁₃⁻ has a 3D structure but incorrectly predicts the dimensionality for Au₁₂⁻. However it has been shown that for main-group atomization energies PBEsol increases the mean unsigned error per bond from 0.13 eV for PBE to 0.31 eV, so it might not be a good choice for modeling catalysis.

As compared to PBE, TPSS reduces the mean unsigned error for transition-metal bond energies to 0.30 eV (Ref. 93) and it reduces the mean unsigned error for main group atomization energies to 0.05 eV;⁷⁹ Table I shows that like PBEsol it predicts the 2D \rightarrow 3D transition only one unit of n too late. TPSSh substitutes 10% of the TPSS exchange by nonlocal Hartree-Fock exchange. Since 10% is a fairly small change, the functional is very similar to TPSS, with the mean errors for transition-metal bond energies and main-group atomization energies (which are always given on a per bond basis) changing to 0.36 (Ref. 93) and 0.04 eV,⁹⁵ respectively. TPSSh gives results very similar to those for TPSS in Table I.

Next we discuss the new results of the present article in chronological order of the development of the four functionals. The M05 functional was developed⁷⁶ as the first functional to be simultaneously reasonably accurate for transition-metal bond energies, main-group atomization energies, barrier heights, and noncovalent interaction energies. The former two errors are 0.27 (Ref. 96) and 0.04 eV (Ref. 76) and the mean unsigned error in barrier heights is 0.11 eV.⁹⁷ The barrier height error may be compared to barrier height errors of 0.63 eV for LSDA, 0.37 eV for BP86, 0.36 eV for PBE and PBEsol, 0.35 eV for TPSS, and 0.28 eV

for TPSSh.⁹⁷ On the basis of these comparisons, M05 would be a good functional for transition metal catalysis. M05 is a hybrid metafunctional like TPSSh, but it has 28% Hartree–Fock exchange. Table I shows performance roughly comparable to TPSSh for Au_n^- .

The M06-L functional⁷⁷ is a step back down to rung 3. The reason for this is that functionals on rungs 1–3 are much more economical (in terms of computer resources) for calculations on extended systems like solids or very large molecules. M06-L has mean unsigned errors of 0.22,⁷⁷ 0.04,⁷⁷ and 0.17 eV (Ref. 97) for transition-metal bond energies, main-group atomization energies, and barrier heights, respectively. Table I shows that it also correctly predicts the dimensionality of all three Au_n^- clusters.

Having improved the functional form of the exchange functional during the design of M06-L, we returned to rung 4 and incorporated this improved form, thereby replacing M05 with M06.⁷⁸ M06 has mean unsigned errors of 0.22,⁷⁸ 0.02,⁷⁸ and 0.10 eV (Ref. 97) for transition-metal bond energies, main-group atomization energies, and barrier heights, respectively, and it performs better than any other functional mentioned in this article for noncovalent interactions.⁷⁸ Table I again shows correct predictions of the dimensionality for all three Au_n^- clusters. Clearly either M06-L or M06 would be a good choice of functional for studying gold catalysis.

Finally we consider SOGGA. Whereas M05, M06-L, and M06 were designed with the goal of making a broadly successful functional, SOGGA—like PBEsol—was designed with a more specialized objective. Other differences from the M05, M06-L, and M06 functionals are that SOGGA is on rung 2 and it has no fitting parameters. Whereas PBEsol has two fitting parameters, SOGGA—like PBE—has none. SOGGA has a functional form similar to PBE and PBEsol, but the form is constrained theoretically to have the whole exchange-correlation energy depend correctly on s_σ through second order.⁷⁹ SOGGA leads to mean unsigned errors of 0.32 (Ref. 79) and 0.45 eV (Ref. 97) for main-group atomization energies and barrier heights and it was not designed to be used for calculating such quantities. It is interesting though that SOGGA performs 20% better than PBEsol for the lattice constants of 18 test solids for which PBEsol had been previously tested and it also performed 10% better for the geometry of hypervalent SF_6 , a factor of 2 better for the lattice constants of two phases of PbTiO_3 , and 7% better for the lattice constants of graphite and graphitic BN. The good accuracy for geometric predictions correlates well with the fact that Table I shows excellent performance for predicting the dimensionality of Au_n^- . Although SOGGA is not recommended in comparison to M06-L and M06, it does perform better than PBEsol, although it is equally simple (rung 2) and has no parameters determined by fitting.

LSDA performs much worse than PBEsol, TPSS, and TPSSh for the jellium surface energy and M06-L, M06, and SOGGA have not been tested for the jellium surface but probably do not do as well for that property as PBEsol, TPSS, and TPSSh do. Yet LSDA, M06-L, M06, and SOGGA do better than these functionals for predicting the 2D \rightarrow 3D transition in Au_n^- . This casts doubt on the hypothesis that the partial success of PBEsol, TPSS, and TPSSh follow from the

relatively accurate jellium surface energies of these functionals. The performance of the different functionals for properties of the gold atom such as $s \rightarrow d$ excitation energies and IP also do not show a clear correlation with the right prediction of the 2D \rightarrow 3D transition.

V. SUMMARY AND CONCLUSIONS

We tested four recent density functionals developed in our group for the 2D \rightarrow 3D transition of the most stable anionic clusters, Au_n^- , as a function of their size and for two properties of gold atoms. The 2D \rightarrow 3D transition is found experimentally to occur between $n=11$ and $n=12$ and we find that M06-L, M06, and SOGGA are the only functionals of those tested so far besides LSDA (which is known to be too inaccurate for modeling most chemical properties) that predict the 2D \rightarrow 3D transition at the correct value of n . The prediction of the right transition size does not correlate with the $s \rightarrow d$ excitation energy of the gold atom, as had been expected based on arguments of the importance of sd^m hybridization to the 2D \rightarrow 3D transition. Also, it is doubtful that the previously reported partial success of the PBEsol, TPSS, and TPSSh density functionals is due to their good performance on jellium surface energies. The accurate prediction of the 2D \rightarrow 3D transition size of Au clusters apparently results from a subtle interplay of energetic effects and there is no simple way to design density functionals that get this right. It is encouraging therefore that the M06-L and M06 functionals, which have been very successful for many transition metal bond energies and reaction energies, as well as for main group chemistry, perform well for the $s \rightarrow d$ excitation energy and the IP of gold atoms and for the cluster size at which the 2D \rightarrow 3D transition of anionic clusters occurs. Based on this good performance, the M06-L and M06 density functionals are recommended for simulating processes catalyzed by gold clusters.

ACKNOWLEDGMENTS

This work was supported in part by the Air Force Office of Scientific Research (AFOSR) by Grant No. FA9550-08-1-018.

¹M. Haruta, *Catal. Today* **36**, 153 (1997).

²M. Valden, X. Lai, and D. W. Goodman, *Science* **281**, 1647 (1998).

³G. C. Bond and D. T. Thompson, *Catal. Rev.-Sci. Eng.* **41**, 319 (1999).

⁴M. Haruta, *Chem. Rec.* **3**, 75 (2003).

⁵R. Meyer, C. Lemire, S. K. Shaikhutdinov, and H.-J. Freund, *Gold Bull.* **37**, 72 (2004).

⁶G. J. Hutchings and M. Haruta, *Appl. Catal.* **291**, 2 (2005).

⁷G. J. Hutchings, M. Brust, and H. Schmidbaur, *Chem. Soc. Rev.* **37**, 1759 (2008).

⁸G. Mills, M. S. Gordon, and H. Metiu, *J. Chem. Phys.* **118**, 4198 (2003).

⁹K. S. A. Varganov, R. M. Olson, M. S. Gordon, and H. Metiu, *J. Chem. Phys.* **119**, 2531 (2003).

¹⁰H. M. Lee, M. Ge, B. R. Sahu, P. Terakeshwas, and K. S. Kim, *J. Phys. Chem. B* **107**, 9994 (2003).

¹¹Q. Fu, H. Saltsburg, and M. Flytzani-Stephanopoulos, *Science* **301**, 935 (2003).

¹²C. Lemire, R. Meyer, S. Shaikhutdinov, and H.-J. Freund, *Angew. Chem. Int. Ed.* **43**, 118 (2004).

¹³L. Xiao and L. Wang, *Chem. Phys. Lett.* **392**, 452 (2004).

¹⁴M.-C. Daniel and D. Astruc, *Chem. Rev. (Washington, D.C.)* **104**, 293 (2004).

- ¹⁵G. J. Hutchings, *Gold Bull.* **37**, 3 (2004).
- ¹⁶N. Lopez, T. V. W. Janssens, B. S. Clasen, Y. Xu, M. Mavrikas, T. Bligaard, and J. K. Nørskov, *J. Catal.* **223**, 232 (2004).
- ¹⁷S. A. Varganov, R. M. Olson, M. S. Gordon, and H. Metiu, *J. Chem. Phys.* **120**, 5169 (2004).
- ¹⁸S. Chretien, M. S. Gordon, and H. Metiu, *J. Chem. Phys.* **121**, 3756 (2004).
- ¹⁹P. Landon, J. Ferguson, B. E. Solsona, T. Garcia, A. F. Carley, A. A. Herzing, C. J. Kiely, S. E. Golunski, and G. J. Hutchings, *Chem. Commun. (Cambridge)* **2005**, 3385.
- ²⁰T. M. Bernhardt, *Int. J. Mass Spectrom.* **243**, 1 (2005).
- ²¹R. M. Olson, S. Varganov, M. S. Gordon, H. Metiu, S. Chretien, P. Piecuch, K. Kowalski, S. A. Kucharski, and M. Musial, *J. Am. Chem. Soc.* **127**, 1049 (2005).
- ²²A. V. Walker, *J. Chem. Phys.* **122**, 094310 (2005).
- ²³Y. W. Heo, L.-C. Tien, and D. P. Norton, *J. Mater. Res.* **20**, 3028 (2005).
- ²⁴H. Grönbeck and P. Broqvist, *Phys. Rev. B* **71**, 073408 (2005).
- ²⁵W. Fa, C. Luo, and J. Dong, *Phys. Rev. B* **72**, 205428 (2005).
- ²⁶G. Li, J. Edwards, A. F. Carley, and G. J. Hutchings, *Catal. Today* **114**, 369 (2006).
- ²⁷M. Chen, Y. Cai, Z. Yan, and D. W. Goodman, *J. Am. Chem. Soc.* **128**, 6341 (2006).
- ²⁸L. M. Liu, B. McAllister, H. Q. Ye, and P. Hu, *J. Am. Chem. Soc.* **128**, 4017 (2006).
- ²⁹S. H. Overbury, V. Schwartz, D. R. Mullins, W. Yan, and S. Dai, *J. Catal.* **241**, 56 (2006).
- ³⁰Y.-K. Han, *J. Chem. Phys.* **124**, 024316 (2006).
- ³¹W. Fa and J. Dong, *J. Chem. Phys.* **124**, 114310 (2006).
- ³²L. Barrio, P. Liu, J. A. Rodriguez, J. M. Campos-Martin, and J. L. G. Fierro, *J. Chem. Phys.* **125**, 164715 (2006).
- ³³W. Ma and Y. Fang, *J. Nanopart. Res.* **8**, 761 (2006).
- ³⁴M. Diefenbach and K. S. Kim, *J. Phys. Chem. B* **110**, 21639 (2006).
- ³⁵A. Lechtken, D. Schooss, J. R. Stairs, M. N. Blom, F. Furche, N. Morgner, O. Kostko, B. von Issendorff, and M. M. Kappes, *Angew. Chem. Int. Ed.* **46**, 2944 (2007).
- ³⁶B. Yoon, P. Koskinen, B. Huber, O. Kostko, B. von Issendorff, H. Häkkinen, M. Moseler, and U. Landman, *ChemPhysChem* **8**, 157 (2007).
- ³⁷S. Chretien and M. Metiu, *J. Chem. Phys.* **126**, 104701 (2007).
- ³⁸M. Baron, D. Stacchiola, S. Ulrich, N. Nilus, S. Shaikhutdinov, H.-J. Freund, U. Martinez, L. Giordano, and G. Pacchioni, *J. Phys. Chem. C* **112**, 3405 (2008).
- ³⁹S. Bulusu, X. Li, L.-S. Wang, and X. C. Zeng, *J. Phys. Chem. C* **111**, 4190 (2007).
- ⁴⁰X. Gu, S. Bulusu, X. Li, X. C. Zeng, J. Li, X. G. Gong, and L.-S. Wang, *J. Phys. Chem. C* **111**, 8228 (2007).
- ⁴¹E. A. I. Shor, V. A. Nasluzov, A. M. Shor, G. N. Vayssilov, and N. Rösch, *J. Phys. Chem. C* **111**, 12340 (2007).
- ⁴²M. Sterrer, T. Risse, U. M. Pozzoni, L. Giordano, M. Heyde, H.-P. Rust, G. Pacchioni, and H.-J. Freund, *Phys. Rev. Lett.* **98**, 096107 (2007).
- ⁴³Y. Gao, N. Shao, and X. C. Zeng, *ACS Nano* **2**, 1497 (2008).
- ⁴⁴Y. Li, G. Galli, and F. Gygi, *ACS Nano* **2**, 1896 (2008).
- ⁴⁵H.-J. Freund and G. Pacchioni, *Chem. Soc. Rev.* **37**, 2224 (2008).
- ⁴⁶M. Chen and D. W. Goodman, *Chem. Soc. Rev.* **37**, 1860 (2008).
- ⁴⁷P. Pyykkö, *Chem. Soc. Rev.* **37**, 1967 (2008).
- ⁴⁸E. S. Kryachko and F. Remacle, *Int. J. Quantum Chem.* **107**, 2922 (2007).
- ⁴⁹V. Simic-Milosevic, M. Heyde, N. Nilus, T. König, H.-P. Rust, M. Sterrer, T. Risse, H.-J. Freund, L. Giordano, and G. Pacchioni, *J. Am. Chem. Soc.* **130**, 7814 (2008).
- ⁵⁰G. Pacchioni, S. Siculo, C. Di Valentin, M. Chiesa, and E. Giamello, *J. Am. Chem. Soc.* **130**, 8690 (2008).
- ⁵¹T. A. Baker, C. M. Friend, and E. Kaxiras, *J. Chem. Phys.* **129**, 104702 (2008).
- ⁵²A. Castro, M. A. L. Marques, A. H. Romero, M. J. T. Oliveira, and A. Rubio, *J. Chem. Phys.* **129**, 144110 (2008).
- ⁵³M. P. Johansson, A. Lechtken, D. Schooss, M. Kappes, and P. Furche, *Phys. Rev. A* **77**, 053202 (2008).
- ⁵⁴Y. Chen, P. Hu, M.-H. Lee, and H. Wang, *Surf. Sci.* **602**, 1736 (2008).
- ⁵⁵T. V. W. Janssens, B. S. Clausen, B. Hvolbaek, H. Falsig, C. H. Christensen, T. Bligaard, and J. K. Nørskov, *Top. Catal.* **44**, 15 (2007).
- ⁵⁶D. M. Cox, R. Brickman, K. Creegan, and A. Kaldor, *Z. Phys. D: At., Mol. Clusters* **19**, 353 (1991); D. M. Cox, R. Brickman, K. Creegan, and A. Kaldor, *Mater. Res. Soc. Symp. Proc.* **206**, 43 (1991).
- ⁵⁷F. Furche, R. Ahlrichs, P. Weis, C. Jacob, S. Gilb, T. Bierweiler, and M. Kappes, *J. Chem. Phys.* **117**, 6982 (2002).
- ⁵⁸H. Häkkinen, B. Yoon, U. Landman, X. Li, H.-J. Zhai, and L.-S. Wang, *J. Phys. Chem. A* **107**, 6168 (2003).
- ⁵⁹X. Xing, B. Yoon, U. Landman, and J. H. Parks, *Phys. Rev. B* **74**, 165423 (2006).
- ⁶⁰C. Zhang, B. Yoon, and U. Landman, *J. Am. Chem. Soc.* **129**, 2228 (2007).
- ⁶¹P. Weis, O. Welz, E. Wollmer, and M. M. Kappes, *J. Chem. Phys.* **120**, 677 (2004).
- ⁶²S. Gilb, P. Weis, F. Furche, R. Ahlrichs, and M. M. Kappes, *J. Chem. Phys.* **116**, 4094 (2002).
- ⁶³P. Weis, T. Bierweiler, S. Gilb, and M. M. Kappes, *Chem. Phys. Lett.* **355**, 355 (2002).
- ⁶⁴Z. H. Li, A. W. Jasper, and D. G. Truhlar, *J. Am. Chem. Soc.* **129**, 14899 (2007).
- ⁶⁵H. Häkkinen, M. Moseler, and U. Landman, *Phys. Rev. Lett.* **89**, 033401 (2002).
- ⁶⁶J. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ⁶⁷A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ⁶⁸J. P. Perdew, *Phys. Rev. B* **33**, 8822 (1986).
- ⁶⁹J. P. Perdew, in *Electronic Structure of Solids, '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), pp. 11–20.
- ⁷⁰J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Lett.* **100**, 136406 (2008).
- ⁷¹J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).
- ⁷²V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, *J. Chem. Phys.* **119**, 12129 (2003); **121**, 11507(E) (2004).
- ⁷³W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ⁷⁴J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- ⁷⁵V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, *Phys. Rev. B* **69**, 075102 (2004).
- ⁷⁶Y. Zhao, N. E. Schultz, and D. G. Truhlar, *J. Chem. Phys.* **123**, 161103 (2005).
- ⁷⁷Y. Zhao and D. G. Truhlar, *J. Chem. Phys.* **125**, 194101 (2006).
- ⁷⁸Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* **120**, 215 (2008); **119**, 525(E) (2008).
- ⁷⁹Y. Zhao and D. G. Truhlar, *J. Chem. Phys.* **128**, 184109 (2008).
- ⁸⁰A. Schweizer, J. M. Weber, S. Gilb, H. Schneider, D. Schoos, and M. M. Kappes, *J. Chem. Phys.* **119**, 3699 (2003).
- ⁸¹D. Andrae, U. Haeusserman, M. Dolg, H. Stoll, and H. Preuss, *Theor. Chim. Acta* **77**, 123 (1990).
- ⁸²Y. Zhao and D. G. Truhlar, *MN-GFM-Version 4.1* (University of Minnesota, Minneapolis, 2009).
- ⁸³M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al.*, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
- ⁸⁴R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.* **256**, 454 (1996).
- ⁸⁵M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, *J. Chem. Phys.* **108**, 4439 (1998).
- ⁸⁶R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, *J. Chem. Phys.* **109**, 8218 (1998).
- ⁸⁷K. S. Pitzer, *Acc. Chem. Res.* **12**, 271 (1979).
- ⁸⁸P. Pyykkö and J. P. Desclaux, *Acc. Chem. Res.* **12**, 276 (1979).
- ⁸⁹J. P. Perdew and K. Schmidt, *AIP Conf. Proc.* **577**, 1 (2001).
- ⁹⁰W. Kohn, *Rev. Mod. Phys.* **71**, 1253 (1999).
- ⁹¹F. S. Legge, G. L. Nyberg, and J. B. Peel, *J. Phys. Chem. A* **105**, 7905 (2001).
- ⁹²G. T. de Jong, D. P. Geerke, A. Diefenbach, and F. M. Bickelhaupt, *J. Chem. Phys.* **123**, 261 (2005).
- ⁹³N. E. Schultz, Y. Zhao, and D. G. Truhlar, *J. Phys. Chem. A* **109**, 11127 (2005).
- ⁹⁴F. Furche and J. P. Perdew, *J. Chem. Phys.* **124**, 044103 (2006).
- ⁹⁵Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A* **109**, 5656 (2005).
- ⁹⁶Y. Zhao, N. E. Schultz, and D. G. Truhlar, *J. Chem. Theory Comput.* **2**, 364 (2006).
- ⁹⁷J. Zheng, Y. Zhao, and D. G. Truhlar, *J. Chem. Theory Comput.* **5**, 808 (2009).
- ⁹⁸C. E. Moore, *Natl. Bur. Stand. Circ. (U.S.)* **467**, 3/186 (1958).