
The Application of Effective Core Potentials in Heavy Atom Molecules: A Study of Small Gold Clusters and Molecules as a Function of Theoretical Method

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ABSTRACT: *Geometric parameters and energies have been calculated for the ground and first excited states of the gold dimer using effective core potentials (ECPs) and a range of standard density functional theory (DFT) models. After initial evaluation, the B3P86 theoretical model was the procedure employed, although other DFT methods provided similar results, based on comparison of the equilibrium bondlength and dissociation energy to experimental values. A number of ECPs were evaluated, and those potentials for which the valence electrons are described by at least a double zeta quality representation all provide similar predictions for the parameters of gold dimers and tetramers. These predictions were in good agreement with the results of more extensive calculations and experiment. The LANL2 ECP for Au combined with the B3P86 density functional method proved effective in reproducing the accepted structure of a number of small organogold molecules. The implication is that the relativistic terms are adequately represented by the ECP and that standard, computationally cost-effective methods may be used for large cluster-ligand molecules. The results are expected to be useful in the continuing study of small gold clusters and gold clusters modified with organic ligands. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 651–657, 1998*

INTRODUCTION

Gold clusters have been the subject of much recent experimental and theoretical interest [1–3]. Naked gold clusters of as many as 55 atoms, as well as polynuclear clusters in which ligands are used to modify the cluster properties, are the particular foci of these studies. The cluster studies aim to explore whether or not the Au₅₅ cluster has metallic properties and whether the attachment of ligands to this cluster can be used to tune those properties. A number of substituted clusters have been prepared [4–6]. In general, these clusters are large and pose computational challenges owing to the number of electrons in the molecule. To test the applicability of various theoretical methods, a number of simpler, ligand-substituted clusters have been used as models for the larger molecules of interest, and the gold dimer has been used as a test system for the naked clusters. An additional challenge for the calculation of the properties of gold-containing molecules is the importance of relativistic effects. Many of the interesting characteristics of these compounds may be attributed to these effects. A description of even the model compounds just noted must take relativistic effects into account.

There have been a number of previous computational studies of gold clusters and organogold complexes. A number of these structure calculations for gold-containing molecules involved extensive basis sets and relativistic computational methods. These have been both all-electron and frozen core calcu-

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lations, using both *ab initio* methods as well as relativistic variants of density functional theory (DFT). For example, Lamare and Michel-Calandini [7] have explored the structure of the Au₁₃ cluster using the local density approximation (LDA) framework. Rösch and co-workers [8] have developed a quasi-relativistic variant of the linear combination of Gaussian-type orbitals density functional (LCGTO-DF) method and applied it extensively to naked and ligated gold clusters as well as to ligated single Au atoms [9]. The method employs large basis sets and has been shown to be very effective in reproducing available experimental data. Boettger [10] has recently explored some of the approximations used in the LCGTO-DF method and found that the basis set dependence for atoms in which relativistic effects are important, such as Au, are no greater than for nonrelativistic cases. Belanzoni, et al. [11] employed the Amsterdam Density Functional suite of programs to complete relativistic calculations for polynuclear aryl derivatives of metals that included gold, using the basis sets delivered within the software. The results indicated an increasing stability with cluster size, but little variation in the Au–Au bond-length. Finally, Matusuoka [12] and Watanabe and Matusuoka [13] applied the Dirac-Fock-Roothan method and contracted basis sets to gold and other heavy atoms with excellent results.

The performance of DFT as applied to metal-containing molecules has recently become a focus of research. The reasons are clear, in that the computational savings for systems with large numbers of electrons, for example metals, are significant. Deeth and Jenkins [14] have compared the accuracy of the LDA method [15] with the more complex gradient corrected methods of Becke [16–18] and found the latter superior for divalent octahedral metal complexes. Perhaps more relevant to the studies described here, Bach and coworkers [19] have examined the performance of DFT methods combined with effective core potentials (ECPs) as applied to iron-containing compounds and found the results in good agreement with available experimental data and/or higher level calculations. We have been interested in the relative merits of various *ab initio* and DFT techniques as applied to radicals and molecules found in chemical vapor deposition systems and other nanoscale and mesoscale processes. Our previous work, as well as that of other groups [20] has shown that perturbation methods are not sufficient for these particular metal-containing systems and that configuration interaction (CI) calculations and the CASSCF method are often equivalent in their agreement with experiments. Perhaps more importantly, we have shown that for many systems, DFT

outperforms the CI calculations when the two techniques are applied to the computation of ground-excited state energy differences and bond dissociation energies. Moreover, DFT generally involves a significantly reduced computational cost.

There have been two recent reviews of the accuracy of relativistic ECPs applied to metal-containing systems. Basch [21] examined small molecules containing Ag, Au and Ni and found the potentials to be effective in describing the molecules. Titov and Mosyagin [22] explored the applicability of relativistic ECPs to Au, Ag and Cu with similar results. Two of the most common basis sets available for gold and involving an ECP representation for the core electrons, including relativistic or quasirelativistic corrections, are those from the Los Alamos National Laboratory, known as LANL2MB and LANL2DZ and developed by Hay and Wadt [23]. These share the same relativistic core potential, but use a minimal basis set and a basis set of double zeta quality, respectively, for the valence electrons. The SBKJC basis set [24] also involving a relativistically corrected ECP for the core electrons, is similar in quality and performance to the LANL2DZ basis set. Pitzer and coworkers [25] proposed alternative ECP-based basis sets and tested the applicability [26] using molecules such as Au₂⁺, TlH and PbSe. Spin-orbit splittings were adequately represented, and the results were in good agreement with numerical Dirac-Hartree-Fock calculations. Other reported ECP basis sets include a very successful basis set (SC) developed by Schwerdtfeger [27], an energy-adjusted potential (PR) reported by Preuß, et al. [28,29] and two different potentials from Ermler and coworkers [30] one with a small core potential and a large basis set (CREL) and one having a large core potential and a small basis set (CRES).

In this article, we employ a series of standard theoretical models with various effective core potentials for the gold atom, to assess the applicability of cost-effective techniques to the calculation of molecular properties. The target molecules are the gold dimers and tetramers as well as simple gold–ligand complexes. The goal is to determine whether these methods are suitable for the relative study of ligand substitution in attempts to fundamentally change the physical properties of gold clusters of interest to experimentalists. Comparison is made with literature results employing higher level relativistic calculations and more extensive basis sets. Discussion of the suitability of the ECPs to structure calculations of large ligated clusters is presented.

COMPUTATIONAL METHODS

Calculations were carried out using the Gaussian 94 system of programs [31]. The only Au-containing

ECP basis set included as part of the computational package is LANL2DZ, which uses the LANL2 effective core potential for the heavy atoms and a double zeta basis set for the lighter atoms. Other ECPs are available and have previously been described here. These potentials were entered as custom basis sets. All of these ECPs include relativistic corrections in the core potential. The advantage of these potentials is that no compensation is required in the theoretical method and the standard techniques may be readily applied. We have applied three DFT models, B3LYP, B3PW91 and B3P86, to gold atoms, gold dimers, and tetramers and to simple organogold molecules.

Initial geometry optimizations were performed at the HF/LANL2DZ level to locate the lowest energy singlet and triplet structures. These minimized structures were further optimized using the DFT theoretical models with the LANL2DZ basis set. No symmetry constraints were imposed on any of the structural calculations. Harmonic vibrational frequencies were also calculated at each level of theory to confirm a structure as a stationary state. Subsequently, the theoretical method was fixed at B3P86 and each of the ECPs was implemented in a comparison test. Again, harmonic frequencies, dissociation energies, and singlet-triplet energy differences were computed in the absence of symmetry constraints. Some of the ECPs could not be combined with density functional methods for optimization using the standard Gaussian convergence criteria for optimization. In these cases, reduced convergence criteria were used to generate an improved starting point and the standard criteria were employed in subsequent calculations.

Finally, the same theoretical methods were applied, using the LANL2 ECP for Au and the 3-21G* basis set for all other atoms, to simple gold-containing molecules to test the applicability of these simple techniques to "real" compounds. Included among these molecules were Au₂(PH₃)₂, CH₃Au(PR₃)₃, Au_n(C₆H₅)_n, AuCH₃ and, most extensively, CH₃AuPH₃. The goal here was to test whether the selection of a computational method, based on the results for Au and Au₂, was also valid for the larger organogold structures. Selected calculations using the more extensive 6-31G* basis set for the light atoms were also completed.

RESULTS AND DISCUSSION

Atomic Properties

The logical first check on the suitability of effective core potentials (and DFT) involves calculation of the atomic ionization potential. The results, obtained with the LANL2DZ basis set, indicate that all three

DFT models do a reasonably good job in the representation of the inner electrons of Au. Two of the DFT models, B3LYP and B3PW91, provide agreement, within approximately 2% of the experimental value, for the ionization potential (IP) (9.45 eV and 9.36 eV, respectively, in comparison to 9.22 eV). The B3P86 method provides a result within approximately 7% of the experimental value. These results indicate that in spite of the difficulties DFT is known to have with excited states, the LANL2DZ effective core potential provides adequate representations of the ground state Au atom and ion and, moreover, confirm that the use of standard, nonrelativistic techniques, with the relativistic effects accounted for by the effective core potential, is a feasible method for the study of gold-containing molecules.

The effectiveness of the various effective core potentials was examined by applying the B3P86 method with all possible ECP representations. Table 1 indicates that the agreement between the experimental IP and the calculated values is similar for most of the ECPs. The minimal valence representation CRES potential provides the best agreement for the ionization. Comparison is also made in Table 1 to previously calculated values of the IP. The best agreement with the current work is found with the results of a study using a related DFT technique and the LANL2MB basis set [32]. The remaining literature results include a Hartree-Fock (HF) calculation [27] employing an earlier version of the LANL2MB basis set (designated as PP), configuration interac-

TABLE 1 Atomic and Diatomic Results as a Function of ECP, Using the B3P86 DFT Model

ECP	IP, eV (Au)	r_e , Å (Au ₂)	D_e , kJ mol ⁻¹ (Au ₂)
Current work			
LANL2MB	9.91	2.646	147
LANL2DZ	9.95	2.540	195
SBKJC	9.81	2.541	197
SC	9.87	2.553	184
PR	9.99	2.550	191
CRES	9.10	2.556	175
CREL	9.95	2.533	196
Previous work			
PP [28]	7.66	—	—
QCISD(T) [28]	8.93	2.537	205
CI(SD) [30]	8.75	2.536	—
CEPA1 [42]	8.78	2.539	—
LCGTO-DF [8]	9.89	2.47	278
B3PW91 [33]	9.34	2.547	182
Expt.	9.22 [34]	2.472 [35]	222 [35]

ECP = effective core potential; DFT = density functional theory; IP = ionization potential.

tion calculations at both the singles + doubles level [28] and also with triplet energy corrections [8], the LCGTO-DF method described earlier [8] and a coupled electron pair approximation (CEPA) calculation using a pseudopotential [33]. With the exception of the LCGTO-DF results, all of these cited calculations underestimate the IP. In general, all three of the DFT methods and all of the ECPs may be noted as providing satisfactory agreement with the experimental values.

Au₂ and Au₄

The results of a series of bondlength and dissociation energy calculations for the gold dimer, for which the basis set has been fixed at LANL2DZ and the three DFT methods are employed, indicated that the B3P86 method was slightly superior to the other two techniques. This conclusion is derived from a comparison of the calculated bondlength values ($r_e = 2.574\text{\AA}$, 2.547\AA , and 2.540\AA , for B3LYP, B3PW91, and B3P86, respectively) to the experimental value shown in Table 1, as well as comparison of the calculated dissociation energies ($D_e = 181$, 183 and 195 kJ mol^{-1} , respectively). Table 1 contains a comparison of the calculated dimer bondlength and dissociation energies as a function of the ECP. In this comparison, the minimum valence basis set/effective core potentials (LANL2MB and CRES) do not fare well as those of at least double zeta quality, whereas the remaining ECPs provide similar results. The conclusion is that for atomic and diatomic gold, all the ECPs adequately represent the core electrons, and it is the quality of the valence electron representation that differentiates the final computational results. With the exceptions already noted all the representations are of at least double zeta quality. We note that the current results, with the exception of the bondlength agreement provided by the LCGTO-DF method, are at least equal to all of the previous calculations in terms of agreement with experiment. The calculated dissociation energy from the current work does provide better agreement with experiment than the LCGTO-DF result. Our predicted ground state harmonic frequency is 173 cm^{-1} from the B3P86/LANL2DZ calculation. This is within approximately 9% of the experimental value [35] of 191 cm^{-1} .

The calculations were also used to explore the lowest triplet state of the dimer. The standard sources of experimental data do not indicate the existence of a triplet state at low excitation energies, and our results give an indication of why this is so. The binding energy of the triplet is estimated by the B3P86/LANL2DZ model to be 21 kJ mol^{-1} . In fact,

an HF calculation does not predict a bound triplet molecule at all. The equilibrium bondlength, by means of the same DFT model, is predicted to be 2.927\AA . A triplet state harmonic frequency of 72 cm^{-1} results from the calculations. The only other prediction of a bound triplet state has just appeared in the literature [32] using a minimum basis set representation for the valence electrons. The predicted bondlength was longer than that from the current work, 2.961\AA vs. 2.927\AA , and, correspondingly, a weaker bond was predicted ($D_e = 12$ kJ mole^{-1} vs. 21).

The final test of the suitability of various effective core potentials was the calculation of the structural and energetic parameters for the gold tetramer. The results are shown in Table 2. Initial geometries were assumed to be planar in a rhombus configuration after the recent work of Bauschlicher, et al. [1]. With a single exception (LANL2MB), variation of the ECP does not have a significant effect on the calculated geometry, but it does impact the energy for dissociation into dimers. The minimal basis sets result in a low value for this dissociation process using the B3P86 model. The highest dissociation energy resulted from use of the LANL2DZ representation. One comparison point, shown in Table 2, is the modified coupled pair functional approach using the equivalent of the LANL2MB basis set. There is a second calculation in Table 2, available from the recent literature [33], in which the authors report that the minimum energy configuration, based on a calcula-

TABLE 2 Tetramer Results as a Function of ECP Using the B3P86 DFT Model

ECP	r_e , \AA	α°	$\Delta E, E(\text{Au}_4) - 2E(\text{Au}_2)$, kJ mol^{-1}
LANL2MB	2.846	61.1	76
LANL2DZ	2.729	61.1	195
SBKJC	2.709	60.7	134
SC	2.730	61.0	121
PR	2.723	60.9	124
CRES	2.709	61.2	101
CREL	2.700	60.9	134
LANL2DZ (isosceles form)	2.750 (2) 2.602 2.552	—	195
MCPF/MB [1]	2.732	58.8	173
B3PW91/DZ [33] (isosceles form)	2.761 (2) 2.608 2.560	—	110

All structures are of the rhombus form, unless noted.
ECP = effective core potential; DFT = density functional theory.

tion very similar to our own, is a substituted tricyclo molecule. We have also calculated the energy of this isomer using the same B3P86/LANL2DZ model that resulted in the rhombus geometry and find that the isosceles form has essentially the same energy as the rhombus, indicating that the predicted geometry for this polymer is still uncertain and additional experimental effort is necessary.

Organogold Molecules

One of the simplest organogold molecules and an excellent test case for the applicability of relativistic ECPs to this class of molecules is CH_3AuPH_3 , a model for the more realistic gold methyltriphenylphosphine. For these studies, the set of theoretical methods has been combined with a basis set consisting of the LANL2DZ representation for the gold atom and the 3-21G* basis set for the light atoms. The basis set will be our "standard." The results reported in previous sections for the smaller fragments, indicate similar agreement of all ECPs with more extensive calculations or experiment. Selection of LANL2DZ as the standard is arbitrary. Although more elaborate basis sets could be chosen for the light atoms, the exploratory nature of this study led us to use of the simpler one cited and relegated the more elaborate basis sets to selected studies.

Differences in bond angles and C–H and P–H bondlengths, with variation in the DFT technique, are minimal, as expected. The remaining structural results are shown in Table 3. The difference in theoretical method is evident in a comparison of the Au–P and Au–C bondlengths. The experimental values are unknown, but the experimental results [36] for the trimethylphosphine rather than PH_3 ligand are 2.03 Å and 2.28 Å for Au–C and Au–P, respectively. Table 3 shows both bondlengths to be decreasing, with the B3P86 method providing a value closer to that one might expect from experiment. Our results provide good agreement in comparison to the experi-

TABLE 3 CH_3AuPH_3 Bondlengths (Å) as a Function of DFT Model Using LANL2DZ^a with 3-21G*^b

DFT model	Au–P, Å	Au–C, Å
B3LYP	2.402	2.078
B3PW91	2.366	2.062
B3P86	2.360	2.058
LCGTO-DF [8]	2.29	2.00
Expt ^c	2.28	2.03

^aBasis set for Au.

^bBasis set for C, H, and P.

^cReference 36, experimental data for $\text{CH}_3\text{AuP}(\text{CH}_3)_3$.

DFT = density functional theory.

mental properties. The only previous study has been that of Rösch et al. [8] and Häberlen and Rösch [9], using the LGGTO-DF method and a large basis set. The authors report a Au–C bondlength of 2.00 Å and a Au–P bondlength of 2.29 Å, nearly identical to the experimental values.

To assess the error introduced by use of the 3-21G* rather than, for example, the 6-31G* basis set for the light atoms, we used the latter along with the LANL2DZ ECP in both HF and B3P86 calculations. The Au–P and Au–C bondlengths were calculated to be 2.469 Å and 2.084 Å for the HF model and 2.413 Å and 2.100 Å in the DFT model. The agreement with experiment is not as good as it was in the case of the smaller basis set for the lighter atoms.

The choice of DFT method, from among the three sampled, did not appear to be a critical factor. For ease of application, the goal in this study, the B3P86 was chosen as the median in effectiveness and computational simplicity. This method, combined with the LANL2 ECP and the 3-21G* basis set for light atoms, was applied to the remaining organogold molecules.

Two molecules that extend the discussion of atoms and dimers are $\text{Au}_2(\text{PH}_3)_2$ and $\text{CH}_3\text{Au}(\text{PCH}_3)_3$. We were particularly interested in the Au–Au bondlength, in comparison with the naked dimer, of the former and in any changes of the Au–P and Au–C bondlengths in comparison to CH_3AuPH_3 in the latter. The relevant results are shown in Table 4. The agreement with previously reported values is also shown in Table 4. The Au–P and Au–C bondlengths in the trimethylphosphine ligated molecule are

TABLE 4 Calculated Bondlengths (Å) for Organogold Molecules Using the B3P86 DFT Model and LANL2DZ^a with 3-21G*^b

Molecule/ <i>r</i> _e	B3P86	Other studies
$\text{CH}_3\text{AuP}(\text{CH}_3)_3$		
Au–P	2.390	2.25 [36]
Au–C	2.110	2.03
$\text{Au}_2(\text{PH}_3)_2$		
Au–Au	2.547	—
Au–P	2.394	—
AuCH_3		
Au–C	2.041	2.017 [37]
AuC_6H_5		
Au–C	1.992	1.98 [37]
$\text{Au}_2(\text{C}_6\text{H}_5)_2$		
Au–Au	2.651	2.65 ^c
Au–C	2.000	2.03

^aBasis set for Au.

^bBasis set for C, H, and P.

^cReference 11; results are for the pentamer.

DFT = density functional theory.

slightly longer than in the parent molecule. This may be attributed to the electron-rich nature of the methyl substitution in comparison to the hydrogen atom. In the gold phosphine dimer molecule, the Au–Au bondlength is nearly identical to that calculated for the naked gold dimer. The phosphine ligand does not seem to have any effect on the metal–metal bond. No literature comparison is available for this molecule.

The effect of the size of the organic molecule bound to the metal atom may be examined by a comparison of the AuCH₃ and AuC₆H₅ ground state species. The length of the Au–C bond varies by less than 3%, but a comparison between the bondlengths calculated in this study and those from a CCSD(T) study [37] using a relativistic pseudopotential [28,29] are in excellent agreement. The final comparison is between the monomer and dimer of AuC₆H₅ in Table 4. The Au–C bondlength of the dimer is approximately equal to that of the monomer, and the Au–Au bondlength in the dimer is somewhat longer than that of the phosphine dimer and nearly identical to that of the AuC₆H₅ pentamer calculated by a relativistic DFT method using an all electron basis set [11]. The results indicate that the computational method utilized for these smaller complexes provides great promise, at a reasonable computational effort, for larger molecules as well.

SUMMARY

Our calculations involving simple gold molecules, employed as models for more elaborate gold complexes, have been carried out using several different relativistic ECPs and three different DFT techniques. The results lead to the following conclusions:

1. ECPs, in conjunction with density functional methods such as B3P86, are capable of providing reliable structural results for small gold clusters and small organogold molecules at a reasonable computational cost for complete optimization. The available ECPs tested provided adequate representation of the core electrons, including relativistic effects. A minimum of double zeta quality is required for the representation of the valence electrons, however, a number of ECPs provide such quality and result in approximately equivalent results.
2. B3P86/3-21G*-LANL2 calculations should provide reasonable estimates of the relative properties of larger organogold molecules and organogold clusters. The use of these

ECP calculations will provide data, not easily obtained by higher-order calculations, for a number of systems of interest.

3. More elaborate basis sets for the light atoms do not appear to improve agreement with experimental results for organogold molecules.

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