

Assessing the validity of theoretical results

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Abstract. We present recent theoretical results for the V_3 and Au_4 clusters. Calculations of the V_3 doublet system indicate that the 6-311+G(d) basis set is sufficiently flexible to provide reliable minimum energy structures and vibrational frequencies, that these structures and frequencies are insensitive to spin contamination of the wave function when the BPW91 functional is used, and that changing to the B3LYP functional may result in very different structures and frequencies. A computationally less expensive scalar relativistic treatment of Au_4 clusters gives structural properties that are in good agreement with those obtained using a four-component method.

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1 Introduction

Results obtained from different theoretical methods can sometimes show substantial disagreement, and it may be difficult to identify which result and/or method is the most reliable. In this paper we discuss results obtained from previous and current investigations of the V_3 and Au_4 clusters, highlighting discrepancies in the results and shedding light into possible reasons for these discrepancies.

The structure of the neutral V_3 cluster has recently been calculated by three groups [1–3], with each group obtaining a different minimum energy structure. Grönbeck and Rosén (hereafter referred to as GR) [1] obtained an acute isosceles triangular structure, Wu and Ray (referred to as WU) [2] obtained an obtuse isosceles structure and Calaminici *et al.* (referred to as CA) [3] obtained an equilateral triangular structure. Although all three groups used density functional theory (DFT), they used different basis sets and different functionals, hence making it difficult to assess (purely on a theoretical basis) which result is the most reliable.

Additional complications that may arise when performing DFT calculations of the V_3 cluster concern spin contamination and spin polarization. For example, CA used a restricted wave function since their unrestricted calculations yielded an optimized wave function that was significantly spin contaminated. However, although the restricted calculations ensure that the wave function is spin uncontaminated, spin polarization is excluded. Since the effect of spin polarization on the minimum energy structure and vibrational frequencies is not known, it is difficult

to assess the quantitative reliability of data obtained from restricted DFT calculations.

In this paper we present new calculations of the V_3 cluster aimed at providing insight into the reasons for the differences in the previous results. The DFT method with the BPW91 [4] and B3LYP [5] functionals are used to study the effect of spin polarization, spin contamination and changes in basis set size on the minimum energy structures.

The other investigation reported here concerns gold clusters, which have been the focus of attention in many recent studies [6–8]. The gold atom has the peculiarity that, compared to all other elements, it has very strong relativistic effects caused mainly by the relativistic stabilization and the contraction of the $6s$ orbital (the gold maximum, [9]). Thus, from a methodological point of view, clusters or compounds containing gold atoms are a “test-field” of computational methods since a valid description of the relativistic effects is required. In quantum chemical calculations, these effects can be included on different levels of theory. In the scalar relativistic approaches, the Hamiltonian is diagonalized in the basis of one-component wave functions. Relativistic effects are included perturbatively by adding the expression for the mass-velocity and Darwin contribution. The two-component approaches are designed to treat the spin-orbit coupling to some extent on the basis of the double point group symmetry. The use of these less computationally expensive schemes, compared with a fully four-component approach, makes them more suitable for quantum chemical applications, at least for s -bound systems. We present the results for planar rhombic D_{2h} tetramer in this contribution.

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2 Computational methods

2.1 The V_3 cluster

Standard optimization methods available in the Gaussian suite of programs [10] were used to obtain the minimum energy V_3 structures. This software provides the option of using restricted or unrestricted DFT with the standard BPW91 and B3LYP functionals, as well as offering 6-311+G(d) and 6-311+G(3df) basis sets. These basis sets are used in this study to determine the effect of increasing the wave function flexibility on the minimum energy structure and vibrational frequencies. The software also determines the spin of (unrestricted) wave functions, which should correspond to $S^2 = 0.75$ for a doublet wave function. All optimizations were performed on a 195 MHz R10000 SGI processor.

2.2 The Au_4 cluster

The geometrical structure of the Au_4 cluster was investigated within a four-component relativistic DFT [11]. Extended numerical basis sets including $5f$, $6p$ and $6d$ wave functions were used in order to be more complete and to provide flexibility in the valence region. In the method used here, the relativistic local density approximation and semi-local schemes *via* different types of the relativistic generalized gradient approximation can be applied [12]. Particularly, we have used the Becke 88 functional for the exchange [13] and the Perdew 86 functional [14] for the correlation.

3 Results and discussion

3.1 The V_3 cluster

Fig. 1 shows the three minimum energy structures obtained in the previous calculations [1–3]. These structures were used as starting geometries for the optimizations performed in the present study. The structure in panel A, which is a V_3 doublet, was obtained by GR using a local spin density (LSD) functional, augmented with gradient corrections according to Becke and Perdew [1]. A triple-zeta basis set with polarization functions was used in the calculations, which were spin restricted. The structure in panel B was obtained by WU using the BPW91 functional and a 6-311G basis set [2]. The structure in panel C, which is also for a doublet wave function, was obtained by CA using the Perdew and Wang (PW86) and Perdew (P86) generalized gradient approximation in conjunction with the local exchange correlation proposed by Vosko, Wilk and Nusair [15]. The calculations were based on a DZVP basis set optimized for gradient corrected functionals [3]. This structure was obtained using a restricted wave function since, as mentioned above, there was significant spin contamination in their optimized unrestricted wave function (the unrestricted calculations yielded the quartet state as the ground electronic state).

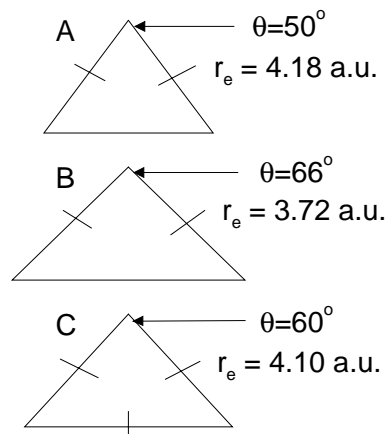


Fig. 1. The three minimum energy V_3 structures obtained in previous studies [1–3] and that were used as initial structures in the present geometry optimizations.

The present work focuses solely on the doublet electronic state, which is the state identified as the ground state in at least two of the previous studies. The quartet state will be considered in future investigations.

Optimization using the BPW91 functional with a 6-311+G(d) basis set and an unrestricted wave function gave the following results: When the initial geometry was that obtained by GR (Fig. 1A) an acute isosceles minimum energy geometry was obtained. However, the S^2 value (after spin annihilation) was 1.27. Spin contamination is thus large under these conditions, and one cannot assume that the results are reliable. Optimization from WU (Fig. 1B) and CA (Fig. 1C) structures yielded a transition state geometry that had an obtuse isosceles structure. Since the optimized wave function was spin contaminated, further optimization to locate a minimum energy structure was not performed.

Optimizing with the B3LYP functional (with the same basis set and an unrestricted wave function) led to significantly different results with an S^2 value larger than 5 in all cases. Since there is a large change in the spin contamination it is not possible to identify if the changes in the optimized structures and vibrational frequencies is due directly to the different functional, or indirectly due to the change in spin contamination.

Optimization with the 6-311+G(3df) basis set (using the BPW91 and B3LYP functionals) gave nearly identical structures, vibrational frequencies and S^2 values as those obtained using the 6-311+G(d) basis. The smaller basis set is thus sufficiently flexible for this system, and the results presented below were obtained with this basis.

Since the spin contamination found for the optimized unrestricted wave functions is fairly large, the above optimizations were repeated using a restricted (open shell) wave function. When using the BPW91 functional, all three initial geometries (see Fig. 1) led to the acute triangular minimum energy structure shown in Fig. 2. The lengths of two equal sides are 4.06 a.u. and the angle they subtend is 49° . The vibrational frequencies are 191, 237 and 466 cm^{-1} . This structure is similar to the minimum

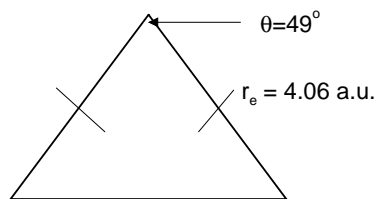


Fig. 2. The BPW91/6-311+G(d) V_3 minimum energy structure obtained using a restricted open shell wave function.

energy structure obtained in the unrestricted calculation, where the lengths of the equal sides are 4.20 a.u., the subtended angle is 47° , and the vibrational frequencies are 174, 211 and 486 cm^{-1} . Thus, within the limitations of the BPW91 functional, the combined effect of spin polarization and spin contamination is sufficiently small to be able to obtain meaningful semi-quantitative results from these calculations.

Optimizations using a restricted wave function in combination with the B3LYP functional are in progress. Large differences between the restricted and unrestricted minimum energy structures may arise in this case, since the spin contamination is larger for this functional. Indeed, preliminary results indicate that a (the) minimum energy structure for this functional using a restricted wave function is an equilateral triangle similar to that obtained by CA.

3.2 Results for Au_4

The planar rhombic (D_{2h}) Au_4 minimum energy structure is shown in Fig. 3. The LDA functional yields a bond length, $r_e = 5.01$ a.u. and the acute angle is 59° . These results compare well with those reported previously [8]. In Ref. [8], where relativistic effects were treated using a scalar relativistic pseudopotential, $r_e = 4.95$ a.u. and the angle is 59° . The results are also in good agreement with those of Häkkinen and Landman [7] who used the Perdew, Burke and Ernzerhof (PBE) functional with a scalar relativistic treatment. Thus, in this case, the structural properties are well described by the computationally cheaper relativistic pseudopotential. For the GGA optimized D_{2h} structure the results are $r_e = 5.10$ a.u. and the acute angle is 59.5° . The increase in the bond length when including gradient corrections follows previously reported trends [8].

4 Conclusions

4.1 The V_3 cluster

The work presented here shows that the 6-311+G(d) basis set is sufficiently flexible to provide accurate results for the V_3 system, at least when the BPW91 and B3LYP functionals are employed. It also shows that minimum energy structures and vibrational frequencies obtained from unrestricted wave function optimizations may be (semi-quantitatively) reliable even though the spin contamination may be large. For example, even though a value of

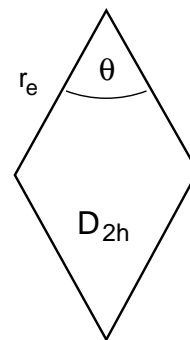


Fig. 3. The planar (D_{2h}) structure of Au_4 investigated in this work.

$S^2 = 1.27$ was obtained for the optimized wave function when using the BPW91 functional, the associated structure and vibrational frequencies were very similar to those obtained from the restricted wave function. However, it is also important to note that results obtained from spin contaminated wave functions cannot be *assumed* to be accurate.

Preliminary results based on a B3LYP functional indicate that the minimum energy structure may be sensitive to the functional. This is in agreement with similar comparisons made using other functionals [2,3]. The B3LYP studies, together with the results of quartet electronic state structures, will appear later.

4.2 The Au_4 cluster

In this study we have also investigated the planar rhombic (D_{2h}) structure of an Au_4 cluster. There are minor differences in the structural properties compared to the scalar relativistic calculations. The extent to which these differences increase when going to clusters of other heavy transition metals remains an open question.

4.3 Summary

Although the present work has shed important light on some of the problems associated with DFT calculations, it has not resolved the discrepancy of the previously published results. A possible way of obtaining a more conclusive answer is to compare calculated properties with experiment, taking care that the calculated results are converged, for example, with respect to the basis set, and that the experimental data is relevant to the calculations. For example, in the case of the vanadium cluster, the better agreement between the experimental and calculated properties of the V_1 cluster obtained by WU and CA, compared to those obtained by GR, favors the WU and CA results. But, since WU obtained results for the V_1 system that contradict experiment when *increasing* the flexibility of the basis set, the CA results may be the most reliable. In addition, the CA results for V_3 are in good

agreement with the pulsed-field-ionization-zero-electron-kinetic-energy (PFI-ZEKE) spectrum, which provides additional support to their results. However, the structures obtained by GR and WU were not compared to the PFI-ZEKE data, and can thus not be excluded on this basis. Moreover, as noted above and by Calaminici *et al.* [3], the results may be strongly dependent on the functional used. Hence the reliability of the CA results would be strongly supported if a different functional gave V_1 , V_2 and V_3 properties that agreed with their results.

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