Geometries and energy separations of 14 electronic states of \( \text{Au}_4 \)

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Multiconfiguration SCF (MCSCF) followed by multireference configuration interaction calculations are carried out on 14 electronic states of \( \text{Au}_4 \). The low-lying electronic states are studied further using multireference singles + doubles CI (MRSDCI) calculations including excitations from the \( d \) shells. The ground state of \( \text{Au}_4 \) is found to be a closed shell \( 1A_g \) state with an equilibrium geometry of rhombus. Two excited states of \( 1B_2 \) symmetry with rhombus and square geometries were found to lie 0.98 and 1.12 eV above the ground state. The spin–orbit effects were included using the relativistic configuration interaction method (RCI). Accurate MRSDCI calculations which included up to 1.5 million configurations on the ground states of \( \text{Au}_2 \) and \( \text{Au}_3 \) are also performed with the objective of comparing the binding energies of \( \text{Au}_2 - \text{Au}_4 \). The gold tetramer is found to be much more stable in comparison to the trimer and dimer.

I. INTRODUCTION

The spectroscopic and electronic structural properties of transition metal clusters have been the topics of many investigations in recent years. 1−30 Such clusters are formed in a cool supersonic beam using a jet-expansion method and probed using laser spectroscopic methods such as laser-induced fluorescence, resonant two-photon ionization spectroscopy, resonant two-photon dissociation spectroscopy, photoelectron and photodetachment spectroscopy. These experimental methods have provided a wealth of information on the spectroscopic properties of transition metal dimers and trimers such as \( \text{Pt}_2 \), \( \text{Pd}_2 \), \( \text{Pt}_3 \), \( \text{Au}_2 \), \( \text{Ag}_2 \), etc. 1−22

The experimental investigations on gold and silver clusters have been on the rise in recent years. 13−23,29,30 In summary, the silver and gold clusters have been investigated using both matrix-isolation and jet-cooled supersonic nozzle expansion methods. The Raman bands of the two clusters have been obtained. Ozin and co-workers 15−17 have obtained the UV-visible spectra of silver clusters. The ESR spectrum of matrix-isolated \( \text{Au}_2 \) was obtained by Howard and co-workers. 21 Hilpert and Gingerich 21 have obtained the atomization enthalpies of both gold and silver trimers.

Theoretical interest in the clusters of gold stems from the unusual bonding and behavior of gold clusters in comparison to the lighter analogs of that group. 24−37 One would expect \( \text{Au}_2 \) to be bound less in comparison to \( \text{Ag}_2 \). However, as shown by Pitzer and co-workers 24−25 \( \text{Au}_2 \) is more strongly bound in comparison to \( \text{Ag}_2 \) due to relativistic effects. This phenomenon is attributed to relativistic mass-velocity contraction of the outer 6s orbital of the gold atom which enhances the stability of the gold dimer in comparison to silver dimer. The mass-velocity contraction of the 6s orbital has many other interesting impacts in the chemistry of molecules containing gold, mercury, thallium, etc. For example, in a recent investigation by Neisler and Pitzer 23, it was demonstrated that the unusual stability of \( \text{Hg}_2^{1+} \) is attributable to relativistic mass-velocity contraction. The color of gold in contrast to silver is attributed to relativistic effects. 24

Theoretical investigation of gold clusters is quite challenging both due to the above mentioned relativistic effects and electron correlations. As shown by Lee and McLean 27,28 electron correlation effects arising from both the 5d 10 and 6s shells of the gold atom are quite important for \( \text{AuH} \). Ross and Ermler 29 have also investigated gold and silver containing compounds such as \( \text{Au}_2 \), \( \text{AgAu} \), etc. In earlier investigations, two of the present authors 29,30 have carried out MCSCF/CI calculations including \( d \) correlations on both gold and silver trimers. It was shown that both \( d \)-correlation effects and spin–orbit effects are important for the electronic states of \( \text{Au}_3 \).

The objective of the present investigation is to obtain the geometries and energy separations of the low-lying electronic states of \( \text{Au}_4 \). We employ MCSCF/MRSDCI method which includes excitations from the \( d \) shells of the gold atoms. The effect of spin–orbit term is also studied using the relativistic CI (RCI) method. The geometries were optimized for 14 low-lying states of \( \text{Au}_4 \). Many possible structures which include rhombus, square, tetrahedron, linear, etc. were considered as candidates for the various electronic states. The atomization energies of \( \text{Au}_2 \), \( \text{Au}_3 \), and \( \text{Au}_4 \) are calculated including \( d \) correlations and compared. For \( \text{Au}_4 \), CI calculations which included about 1.5 million configurations were carried out with the objective of calculating the atomization energies. Section II describes our method while Sec. III comprises results and discussions.

II. METHOD OF CALCULATIONS

In analogy with the gold dimer, \( \text{Au}_4 \) is expected to have a closed shell singlet ground state. In \( C_{3v} \) symmetry, this would correspond to a \( 1A_g \) state. The bonding in \( \text{Au}_4 \) should primarily arise from the 6s orbitals of the gold atoms since the ground state of the atom is 5d 10 6s 2 (\( ^2S \)). However, it has been well documented by the present authors 29, 30 Ross and

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Ermier, and McLean that d-correlation effects would be especially important for computing the dissociation energies and energy separations of electronic states. Thus the present method of calculations is aimed at investigating low-lying electronic states with a method that includes d-correlation and relativistic effects and yet does not become too large that it becomes almost impossible to do. This is achieved through the MCSCF/CI/RCI method described below.

We first carry out multiconfiguration self-consistent field (MCSCF) calculations which employed the complete active space MCSCF (CASSCF) method. In this method, the wave functions are constructed in the complete configuration space of strongly occupied orbitals of the separated atoms. The MCSCF calculations included a total of 44 electrons with the four outer electrons explicitly retained in the active space. The remaining 40 electrons of Au were kept in the orbitals which were allowed to relax but no excitations were allowed from these orbitals at the CASSCF level of calculations; these orbitals correspond to the d orbitals of the separated atoms. The active space in the CASSCF for rhombus and square geometries included three a1 and one b2 orbitals in the C3v group which correlated into the 6s orbitals of the separate atoms at infinite separation. The CASSCF calculations of the tetrahedral geometry included two a1 and one b1 orbital and one b2 orbital due to different orientations. Similarly, CASSCF calculations of linear geometry included four a1 orbitals since the molecular axis coincides with C2 axis. Separate CASSCF calculations were carried out for each state of different spatial symmetry and spin multiplicity.

Relativistic effective core potentials with the outer 5d10 6s1 shells of the four gold atoms explicitly retained in the valence space, generated in Ref. 38 together with the (3s3p3d) valence Gaussian basis sets are used here. These potentials and basis sets were employed in an earlier investigation on Au, which proved to be satisfactory for Au.

The effects of 10-component 4f-type functions could be important for both the equilibrium geometries and binding energies of gold clusters. Thus the (3s3p3d) basis set of the gold atom was extended further by augmenting it with a set of 10-component 4f-type functions with a = 0.36. The effects of these additional functions on Au were tested by including these at both CASSCF and MRSDCI levels of theory. For Au, the inclusion of 4f functions resulted in a basis set of 160 Gaussian functions. Thus MRSDCI calculations of Au, which included these functions could not be carried out. However, the effects of these functions were tested at the CASSCF level by comparing CASSCF calculations with and without 4f functions in the basis set.

Two types of configuration interaction (CI) calculations were carried out following CASSCF. Both the calculations included excitations from the d shells since it is well documented that d-correlation effects could play an important role in accurate determination of energy separations.

The CI calculations which included d-correction effects to a less degree are labeled d-POLCI. The POLCI calculations included those configurations in the CASSCF with coefficients ≥0.07 as reference configurations but with explicit retention of some of the core orbitals in the CASSCF in the internal space for CI using the following procedure. The POLCI configurations form a subset of MRSDCI (multireference singles + doubles) in which the configurations generated by distributing two electrons in the MCSCF-orthogonal space are omitted. The d-POLCI calculations thus included all single and most important double excitations from the various reference configurations. The CASSCF calculations revealed that some of the d orbitals of Au are much lower in energy in comparison to the other orbitals. There were six orbitals which were found to be considerably lower in energy (orbital ε < −0.512 hartrees) and two orbitals with eigenvalues < −0.495 hartrees. Inclusion of these eight orbitals in core gave a truncated space for POLCI. The POLCI calculations included all the external orbitals and 28 electrons. The geometries were fully optimized at both CASSCF and POLCI levels of calculations. Our earlier investigation on Au has revealed that POLCI calculations yield geometries in very good agreement with more accurate MRSDCI calculations.

We carried out multireference singles + doubles CI (MRSDCI) calculations including d correlation for three low-lying states of Au with the objective of scaling the POLCI calculations and calculating the atomization energies. The MRSDCI calculations included 32 electrons obtained by retaining orbitals with eigenvalues lower than — 0.51 hartrees in the core. The natural orbitals obtained from the POLCI calculations were used in the MRSDCI. All the external orbitals in the POLCI with densities less than 10−4 were separated into another external subset. Then all possible single excitations into all orbitals and double excitations into internal and first external subsets were allowed. This method of truncation of the external space brought down the CSF count to a manageable number of less than 500 000 for both the 1A1 and 1B1 states of Au. We also did comparable MRSDCI calculations which included 28 electrons. It was gratifying that the two calculations did not differ significantly. Further, as seen in Sec. III, the analysis of densities of the d orbitals reveals that this is a justified approach.

We considered a number of possible geometries for both singlet and triplet states of different symmetries in the C2v group. These geometries included rhombus, square, linear structure, tetrahedron, trapezium, etc. The POLCI calculations included between 44 000–90 000 configurations depending on the electronic state while the MRSDCI calculations included up to 500 000 configurations.

The spin–orbit coupling effects could be important for gold clusters since the 5d and 6p spin-orbit splittings are quite large for the gold atom. However, to first order, the spin–orbit coupling effect would be zero for the 1A1 ground state of Au, primarily due to symmetry considerations. The second-order off-diagonal spin–orbit matrix elements could be large for Au and thus could alter the electronic states. There could also be spin–orbit effects from the mixing of the 6p orbitals and fractional vacancies created in the nearly full d shells in higher-order CI. Consequently, the spin–orbit effects were investigated using the recently developed relativistic CI (RCI) for polyatomic.
were used as the orbital space for the relativistic configuration interaction calculations. The spin-orbit operator was expressed as the difference of $I + \frac{1}{2}$ and $I - \frac{1}{2}$ relativistic effective potentials. The spin–orbit integrals were obtained using Pitzer’s modified version of the ARGOS integral package to calculate these integrals. The relativistic configuration interaction calculations were carried out by adding the transformed spin–orbit integrals over the $\delta$-MRSACI natural orbitals into the CI matrix. Since the inclusion of the spin–orbit term into the Hamiltonian changes the symmetry group into a spin double group, all low-lying electronic configurations which have the same symmetry in the spin double group would mix in the relativistic CI.

The RCI calculations of the $^1A_1 (A_1)$ state included all important configurations for the $^1A_1$ state and the configurations which describe the $^1B_1 (A_1)$ state as reference configurations. Then single and double excitations were included from these reference configurations. To facilitate these calculations, the less important orbitals in the external space were omitted in the RCI based on the densities of the MRSACI natural orbitals. Another set of calculations without the spin–orbit integrals were also made. The difference between the two energies was taken as the spin–orbit correction and applied to the MRSACI results obtained without the spin–orbit term. The RCI calculations were made for the spin–orbit components of the two lowest states, namely, $^1A_1 (A_1)$, $^3B_2 (A_1)$, $^3B_1 (A_2)$ and $^3B_2 (B_1)$. The $^3B_2 (A_1)$ state was obtained as the second root of the RCI calculations which included all configurations of $A_1$ symmetry in the $C_{2v}$ double group.

We also carried out CASSCF/MRSACI calculations on Au$_3$ and Au$_4$, which included 22 and 33 electrons, respectively, at both equilibrium geometries and very long distances to compute and compare the atomization energies of these species with the tetramer. The MRSACI calculations on Au$_3$ included 1.5 million configurations while the MRSACI calculations on Au$_2$ included about 60,000 configurations. The MRSACI calculations of Au$_4$ were carried out using the contracted CI (CCI) method of Siegbahn.\(^{45}\)

All CASSCF/CCI calculations reported here were carried out using one of the author’s (K. Balasubramanian)\(^{41}\) modified version of ALCHEMY II codes\(^{42}\) to include relativistic effective core potentials as described in Ref. 41.

### III. RESULTS AND DISCUSSION

Table I shows the calculated equilibrium geometries of 14 electronic states of Au$_4$, and their energy separations. The computed geometries of these states are shown in Fig. 1. As can be seen from Table I, the ground state of Au$_4$ is unambiguously of $^4A_1$ symmetry ($^4A_1$ in $D_{2h}$ symmetry) of rhombus geometry. The four sides have the same length of 2.69 Å at the POLCI level. As we will discuss later, this geometry is very close to more accurate MRSACI geometry.

The $^2B_2$ excited state of Au$_4$ exhibits two potential stationary points one with rhombus structure ($\theta_2 = 67^\circ$) and the other with square geometry. The two extrema are separated by only 0.09 eV. Although, we did not calculate the barrier to convert the rhombus structure into square structure based on the fact that the geometry differences between these two minima are small, we predict that these two structures should be interconvertible into each other. Thus, Au$_4$ in the $^2B_2$ excited state could be floppy.

The $^1A_1$ ground state, in comparison to $^2B_2$ is well separated from its square counterpart. This separation of 1.43 eV is even larger than the separation of the $^3\Sigma_g^+$ linear geometry (1.26 eV) indicating that interconversion of rhombus into square geometry might be difficult in the $^1A_1$ state. For the $^1A_1$ state, the square structure is a maximum in the potential energy surface.

The tetrahedral geometries of both $^1A_1$ and $^3B_2$ symmetries are quite high in energy ( $> 1.5$ eV). This is anticipated

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<th>Geometry</th>
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<th>$\theta_{\text{deg}}$</th>
<th>$E$(eV)</th>
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</table>

* $R_{12}$ stands for the four equal sides of rhombus; for linear states $R_{12}$ represents the corner bond lengths while $R_{23}$ represents the center bond length. $\theta$ is the shortest Au-Au-Au bond angle.

* Zero energy for CASSCF is $-133.311407$ hartrees; for POLCI it is $-133.363715$ hartrees.

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since the four $s$ orbitals on the gold atoms are unlikely to form tetrahedral bonding unless considerable contamination arises from the $6p$ orbitals of the gold atoms. The other electronic states in Table III are quite excited in comparison to the ground state.

The rhombus structure of Au$_4$ is analogous to the Si$_4$ cluster which also exhibits a rhombus structure in the $^1A_1$ ground state.$^{43,44}$ Unlike Au$_2$, there are no other candidates for the ground state of Au$_4$ since the $^1A_1$ state with rhombus structure is about 0.9 eV lower than any other structure.

The equilibrium geometry of the ground state of Au$_4$ ($^1A_1$) is reminiscent of the rhombus structure of the ground state of Na$_4$ and K$_4$ found by Spiegelman and Pavolini$^{45}$ in a recent SCF/CIPSI calculation. The rhombic structure of the $^1A_1$ state of alkali tetramers is well known.$^{46-49}$ The Na–Na and K–K bond lengths in the rhombus structure are 6.5 and 8.4 bohr, respectively.

The $d$-correlation effects not included in a POLCI method could be important especially for energy separations, although we were fairly certain that POLCI geometries would be in very good agreement with MRSDCI geometries based on our earlier calculations on Au$_3$.$^{30}$ We carried out MRSDCI calculations for the three lowest-lying electronic states of Au$_4$, namely, $^1A_1$ (rhombus), $^1B_2$ (rhombus), and $^3B_2$ (square). The results of MRSDCI geometries and energy separations for these three states are compared with POLCI in Table II. As can be seen from Table II, the geometries obtained by POLCI are in good agreement with the MRSDCI geometries. For the rhombus structure, only the bond angle changes by about 2%. The energy separations are, however, more sensitive to higher-order $d$ correlations not included in the POLCI method. The separation of the $^1B_2$ (rhombus) state changes by 10% while the $^3B_2$ (square) state changes by 15%. However, it must be pointed out that the POLCI method included only 79 000 configurations while the MRSDCI method included up to 500 000 configurations. The difference in the energy separations was only 3% between a calculation that included 28 electrons as opposed to 32 electrons. Inclusion of more than 32 electrons would lead to a calculation that must include all 44 electrons since the other six core orbitals were nearly degenerate. The MRSDCI calculations which include all 44

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electrons are beyond our theoretical method at present.

As mentioned in Sec. II, the effects of 4f functions were tested on the geometry of the \(^1A_1\) ground state of Au\(_4\). CASSCF calculations which included 4f-type functions were made and geometries were reoptimized. At the CASSCF level, the bond length of the side of the rhombus \((1A_1)\) decreased by 0.1 Å and the bond angle changed by 2°. However, a comparison of CASSCF and MRSDCI calculations on the Au\(_4\) dimer reveals that the bond length decrease brought about by 4f functions is nullified at the MRSDCI level. Alternatively, MRSDCI geometries are nearly the same with or without 4f functions. Consequently, we believe that for Au\(_4\) the geometry changes at the MRSDCI level due to 4f functions will be much smaller than the values obtained above.

Table III shows the important configurations in the CASSCF wave function of the electronic states of Au\(_4\). As can be seen from that table, the \(^1A_1\) state has three important configurations, although the leading configuration has a coefficient of 0.977. Analysis of the highest-occupied MRSDCI natural orbitals of the \(^1A_1\) and other states reveals the following information. In the \(^1A_1\) state, the highest occupied 9a\(_1\) orbital is predominately made of the 6s orbitals of the gold atoms located on the z axis and it is antibonding. In the rhombus structure, the two atoms along the z axis (vertical atoms of the rhombus) are at the corners of the longer diagonal. There is considerable d\(_{xy}\) participation also in this orbital. The 6p\(_{z}\) interaction of the atoms located on the y axis was noticeable in the 9a\(_1\) orbital. The 8a\(_1\) orbital on the other hand involves all the four gold atoms in contrast with the 9a\(_1\) orbital which includes primarily the 6s orbitals along the z axis. Thus the square geometry elongates along the z axis due to the antibonding type of interaction along this axis leading to a rhombus structure. The 5b\(_2\) natural orbital is a mixture of both Au d(3yz) orbitals of the gold atoms situated on the z axis, the Au d(3z\(^2\) – 2x\(^2\)) orbitals of the gold atom situated on the y axis, and to some extent the antibonding combination of the 6s orbitals of the gold atoms along the y axis (see Fig. 1). It must be noted that the densities of 4b\(_2\) and 5b\(_2\) orbitals are very close.

The above analysis of the natural orbitals of the Au\(_4\) \(^1A_1\) state clearly indicates the importance of d orbital participation and d correlation effects in the highest-occupied orbitals of Au\(_4\), especially in the 4b\(_2\) and 5b\(_2\) orbitals. At the CASSCF level the only active d orbital, namely, 6b\(_2\) is predominantly made up of the antibonding combination of the s orbitals along the y axis. However, at the equilibrium geometry of the rhombus structure this orbital has a density of only 0.0195 at the CASSCF level and 0.024 at the MRSDCI level.

As seen in Table III, the first excited \(^3B_2\) state arises from the promotion of one of the 9a\(_1\) electrons into the 5b\(_2\) orbital. Since the 9a\(_1\) orbital is antibonding along the z axis while 5b\(_2\) is antibonding along the y axis, the two atoms along the y axis move a bit apart leading to a bigger Au–Au–Au angle (see Fig. 1). The second minimum in the \(^3B_2\) is explained based on the balance of two antibonding types of interaction thus making the two diagonal bond lengths equal. In the first case, the antibonding interaction along the z axis is a bit larger than the interaction along the y axis.

The linear \(^3Σ^+\) state and square \(^1A_1\) extrema are the other excited states of \(^1A_1\) symmetry with energy separations of 29–33 kcal/mol. As seen from Table I, the linear geometry has Au–Au bond lengths of 2.40 and 2.50 Å (see Fig. 1). The Au\(_4\) dimer has a bond length of 2.56 Å at the MRSDCI level of theory. Thus, the shorter bond lengths of 2.40 Å at the corner bonds imply partial bonding at the corners of the linear structure arising from 5d–5d and 6p–6p overlaps. This will be discussed further later by comparing Mulliken populations. The other states and structures are quite excited for Au\(_4\). While most of the states of Au\(_4\) have leading configurations with coefficient > 0.95, the \(^1A_1\) state with tetrahedral geometry and the \(^3A_1\) state with square geometry are exceptions (see Table III). However, the \(^3A_1\) state (tetrahedron) is quite excited \((T_\epsilon \sim 5.1 \text{ eV})\) and has an occupied 10a\(_1\) orbital which is antibonding. This is reflected in longer bond lengths for the \(^3A_1\) (rhombus) and \(^1A_1\) (tetrahedron) structures.

The importance of d-correlation effects and the participation of d orbitals in bonding can be realized by investigating the densities of the MRSDCI natural orbitals of Au\(_4\). Table IV shows the densities of natural orbitals with \((D > 0.01)\) for three low-lying electronic states obtained from MRSDCI calculations. The orbitals labeled 8a\(_1\), 9a\(_1\), 10a\(_1\) and 5b\(_2\) are the active orbitals at the CASSCF level for the rhombus geometry. Thus at the CASSCF level of theory, the orbitals 1a\(_1\)–7a\(_1\), 1b\(_2\)–4b\(_2\), 1b\(_1\)–4b\(_1\), and 1a\(_2\)–4a\(_2\) are all predominantly d orbitals of gold atoms and are fully occupied. At the MRSDCI level of calculations, however, the densities of many of these orbitals deviate from 2.0 indicating the extent of d-correlation effects. The larger the deviation of density of an orbital from 2.0, the larger is the participation of that orbital in higher-order correlations. The 5a\(_1\)–7a\(_1\), 4b\(_2\)–5b\(_2\), 3b\(_1\)–4b\(_1\), and 3a\(_2\)–4a\(_2\) orbitals all have densities of 1.986 or 1.985 indicating the participation of these orbitals more heavily in higher-order correlation effects in comparison to the 2b\(_1\), 3b\(_2\), 1a\(_1\), and 2a\(_2\) orbitals. For the
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* The linear and tetrahedral geometries were oriented differently in comparison to rhombus and square geometries.

\(B_2\) state, the \(b_2\) and \(a_2\) orbitals participate slightly more in comparison to the \(a_s\) orbitals.

Next, we analyze the Mulliken population analyses of the MRSDCI and POLCI natural orbitals of the electronic states of \(Au_4\). Table V shows the Mulliken populations of some of the low-lying electronic states of \(Au_4\). In the \(1\)A\(_{1}\) ground state with rhombus structure, the metal atoms along the \(z\) axis have slightly greater gross populations in comparison to the atoms along the \(y\) axis (M\(_z\)). The fact that the gross \(d\) populations of most of the electronic states are lower than 10.0 (~9.92–9.96) is consistent with our earlier statement on the importance of \(d\)-correlation effects. Similarly, we would like to point out that the 6\(p\) populations also deviate significantly from zero value. For the \(1\)A\(_{1}\) rhombus ground state, the M\(_z\) (\(p\)) population is about 0.24. Note that the M\(_z\) atoms are located on the \(y\) axis and thus there is considerable overlap of the 6\(p\) orbitals of these two atoms. This is the other reason why the two Au atoms located on the \(y\) axis come closer in the rhombus structure which results in the acute apex angle (Fig. 1).

It was noted that the corner bonds of the linear \(1\Sigma^+_g\) state are shorter than the central metal–metal bonding. The
shorter terminal bonds were attributed to partial 5d–5d bonding. As seen from Table V, the corner atoms of the 1Σg state have gross d populations smaller than 10.0 (9.917) consistent with the above partial 5d–5d bonding in the terminal bonds.

The participation of the 6p orbitals in excited electronic states of Au4 is noticeable only in the 3B2 states and the 1A1 state of tetrahedral geometry. It is natural that the 6p orbitals to have to hybridize with the 6s orbitals to some extent to form the tetrahedral bonds.

Table VI compares the POLCI and MRSDCI Mulliken populations of the three lowest electronic states of Au4. This comparison is important since it gives some insight into the extent of d correlations and higher-order correlations. For the 1A1 ground state, the metal d populations decrease a bit while the p populations increase in going from POLCI to a MRSDCI level of theory. There is a slight increase in the M1 total gross population in comparison to the M1 total gross population. The drop in the d population is somewhat larger for the 3B2 states. However, it is comforting that the overall change in the Mulliken populations is not substantial in comparing the POLCI and MRSDCI calculations.

The spin–orbit effects could be large for Au4 considering the fact that the participation of the 6p orbitals even in the closed-shell 1A1 ground state is large and that the 5d3/2 – 5d3/2 and 6p1/2 – 6p1/2 atomic spin–orbit splittings of the gold atom are 12 274 and 3815 cm⁻¹, respectively (Table VII). Thus, we decided to carry out relativistic CI calculations including the spin–orbit term for the ground state and the first excited state of Au4. The spin–orbit term lowers the energy of the 1A1 (A1) state by 0.01 eV (0.23 kcal/mol). The 1A1 (A1) state mixes with the A1 component of the first excited 3B2 state. Table VIII shows the actual weights of the different states mixing in the RCI wave functions of Au4.

As can be seen from Table VIII, the 1A1 (A1) ground state is a 96%-0.1% mixture of 1A1 and 3B2 (A1). The 3B2 (A1) excited state however, is a 91%-5% mixture of 3B2 with 1A1. This spin–orbit contamination lowers the 1A1 state by 0.23 kcal/mol relative to 1A1 without the spin–orbit term and rises the 3B2 (A1) by 0.3 kcal/mol relative to the 3B2 state without the spin–orbit term. The total spin–orbit splitting of the 3B2 state [i.e., 3B2 (A1) – 3B2 (A1) separation] is 0.51 kcal/mol. Consequently, while the total spin–orbit splitting of the lowest-lying states of Au4 is not very large, the spin–orbit contamination is significant. At least, for the ground state most of the lowering comes from this spin–orbit contamination.

As noted in Sec. II, we also carried out CASSCF/MRSDCI calculations of Au4 and Au5 at the equilibrium and long distance geometries to calculate the atomization energies for the clusters Au4–Au5. Table IX summarizes these results using various methods. The atomization energy of the cluster Au4 is defined as the energy for the following reaction:

\[ \text{Au} _4 \rightarrow n \text{Au} \]

### Table V: Mulliken population analyses of the natural orbitals of Au4

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* M1 stands for one of the two atoms along the z axis for the rhombus and square geometries. M2 stands for one of the atom atoms along the y axis. The overlap is between M1 and M2 atoms. For the linear geometries, M1 is one of the corner atoms.

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To maintain consistency, atomization energies were calculated for Au₂–Au₄ clusters using the same type of calculation for the cluster at the equilibrium geometry and linear geometry with Au–Au bond lengths set to 8.0 Å.

The best results in Table IX are obtained using the full d-MRSDCI calculations including excitations from the d shells. For the gold dimer, the d-MRSDCI method yields a \( D_e \) value of 46 kcal/mol only 7 kcal/mol (13% error) lower than the experimental value of 53 kcal/mol. The full d-MRSDCI, however, represents a significant improvement over the SOCI (which did not include excitations from the d shells) \( D_e \) value of Au₂ which is only 27 kcal/mol. Thus d-correlation effects improve the binding energy of Au₂ by 19 kcal/mol (almost 41%). The present \( D_e \) value obtained using the full MRSDCI is much improved in comparison to a value of 39 kcal/mol obtained using only excitations from the d shells of \( 1\text{A}_1 \), symmetry block of Au₂ and a calculation reported by Ross and Ermel in which a \( D_e \) value of 36 kcal/mol by allowing only single excitations from the d shells of the gold atoms. Thus, it is clear that double excitations from the d shells are important for accurate computations of the dissociation energies.

For the gold trimer, the SOCl method without d correlations yields only about half of the atomization energy. The d-POLCI calculations which included the most important double excitations from the 5d and 6s and all single excitations from the 5d orbitals yield an improved value of 62 kcal/mol in comparison to the Hilpert–Gingerich experimental value of 88 kcal/mol. Thus the POLCI method seems to pick up 70% of the correlation effects and has a manageable number of CSFs for gold trimers. A full MRSDCI method including Davidson’s correction for higher-order correlations for Au₃ yields an atomization energy of 76 kcal/mol. Thus full MRSDCI including excitations from the d shells seems to yield more accurate atomization energies than other calculations which included correlations to less degree.

As mentioned in Sec. II, the effects of 10-component 4f-type functions were tested on the atomization energy of the dimer by carrying out CASSCF/MRSDCI calculations with and without 4f functions. However, it was found that the \( D_e \) changed by less than 0.1 kcal/mol for the dimer. Thus, 4f functions do not have significant effects on atomization energies.

There are no experimental values available for the atomization energy of the gold tetramer. Our d-MRSDCI calculations (28 electrons) yield a value of 158 kcal/mol for the atomization energy of the ground state of Au₄. We believe that this value should be within 10%–15% of the experimental result. Thus we predict that atomization energy of Au₄ should be 180 ± 10 kcal/mol. Note that Au₄ is unusually more stable in comparison to the trimer. The binding energy per site for the tetramer is 40 kcal/mol in comparison to 25 and 23 kcal/mol for the trimer and dimer, respectively. This enhanced stability of the tetramer is attributed to the closed shell stable ground state of Au₄. Among the dimer, trimer, and tetramer of gold, the tetramer is unusually more stable.

To maintain consistency, atomization energies were calculated for Au₂–Au₄ clusters using the same type of calculation for the cluster at the equilibrium geometry and linear geometry with Au–Au bond lengths set to 8.0 Å.

The best results in Table IX are obtained using the full d-MRSDCI calculations including excitations from the d shells. For the gold dimer, the d-MRSDCI method yields a \( D_e \) value of 46 kcal/mol only 7 kcal/mol (13% error) lower than the experimental value of 53 kcal/mol. The full d-MRSDCI, however, represents a significant improvement over the SOCI (which did not include excitations from the d shells) \( D_e \) value of Au₂ which is only 27 kcal/mol. Thus d-correlation effects improve the binding energy of Au₂ by 19 kcal/mol (almost 41%). The present \( D_e \) value obtained using the full MRSDCI is much improved in comparison to a value of 39 kcal/mol obtained using only excitations from the d shells of \( 1\text{A}_1 \), symmetry block of Au₂ and a calculation reported by Ross and Ermel in which a \( D_e \) value of 36 kcal/mol by allowing only single excitations from the d shells of the gold atoms. Thus, it is clear that double excitations from the d shells are important for accurate computations of the dissociation energies.

For the gold trimer, the SOCl method without d correlations yields only about half of the atomization energy. The d-POLCI calculations which included the most important double excitations from the 5d and 6s and all single excitations from the 5d orbitals yield an improved value of 62 kcal/mol in comparison to the Hilpert–Gingerich experimental value of 88 kcal/mol. Thus the POLCI method seems to pick up 70% of the correlation effects and has a manageable number of CSFs for gold trimers. A full MRSDCI method including Davidson’s correction for higher-order correlations for Au₃ yields an atomization energy of 76 kcal/mol. Thus full MRSDCI including excitations from the d shells seems to yield more accurate atomization energies than other calculations which included correlations to less degree.

As mentioned in Sec. II, the effects of 10-component 4f-type functions were tested on the atomization energy of the dimer by carrying out CASSCF/MRSDCI calculations with and without 4f functions. However, it was found that the \( D_e \) changed by less than 0.1 kcal/mol for the dimer. Thus, 4f functions do not have significant effects on atomization energies.

There are no experimental values available for the atomization energy of the gold tetramer. Our d-MRSDCI calculations (28 electrons) yield a value of 158 kcal/mol for the atomization energy of the ground state of Au₄. We believe that this value should be within 10%–15% of the experimental result. Thus we predict that atomization energy of Au₄ should be 180 ± 10 kcal/mol. Note that Au₄ is unusually more stable in comparison to the trimer. The binding energy per site for the tetramer is 40 kcal/mol in comparison to 25 and 23 kcal/mol for the trimer and dimer, respectively. This enhanced stability of the tetramer is attributed to the closed shell stable ground state of Au₄. Among the dimer, trimer, and tetramer of gold, the tetramer is unusually more stable.
TABLE IX. The atomization energies of Au$_2$--Au$_6$ by various methods.

<table>
<thead>
<tr>
<th>System</th>
<th>AE (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_2$</td>
<td>SOCI*</td>
</tr>
<tr>
<td>Au$_2$</td>
<td>R-MRSDCI*</td>
</tr>
<tr>
<td>Au$_3$</td>
<td>MRSDCI*</td>
</tr>
<tr>
<td>Au$_4$</td>
<td>Expt</td>
</tr>
<tr>
<td>Au$_4$</td>
<td>SOCI*</td>
</tr>
<tr>
<td>Au$_5$</td>
<td>POLCI</td>
</tr>
<tr>
<td>Au$_6$ d-MRSDCI*</td>
<td>76</td>
</tr>
<tr>
<td>Au$_6$</td>
<td>POLCI</td>
</tr>
<tr>
<td>Au$_6$ d-MRSDCI*</td>
<td>158</td>
</tr>
</tbody>
</table>

*SOCI; does not include excitations from the d shells.
*R-MRSDCI: restricted MRSDCI including d excitations but allowing excitation only from the A block.
*MRSDCI: full multireference single + double CI including excitations from all d orbitals.
*MRSDCI calculations which included 28 electrons and all the external orbitals with $D>10^{-4}$ in the CI.

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41The major authors of Alchemie II are B. Liu, B. Lengsfeld, and M. Yoshimine.