

## ARTICLE

# Density Functional Study on Relative Energies, Structures, and Bonding of Low-lying Electronic States of Lutetium Dimer

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Low-lying electronic states of the lutetium dimer ( $\text{Lu}_2$ ) were studied based on density functional theory (DFT) using ten different density functionals together with three different relativistic effective core pseudopotentials (RECPs). Relative state energies, equilibrium bond lengths, vibrational frequencies, and ground-state dissociation energies were evaluated. It was found that the ground state is a triplet state irrespective of the type of functional and RECP used. This result is in contrast with a previous DFT calculation which gave a singlet ground state for  $\text{Lu}_2$ . By comparing with the high-level *ab initio* and available experimental results, it is evident that the hybrid-GGA functionals combined with the Stuttgart small-core RECP yield the best overall agreement for the properties under study. The effects of Hartree-Fock exchange in B3LYP functional on the calculated bond length and dissociation energy of the ground state were examined, and rationalized in terms of 5d participation in Lu–Lu covalent bonding.

**Key words:** Lutetium dimer, Density functional theory, Relativistic effective core pseudopotential, Hartree-Fock exchange, Covalent bonding

## I. INTRODUCTION

Lanthanide clusters have been the subject of considerable study in diverse research areas such as nuclear and solid-state physics [1]. Understanding physical properties of these clusters is crucial for appreciating their behaviors in potential applications. Among these, lanthanide dimers are the smallest ones and have been subjected to a number of experimental and theoretical studies, the latter including those using the methods based on density functional theory (DFT) [2–6] and high-level *ab initio* MO theory [7,8]. Physical effects that challenge the theoretical modeling are mainly those associated with the 4f electrons, including large relativistic effects and strong (static and dynamic) electron correlations.  $\text{Lu}_2$  is among the simplest representatives of the lanthanide dimers owing to its atomic ground-state configuration ( $\text{Lu } 4f^{14}5d6s^2$ ). This closed 4f-shell configuration allows one to neglect the 4f spin-orbit coupling and the 4f static electron correlation in the first approximation.

Very few experiments have been performed on  $\text{Lu}_2$ . A recent experimental investigation, using Raman and absorption spectroscopy in Ar matrices, provides a value of  $121.6 \pm 0.8 \text{ cm}^{-1}$  for the ground-state vibrational fre-

quency [9]. This value of dissociation energy differs substantially from that of  $1.43 \pm 0.34 \text{ eV}$  determined thermochemically [10]. Cao and Dolg studied low-lying electronic states theoretically using the *ab initio* MO theory methods at the multireference configuration interaction with the cluster correction of Siegbahn (MRCI+Q) and the coupled-cluster singles and doubles with a perturbative treatment of triple excitations (CCSD(T)) levels [4,6]. They found that the ground state of  $\text{Lu}_2$  is most likely the triplet state  $^3\Sigma_g^-$ , the computed spectroscopic constants being in good agreement with experimental data [4]. Using the singles and doubles quadratic configuration interaction (QCISD) method, Yang *et al.* also obtained a triplet ( $^3\Sigma_g$ ) ground state for  $\text{Lu}_2$ , the computed spectroscopic parameters agreeing well with experiments [5]. Recently, Wu *et al.* performed DFT calculations on lanthanide dimers which predicted a singlet rather than a triplet ground state for  $\text{Lu}_2$ , in disagreement with the aforementioned *ab initio* MO results [8]. They also suggested that further theoretical studies were needed to resolve this discrepancy.

DFT has been attracting attention of theoreticians because it can accurately estimate the physical and chemical properties of a wide variety of systems with much less computational effort when compared to high-level *ab initio* MO theory methods. Even though there are many different DFT functionals available presently, using which a large number of DFT studies on transition metal containing systems have been performed, the applicability of DFT methods to lanthanide-containing

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systems is far from definite. In this work, we have performed DFT calculations on low-lying electronic states of Lu<sub>2</sub> using ten different functionals with three different relativistic effective core pseudopotentials (RECPs). The motivation for this work is two-fold: (i) to investigate the relative stability of the lowest-energy singlet and triplet states and to see if this property has any dependence on the type of functional and RECP used, and (ii) to examine the performance of different functionals and RECPs on prediction of Lu<sub>2</sub> properties by comparing against higher-level *ab initio* and experimental results, with the hope to provide some guidance for future DFT studies on lanthanide clusters. The relative state energies, equilibrium bond lengths, harmonic vibrational frequencies, and ground-state dissociation energies were calculated. The accuracy of the results was then used as the criterion to assess the different methods used. The effect of changing the fraction of Hartree-Fock (HF) exchange in B3LYP functional on calculated properties was addressed.

## II. COMPUTATIONAL METHODS

The calculations were carried out for the lowest-energy singlet, triplet, and quintet states of Lu<sub>2</sub>. The singlet and triplet states stem from the dominant  $4f^{14}4f^{14}(6s\sigma_g)^2(6s\sigma_u)^2(5d\pi_u)^2$  configuration and the quintet state from the dominant  $4f^{14}4f^{14}(6s\sigma_g)^2(6s\sigma_u)^1(5d\sigma_g)^1(5d\pi_u)^2$  configuration. Because DFT is generally implemented as a single-determinant method within the Kohn-Sham formalism, pure spin states with multi-configuration wave functions are difficult to describe. The single-determinant description of the high-spin triplet and quintet states is not a problem, except for the small spin contaminations inherent to the use of DFT (as shown later). For the singlet that is an open-shell state, the spin eigenfunction is two-determinant in character, and therefore it is not amenable to direct DFT calculations. In the present work, we employed the broken-symmetry approach to correct for the inadequacy in the single-determinant treatment of the open-shell singlet state. That is, an unrestricted DFT is applied and the wave function for the singlet is allowed to break spin symmetry. The energy of the open-shell singlet was then determined using the so-called sum method [11], *i.e.*,  $E_s = 2E_{bs} - E_T$ , where  $E_{bs}$  and  $E_T$  are the computed energies for the broken-symmetry and triplet states, respectively, the latter being readily computed from single-determinant DFT formalism. The symmetries of the triplet and quintet states are  $^3\Sigma_g$  and  $^5\Sigma_u$ , respectively, as determined from the orbital symmetries. For the singlet state, however, the symmetry cannot be determined because some occupied orbitals have undefined symmetries due to the broken-symmetry approach used. In all cases under study, we found only little spin contamination in the DFT calculations,

*i.e.*,  $\langle S^2 \rangle \approx S(S+1)$ . For instance, for the triplet and quintet states, the  $\langle S^2 \rangle$  values are in the ranges of 2.012–2.039 and 6.003–6.006, respectively, very close to the proper eigenvalues of 2.0 and 6.0. For the broken-symmetry state, the  $\langle S^2 \rangle$  values are in the range of 1.019–1.082, very close to 1.0. This indicates that the broken-symmetry state is almost an equal mixture of pure-spin singlet and triplet, which validates the use of the sum method to estimate the singlet energies.

All the calculations in this work were carried out using the Gaussian03 package [12]. Ten density functionals were employed: (i) the Slater exchange only (S-null) [13], (ii) the Becke 1988 exchange (B88) only [14], (iii) the Slater exchange+Vosko-Wilk-Nusair (VWN5) [15] correlation (SVWN5), (iv) the B88 exchange+Perdew-Wang 1991 (PW91) [16–19] correlation (BPW91), (v) the B88 exchange+Lee-Yang-Parr (LYP) [20] correlation (BLYP), (vi) the 1996 exchange-correlation (XC) functional of Perdew, Burke and Ernzerhof (PBE) [21], (vii) the XC functional of Tao, Perdew, Staroverov, and Scuseria (TPSS) [22], (viii) the Becke three-parameter hybrid exchange (B3) [23]+PW91 correlation (B3PW91), (ix) the Becke three-parameter hybrid exchange (B3)+LYP correlation (B3LYP), (x) the 1997 hybrid XC functional of Perdew, Burke, and Ernzerhof (PBE1) [24]. These ten functionals are commonly used in DFT calculations, and each has various degrees of success and merit as documented in the literature. Among these, TPSS is a nonempirical meta-GGA functional that includes the kinetic energy density in addition to the electron density and its gradient. In addition, HF calculations were also included for comparative purposes.

Three different RECPs with the associated basis sets were used for the lutetium atom. The first two are the Stuttgart energy-consistent small- and large-core RECPs [25,26], denoted by SSC and SLC, respectively, in this work. The SSC pseudopotential includes 28 electrons in the core, and treats the 4s, 4p, 4d, 5s, 5p, 4f, 6s, and 5d electrons (43 electrons) explicitly. The corresponding optimized basis set for the valence electrons has the (14s13p10d8f6g)/[10s8p5d4f3g] contraction. The SLC pseudopotential includes f orbitals in the core, so that the atom is modeled as an 11-valence electron (5s<sup>2</sup>5p<sup>6</sup>6s<sup>2</sup>5d) system. The valence basis set has the (7s6p5d)/[5s4p3d] contraction. These two RECPs were adjusted on the basis of relativistic all-electron calculations using the so-called Wood-Boring (WB) scalar-relativistic HF approach to reproduce the total valence energies of low-lying electronic states of the neutral Lu atom and its ion [27]. It has been established that the energy-consistent RECPs can capture the relativistic effects from all electron scalar-relativistic Douglas-Kroll-Hess calculations [28]. The third RECP considered in this work is a shape-consistent one developed by Stevens and coworkers (hereafter denoted as CEP), where the 5s, 5p, 4f, 6s, and 5d electrons

TABLE I Relative state energies (in eV) of the lowest-energy singlet, triplet, and quintet states of Lu<sub>2</sub>.

Method	SSC			SLC			CEP		
	Singlet	Triplet	Quintet	Singlet	Triplet	Quintet	Singlet	Triplet	Quintet
HF	1.01	0	1.61	0.94	0	1.06	1.18	0	1.47
S-null	0.60	0	0.44	0.59	0	0.40	0.83	0	1.26
B88	1.00	0	0.71	0.41	0	0.59	0.70	0	1.49
SVWN5	1.18	0	0.54	0.39	0	0.51	0.50	0	1.37
BPW91	1.06	0	0.64	0.29	0	0.54	0.44	0	1.42
BLYP	0.84	0	0.91	0.23	0	0.83	0.32	0	1.70
PBE	1.08	0	0.67	0.30	0	0.57	0.46	0	1.45
TPSS	1.08	0	0.57	0.25	0	0.57	0.44	0	1.32
B3PW91	0.36	0	0.78	0.34	0	0.67	0.48	0	1.49
B3LYP	0.28	0	0.99	0.27	0	0.90	0.38	0	1.71
PBE1	0.38	0	0.82	0.35	0	0.70	0.52	0	1.51
MRCI+Q [4]	0.54	0							
CCSD(T) [4]		0	1.23						
QCISD [5]				0.75	0				
DFT [8]							-1.28±0.18	0	

(25 electrons) are treated explicitly [29]. The contraction scheme for the optimized valence basis set is (6s6p3d7f)/[4s4p2d2f]. This pseudopotential was adjusted based on relativistic Dirac-Hartree-Fock computations to reproduce the shapes of atomic spin orbitals.

In all calculations, the ultrafine integration grid was used, the SCF convergence criterion for energy was set at  $10^{-8}$  a.u., and the “tight” convergence for geometry optimization was used. For the calculation of dissociation energies, the corrections due to the zero point vibrational energy (ZPVE) and the basis set superposition error (BSSE) were included.

### III. RESULTS AND DISCUSSION

#### A. Relative state energies

The relative state energies are particularly interesting because they include two states (singlet and triplet) both with four electrons in 6s orbitals and two electrons in 5d orbitals, and one state (quintet) with 6s and 5d orbitals each occupied by three electrons. The singlet state has the same dominant configuration as the triplet state but differs in the spin coupling between the two electrons in  $5d\pi_u$  orbitals. Previous *ab initio* MO calculations using the SSC pseudopotential at the MRCI+Q and CCSD(T) levels predicted a triplet ground state ( $^3\Sigma_g$ ) for Lu<sub>2</sub> [4]. Also, the QCISD calculations with the SLC pseudopotential gave a triplet ground state with the same symmetry [5]. However, recent DFT calculations using the CEP pseudopotential predicted a singlet ground state for Lu<sub>2</sub> [8]. The calculated results for relative state energies are shown in Table I. From the DFT results, we notice that the ground electronic state

of Lu<sub>2</sub> is indeed the triplet state  $^3\Sigma_g$ , regardless of what DFT functional and pseudopotential are used. This observation is consistent with previously reported *ab initio* MO calculations [4–6], but in sharp contrast with the DFT prediction by Wu *et al.* [8]. We want to stress that the singlet state is an open-shell state that requires a broken-symmetry approach in DFT. Unfortunately, Wu *et al.* did not give the calculation details for this state [8]. The obtained energy ordering of the three electronic states is triplet<singlet<quintet, except for the cases using the exchange-only, LSDA, pure- and meta-GGA functionals with the SSC pseudopotential, where the singlet was predicted too high in energy so that the ordering becomes triplet<quintet<singlet.

Among all the DFT functionals used with the SSC pseudopotential, B3LYP predicts the smallest singlet-triplet energy splitting ( $\Delta E_{ST}$ ) and the largest quintet-triplet energy difference ( $\Delta E_{QT}$ ). The exchange-only S-null functional gives the smallest  $\Delta E_{QT}$ . Including gradient correction in the exchange functional (comparing B88 with S-null) increases  $\Delta E_{QT}$  by 0.27 eV. However, the effect of correlation on this quantity is not definite; for instance, PW91 introduces a decrease while LYP an increase in  $\Delta E_{QT}$  when BPW91 and BLYP are compared with B88. The differences in  $\Delta E_{ST}$  and  $\Delta E_{QT}$  between the PW91 and LYP correlation functionals (comparing BPW91 with BLYP, and B3PW91 with B3LYP) are smaller than 0.08 and 0.25 eV, respectively. The results from the TPSS functional are very close to those from the PBE functional. Including HF exchange in the GGA functionals leads to an increase (smaller than 0.14 eV) of  $\Delta E_{QT}$ . Compared with the values derived at the MRCI+Q and CCSD(T) levels using the same SSC pseudopotential (see Table I), the best agreements are obtained when the hybrid-GGA func-

TABLE II Equilibrium bond lengths (in Å) of Lu<sub>2</sub> in the lowest-energy singlet, triplet, and quintet states.

Method	SSC			SLC			CEP		
	Singlet	Triplet	Quintet	Singlet	Triplet	Quintet	Singlet	Triplet	Quintet
HF	3.135	3.167	2.832	3.272	3.277	3.033	3.031	3.043	2.766
S-null	3.068	3.064	2.790	3.208	3.197	2.932	3.035	3.037	2.806
B88	3.326	3.183	2.888	3.316	3.296	3.003	3.124	3.119	2.885
SVWN5	3.120	2.997	2.729	3.217	3.116	2.855	2.990	2.986	2.755
BPW91	3.204	3.067	2.792	3.181	3.165	2.896	3.040	3.031	2.803
BLYP	3.237	3.097	2.808	3.129	3.201	2.914	3.064	3.053	2.818
PBE	3.198	3.063	2.789	3.179	3.164	2.894	3.036	3.027	2.800
TPSS	3.197	3.048	2.784	3.182	3.163	2.904	3.025	3.015	2.794
B3PW91	3.058	3.050	2.778	3.158	3.144	2.883	3.019	3.012	2.767
B3LYP	3.079	3.067	2.787	3.180	3.165	2.893	3.035	3.026	2.787
PBE1	3.054	3.047	2.775	3.153	3.139	2.881	3.013	3.006	2.770
MRCI+Q [4]	3.142	3.072							
CCSD(T) [4]		3.058	2.801						
QCISD [5]				3.309	3.242				
CCSD(T) [6]					3.079				

tionals are used, especially for  $\Delta E_{ST}$ , although the DFT values are still a little smaller. From the results calculated with the SLC and CEP pseudopotentials, we first note that gradient correction in the exchange functional decreases  $\Delta E_{ST}$  by  $\sim 0.15$  eV while increasing  $\Delta E_{QT}$  by  $\sim 0.21$  eV. Secondly, correlation functionals decrease  $\Delta E_{ST}$ , whereas no definite behavior is observed for  $\Delta E_{QT}$ . The differences in  $\Delta E_{ST}$  and  $\Delta E_{QT}$  between the PW91 and LYP correlation functionals amount to 0.12 and 0.28 eV, respectively. Thirdly, HF exchange increases  $\Delta E_{ST}$  by at most 0.06 eV and  $\Delta E_{QT}$  by at most 0.07 eV. This can be attributed to their larger values predicted at the HF level.

From the results in Table I, one can see that, when using the hybrid-GGA functionals, the predicted values for  $\Delta E_{ST}$  with all three pseudopotentials are comparable, with the SLC (CEP) values slightly smaller (larger) than the SSC ones. Hence, the hybrid-GGA methods seem to be more accurate in predicting  $\Delta E_{ST}$  than the other DFT methods tested, due to their good performance on energies of the broken-symmetry state. A similar observation has been made based on studies of open-shell singlet states for antiferromagnetically coupled spin-dimers using the broken-symmetry approach [30]. For  $\Delta E_{QT}$ , the SLC and CEP values are respectively slightly smaller and much larger than the SSC values, no matter what DFT functional was used. Finally, we note that the predicted  $\Delta E_{ST}$  values using the SLC pseudopotential are all smaller than the QCISD value obtained with the same large-core pseudopotential.

To summarize this part, we find that all DFT methods studied in this work predict a triplet ground state ( $^3\Sigma_g$ ) for Lu<sub>2</sub>, irrespective of the functional and the pseudopotential used. Including gradient correction in the exchange functional decreases (increases) the value

of  $\Delta E_{ST}$  ( $\Delta E_{QT}$ ). Introducing correlation effects decreases the  $\Delta E_{ST}$  value. The magnitude of  $\Delta E_{ST}$  is more sensitive to the change in the exchange functional than in the correlation functional, whereas for  $\Delta E_{QT}$ , the situation is reversed. The hybrid-GGA functionals combined with the SSC pseudopotential result in  $\Delta E_{ST}$  and  $\Delta E_{QT}$  values in best agreement with the high-level *ab initio* MO results at the MRCI+Q and CCSD(T) levels, with the energy ordering of triplet < singlet < quintet. The SLC and CEP calculations give respectively smaller and larger values for both  $\Delta E_{ST}$  and  $\Delta E_{QT}$ , when compared with the SSC calculations.

## B. Equilibrium bond lengths

The calculated results for equilibrium internuclear distances are listed in Table II, which indicates that, among all the DFT methods tested, the B88 calculation predicts the longest bond length, and the SVWN5 calculation gives the shortest one (except for the singlet state using the SSC and SLC pseudopotentials), the latter being consistent with prior observation of overbinding in LSDA. A comparison of S-null and B88 calculations shows that gradient correction to the Slater exchange leads to an increase in the bond length, up to 0.258 Å for the singlet state, 0.119 Å for the triplet state, and 0.098 Å for the quintet state. Inclusion of correlation effects decreases the calculated bond lengths (when S-null and SVWN5, or B88, BPW91, and BLYP are compared). This behavior is opposed to the usual increase in the bond length when correlation effects are included. It is likely to be the result of important contributions of the excitations starting from the  $6s\sigma_u$  orbital of antibonding character to orbitals of bonding charac-

ter in higher energies. The exceptions are again the singlet state with SSC and SLC pseudopotentials for which the SVWN5 bond lengths are longer than the S-null ones. The meta-GGA TPSS yields bond lengths are very close to those from the pure-GGA PBE functional. Including HF exchange in the calculation (comparing BLYP with B3LYP, BPW91 with B3PW91) decreases the bond length, indicating that the hybrid B3 exchange functional predicts shorter bond lengths than the pure B88 one. This may be explained by the fact that the B3 exchange functional contains about 20% HF exchange and about 72% B88 exchange, with HF predicting a shorter bond length than B88 (see Table II). Similar reasoning may be applied when comparing the PBE and PBE1 results. The difference in bond lengths by various correlation functionals is smaller than 0.052 Å (when BPW91, BLYP, and PBE, or B3PW91, B3LYP, and PBE1 are compared). Hence, the bond length studied is more sensitive to the exchange functional than the correlation functional. Moreover, except for S-null, all the DFT methods employed predict the Lu–Lu bond length to decrease with increasing spin multiplicity, no matter what pseudopotential was used. The decrease of bond lengths in the triplet state with respect to the singlet one may be ascribed to the lower Pauli repulsion in the former state as a result of having two electrons in parallel spin. The reduction of bond lengths when going from triplet to quintet is the result of the electron excitation from the antibonding  $6s\sigma_u$  orbital to the bonding  $5d\sigma_g$  orbital, as manifested by their dominant electronic configurations.

With the SSC pseudopotential for Lu, the predicted bond lengths for the ground triplet state by all the DFT functionals employed (except for B88 and SVWN5) agree well with those obtained at the MRCI+Q and CCSD(T) levels (within 0.039 Å), with the meta- and hybrid-GGA functionals giving the best agreement (within 0.005 Å). For the quintet state, the bond lengths predicted by these functionals also agree closely with the CCSD(T) value (within 0.026 Å). For the singlet state, however, the calculated bond lengths using the pure- and meta-GGA functionals are a little too large (by at least 0.055 Å), while those using the hybrid-GGA functionals are a little too small (by at least 0.065 Å), when compared with the CCSD(T) result. This is presumably due to the fact that the obtained equilibrium distance is for a singlet state that is a broken-symmetry solution, the wave function of which is not a spin eigenfunction but rather is a linear combination of pure singlet and triplet eigenfunctions with similar weights. Yet, the hybrid-GGA functionals seem again to be more suitable than the other ones when used with the SSC pseudopotential in studying the equilibrium Lu–Lu bond length for the broken-symmetry state.

With the SLC pseudopotential, the calculated bond lengths for the triplet state by all the DFT functionals (except for B88) fall in the range between the CCSD(T) and QCISD values, *i.e.* 3.079 and 3.242 Å, respectively.

The predicted bond lengths for the singlet state are all smaller than the QCISD value. Comparison of the calculated bond lengths with different pseudopotentials indicates that the SLC values for the triplet and quintet states are generally larger than the corresponding SSC values by  $\sim 0.1$  Å. This result is consistent with the expected performance of large-core pseudopotentials, which presumably overestimate the bond lengths due to poor treatment of the core-valence correlation relative to the small-core calculations. For the singlet state, only the LSDA and hybrid-GGA results show the expected lengthening of bond lengths. Interestingly, the predicted bond lengths for the ground triplet state using the CEP pseudopotential are smaller (by 0.01–0.04 Å) than those using the SSC pseudopotential, although the number of core electrons is larger in the former pseudopotential. This situation is also pronounced in the singlet state, but less in the quintet state. The difference in the pseudopotential construction and in the basis set for the valence electrons might be partially responsible for these observations.

### C. Harmonic vibrational frequencies

Theoretical harmonic vibrational frequencies for Lu<sub>2</sub> in various electronic states are listed in Table III. The exchange-only B88 functional gives the smallest vibrational frequencies among all the methods studied. In accord with the case of bond lengths, including gradient correction in the exchange functional decreases the vibrational frequencies, and introducing correlations in the DFT functionals increases them. Also, the hybrid-GGA affects the pure-GGA calculations in the same directions as HF calculations affect the corresponding quantity. One minor exception is the BLYP frequency for the singlet state with the SSC pseudopotential. The calculated vibrational frequencies are again more sensitive to the change of exchange functionals than the change in correlation functional, which is similar to the case of bond length calculations. Moreover, the vibrational frequencies increase with increasing spin multiplicity, irrespective of the DFT functional and the pseudopotential used. This observation is again in accord with that for the bond length, which shortens with increasing spin multiplicity.

From the SSC results listed in Table III, one sees that, for the ground triplet state, the TPSS functional gives the best agreement with the experimental frequency, with B3PW91 being the second best. The vibrational frequencies predicted by the meta- and hybrid-GGA calculations are comparable or even superior to those by the *ab initio* MO methods at MRCI+Q and CCSD(T) levels, when compared with the experimental value. For the quintet state, the pure-, meta-, and hybrid-GGA functionals all perform reasonably well, with the frequencies from the hybrid variety being a little larger. It is interesting to see that the SVWN5 functional gives a

TABLE III Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) of  $\text{Lu}_2$  in the lowest-energy singlet, triplet, and quintet states.

Method	SSC			SLC			CEP		
	Singlet	Triplet	Quintet	Singlet	Triplet	Quintet	Singlet	Triplet	Quintet
HF	121.9	120.2	159.5	105.9	105.5	114.6	144.8	146.4	144.6
S-null	115.6	117.6	145.5	105.0	107.1	133.5	136.4	138.2	158.3
B88	99.8	105.9	134.7	92.1	95.0	123.8	126.4	129.1	148.3
SVWN5	108.0	123.3	152.0	113.2	115.1	142.6	140.9	142.8	165.8
BPW91	102.6	117.9	146.6	108.1	110.3	138.3	137.4	139.6	161.0
BLYP	97.3	111.1	142.5	101.4	103.3	134.0	132.2	134.3	157.1
PBE	103.7	118.7	147.2	108.7	111.0	138.8	138.4	140.6	161.7
TPSS	104.5	121.9	149.3	110.6	113.1	140.1	140.8	143.0	174.9
B3PW91	121.6	123.2	152.1	113.3	115.4	143.3	141.6	143.7	165.9
B3LYP	116.9	118.8	149.7	108.8	110.8	139.6	137.9	140.1	162.6
PBE1PBE	123.7	125.3	153.3	115.1	117.3	143.2	143.5	145.6	166.5
MRCI+Q [4]	108.0	124.0							
CCSD(T) [4]		122.0	146.0						
CCSD(T)					120.0				
QCISD				95.5	113.3				
Experiment [9]		121.6±0.8							

singlet frequency in best agreement with the MRCI+Q value, with the TPSS functional being the second best.

With the SLC pseudopotential, all DFT functionals (except B88 and BLYP) predict the ground state vibrational frequencies lower than the CCSD(T) value by at most  $10 \text{ cm}^{-1}$ , but close to the QCISD value (within  $4 \text{ cm}^{-1}$ ). For the singlet state, all functionals yield smaller values (by  $3.2\text{--}19.6 \text{ cm}^{-1}$ ) than the one obtained at the QCISD level. Comparing the calculated SLC with SSC results (Table III) indicates that the SLC values for the triplet and quintet states are smaller by  $7\text{--}10 \text{ cm}^{-1}$  than the corresponding SSC values, as in the case of bond lengths. For the singlet state, however, only the vibrational frequencies from the hybrid-GGA calculations show the expected decreases when increasing the core-size. The calculated CEP vibrational frequencies are higher than the corresponding SSC ones, no matter what electronic state was studied. These observations are consistent with those in the case of bond lengths.

#### D. Ground-state dissociation energies

The calculated dissociation energies for  $\text{Lu}_2$  in the ground triplet state are summarized in Table IV. We first note that, among all the methods studied in this work, the B88 calculation predicts the largest dissociation energy and the SVWN5 calculation gives the smallest one, the latter due to the well-known overbinding in LSDA. Inclusion of gradient correction in exchange functional (comparison of S-null with B88) increases the calculated dissociation energies by about  $0.80 \text{ eV}$ . When correlation was added to the calculations (BPW91 and

TABLE IV Dissociation energies (in eV) of  $\text{Lu}_2$  in the ground triplet state.

Method	SSC	SLC	CEP
HF	1.54	1.15	1.83
S-null	2.02	1.98	2.13
B88	1.19	0.97	1.32
SVWN5	2.17	1.95	2.36
BPW91	1.74	1.16	1.95
BLYP	1.44	1.23	1.59
PBE	1.83	1.61	2.06
TPSS	1.77	1.55	2.01
B3PW91	1.63	1.40	2.33
B3LYP	1.37	1.18	2.00
PBE1	1.71	1.52	2.00
MRCI+Q [4]	1.73		
CCSD(T) [4]	1.67		
QCIS [5]		1.79	
Experiment [10]	1.43±0.34		

BLYP compared to B88), the dissociation energies increase by up to  $0.63 \text{ eV}$  for the PW91 correlation functional and  $0.27 \text{ eV}$  for the LYP one. Upon inclusion of HF exchange (comparison of B3LYP and BLYP, B3PW91 and BPW91, or PBE1 and PBE), the predicted dissociation energies decrease by about  $0.10 \text{ eV}$  when using the SSC pseudopotential. However, this decrease is not observed when using the CEP and SLC pseudopotentials, for which diverse behaviors are exhibited. As in the cases of bond lengths and vibrational frequencies, the calculated dissociation energies are again

more sensitive to the change of exchange functionals than the change in correlation functional.

Within the SSC results, the BLYP functional gives a dissociation energy in best agreement with the experimental value, with B3LYP being the second best. The BPW91, TPSS, B3PW91, and PBE1 functionals all predict dissociation energies very close to the MRCI+Q and CCSD(T) values, which are also within the range of the experimental uncertainty; see Table IV. With the SLC pseudopotential, the PBE functional gives the best agreement with the QCISD result, the TPSS functional being next best. It is interesting to see that the TPSS, B3PW91, and PBE1 functionals all yield dissociation energies very close to the experimental value of 1.43 eV. Compared with the SSC results, all the methods with the SLC pseudopotential predict smaller dissociation energies, in line with the cases of bond lengths and vibrational frequencies. Of the three pseudopotentials used, the CEP pseudopotential gives the largest dissociation energy, no matter what DFT functional was used.

It should be noted that the ZPVE and BSSE corrections to the dissociation energy were included in the calculations. The ZPVE was found to be at most 0.008 eV, and thus may be safely neglected. The BSSE magnitude was estimated, using the counterpoise correction [31], to be up to 0.3 eV for the SSC calculations, 0.2 eV for the SLC calculations, and 0.6 eV for the CEP results. It is known that the counterpoise correction tends to overestimate the BSSE magnitude. We therefore believe that the true results are bracketed by the estimates with and without this correction.

To summarize, we observe that the behaviors of calculated bond lengths, vibrational frequencies, and ground-state dissociation energies with respect to changing the DFT functional and pseudopotentials are generally consistent with each other. Compared with the *ab initio* MO theory and experimental results, the values of these quantities predicted by the meta- and hybrid GGA functionals give the best overall agreement, when used with the SSC pseudopotential.

### E. Effects of HF exchange on covalent bonding

The atomic ground-state of Lu is  $4f^{14}5d^{16}s^2$   $^2D$ , and the low-lying excited states  $4f^{14}6s^26p^1$   $^2P$  and  $4f^{14}5d^26s^1$   $^4F$  are 0.72 and 2.34 eV higher in energy, respectively [27]. Hence, the 6p orbitals are expected to participate in Lu–Lu bonding by a significant degree. Indeed, a natural orbital analysis of the ground triplet state at the B3LYP/SSC level shows that the 6p orbitals are admixed into the occupied  $6s\sigma_u$  and  $5d\pi_u$  orbitals by 30% and 16% via s-p and p-d hybridizations, respectively.

The participation of 6p orbitals in chemical bonding is also manifested when studying calculated ground-state properties, such as bond length and dissociation

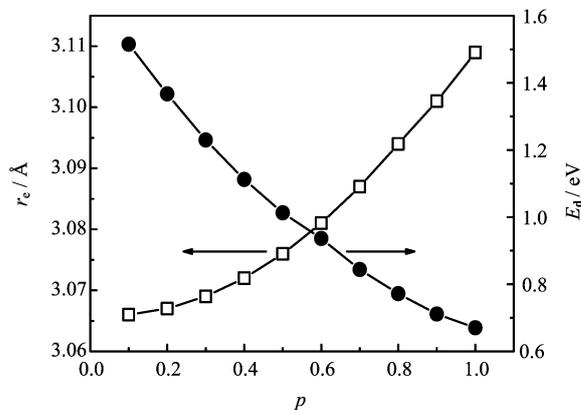


FIG. 1 Equilibrium bond length ( $r_e$ ) and dissociation energy ( $E_d$ ) of  $\text{Lu}_2$  in the ground triplet state computed with the B3LYP method using different amounts of HF exchange.

energy, as a function of percentage of HF exchange in the B3LYP-like calculations. The original B3LYP functional can be written as

$$pE_x^{\text{HF}} + (1-p)E_x^{\text{Slater}} + 0.72\Delta E_x^{\text{Becke}} + 1.0E_c^{\text{VWN}} + 0.81\Delta E_c^{\text{LYP}}$$

with  $p=0.2$  and  $q=0.8$ , where  $E_x^{\text{HF}}$  is the HF exchange,  $E_x^{\text{Slater}}$  is the local Slater exchange [13], and  $\Delta E_x^{\text{Becke}}$  is the nonlocal Becke exchange correction [14].  $E_c^{\text{VWN}}$  is the local VWN correlation functional [15], and  $\Delta E_c^{\text{LYP}}$  is the LYP nonlocal correlation functional [20]. We changed the  $p$  parameter in the interval  $0.1 \leq p \leq 1.0$  by an increment of 0.1. Figure 1 depicts the calculated ground-state bond length and dissociation energy as a function of  $p$  value. It shows that the bond length increases from 3.066 Å to 3.109 Å whereas the dissociation energy decreases from 1.515 eV to 0.670 eV, when increasing the HF percentage from  $p=0.1$  to  $p=1.0$ . While both behaviors are consistent with the longer bond length of 3.167 Å and the larger dissociation energy of 1.54 eV predicted at the HF level, the underlying reasons may be connected to the covalent bonding in  $\text{Lu}_2$ . It has been shown that covalent bonding can be described in terms of charge fluctuations [32], which in the case of  $\text{Lu}_2$ , depends strongly on the participation of 5d orbitals in bonding. Wang *et al.* have already reported a significant contribution of 5d orbital to the covalent bonding in the case of ytterbium clusters [33]. A similar 5d contribution to Lu–Lu covalent bonding is thus expected. As shown above, the 6p orbitals are admixed into the occupied 5d orbitals by a sizable amount, which diminishes the contribution of 5d orbitals to covalent bonding. Table V gives the electron configurations for Lu atom as derived from the natural population analysis of the B3LYP-like/SSC results with  $p=0.1-1.0$ . The calculated bond lengths and dissociation energies are also listed. One can see that, in going from  $p=0.1$  to  $p=1.0$ , the occupation number of 5d (6p) orbitals decreases (increases), and hence, the covalent

character of the Lu–Lu bonding decreases, consistent with the observed trends for the bond length and the dissociation energy. It is interesting to see that, when  $p=0.40$ , the calculation reproduces the bond length of 3.072 Å obtained at the MRCI+Q level, whereas, with  $p=0.16$ , the calculated dissociation energy matches the experimental value of 1.43 eV [4].

TABLE V Equilibrium bond lengths ( $r_e$ ), dissociation energies ( $E_d$ ), and natural electron configurations of Lu<sub>2</sub> in the ground triplet state computed with the B3LYP-like method using different fractions of HF exchange.

$p$	$r_e/\text{Å}$	$E_d/\text{eV}$	Natural electron configuration
0.1	3.066	1.515	$6s^{1.94}5d^{0.99}6p^{0.07}$
0.2	3.066	1.367	$6s^{1.94}5d^{0.97}6p^{0.08}$
0.3	3.067	1.230	$6s^{1.94}5d^{0.96}6p^{0.10}$
0.4	3.069	1.112	$6s^{1.95}5d^{0.94}6p^{0.11}$
0.5	3.072	1.013	$6s^{1.95}5d^{0.92}6p^{0.13}$
0.6	3.076	0.936	$6s^{1.95}5d^{0.91}6p^{0.15}$
0.7	3.081	0.844	$6s^{1.95}5d^{0.89}6p^{0.17}$
0.8	3.087	0.772	$6s^{1.95}5d^{0.87}6p^{0.18}$
0.9	3.094	0.711	$6s^{1.94}5d^{0.85}6p^{0.20}$
1.0	3.101	0.670	$6s^{1.94}5d^{0.83}6p^{0.22}$

#### IV. CONCLUSION

In the work, we report a comparative theoretical study on the lowest-energy singlet, triplet, and quintet states of Lu<sub>2</sub> using DFT with ten different density functionals and three types of RECP for Lu. Relative state energies, equilibrium bond lengths, vibrational frequencies, and ground-state dissociation energies were examined. Factors that influence the calculated properties were explored, including the nature of the density functional chosen, the type of RECP used, and the percentage of HF exchange in the density functional. All the DFT calculations performed in this work predicted the triplet state ( ${}^3\Sigma_g$ ) as the ground state, no matter what DFT functional and pseudopotential were used. This result agrees with those by high-level *ab initio* MO calculations, but contrasts with that of a recent DFT calculation, where the ground state was predicted to be a singlet state. Compared with high-level *ab initio* calculations and experiments, the best overall results were obtained using hybrid-GGA functionals in combination with the SSC pseudopotential, especially for the open-shell singlet state that was studied with the broken-symmetry approach. The predicted behaviors of bond lengths, vibrational frequencies, and ground-state dissociation energies with respect to changing the DFT functional and pseudopotentials are generally consistent with each other. The obtained values of these quantities by meta-GGA TPSS functional also agree well with those by higher-level *ab initio* calculations

and experiments. Finally, the effect of HF exchange in B3LYP functional on the calculated ground-state bond length and dissociation energy was addressed. It was found that with increasing amount of HF exchange, the bond length increases whereas the dissociation energy decreases. These behaviors are explained in terms of the contribution of Lu 5d orbitals to the covalent bonding.

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