The Journal of Chemical Physics

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Cite as: J. Chem. Phys. **156**, 104103 (2022); https://doi.org/10.1063/5.0085213
Submitted: 13 January 2022 • Accepted: 14 February 2022 • Accepted Manuscript Online: 18 February 2022 • Published Online: 09 March 2022

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The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

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Submitted: 13 January 2022 • Accepted: 14 February 2022 •
Published Online: 9 March 2022



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## ABSTRACT

Aurophilicity is a $d^{10}$–$d^{10}$ closed-shell interaction, which is repulsively calculated by the Hartree–Fork (HF) method, whereas binding energies ($E_b$) are largely overestimated under the second-order Møller–Plesset (MP2) method, compared to the coupled cluster singles and doubles with perturbative triples [CCSD(T)] method. The unusual energy errors between different wave functional methods were also verified in other closed-shell metallophilic systems and even were taken as a label of metallophilic interaction. Here, we performed a benchmark study on a collection of structures with weak interactions, sp–sp bonds, sp–d bonds, and d–d bonds, to investigate the influence factor of the errors of HF and MP2 methods. It was found that the large energy errors of HF and MP2 methods were not specified for closed-shell interactions, and the errors could also be very large for many covalent bonds, which was strongly related to the azimuthal quantum number of interaction orbitals. Compared to the CCSD(T) method, the MP2 method weakens the s–s covalent interactions slightly, strengthens the p–p covalent interactions slightly, and overestimates the d–d covalent interactions largely (can be −170 kcal/mol for the Re–Re quadruple bond). This benchmark study suggests that the special energy errors in metallophilicity may result from the participation of d orbitals. Benchmark studies on various density functional methods were also given for calculating binding energies of d–d bonds.



## I. INTRODUCTION

Metallophilic interactions, the tendency of complexes containing metal atoms with closed electron shells to establish attractive short metal–metal contacts, are interesting research targets from both an experimental and theoretical perspective.[1–7] Jiang *et al.*[8] pioneered the theoretical study of $Au^I\cdots Au^I$ complexes and thought that the unusual interaction was due to the hybridization between the 5d, 6s, and 6p orbitals of gold, which were then named "aurophilicity" in gold chemistry. Afterward, similar strong closed-shell interactions were also found in other transition metals, such as $Cu^I$, $Ag^I$, $Hg^{II}$, and $Au^{III}$, and they were called "metallophilicity."[5,6,9–14] The binding energies ($E_b$) of the closed-shell interactions can be up to 12 kcal/mol,[5] much stronger than van der Waals interactions and even comparable with strong hydrogen bonds.[2]

Sometimes it is difficult to evaluate the binding energies of closed-shell interactions by wave functional methods because of large energy errors. Pyykkö and Zhao[15,16] first found that there were no attractions at the Hartree–Fork (HF) level for a perpendicular $(ClAuPH_3)_2$ dimer, while stronger attractions appeared at the second-order Møller–Plesset (MP2) level, compared with the results of the coupled cluster singles and doubles with perturbative triples [CCSD(T)] level. They also found that the metallophilic interaction strength and Au–Au distance oscillate quite strong along the series HF, MP2, MP3, MP4, CCSD, and CCSD(T). It was, therefore, concluded that $Au^I\cdots Au^I$ aurophilicity is attributed to electron correlation effects. Subsequently, similar energy errors were widely verified in many metallophilic interactions.[4,17–28] Hermann *et al.*[20] focused on cuprophilicity in $[CH_3–Cu–X]_2$ (X = $OH_2$, $NH_3$, $SH_2$, $PH_3$, etc.), in which all interaction potential curves are attractive under the MP2 level and are repulsive under the HF level. Thus,

they thought cuprophilic interactions could be explained by electron correlation effects. The energy difference of HF and MP2 methods calculated by Barreiro *et al.*[18] on the model system $[Ag_6(SH)_6]$ was up to 300 kJ/mol, which suggested that considering the correlation effect was essential to reproduce argentophilic structures. The energy errors of HF and MP2 methods were calculated to indicate the existence of metallophilic interactions, which seems to be regarded as a label of metallophilic interactions. However, this energy error was also found in some covalent bonds.[29,30] It is necessary to verify the origin of the large energy errors of HF and MP2 methods.

Here, we carry out extensive calculations on the binding energies of a series of selected systems, including closed-shell interactions, covalent bonds, and weak interactions. The oscillation of bonding energy displays intriguing rules under different calculation methods, where the energy errors are mainly determined by azimuthal quantum number of the interaction orbitals. We also provide a benchmark study on various density functional (DFT) methods for calculating the binding energies of d–d interactions.

## II. COMPUTATIONAL METHODS

Geometry optimization and frequency analysis are performed under LC-$\omega$PBE functional with D3(BJ)[31–33] dispersion correlation, and relativistic effective core potential basis set (def2-QZVP) is used for each atom.[34] Binding energy ($E_b$) is calculated under HF, MP2, and CCSD(T) methods at def2-QZVP basis set and defined as $E_b = E(AB) - E(A) - E(B)$, where $E(AB)$, $E(A)$, and $E(B)$ represent the absolute energy of the whole system and two parts of system, respectively.[35,36] The energy error is defined as $Error\ (Y) = E_b(Y) - E_b[CCSD(T)]$, where Y = HF, MP2, MP3, and MP4. Chemical bonding analysis for the selected complexes is performed from the natural bonding orbital (NBO) analysis, adaptive natural density partitioning (AdNDP)[37–39] analysis, and electron localized function (ELF)[40–43] method. All calculations are based on the Gaussian 16 package[44] and the MOLPRO program.[45] Analyses of the electronic structure are performed by the Multiwfn package, and molecular visualization is performed by the VMD package.[46]

## III. RESULTS AND DISCUSSION

### A. Closed-shell interactions

To explore energy errors of HF and MP2 methods in metallophilic interactions, we selected several closed-shell structures for systematic calculations based on the results of Pyykkö.[16] Perpendicular $(XMPH_3)_2$ (M = Au, Ag, Cu; X = F, Cl, Br) and $(HgX_2)_2$ (X = H, Cl, Br, Me) with $d^{10}$–$d^{10}$ closed-shell interactions were fully optimized at the LC-$\omega$PBE-D3(BJ)/def2-QZVP level of theory, as shown in Fig. 1. Dihedral angles of P–Au–Au–P and X–Hg–Hg–X are fixed at 90° to decrease the influence of ligands. Table I lists the binding energies of the interaction at the CCSD(T)/def2-QZVP level and energy errors of HF and MP2 methods referred to the CCSD(T) method. $E_b$[CCSD(T)] of these metallophilic interactions range from −1 to −7 kcal/mol, which belongs to weak interactions. It is clear that the binding energy is overestimated by MP2 and underestimated by HF for all listed dimers with $d^{10}$–$d^{10}$ interactions, which even shows repulsion under the HF method.

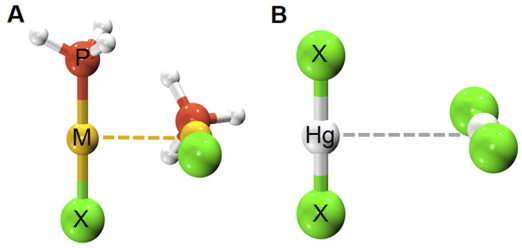


**FIG. 1.** (a) $(XMPH_3)_2$ (M = Au, Ag, Cu; X = F, Cl, Br) and (b) $(HgX_2)_2$ (X = H, Cl, Br, Me) with perpendicular conformation optimized at the LC-$\omega$PBE-D3(BJ)/def2-QZVP level.

For comparison, other closed-shell interactions ($d^8$–$d^{10}$, $d^8$–$d^8$, and $d^{10}$–$s^2$) were also performed in $(ClMPH_3)_2Cl_2$ (M = Au and Ag), $[Cl_2Pt(CO)_2]_2$, $[Pt(PH_3)_3Tl]^+$, and $[ClAu(PH_3)_2Tl]^+$, based on previous literature studies.[23–25,47,48] The optimized structures are shown in Fig. S1 of the supplementary material, and the energy errors are also listed in Table I. As same as the $d^{10}$–$d^{10}$ closed-shell interactions, $E_b$[CCSD(T)] of $d^8$–$d^{10}$, $d^8$–$d^8$, and $d^{10}$–$s^2$ interactions are also overestimated by the MP2 method and underestimated by the HF method. The results demonstrate that the energy errors of HF and MP2 methods widely exist in metallophilic interactions.

### B. Covalent interactions and weak interactions

Besides closed-shell interactions, comprehensive investigations on s–s, p–p, and d–d covalent bonds and other weak interactions were carried out to explore the energy errors of HF and MP2 methods.

#### *1. s–s bonds*

We considered elements in IA and IIA to form a series of small molecules with s–s bonds, including diatomic molecules, H–H, Li–Li, Na–Na, LiH, NaH, etc., $sp^3$ hybridization molecules, $CH_4$, $NH_3$, $PH_3$, etc., and a special molecule $OsH_4$ with $d^3s$ hybridization AdNDP orbitals of $OsH_4$ are shown in Fig. S2. The above 25 molecules were optimized at the LC-$\omega$PBE-D3(BJ)/def2-QZVP level of theory, and data of binding energies are listed in Table II. $E_b$ of s–s bonds calculated by the CCSD(T) method ranges from −9 to −109 kcal/mol, and the energy errors of HF and MP2 methods are all positive values. It is clear that the HF method underestimates the strength of s–s bonds, while the binding energies of the MP2 method are only slightly higher than that of the CCSD(T) method with errors of 0–6 kcal/mol. Evaluations of the MP2 method for s–s bonds are relatively reasonable, which means the situation of energy errors is different from that of closed-shell interactions.

#### *2. p–p bonds*

Several small molecules with p–p bonds, including the single bond, double bond, and triple bond, such as $CH_3$–$CH_3$, $CH_2$=$CH_2$, and CH≡CH, were optimized at the LC-$\omega$PBE-D3(BJ)/def2-QZVP level. Table III lists the results of bonding energy calculated by the CCSD(T) method and the energy errors of HF and MP2 methods.

**TABLE I.** Binding energies ($E_b$) for $d^{10}$–$d^{10}$, $d^{10}$–$d^8$, $d^8$–$d^8$, and $d^{10}$–$s^2$ closed-shell interactions at the CCSD(T)/def2-QZVP level of theory and energy errors (*Error*) of HF and MP2 methods compared to the CCSD(T) method in kcal/mol.

| Type | Structure | Bond | $E_b$ [CCSD(T)] | *Error* (HF) | *Error* (MP2) |
|---|---|---|---|---|---|
| $d^{10}$–$d^{10}$ | $(ClCuPH_3)_2$ | Cu–Cu | −6.73 | +11.74 | −0.14 |
| | $(ClAgPH_3)_2$ | Ag–Ag | −6.29 | +10.19 | −2.00 |
| | $(BrAuPH_3)_2$ | Au–Au | −6.27 | +10.59 | −3.69 |
| | $(ClAuPH_3)_2$ | Au–Au | −5.78 | +10.11 | −3.46 |
| | $(FAuPH_3)_2$ | Au–Au | −5.04 | +8.01 | −2.44 |
| | $(HgMe_2)_2$ | Hg–Hg | −2.79 | +5.98 | −1.78 |
| | $(HgBr_2)_2$ | Hg–Hg | −3.97 | +8.84 | −3.90 |
| | $(HgCl_2)_2$ | Hg–Hg | −1.76 | +5.01 | −1.45 |
| | $(HgH_2)_2$ | Hg–Hg | −1.20 | +3.44 | −1.19 |
| $d^{10}$–$d^8$ | $(ClAuPH_3)_2Cl_2$ | Au–Au | −3.53 | +7.53 | −3.09 |
| | $(ClAgPH_3)_2Cl_2$ | Ag–Ag | −3.12 | +7.07 | −2.08 |
| $d^8$–$d^8$ | $[Cl_2Pt(CO)_2]_2$ | Pt–Pt | −11.87 | +7.98 | −3.37 |
| $d^{10}$–$s^2$ | $[ClAu(PH_3)_2Tl]^+$ | Au–Au | −22.16 | +11.49 | −5.92 |
| | $[(PH_3)_3PtTl]^+$ | Pt–Pt | −36.80 | +12.94 | −8.83 |

Similar to s–s bonds, the bonding energy of p–p bonds is underestimated by the HF method and is relatively accurate under the MP2 method, but the results of MP2 are slightly overestimated compared to the CCSD(T) method.

In Table III, p–p single bonds are overestimated by MP2 with 0–7 kcal/mol, p–p double bonds with 8–13 kcal/mol, and p–p triple bonds with 12–16 kcal/mol. However, in proportion, the binding energies calculated by the MP2 method is only slightly lower than

**TABLE II.** Binding energies ($E_b$) for s–s bonds at the CCSD(T)/def2-QZVP level of theory and energy errors (*Error*) of HF and MP2 methods compared to the CCSD(T) method in kcal/mol.

| Type | Structure | Bond | $E_b$ [CCSD(T)] | *Error* (HF) | *Error* (MP2) |
|---|---|---|---|---|---|
| s–s | $H_2$ | H–H | −108.38 | +24.74 | +4.85 |
| | $Li_2$ | Li–Li | −23.76 | +19.84 | +6.67 |
| | $Na_2$ | Na–Na | −16.50 | +17.07 | +5.07 |
| | $K_2$ | K–K | −12.16 | +14.94 | +4.83 |
| | $Rb_2$ | Rb–Rb | −10.77 | +14.13 | +4.63 |
| | $Cs_2$ | Cs–Cs | −9.72 | +13.41 | +4.52 |
| | LiH | Li–H | −56.38 | +22.40 | +5.34 |
| | NaH | Na–H | −95.86 | +22.97 | +5.82 |
| | KH | K–H | −43.64 | +21.75 | +5.49 |
| | $BeH_2$ | Be–H | −40.88 | +20.78 | +3.49 |
| | $MgH_2$ | Mg–H | −72.14 | +19.94 | +3.84 |
| | $CaH_2$ | Ca–H | −61.35 | +20.32 | +4.45 |
| $sp^3$–s | $CH_4$ | C–H | −118.08 | +24.05 | +0.81 |
| | $NH_3$ | N–H | −113.21 | +28.83 | +0.37 |
| | $SiH_4$ | Si–H | −94.87 | +18.32 | +2.40 |
| | $PH_3$ | P–H | −85.34 | +18.99 | +2.28 |
| | $GaH_3$ | Ga–H | −83.19 | +17.77 | +2.75 |
| | $GeH_4$ | Ge–H | −87.85 | +18.09 | +2.60 |
| | $AsH_3$ | As–H | −49.29 | +20.40 | +2.01 |
| | $H_2Se$ | Se–H | −82.59 | +21.44 | +2.04 |
| $d^3s$–s | $OsH_4$ | Os–H | −85.63 | +23.87 | +1.42 |

**TABLE III.** Binding energies ($E_b$) for p–p bonds at the CCSD(T)/def2-QZVP level of theory and energy errors (*Error*) of HF and MP2 methods compared to the CCSD(T) method in kcal/mol.

| Type | Structure | Bond | $E_b$ [CCSD(T)] | *Error* (HF) | *Error* (MP2) |
|---|---|---|---|---|---|
| p–p (single bond) | $C_2H_6$ | C–C | −111.86 | +26.05 | −3.69 |
| | $N_2H_4$ | N–N | −70.88 | +31.64 | −6.52 |
| | $H_2O_2$ | O–O | −50.47 | +46.26 | −7.00 |
| | $CH_3OH$ | C–O | −103.23 | +32.52 | −6.44 |
| | $CH_3CH_2NO_2$ | C–N | −72.67 | +16.16 | −3.43 |
| | $Si_2H_6$ | Si–Si | −76.89 | +18.19 | −0.05 |
| | $P_2H_4$ | P–P | −56.34 | +18.08 | −2.17 |
| | $S_2H_2$ | S–S | −54.87 | +22.55 | −3.47 |
| p–p (double bond) | $C_2H_4$ | C=C | −201.89 | +24.11 | −13.25 |
| | $N_2H_2$ | N=N | −122.84 | +64.76 | −8.23 |
| | $O_2$ | O=O | −115.28 | +80.61 | −11.20 |
| | $CH_2O$ | C=O | −182.61 | +76.51 | −9.79 |
| | $CH_3CH_2NO_2$ | N=O | −93.07 | +52.46 | −12.78 |
| | $H_2CNH$ | C=N | −162.09 | +58.51 | −6.54 |
| | $H_2CS$ | C=S | −129.94 | +52.23 | −3.51 |
| p–p (triple bond) | $C_2H_2$ | C≡C | −231.93 | +45.04 | −15.93 |
| | $N_2$ | N≡N | −215.79 | +96.38 | −12.25 |
| | HCN | C≡N | −220.13 | +72.27 | −14.51 |

those calculated by the CCSD(T) method. For the HF method, p–p single bonds are underestimated with 12–16 kcal/mol, p–p double bonds with 24–80 kcal/mol, and p–p triple bonds with 45–96 kcal/mol. In summary, with the increase in the bond order and enhancement of interactions, it is obvious that underestimation of the HF method and overestimation of the MP2 method become strong.

### 3. d-p and d-d bonds

We selected several molecules with d–p and d–d bonds to discuss the energy errors in different calculation methods. Figure 2 displays the optimized structures of $MX_4$ (M = Os, Ti, X = F and Cl), perpendicular $(Cl_2AuPH_3)_2$ and $[PtCl(CO)_2]_2$, $Mo_2Cl_6$, $(Re_2Cl_8)^{2-}$, and $W_2$ (full AdNDP bonding analyses of these structures are shown in Figs. S3–S7).[49–52] Figure 2 shows the d–p single bond in $MX_4$ (M = Os, Ti, X = F and Cl), the d–d single bond in perpendicular $(Cl_2AuPH_3)_2$ and $[PtCl(CO)_2]_2$, the d–d triple bond in $Mo_2Cl_6$, the d–d quadruple bond in $(Re_2Cl_8)^{2-}$, and the d–d sextuple bond in $W_2$.

The binding energies of d–p and d–d bonds in these structures at the CCSD(T) level and the energy errors of HF and MP2 methods are summarized in Table IV. For structures $OsX_4$ and $TiX_4$ (X = F and Cl), $MX_4$ process $T_d$ geometric symmetry, where d orbitals of Os (Ti) atom and p orbitals of Cl (F) hybrid to form $d^3s$–$p_z$ orbitals.[53] The binding energies of $d^3s$–p bonds calculated by the CCSD(T) method ranges from −89 to −145 kcal/mol, which are underestimated by the HF method and overestimated by the MP2 method. For d–d bonds, $E_b$[CCSD(T)] of Au–Au and Pt–Pt single bonds are −44.50 and −67.17 kcal/mol, and the energy errors are still very large for HF and MP2 methods. In addition, $E_b$[CCSD(T)] of the d–d triple bond in $Mo_2Cl_6$ is −70.86 kcal/mol, the d–d quadruple bond in $(Re_2Cl_8)^{2-}$ is −97.37 kcal/mol, and the d–d sextuple bond in $W_2$ is −106.76 kcal/mol. For these d–d multiple bonds, it is surprising that the energy errors of the HF method are +153.45, +153.37, and +268.87 kcal/mol, respectively, while the errors of the MP2 method are −93.18, −171.31, and −188.46 kcal/mol, respectively. The errors are unreasonably large and increase with d–d bond orders, which indicates that the MP2 method cannot give reasonable results for the binding energy of d–d bonds.

### 4. Weak interactions

Metallophilic interaction is classified into weak interactions, and so we are curious about the energy errors of HF and MP2 methods in other weak interactions. Table V lists several molecules with intermolecular hydrogen bonds involving H···N, H···P, and H···O, as well as halogen bonding involving Br···P, I···P, and I···N. In addition, gold–hydrogen bonding (Au···H bond), which are also calculated in structure $(FAuF)^{-1}$···HF and $(XAuPH_3)^{-1}$···HF (X = F and Cl), has been proved by convincing and consistent evidence.[54–56] All structures optimized at the LC-ωPBE-D3(BJ)/def2-QZVP level are shown in Fig. S8. For these structures with weak interactions in Table V, $E_b$[CCSD(T)] ranges from −2 to −16 kcal/mol, which is still underestimated by the HF method and little overestimated by the MP2 method.

The errors of these weak interactions are smaller than those of metallophilic interactions. Moreover, the errors of the hydrogen bond and the Au···H bond are obviously smaller than those of the halogen bond. Interestingly, the tendency of the

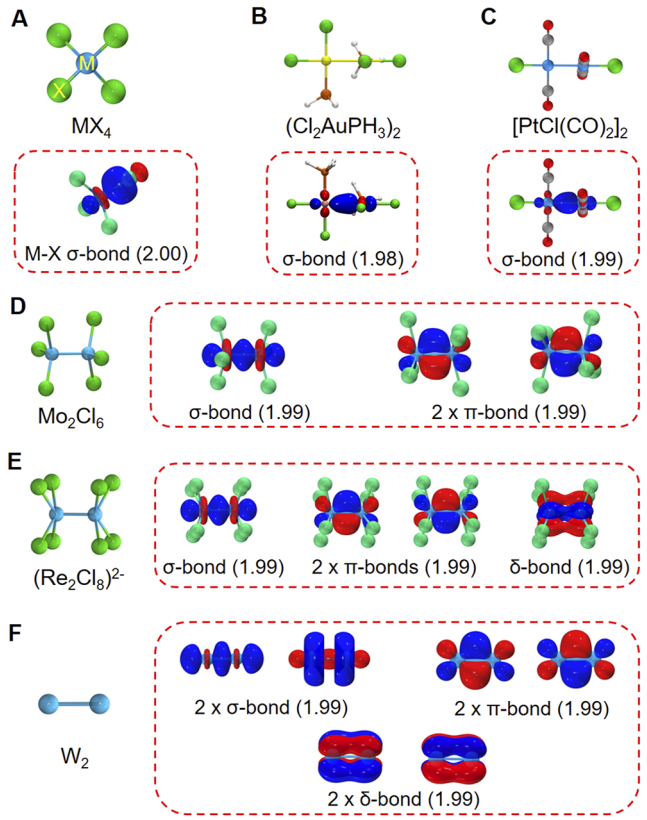


**FIG. 2.** Optimized structures at the LC-$\omega$PBE-D3(BJ)/def2-QZVP level and AdNDP bonding orbitals for (a) $MX_4$ ($T_d$, M = Os and Ti, X = F and Cl), (b) $(Cl_2AuPH_3)_2$, (c) $[PtCl(CO)_2]_2$, (d) $Mo_2Cl_6$, (e) $(Re_2Cl_8)^{2-}$, and (f) $W_2$. Occupation numbers are in parentheses.

errors in weak interactions is similar to that in covalent interactions, which is also related to the azimuthal quantum number of the interaction orbitals. Actually, the hydrogen bond, the Au···H bond, halogen bond, and the metallophilic interaction can be regarded as s–p, s–d, p–p, and d–d weak interactions, respectively.

### C. Discussions on d–d bonding

Previous works have shown that $d^{10}$–$d^{10}$ aurophilic interactions may due to the strong relativistic effect and s–d hybridization of the Au atom.[16,21,27,57] However, as shown in Table II, for $Li_2$, $Na_2$, $K_2$, $Rb_2$, and $Cs_2$ series with s–s bonds, the interactions are underestimated for both HF and MP2 methods, and the errors are not related to atomic mass. To further investigate the relationship between the relativistic effect and energy errors, Table VI compares the energy errors of HF and MP2 methods of $Cu_2$, $Ag_2$, and $Au_2$ molecules with reference to the CCSD(T) method. Different from the s–s bond in IA series, the values of energy errors of the MP2 method decrease obviously from $Cu_2$ to $Ag_2$, and to $Au_2$. This phenomenon may result from the relativistic effect and s–d hybridization. The component of the d orbital for the Au–Au bond is about 5.4%, much greater than those of Ag–Ag (1.0%) and Cu–Cu (1.2%) bonds. Therefore, the reason for the overestimation of $E_b$ of the Au–Au bond (−6.25 kcal/mol) at the MP2 level is also the azimuthal quantum number of interaction orbitals (large component of d orbital), resulting from a strong relativistic effect.

Previous works have shown that the strength of metallophilic interaction oscillates quite strong along the series HF, MP2, MP3, MP4, and CCSD(T) methods.[1,16] Figure 3(a) gives the energy error curves of HF, MP2, MP3, and MP4 methods for several typical structures with Au···Au, Ag···Ag, and Hg···Hg closed-shell interactions, where $E_b$ of the CCSD(T) method is set to zero for comparison. It is clear that $E_b$ of metallophilic interactions are underestimated by HF and MP3 methods and are overestimated by MP2 and MP4 methods, consistent with previous studies. For comparison, the energy error curves of s–s, p–p, and d–d bonds are also given in Fig. 3. For s–s bonds, the binding energies of HF, MP2, MP3, and MP4 methods are all underestimated but gradually approach to that of the CCSD(T) method [Fig. 3(b)]. For p–p bonds, MP2 and MP4 methods all overestimate binding energies, but the MP3 method is close to the CCSD(T) method [Fig. 3(c)]. Oscillation in p–p bonds is greater than that in s–s bonds but smaller than that in metallophilic interactions. It is worth noting that the absolute values of the energy error of d–d bonds are much larger than those of $d^{10}$–$d^{10}$ metallophilic interactions [Fig. 3(d)], and they display consistent oscillation. Consistence of the energy error curves indicates a certain similarity between the metallophilic interactions and d–d bonds, and there may be a confirmative d–d covalent component in metallophilic interactions.

### D. Benchmark studies on DFT methods for d–d bonds

As discussed earlier, HF and MP2 methods cannot give accurate results when calculating binding energies of d–d bonds and may even carry out completely wrong results. Besides, calculating large molecules by the CCSD(T) method is time-consuming. Therefore, DFT methods are taken into consideration to evaluate $E_b$ with large errors of the MP2 method, which is expected to obtain more reasonable results.

The bonding energy of d–d bonds at the CCSD(T) level in four structures, including Au–Au and Pt–Pt single bonds, the Mo–Mo triple bond, and the Re–Re quadruple bond, is given in Table VII. Compared to the CCSD(T) method, Table VII also lists the energy errors of HF, MP2, SCS-MP2, and DFT methods, including TPSS(h),[58,59] PBE(0),[60–62] M062X,[63] BP86,[64] B3LYP,[62,65,66] CAM-B3LYP,[67] and LC-$\omega$PBE.[31,32] The smallest absolute values of errors with percentage less than 10% in each structure are given in bold. The binding energy of the Au–Au bond in $(Cl_2AuPH_3)_2$ is −44.50 kcal/mol in the CCSD(T) method, and three PBE-based methods (PBE, PBE0, and LC-$\omega$PBE) are more accurate in which the error percentages are less than 3%. For the Pt–Pt single bond in $[PtCl(CO)_2]_2$, BP86, TPSS, and LC-$\omega$PBE functionals can give more accurate results, compared to the CCSD(T) method. For $Mo_2Cl_6$, $E_b$ of the Mo–Mo triple bond is −70.86 kcal/mol in the CCSD(T) method where B3LYP seems to give a tight approximation with the error of −0.68 kcal/mol and hybrid functionals TPSSh and PBE0 also perform well. Finally, for anion $(Re_2Cl_8)^{2-}$, TPSS, PBE, and PBE0 methods are more accurate to evaluate the

**TABLE IV.** Binding energies ($E_b$) for d-p and d–d bonds at the CCSD(T)/def2-QZVP level of theory and energy errors (*Error*) of HF and MP2 methods compared to the CCSD(T) method in kcal/mol.

| Type | Structure | Bond | $E_b$ [CCSD(T)] | *Error* (HF) | *Error* (MP2) |
|---|---|---|---|---|---|
| $d^3s$–p | $OsF_4$ | Os–F | −106.89 | +34.50 | −7.58 |
| | $OsCl_4$ | Os–Cl | −89.52 | +24.92 | −6.58 |
| | $TiF_4$ | Ti–F | −144.06 | +35.27 | −12.25 |
| | $TiCl_4$ | Ti–Cl | −99.86 | +35.97 | −6.64 |
| d–d | $(Cl_2AuPH_3)_2$ | Au–Au | −44.50 | +29.94 | −16.36 |
| | $[PtCl(CO)_2]_2$ | Pt–Pt | −67.17 | +29.22 | −16.08 |
| | $Mo_2Cl_6$ | Mo≡Mo | −70.86 | +153.45 | −93.18 |
| | $(Re_2Cl_8)^{2-}$ | Re//Re(4) | −97.37 | +153.37 | −171.31 |
| | $W_2$ | W//W(6) | −106.76 | +268.87 | −188.46 |

**TABLE V.** Binding energies ($E_b$) for the hydrogen bond, halogen bond, and Au···H bond at the CCSD(T)/def2-QZVP level of theory and energy errors (*Error*) of HF and MP2 methods compared to the CCSD(T) method in kcal/mol.

| Type | Structure | Bond | $E_b$ [CCSD(T)] | *Error* (HF) | *Error* (MP2) |
|---|---|---|---|---|---|
| Hydrogen bond | F–H···$NH_3$ | H···N | −13.90 | +1.82 | −0.41 |
| | F–H···$PH_3$ | H···P | −4.84 | +1.13 | −0.23 |
| | Cl–H···$OH_2$ | H···O | −6.07 | +1.63 | −0.61 |
| | Br–H···$OH_2$ | H···O | −5.10 | +1.66 | −0.62 |
| | Br–H···$NH_3$ | H···N | −9.10 | +3.65 | −1.63 |
| Halogen bond | F–Br···$PH_3$ | Br···P | −11.28 | +5.68 | −4.27 |
| | F–I···$NH_3$ | I···N | −15.89 | +2.69 | −1.96 |
| | F–I···$PH_3$ | I···P | −11.29 | +4.37 | −3.21 |
| | Cl–Br···$PH_3$ | Br···P | −3.92 | +4.00 | −1.79 |
| | Cl–I···$PH_3$ | I···P | −6.25 | +4.84 | −2.81 |
| Au···H bond | $(FAuF)^{-1}$···HF | Au···H | −11.27 | +3.64 | −0.38 |
| | $FAuPH_3$···HF | Au···H | −2.29 | +2.85 | −0.41 |
| | $ClAuPH_3$···HF | Au···H | −2.27 | +2.98 | −0.52 |

Re–Re quadruple bond in which the error percentages are all less than 9.0%. What is more, the average percentage errors (APE) in the last column of Table VII suggest that TPSS, PBE0, and B3LYP functionals perform well with percentage less than 10%. Overall, considering the energy errors and APE of all DFT methods in four typical structures, TPSS and PBE0 functionals are recommended for calculating the binding energies of d–d bonds between transition metals.

**TABLE VI.** Binding energies ($E_b$) of $Cu_2$, $Ag_2$, and $Au_2$ at the CCSD(T)/def2-QZVP level, energy errors of HF and MP2 compared to the CCSD(T) method (in kcal/mol), and orbital components of Cu–Cu, Ag–Ag and Au–Au bonds by NBO analysis under the LC-ωPBE-D3(BJ)/def2-QZVP level.

| | | | | | Orbital components | | |
|---|---|---|---|---|---|---|---|
| Structure | Bond | $E_b$ [CCSD(T)] | *Error* (HF) | *Error* (MP2) | s (%) | p (%) | d (%) |
| $Cu_2$ | Cu–Cu | −44.25 | +32.49 | +0.17 | 94.1 | 4.7 | 1.2 |
| $Ag_2$ | Ag–Ag | −35.66 | +26.20 | −3.17 | 94.1 | 4.9 | 1.0 |
| $Au_2$ | Au–Au | −48.05 | +29.63 | −6.25 | 90.7 | 3.9 | 5.4 |

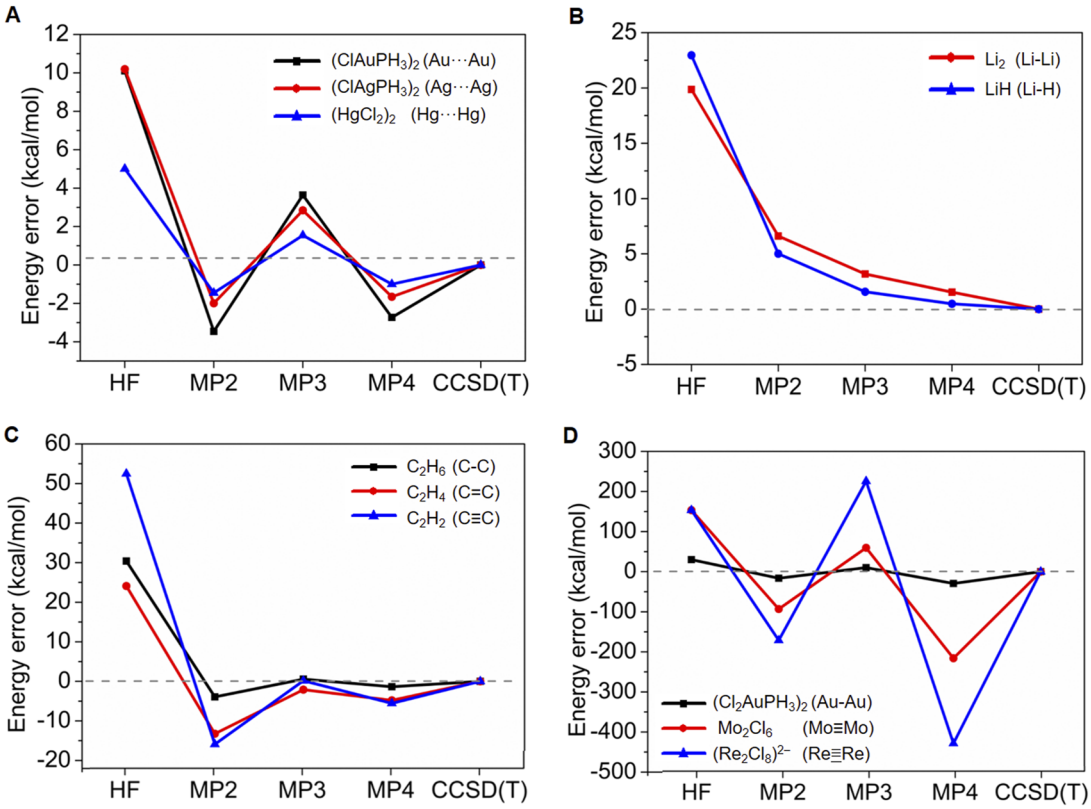


**FIG. 3.** Energy errors calculated by HF, MP2, MP3, MP4, and CCSD(T) methods for (a) metallophilic interactions, (b) s–s bonds, (c) p–p bonds, and (d) d–d bonds. $E_b$ of CCSD(T) method are set to zero for comparison.

**TABLE VII.** Bonding energies ($E_b$) of four selected structures with the d–d bond at the CCSD(T) level, energy errors under wave functional, and DFT methods related to CCSD(T) and the average values in kcal/mol.

| Structure<br>bond | $(Cl_2AuPH_3)_2$<br>Au–Au | $[PtCl(CO)_2]_2$<br>Pt–Pt | $Mo_2Cl_6$<br>Mo≡Mo | $(Re_2Cl_8)_2^-$<br>Re–Re(4) | APE[a] (%) |
|---|---|---|---|---|---|
| $E_b$ [CCSD(T)] | **−44.50** | **−67.17** | **−70.86** | **−97.37** | ··· |
| *Error* (HF) | +29.94 (67.3%) | +29.22 (43.5%) | +153.45 (216.6%) | +153.37 (157.5%) | 121.2 |
| *Error* (MP2) | −16.36 (36.8%) | −16.08 (23.9%) | −93.18 (131.5%) | −171.31 (175.9%) | 92.0 |
| *Error* (SCS-MP2) | −54.38 (122.2%) | −8.10 (12.1%) | −139.60 (197.0%) | −223.07 (229.1%) | 140.1 |
| *Error* (TPSS) | −3.64 (8.2%) | **+1.46 (2.2%)** | −15.36 (21.7%) | **−5.08 (5.2%)** | **9.3** |
| *Error* (TPSSh) | +7.07 (15.9%) | +8.56 (12.7%) | **+6.00 (8.5%)** | +14.64 (15.0%) | 13.0 |
| *Error* (PBE) | **−0.57 (1.3%)** | +3.66 (5.4%) | −19.58 (27.6%) | **+7.70 (7.9%)** | 10.6 |
| *Error* (PBE0) | **+1.21 (2.7%)** | +3.74 (5.6%) | **+7.52 (10.6%)** | **+8.68 (8.9%)** | **7.0** |
| *Error* (M062X) | +15.51 (34.9%) | +17.84 (26.6%) | +27.46 (38.8%) | +48.40 (49.7%) | 37.5 |
| *Error* (BP86) | −6.51 (14.6%) | **−0.08 (0.1%)** | −28.19 (39.8%) | −28.90 (29.7%) | 21.1 |
| *Error* (B3LYP) | +2.01 (4.5%) | +6.15 (9.2%) | **−0.68 (1.0%)** | −23.51 (24.1%) | **9.7** |
| *Error* (CAM-B3LYP) | +5.17 (11.6%) | +6.58 (9.8%) | +17.83 (25.2%) | −18.62 (19.1%) | 16.4 |
| *Error* (LC-$\omega$PBE) | **+0.72 (1.6%)** | **+1.80 (2.7%)** | +28.39 (40.1%) | +29.68 (30.5%) | 18.7 |

[a]Percentage errors (PE) are defined as PE = $|Error(Y)/E_b|$ * 100% in brackets of four structures and average percentage errors (APE) are defined as APE = PE/4.

## IV. CONCLUSIONS

In this work, we give a benchmark study on the errors of binding energies calculated by different wave functional and DFT methods. Specifically, systematic research studies on a series of structures, including metallophilic interactions, covalent bonds, and weak interactions, are performed to investigate the influence factor of the energy errors. The analysis of the results presented offers the following conclusions.

(1) The energy errors of HF and MP2 methods are not unique to metallophilic interactions, which extensively appear in numerous covalent bonds.
(2) In covalent bonds, it is found that energy errors were related to the azimuthal quantum number of interaction orbitals. As the interaction orbital changes from s to p, and to d, the calculated energy errors of HF and MP2 methods increase apparently, and the errors are even more than 170 kcal/mol in d–d multiple bonds.
(3) In weak interactions, the energy errors of HF and MP2 methods also increase with the increase in the azimuthal quantum number of interaction orbitals (hydrogen bond < halogen bond < metallophilic interaction).
(4) The binding energies calculated by HF, MP2, MP3, MP4, and CCSD(T) methods suggest that the metallophilic interaction has similar error curves with d–d covalent bonds. Thus, we speculate that the energy errors in metallophilic interactions are caused by the participation of the d orbital.
(5) Benchmark studies on DFT methods suggest that the TPSS and PBE0 functionals can give more accurate estimates of binding energies for d–d bonds.

## SUPPLEMENTARY MATERIAL

See the supplementary material for all structures, AdNDP analyses with d–d bonds, and absolute binding energies of some molecules.

## ACKNOWLEDGMENTS

This research was financially supported by the National Natural Science Foundation of China (Grant No. 21873001). The calculations were carried out at the High-Performance Computing Center of Anhui University.

## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

### Author Contributions

X.Y. and T.J. contributed equally to this work.

## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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