

Explanation of the Source of Very Large Errors in Many Exchange–Correlation Functionals for Vanadium Dimer

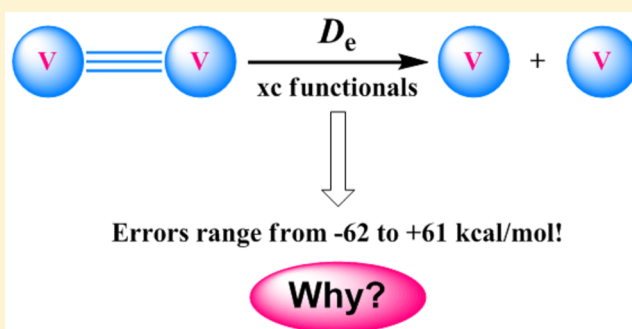
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S Supporting Information

ABSTRACT: Vanadium dimer is a notoriously difficult case for Kohn–Sham (KS) density functional theory with currently available approximations to the exchange–correlation (xc) functionals, and many approximate xc functionals yield an exceedingly large error in the calculated bond energy. In this paper, we first test the bond energies estimated by 43 xc functionals and the Hartree–Fock (HF) method. The results further confirm the large errors and show that, with the experimental bond energy being 64.2 kcal/mol, the KS calculations give predictions all over the map with errors ranging from –61.5 to +60.5 kcal/mol, and the HF method performs much worse with an error of –124.4 kcal/mol! The reason for these very large errors is examined in this article by analyzing the atomic and molecular orbital energies calculated by various xc functionals. The results show that the errors in estimates of the bond energy of vanadium dimer can primarily be related to the calculated energy gap between the 4s and 3d_{z²} atomic orbitals of the vanadium atom and especially to the 3d_{z²} orbital energy. This interesting relation between the errors in the calculated bond energy and the magnitudes of the single-particle orbital energies provides a constructive alternative to the common but more sterile explanation that it is the static correlation energy due to multicenter left–right correlation that makes the vanadium dimer and many other transition metal compounds so difficult for Kohn–Sham calculations. One of the most important factors in determining the critical atomic orbital energy is the amount of nonlocal HF exchange that is included in the xc functional, but it is still difficult to explain why different local functionals (functionals with no HF exchange) yield quite different results. We conclude that improving calculations of orbital energies of atoms may provide a route to improving the accuracy of theoretical predictions of molecular bond energies for systems containing metal atoms.



1. INTRODUCTION

Kohn–Sham (KS) density functional theory^{1,2} has become the most popular method for calculating a variety of molecular properties. It uses the single-particle electron density distribution $\rho(r)$, rather than the many-electron wave function or the two-particle density matrix, to describe the electronic structure of a system, and it represents the density as the square magnitude of a Slater determinant (which is an antisymmetrized product of spin–orbitals) for the purpose of computing an approximation to the noninteracting kinetic energy from the spin–orbitals. The spin–orbitals and their orbital energies may also be used for molecular orbital analysis of molecular structure and energetics.³

We will use the shorthand language of labeling inherently multiconfigurational systems, that is, those whose wave functions are not well represented as a single antisymmetrized product of spin–orbitals, as “multireference” systems and labeling systems whose wave functions are reasonably well represented by a single Slater determinant as single-reference systems. KS theory is in principle exact for all systems, even for

multireference systems. However, the accuracy depends on the quality of the approximation to the exchange–correlation (xc) functional, and presently available xc functionals sometimes have serious problems in calculating energies of multireference systems, not only because KS theory uses a single-determinantal noninteracting reference state to compute the dominant portion of the kinetic energy but also because it uses a single Slater determinant to represent the density in solving the self-consistent-field (SCF) equations.

Transition metals are very important elements for many applications, including industrially and biologically important catalysts. However, KS theory often shows larger errors for transition metal species than for typical main-group compounds. It is usually assumed that these larger errors arise from high multireference character in transition metal compound since molecules containing transition metals often present multiconfigurational characteristics. For the 3d transition metal

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Table 1. Calculated Bond Energies of V_2 and Errors (kcal/mol), Arranged in Order of Increasing MUEs

functional	refs	X^a	$D_e(\text{opt})$	$D_e(\text{con})$	Err(opt)	Err(con)	MSE	MUE
τ -HCTHhyb	24	15	61.4	59.9	−2.8	−4.3	−3.6	3.6
M06-L	25	0	57.7	57.0	−6.5	−7.2	−6.9	6.9
OLYP	20, 21	0	66.5	80.1	2.3	15.9	9.1	9.1
MPWLYP1M	22	5	70.3	78.0	6.1	13.8	10.0	10.0
MOHLYP	22	0	69.1	79.9	4.9	15.7	10.3	10.3
revTPSS	26	0	64.2	87.0	0.0	22.8	11.4	11.4
OreLYP	20, 21, 23	0	73.9	79.5	9.7	15.3	12.5	12.5
TPSSh	27	10	40.8	60.5	−23.4	−3.7	−13.6	13.6
OLYP-D3(BJ)	20, 21, 28, 29	0	71.2	84.8	7.0	20.6	13.8	13.8
M11-L	30	0	51.9	46.4	−12.3	−17.8	−15.1	15.1
MN12-L	31	0	50.2	45.8	−14.0	−18.4	−16.2	16.2
M05	32	28	48.7	46.0	−15.5	−18.2	−16.9	16.9
O3LYP	33	11.61	38.1	50.8	−26.1	−13.4	−19.8	19.8
M06-D3(BJ)	28, 29, 34	27	44.6	41.9	−19.6	−22.3	−21.0	21.0
M06	34	27	44.6	41.9	−19.6	−22.3	−21.0	21.0
BLYP	21, 35	0	79.6	91.1	15.4	26.9	21.2	21.2
OHLYP	20, 21	0	27.7	55.9	−36.5	−8.3	−22.4	22.4
B97-1	36	21	42.3	39.1	−21.9	−25.1	−23.5	23.5
PBE	37	0	73.4	102.2	9.2	38.0	23.6	23.6
SOGGA11	38	0	76.2	100.4	12.0	36.2	24.1	24.1
τ -HCTH	24	0	92.1	90.3	27.9	26.1	27.0	27.0
B3LYP	39	20	32.3	37.4	−31.9	−26.8	−29.4	29.4
MPW3LYP	40	21.8	32.7	33.4	−31.5	−30.8	−31.2	31.2
N12	41	0	80.6	113.8	16.4	49.6	33.0	33.0
PW6B95-D3(BJ)	28, 29, 42	28	27.5	30.1	−36.7	−34.1	−35.4	35.4
SOGGA	43	0	82.4	117.7	18.2	53.5	35.9	35.9
HSE	44, 45	0–25	22.7	33.1	−41.5	−31.1	−36.3	36.3
PW6B95	42	28	25.9	28.4	−38.3	−35.8	−37.1	37.1
PBE0	46	25	22.5	31.6	−41.7	−32.6	−37.2	37.2
B97-3	47	26.93	33.4	19.7	−30.8	−44.5	−37.7	37.7
MN12-SX	48	0–25	29.2	23.0	−35.0	−41.2	−38.1	38.1
ω B97X-D	49	22.2–100	28.2	22.9	−36.0	−41.3	−38.7	38.7
M11	50	42.8–100	18.6	31.1	−45.6	−33.1	−39.4	39.4
B1LYP	51	25	27.7	19.5	−36.5	−44.7	−40.6	40.6
MPW1B95	40	31	23.5	23.5	−40.7	−40.7	−40.7	40.7
ω B97X	52	15.77–100	27.9	16.1	−36.3	−48.1	−42.2	42.2
M08-SO	53	56.79	31.1	−10.8	−33.1	−75.0	−54.1	54.1
M08-HX	53	52.23	30.6	−17.6	−33.6	−81.8	−57.7	57.7
MPWB1K	40	44	19.9	−8.3	−44.3	−72.5	−58.4	58.4
SOGGA11-X	54	40.15	20.8	−10.4	−43.4	−74.6	−59.0	59.0
M05-2X	55	56	24.2	−15.7	−40.0	−79.9	−60.0	60.0
GVWN5 ^b	2, 56, 57	0	110.0	139.4	45.8	75.2	60.5	60.5
M06-2X	34	54	26.0	−20.5	−38.2	−84.7	−61.5	61.5
HF		100	−6.0	−114.4	−70.2	−178.6	−124.4	124.4

^aPercentage of HF exchange. ^bGVWN5 denotes an LSDA functional with the Gáspár–Kohn–Sham approximation for exchange and VWN5 for correlation (keyword SVWN5 in *Gaussian 09*).

dimers, for example, only two (i.e., Cu_2 and Zn_2) of the ten dimers are single-reference systems as defined by diagnostics of $C_0^2 > 0.90$, $T_1 < 0.05$, and $D_1 < 0.10$.⁴ (The precise definitions of these diagnostics do not concern us here; they are explained in ref 4.) One of these dimers, namely, vanadium dimer (V_2), is notoriously difficult for KS theory in that many xc functionals show an exceedingly large error in the calculated bond energy. To confirm this, the first step in the present paper is to test the predictions of KS theory on the bond energy of the V_2 molecule for 43 choices of xc functional, with particular attention to those that are historically important, popular, especially generally accurate, or recently developed or that have not been widely tested in previous reports. We also test the

Hartree–Fock (HF) method, which can be viewed as using a functional with 100% nonlocal HF exchange and no correlation.

Results of this first step are shown in Table 1, where X is the percentage of HF exchange included in a given xc functional; $D_e(\text{opt})$ denotes the optimized equilibrium bond energy, which means the energy required to dissociate the V_2 molecule from the geometry of the ground state (GS) as optimized with the xc functional under consideration to whatever state is predicted to be the GS of the vanadium atoms by the xc functional under consideration; Err(opt) is the error of the corresponding calculated $D_e(\text{opt})$ as compared to the experimental equilibrium dissociation energy. We also show $D_e(\text{con})$ and Err(con) in the table; these correspond to a different way to compute the

bond energy and error and will be explained in detail below. The numbers in Table 1 are a dramatic confirmation of how hard this problem is. The experimental D_e is 64.2 kcal/mol, but KS calculations give a wide range of results with mean signed errors of the two ways of computing the error ranging from -61.5 kcal/mol to $+60.5$ kcal/mol. An error of -61.5 means the predicted bond energy is only 2.7 kcal/mol, and an error of $+60.5$ indicates the predicted bond energy as 124.7 kcal/mol, a span of 122.0 kcal/mol! In this article, we explore the source of these extremely large errors.

2. BOND ENERGIES

The experimental ground state of the vanadium atom is 4F , derived from the $4s^23d^3$ electronic configuration, and its lowest excited state is 6D , derived from the $4s^13d^4$ electronic configuration. We denote the $^4F(4s^23d^3)$ state as the low-spin (LS) state and the $^6D(4s^13d^4)$ state as the high-spin (HS) state, so LS denotes the experimental ground state of the vanadium atom. For the vanadium dimer, the experimental result⁵ is that it has a $^3\Sigma_g^-$ ground state, and the experimental equilibrium bond length (r_e) is 1.77 Å.

The equilibrium dissociation energy (also called the equilibrium bond energy or the equilibrium atomization energy) of a diatomic molecule is the potential energy required to dissociate the bond to form infinitely separated atoms in their ground states; this is conventionally called D_e . The dissociation energy at 0 K is called D_0 , which denotes the ground-state dissociation energy; D_0 is smaller than D_e by the zero-point energy (ZPE). In this paper, we calculated the ZPE energy of vanadium dimer from its experimental vibrational frequency ω_e (536.9 cm^{-1}),⁶ and then, we added it to the experimental ground-state dissociation energy (63.4 kcal/mol).⁶ The resulting D_e value of 64.2 kcal/mol is used to evaluate how well or badly an xc functional or the HF method performs.

The KS self-consistent-field (SCF) calculations do not include spin-orbit coupling, and to compare to experiment, the spin-orbit energies must be included. In this paper, the theoretical dissociation energies are calculated by

$$D_e = D_e(\text{SCF}) + \Delta E_{\text{SO}} \quad (1)$$

where

$$\Delta E_{\text{SO}} = 2E_{\text{SO}}(\text{V}) - E_{\text{SO}}(\text{V}_2) \quad (2)$$

$E_{\text{SO}}(\text{V})$ and $E_{\text{SO}}(\text{V}_2)$ are the spin-orbit energies of the V atom and the V_2 molecule, respectively. The experimental value of ΔE_{SO} of vanadium dimer is -1.83 kcal/mol,⁷ and this negative value is added to each SCF bond energy (of each xc functional or HF calculation) in order to obtain the calculated D_e values that are compared to experiment.

There are two ways to calculate D_e from a quantum mechanical calculation; we will denote them “opt” (optimized) and “con” (constrained). In an opt calculation, the bond energy is calculated as the potential energy required to dissociate the V_2 molecule from its theoretically optimized geometry in whatever symmetry is predicted by the xc functional to have the lowest energy to free atoms in whatever state is predicted to be the ground state of the vanadium atoms by the xc functional under consideration. In contrast, $D_e(\text{con})$ denotes the potential energy to take the V_2 molecule from the experimental bond length in the experimental molecular ground electronic state to two V atoms in the experimental ground state of a vanadium

atom, that is, it equals the potential energy in the LS state of the two atoms minus the potential energy of the V_2 molecule in the $^3\Sigma_g^-$ state with bond length fixed to be 1.77 Å. If the xc functional were to predict the correct states and the correct equilibrium bond length, then $D_e(\text{con})$ would equal $D_e(\text{opt})$.

In summary we have

$$D_e(\text{opt}) = 2E(\text{V, GS}) - E(\text{V}_2, \text{opt}) \quad (3)$$

$$D_e(\text{con}) = 2E(\text{V, LS}) - E(\text{V}_2, \text{con}) \quad (4)$$

where $E(\text{V, GS})$ and $E(\text{V, LS})$ are Born–Oppenheimer energies of the vanadium atom in predicted ground state (for a given functional) and in the LS state, respectively; $E(\text{V}_2, \text{opt})$ and $E(\text{V}_2, \text{con})$ are Born–Oppenheimer energies of the V_2 molecule in the theoretically predicted ground state at the theoretically predicted bond length and of the V_2 molecule in the experimental ground state ($^3\Sigma_g^-$) at the experimental equilibrium geometry (bond length equals to 1.77 Å). Analogously, we have two ways to compute the error:

$$\text{Err}(\text{opt}) = D_e(\text{opt}) - 64.2\text{ kcal/mol} \quad (5)$$

$$\text{Err}(\text{con}) = D_e(\text{con}) - 64.2\text{ kcal/mol} \quad (6)$$

Ideally, both $D_e(\text{opt})$ and $D_e(\text{con})$ would equal the experimental D_e of 64.2 kcal/mol,⁶ and both errors would be zero.

Both kinds of errors are listed in Table 1, and we find most functionals give quite different $\text{Err}(\text{opt})$ and $\text{Err}(\text{con})$. Since both dissociation energies are interesting in their own right, we find it most useful to average over these two ways to define the error. The average of the two errors is called the mean signed error (MSE); the average of the absolute values of the two errors is called the mean unsigned error (MUE). In the rest of the article, we will simply refer to these mean errors because an accurate functional would give a small error in both of these quantities (the exact functional would have zero error for both), and the mean unsigned error is a composite quantity that reflects the ability of an individual xc functional to predicting the geometry, the states, and the energetics.

3. MOLECULAR ORBITAL DIAGRAMS

Molecular orbital (MO) diagrams^{8,9} provide ways to qualitatively describe chemical bonding in molecules in terms of molecular orbital theory^{10,11} in general and in terms of the linear combination of atomic orbitals (LCAO)¹² molecular orbital method in particular. Such diagrams for diatomic molecules are well suited to explain how the atoms interact with each other to form a molecule and to predict bond strength. There are four general rules for MO diagram construction.

- LCAO principle: the number of molecular orbitals is equal to the number of atomic orbitals (AOs) included in the linear expansion.
- Aufbau principle: electrons fill orbitals starting with the lowest available energy levels and then filling higher levels.
- Pauli exclusion principle: the maximum number of electrons occupying an orbital is two, with opposite spins.
- Hund's rule: when there are several MOs with equal energy (degenerate MOs), electrons occupy them singly before filling them in pairs.

The LCAO expansion for the i th MO of a molecule can be expressed as

$$\Psi_i = \sum_m c_{mi} \Phi_m \quad (7)$$

where Ψ_i is the MO, Φ_m is an AO, and c_{mi} is the combination coefficient whose absolute square represents the relative contribution of AO Φ_m to MO Ψ_i . In this article, we do not concern ourselves with the MOs of the V_2 molecule formed mainly from 1s, 2s, 2p, 3s, and 3p AOs of the vanadium atom; we are concerned only with valence MOs, formed mainly from 4s and 3d AOs.

There are three steps to construct an MO diagram for a given homonuclear diatomic molecule, in particular (1) determine the AO energy levels and fill electrons into these orbitals; (2) determine the MO energy levels and fill electrons into these orbitals; (3) connect MOs with their constituent AOs according to their dominant combination coefficients. In this article we will provide the MO diagrams of V_2 molecule using Kohn–Sham calculations with various xc functionals in order to see if the MO diagrams can give clues as to the source or sources of the very large errors in using many xc approximations to calculate the V_2 bond energy.

4. COMPUTATIONAL DETAILS

The xc functionals employed in the present study along with the HF method are listed in Table 1. This table also gives the original references for the functionals and the percentages X of nonlocal Hartree–Fock exchange; the remaining exchange energy density and all of the correlation energy density at a point in space are functions of local variables (always the α and β spin densities at the point, usually also the local magnitudes of their gradients, and in some cases also the local spin-labeled noninteracting kinetic energy densities).

All calculations in the present paper were carried out with the Gaussian 09 software package,¹³ locally modified.¹⁴

The all-electron def2-TZVP basis set is used for all calculations in this project,¹⁵ and we neglect relativistic effects. The good performance of nonrelativistic def2-TZVP calculations has been documented elsewhere¹⁶ and is further confirmed in our recently published paper testing various xc functionals in bond energy calculations on the 3dBE70 database.¹⁷

Calculations with electron spin component $M_S = 0, 1, 3/2$, and $5/2$ are called singlets, triplets, quartets, and sextets, respectively. In the opt calculations, for the atom, we calculated both the LS and HS state with each functional to see which one has a lower energy; for the molecule, we performed calculations on the $^1\Sigma_g^+$, $^3\Sigma_g^-$, and $^3\Delta_g$ states for each functional to see which has the lowest energy. We employ broken-spatial-symmetry solutions of the Kohn–Sham equations since the optimum Kohn–Sham orbitals do not necessarily belong to the irreducible representations of the atomic or molecular point group. Therefore, the energy calculations for the vanadium atom and the geometry optimizations and energy calculations for the V_2 molecule were performed for all xc functionals and for the HF method by a calculation in which the orbitals were optimized until the wave function is stable; if the solution with symmetry orbitals is unstable, we break symmetry to get a stable solution. However, we use collinear orbitals, and we constrain M_S to equal the total electron spin quantum number S .

The theoretically predicted ground state of the vanadium atom and dimer are shown for each method in Table 2. It is

Table 2. Ground States of V Atom [GS(V)] and V_2 Molecule [GS(V_2)] Predicted by Various Functionals and the HF Method

functional	GS(V)	GS(V_2)	functional	GS(V)	GS(V_2)
B1LYP	HS	$^1\Sigma_g^+$	MPW3LYP	HS	$^1\Sigma_g^+$
B3LYP	HS	$^1\Sigma_g^+$	MPWB1K	HS	$^1\Sigma_g^+$
B97-1	LS	$^1\Sigma_g^+$	MPWLYP1M	HS	$^3\Sigma_g^-$
B9-3	LS	$^1\Sigma_g^+$	N12	HS	$^3\Delta_g$
BLYP	HS	$^3\Sigma_g^-$	O3LYP	HS	$^3\Sigma_g^-$
GVWN5	HS	$^3\Sigma_g^-$	OHLYP	HS	$^3\Sigma_g^-$
HF	LS	$^3\Delta_g$	OLYP	HS	$^3\Sigma_g^-$
HSE	HS	$^1\Sigma_g^+$	OLYP-D3(BJ)	HS	$^3\Sigma_g^-$
M05	LS	$^3\Sigma_g^-$	OreLYP	HS	$^3\Sigma_g^-$
M05-2X	LS	$^1\Sigma_g^+$	PBE	HS	$^3\Sigma_g^-$
M06	LS	$^3\Sigma_g^-$	PBE0	HS	$^1\Sigma_g^+$
M06-2X	LS	$^1\Sigma_g^+$	PW6B95	HS	$^1\Sigma_g^+$
M06-D3(BJ)	LS	$^3\Sigma_g^-$	PW6B95-D3(BJ)	HS	$^1\Sigma_g^+$
M06-L	LS	$^3\Sigma_g^-$	revTPSS	HS	$^3\Sigma_g^-$
M08-HX	LS	$^1\Sigma_g^+$	SOGGA	HS	$^3\Sigma_g^-$
M08-SO	HS	$^1\Sigma_g^+$	SOGGA11	HS	$^3\Sigma_g^-$
M11	HS	$^1\Sigma_g^+$	SOGGA11-X	LS	$^1\Sigma_g^+$
M11-L	LS	$^1\Sigma_g^+$	TPSSH	HS	$^1\Sigma_g^+$
MN12-L	LS	$^1\Sigma_g^+$	τ -HCTH	LS	$^3\Sigma_g^-$
MN12-SX	LS	$^1\Sigma_g^+$	τ -HCTHhyb	LS	$^3\Sigma_g^-$
MOHLYP	HS	$^3\Sigma_g^-$	ω B97X	LS	$^1\Sigma_g^+$
MPW1B95	HS	$^1\Sigma_g^+$	ω B97X-D	HS	$^1\Sigma_g^+$

found that all the 43 functionals and the HF method predict that the stable singlet solution for the molecule is an open-shell solution (the closed-shell singlet is unstable), and almost half of the functionals give the $^1\Sigma_g^+$ state as the ground state. This seems to be inconsistent with previous theoretical studies^{7,18,19} that employ the $^3\Sigma_g^-$ state as the ground state. However, from the statements of the papers by Barden et al.¹⁸ and Yanagisawa et al.,¹⁹ it is not clear whether or not they have checked the singlet state of the molecule or, if they did, whether they checked for the stability of the solution. As to the previous work reported by our group,⁷ we used broken-spatial-symmetry solutions for Cr_2 and Mn_2 calculations, but not for V_2 . For further confirmation of the present findings, we calculated the energies of singlet and triplet V_2 molecule without breaking the spatial symmetry by using the HF method and the functionals that appear both in ref 7 and in the present study, in particular, BLYP, OLYP, B3LYP, B97-1, O3LYP, MPW1B95, and TPSSH. These calculations give a closed-shell singlet state and a $^3\Sigma_g^-$ ground state. Thus, the difference from previous work is confirmed to be due to the previous work not finding the stable solutions.

Although the LS state [$^4F(4s^23d^3)$] is the experimental ground state of V atom, we chose to use the HS state [$^6D(4s^13d^4)$] to calculate the atomic orbital (AO) energy levels shown in the MO diagrams in the present paper because all five valence electrons are singly filled into corresponding atomic orbitals in this state, and orbital energies shown in diagrams are more consistent if they correspond to occupied orbitals. The $3d_{z^2}$ atomic orbital of the vanadium atom is important in the dimer but is unoccupied even in the HS state. The α orbital energies of the five occupied orbitals and the unoccupied $3d_{z^2}$

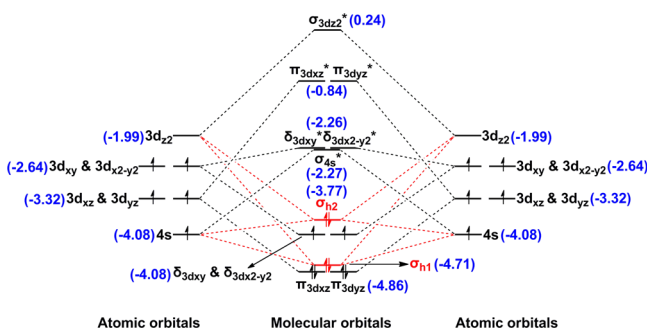


Figure 2. Same as Figure 1 except for the M06-L functional.

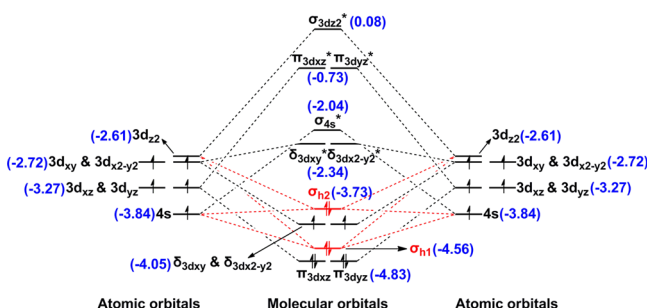


Figure 3. Same as Figure 1 except for the OreLYP functional.

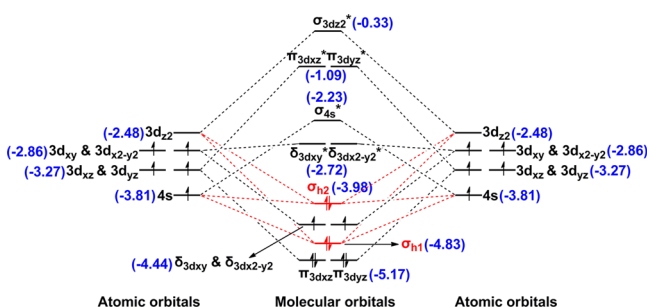
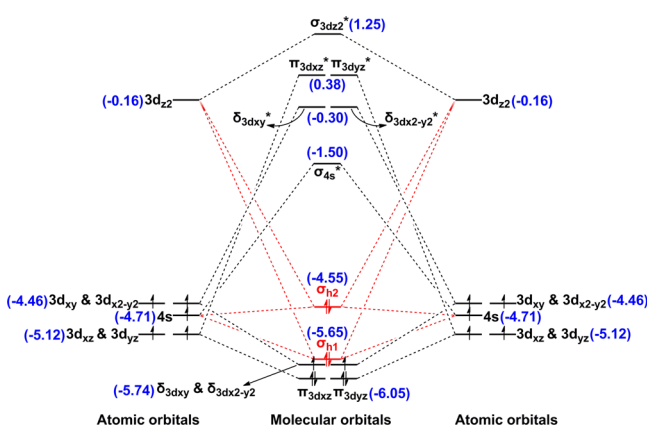
Figure 4. Same as Figure 1 except for the τ -HCTH functional.

Figure 5. Same as Figure 1 except for the MPW1B95 functional.

These five AOs are shown as singly occupied in the figure, where an upward barb denotes majority α spin, and a downward barb denotes minority β spin.

To determine the MO energy levels, we first checked all the occupied MOs that are composed mainly of the 4s and/or 3d AOs of vanadium atoms. According to the procedure described in the Computational Details section, we get the molecular

orbital energies (shown in Figure 1 in blue) for four doubly occupied molecular orbitals as -5.66 eV for $\pi_{3d_{xz}}$ and $\pi_{3d_{yz}}$, -5.36 eV for σ_{h1} , and -4.38 eV for σ_{h2} , where $\pi_{3d_{xz}}$ or $\pi_{3d_{yz}}$ is the π_u MO obtained by combining either the two $3d_{xz}$ or $3d_{yz}$ AOs of the two V atoms, while σ_{h1} or σ_{h2} are σ_g MOs obtained by combining the 4s orbital with the $3d_{z^2}$ AO on each V atom (to make a hybrid orbital), and then combining the hybrids on the two centers to generate the MOs called σ_{h1} or σ_{h2} . In particular, the σ_{h1} and σ_{h2} MOs are obtained by combining the same AOs ($\Phi_m = 4s, 3d_{z^2}$), but with different weights of contributions from each AO (See Table S1 in Supporting Information). For brevity, we will label σ_{h1} and σ_{h2} as the hybrid MOs in the rest of this paper. Finally, the remaining two electrons are in singly occupied orbitals $\delta_{3d_{xy}}$ and $\delta_{3d_{x^2-y^2}}$ which are δ_g MOs obtained by combining the two $3d_{xy}$ or $3d_{x^2-y^2}$ AOs of the two V atoms; these two MOs have equal orbital energies of -4.90 eV.

Although it is not an occupied orbital, the $3d_{z^2}$ AO is also included in our considerations and in the diagrams because it is crucial to understanding the origin of the hybrid MOs σ_{h1} and σ_{h2} . Consequently, there are 12 AOs in the diagram (six from each vanadium atom corresponding to the 4s and 3d subshells), and therefore, 12 MOs are generated. As a result, in addition to the aforementioned six occupied MOs (four doubly occupied and two singly occupied), six unoccupied MOs that consist of the 4s and/or 3d AOs are also shown, in particular σ_{4s}^* (which is a σ_u MO obtained by combining the 4s AOs of the two V atoms), $\delta_{3d_{xy}}^*$ (δ_u MO corresponding to $\delta_{3d_{xy}}$), $\delta_{3d_{x^2-y^2}}^*$ (δ_u MO corresponding to $\delta_{3d_{x^2-y^2}}$), $\pi_{3d_{xz}}^*$ (π_g MO corresponding to $\pi_{3d_{xz}}$), $\pi_{3d_{yz}}^*$ (π_g MO corresponding to $\pi_{3d_{yz}}$) and $\sigma_{3d_{z^2}}^*$ (σ_u MO obtained by combining the $3d_{z^2}$ AOs of the two V atoms). The δ_u and the π_g MOs are each a degenerate pair, and they have orbital energies of respectively -1.71 and -0.41 eV.

The two hybrid MOs (i.e., σ_{h1} and σ_{h2}) deserve particular attention because they involve contributions from the virtual $3d_{z^2}$ AOs. Furthermore, all MOs in Figure 1 except σ_{h1} and σ_{h2} derive from only one and the same AO from each of the two vanadium atoms; they thus consist of AOs with exactly the same energy levels. However, the hybrid orbitals involve a mix of orbitals with different energies. This is important because covalent bonding in MOs is enhanced when the AO energy levels are the same. Consequently we examine the relative energies of the 4s and $3d_{z^2}$ AOs of the vanadium atom in the HS state, and we quantify this energy difference by defining an orbital energy gap by

$$\Delta\epsilon = \epsilon_{3d_{z^2}} - \epsilon_{4s} \quad (8)$$

where ϵ_{4s} and $\epsilon_{3d_{z^2}}$ are respectively the 4s and $3d_{z^2}$ orbital energies of the vanadium atom in its HS state. Figure 1 shows that the τ -HCTHhyb xc functional predicts $\Delta\epsilon$ to be 2.93 eV.

5.2. MO Diagrams of M06-L, OreLYP, and τ -HCTH. All other MO diagrams are constructed following the same method as described above for making the τ -HCTHhyb MO diagram.

Figures 2–4 display the MO diagrams for M06-L, OreLYP, and τ -HCTH, respectively, and Tables S2–S4 in Supporting Information show the details of the corresponding MOs. It turns out that these three xc functionals predict the same order of AO energy levels that τ -HCTHhyb does; in particular, the order is $4s < 3d_{xz} = 3d_{yz} < 3d_{xy} = 3d_{x^2-y^2} < 3d_{z^2}$. For MO energy levels, M06-L gives the same order as τ -HCTHhyb, namely $\pi_u < \sigma_{h1} < \delta_g < \sigma_{h2} < \sigma_{4s}^* < \delta_u < \pi_g < \sigma_{3d_{z^2}}^*$, but OreLYP and τ -HCTH reverse the order of the virtual orbitals σ_{4s}^* and δ_u . In

summary, these four functionals give qualitatively similarly structured MO diagrams; they do, however, differ from each other quantitatively in their orbital energies. Particularly significant is that the energy gaps $\Delta\epsilon$ obtained by M06-L, OreLYP, and τ -HCTH calculations are 2.09, 1.23, and 1.33 eV, respectively, as compared to the much larger 2.93 eV for the more accurate τ -HCTHhyb functional.

5.3. MO Diagram of MPW1B95. The MO diagram for MPW1B95 calculations is illustrated in Figure 5, and details of MOs are shown in Table S5 in Supporting Information. Even at first glance, one sees a significant difference in the MPW1B95 diagram as compared with those for the previous four functionals. In particular, there is a much wider energy gap between the virtual $3d_{z^2}$ AO and the five occupied valence AOs and there are wider gaps between the bonding and antibonding MOs. Also, the 4s atomic orbital is at -4.71 eV, which is higher than the pair of degenerate valence 3d orbitals— $3d_{xz}$ and $3d_{yz}$ (-5.12 eV), and the $3d_{z^2}$ orbital is at -0.16 eV, leading to $\Delta\epsilon = 4.55$ eV. For molecular orbitals, MPW1B95 predicts generally the same order of energy levels as τ -HCTHhyb does, except it reverses the order of the occupied orbitals σ_{h1} and δ_g .

5.4. Source of the Very Large Errors Predicted by Many xc Functionals. Based on the above discussion of five selected MO diagrams, we see that the magnitude of the predicted bond energy of the vanadium dimer by a specific xc functional is strongly correlated with the energy gap $\Delta\epsilon$ between the 4s and $3d_{z^2}$ AOs of the vanadium atom in its HS state. In particular, if we put the five functionals in order of increasing gap, the gaps are 1.23, 1.33, 2.09, 2.93, and 4.55 eV, and—with the functionals in the same order—the $D_e(\text{con})$ values are 80, 90, 58, 60, and 24 kcal/mol, respectively. To further illustrate this correlation, we checked the orbital energies of the 4s and $3d_{z^2}$ AOs obtained by using all the 43 xc functionals and the HF method, and we calculated their relative energies $\Delta\epsilon$; these results are shown in Table 3. For the sake of convenient analysis, the percentage X of HF exchange and the MSEs that are given in Table 1 are also listed in Table 3, and all methods are arranged in order of increasing $\Delta\epsilon$.

As we can see, arranging the table in order of increasing $\Delta\epsilon$ roughly separates the MSEs into two groups: the M06-L functional and all xc functionals (including the HF method as well) listed below M06-L give negative MSEs; whereas all functionals listed above M06-L give positive MSEs with only one exception, namely OHLYP, which underestimates the bond energy with an MSE of -22.4 kcal/mol. This separation confirms the hypothesized correlation between bond energy and $\Delta\epsilon$. If the AO energy gap $\Delta\epsilon$ is predicted by an xc functional to be smaller than that given by M06-L ($\Delta\epsilon = 2.09$ eV), then the bond energy is probably overestimated, whereas if $\Delta\epsilon$ is calculated to be larger than 2.09 eV, the bond energy of the V_2 molecule tends to be underestimated by the xc functional.

Another correlation apparent in the table is that the percentage X of HF exchange anticorrelates with the MSE. As shown in Table 3, almost all xc functionals that have no HF exchange ($X = 0$) tend to give positive MSEs, and almost all functionals with nonzero X have negative MSEs; there are only five exceptions: MPWLYP1M ($X = 5$, positive MSE) plus OHLYP, M06-L, M11-L, and MN12-L ($X = 0$, negative MSEs). MSE anticorrelates with both the energy gap and the percentage of Hartree–Fock exchange because those two quantities correlate with one another: local xc functionals tend to give small energy gaps between 4s and $3d_{z^2}$ AOs, whereas

Table 3. Calculated 4s and $3d_{z^2}$ Orbital Energies of the V Atom in Its HS State (ϵ_{4s} and $\epsilon_{3d_{z^2}}$ in eV), the Energy Gaps between These Two AOs ($\Delta\epsilon$ in eV), and the MSEs over the Two Ways to Calculate the Bond Energy of V_2 (in kcal/mol)^a

functional	X^a	ϵ_{4s}	$\epsilon_{3d_{z^2}}$	$\Delta\epsilon$	MSE
GVWNS	0	-4.38	-3.37	1.01	60.5
SOGGA11	0	-3.95	-2.88	1.07	24.1
N12	0	-3.56	-2.42	1.14	33.0
SOGGA	0	-4.16	-2.94	1.22	35.8
OreLYP	0	-3.84	-2.61	1.23	12.5
OLYP	0	-3.84	-2.56	1.28	9.1
OLYP-D3(BJ)	0	-3.84	-2.56	1.28	13.8
MOHLYP	0	-3.89	-2.56	1.33	10.3
τ -HCTH	0	-3.81	-2.48	1.33	27.0
PBE	0	-4.22	-2.86	1.36	23.6
BLYP	0	-4.00	-2.56	1.44	21.2
OHLYP	0	-3.84	-2.39	1.45	-22.4
revTPSS	0	-4.16	-2.48	1.68	11.4
MPWLYP1M	5	-4.11	-2.12	1.99	10.0
M06-L	0	-4.08	-1.99	2.09	-6.8
M11-L	0	-3.59	-1.20	2.39	-15.0
O3LYP	11.61	-4.16	-1.61	2.55	-19.8
TPSSh	10	-4.35	-1.61	2.74	-13.6
τ -HCTHhyb	15	-4.35	-1.42	2.93	-3.6
MN12-L	0	-4.14	-1.20	2.94	-16.2
HSE	0–25	-4.35	-1.06	3.29	-36.3
B3LYP	20	-4.54	-0.95	3.59	-29.4
B97-1	21	-4.38	-0.71	3.67	-23.5
M05	28	-4.00	-0.33	3.67	-16.8
M06	27	-4.46	-0.73	3.73	-21.0
M06-D3(BJ)	27	-4.46	-0.73	3.73	-21.0
MPW3LYP	21.8	-4.54	-0.76	3.78	-31.1
MN12-SX	0–25	-3.81	0.03	3.84	-38.1
PBE0	25	-4.68	-0.63	4.05	-37.2
B1LYP	25	-4.49	-0.35	4.14	-40.6
B97-3	26.93	-4.54	-0.27	4.27	-37.6
PW6B95	28	-4.71	-0.44	4.27	-37.1
PW6B95-D3(BJ)	28	-4.71	-0.44	4.27	-35.4
MPW1B95	31	-4.71	-0.16	4.55	-40.7
SOGGA11-X	40.15	-5.14	0.49	5.63	-59.0
MPWB1K	44	-4.95	0.84	5.79	-58.4
M08-HX	52.23	-5.06	1.25	6.31	-57.7
M05-2X	56	-4.95	1.44	6.39	-59.9
M06-2X	54	-5.17	1.36	6.53	-61.4
M08-SO	56.79	-5.58	1.09	6.67	-54.0
ω B97X-D	22.2–100	-5.99	1.55	7.54	-38.7
M11	42.8–100	-5.82	2.37	8.19	-39.3
ω B97X	15.77–100	-6.04	2.23	8.27	-42.2
HF	100	-5.85	3.62	9.47	-124.4

^aPercentage of HF exchange. ^aThe table is arranged in order of increasing $\Delta\epsilon$.

including some HF exchange leads to wider energy gaps. The correlation also illustrates why τ -HCTH ($X = 0$) and τ -HCTHhyb ($X = 15$) give quite different predictions.

For the purpose of further confirmation of relations between these quantities, we have plotted some scattergrams of various possible correlates with the MSE of vanadium dimer bond energy calculation or with percentage X of HF exchange included in the xc functional (the range-separated functionals M11, MN12-SX, HSE, ω B97X and ω B97X-D are excluded

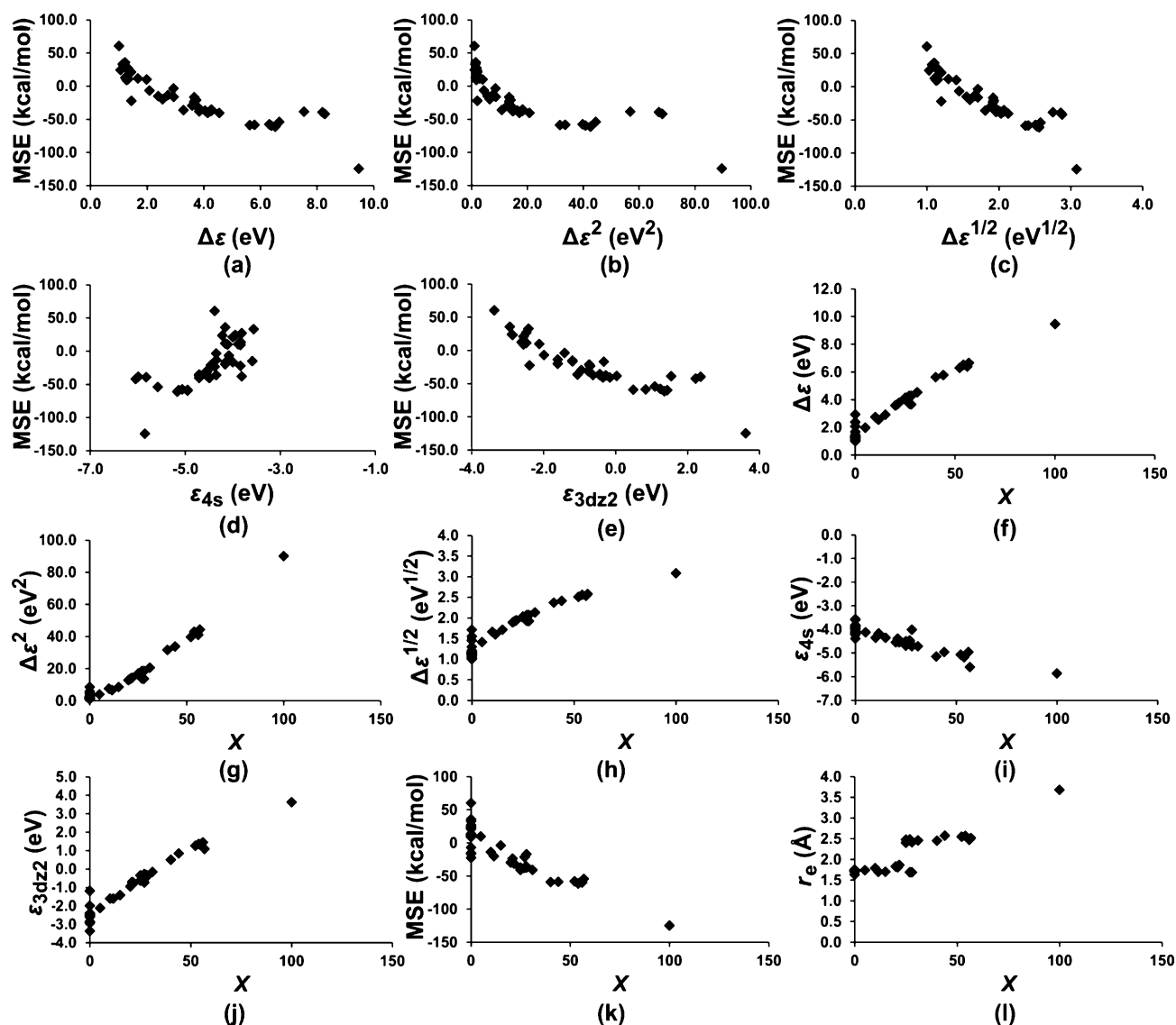


Figure 6. Scattergrams. (a) Mean signed error MSE versus $\Delta\epsilon$. (b) MSE vs $\Delta\epsilon^2$. (c) MSE vs $\Delta\epsilon^{1/2}$. (d) MSE vs ϵ_{4s} . (e) MSE vs ϵ_{3dz^2} . (f) $\Delta\epsilon$ vs percentage X of Hartree–Fock exchange. (g) $\Delta\epsilon^2$ vs X . (h) $\Delta\epsilon^{1/2}$ vs X . (i) ϵ_{4s} vs X . (j) ϵ_{3dz^2} vs X . (k) MSE vs X . (l) r_e vs X .

from plots involving X because they use different X for the long-range and short-range parts of the Coulomb operator). Several possible correlates are considered, in particular $\Delta\epsilon$, $\Delta\epsilon^2$, $\Delta\epsilon^{1/2}$, ϵ_{4s} , ϵ_{3dz^2} , and r_e (which means the bond length optimized by an xc functional). All these scattergrams are shown in Figure 6, and the corresponding Pearson product-moment correlation coefficients (PPMCCs, denoted as R) are listed in Table 4.

Figure 6 and Table 4 show that the MSE negatively correlates with $\Delta\epsilon$, $\Delta\epsilon^2$, $\Delta\epsilon^{1/2}$, and ϵ_{3dz^2} , while it positively correlates with ϵ_{4s} . These are consistent since $\Delta\epsilon$ involves $-\epsilon_{4s}$ (and plus ϵ_{3dz^2} ; see eq 8). The correlation coefficients R indicate that MSE correlates strongly with the square root of the energy gap, the percentage HF exchange that is included in the xc functional, and the energy gap itself. It is very interesting to notice that MSE correlates most strongly with the $3d_{z^2}$ orbital energies of vanadium atom ϵ_{3dz^2} , but less strongly with the $4s$ atomic orbital energy ϵ_{4s} , which indicates that it is actually the virtual $3d_{z^2}$ orbital energy that matters for the magnitude of MSE. It was mentioned above that the quantities $\Delta\epsilon$ and X correlate with one another; here, that is validated quantitatively

by the large value of the correlation coefficient ($R = 0.9790$). Given these correlations, we also see correlations of X with $\Delta\epsilon^2$, $\Delta\epsilon^{1/2}$, ϵ_{4s} , and ϵ_{3dz^2} , but with signs of R opposite to those of the MSE correlations. This confirms that the accuracy of the KS calculation on bond energy of vanadium dimer can be linked with the percentage X of HF exchange that is used to replace the local exchange in an xc functional, and it explains why atomic orbital energies are the bridge. The correlation between MSE and X has $R = -0.8978$, which confirms that MSE predicted by a functional tends to be more negative if one increases the nonlocal HF exchange. The correlation between the optimized r_e and the percentage X is positive such that greater HF exchange tends to give longer bond lengths. Therefore, the content of HF exchange in a KS functional plays a significant role in the bond energy and bond length calculations on vanadium dimer, but it is not the only part of story because ϵ_{4s} and ϵ_{3dz^2} are almost equally sensitive to X , while ϵ_{3dz^2} is much more sensitive to MSE than ϵ_{4s} .

Because orbital energies are theoretical quantities, the question arises of whether we can find a correlation with the

Table 4. Pearson Product-Moment Correlation Coefficients (PPMCCs, denoted as R) between Various Pairs of Variables^a

variable pairs	R
$(X, \Delta\epsilon)$	0.9790
$(X, \Delta\epsilon^2)$	0.9757
$(X, \epsilon_{3d_{z^2}})$	0.9660
$(X, \Delta\epsilon^{1/2})$	0.9460
(X, ϵ_{4s})	-0.9187
$(\epsilon_{3d_{z^2}}, \text{MSE})$	-0.9018
$(\Delta\epsilon^{1/2}, \text{MSE})$	-0.8983
(X, MSE)	-0.8978
(X, r_e)	0.8896
$(\Delta\epsilon, \text{MSE})$	-0.8706
$(\Delta\epsilon^2, \text{MSE})$	-0.7864
(ϵ_v, MSE)	0.7014
$(\Delta E, \text{MSE})$	-0.4014
$(\Delta E, X)$	0.3986
$(\Delta E, \Delta\epsilon)$	0.3189

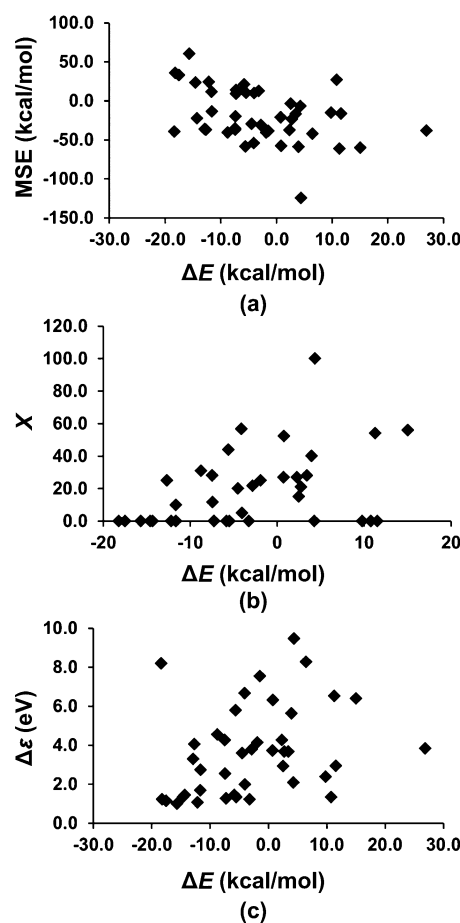
^aThe table is arranged in order of decreasing absolute value of R . For this table (just as in the figures), the atomic orbital energies are the α orbital energies taken from the HS state of the atom.

predicted value of an experimentally observable quantity. A quantity that might be expected to carry similar information to the orbital energy of the $3d_{z^2}$ orbital or the orbital energy gap $\Delta\epsilon$ is the energy difference ΔE between the $3d^4 4s$ sextet excited state of V and the $3d^3 4s^2$ quartet ground state. Figure 7 and Table 4, however, show little if any correlation between ΔE and $\Delta\epsilon$, MSE, or X .

A summary of the major findings is as follows. Hartree–Fock exchange tends to raise the energies of the 3d orbitals. This, or any other aspect of the functionals that raises the 3d orbital energies makes them participate less readily in $4s3d$ bonding hybrid orbitals; and this in turn causes this an underestimate of the bond energy. Density functional exchange tends to underestimate the 3d orbital energy; this makes the hybrid orbital bonding stronger and overestimates the bond energy.

These findings deserve particular attention for future functional development. When one derives or parametrizes a new xc functional or tries to improve an existing one, it would seem to be very valuable to examine the orbital energies of the vanadium atom, especially the energy of the virtual $3d_{z^2}$ atomic orbital. The interesting and unexpected correlation between the error in the calculated bond energy and the magnitude of the single-particle atomic orbital energies reminds us that accurate predictions of bond formation energies start with realistic descriptions of the atomic orbitals of the atoms involved in the bond. The nonlocal exchange that is included in a KS functional can be useful in functional design, but it is not the only handle for improving the bond energy and bond length calculations.

A common working assumption about the very large errors of many KS calculations for the vanadium dimer and other difficult-to-predict transition metal bonding situations is to attribute the errors to significant multiconfigurational characteristics of the transition metal compound. However, according to our present investigation, it may be more effective to first concentrate on accurate description to the orbital energy of the virtual $3d_{z^2}$ atomic orbital. Much more remains to be understood though, and we suggest a deeper study in the future. For example, it seems from Table 3 that whether the MSE calculated by a specific functional should be positive or

**Figure 7.** Scattergrams: (a) MSE vs ΔE , (b) ΔE vs X , and (c) energy difference of vanadium atom between its HS and LS state ΔE vs $\Delta\epsilon$.

negative depends highly upon whether the functional is local or hybrid.

As already summarized, including more HF exchange tends to cause more negative MSEs, but the percentage of HF exchange is only part of story. For example, the 16 local functionals studied here all have the same percentage of HF exchange, that is, $X = 0$, but their MSEs span a very wide range from -22.4 to +60.5 kcal/mol. So there must be some other aspects that the accuracy of density functional depends on. The problem is what are they? What is necessary to get the right answer for the right reason? Next, we consider some other possible contributing factors.

OHLYP is a functional constructed by combining the OptX exchange²⁰ with half of the LYP correlation²¹ instead of full LYP correlation, and it is interesting to compare its performance with the closely related OLYP (which is like OHLYP but without the one-half), MOHLYP (which consists of modified OptX exchange²² and the half-LYP correlation) and OreLYP (which is like OLYP but with Thakkar's reoptimized LYP correlation²³). Table 3 shows that the most standard of these functionals, OLYP, has a rather small gap of only 1.28 eV, and this is hardly changed by switching the correlation functional to the new reLYP and is not changed at all by adding molecular mechanics dispersion, as in OLYP-D3(BJ). It is well-known that LYP tends to overestimate the correlation energy; therefore it is interesting to see that scaling back the correlation energy by a full factor of 2, as in OHLYP, leads to a larger gap of 1.45 eV. However, if one simultaneously modifies

the OptX exchange functional to tend to the uniform electron gas limit when the density gradient goes to zero (the OptX functional does not satisfy this constraint), one gets MOHLYP, which is very close to the original OLYP; this clearly shows that a judicious and balanced choice of modification of both exchange and correlation could get an answer between OHLP on the one side and OLYP or MOHLYP on the other and could conceivably get the right answer for the wrong reason, which motivates a deeper study. In O3LYP, the correlation energy is scaled back empirically but less than a factor of 2, and 11.61% of the local exchange is replaced by nonlocal HF exchange. Table 3 shows that this is reasonably successful, but we do not know if it getting the right answer for the right reason.

Since we have emphasized, among other issues, the correlation between the amount of Hartree–Fock exchange in an exchange–correlation functional and the accuracy of the calculated binding energies, it is worthwhile to also emphasize that the correlation between the amount of exact exchange in the functional and various properties of transition metal complexes is well-known in other contexts as well, such as spin-splitting energetics.⁵⁸ A key point in the present analysis is that the effect of the treatment of exchange is associated more with its indirect effect on intra-atomic s–d orbital energy differences than with its direct effect on the exchange energies of different spin states,⁵⁸ with the effect of increasing static correlation error by increasing the fraction of Hartree–Fock exchange,⁵⁹ or with the inability of Hartree–Fock exchange to “to describe weakly overlapping orbitals on different centers.”⁶⁰ To illustrate the qualitative difference between considerations based on orbital energies and those based on spin splittings, note that the intra-atomic orbital energy difference can be seen in a single calculation on a single spin state of V and does not require comparing the energies of triplet V₂ to the sum of the energies of two quartet V atoms or comparing the energy of V or V₂ in its ground state to its energy in an excited state with a different number of unpaired electrons.

6. CONCLUSIONS

The bond energies relative to high-spin and low-spin fragments of the very difficult case—vanadium dimer—have been calculated using 43 xc functionals and the HF method. The results show that the mean signed errors (MSEs) of the two bond energies range from –124 kcal/mol to +61 kcal/mol, with a median mean unsigned error of 29 kcal/mol (29.4 if we exclude HF and 30.3 if we include it), demonstrating that V₂ is definitely a difficult case for the present available xc functionals. To explore the source of these exceedingly large errors, the molecular orbital (MO) diagrams of V₂ using results of five xc functionals, in particular τ -HCTHhyb, M06-L, OreLYP, τ -HCTH, and MPW1B95 are constructed and analyzed. These functionals are selected because they give respectively the two best predictions with negative MSE, the best prediction with positive MSE, the poorest prediction with positive MSE, and the poorest prediction with negative MSE, among all functionals that have similar values of Err(opt) and Err(con).

The results show the key importance of two molecular orbitals (σ_{h1} and σ_{h2}) that are linear combinations of two singly occupied 4s and two virtual 3d_{z²} AOs of the vanadium atoms. Further consideration of the MO diagrams revealed that the error of the calculated bond energy of the vanadium dimer given by an xc functional can be related to the error of the predicted energy gap ($\Delta\epsilon$) between the 4s and 3d_{z²} AOs and

especially with the energy of the 3d_{z²} AO. Furthermore, considering all 43 functionals, we find that those giving $\Delta\epsilon$ larger than that predicted by M06-L (2.09 eV) tend to predict negative MSEs, while if $\Delta\epsilon$ is smaller than 2.09 eV, then positive MSEs are found, with the only exception being OHLYP, which gives $\Delta\epsilon$ and MSE as 1.45 eV and –22.4 kcal/mol, respectively. This interesting relation between the accuracy of the calculated bond energies of V₂ molecule and the accuracy of the orbital energies of the vanadium atom fundamentally alters the common view that it is the quite significant multiconfigurational characteristics of transition metal compounds, leading to static correlation energy, that makes many of them, with the vanadium dimer being a prime example, such difficult cases for many xc functionals. Furthermore, the finding that it is the atomic orbital energies that control the accuracy allows for constructive approaches for improving the exchange–correlation functionals, whereas it is much harder to use the static correlation energy explanation constructively.

One of the most important contributing factors to this relationship is found to be the amount of nonlocal HF exchange that is used to replace the local exchange of an individual xc functional. Specifically, all local density functionals, except M06-L, M11-L, and MN12-L, turn out to overestimate the bond energies (positive MSEs), while the HF method and all the nonlocal density functionals, with the only exception being MPWLYP1M, predict negative MSEs, and roughly speaking, the more HF exchange that is included, the more negative are the MSEs.

The PPMCC analyses show that MSE is most correlated with $\epsilon_{3d_{z^2}}$ and less correlated with ϵ_{4s} , namely it is actually the virtual 3d_{z²} atomic orbital that matters most for the errors of the bond energy calculations. The percentage X of nonlocal exchange of a KS functional is also well correlated with MSE, but $\epsilon_{3d_{z^2}}$ and ϵ_{4s} are almost equally sensitive to X. Therefore, the nonlocal exchange should play an important role for improvement of the KS functional, but it is not the only part of story.

■ ASSOCIATED CONTENT

Supporting Information

MO energies, dominant atomic orbital contributions, and MO shapes that are predicted by “constrained” calculations by the τ -HCTHhyb, M06-L, OreLYP, τ -HCTH, and MPW1B95 xc functionals. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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