

Performance of Effective Core Potentials for Density Functional Calculations on 3d Transition Metals

Xuefei Xu[†] and Donald G. Truhlar^{*,†}

[†]Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States

S Supporting Information

ABSTRACT: The performance of popular Hartree–Fock-based effective core potentials in Hartree–Fock and density functional calculations of 3d transition metals has been evaluated by basis-set convergence studies for ten cases: the equilibrium bond dissociation energy (D_e) for dissociation of ground-state Ti_2 to ground and excited atoms, the ground-state dissociation energies of FeO , Cu_2 , ScH , TiH , Sc_2 , Fe_2 , and TiV^+ , and the first excitation energy (E_x) of Ti atom. Each case is studied with 11 or 13 density functionals. For comparison, the accuracy of the all-electron def2-TZVP basis set is tested with both relativistic and nonrelativistic treatments. Convergence and accuracy are assessed by comparing to relativistic all-electron calculations with a nearly complete relativistic basis set (NCBS-DK, which denotes the cc-pVSZ-DK basis set for 3d metals and hydrogen and the ma-cc-pVSZ-DK basis set for oxygen) and to nonrelativistic all-electron calculations with a nearly complete nonrelativistic basis set (NCBS-NR, which denotes the cc-pVSZ basis set for 3d metals and hydrogen and the ma-cc-pVSZ basis set for oxygen). As compared to NCBS-DK results, all ECP calculations perform worse than def2-TZVP all-electron relativistic calculations when averaged over all 130 data (13 functionals and ten test cases). The compact effective potential (CEP) relativistic effective core potential (RECP) combined with a valence basis set developed for the many-electron Dirac–Fock (MDF10) RECP performs best in effective core potential calculations and has an average basis-set incompleteness error of 3.7 kcal/mol, which is much larger than that (0.9 kcal/mol) of def2-TZVP relativistic all-electron results. Hence, the def2-TZVP relativistic all-electron calculations are recommended for accurate DFT calculations on 3d transition metals. In addition to our general findings, we observed that all kinds of density functionals do not show the same trends. For example, when ECPs are used with hybrid functionals, which sometimes are not recommended for calculations of transition metal systems, they are found to perform better at achieving the basis-set limit than when used with local functionals and meta-GGA functionals. The most successful combination of RECP and basis set has a basis-set incompleteness error of 1.7–2.4 kcal/mol for hybrid generalized gradient approximations, which is smaller than that of nonrelativistic NCBS calculations (whose average basis-set incompleteness error for hybrid functionals is 2.7–2.9 kcal/mol). The average basis-set incompleteness error in Hartree–Fock calculations is 1.0–4.4 kcal/mol for five of the ECP basis sets but is 5.8–10.8 kcal/mol for six others.

1. INTRODUCTION

Accurate computational study of transition metal (TM) containing systems has been recognized as a challenge for several decades because of the large computational cost, significant relativistic effects, and particularly the presence of low-lying electronic states arising from partially filled d shells. Because of the complexity, the present most widely used computational method for large TM system is density functional theory (DFT) combined with the use of effective core potentials (ECPs).¹ Following this strategy, there are several issues to which one should pay attention.

The first issue is the decision whether to use an ECP. An ECP is a potential energy function added to an electronic structure calculation to replace the explicit treatment of core electrons. The use of an ECP allows one to significantly reduce the cost of calculations in three ways: (i) by decreasing the number of basis functions (because no basis functions are required to treat core orbitals), (ii) by decreasing basis-set superposition error; and (iii) by solving a nonrelativistic (NR) wave equation for valence orbitals in the presence of a relativistic ECP (RECP, which is an ECP fitted to relativistic calculations) rather than having to use a relativistic all-electron (AE) wave equation to include the relativistic effects. The second issue is that ECP requirements for DFT are different from those for wave function theory (WFT).

The most popular ECPs for DFT calculations with Gaussian basis functions have been developed with Hartree–Fock (HF) wave functions, and their application in DFT studies needs further validation because of the nonlinear dependence of exchange–correlation (xc) functional on density. The importance of nonlinear core corrections (NLCC) in DFT calculations with ECPs has been stressed in several studies,² and a few systematic investigations³ have been carried out to validate the use of some HF-derived ECPs in Gaussian-based DFT calculations. In our recent work on ECPs for As-containing compounds, we investigated⁴ the need for NLCCs for Gaussian-based DFT calculations. The limited transferability of HF-derived ECPs in DFT calculations was observed, but the errors introduced relative to the nearly complete all-electron (AE) basis set calculations by using small-core ECPs with appropriate valence basis sets for arsenic were found to be small enough to be acceptable for many purposes. However, for transition metals, the conclusions could change, especially due to the variability of s and d orbital occupations upon bonding or electronic excitation. With different valence occupancies, the electron density in the

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core region of a particular TM atom could differ significantly from the density of the reference state used in the ECP construction; this makes stronger demands on the transferability of ECPs for accurate calculations with either HF or DFT.²

A related issue is that ECPs do not eliminate electron density in the core region. They do remove the density due to core orbitals, and they replace the core-region density of the true core orbitals by the core-region density of the pseudovalence orbitals (which are the nodeless valence orbitals determined in the presence of ECPs rather than in the presence of explicit core orbitals). Different ECPs change the core-region density and density gradient in different ways, and different density functionals may be more or less suitable for use in the presence of such changes as caused by a particular ECP. Meta-GGA functionals that involve orbital-dependent kinetic energy density make the importance of this complication even more difficult to pre-judge.

Another issue is that, despite the success of DFT for systems composed of main-group elements, density functionals have special problems for the investigation of TM systems.⁵ The main one is that, as a single reference method, DFT is expected to be less accurate for some TM systems, because of their strong multireference character. The performance of various density functionals when applied to TM-containing systems has been extensively investigated using AE basis sets in the past decade.⁶ One conclusion^{6b} is that local generalized gradient approximations (GGA) and meta-GGA functionals usually perform better for TM species than do the nonlocal hybrid functionals that are the recommended functionals for most main-group species; this results because the Hartree–Fock (HF) exchange involved in hybrid functionals does not incorporate the important static correlation effects of multireference systems, whereas density functional exchange includes a portion of the nondynamical correlation energy,⁷ this is particularly important in TM bonding.⁸ The various exchange and correlation functionals include different approximations to Hartree–Fock exchange, nondynamical correlation, and dynamical correlation, and the resulting errors introduced by each density functional interact nonlinearly with errors introduced by each ECP, by the NLCC, and by the pseudovalence orbital density. Ultimately we need to find an ECP that works well for a given density functional.

In the present work, we investigate the performance of popular HF-derived ECPs for DFT study of 3d TM-containing species. A key issue in the construction of effective core potentials is that they do not represent just the interaction of a single electron with the core. Rather they must be constructed from the neutral atom wave function so that they take account, in an effective way, of the valence–valence interaction energy between the pseudovalence orbitals without modifying the form of the two-electron Coulomb interaction that is appropriate for interactions among the original valence orbitals.⁹ This indicates that effective core potential cannot be completely transferable among molecules that have different valence electron distributions or different partial atomic charges. Therefore, in testing the performance of effective core potentials we should consider molecules with bonds having both high and low partial ionic character, and we should consider molecules in which the valence electron distribution is significantly different than that in the atoms, for example a case where s and d orbital occupancies have changed. The test set used here includes this kind of diversity. The first and major part of the present investigation involves determining how well one can find a generally applicable ECP for DFT methods;

this is accomplished by averaging ECP performance on up to 130 data (as explained above). The second part is a study of whether particular ECPs are well suited for use with specific density functionals. The appropriate valence basis sets to be combined with ECPs for DFT calculations are also discussed. In addition we carry out HF calculations for sorting out the special ECP needs of DFT as compared to those of WFT.

2. COMPUTATIONAL DETAILS

It is well-known that core–valence interactions are too strong to allow one to replace the 3s and 3p electrons by an ECP in 3d TMs.¹⁰ Therefore, we consider only “small-core” ECPs that replace the innermost 10 electrons. Finally we note that the relativistic effects considered in the present article are only the one-electron scalar relativistic effects, that is, the mass-velocity and Darwin terms; we do not consider spin–orbit coupling at all.

Our investigation starts by calculating the equilibrium bond energy (D_e) of Ti_2 using a variety of combinations of popular ECPs and valence basis sets and 11 popular and prototypical functionals (M05,¹¹ M06-L,¹² M06,¹³ BLYP,¹⁴ ω B97X-D,¹⁵ τ HCTHhyb,¹⁶ G96LYP,^{14b,17} mPWLYP,^{14b,18} B3LYP,^{14,19} X3LYP,²⁰ and BPBE^{14a,21}). We investigate the $^3\Delta_g$ state of Ti_2 and consider the two dissociation limits of this state: one dissociation limit is the ground state (3F , $4s^23d^2$) of two Ti atoms; another dissociation limit is the first excited state (5F , $4s^13d^3$) of two Ti atoms; the former may be called adiabatic dissociation, and the latter may be called diabatic dissociation because the bonding of Ti_2 ($^3\Delta_g$) is derived from the $4s^13d^3$ occupations of Ti atoms.

For each kind of dissociation and each given functional, we carry out a Douglas–Kroll–Hess second-order scalar relativistic calculation (labeled, as usual, as either DKH or DK)²² with a large AE basis set called cc-pV5Z-DK.²³ This basis set is specifically optimized for relativistic calculations and is used to obtain a D_e reference value for that functional. For brevity, this reference value is labeled NCBS-DK (NCBS denotes “nearly complete basis set”). For each ECP calculation, with either a nonrelativistic (NR) or a DKH relativistic treatment of valence electrons, we calculate a deviation from the relativistic NCBS-DK value; we will call this the complete error. The complete mean unsigned error (C-MUE) is the mean unsigned deviation of the 11 calculated values for each kind of dissociation limit from their corresponding NCBS-DK reference values, and it is a measure of how well the whole treatment approaches the complete basis set limit including relativistic effects. The C-MUE is also called the basis-set incompleteness error.

Similarly, we use a nonrelativistic calculation with the cc-pV5Z basis set (which is specifically optimized for nonrelativistic calculations) to obtain a nearly complete-basis-set nonrelativistic reference value, labeled NCBS-NR, of D_e of Ti_2 for each dissociation limit and for a given functional. The mean unsigned deviation of calculations with each ECP and its corresponding valence basis set from the corresponding NCBS-NR reference values is calculated for the 11 functionals and is called the nonrelativistic mean unsigned error (NR-MUE). The NR-MUE is a measure of how well this treatment approaches the nonrelativistic complete basis set limit.

As mentioned in Introduction, the error from the density functional itself interacts with the error from the basis set; therefore, instead of comparing to experimental results, we compare the ECP results to the AE NCBS values obtained with the same functional. We do this for both relativistic and nonrelativistic ECPs.

In this way, one can largely decouple the errors that are intrinsic to a given functional, errors from the treatment of relativistic effects, and errors resulting from the choice of ECP and valence basis set. By averaging over 11 functionals we get a robust estimation of the typical errors incurred by use of a given ECP to represent the core electrons for DFT calculations because averaging over 11 functionals avoids the bias due to the choice of a particular functional.

In this first test set, we first test the five popular small-core ECPs, each used with its own valence basis set, that is, with the basis set originally proposed by the developers of that ECP. Next we test some nonstandard combinations of these ECPs with AE basis sets or with valence basis sets designed, optimized, or designated for other ECPs. The five tested ECPs include three RECPs:

- the multiconfiguration Hartree–Fock adjusted relativistic Stuttgart ECP with perturbative corrections added from Dirac–Hartree–Fock results (originally called MDF10²⁴ and also often called SDD),
 - the relativistic compact effective potential (CEP,²⁵ which is also sometimes called the Stevens–Basch–Krauss–Jasien (SBKJ) potential),
 - the CRENBL RECP derived from numerical Dirac–Fock calculations;²⁶
- and two nonrelativistic ECPs (NRECPs):
- the Los Alamos²⁷ small-core NRECP,
 - the MHF10²⁴ Stuttgart NRECP.

MDF10 and MHF10 are energy-adjusted ECPs, and the others are shape-consistent ECPs. The energy-adjusted ECPs are adjusted to more than a single reference state so that they are expected to describe states with different d occupation in a more balanced way. The CEP shape-consistent ECP is also obtained in this way. In all ECP calculations in the paper itself (whether employing an NRECP or an RCP), the valence electrons are treated nonrelativistically. Two calculations presented in the Supporting Information confirm the expected small effect of including scalar relativistic effects in the treatment of noncore electrons.

For comparison, we also test the performance of popular AE def2 basis sets²⁸ def2-TZVP and def2-QZVP and the minimally augmented def2 basis sets²⁹ ma-TZVP and ma-QZVP. The relativistic def2-QZVP calculations have been recommended for accurate calculations of small arsenic species in our recent work, and the nonrelativistic def2-TZVP calculations have been found to be reasonably accurate for the properties in which relativistic effect is not significant.

For brevity, we will sometimes label the combination of an ECP and a valence basis set as an “ECP basis set”. We denote each nonstandard ECP basis set by “basis[ECP]”, where “basis” is the well-known name of the basis set and “ECP” is an abbreviation for the ECP. Lanl2 denotes the small-core Los Alamos NRECP; CEP denotes the CEP RECP; MDF denotes the MDF10 RECP; and MHF denotes the MHF10 NRECP. For the standard ECP basis sets, that is, using an ECP and its own designated basis set, or for the use of an AE basis set, we just use the well-known name for it, for example, Lanl2DZ, CEP-121G, or def2-TZVP. A suffix “-C” is added in the denotation if Cartesian d, f, or g subshells are used in calculations instead of the default spherical harmonic d, f, or g basis functions.

Based on the averages of obtained C-MUEs and NR-MUEs for D_e values of two kinds of dissociation of Ti_2 , we selected several more accurate ECP basis sets and the def2-TZVP AE basis set for further tests with a larger test set using the same 11 density functionals. The test set includes 10 cases: the two kinds of

dissociation energy of Ti_2 of the first test set, the first excitation energy E_x ($4s^23d^2 \rightarrow 4s^13d^3$) of Ti atom, and D_e values of TiV^+ ($^3\Delta$ state, dissociating to a neutral Ti atom and a V^+ cation), TiH ($^4\Phi$), Fe_2 ($^7\Delta_u$), FeO ($^5\Delta$), Sc_2 ($^5\Sigma_u^-$), ScH ($^1\Sigma^-$), and Cu_2 ($^5\Sigma_g^+$). For the cases of TiH , Fe_2 , FeO , Sc_2 , ScH , and Cu_2 , only the ground-state dissociation limit is considered. In calculations with these selected ECP basis sets and in the def2-TZVP AE calculations, the ma-TZVP AE basis set always is used for the oxygen atom of FeO , and the def2-TZVP AE basis set is used for hydrogen in the cases of ScH and TiH .

The same strategy is used for this second test set, and the performance of ECP basis sets for all 11 functionals is estimated by calculating C-MUE and NR-MUE for each case and then averaging over the ten cases. Errors averaged over the ten cases are prefixed by “A-” (which should not be confused with the “M” that denotes a mean over several density functionals). In the calculations of NCBS-DK (NCBS-NR) reference values for each functional and each case, the NCBS-DK (NCBS-NR) basis set for 3d TM metals and H atom is always cc-pV5Z-DK (cc-pV5Z),^{22,30} and the NCBS-DK (NCBS-NR) basis set for O atom is a minimally augmented cc-pV5Z-DK (cc-pV5Z) basis set (ma-cc-pV5Z-DK (ma-cc-pV5Z)) because of the negative partial charge on O. The minimally augmented basis set ma-cc-pV5Z-DK or ma-cc-pV5Z is obtained by adding a set of diffuse s and p functions to the cc-pV5Z-DK or cc-pV5Z basis set for non-hydrogenic elements, with the exponents of the most diffuse s or p functions of cc-pV5Z-DK or cc-pV5Z basis set divided by a factor of 3, as recommended previously.^{4,29}

To identify an ECP that works well for a given functional, we also calculate the mean unsigned deviation of various ECP basis sets from the NCBS-DK reference value over ten cases for each given functional. In addition, for further understanding, the use of these ECP basis sets for HF calculations and for calculations with two additional functionals SVWN³¹ and HSE³² will be also tested in this part of the investigation. Through comparison with the performance of the def2-TZVP AE basis set for each functional, the use of each special ECP basis set is discussed in detail.

All calculations are carried out using the Gaussian 09³³ electronic-structure package. For each molecule, the same geometry was used for all calculations because the use of any reasonable bond length is equally good for testing whether the ECP represents the effect of the core electrons. (Nevertheless, for completeness, we confirm at the beginning of section 3 that the complete mean unsigned errors in dissociation energies with a fixed reasonable bond length are in good agreement with those obtained with individually optimized bond lengths.) The experimental bond lengths are used for $R_{\text{Ti}-\text{Ti}} = 1.943 \text{ \AA}$,³⁴ $R_{\text{Fe}-\text{Fe}} = 2.02 \text{ \AA}$,³⁴ $R_{\text{Cu}-\text{Cu}} = 2.219 \text{ \AA}$,³⁴ $R_{\text{Ti}-\text{H}} = 1.779 \text{ \AA}$,³⁵ and $R_{\text{Fe}-\text{O}} = 1.616 \text{ \AA}$.³⁶ The value of $R_{\text{Sc}-\text{Sc}}$ equal to 2.63 \AA is taken from the DFT calculation in ref 34; $R_{\text{Sc}-\text{H}} = 1.7709 \text{ \AA}$ is obtained here by the M05/NCBS-DK method; and $R_{\text{TiV}^+} = 2.4287 \text{ \AA}$ is obtained here by the M05/def2-TZVP method. For each single-point electronic structure calculation, the internal stability³⁷ of wave function has been tested. If instability is found, the wave function is reoptimized with the appropriate reduction in constraints, until it is stable.

3. RESULTS AND DISCUSSION

For convenience of the reader understanding the trends, all values of errors in the tables are rounded to the nearest 0.1 kcal/mol. For specialists, another set of tables showing the hundredths place is given in the Supporting Information.

Table 1. C-MUE of Equilibrium Bond Length R_e (Å) and C-MUE of D_e (kcal/mol) of TiH and Cu₂ over 11 Density Functionals

	TiH			Cu ₂		
	R_e	D_e^a	D_e^b	R_e	D_e^a	D_e^b
NCBS-DK	0	0	0	0	0	0
NCBS-NR	0.0032	1.7	1.7	0.0303	2.7	2.9
def2-TZVP (DK)	0.0019	1.0	1.0	0.0146	0.8	0.9
def2-TZVP (NR)	0.0012	0.8	0.8	0.0445	3.7	4.0
Lan12DZ	0.0220	2.3	2.4	0.0163	1.8	1.8
ma-sc-SVP	0.0338	2.6	2.6	0.0122	13.2	13.1
MDF[Lan12]-C	0.0035	1.0	1.0	0.0316	3.8	4.0

^a D_e is calculated with individually optimized bond length. ^b D_e is calculated with fixed bond length.

Before the systematic studies, we take TiH and Cu₂ as examples to compare the errors calculated from D_e values with particularly optimized bond length R_e for a certain method and basis to those obtained with a fixed reasonable bond length. As shown in Table 1, for both molecules, the C-MUE values of the calculated D_e with the optimized bond length over 11 density functionals (M05, M06-L, M06, BLYP, ω B97X-D, τ HCTHhyb, G96LYP, mPWLYP, B3LYP, X3LYP, and BPBE) are similar to those obtained with the fixed bond length, even for some basis choices which give a large geometry deviation from the NCBS-DK limit; this indicates that the protocol used here is insensitive to choice of geometry within the near equilibrium region.

3.1. D_e of Ti₂. Table 2 lists the calculated MUEs (NR-MUE, C-MUE) using four AE basis sets (def2-QZVP, def2-TZVP, ma-QZVP, and ma-TZVP) and 24 ECP basis sets (the details are in Table 2, and more ECP basis sets test results can be found in the Supporting Information), for D_e values of two kinds of dissociations of Ti₂, averaged over the 11 density functionals (M05, M06-L, M06, BLYP, ω B97X-D, τ HCTHhyb, G96LYP, mPWLYP, B3LYP, X3LYP, and BPBE). The last two columns give the average of MUEs (A-NR-MUE, A-C-MUE) of the two kinds of D_e values of Ti₂, so each value in these columns is an average over 22 data.

3.1.1. AE Basis Sets. As shown in Table 2, the nonrelativistic calculations with def2- π ZVP and ma- π ZVP ($\pi \geq T$) AE basis sets all have A-NR-MUE values of <0.5 kcal/mol; it is not necessary to use an ma- basis set instead of a def2- basis set on the metal in the D_e calculations of 3d transition metal–metal bond. In a similar way, the def2- basis sets tested with relativistic treatment show acceptably small errors with A-C-MUE being smaller than 0.7 kcal/mol, even though these basis sets are optimized for nonrelativistic calculations. It is noted that in our previous study⁴ for arsenic, relativistic calculations with def2-TZVP were not recommended because the def2-TZVP basis set is overpolarized by f functions for relativistic valence orbitals of arsenic. We note that def2-TZVP is as good as or slightly better for the two kinds of dissociations of Ti₂ than the def2-QZVP basis set for relativistic treatment. Using the C-MUEs of nonrelativistic calculations with cc-pVSZ, which is the NCBS-NR basis set, we can roughly estimate the relativistic effect for the two dissociation limits of Ti₂. The ground state dissociation limit of Ti₂ is found to have a larger relativistic effect, which is about twice that of the dissociation to the first excited state of Ti atom. The average of the absolute values of relativistic effect for the two dissociation

limits of Ti₂ is ~ 3.2 kcal/mol, which should be the smallest error for AE nonrelativistic treatment for Ti₂ dissociations. In order to get more accurate results, a relativistic treatment must be used.

3.1.2. ECP Basis Sets. According to Table 2, relativistic DFT calculations with the def2-TZVP AE basis set can decrease the complete error to 0.6 kcal/mol. Can one also achieve this with an RECP? If not, can the RECP at least reduce the A-C-MUE to a value below the 3 kcal/mol achievable with NR AE calculations? We shall see that the answers are no and no. (We remind the reader that all errors in and all conclusions in this section are for errors averaged over 11 density functionals.)

Table 2 shows a large number of calculations on Ti₂, which was studied in the most detail because it turned out to be a very difficult test case. The table shows that the performance of all the ECP basis sets tested (including both RECPs and NRECPs) is much worse than those of the AE basis sets, even worse than those of the nonrelativistic AE basis set calculations. Most standard ECP basis sets and some nonstandard ECP basis sets are singled out for having relatively better performance in Table 2. Next we discuss a few examples showing this.

The smallest A-C-MUE is 7.6 kcal/mol obtained with the MDF[CEP]-C ECP basis set, which is a nonstandard combination of CEP RECP and the valence basis set particularly developed for use with the MDF10 RECP except that “-C” denotes the Cartesian d and f functions are used in calculations. The CEP-121G standard ECP basis adopts the same CEP RECP but has larger A-C-MUE value (10.4 or 10.6 kcal/mol for spherical harmonic or Cartesian d functions) due to using a relatively smaller valence basis set. This example provides an illustration of why we considered nonstandard ECP basis sets. It shows that sometimes the error in a standard ECP basis set is not due entirely to the ECP itself but rather has a significant component due to the originally proposed valence basis set. But in this case we can still reduce the average complete error by only 26% by using a better valence basis set.

The Los Alamos small-core NRECP is also a relatively good ECP. Since it is fitted to nonrelativistic calculations, the relativistic effect is not taken account. Hence, although the Los Alamos NRECP with its own valence basis sets (Lan12DZ-C and Lan12DZ) has a worse performance than MDF[CEP]-C as compared to NCBS-DK reference values, it has the best performance compared to NCBS-NR values. We tried to improve the performance of the Los Alamos ECP by adding more polarization functions and by decontraction, as discussed next. Lan12DZ(f)-C has an additional f polarization shell for the valence basis set as compared to Lan12DZ-C; these additional f polarization functions slightly improve its performance relative to Lan12DZ-C with the average error decreasing by 0.3–0.5 kcal/mol. Lan12TZ and Lan12TZ(f) decontract the s and p functions of valence basis set of Lan12DZ, and Lan108 decontracts all s, p, and d functions; these basis sets, although further flexibilized by uncontractions, still lead to large MUEs due to the incompleteness of the basis set.

Although MDF10 and CRENL are both RECPs fitted to relativistic calculations, they perform worse than Los Alamos and MHF10 NRECPs for the Ti₂ dissociation energies, especially the CRENL RECP, which has an A-C-MUE of 12.5 kcal/mol. When spherical harmonic d, f, or g functions are used, MDF2fg has a smaller A-C-MUE value than that of MDF due to one additional f shell and one g shell added to valence basis set, which was recommended by Martin.³⁸ However, the use of Cartesian functions gets the opposite results: the AMUEs of MDF2fg-C are found to be larger than those of MDF-C.

The nonstandard ECP basis sets in which an ECP is simply combined with an AE basis set usually perform very badly. This is

Table 2. MUE (kcal/mol) over 11 Density Functionals for D_e of Ti_2 ^a

	basis function	ECP	RECP	type ^b	$Ti_2 \rightarrow 2Ti$ (³ F)		$Ti_2 \rightarrow 2Ti$ (⁵ F)		A-NR-MUE	A-C-MUE
					NR-MUE	C-MUE	NR-MUE	C-MUE		
cc-pV5Z-DK	9s,8p,6d,4f,3g,2h,1i			DK	4.3	0.0	2.1	0.0	3.2	0.0
def2-TZVP	6s,4p,4d,1f			DK	5.2	0.9	2.0	0.3	3.6	0.6
def2-QZVP	11s,6p,5d,3f,1g			DK	3.4	0.9	2.6	0.5	3.0	0.7
def2-TZVP	6s,4p,4d,1f			NR	0.6	3.7	0.3	2.4	0.5	3.0
ma-TZVP	7s,5p,4d,1f			NR	0.5	4.0	0.2	2.1	0.3	3.0
def2-QZVP	11s,6p,5d,3f,1g			NR	0.6	4.5	0.4	1.7	0.5	3.1
cc-pV5Z	9s,8p,6d,4f,3g,2h,1i			NR	0.0	4.3	0.0	2.1	0.0	3.2
ma-QZVP	12s,7p,5d,3f,1g			NR	0.4	4.7	0.3	1.7	0.4	3.2
MDF[CEP]-C	6s,5p,3d,1f	CEP	yes	NR	9.6	6.8	7.9	8.5	8.7	7.6
Lanl2DZ(f)-C	3s,3p,2d,1f	Los Alamos	no	NR	6.7	5.7	9.5	10.1	8.1	7.9
MDF[Lanl2]	6s,5p,3d,1f	Los Alamos	no	NR	8.3	5.8	10.1	10.7	9.2	8.3
MD[Lanl2]-C	6s,5p,3d,1f	Los Alamos	no	NR	9.9	7.1	8.9	9.5	9.4	8.3
Lanl2DZ-C	3s,3p,2d	Los Alamos	no	NR	7.1	6.0	10.1	10.7	8.6	8.3
MHF-C	6s,5p,3d,1f	MHF10	no	NR	10.4	7.6	10.1	10.7	10.2	9.2
def2-QZVP[Lanl2]	11s,6p,5d,3f,1g	Los Alamos	no	NR	8.1	12.4	7.9	6.0	8.0	9.2
Lanl2DZ	3s,3p,2d	Los Alamos	no	NR	5.9	8.2	10.0	10.6	8.0	9.4
m-Lanl2DZ	3s,3p,2d	Los Alamos	no	NR	6.0	8.8	9.8	10.4	7.9	9.6
MDF2fg	6s,5p,3d,2f,1g	MDF10	yes	NR	13.2	9.9	9.3	9.8	11.2	9.9
MDF-C	6s,5p,3d,1f	MDF10	yes	NR	13.6	10.2	9.2	9.8	11.4	10.0
CEP-121G[Lanl2]-C	4s,4p,3d	Los Alamos	no	NR	13.1	9.6	9.9	10.5	11.5	10.1
MDF	6s,5p,3d,1f	MDF10	yes	NR	13.4	10.0	9.6	10.1	11.5	10.1
CEP-121G	4s,4p,3d	CEP	yes	NR	13.9	10.3	9.8	10.4	11.9	10.4
CEP-121G-C	4s,4p,3d	CEP	yes	NR	14.4	10.8	9.8	10.4	12.1	10.6
MDF2fg-C	6s,5p,3d,2f,1g	MDF10	yes	NR	14.8	11.2	9.5	10.1	12.1	10.7
Lanl2TZ(f)	5s,5p,3d,1f	Los Alamos	no	NR	14.5	11.7	10.0	10.6	12.3	11.1
Lanl2TZ	5s,5p,3d	Los Alamos	no	NR	14.9	12.0	10.3	10.9	12.6	11.4
CEP-121G[MDF]-C	4s,4p,3d	MDF10	yes	NR	14.9	11.3	11.1	11.7	13.0	11.5
Lanl08	5s,5p,5d	Los Alamos	no	NR	14.9	12.1	10.4	11.0	12.7	11.6
def2-TZVP[Lanl2]	6s,4p,4d,1f	Los Alamos	no	NR	12.8	17.1	5.5	6.1	9.1	11.6
CRENBL	7s,6p,6d	CRENBL	yes	NR	17.2	13.6	10.8	11.4	14.0	12.5
Lanl2MB	2s,2p,1d	Los Alamos	no	NR	10.8	9.8	19.1	20.1	15.0	15.0
ma-sc-SVP	5s,4p,2d,2f	MDF10	yes	NR	5.8	5.9	26.7	24.6	16.2	15.3

^a The well-known names of AE basis sets and standard combinations of ECP and valence basis sets are used. The nonstandard combinations of ECP and basis set are denoted as “basis[ECP]”, where “basis” is the well-known name of the basis set and “ECP” is an abbreviation for the name of ECP that is used. Lanl2 denotes small-core (10e) Los Alamos NRECP; CEP denotes CEP RECP; MDF denotes MDF10 RECP; MHF denotes MHF10 NRECP. If Cartesian d, f, or g functions are used in calculations, a suffix “-C” is used. ^b This column refers to how the valence electrons are treated; some calculations in which they are treated relativistically are presented in the Supporting Information.

attributed to these AE basis sets being incomplete and not flexible enough. The pseudovalence orbitals in ECP calculations are different from the valence orbitals in AE calculations in shape and size extent. The exponents of basis functions and the contraction coefficients from an incomplete AE bases sets are therefore not suitable for description of pseudovalence orbitals. Relatively good results for combinations of this type are only observed for def2-QZVP[Lanl2], where the relatively complete AE basis set def2-QZVP is used as the valence basis set.

3.2. D_e of FeO, Cu₂, ScH, TiH, Sc₂, Fe₂, and TiV⁺ and E_x of Ti. Based on A-C-MUE values in Table 2 for Ti_2 dissociation energies, we selected several ECP basis sets with relatively good performance averaged over 11 density functionals for further tests. The criterion is that A-C-MUE in Table 2 is smaller than 10.0 kcal/mol. In addition, the MDF2fg-C and ma-sc-SVP with relatively larger A-C-MUE values are also selected for special

interest (which will be specified in the later discussion). However the def2-QZVP[Lanl2] and m-Lanl2DZ choices are excluded although their A-C-MUEs are smaller than 10.0 kcal/mol. The def2-QZVP[Lanl2] is excluded because it has the same CPU time as def2-QZVP AE calculations but behaves worse due to the use of an ECP. So it is not very attractive to further test this ECP basis set. The m-Lanl2DZ is a slightly modified Lanl2DZ ECP basis set, and its valence basis set has one more p primitive function and different p contracted functions compared with Lanl2DZ. This small change of valence basis sets affects the performance only very slightly. Therefore, we only choose Lanl2DZ for later tests. Thus, in the rest of this section, we employ 11 ECP basis sets (MDF[CEP]-C, Lanl2DZ(f)-C, MDF[Lanl2], MDF[Lanl2]-C, Lanl2DZ-C, MHF-C, Lanl2DZ, MDF2fg, MDF-C, MDF2fg-C, ma-sc-SVP) to perform DFT calculations with the same 11 density functionals as used in section 3.1, but here we apply them to D_e of

Table 3. NR-MUE (kcal/mol) for D_e of Diatomic Molecules and the First Excitation Energy E_x of Ti Atom Using Different ECP and Basis Set over 11 Functionals

	D_e of diatomic molecules									E_x of Ti	A-NR-MUE(10)
	FeO ^a	Cu ₂	ScH ^b	TiH ^b	Sc ₂	Fe ₂	Ti ₂ ^c	Ti ₂ ^d	TiV ⁺		
NCBS-NR ^e	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
def2-TZVP (DK) ^f	2.6	2.0	0.6	2.7	1.5	6.0	5.2	2.0	1.3	3.6	2.7
def2-TZVP (NR) ^g	1.6	1.1	0.6	1.0	0.4	1.0	0.6	0.3	0.8	0.2	0.8
Lanl2DZ-C	4.0	3.5	1.0	1.2	1.7	5.6	7.1	10.1	4.3	1.5	4.0
Lanl2DZ(f)-C	4.2	3.6	1.0	1.5	2.1	6.5	6.7	9.5	4.3	1.4	4.1
Lanl2DZ	4.2	4.2	0.7	1.5	4.1	6.6	5.9	10.0	4.0	3.0	4.4
MDF[Lanl2]	3.7	2.4	0.8	1.5	1.7	8.4	8.3	10.1	6.6	1.2	4.5
MDF[CEP]-C	7.1	0.5	1.0	2.6	2.3	9.5	9.6	7.9	4.1	2.5	4.7
MDF[Lanl2]-C	5.3	1.1	0.9	2.6	2.1	9.4	9.9	8.9	5.2	2.7	4.8
MHF-C	7.0	1.8	1.3	2.9	3.9	9.3	10.4	10.1	6.7	2.2	5.6
MDF2fg	6.9	1.2	1.7	4.7	5.4	13.4	13.2	9.3	5.4	5.1	6.6
MDF-C	8.0	1.2	1.5	4.6	5.4	14.5	13.6	9.2	5.9	5.5	6.9
MDF2fg-C	6.9	1.8	1.5	4.7	5.8	16.1	14.8	9.5	5.3	6.1	7.2
ma-sc-SVP	3.1	16.1	1.1	4.4	3.2	13.9	5.8	26.7	2.6	12.8	8.9

^aIn the calculations with ECP for metals, the basis set for O is ma-TZVP. ^bIn the calculations with ECP for metals, the basis set for H is def2-TZVP. ^cTi₂ → 2Ti (³F). ^dTi₂ → 2Ti (⁵F). ^eNCBS-NR: nonrelativistic results with NCBS-NR basis set. NCBS-NR basis set is cc-pVSZ for all transition metals and H atom, ma-cc-pVSZ for O atom. ^fRelativistic calculations with the def2-TZVP basis set. ^gNonrelativistic calculations with the def2-TZVP basis set.

Table 4. C-MUE (kcal/mol) for D_e of Diatomic Molecules and the First Excitation Energy E_x of Ti Atom Using Different ECP and Basis Set over 11 Functionals

	D_e of diatomic molecules									E_x of Ti	A-C-MUE(10)
	FeO ^a	Cu ₂	ScH ^b	TiH ^b	Sc ₂	Fe ₂	Ti ₂ ^c	Ti ₂ ^d	TiV ⁺		
NCBS-DK ^e	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NCBS-NR ^f	1.4	2.9	0.2	1.7	1.4	5.1	4.3	2.1	1.0	3.2	2.3
def2-TZVP (DK) ^g	1.8	0.9	0.5	1.0	0.2	1.5	0.9	0.3	0.8	0.4	0.8
def2-TZVP (NR) ^h	1.6	4.0	0.6	0.8	1.5	4.3	3.7	2.4	1.1	3.0	2.3
MDF[CEP]-C	5.7	2.7	0.9	1.2	1.2	7.1	6.8	8.5	4.7	1.4	4.0
MDF[Lanl2]-C	3.9	4.0	0.9	1.0	1.3	7.1	7.1	9.5	5.8	1.4	4.2
Lanl2DZ(f)-C	3.3	1.5	1.0	1.4	2.3	8.7	5.7	10.1	4.8	3.2	4.2
Lanl2DZ-C	3.0	1.5	0.9	1.5	2.1	8.5	6.0	10.7	4.7	3.6	4.2
MDF[Lanl2]	3.2	5.3	0.7	1.3	1.7	8.7	5.8	10.7	7.2	3.5	4.8
MHF-C	5.6	4.7	1.3	1.2	2.5	7.4	7.6	10.7	7.4	1.9	5.0
MDF2fg	5.5	1.7	1.7	2.9	4.0	9.1	9.9	9.8	6.1	1.9	5.3
Lanl2DZ	3.4	1.8	0.8	2.4	5.4	10.4	8.2	10.6	4.4	5.5	5.3
MDF-C	6.6	1.7	1.5	2.9	4.0	9.9	10.2	9.8	6.5	2.3	5.4
MDF2fg-C	5.5	1.1	1.5	3.0	4.4	11.2	11.2	10.1	6.0	2.9	5.7
ma-sc-SVP	2.4	13.1	1.0	2.6	4.3	8.9	5.9	24.6	2.7	9.6	7.5

^aIn the calculations with ECP for metals, the basis set for O is ma-TZVP. ^bIn the calculations with ECP for metals, the basis set for H is def2-TZVP. ^cTi₂ → 2Ti (³F). ^dTi₂ → 2Ti (⁵F). ^eRelativistic results with the NCBS-DK basis set. The NCBS-DK basis set is cc-pVSZ-DK for all transition metals and H atom, ma-cc-pVSZ-DK for O atom. ^fNonrelativistic results with the NCBS-NR basis set. The NCBS-NR basis set is cc-pVSZ for all transition metals and H atom, ma-cc-pVSZ for O atom. ^gRelativistic calculations with the def2-TZVP basis set. ^hNonrelativistic calculations with the def2-TZVP basis set.

FeO, Cu₂, ScH, TiH, Sc₂, Fe₂, and TiV⁺ and E_x of Ti. For comparison, relativistic and nonrelativistic calculations with the def2-TZVP AE basis set are also carried out. All the NR-MUEs and C-MUEs of 11 ECP basis sets and of def2-TZVP AE calculations are given respectively in Tables 3 and 4, which also includes those for two kinds of dissociations of Ti₂ from section 3.1. For each basis, the average of MUEs over the ten cases (A-NR-MUE(10) and A-C-MUE(10)) are calculated and shown in the last columns of

Tables 3 and 4, so that each value in the final columns of these tables is an average over 110 data.

3.2.1. Comparison with Nonrelativistic NCBS Results. According to the NR-MUEs shown in Table 3, the Los Alamos NRECP is the best ECP. The valence basis set normally designated for use with the Los Alamos NRECP performs slightly better when Cartesian d functions are used in calculations (Lanl2DZ-C has a 0.4 kcal/mol smaller A-NR-MUE(10) than Lanl2DZ).

By comparison of the performance of Lanl2DZ(f)-C and Lanl2DZ-C, the additional *f* polarization functions in valence basis set are found to have less effect on the present investigations. MDF-[Lanl2], which is a combination of the valence basis set originally developed for the MDF10 RECP and the Los Alamos NRECP, works better when using spherical harmonic *d* and *f* functions. Lanl2DZ and MDF[Lanl2] are observed to have similar values of A-NR-MUE(10). Thus, when the Los Alamos NRECP is used, Lanl2DZ-C and MDF[Lanl2]-C have the smallest and largest A-NR-MUE(10) values respectively. Altogether though, the performance of all the ECPs is poor in this test. In particular, if relativistic effects are not taken into account, the use of ECP basis sets has a 5–12 times larger A-NR-MUE(10) than that of def2-TZVP nonrelativistic AE calculations.

The relativistic effects for 3d TM metals are usually not negligible, and they must be taken into account. For the present tests, the relativistic effect is estimated to be up to 5 kcal/mol. Hence, it is more important to check the performance of the 11 ECP basis sets and def2-TZVP AE basis set relative to NCBS-DK results, i.e. to check their C-MUEs. We do this in section 3.2.2.

3.2.2. Comparison with Relativistic NCBS Results. Comparison of Tables 3 and 4 shows that the A-C-MUE(10) of def2-TZVP relativistic calculations is similar to the A-NR-MUE(10) of def2-TZVP nonrelativistic calculations. This indicates that relativistic calculations with the def2-TZVP basis set optimized for nonrelativistic calculations are feasible for DFT calculations of 3d TM metals, in spite of their relatively bad performance for arsenic. Therefore, in succeeding discussions, we will compare the C-MUEs of ECP basis sets with those of def2-TZVP relativistic calculations.

Again, as seen in Table 4, the CEP RECP and Los Alamos NRECP are the two best ECPs for the present DFT study as compared to NCBS-DK calculations. Here, because the comparison is now to reference values including relativistic effects, the relativistic CEP performs better than the Los Alamos NRECP. It is surprising that MDF-C using the relativistic MDF10 ECP has a larger A-C-MUE(10) than MHF-C employing the nonrelativistic MHF10 ECP. Overall though, the performance of the ECPs is disappointing. In particular, Table 4 shows that A-C-MUE(10) values of calculations employing ECP basis sets are 5–9 times larger than the A-C-MUE(10) of def2-TZVP relativistic AE calculations.

The ma-sc-SVP basis set is an ma-SVP basis set specially modified for combination as a valence basis set with the MDF10 RECP, and in our recent work,⁴ this ECP basis set was found to perform relatively well for arsenic; therefore, it was recommended for large TM-containing arsenic systems because it is available for all elements up to radon. We also mentioned that one must be careful about using it because it had not been tested systematically for 3d TM elements. According to the present investigation, ma-sc-SVP is not a stable enough ECP basis set; although it does perform relatively well for some cases, such as D_e of FeO, ScH, TiV⁺, and ground state dissociation of Ti₂, it performs very badly for D_e of Cu₂, for the excited dissociation limit of Ti₂, and for excitation of Ti. This leads to the result that ma-sc-SVP has the worst performance of all 11 tested ECP basis sets in this section, and it shows why broad testing is required to draw reliable conclusions. We note that the MDF10³⁹ ECP used in the ma-sc-SVP basis set for As is a multiconfiguration Dirac-Hartree–Fock adjusted fully relativistic ECP.

3.2.2.1. D_e of Diatomic Molecules. All ECP basis sets for D_e calculations of transition metal–metal bonds of Fe₂, Ti₂, and

TiV⁺ have very bad performance as compared to NCBS-DK reference calculations that include the relativistic effect. However, ECP calculations work for Cu₂ and Sc₂. For Cu₂, although they still perform worse than def2-TZVP relativistic AE calculations, most ECP basis sets, except for MDF[Lanl2], MHF-C, and ma-sc-SVP, give much better results than def2-TZVP nonrelativistic AE calculations. MDF2fg-C is especially good for D_e of Cu₂, and it almost behaves as well as def2-TZVP relativistic calculations. Its C-MUE value is only 1.1 kcal/mol, much smaller than the error (2.9 kcal/mol) introduced by nonrelativistic NCBS calculations. The relatively good performance of ECPs for Cu₂ can be attributed to the fully occupied *d* shell of Cu, which avoids the variable *s*–*d* occupancy problem mentioned in the second paragraph of section 1. The ECP calculations with MDF[CEP]-C and MDF[Lanl2]-C work well for D_e of Sc₂, for which their C-MUEs are about 1.2 kcal/mol. Other ECP basis sets also perform better for Sc₂ than for Fe₂, Ti₂, and TiV⁺. We note that the valence electron configuration of Sc₂ ($^5\Sigma_u$) is $[\sigma_g^2 \pi_u^1 \pi_u^1 \sigma_g^1 \sigma_u^1]$, while the valence electron configurations of Fe₂ ($^7\Delta_u$), Ti₂ ($^3\Delta_g$), and TiV⁺ ($^3\Delta$) are respectively $[\sigma_g^2 \pi_u^2 \pi_u^2 \sigma_g^2 \delta_g^2 \delta_g^1 \delta_u^1 \delta_u^1 \pi_g^1 \pi_g^1 \sigma_u^1]$, $[\sigma_g^2 \pi_u^2 \pi_u^2 \sigma_g^2 \delta_g^1]$, and $[\sigma^2 \pi^2 \pi^2 \sigma^1 \delta^1]$. In the latter three cases, two degenerate δ orbitals have different electron occupations. This implies larger multireference character of these bonds. The accurate description of multireference character with DFT methods can place a greater demand on the transferability of ECPs, as discussed in the fourth paragraph of section 1.

The calculations employing suitable ECP basis sets for ScH and TiH can obtain very similar results to def2-TZVP relativistic calculations. This may result because metal–hydrogen bonding causes less changes the electronic environment of the transition metal atom than does bonding to other elements.

3.2.2.2. E_x of Ti. To some extent, the C-MUEs for E_x of Ti can represent the transferability of ECPs for different *s*–*d* occupancies. C-MUE values of MDF[CEP]-C and MDF[Lanl2]-C are 1.4 kcal/mol for E_x of Ti. This is a 7.5% error since the experimental E_x of Ti is only 18.68 kcal/mol.⁴⁰ The ma-sc-SVP ECP basis set performs very badly for E_x of Ti, which explains its large C-MUE for Ti₂ dissociation to excited states of Ti atom. The ECP basis sets which perform well for E_x of Ti gives relatively better results for diabatic dissociation of Ti₂ than for ground dissociation.

3.3. Specific Accuracies of ECP Basis Sets for Particular Density Functionals. According to the above results, in the four ECPs tested for all ten cases, the CEP RECP and the Los Alamos NRECP have been found to be relatively better ECPs, and MDF10 and MHF10 to be relatively worse for DFT calculations of 3d TM metals when the results are averaged over 11 density functionals. However, we do expect that specific ECP basis sets can be better for certain specific functionals. Our goal in this subsection is to look for an ECP basis set that, although it is not the best one when averaged over a diverse set of DFT methods, works well for a given functional. Therefore, for each of the 11 functionals in the present study so far (M05, M06-L, M06, BLYP, ω B97X-D, τ HCTHhyb, G96LYP, mPWLYP, B3LYP, X3LYP, and BPBE) and for two additional functionals (SVWN and HSE), we also calculate the average complete unsigned deviation (A-C-UE) for the 11 most promising ECP basis sets and for the def2-TZVP basis set from the NCBS-DK reference values over the ten cases tested in previous sections. For comparison, the performance of these ECP basis sets for the HF method is also investigated in the same way, which is particularly interesting

Table 5. A-C-UEs (kcal/mol) over All 10 Cases for Each Density Functional and for HF

	SVWN	BLYP	G96LYP	mPWLYP	BPBE	τ HCTHhyb	B3LYP	X3LYP	ω B97X-D	HSE	M06-L	M05	M06	HF
X	0	0	0	0	0	15	20	21.8	22.2–100	25–0	0	28	27	
NCBS-DK ^a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NCBS-NR ^b	1.9	1.8	1.6	1.9	1.5	2.7	2.7	2.8	2.9	2.8	2.5	2.7	2.6	4.9
def2-TZVP (DK) ^c	1.1	0.7	0.7	0.6	0.8	1.1	0.7	0.7	1.1	0.9	1.0	1.4	0.4	2.9
def2-TZVP (NR) ^d	1.9	1.9	1.8	1.9	1.6	2.3	2.7	2.5	2.8	2.4	2.4	2.7	2.7	5.8
MDF[CEP]-C	1.9	4.1	4.6	4.0	3.5	3.7	2.1	2.0	2.4	1.7	3.6	6.6	7.4	4.2
MDF[Lan12]-C	2.5	4.4	5.1	4.2	4.1	4.0	2.4	2.2	2.8	2.0	4.3	5.9	6.5	4.4
Lan12DZ(f)-C	1.9	3.1	4.0	3.0	3.3	3.4	2.6	2.7	2.6	3.1	4.5	7.5	9.6	10.2
Lan12DZ-C	2.0	3.4	3.0	3.3	3.5	3.6	2.9	3.0	3.1	3.3	4.0	7.5	9.4	10.8
MDF[Lan12]	3.3	4.9	5.6	4.7	5.0	4.1	3.0	4.4	3.2	3.3	3.8	6.6	7.6	5.8
MHF-C	3.2	5.4	6.2	5.1	5.4	4.8	3.1	3.0	3.8	2.8	5.3	6.3	7.0	6.7
MDF2fg	3.3	5.7	6.3	5.5	5.0	6.0	4.1	3.9	4.6	3.3	5.6	5.6	5.8	2.4
Lan12DZ	2.9	4.2	4.3	4.1	4.1	3.5	4.7	4.9	4.8	4.5	4.8	7.6	11.3	9.0
MDF-C	3.7	5.9	6.4	5.8	5.0	6.3	4.4	4.2	5.1	3.5	6.1	5.7	6.2	2.2
MDF2fg-C	3.4	6.3	6.7	6.2	5.2	6.6	4.8	4.6	5.5	3.7	5.8	5.6	5.3	1.0
ma-sc-SVP	7.5	6.5	6.4	6.4	6.7	6.8	5.8	5.7	6.5	6.1	9.6	10.2	11.9	7.2

^a All-electron relativistic results with the NCBS-DK basis set, which is cc-pVSZ-DK for all transition metals and the H atom and ma-cc-pVSZ-DK for the O atom. ^b All-electron nonrelativistic results with the NCBS-NR basis set, which is cc-pVSZ for all transition metals and the H atom and ma-cc-pVSZ for the O atom. ^c All-electron relativistic calculations with the def2-TZVP basis set. ^d All-electron nonrelativistic calculations with the def2-TZVP basis set.

since the HF method does not require NLCC, as discussed in section 1. The calculated A-C-UEs for each functional and HF method are shown in Table 5.

We will arrange the discussion of density functionals into three groups. Subsection 3.3.1 considers the local spin density approximation (SVWN) and four local generalized gradient approximations (GGAs, in particular BLYP, G96LYP, mPWLYP, and BPBE). Subsection 3.3.2 considers two global-hybrid GGAs (B3LYP and X3LYP) and two range-separated hybrid GGAs (ω B97X-D and HSE). Subsection 3.3.3 considers one meta-GGA (M06-L) and three hybrid meta-GGAs (τ HCTHhyb, M05, and M06).

The percentage X of Hartree–Fock exchange in each functional is shown in the first row of Table 5. Note that for range-separated functionals, X depends on interelectronic distance r_{12} , and for these functionals it is shown as a range, with the first number being X at small r_{12} and the second number being X at large r_{12} .

3.3.1. SVWN, HF, and GGAs. Table 5 shows that the local spin density approximation SVWN to the exchange-correlation functional is less sensitive to the choice of ECP basis sets than are any of the other functionals tested. One main obstacle to the reliable use of ECPs in DFT studies is that ECPs convert small- s core regions into large- s core regions, where s is the reduced density gradient. Most functionals depend on s , with the local spin-density approximation being the only significant exception. Since we find that ECPs perform much better for the local spin-density approximation, we conclude that the s issue is one of the dominant error sources of DFT calculations employing ECPs. Since the local-spin density approximation is independent of s , it is expected, on that basis, to have the same ECP requirements as the HF method. However the last column of Table 5 shows that, except for the MDF10 RECP, the ECPs tested here, even though they were derived for HF methods, have even larger basis-set incompleteness error for HF than for most density functionals. However, we must recall that here we compare our ECP basis set results to the nearly complete basis set limit including relativistic

effects. The HF method significantly overestimates relativistic effects relative to DFT methods, as evidenced by their larger A-C-UE values for cc-pVSZ nonrelativistic (NCBS-NR) calculations. This explains the much worse performance of Los Alamos and MHF10 NRECPs, which are fitted to nonrelativistic AE results, when compared to that of the MDF10 RECP which is fitted to relativistic AE results. In addition, as shown in Table 5, the A-C-UEs of def2-TZVP AE calculations using the HF method are more than twice those of DFT methods, which implies slower basis set convergence in HF. Hence, due to using larger valence basis sets, the HF calculations of MDF[Lan12]-C and MDF[Lan12] perform much better than those using Lan12DZ(f)-C, Lan12DZ-C, and Lan12DZ. These complications of the HF results make it hard to compare their A-C-UEs in Table 5 directly with those of DFT.

Therefore, we instead compare the results of the local spin density approximation to those of GGAs, where the energy density definitely depends on the reduced density gradient s . Although the def2-TZVP calculations with SVWN and GGAs have similar A-C-UEs, GGA calculations using ECP basis sets are observed to have relatively larger basis-set incompleteness errors. As mentioned above, this shows that the s issue is significant. It is also noted that Lan12DZ(f)-C and Lan12DZ-C ECP basis sets are preferred for both GGAs and SVWN. MDF[CEP]-C is also reasonable for SVWN and GGAs.

3.3.2. Hybrid GGAs. Hybrid GGAs functionals (B3LYP, X3LYP, ω B97X-D, and HSE) have worse ECP performance than the local spin density approximation but better performance than GGAs. This must be due to the component of HF exchange. The DFT exchange and correlation parts of these hybrid functionals can yield reasonably accurate estimates of relativistic effects and ensure fast basis set convergence, while the portion of HF exchange that replaces a portion of GGA exchange reduces the s difficulty of the GGA functionals. MDF[CEP]-C works best for all hybrid GGAs, and it has a smaller A-C-UE value than def2-TZVP nonrelativistic AE calculations.

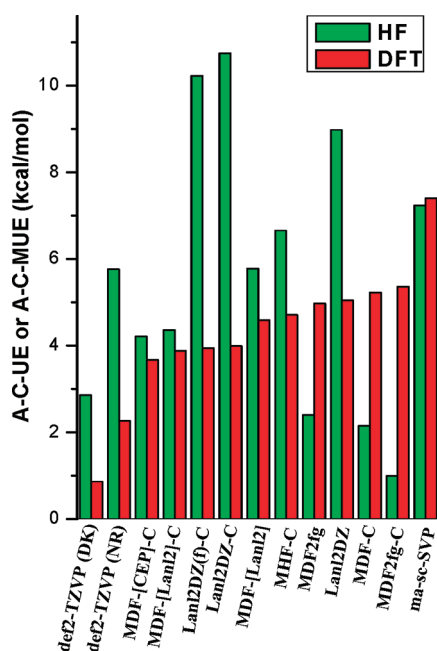


Figure 1. Average complete unsigned error (A-C-UE in kcal/mol) of HF and average complete mean unsigned error (A-C-MUE in kcal/mol) of DFT (averaged over 13 functionals) for ten cases, where the “errors” are deviations as compared to the corresponding NCBS-DK reference values.

The ω B97X-D and HSE range-separated hybrid functionals use different amounts of HF exchange for different interelectronic separation ranges. The ω B97X-D uses full HF exchange at large electron–electron distances and uses a small fraction of 22% HF exchange at short-range. HSE is a screened-Coulomb range-separated hybrid GGA, and it uses pure DF exchange (0% HF exchange) at large interelectronic separation and 25% HF exchange at short-range. Since the most important electron–electron interactions for core electrons that are described by an ECP are short-range interactions, although the two tested range-separated hybrid functionals have very different HF exchange percentages at long-range, they both behave like the two global hybrid functionals.

3.3.3. Meta-GGA Functionals. Meta-GGA functionals not only depend on the up and down spin densities and reduced density gradients but also on the up and down spin kinetic energy densities. The dependence on the kinetic energy densities makes them behave differently with regard to using ECPs. The M06-L meta-GGA is a local functional, but it behaves more like hybrid GGAs than like local GGAs. The hybrid meta-GGAs calculations (M05 and M06) with ECPs are found to have very large basis-set incompleteness error. The MDF10 RECP, which has the worst performance for both local and hybrid functionals, works best for the M05 and M06 functionals. This could be partially due to larger HF exchange. It is noted in this regard that the τ HCTHhyb hybrid meta-GGA functional with smaller HF exchange behaves more like local GGAs.

3.4. Comparison of HF and DFT for the Use of ECPs. Figure 1 is the plot of A-C-UE of HF method and A-C-MUE of DFT for all ten test cases. The A-C-MUEs of DFT methods are averaged for all 13 functionals tested in present study. As shown in Figure 1, except for the MDF10 RECP, the HF-derived ECPs have smaller basis-set incompleteness errors in DFT calculations than in HF calculations, which is surprising in light of

the theoretical underpinning of the need for NLCCs in DFT (no NLCCs are employed in the present work). As discussed in section 3.3.1, the intrinsic error of the HF method seems to dominate the complete error. Therefore, from the present investigation, it is hard to tell how important the NLCC correction is in DFT calculations.

The smallest complete mean unsigned error introduced for DFT calculations is about 3.7 kcal/mol with an appropriate ECP basis set, namely MDF[CEP]-C. Accuracies nearly as good are attained with MDF[Lan12]-C, 3.9 kcal/mol, Lan12DZ(f)-C, 3.9 kcal/mol, and Lan12DZ-C, 4.0 kcal/mol. However, none of these values is as good as an all-electron def2-TZVP relativistic (DK) calculation, 0.9 kcal/mol, or even an all-electron def2-TZVP nonrelativistic calculation, 2.3 kcal/mol. Since the results in Figure 1 are in a sense the culmination summary of the paper, they are presented in tabular form in the Supporting Information (Table S6).

4. SUMMARY

The present work systematically investigates the performance of ECPs and ECP basis sets in Hartree–Fock and DFT calculations of 3d transition metal species, where an ECP basis set is defined as a valence and subvalence basis set plus an effective core potential for a small core (for 3d transition metals, a small core is the innermost ten electrons). The investigation starts from calculations of two kinds of dissociation energy for Ti_2 using 11 common density functionals (M05, M06-L, M06, BLYP, ω B97X-D, τ HCTHhyb, G96LYP, mPWLYP, B3LYP, X3LYP, and BPBE). The performance of some Hartree–Fock-derived ECP basis sets (including three relativistic ECPs and two non-relativistic ECPs) and four popular all-electron basis sets with relativistic or nonrelativistic treatments is evaluated by comparing their predictions to what is obtained with relativistic NCBS-DK calculations and with nonrelativistic NCBS-NR calculations, where NCBS denotes the nearly complete basis set limit, where DK denotes a relativistic calculation, and NR denotes a non-relativistic one.

Based on their performance and on some special considerations, eleven ECP basis sets and the def2-TZVP all-electron basis set are chosen for further tests on the equilibrium bond dissociation energy (D_e) of FeO , Cu_2 , ScH , TiH , Sc_2 , Fe_2 , and TiV^+ and the electronic excitation energy of Ti , using the same 11 functionals. The eleven ECP basis sets chosen for this study are MDF[CEP]-C, Lan12DZ(f)-C, MDF[Lan12], MDF[Lan12]-C, Lan12DZ-C, MHF-C, Lan12DZ, MDF2fg, MDF-C, MDF2fg-C, and ma-sc-SVP. Both relativistic and nonrelativistic calculations are carried out with the def2-TZVP basis set. ECP calculations (except for a couple of tests in the Supporting Information) treat the valence electrons nonrelativistically. The general performance of eleven ECP basis sets and the def2-TZVP all-electron DFT calculations is evaluated based primarily on the average complete mean unsigned deviations (A-C-MUE) from the NCBS-DK all-electron relativistic results, averaged over ten cases including D_e of two kinds of dissociation limits of Ti_2 and over 11 functionals at first and then over 13 functionals. The numbers mentioned below refer to the average over 13 functionals.

The relativistic all-electron def2-TZVP DFT calculations for 3d transition metal species are found to be close to the basis-set limit and to have an A-C-MUE error value of only 0.9 kcal/mol. This result is qualitatively different from what we found in our previous study⁴ of arsenic DFT calculations, where relativistic

calculations with the def2-TZVP basis set for arsenic were not recommended. The use of ECP basis sets in DFT calculations for 3d transition metal species gives much worse results than def2-TZVP relativistic all-electron calculations for the density functionals employed in the various tests. The CEP relativistic ECP and the Los Alamos nonrelativistic ECP are, on average, the best general ECP choices for DFT calculations, and, in particular, the MDF[CEP]-C ECP basis set, which is a combination of the CEP relativistic ECP and valence basis sets developed for the MDF10 relativistic ECP, has the smallest average mean complete unsigned error (A-C-MUE), 3.7 kcal/mol, where “complete error” denotes the deviation from the nearly complete-basis-set relativistic calculations for a given functional, “mean” denotes averaging over the 13 functionals, and “average” denotes averaging over the ten cases.

The main goals in using relativistic ECPs are to decrease the size of the basis sets and to include relativistic effects in calculations in which the explicitly included electrons are still treated nonrelativistically. The second goal cannot be considered to be achieved satisfactorily since we find that results obtained using relativistic ECPs are farther from the nearly complete-basis-set relativistic limit than are polarized triple- ζ nonrelativistic all-electron calculations. Along the same lines, it is also disappointing that when DFT calculations are compared to nearly complete-basis-set relativistic results with the same density functional, the MDF10 relativistic ECP fitted to relativistic calculations has a larger A-C-MUE than does the MHP10 nonrelativistic ECP fitted to nonrelativistic calculations.

We also examined the question of whether some ECPs perform better for certain density functionals than their performance averaged over a set of diverse density functional calculations. To examine this, for each of the 11 selected common density functionals and for two additional density functionals (SVWN and HSE), the average complete unsigned deviation (A-C-UE) from the NCBS-DK reference values has been calculated for the eleven ECP basis sets and for the def2-TZVP all-electron basis set for all ten cases. For comparison, Hartree–Fock calculations are performed in the same way. In these tests, the local spin density approximation functional SVWN has the smallest A-C-UE error value, which we interpret as being due to its independence of the reduced density gradient s . GGAs (in which the energy density depends on s) have relatively worse performance than SVWN for the use of Hartree–Fock-derived ECPs. Both LSDA and GGAs are local functionals, and they work best with the Lanl2DZ(f)-C and Lanl2DZ-C ECP basis sets. The Hartree–Fock exchange used in hybrid GGAs partially avoids the difficulty caused by the s dependence of GGAs in ECP calculations, so that, even though hybrid GGAs are often not recommended functionals for transition metal chemistry, the use of ECPs with this kind of density functional introduces less basis-set incompleteness error than with GGAs. The calculations with hybrid functionals using appropriate ECP basis sets often show better basis set convergence than def2-TZVP nonrelativistic calculations. MDF-CEP-C and MDF[Lanl2]-C are the preferred ECP basis sets for hybrid functionals. The average ECP basis-set-incompleteness error for hybrid functionals calculations with the best performing ECP basis set is ~ 2 kcal/mol.

The meta-GGA density functionals, which depend not only on the up and down spin density and s but also on the up and down spin kinetic energy density, show different behaviors. The M06-L local meta-GGA behaves more like hybrid GGAs, the τ HCTHhyb meta-hybrid GGA behaves more like local functionals as far as its

compatibility with ECPs, and the M05 and M06 hybrid meta-GGAs have the largest errors introduced by ECPs. M05 and M06 with higher HF exchange work best with the MDF10 RECP as does the Hartree–Fock method.

The present investigations show that different functionals have different needs for ECP basis sets. Except for using hybrid functionals and the local spin density approximation, the use of ECP basis sets for 3d transition metals introduces an error of at least 3 kcal/mol for DFT calculations compared to the nearly complete basis set limit including the relativistic effect. Although hybrid functionals are not recommended for transition metal species with high multireference character, they work better with ECPs than do local functionals and meta-GGA functionals.

DFT calculations with an ill-suited ECP basis set can lead to a basis set error larger than 10 kcal/mol. Great caution is urged when using Hartree–Fock-derived ECPs in either HF or DFT studies of 3d transition metal systems. In order to get better results, relativistic or even nonrelativistic DFT calculations with the def2-TZVP all-electron basis set are recommended. It is emphasized again that the conclusions are for 3d transition metals and that they are obtained based on comparisons to the HF and DFT complete-basis-set limit including relativistic effects rather than by comparison to experimental data because comparison to experiment makes it is hard to disentangle basis-set incompleteness from the quality of the Hartree–Fock approximation or the approximate density functional.

■ ASSOCIATED CONTENT

S Supporting Information. (1) Another version of Tables 1–5 showing the deviations rounded in the hundredths place (0.01 kcal/mol) rather than the tenths place; (2) some additional combinations of ECP and basis set for Ti_2 calculations and more details for the specialist and readers interested in this kind of detail; (3) NCBS-DK values for each case and each functional investigated in the present work and for Hartree–Fock calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: truhlar@umn.edu.

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