Extended separated-pair approximation for transition metal potential energy curves

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ABSTRACT. Developing a computational method that is both affordable and accurate for transition-metal chemistry is major challenge. The bond dissociation energies and the potential energy curves are two important targets for theoretical prediction. Here we investigate the performance of multiconfiguration pair-density functional theory (MC-PDFT) based on wave functions calculated by the complete-active-space (CAS) and generalized active space (GAS) self-consistent-field (SCF) methods for three transition-metal diatomics (TiC, TiSi, and WCl) for which accurate bond energies are available from recent experiments. We compare the results to those obtained by complete-active-space second-order perturbation theory (CASPT2) and Kohn-Sham density functional theory (KS-DFT). We use six systematic methods to choose the active spaces: (1) We put the bonding orbitals, antibonding orbitals and singly occupied nonbonding orbitals into the active space in the first method; (2) we also put s and p valence orbitals into the active space; (3,4)we tried two levels of correlated participating orbitals (CPO) active spaces, nominal CPO (nom-CPO) and extended CPO (ext-CPO); (5,6) we used the separated-pair (SP) approximation, and a new method presented here called extended separate pairs (ESP) approximation to divide the nom-CPO active space into subspaces. Schemes 1-4 are carried out within the CAS framework, and schemes 5 and 6 are carried out in the GAS framework to eliminate deadwood configurations. For TiC and TiSi, we used all six kinds of active space. For WCl, we used three active spaces (nom-CPO, SP, ESP). We found that MC-PDFT performs better than both CASPT2 and KS-DFT, and we found that the SP (for TiSi) and ESP (for TiC and WCl) approximations are particularly appealing because make the potential curves smoother and significantly decrease the computational cost of CASSCF calculations. Furthermore, ESP-PDFT can be as accurate as CAS-PDFT.

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I. INTRODUCTION

The current situation in quantum mechanical electronic structure is that strategies for accurate calculations are more straightforward for weakly correlated systems than for strongly correlated ones.^{1,2,3,4} Strongly correlated systems are also called multireference systems and are inherently multiconfigurational systems. Strong correlation is usually a consequence of near degeneracy of low-energy electronic configurations, and it is very common in transition metal systems.

Systems exhibiting this type of correlation are usually treated by a two-step procedure, with the first step being a multiconfiguration self-consistent field (MCSCF) calculation to obtain a reference wave function and the second being a post-SCF step. Such methods are called multireference methods. In the present work we consider two kinds of MCSCF wave function, namely complete-active-space self-consistent field (CASSCF) calculations⁵ and generalized-active-space self-consistent-field (GASSCF) calculations.⁶ We also consider three kinds of post-SCF calculation: (1) complete active space second-order perturbation theory,^{7,8,9} (CASPT2), which starts with a CASSCF calculation, and (2, 3) two forms of multiconfiguration pair-density functional theory^{1,10} (MC-PDFT), namely CAS-PDFT, starting from CASSCF, and GAS-PDFT, starting from GASSCF.

MCSCF calculations can account well for the portion of correlation energy arising from near-degeneracy^{11,12,13,14} but they do not provide most of the dynamic correlation,^{15,16} which is necessary for quantitative accuracy. In principle, one could include the rest of the dynamic correlation by increasing the active space; however for almost all systems, it is impractical to converge the dynamic correlation this way. Therefore, practical multireference methods add the correlation in the space external to the MCSCF calculation by multireference configuration interaction (MR-CI),^{17,18,19} multireference perturbation theory^{20,21,22}(MR-PT) (for example, CASPT2), multireference coupled cluster theory (MR-CC),^{23,24,25} or MC-PDFT. We next stress three important considerations for these post-MCSCF methods.

First, MR-CI, MR-PT, and MR-CC involve considerable expense beyond the cost of the MCSCF step. They require significantly more memory and computational time, which is unaffordable in many cases. This is the main reason why MC-PDFT was developed. In MC-PDFT, the electronic kinetic energy, density, and on-top density are calculated by using a MCSCF wave function. Then, the classical Coulomb energy is

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calculated from the density and an "on-top energy" is computed by using an on-top density functional of the density and on-top density. MC-PDFT can be compared with Kohn-Sham density functional theory²⁶ (KS-DFT). In KS-DFT, the energy is obtained by calculating the kinetic energy and density from a Slater determinant. Then, the classical Coulomb energy is calculated from the density, and the rest of the energy is computed by using an exchange–correlation functional of the density.

A difficulty for all four of these kinds of post-MCSCF methods is active space selection, where "active space" refers to the set of active orbitals and electrons that generate the configuration state functions (CSFs) included in the MCSCF wave function. The results of these methods may depend strongly on the active space. "Complete" active spaces are defined by selecting a set of active orbitals and a number of electrons occupying them and including all CSFs that can be made by various occupancies of these orbitals by these electrons – but the choice of which orbitals to make active is often based on unsystematic trial runs and chemical insight. Incomplete active spaces (as used, for example, in GASSCF) are even less systematic, and choosing a scheme for which CSFs are to be included is often based on trial runs. This precludes defining a model chemistry²⁷ that can be tested systematically. Therefore, finding a systematic way to choose an active space is important for the development of multireference methods, and it is one of the subjects of the present paper.

The third source of difficulty is the large size of complete active spaces. Thus, although methods for systematically selecting complete active spaces are valuable, it is also of great practical interest to define and test systematic methods for incomplete active spaces, and we also consider this issue in the present paper. In the present article we test previously proposed methods for selecting an active space, and we also propose a new method. The present tests are made for the molecules TiC, TiSi, and WCl, for which we compare to accurate experimental bond energies from recent papers by Morse and coworkers,^{28,29,30} and the calculations are carried out by CASSCF, GASSCF, CASPT2, and both the CAS-PDFT and GAS-PDFT versions of MC-PDFT.

For context we here cite a variety of previous work on systematizing or automating the selection of an active space, namely methods based on MP2 natural orbital occupations,³¹ UHF natural orbitals,^{32,33} correlated participating

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II. ACTIVE SPACES

The choice of an active space requires two kinds of decision: (*i*) how many active electrons in how many active orbitals, and (*ii*) how to choose a scheme for which configurations are to be included among the configurations that can be generated with choice *i*. Next we consider issue *ii*, and after that we consider issue *i*.

We have previously developed MC-PDFT as an efficient way to calculate strongly correlated systems, especially when it can be applied successfully with small active spaces for the required first step of a multiconfiguration self-consistent-field (MCSCF) calculation^{1,10}. Motivated by that consideration, we proposed the separated pair (SP) approximation⁴² for active space selection, and we showed that it worked well for several systems in both main-group and transition metal molecules. However, the present study, which is concerned with two titanium tetrals (TiC and TiSi) and a molecule, WCl that contains a heavy transition metal, shows that the SP approximation is inadequate for two of the three systems studied. We then propose a straightforward extension, called the extended separated pair (ESP) approximation, that yields good results as a first step for PDFT calculations on both systems where the SP approximation is insufficient.

An SP wave function is a special case of GASSCF wave function. In GASSCF, the active space is divided into a number of subspaces, and in the SP approximation, every GAS subspace only contains one or two orbitals. One electron is distributed in one or two orbitals or two or three electrons are distributed in two orbitals. All interspace excitations are excluded, and this decreases the number of CSFs as compared to a CAS with the same number of active electrons in the same active orbitals. In practice, we have found that SCF convergence can be difficult in SP calculations if the subspaces are too restrictive (making them unphysical for the system in question); in particular we will see this problem in two of the molecules investigated in the present paper. Therefore, in the present paper we propose the ESP approximation. In the ESP approximation, for each certain symmetry, we put all singly occupied orbitals (which may be bonding, antibonding, or nonbonding orbitals) and their correlating orbitals into a single subspace. For doubly occupied orbitals we

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use the SP approximation. The ESP approximation leads to larger subspaces than the very economical SP approximation can, but it still decreases the number of CSFs as compared to CAS, and it eliminates the SCF convergence problems for the two cases mentioned. Furthermore, we will show in this paper that using ESP wave functions as the reference for PDFT is as accurate as using CASSCF wave functions for two systems to which it is applied.

Next we consider the choice of active orbitals. Our first four choices of active space are based on CAS. The first is to put all the bonding orbitals, antibonding orbitals, and singly occupied nonbonding orbitals into the active space. Second, we test a larger active space that includes s-subshell and p-subshell orbitals. Our third and fourth choices are based on the correlated-participating-orbitals (CPO)^{34,35,36} scheme, which includes the orbitals that participate most strongly in bond breaking and forming. There are three levels of CPO active spaces, based on the way we define participating orbitals: nominal (nom-CPO), moderate (mod-CPO) and extended (ext-CPO), but for TiC and TiSi, nom and mod are the same, so we need only consider nom and ext. The fifth and sixth choices are based on GASSCF. Next we give details of these active space choices.

(1) For active space 1, we put the bonding orbitals, antibonding orbitals and singly occupied nonbonding orbitals into the active space. For TiC, the a_1 symmetry orbitals include a singly occupied σ bond, an empty σ^* bond, and a singly occupied 4s orbital. The b_1 and b_2 symmetries each have a doubly occupied π orbital and an empty π^* orbital. We put these orbitals into the active space, and this gives a (6, 7) active space, where an active space consisting of *n* electrons in *m* orbitals is denoted as (*n*, *m*). For TiSi, a_1 symmetry has a doubly occupied σ bond, an empty σ^* bond, and a singly occupied 3d orbital. In a_2 symmetry, it includes a singly occupied 3d orbital; b_1 and b_2 symmetries both have a singly occupied π orbital and an empty π^* orbital. We put these orbitals into the active space, and this yields a (6, 8) active space. For WCl, we only considered active spaces choices 3, 5, and 6.

(2) For active space 2, in addition to the orbitals in active space 1, we added the p-subshell s-subshell valence orbitals for both atoms. For TiC, this involves a doubly occupied 3s orbital and all doubly occupied 3p orbitals for Ti and a doubly occupied 2s orbital for C; this yields a (16, 12) active space. Similarly, for TiSi, this yields a (16, 13) active space.

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(3) We employed two CPO choices, nom-CPO and ext-CPO. The details of CPO active spaces are laid out in ref. 35. For TiC, nom-CPO it includes one more orbital, an empty correlating orbital for 4s, added to active space 1, so we get a (6, 8) active space. For TiSi, nom-CPO adds two orbitals active space 1, in particular two empty correlating orbitals for two singly occupied 3d orbitals; this yields a (6, 10) active space.

For WCl, the nom-CPO active space in a_1 symmetry has a doubly occupied σ bond, an empty σ^* bond, a singly occupied 6s orbital and its correlating orbital, and a singly occupied 5d orbital and its correlating orbital. The b_1 , b_2 , and a_2 symmetries each have a singly occupied 5d orbital and its correlating orbital. Therefore, nom-CPO for WCl is a (7, 12) active space.

(4) For TiC and TiSi, the ext-CPO active spaces include two more orbitals in addition to the nom-CPO active spaces. These are a doubly occupied 2s orbital for C or 3s orbital for Si and its empty correlating orbital. This yields an (8, 10) active space for TiC and an (8, 12) active space for TiSi.

(5) We used the separated-pair (SP) approximation⁴² and a new method presented here called extended separate pairs (ESP) approximation for all three molecules. In these schemes, for the molecules considered here, we use the same number of electrons and the same active orbitals as in nom-CPO, but we divided the orbitals into subspaces to reduce the number of CSFs. For SP, each subspace includes an orbital (bonding orbital, antibonding orbital, or singly occupied nonbonding orbital) and its correlating orbital.

(6) In the ESP approximation, for each certain symmetry, we combined all singly occupied orbitals (bonding, antibonding, and nonbonding) and their correlating orbitals into a larger subspace. For the other orbitals, ESP is the same as SP.

The number of CSFs in each of the active spaces is summarized in Table I.

III. BOND ENERGY CALCULATIONS

We consider three diatomics in their ground electronic states. The ground term for TiC is ${}^{3}\Sigma^{+}$ (Ref. 28); the ground term for TiSi is ${}^{5}\Delta$ (Ref. 29); the ground term for WCl is ${}^{6}\Sigma^{+}$ (Ref.30).

The experimental data^{28,29,30} are ground-state dissociation energies (D_0). The experimental values include spin-orbit coupling (SOC) since it is a real effect, but the theoretical calculations are carried out without SOC, except for the one separate

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calculation (see below) where we calculated the SOC of TiSi.

The electronic structure calculations directly yield not D_0 but rather the equilibrium dissociation energies (D_e). Therefore, and because the theoretical calculations of D_e are carried out without SOC, we calculate D_0 for diatomic molecule AB by

$$D_0 = D_e - ZPE(AB) + SOC(A) + SOC(B) - SOC(AB)$$
(1)

where SOC is a negative number equal to the energy lowering by SOC.

The ZPEs were calculated by KS-DFT; for TiC and TiSi, we used MN15⁴⁶/jun-cc-pVTZ, and for WCl, we used MN15/ANO-RCC.

For atoms, we calculated the spin-orbit coupling from the NIST tables⁴⁷.

The SOC for molecules is treated only to first order, which is usually sufficient. SOC(AB) is zero for TiC and WCl because they have Σ ground states. For TiSi, which is in a Δ state,²⁹ we calculated the spin-orbit coupling using *Molpro*^{48,49} (version 2015.1). We first performed a ten-state SA-CASSCF calculation using nom-CPO active space without SOC by averaging over ${}^{3}\Sigma$, ${}^{3}\Pi$, and ${}^{3}\Delta$, ${}^{5}\Sigma$, ${}^{5}\Pi$, and ${}^{5}\Delta$ to generate the initial guess for a two-state SA-CASSCF calculation of the ${}^{5}\Delta$ state pair using nom-CPO active space without SOC (in *C*_{2v} symmetry, the degenerate Δ state appears in a₁ and a₂ irreps). The off-diagonal SOC matrix elements⁵⁰ were added to the diagonal CASSCF Hamiltonian (we did not make CASPT2 corrections) of the states resulting from the second SA-CASSCF calculation, and the eigenvalues of this Hamiltonian give the spin-orbit splitting.

The quantities entering eq 1 are summarized in Table II.

In all subsequent tables the theoretically calculated bond energies were calculated by eq 1.

IV. METHODS AND COMPUTATIONAL DETAILS

For TiSi and TiC calculations, we performed nonrelativistic calculations with the jun-cc-pVTZ basis set⁵¹. For WCl calculations, we used the second-order Douglas-Kroll-Hess relativistic Hamiltonian with the ANO-RCC⁵² basis set (except that we used the def2-TZVP basis set⁵³ with a relativistic effective core potential for KS-DFT²⁶ calculations on WCl). CASSCF, GASSCF, and multireference calculations (CASPT2, MC-PDFT) are carried out with *OpenMolcas* v. 18.09.^{54,55} KS-DFT calculations were all carried out with the *Gaussian 09* program⁵⁶ or an in-house modified version⁵⁷ of *Gaussian 09*.

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This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0003048 The PDFT calculations begin with CASSCF or GASSCF (which are special cases of MCSCF), and the CASPT2 calculations begin with a CASSCF calculation. We report results obtained via CASSCF, CASPT2, CAS-PDFT, ESP-PDFT, and KS-DFT. CASSCF, CASPT2 and MC-PDFT (CAS-PDFT and ESP-PDFT) calculations were performed using *OpenMolcas* v. 18.09.^{54,55} For all the curves we got from MCSCF calculations, we optimized the molecule near the equilibrium point first and scan the whole curves from the equilibrium point to both sides using the former point as the initial guess.

For CASPT2, an imaginary shift⁵⁸ is introduced to remove problems with intruder states (states giving small denominator in the second-order perturbation, and hence having a spuriously large effect on the energy, even when they are weakly coupled to the ground state). We use 0.25 E_h for the imaginary shift (1 E_h = 1 hartree = 27.2116 eV). We used the default value of 0.25 E_h for the ionization-potential-electron-affinity (IPEA) shift⁵⁹.

In the CASPT2 calculations, we froze (did not correlate) the 1s shell on all atoms and the 2s and 2p shell on silicon and titanium.

We used eight on-top functionals for the MC-PDFT calculations (CAS-PDFT and ESP-PDFT), namely translated¹⁰ (prefix t) and fully translated⁶⁰ (prefix ft) versions of BLYP^{61,62}, PBE⁶³, revPBE⁶⁴, and OreLYP^{62,65,66}.

We tested the functionals mentioned above (BLYP, PBE, revPBE and OreLYP) and also M06-L⁶⁷, M06⁶⁸, MN15⁴⁶, MN15-L⁶⁹, revM06⁷⁰, and revM06-L⁷¹.

V. RESULTS AND DISCUSSION

A. CAS-PDFT and CASPT2 for TiC

Table III gives the bond dissociation energies and the signed errors for TiC with various methods and active spaces. Figure 1 shows four of the potential energy curves obtained using various active spaces. The CAS-PDFT potential curves with other on-top functionals and active spaces are shown in the Supplementary Material.

Table III shows that CASPT2 gives a very inaccurate bond energy (an error of 46.0 kcal/mol) when we add s-subshell and p-subshell into the active space in addition to the bonding orbitals, antibonding orbitals, and singly occupied nonbonding orbitals. In contrast, the results with CAS-PDFT are reasonably stable to changes in the active space for all of the functionals studied here. Furthermore, with tBLYP the results are more accurate than CASPT2 with all four active spaces, and with ftBLYP they are

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more accurate with 3 of the 4 active spaces. It should be recognized though that although CASPT2 performs well when we use ext-CPO active space, that kind of large active space is impractical for larger molecules.

We previously found good results with tBLYP and ftBLYP for FeC, VN, and TiO.³⁵ so the good performance of these functionals is not surprising.

The potential energy curves in Fig. 1 are not completely smooth with any of the methods, although in most cases their nonsmoothness is minor; the exception is CASPT2 with the (16,12) active space, where the results are very unsmooth. We checked the reference weights of CASPT2 calculations and found there is a big jump at the same place as the jump in CASPT2 energy curve (the reference weights are given in the supplementary material). The reason for both jumps is that at this point, the $2p\sigma$ orbital of Ti, which is uncorrelated, rotates into the active space, replacing the correlated 2s orbital of C, which is correlated. CASPT2 is sensitive to this change whereas CAS-PDFT, which uses only the kinetic energy, density, and on-top energy but not the orbitals or the structure of the wave function, is not. This kind of problem has been discussed previously.⁷²

The good performance of the systematic, small nom-CPO active space is particularly encouraging since that kind of active space remains practical for considerably larger systems.

B. CAS-PDFT and CASPT2 for TiSi

Table IV gives the bond dissociation energies and the signed errors for various methods with various active spaces. Figure 2 shows four of the potential energy curves using various active spaces. The CAS-PDFT potential curves with other on-top functionals and active spaces are shown in the Supplementary Material.

Based on Table IV, we find that again that CASPT2 with an active space (16,13) gives inconsistent results with respect to the other active spaces. However, for TiSi, CAS-PDFT also performs inconsistently for this molecule in that it gives poor results if we use ext-CPO active space. Nevertheless, as we mentioned in the previous part of this paper, it is not practical to use ext-CPO in larger systems because it contains too many active orbitals. CAS-PDFT is more consistent for the three more practical active spaces.

For this molecule the best performance among the on-top functionals, averaged over the three smaller active space is provided by tPBE, ftBLYP, and trevPBE. It is

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encouraging that ftBLYP does well for both TiC and TiSi.

The plots of potential energy curves (Fig. 2) show that CASSCF gives us smooth curves for all four active spaces. CAS-PDFT gives smooth curves when we add s-subshell and p-subshell orbitals into the active space in addition to bonding orbitals, antibonding orbitals and singly occupied nonbonding orbitals, as well as when we use the ext-CPO active space. However, it gives us slightly irregular curves when we use the other two kinds of active spaces. CASPT2 always gives irregular curves for TiSi, especially when we used the (16, 13) active space. Most likely, the jump we see in CASPT2 calculation using the (16, 13) active occurs for a reason similar to that which we explained in detail for TiC in the section above. We should point out that there are some small irregularities close to the minimum for the CAS-PDFT curves and CASPT2 curves when we used (6, 8) active space. We used the lowest energies for these curves in this part when we calculated the bond energies.

Considering both bond energies and potential energy curves, CAS-PDFT performs better than CASPT2 for both TiC and TiSi when we use the jun-cc-pVTZ basis set.

C. SP and ESP approximations

For TiC, we tried three different ways to calculate the potential energy curves for SP calculations. (1) We optimized the orbitals for a geometry near the equilibrium geometry, and we scanned the whole potential energy curve from this point to both sides using the previous point as the initial guess. (2) We optimized a point at long distance and scanned the whole potential energy curve from long distance to short distance using the previous point as the initial guess. (3) We used the natural orbitals we got from CASSCF calculations as the initial guess for each point. However, we found that the we could not converge the SCF iterations at most geometries with any of the three methods. This can be explained as follows. TiC, Ti, are C are all triplets; in TiC, the configuration on Ti is $3d^34s$, whereas in Ti atom, the configuration is $3d^{2}4s^{2}$; similarly C is $2s2p^{3}$ in the molecule and $2s^{2}2p^{2}$ in the atom. In the diatomic, Ti uses a $3d_{z^2}$ orbital, to form a σ bond with the $2p_z$ orbital for C, and it uses $3d_{xz}$ and $3d_{yz}$ orbitals to form π bonds with $3p_x$ and $3p_y$ orbitals for C. Therefore the molecule has only one 4s electron. If we used the separated pair active space, we would put the 4s orbital and its correlating orbital into a subspace and with one electron. However, although this would be reasonable near the equilibrium distance geometry, it is

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unphysical when the distance between two atoms is long since the ground state for Ti atom is $3d^24s^2$. This situation is apparently the reason for the poor SCF convergence of SP for TiC.

To remedy the above problem, we used ESP-PDFT, and this gives us good results. Both the shape of potential energy curves and the bond energy are quite similar with in ESP-PDFT and CAS-PDFT. However, CAS-PDFT involves 360 CSFs when we use the nom-CPO active space. In ESP-PDFT, ESP/nom-CPO only contains 178 CSFs (see Table I); therefore ESP decreases the number of configurations by a factor of 2.0. Table V compares the results of TiC calculations using ESP/nom-CPO-PDFT and CAS/nom-CPO-PDFT, and Fig. 3 compares the potential energy curves. (The ESP-PDFT potential curves with other on-top functionals are in the Supplementary Material.) The encouraging fact in Table V is that the ESP and CAS-PDDFT calculations with the same set of active orbitals agree within with 0.7 kcal/mol for all 8 on-top functionals.

For TiSi, we were able to use the SP approximation. Ti uses its doubly occupied 4s orbital to form a σ bond with the empty $3p_z$ orbital for Si and uses its empty $3d_{xz}$ and $3d_{yz}$ orbitals to form two π bonds with two singly occupied $3p_x$ and $3p_y$ orbitals for Si. There are no excitations from 4s orbital to 3d orbital and therefore the SP approximation can be applied to TiSi system. However, ESP approximation is same as SP approximation for this system. Therefore the ESP approximation also works. Table VI compares the results of ESP-PDFT and CAS-PDFT for the same set of active orbitals, and Figure 4 compares the potential energy curves. (The ESP-PDFT potential curves with other on-top functionals are in the Supplementary Material.) Table VI shows that ESP-PDFT can be as good as CAS-PDFT for the bond dissociation energy. However, Figure 4 shows that ESP-PDFT performs much better than CAS-PDFT for the potential energy curve. Furthermore, ESP-PDFT is much less expensive than CAS-PDFT. The CAS-PDFT calculation with the nom-CPO active space contains 594 CSFs, but the ESP calculation with the same active orbitals has only 112 CSFs (see Table I). Therefore, ESP-PDFT is a better choice than CAS-PDFT for this system.

We also applied the ESP methods to WCl and tried to apply the SP method. We tried to get the potential energy curve for the SP approximation using the three methods discussed for TiC. All the three methods failed at almost all the points. For W, the experimental ground state is 5d⁴6s², but without SOC the ground state is 5d⁵6s¹,

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and this is the relevant state for our spin-orbit-free calculation of the potential energy curve. In WCl, W uses its singly occupied $5d_{z2}$ orbital to form a σ bond with the singly occupied $3p_z$ orbital for Cl. The 6s orbital is singly occupied. Since the energy difference between $5d^46s^2$ and $5d^56s^1$ is small, the $5d^46s^2$ state contributes significantly when the distance between two atoms becomes longer. Therefore, it is not adequate to simply put the 6s orbital and its correlating orbital into a subspace with one electron, and we find that SP-PDFT does not converge in this system. However, the ESP approximation works well. When we compare the results of ESP-PDFT and CAS-PDFT, we find that ESP-PDFT gives smoother curves than CAS-PDFT does, and it give a very similar bond dissociation energy. Furthermore, the ESP approximation can also significantly decrease the number of CSFs in this system. The CAS-PDFT calculation with the nom-CPO active space includes 2652 CSFs, whereas ESP-PDFT calculation includes only 416 CSFs (see Table I). Thus in this larger system the reduction in the number of configurations is a factor of 6.4, whch is larger than the factor of 2.0 seen above for TiC. This result is very promising.

Table VII compares the results of ESP-PDFT and CAS-PDFT for WCl. Figure 5 compares the potential energy curves of ESP-ftrevPBE and CAS-ftrevPBE with the nom-CPO active space. The ESP-PDFT potential curves with other on-top functionals are s in the Supplementary Material.

The orbitals of the ESP subspaces are shown in Appendix B.

D. Comparison to KS-DFT

We also carried out KS-DFT calculations, and the results are shown in Table VIII. We find that the PBE, revPBE, and BLYP exchange-correlation functionals all perform poorly for TiC and TiSi; the corresponding MC-tPBE, MC-ftPBE, MC-ftrevPBE, MC-trevPBE, MC-ftBLYP and MC-tBLYP calculations are much better for these two systems. The MN15 and MN15-L functionals perform well for both TiC and TiSi, but these are meta functionals, and so far there are no meta functionals available for MC-PDFT.

Table VIII shows that KS-DFT performs better than MC-PDFT for WCl. Appendix A shows that WCl is a weakly correlated system, whereas TiC and TiSi are strongly correlated, and this distinction is consistent with the better performance of KS-DFT for WCl.

VI. CONCLUSIONS

We have four major conclusions from this project:

First, CAS-PDFT performs better than CASPT2 for TiC and TiSi. It performs more consistently when we use different active spaces and it can always give us better results than CASPT2. Therefore, the strategy of adding external correlation by using a translated on-top density functional rather than perturbation theory not only requires less computer time and memory, also it is more accurate.

Second, by testing several different systematic methods for complete active space selection, we show that our previously proposed method, nom-CPO, is particularly encouraging.

Third, we developed a new method, the ESP approximation, for choosing an incomplete active space in GASSCF calculations. In particular, the ESP approximation is more robust than the SP approximation since it is more physical and therefore overcomes the convergence problems of SP for two of the systems. The ESP approximation can significantly decrease the number of CSFs in a CASSCF calculation, it makes the potential energy curve smoother, and it is as accurate as CAS-PDFT. It will be interesting to test the ESP approximation more broadly.

Third, the dependence of both MC-PDFT and KS-DFT on the choice of density functional is significant, and work to develop broadly accurate on-top functionals would be useful.

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APPENDIX A. MULTIREFERENCE DIAGNOSTICS

Multireference diagnostics are helpful for putting the results in perspective. Here we apply three such diagnostics, the M diagnostic,³⁴ the T₁ diagnostic,⁷³ and the B₁ diagnostic⁷⁴. We used the jun-cc-pVTZ basis for TiC and TiSi; we used the ANO-RCC basis for WCl.

A large T_1 indicates a multireference system; the borderline between weak and strong correlation is often taken as 0.02 for closed-shell systems and 0.045 for open-shell systems; the molecules here are open-shell systems. For geometries near the equilibrium structure, we calculated T_1 values 0.05 for TiC, 0.07 for TiSi, and 0.02 for WCl. These three calculations were performed with *Molpro* (version 2015.1).

With the B₁ diagnostic, the nominal border between small and large multireference character is 10 kcal/mol. We calculated B₁ diagnostic values (in kcal/mol) of 23.6 for TiC, 13.2 for TiSi, and 1.6 for WCl. These calculations were performed in *Gaussian 16*.⁷⁵

The standard criteria for the M diagnostic are small multireference character for M in the range 0–0.05, modest multireference character in the range 0.05 – 0.10, and large multireference character when M is greater than 0.10. At the equilibrium geometries we find M values of 0.14, 0.30, and 0.04 for TiC, TiSi, and WCl, respectively. These calculations were performed using *OpenMolcas* v. 18.09.^{54,55}

The three diagnostics agree that at the equilibrium geometry, TiC and TiSi are multireference systems, and WCl is a single-reference system.

Figures 6 and 7 show the multireference diagnostic M for TiC and TiSi with various active spaces and various geometries: Figure 8 shows the multireference diagnostic M for WCl with the nom-CPO active space. These figures show that the multireference characters increase significantly as the bonds are stretched.

APPENDIX B. ESP ORBITALS

The orbitals of the ESP subspaces are shown in Figs. 9, 10, and 11.

NOTE

The authors declare no competing financial interest.

SUPPLEMENTARY MATERIAL

As described throughout the text, a number of files are provided as the supplementary material: (1) The absolute energies in hartrees and potential energy



This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0003048 curves of CASSCF, CASPT2, CAS-PDFT and ESP-PDFT calculations for TiC, TiSi and WCl; (2) energies (kcal/mol) of singlet and quintet with the triplet energy as the reference for TiC; (3) the weights of reference wave function in the CASPT2 calculations with various active spaces for TiC and TiSi.

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The authors are grateful to Jie Bao, Zoltan Varga, and Chen Zhou for helpful assistance and are grateful to Prachi Sharma for adding the tOreLYP and ftOreLYP functionals to *OpenMolcas*. This work was supported in part by the National Science Foundation under grant CHE– 1746186.

Active Space ^{<i>a</i>}	TiC	TiSi	WCl
	complete active spaces		
$(6, 7 \text{ or } 8)^a$	140	111	\mathbf{NU}^{b}
$(16, 12 \text{ or } 13)^a$	28,248	97,497	NU
nom-CPO	360	594	2,652
ext-CPO	5,154	12,888	NU
	generalized active spaces		
SP	100	112	256
ESP	178 ^c	112	416

TABLE I. Number of configuration state functions for various calculations

^a7 and 12 refer to TiC; 8 and 13 refer to TiSi. Note that there are two (2,2) spaces and two (1,2) spaces for TiC.

^bNU denotes not used.

^{*c*}The ESP approximation for TiC has two (2,2) spaces and one (2,4) space.

AB	D_0 (exp.)	ZPE (AB)	$SOC(A)^a$	SOC(B)	SOC(AB)
TiC	88.94	1.48	-0.64	-0.08	0.00
TiSi	50.76	0.54	-0.64	-0.43	-0.31
WCl	88.05	0.57	-8.44	-0.84	0.00

TABLE II. Experimental dissociation energies and data for eq 1 (all data in kcal/mol)

^{*a*}The spin-orbit energy of the species is defined as the energy of the ground state including spin-orbit coupling minus the energy of the of the spin-orbit-free ground state. This is straightforward except for W. For W the spin-orbit-inclusive ground state (i.e., the true ground state) is $5d^46s^2$ ⁵D, with energy 0 (by definition), the spin-orbit-free $5d^46s^2$ ⁵D configuration has energy 12.74 kcal/mol, and the spin-orbit free $5d^56s^1$ ⁷S configuration has energy 8.44 kcal/mol. Therefore SOC(W) is -8.44 kcal/mol. For the other cases the lowest-energy electron configuration is the same with and without spin-orbit coupling.

A ative Spaced	CARCE	CACDTO	CAS-PDFT									
Active Space	CASSCF	CASP12	ftrevPBE	trevPBE	ftBLYP	tBLYP	ftPBE	tPBE	ftOreLYP	tOreLYP		
Bond	lenergies											
CAS $(6, 7)^b$	63.81	95.08	96.69	97.91	91.54	89.90	102.73	102.93	95.98	96.82		
CAS $(16, 12)^c$	76.60	134.93	96.82	98.05	90.47	89.13	102.69	103.19	95.02	96.08		
nom-CPO (6, 8) ^d	65.29	95.38	95.58	96.69	91.01	88.96	101.69	101.70	95.41	96.20		
ext-CPO (8, 10) ^e	67.77	91.48	95.92	97.02	91.93	89.97	102.03	101.97	94.70	96.24		
Sign	ed errors											
CAS (6, 7)	-25.1	6.1	7.8	8.97	2.6	1.0	13.8	14.0	7.0	7.9		
CAS (16, 12)	-12.3	46.0	7.9	9.1	1.5	0.2	13.8	14.2	6.1	7.1		
nom-CPO (6, 8)	-23.6	6.4	6.6	7.75	2.1	0.0	12.8	12.8	6.5	7.3		
ext-CPO (8, 10)	-21.2	2.5	7.0	8.08	3.0	1.0	13.1	13.0	5.8	7.3		

TABLE III. Bond dissociation energies and signed errors (kcal/mol) of TiC calculated with various methods and active spaces.

^{*a*}An active space consisting of *n* electrons in *m* orbitals is denoted as (n, m).

^bIncluding the bonding orbitals, antibonding orbitals and singly occupied nonbonding orbitals.

^cIncluding the bonding orbitals, antibonding orbitals, singly occupied nonbonding orbitals, p-subshell orbitals for Ti and s-subshell orbitals for Ti and C.

^{*d*}nom-CPO (6, 8); (σ , σ *), 2(π , π *), (4s_{Ti}, 4s_{Ti}')

^{*e*}ext-CPO (8, 10); (σ , σ ^{*}), 2(π , π ^{*}), (4s_{Ti}, 4s_{Ti}), (2s_C, 2s_C)

A sting Sugard	CARCE	CACDTO				CAS-P	DFT			CAS-PDFT									
Active Space ^a	CASSCF	CASP12	ftrevPBE	trevPBE	ftBLYP	tBLYP	ftPBE	tPBE	ftOreLYP	tOreLYP									
Bond	energies																		
CAS $(6, 8)^b$	19.08	44.10	44.25	44.93	39.77	40.47	48.32	48.59	43.33	45.20									
CAS $(16, 13)^c$	25.41	78.49	46.09	46.65	38.97	40.72	49.71	50.40	40.87	42.61									
nom-CPO $(6, 10)^d$	21.96	48.27	49.33	50.11	44.65	45.52	53.01	53.49	47.74	49.56									
ext-CPO (8, 12) ^e	29.66	40.35	35.01	35.66	29.11	29.98	38.48	38.79	29.98	32.47									
Signe	ed errors																		
CAS (6, 8)	-30.4	-6.7	-6.5	-5.8	-11.0	-10.3	-2.4	-2.2	-7.4	-5.6									
CAS (16, 13)	-24.0	27.7	-4.7	-4.1	-11.8	-10.0	-1.0	-0.34	-9.9	-8.1									
nom-CPO (6, 10)	-27.5	-2.5	-1.4	-0.6	-6.1	-5.2	2.2	2.7	-3.0	-1.2									
ext-CPO (8, 12)	-19.8	-10.4	-15.8	-15.1	-21.6	-20.8	-12.3	-12.0	-20.8	-18.3									

TABLE IV. Bond dissociation energies and signed errors (kcal/mol) of TiSi calculated with various methods and active spaces.

^{*a*}An active space consisting of *n* electrons in *m* orbitals is denoted as (n, m).

^bIncluding the bonding orbitals, antibonding orbitals and singly occupied nonbonding orbitals.

^cIncluding the bonding orbitals, antibonding orbitals, singly occupied nonbonding orbitals, p-subshell orbitals for Ti and s-subshell orbitals for Ti and Si.

^{*d*}nom-CPO (6, 10); (σ , σ *), 2(π , π *), 2(3d, 3d')

^eext-CPO (8, 12); (σ , σ ^{*}), 2(π , π ^{*}), 2(3d, 3d'), (3s_{Si}, 3s_{Si}')

Methods	ftrevPBE	trevPBE	ftBLYP	tBLYP	ftPBE	tPBE	ftOreLYP	tOreLYP
Bo	ond energies							
ESP-PDFT	95.07	96.05	90.59	88.32	101.19	101.05	94.91	95.54
CAS-PDFT	95.58	96.69	91.01	88.96	101.69	101.70	95.41	96.20
Si	gned errors							
ESP-PDFT	6.1	7.1	1.6	-0.6	12.2	12.1	6.0	6.6
CAS-PDFT	6.6	7.8	2.1	0.0	12.8	12.8	6.5	7.3

TABLE V. Bond dissociation energies and signed errors (kcal/mol) of TiC calculated with nom-CPO active space, which is (6,8)

TABLE VI. Bond dissociation energies and signed errors (kcal/mol) of TiSi calculated with nom-CPO, which is (6,10)

		-	-					
Methods	ftrevPBE	trevPBE	ftBLYP	tBLYP	ftPBE	tPBE	ftOreLYP	tOreLYP
Bo	ond energies							
ESP-PDFT	50.45	51.94	43.31	46.32	54.03	55.77	44.84	47.83
CAS-PDFT	49.33	50.11	44.65	45.52	53.01	53.49	47.74	49.56
S	igned errors							
ESP-PDFT	-0.3	1.2	-7.4	-4.4	3.3	5.0	-5.9	-2.9
CAS-PDFT	-1.4	-0.6	-6.1	-5.2	2.2	2.7	-3.0	-1.2

Methods	ftrevPBE	trevPBE	ftBLYP	tBLYP	ftPBE	tPBE	ftOreLYP	tOreLYP
Bo	nd energies							
ESP-PDFT	79.54	78.31	81.06	74.76	83.64	81.03	82.69	79.79
CAS-PDFT	79.76	78.61	81.22	75.05	83.86	81.33	82.91	80.14
Si	gned errors							
ESP-PDFT	-8.5	-9.7	-7.0	-13.3	-4.4	-7.0	-5.4	-8.3
CAS-PDFT	-8.3	-9.4	-6.8	-13.0	-4.2	-6.7	-5.1	-7.9

TABLE VII. Bond dissociation energies and signed errors (kcal/mol) of WCl calculated by using nom-CPO, which is (7,12)

TABLE VIII. Bond dissociation energies and signed errors(kcal/mol) of TiC, TiSi and WCl calculated by using KS-DFT with various functionals and their experimental values.

Molecules	BLYP	OreLYP	M06-L	M06	MN15-L	MN15	PBE	revM06-L	revM06	revPBE	Exp.
Bo	ond energie	es									
TiC	103.83	101.91	104.21	91.23	88.29	86.25	117.49	90.82	77.63	110.61	88.94
TiSi	61.70	62.44	68.24	55.38	55.50	48.04	72.72	65.76	50.34	68.89	50.76
WCl	85.21	85.30	90.45	87.21	87.45	90.32	86.30	92.70	88.58	81.59	88.05
Si	gned error	`S									
TiC	14.9	13.0	15.3	2.3	-0.6	-2.7	28.6	1.9	-11.3	21.7	0.0
TiSi	10.9	11.7	17.5	4.6	4.7	-2.7	22.0	15.0	-0.4	18.1	0.0
WCl	-2.8	-2.8	2.4	-0.8	-0.6	2.3	-1.8	4.6	0.5	-6.5	0.0

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22

FIG. 1. Potential energy curves of TiC calculated by using various methods and various active spaces. These calculations do not include spin-orbit coupling.

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FIG. 2. Potential energy curves of TiSi calculated by using various methods and various active spaces. These calculations do not include spin-orbit coupling.



FIG. 3. Potential energy curves of TiC calculated by using ESP-ftrevPBE and CAS-ftrevPBE methods with nom-CPO active space. These calculations do not include spin-orbit coupling.

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FIG. 4. Potential energy curves of TiSi calculated by using ESP-ftrevPBE and CAS-ftrevPBE methods with nom-CPO active space. These calculations do not include spin-orbit coupling.



FIG. 5. Potential energy curves of WCl calculated by using ESP-ftrevPBE and CAS-ftrevPBE methods with nom-CPO active space. These calculations do not include spin-orbit coupling.



FIG. 6. Multireference diagnostics M for TiC in its ground electronic state with various active spaces. The equilibrium value of the bond distance is 1.695 Å.



FIG. 7. Multireference diagnostics M for TiSi in its ground electronic state with various active spaces. The equilibrium value of the bond distance is 2.475 Å.

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FIG. 8. Multireference diagnostics M for WCl in its ground electronic state with nom-CPO active spaces. The equilibrium value of the bond distance is 2.360 Å.

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FIG. 9. The active orbitals and natural orbital occupation numbers of each subspace used in the ESP-PDFT calculations for TiC. The ESP approximation for TiC has two (2,2) spaces and one (2,4) space.



FIG. 10. The active orbitals and natural orbital occupation numbers of each subspace used in the ESP-PDFT calculations for TiSi.



FIG. 11. The active orbitals and the natural orbital occupation numbers of each subspaces used in the ESP-PDFT calculations for WCl.

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