

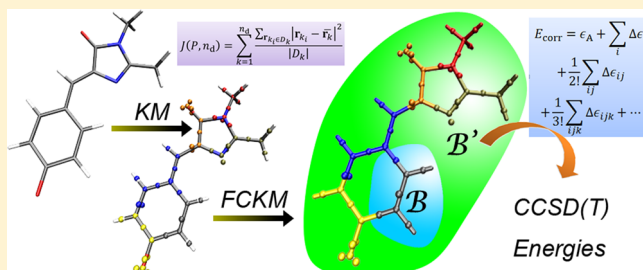
Third-Order Incremental Dual-Basis Set Zero-Buffer Approach for Large High-Spin Open-Shell Systems

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S Supporting Information

ABSTRACT: The third-order incremental dual-basis set zero-buffer approach (inc3-db-B0) is an efficient, accurate, and black-box quantum chemical method for obtaining correlation energies of large systems, and it has been successfully applied to many real chemical problems. In this work, we extend this approach to high-spin open-shell systems. In the open-shell approach, we will first decompose the occupied orbitals of a system into several domains by a K-means clustering algorithm. The essential part is that we preserve the active (singly occupied) orbitals in all the calculations of the domain correlation energies. The duplicated contributions of the active orbitals to the correlation energy are subtracted from the incremental expansion. All techniques of truncating the virtual space such as the B0 approximation can be applied. This open-shell inc3-db-B0 approach is combined with the CCSD and CCSD(T) methods and applied to the computations of a singlet–triplet gap and an electron detachment process. Our approach exhibits an accuracy better than 0.6 kcal/mol or 0.3 eV compared with the standard implementation, while it saves a large amount of the computational time and can be efficiently parallelized.



1. INTRODUCTION

Molecules with unpaired electrons, or “open-shell” electronic structures, are of fundamental importance in chemistry. The ground states of most free atoms as well as of many *d*- and *f*-transition metal complexes are open-shell; the heterolytic cleavage of a covalent bond produces two radicals; radicals and polyradicals often function as reactants or intermediates in organic reactions;^{1–3} the energy conversion processes such as singlet fission⁴ occurring in organic materials also involve open-shell states; for some complex systems, including solvated electrons⁵ or some biological systems,⁶ the open-shell structure is critical for understanding their physical nature.

From a theoretical point of view, when only “vertical” processes (i.e., processes without geometrical change) such as vertical excitation or attachment are considered, one can apply methods related to response theory such as propagator approaches,⁷ time-dependent density functional theory (TDDFT),⁸ or equation-of-motion coupled-cluster (EOM-CC),⁹ avoiding explicitly constructing open-shell wave functions. This is, of course, not always possible in practice. For the explicit computation of open-shell states, DFT and ab initio methods are both available. However, the methods developed for open-shell systems are much less advanced than the corresponding ones for closed-shell systems. DFT is an acceptable choice for large open-shell systems, but besides the problem of unpredictable accuracy of functionals prior to benchmarks, the Kohn–Sham form of DFT has inherent deficiencies in the treatment of open-shell states^{10,11} due to its single determinant nature. Some authors even argued that spin is not a well-defined concept within the framework of DFT.¹²

For polyradicals (which contain many near-degenerate singly occupied orbitals), special techniques such as broken-symmetry calculations^{13,14} have to be used. Ab initio methods are theoretically more rigorous and can treat closed- and open-shell states of different symmetries in a balanced way. The most general multireference (MR) approaches, for example, complete active space self-consistent field (CASSCF),¹⁵ MR configuration interaction (MRCI),¹⁶ or second-order CAS perturbation theory (CASPT2),¹⁷ can treat static and partly also dynamic correlation well. However, these approaches are very complex, partly suffering from intruder states or difficulties in convergence; moreover, they are often time-consuming and thus cannot be applied to very large systems. Coupled-cluster (CC) theory can treat dynamic correlation efficiently, but a widely accepted MR generalization is still not established, although promising developments have appeared.^{18–20}

Fortunately, for a class of *high-spin* systems, in which the *n* unpaired electrons occupy *n* energetically well-separated orbitals and couple ferromagnetically to the highest possible spin *S* = *n*/2, the static correlation is often not significant. Thus, these systems can be treated well in the single-reference (SR) framework. Common CC and its explicit correlation (F12) generalization formulas can be modified to treat high-spin open shell systems.^{21,22} As for closed-shell cases, their application to large systems is hindered by the high scaling of the computational cost. In fact, the problem is more serious, since some tricks used to simplify the computation procedure

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of closed-shell systems, such as additional symmetry due to zero spin projection, cannot be applied. Therefore, it is important to develop fast local correlation methods for open-shell as well as for closed-shell systems. In the last three decades, much effort has been invested to develop local correlation methods. In general, there are two classes. One is to reconstruct the occupied and virtual space by exploiting the locality of electron correlation.^{23–40} Another one is to decompose the system into several fragments and obtain the properties of the entire system from those of the fragments.^{41–60} Some of these methods can be applied to both closed- and open-shell systems, but some cannot.

The incremental scheme has features of both classes. This method, which can be dated back to Nesbet,⁶¹ was first proposed by Stoll^{62,63} and successfully applied to periodic systems^{64–66} as well as to the adsorption of atoms and small molecules on solid surfaces.⁶⁷ We have been developing the incremental scheme for molecules since 2007.^{68–76} By now, this approach can work quite well with CCSD, CCSD(T), and their F12 versions. Unlike most local correlation methods, we do not pursue “awfully large” systems, since, in this case, all local correlation methods including ours have to discard a lot of integrals or other physical quantities to reduce the computational cost, possibly leading to unavoidable large errors. Instead, the incremental scheme aims at treating systems beyond the ability of standard correlation methods *accurately* in an efficient way. Thus, the incremental scheme can provide the most accurate correlation energies for large systems, which is confirmed by extensive calibrations.^{75–79} An example is that for two isomers of a large organic molecule, the incremental scheme gave the correct stability order but another linear-scaling correlation method failed;⁸⁰ using the incremental scheme, we can obtain the most accurate first-principle hydration energies for lanthanoid(III)⁸¹ and actinoid(III)⁸² ions. In fact, the results from the incremental scheme are often used as a benchmark reference.^{81,83}

The latest implementation of incremental scheme is the third-order dual-basis set zero buffer approach (inc3-db-B0).^{75,76} This is an accurate, efficient, parallel, and black-box approach. In this work, we will extend the inc3-db-B0 approach to high-spin open-shell systems. We first describe the theory, then apply it to several different systems that interest chemists, and demonstrate the power of our approach.

2. THEORY

2.1. Incremental Expansion with Active Orbitals. The principle of the inc3-db-B0 approach for closed-shell systems was described in detail in our previous works.^{75,76} The basic idea is that for a system the occupied canonical molecular orbitals (CMOs) to be correlated are localized according to the Boys criterion,⁸⁴ yielding a set of localized MOs (LMOs). This set is decomposed into several nonintersecting subsets called one-site domains, denoted by i, j , etc. The union of n one-site domains i, j, \dots, k is called a n -site domain $X = i \cdots j \cdots k$. For an n -site domain X , define ϵ_X as the correlation energy computed by correlating *only* the orbitals in X . Then, the total correlation energy of the entire system can be expressed as

$$E_{\text{corr}} = \sum_i \Delta\epsilon_i + \frac{1}{2!} \sum_{ij} \Delta\epsilon_{ij} + \frac{1}{3!} \sum_{ijk} \Delta\epsilon_{ijk} + \dots \quad (1)$$

where the n th-order increment $\Delta\epsilon_X$ is defined as

$$\Delta\epsilon_i = \epsilon_i(\mathcal{B}_i) \quad (2)$$

$$\Delta\epsilon_{ij} = \epsilon_{ij}(\mathcal{B}_{ij}) - \Delta\epsilon_i - \Delta\epsilon_j \quad (3)$$

$$\Delta\epsilon_{ijk} = \epsilon_{ijk}(\mathcal{B}_{ijk}) - \Delta\epsilon_{ij} - \Delta\epsilon_{ik} - \Delta\epsilon_{jk} - \Delta\epsilon_i - \Delta\epsilon_j - \Delta\epsilon_k \quad (4)$$

Here, \mathcal{B} denotes the basis set used for the calculation, \mathcal{B}_X is an X -specific basis set, and $\epsilon_X(\mathcal{B}_X)$ means that ϵ_X is computed with basis set \mathcal{B}_X , as will be described below. Previous works^{75,76} show that eq 1 can be truncated at the third-order with little loss of accuracy. The high accuracy of the incremental scheme is due to the locality of electronic correlation, since for molecules with large HOMO–LUMO gap, the CMOs can be well localized.

For open-shell systems, the above principle should also be applicable. However, in some systems, the singly occupied molecular orbitals, or active orbitals (AMOs), tend to be much more delocalized than the localized doubly occupied ones. This means that AMOs may couple with all the other occupied MOs to a considerable extent. In addition, due to technical reasons, it is not possible for most quantum chemistry codes to freeze open shells when correlating closed ones. Thus, for the incremental expansion of high-spin open-shell systems, active orbitals will be correlated in the calculation of each ϵ_X .⁸⁵ An additional advantage is that preserving AMOs in each domain X can keep its spin state identical to that of the entire system. In this way, eq 1 will repeatedly take the correlation of the AMOs into account; therefore, eqs 1–4 can be modified as

$$E_{\text{corr}} = \epsilon^A(\mathcal{B}) + \sum_i \Delta\epsilon_i + \frac{1}{2!} \sum_{ij} \Delta\epsilon_{ij} + \frac{1}{3!} \sum_{ijk} \Delta\epsilon_{ijk} + \dots \quad (5)$$

$$\Delta\epsilon_i = \epsilon_i^A(\mathcal{B}_i) - \epsilon^A(\mathcal{B}_i) \quad (6)$$

$$\Delta\epsilon_{ij} = \epsilon_{ij}^A(\mathcal{B}_{ij}) - \epsilon^A(\mathcal{B}_{ij}) - \Delta\epsilon_i - \Delta\epsilon_j \quad (7)$$

$$\Delta\epsilon_{ijk} = \epsilon_{ijk}^A(\mathcal{B}_{ijk}) - \epsilon^A(\mathcal{B}_{ijk}) - \Delta\epsilon_{ij} - \Delta\epsilon_{ik} - \Delta\epsilon_{jk} - \Delta\epsilon_i - \Delta\epsilon_j - \Delta\epsilon_k \quad (8)$$

where “A” stands for AMO and ϵ^A is the correlation energy of the AMOs. Note that there is no “A” superscript for $\Delta\epsilon_X$ because the contribution from the AMOs has always been deducted. For the singlet (closed-shell) states, $\epsilon^A = 0$. The idea of eliminating duplicated correlation energies of AMOs is critical in the development of MR correlation methods for large systems.^{67,85,86} In this way, the inc3-db-B0 approach can be generalized to high-spin open-shell systems. We will see in the following sections that the incremental scheme shows excellent performance for high-spin open-shell as well as closed-shell systems.

2.2. Domain Decomposition and Virtual Space Truncation. To implement eq 5, we need a way to decompose the orbitals into domains. The K-means clustering algorithm (KM),^{87,88} which is a useful tool in statistics and chemoinformatics,⁸⁹ is used for this purpose. In brief, after obtaining the LMOs for doubly occupied orbitals of a molecule, we compute their centers of charge, which form a set of points \mathcal{P} . The KM algorithm is then applied for \mathcal{P} to decompose it into n_d domains in a way that the distances between the points within a domain are minimized, the essential point of which being minimization of $J(\mathcal{P}, n_d)$ in eq 9. For details, please refer

to our previous works.^{75,76} Note that AMOs are not involved in the decomposition because they will be preserved in all domains.

$$J(\mathcal{P}, n_d) = \sum_{k=1}^{n_d} \frac{\sum_{\mathbf{r}_{k_i} \in D_k} |\mathbf{r}_{k_i} - \bar{\mathbf{r}}_k|^2}{|D_k|} \quad (9)$$

After domain decomposition, we can begin to compute all the ϵ_X values and $\Delta\epsilon_X$ values. Because in each domain X the LMOs are distributed spatially compact, the virtual space can be truncated specifically for X . The scheme we use is the so-called dual-basis set zero-buffer (db-B0) approximation.⁷⁵ Assume that a basis set \mathcal{B} is used in a calculation. At the Hartree–Fock (HF) stage, a truncated basis set \mathcal{B}' , where, for example, for main group elements of the first and second period basis functions of angular momentum higher than p have been removed, is used; then, at the correlation energy computation stage of a domain X , a X -specific basis set \mathcal{B}_X is constructed to obtain the correlation energy as accurately as possible. It was demonstrated that the most compact \mathcal{B}_X can be built in the following way: The fixed-center KM algorithm (FCKM)⁷⁵ is used to find the atoms that contribute most to the correlation energy of domain X . Then, in the correlation calculation stage, only for those atoms we use the original basis set \mathcal{B} , whereas for the rest of the atoms we still use the truncated one, that is, \mathcal{B}' . To use the FCKM algorithm, one can use the geometrical center $\bar{\mathbf{r}}_k$ of the 1-site domains as fixed centers and decompose the set of atomic coordinates \mathcal{A} into n_d subsets M_k (by minimization of $J(\mathcal{A}, n_d)$ in eq 10). The atoms in M_k are those ones that contribute most to the correlation energy of domain D_k .

$$J(\mathcal{A}, n_d) = \sum_{k=1}^{n_d} \frac{\sum_{\mathbf{x}_{k_i} \in M_k} |\mathbf{x}_{k_i} - \bar{\mathbf{r}}_k|^2}{|M_k|} \quad (10)$$

For details of the db-B0 approximation, see refs 75 and 76. With the incremental expansion eq 5 and the db-B0 approximation, one can apply the inc3-db-B0 approach for high-spin open-shell systems. The entire procedure is illustrated Figure 1.

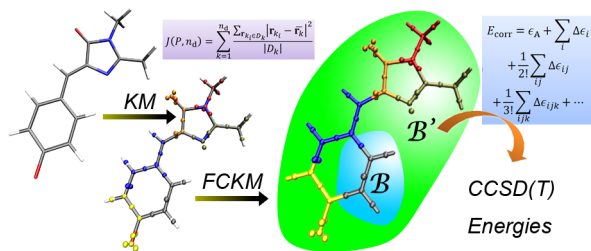


Figure 1. Illustration of the inc3-db-B0 approach.

3. APPLICATIONS

In this section, we show the performance of our inc3-db-B0 approach for some real chemical systems involving high-spin open-shell species. The calculations were performed with in-house developed C++ codes and Molpro 2012.1.⁹⁰

3.1. Singlet–Triplet Gap of Diphenylcarbene. Carbene is a well-known star in organic chemistry. Its singlet and triplet states can lead to different reactivity.⁹¹ A recent work by Costa and Sander argues that the stability of the spin states of

diphenylcarbene can be controlled by the methanol solvent.⁹² In this work, the author⁹² applied dispersion interaction corrected hybrid DFT B3LYP-D3 to compute the energies of singlet and triplet states of diphenylcarbene and diphenylcarbene–methanol complex. We will use the more exact CCSD(T) method to examine these energies.

The results are listed in Table 1. The singlet–triplet gaps (STG) obtained by the inc3-db-B0 approach agree well with

Table 1. Singlet–Triplet Gap (Unit: kcal/mol) of Diphenylcarbene and Its Methanol Complex

method	diphenylcarbene ^a	diphenylcarbene–methanol ^a
	$E(S-T)^b$	$E(S-T)^b$
standard CCSD/VDZ	5.11	−0.41
inc3-db-B0-CCSD/VDZ	4.63 (−0.48)	−0.09 (0.32)
standard CCSD/VTZ	3.78	^c
inc3-db-B0-CCSD/VTZ	3.65 (−0.13)	−2.56 (−)
inc3-db-B0-CCSD, extrapolation ^e	3.50	−3.30
standard CCSD(T)/VDZ	3.25	−2.20
inc3-db-B0-CCSD(T)/VDZ	2.84 (−0.41)	−1.58 (0.62)
standard CCSD(T)/VTZ	^c	^c
inc3-db-B0-CCSD(T)/VTZ	1.57 (−)	−4.75 (−)
inc3-db-B0-CCSD(T), extrapolation ^e	1.31	−5.78
B3LYP-D3/6-311++G(d,p) ^a	5.06	−0.44
CPU time ^d		diphenylcarbene–methanol
standard CCSD(T)/VDZ	1.7 days	14.0 days
inc3-db-B0-CCSD(T)/VDZ	2.3 days	8.8 days
standard CCSD/VTZ	51.0 days	
inc3-db-B0-CCSD(T)/VTZ	42.7 days (1.6 days/30)	187.8 days (6.8 days/30)

^aThe geometries and energies are taken from ref 92. Also see Figure 2.

^bThe number in parentheses is the error of the inc3-db-B0 approach relative to the standard implementation. ^cBeyond our computational ability. ^dThe listed CPU times are for the triplet molecules. Some calculations were parallelized. The wall times and the number of CPU cores for parallelization are given in the parentheses. These calculations were performed with Intel Xeon CPU E5-46200 @2.20 GHz on our cluster. ^eThe extrapolation is performed by $E_{XY} = E_{HF,Y} + ((X^3 E_{corr,X} - Y^3 E_{corr,Y}) / (X^3 - Y^3))$, with $X = 2$ and $Y = 3$ for VDZ and VTZ, respectively.

those of the standard implementations, the largest error being 0.62 kcal/mol. The efficiency is also very good: at the VDZ level one can save about 30% computational cost for the diphenylcarbene–methanol complex, and at the VTZ level, the inc3-db-B0-CCSD(T) calculation is even faster than a standard CCSD one. Thus, the incremental scheme shows excellent accuracy and efficiency for these high-spin open-shell molecules.

In this as well as in the following example, the VTZ calculations were much more expensive than the VDZ ones. One reason is the poor convergence of the open-shell CC calculations, especially for larger basis sets such as VTZ. A shift factor is needed to force convergence, which increases the number of CC iterations and thus made the calculations expensive. Moreover, it was observed (also in previous works^{75,76}) that for some systems the inc3-db-B0 calculation may take a little longer than the standard one when a small basis set such as VDZ is used. The VDZ basis set is already so small that the reduction of the virtual space by the db-B0

approximation is not sufficient to compensate for the overhead introduced by the incremental scheme. For VTZ and larger basis sets inc3-db-B0 is always more efficient than the standard approach.

Based on the reliability of our approach, we can calibrate Costa and Sander's calculations.⁹² CCSD(T) and B3LYP-D3 agree that the ground state of diphenylcarbene changes from a triplet to a singlet state when it complexes with a methanol molecule. The standard CCSD and incremental CCSD results in the VDZ basis agree well with the DFT data. However, both enlarging the basis set and including perturbative triples change the results significantly. Taking inc3-db-B0-CCSD(T)/VTZ as a reference, the STG of diphenylcarbene and diphenylcarbene–methanol complex at B3LYP-D3 level is over- and underestimated by about 3.5 and 4.3 kcal/mol, respectively. The basis set extrapolated results indicate that an improvement of the basis sets would even lead to larger discrepancies. The tendency of DFT exhibiting a large error for the STG can also be found for some didehydroazines,⁹³ where B3LYP/VTZ deviates from CCSD(T)/VTZ by 5–15 kcal/mol. Thus, the STG obtained by DFT should be interpreted with caution. The accurate inc3-db-B0-CCSD(T) results reveal that the methanol molecule can reverse and *enlarge* the STG of diphenylcarbene, rather than reverse and *reduce* the STG as expected by DFT (see Figure 2). This offers a new guide for rational design of organic reactions involving diphenylcarbene and possibly other carbenes.

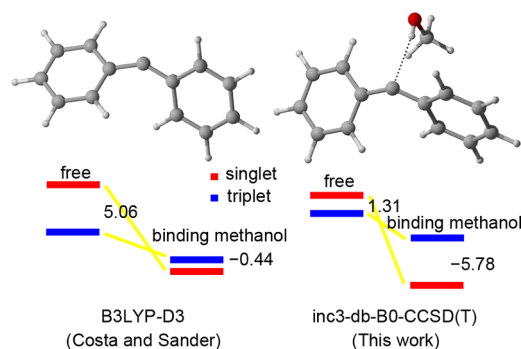


Figure 2. Left top: Diphenylcarbene. Right top: Diphenylcarbene–methanol complex. Bottom: The effect of the methanol molecule suggested by B3LYP-D3⁹² and inc3-db-B0-CCSD(T). The geometries of diphenylcarbene and the diphenylcarbene–methanol complex can be found in the Supporting Information.

3.2. Vertical Detachment Energy of the GFP Chromophore. Green fluorescent protein (GFP)⁶ is an important tool for biological in vivo studies. The impact of the GFP on its chromophore, that is, deprotonated 4-hydroxybenzylidene-2,3-dimethylimidazolinone anion (dHBDI[−]), has been discussed theoretically by several authors.^{94–96} It was argued that the protein can increase the vertical detachment energy (VDE) of the dHBDI[−] by more than 2 eV.⁹⁵ A possible reason is that the positively charged Arg96 residue of the GFP (PDB ID: 1EMA⁹⁷) stabilizes the anionic form of dHBDI. To examine the effect of this arginine we built a model: the complex of dHBDI and a guanidinium cation (Gmd⁺) (see Figure 3). The VDEs we try to compute are defined as

$$\text{VDE}(\text{gas}) = E[\text{dHBDI}] - E[\text{dHBDI}^-] \quad (11)$$

$$\text{VDE}(\text{protein}) = E[\text{dHBDI} \cdot \text{Gmd}^+] - E[\text{dHBDI}^- \cdot \text{Gmd}^+] \quad (12)$$

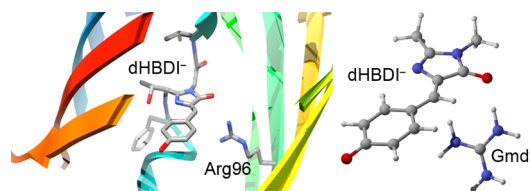


Figure 3. Left: Chromophore part of the GFP. Right: dHBDI[−]·Gmd⁺ model complex. The geometries of the model complexes can be found in the Supporting Information.

The geometries of dHBDI[−] and dHBDI[−]·Gmd⁺ were optimized at the B3LYP/6-311++G(d) with Gaussian03.⁹⁸ The VDEs calculated by the inc3-db-B0 approach in comparison to standard CCSD and CCSD(T) results and DFT data are given in Table 2.

Table 2. VDEs (Unit: eV) of dHBDI in Gas Phase and Protein Environment

method	VDE(gas) ^a	VDE(protein) ^a
standard CCSD/VDZ	2.22	5.53
inc3-db-B0-CCSD/VDZ	2.22 (0.00)	5.52 (−0.01)
standard CCSD/VTZ	^b	^b
inc3-db-B0-CCSD/VTZ	2.67 (−)	5.87 (−)
inc3-db-B0-CCSD, extrapolation ^d	2.84	6.12
standard CCSD(T)/VDZ	2.20	5.51
inc3-db-B0-CCSD(T)/VDZ	2.18 (−0.02)	5.48 (−0.03)
standard CCSD(T)/VTZ	^b	^b
inc3-db-B0-CCSD(T)/VTZ	2.68 (−)	5.81 (−)
inc3-db-B0-CCSD(T), extrapolation ^d	2.88	6.07
B3LYP/6-311++G(d)	2.88	6.05
CPU time ^c	VDE(gas)	VDE(protein)
standard CCSD(T)/VDZ	14.3 days	53.5 days
inc3-db-B0-CCSD(T)/VDZ	9.4 days	55.9 days (5.8 days/10)
standard CCSD(T)/VTZ		
inc3-db-B0-CCSD(T)/VTZ	22.6 days (2.7 days/10)	209.4 days (7.4 days/30)

^aThe number in parentheses is the error of inc3-db-B0 approach relative to the standard implementation. ^bBeyond our computational ability. ^cThe listed CPU times are for the doublet molecules. Some calculations were parallelized. The wall times and the number of CPU cores for parallelization are given in the parentheses. These calculations were performed with Intel Xeon CPU E5-46200 @2.20 GHz on our cluster. ^dThe extrapolation is performed by $E_{XY} = E_{\text{HF},Y} + ((X^3 E_{\text{corr},X} - Y^3 E_{\text{corr},Y}) / (X^3 - Y^3))$, with $X = 2$ and $Y = 3$ for VDZ and VTZ, respectively.

Obviously, for large basis sets such as VTZ, the inc3-db-B0 approach saved considerable computational cost with little loss of accuracy. Using inc3-db-B0-CCSD(T)/VTZ as reference, DFT is observed to overestimate the VDE by about 0.2 eV, whereas here the agreement with basis set extrapolated values is even within 0.02 eV. Indeed, the existence of Gmd⁺ stabilizes the dHBDI[−], yielding the VDE about 3.2 eV larger than that of dHBDI[−] in gas phase, which is very similar to that of dHBDI[−] in GFP. Thus, the positively charged Arg96 residue of GFP could be important in controlling the excitation properties of its chromophore.

4. CONCLUSION

In this work, we have successfully generalized the inc3-db-B0 approach from closed-shell to high-spin open-shell systems. This is important because one can treat both kinds of molecules in a balanced way, extending the application of our method to a larger variety of chemical problems. It is not only proved as accurate as for the closed-shell case but often also exhibits an even higher efficiency for the open-shell case. We have seen that the faster DFT and the more accurate CCSD(T) approach give qualitatively consistent but occasionally quantitatively quite different pictures for some chemical problems, suggesting that one should use and interpret the DFT results carefully. We are also looking for the possibilities of combining our approach with more advanced MR methods or EOM-CC, in order to be able to treat general excitation states.

■ ASSOCIATED CONTENT

● Supporting Information

The geometries of the molecules considered in this work. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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