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A density functional study of the simplest hydrogen abstraction reaction. Effect of self-interaction correction

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Abstract

Twenty-four different local and gradient-corrected density functional methods were used in a study of the reaction $H+H_2 \rightarrow H_2+H$. Barrier heights were calculated with a large basis set. The results were compared to those obtained by ab initio methods and experiment. It was found that conventional Kohn–Sham methods consistently and significantly underestimate the reaction barrier. In particular, the local spin-density approximation (LSDA) in unmodified form completely fails, predicting H_3 to be a stable species. However, the inclusion of a self-interaction correction restores the correct qualitative features of the potential surface, and generally leads to reasonable results when pairing a gradient-corrected exchange functional with a correlation functional.

1. Introduction

One of the most important objectives in combustion chemistry is the characterization of the single steps involved in the complicated chemical reactions occurring in flames. The increased demand for energy and its efficient utilization, combined with the recent public awareness of the negative environmental impact of some of the existing energy alternatives, have led scientists to study the intricacies of combustion in order to provide a more detailed picture of the basic mechanisms governing these processes.

Among the many types of reactions taking place in combustion chemistry, hydrogen abstractions by radical species constitute one of the most important classes. In particular, the abstraction of a hydrogen atom from saturated hydrocarbons has been shown to be the rate-limiting step in some combustion reactions [1,2]. In the past few years, ab initio molecular orbital calculations have been used with reasonable success in the mapping of potential energy surfaces of some of the critical steps in hydrogen abstractions [3–5]. Furthermore, this information has been used, in conjunction with models such as the transition state theory (TST), to describe the kinetics governing such reactions [6–8]. This combination has provided a valuable source of information leading to the accurate description of the mechanisms involved in some hydrogen abstraction reactions.

One of the critical aspects that the computational chemist must consider when using ab initio molecu-

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lar orbital calculations is their inherent computational cost. The simplest ab initio method, Hartree–Fock (HF), is applicable to fairly large chemical systems, as the rate-limiting step in large calculations scales essentially as $\mathcal{O}(N^2)$, where N is the number of basis functions. However, it is well known that HF does not perform well in predicting reaction barriers. For the more sophisticated correlated methods which are required to obtain good results, such as perturbation theory, configuration interaction and coupled-cluster treatments, the scaling of the cost increases substantially ($\mathcal{O}(N^5)$ or greater), and hence the scope of these methods is limited. Thus, it would be highly desirable to find an ab initio method that is both sufficiently accurate and of reasonable computational cost.

A number of recent reviews [9–11] and studies [12–20] have shown that density functional theory (DFT) shows much promise in prediction of various molecular properties such as equilibrium geometries, vibrational frequencies and atomization energies, often attaining accuracy comparable to or even better than conventional correlated ab initio methods. Moreover, DFT methods are more attractive from a computational standpoint, as a description of electron correlation is included at the self-consistent field level; thus, the computational cost is on the order of that of HF, making DFT methods applicable to large systems.

These encouraging results make the prospect of applying DFT to the study of reaction barriers attractive. Even though for the past few years a reasonable amount of work has been devoted to DFT studies of the energetics of a variety of chemical reactions [11,12,21–25], relatively little has been done in the case of reaction barriers where radical species are involved [26–28]. It is therefore desirable to conduct a systematic study of the performance of DFT in the determination of barrier heights of hydrogen abstraction reactions.

The logical first step in a systematic study of hydrogen abstractions is the simplest such reaction, $H+H_2 \rightarrow H_2+H$. A number of groups [29–32] have studied the potential energy surface of this reaction in detail by high-level quantum-mechanical methods. In the present work, a family of DFT methods (involving local and gradient-corrected functionals) are used. Fully optimized geometries and vibrational adiabatic reaction barriers were computed for each of 24 different DFT methods, including an investigation of the performance of a version of self-interaction-corrected DFT. The results were compared to experiment and theoretical values obtained by conventional ab initio methods.

2. Method

In the Kohn–Sham (KS) formulation [33] of DFT, the total electronic energy is given by

$$E_{KS} = E_T + E_V + E_J + E_{XC} , \tag{1}$$

where E_T is the non-interacting kinetic energy, E_V is the electronic-nuclear energy, E_J is the Coulomb energy,

$$E_J = \tfrac{1}{2} \int\int \rho(\boldsymbol{r}_1) r_{12}^{-1} \rho(\boldsymbol{r}_2)\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 , \tag{2}$$

and E_{XC} is the exchange–correlation energy,

$$E_{XC} = \int F(\rho_\alpha(\boldsymbol{r}), \rho_\beta(\boldsymbol{r}))\, d\boldsymbol{r} . \tag{3}$$

Here ρ denotes the one-electron total density, while ρ_α and ρ_β denote the respective spin densities. Of course, many commonly used exchange–correlation functionals depend on the derivatives of the spin densities as well (e.g., gradient-corrected functionals); Eq. (3) merely shows a 'local' functional for conciseness.

For finite systems, the total energy in Eq. (1) contains a spurious contribution arising from the Coulomb self-interaction of the electrons in Eq. (2). In HF theory, this contribution is exactly canceled by an analogous exchange contribution, but in KS theory the cancellation is imperfect, due to the approximate nature of the exchange–correlation energy functional which must be employed in practice. Many previous workers [34–36] have examined various procedures aimed at remedying this deficiency; these are called self-interaction-corrected (SIC) methods. Most SIC theories involve the addition of a correction term to the energy of the form

$$E_{SIC} = -\sum_i \left(E_J^i + E_{XC}^i\right) , \tag{4}$$

where

$$E^i_J = \tfrac{1}{2} \iint \rho_i(\mathbf{r}_1) r_{12}^{-1} \rho_i(\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\,, \tag{5}$$

$$E^i_{\mathrm{XC}} = \int F(\rho_i(\mathbf{r}), 0)\, \mathrm{d}\mathbf{r}\,, \tag{6}$$

$$\rho_i(\mathbf{r}) = |\psi_i(\mathbf{r})|^2\,, \tag{7}$$

with the summation running over all occupied (α and β) molecular orbitals ψ_i.

An important characteristic of SIC DFT methods which is different from ordinary KS methods is that, since the SIC corrections are calculated with the approximate XC functional on an orbital-by-orbital basis (rather than by using the total density), the SIC energy depends upon the set of orbitals used, i.e. the SIC energy is *not* invariant under unitary transformations among the occupied orbitals. As has previously been noted [36], one would therefore expect that the self-interaction might have a significant effect in processes involving a change in the spatial extent of the electronic states, e.g. in reactive systems. For this reason, we feel it is important to investigate the effect of SIC on reaction barriers calculated by DFT. Fois et al. [37] have recently examined the dissociation of Na_2 and the isomerization barrier of Na_3 by SIC LSD theory using a modified Car–Parrinello molecular dynamics scheme, with good results. To our knowledge the present work is the first study of the effect of SIC on reaction barriers for other than metallic systems.

A variety of functionals were used in the present study. The exchange functionals are

(1) The Dirac–Slater (S) local spin density functional [38,39], corresponding to Xα theory with $\alpha = \frac{2}{3}$, correct for the uniform electron gas.

(2) The Becke (B) functional [40], which incorporates a gradient correction to the Dirac–Slater functional.

(3) The gradient-corrected GGA91 functional of Perdew and Wang (PW) [41].

The correlation functionals are

(1) The 'null' functional, indicating that no correlation functional is used.

(2) The local functional of Vosko, Wilk and Nusair (VWN) [42], which is a parameterization of exact results for the uniform electron gas [43].

(3) The gradient-corrected functional of Lee, Yang and Parr (LYP) [44,45].

(4) The gradient-corrected GGA91 functional of Perdew and Wang (PW) [41,46].

Pairing the exchange and correlation functionals in all ways gives rise to twelve different exchange–correlation functionals. The performance of each of these was examined with and without the self-interaction correction described above, for a total of 24 DFT methods.

For comparison, three conventional ab initio methods were also used, covering a wide range in the sophistication of correlation treatment. These are HF theory, second-order Møller–Plesset (MP2) theory and coupled-cluster theory limited to single and double substitutions with triples correction (CCSD(T)) [47].

Optimized geometries and harmonic vibrational frequencies were calculated for H_2 and the linear symmetric H_3 transition structure by all DFT and ab initio methods. Vibrational adiabatic reaction barriers were then calculated, using the harmonic approximation for the zero-point energies. A large orbital basis set, 6-311++G(3df, 3pd) was used throughout. All DFT and HF calculations were carried out using a developmental version of the Q-Chem quantum chemistry program [48], while the MP2 and CCSD(T) calculations were performed with the GAUSSIAN 92 program [49].

Fully self-consistent KS densities were obtained. No auxiliary fitting or projection techniques were used. The standard SG-1 quadrature scheme [50] was used for the XC integrals. The KS canonical orbitals were then localized using the Boys procedure [51]; these were used to evaluate the self-interaction correction in Eq. (4). (Localized orbitals were employed in order to maximize the removal of the self-interaction energy.) Thus, our present implementation of SIC applies the correction perturbatively, rather than including the SIC terms in the self-consistent procedure, which would be more desirable but is more difficult to implement.

3. Results and discussion

3.1. Geometries

Table 1 lists the fully optimized geometries for H_2 and the H_3 $D_{\infty h}$ stationary point obtained by all the

Table 1
Optimized H–H distances (Å) of H_2 equilibrium structure and H_3 $D_{\infty h}$ transition structure [a]

Functional	H_2		H_3	
	KS	SIC	KS	SIC
S-null	0.783	0.735	0.974	0.928
S-VWN	0.766	0.727	0.950	0.911
S-LYP	0.775	0.730	0.959	0.913
S-PW	0.778	0.735	0.963	0.923
B-null	0.753	0.733	0.951	0.935
B-VWN	0.738	0.725	0.927	0.916
B-LYP	0.747	0.727	0.936	0.918
B-PW	0.749	0.732	0.940	0.931
PW-null	0.755	0.733	0.952	0.932
PW-VWN	0.740	0.725	0.928	0.914
PW-LYP	0.748	0.728	0.937	0.916
PW-PW	0.751	0.733	0.941	0.928
HF	0.734		0.933	
MP2	0.737		0.918	
CCSD(T)	0.742		0.930	
expt.	0.741			

[a] The 6-311G++(3df, 3pd)basis set was used in all theoretical calculations.

DFT methods under study. In addition, results obtained by the conventional ab initio methods, as well as the experimental geometry of H_2, are included for comparison purposes. In general, the bond length of H_2 is overestimated by ≈0.03–0.04 Å when the Dirac–Slater local spin density exchange functional is used. The use of gradient corrected exchange functionals (B and PW) improves the agreement with experiment. In cases where gradient-corrected exchange functionals were combined with correlation functionals (local or gradient-corrected), KS H_2 bond lengths in fairly good agreement with the experimental value were obtained. In particular, B-VWN and PW-VWN predict bond lengths in excellent agreement with experiment (0.738 and 0.740 Å, respectively, versus 0.741 Å). The same is true in the case of the ab initio methods MP2 and CCSD(T) (0.737 and 0.742 Å, respectively). It is interesting to note that in all instances, the inclusion of the self-interaction correction shortens the H_2 bond length considerably, underestimating the experimental value by up to 0.016 Å. It is well known that KS methods generally overestimate bond lengths, and this is due in part to the spurious Coulombic electronic repulsion; given this trend, the agreement of KS with experiment in the case of H_2 is most likely fortuitous, and therefore SIC bond lengths may be expected to be of better quality on average than in this case.

In the case of the linear H_3 stationary point, all the KS methods with exchange functionals and no correlation overestimate the H–H bond length by ≈0.02–0.04 Å when compared to the H–H bond length predicted by the highly correlated ab initio method CCSD(T). The use of correlation functionals improves the agreement, with B-VWN and PW-VWN giving the best results. As in the case of H_2, inclusion of the self-interaction correction shortens the H–H bond length, correcting the KS results somewhat.

3.2. Vibrational frequencies

Table 2 lists the harmonic vibrational frequencies obtained for H_2 and the H_3 transition structure. Again, the ab initio results are also listed as well as the experimental harmonic vibrational frequency of H_2. Most of the KS methods underestimate the experimental frequency of H_2 by up to 400 cm^{-1} while the inclusion of SIC produces frequencies that are in general too high. This is consistent with the fact that the KS H–H bond lengths are too long and the corresponding SIC values are too short.

The theoretical frequencies of the H_3 stationary point calculated by the DFT and ab initio methods are also given in Table 2. It is interesting to note that in the case of the KS methods S-VWN, S-LYP and S-PW no imaginary frequency was found, indicating that these stationary points are minima and no transition structure exists at these levels of theory. The imaginary frequencies obtained with B-null and PW-null are in fairly good agreement with the value obtained with CCSD(T). However, the use of correlation functionals predicts imaginary frequencies that are too low (by up to 1400 cm^{-1}). SIC improves the agreement, especially in the case of PW-VWN, PW-LYP, and PW-PW, where the largest error was found to be 56 cm^{-1}. Note in particular that, unlike KS, all SIC stationary points are transition structures. In general, the bending and symmetric stretching frequencies are in reasonable agreement with the CCSD(T) values. As in the case of the imaginary vibrational mode, SIC increases the value of the vibra-

Table 2
Harmonic vibrational frequencies (cm^{-1}) of H_2 equilibrium structure and H_3 $D_{\infty h}$ transition strcture[a]

Functional	H_2		H_3					
	KS	SIC	KS			SIC		
	Σ_g	Σ_g	Σ_u	Π_u	Σ_g	Σ_u	Π_u	Σ_g
S-null	3998	4571	1035i	801	1865	2083i	883	2122
S-VWN	4175	4671	889	846	1985	1476i	900	2226
S-LYP	4083	4648	980	817	1947	1434i	895	2221
S-PW	4069	4586	846	787	1933	1061i	857	2153
B-null	4250	4616	1494i	901	1928	2422i	914	2082
B-VWN	4428	4716	537i	948	2053	1786i	943	2199
B-LYP	4336	4692	235i	917	2016	1739i	930	2159
B-PW	4325	4624	532i	891	2000	1675i	895	2110
PW-null	4232	4610	1486i	895	1924	2285i	905	2098
PW-VWN	4410	4710	506i	942	2049	1577i	918	2214
PW-LYP	4319	4686	171i	914	2012	1518i	913	2208
PW-PW	4307	4618	507i	884	1996	1548i	878	2123
HF	4578		2296i	898	2037			
MP2	4518		1976i	895	2148			
CCSD(T)	4403		1521i	881	2052			
expt.	4401							

[a] The 6-311G++(3df, 3pd) basis set was used in all theoretical calculations.

tional frequency; however, this effect is not as marked as in the previous case.

3.3. Barriers

The total energies for the species involved in the reaction are listed in Table 3, and the classical and vibrational adiabatic (zero-point corrected) barrier heights obtained with the 24 DFT methods and the three ab initio methods are shown in Table 4. For reference, a high-quality quantum Monte Carlo (QMC) result of 9.61 kcal mol^{-1} [30] is used, which is close to the experimental value of 9.7 kcal mol^{-1} [52]. The barriers obtained by most of the KS methods are very low compared to QMC, with S-VWN, S-LYP and S-PW actually predicting H_3 to be stable relative to the $H+H_2$ asymptote, a dramatic failure. However, it is interesting to note that the methods B-null as well as PW-null give barriers that are in fairly good agreement with the QMC result (10.99 and 10.13 kcal mol^{-1}, respectively). This is very surprising, given that exchange-only KS methods have been shown to yield abysmal results for atomization energies [18]. The inclusion of SIC raises the KS barriers by an average of 8 kcal mol^{-1}, indicating that the self-interaction plays a major role in the vicinity of the transition state, where one bond is partially broken while the other is partially formed. The B-null functional gives a barrier height that is approximately 10 kcal mol^{-1} too high after SIC is applied, while PW-null is 7 kcal mol^{-1} too high, which leads to the conclusion that the accuracy of the KS B-null and PW-null results arises from a fortuitous balancing of opposing effects; the underestimation of the true exchange by the approximate exchange functional, and the omission of correlation.

The reaction barrier was also calculated using the restricted open-shell KS (ROKS) formalism, which was found to raise the barrier by on the order of 1 kcal mol^{-1} relative to unrestricted KS (UKS). This amount is somewhat surprising given the small amount of spin contamination found in the UKS re-

Table 3
Total absolute energies (hartree) of H, H_2 and H_3 [a]

Functional	H		H_2		H_3	
	KS	SIC	KS	SIC	KS	SIC
S-null	0.45692	0.49822	1.04414	1.13127	1.49238	1.60600
S-VWN	0.47851	0.49880	1.13728	1.18125	1.62027	1.66952
S-LYP	0.45692	0.49822	1.08180	1.16974	1.54421	1.65835
S-PW	0.46652	0.49871	1.08079	1.14773	1.55301	1.63854
B-null	0.49772	0.49909	1.13152	1.13149	1.61054	1.59728
B-VWN	0.51971	0.49927	1.22621	1.18100	1.74011	1.65928
B-LYP	0.49772	0.49909	1.16962	1.16998	1.66279	1.64904
B-PW	0.50744	0.49946	1.16837	1.14787	1.67129	1.62972
PW-null	0.49424	0.49886	1.12359	1.13115	1.60050	1.60086
PW-VWN	0.51617	0.49910	1.21802	1.18077	1.72981	1.66321
PW-LYP	0.49424	0.49886	1.16161	1.16965	1.65269	1.65280
PW-PW	0.50390	0.49929	1.16023	1.14765	1.66102	1.63346
HF	0.49982		1.13307		1.60488	
MP2	0.49982		1.16495		1.64372	
CCSD(T)	0.49982		1.17253		1.65652	

[a] The 6-311G++(3df, 3pd) basis set was used throughout.

Table 4
Barrier height (kcal mol^{-1}) of $H+H_2 \rightarrow H_2+H$ reaction [a]

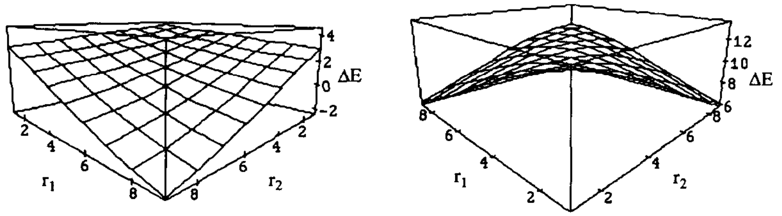
Functional	Classical barrier height		Zero-point correction		Vibrational adiabatic barrier height	
	KS	SIC	KS	SIC	KS	SIC
S-null	5.45	14.74	−0.76	−0.97	4.69	13.77
S-VWN	−2.81	6.61	0.56	−0.92	−2.25	5.69
S-LYP	−3.45	6.03	0.68	−0.91	−2.76	5.12
S-PW	−3.58	4.96	0.41	−1.03	−3.18	3.93
B-null	11.73	20.90	−0.74	−1.01	10.99	19.89
B-VWN	3.65	13.17	−0.68	−0.90	2.95	12.27
B-LYP	2,86	12.57	−0.69	−0.96	2.16	11.61
B-PW	2.84	11.05	−0.78	−1.04	2.05	10.02
PW-null	10.87	18.29	−0.74	−1.00	10.13	17.29
PW-VWN	2.75	10.45	−0.68	−0.94	2.07	9.51
PW-LYP	1.98	9.86	−0.69	−0.93	1.30	8.93
PW-PW	1.95	8.46	−0.78	−1.06	1.18	7.40
HF	17.58		−0.95		16.63	
MP2	13.21		−0.83		12.38	
CCSD(T)	9.91		−0.83		9.08	
QMC [b]					9.61	
expt. [c]					9.7	

[a] The 6-311G++(3df, 3pd) basis set was used in all theoretical calculations.
[b] From ref. [30].
[c] From ref. [52].

sults (e.g. $\langle S^2 \rangle = 0.7565$ for B-LYP); however, this difference is small compared to the total errors in the barriers and does not have a significant impact on the performance of the KS methods.

3.4. Potential energy surfaces

In order to investigate further the effect of SIC on the energetics of the $H+H_2$ reaction, the potential energy surface (PES) has been calculated in the case of the B-null and B-LYP functionals, with and without SIC. Fig. 1 shows plots of the PES differences between these methods and CCSD(T). The CCSD(T) results are expected to be of very high quality for this particular problem. As a check, a full-CI single-point calculation with the same basis set was carried out at the CCSD(T) transition structure geometry, using the GAMESS program [53]; the resulting energy difference was at the microhartree level. To the extent that the DFT surfaces parallel the CCSD(T) surface, the difference plots will be flat. Looking at Fig. 1a, it becomes clear that the agreement between the KS B-null surface and the CCSD(T) results is close only in the vicinity of the TS (point (3.5, 3.5) in Fig. 1a). This confirms that KS B-null KS predicts a barrier height in good agreement with the QMC and CCSD(T) fortuitously. When SIC is included, the B-null functional gives relative energies that deviate considerably from the CCSD(T) results along all regions of potential energy surface (Fig. 1b). KS B-LYP underestimates the relative energies in all regions of the PES, especially at the TS, where the difference with respect to the CCSD(T) barrier becomes almost 7 kcal mol^{-1} (Fig. 1c). On the other hand, as Fig. 1d shows, SIC seems to ameliorate this problem somewhat. In fact, SIC B-LYP predicts a PES in fairly good agreement with the CCSD(T) surface except in the limit of dissociation into three separate H atoms (points farther than (5.0, 5.0) in Fig. 1d), where the difference between the two surfaces can be as large as 8 kcal mol^{-1}. Thus, though the entire difference plot is far from uniformly flat, SIC B-LYP gives the best PES of the four methods plotted in the region of chemical significance. The same situation has been observed in the case of the other gradient-corrected XC functionals.



(a) KS B-null

(b) SIC B-null

(c) KS B-LYP

(d) SIC B-LYP

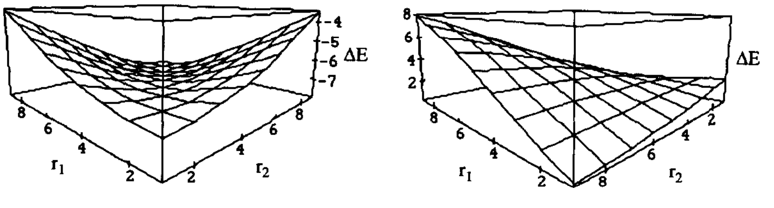


Fig. 1. Potential energy surface differences (kcal mol^{-1}) DFT−CCSD(T). The H–H axes are in arbitrary units, with the transition structure occurring at approximately (3.5, 3.5).

4. Conclusions

Some valuable observations on the performance of DFT in predicting reaction barriers were obtained from the study of this simple open-shell abstraction reaction. First of all, KS methods have severe difficulties in reproducing the barrier height, with three of the four methods employing a local exchange functional incorrectly predicting H_3 to be stable relative to $H+H_2$. In particular, this is a serious indictment of S-VWN, commonly known as LSDA, which is perhaps the most widely used DFT method. Even functionals generally exhibiting good performance elsewhere, such as B-LYP and B-PW, give barriers which are substantially too low, by several kcal mol^{-1}. We note that this is in contrast with the recent results of Fan and Ziegler [28] who have also studied radical hydrogen abstractions including $CH_4+CH_3 \rightarrow CH_3+CH_4$. Their findings indicated that, although the LSDA does not perform well, gradient-corrected methods give sufficiently good agreement with experiment to be useful in practical kinetic studies. However, the results presented here, as well as similarly poor results we have obtained for the reactions $CH_4+H \rightarrow CH_3+H_2$ and $CH_4+{}^3O \rightarrow CH_3+OH$ [54], do not bode well for performance of KS theory with current functionals on radical abstractions in general. Clearly, further examination of this class of reactions is necessary.

In this case, the self-interaction correction is indeed seen to play an important role. Addition of SIC gives a large energy change in the proper direction; even functionals which predicted fundamentally incorrect potential surfaces (e.g. having negative barriers) yield the proper qualitative behavior upon the inclusion of SIC. The best quantitative results were obtained by combining gradient-corrected exchange functionals with a correlation functional, consistent with previous KS studies on other properties for which the effect of SIC would not be expected to be as important (e.g. atomization energies); this resulted in accuracies to within 2 kcal mol^{-1} or less.

It is clear from this work that further investigation of SIC is warranted. In subsequent studies on more complicated reactions it will be determined if the present simple perturbative scheme is sufficient to continue to give good results, or if a more sophisticated SIC treatment is required. This could involve use of other orbital localization schemes (such as Edmiston–Ruedenberg localization [55]), or, more desirably, performing fully self-consistent SIC calculations. As mentioned earlier, implementation of self-consistent SIC is somewhat more complicated than regular KS, but various such implementations have been reported [35,36].

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