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Breaking Bonds with the Left Eigenstate Completely Renormalized Coupled-Cluster Method

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Breaking Bonds with the Left Eigenstate Completely Renormalized Coupled-Cluster Method

Abstract
The recently developed [P. Piecuch and M. Wloch, J. Chem. Phys. 123, 224105 (2005)] size-extensive left eigenstate completely renormalized (CR) coupled-cluster (CC) singles (S), doubles (D), and noniterative triples (T) approach, termed CR-CC(2,3) and abbreviated in this paper as CCL, is compared with the full configuration interaction (FCI) method for all possible types of single bond-breaking reactions between C, H, Si, and Cl (except H2) and the H2Si≡SiH2 double bond-breaking reaction. The CCL method is in excellent agreement with FCI in the entire region $R=1–3R_e$ for all of the studied single bond-breaking reactions, where $R$ and $R_e$ are the bond distance and the equilibrium bond length, respectively. The CCL method recovers the FCI results to within approximately 1mhartree in the region $R=1–3R_e$of the H–SiH3, H–Cl, H3Si–SiH3, Cl–CH3, H–CH3, and H3C–SiH3 bonds. The maximum errors are −2.1, 1.6, and 1.6mhartree in the R=1–3Re region of the H3C–CH3, Cl–Cl, and H3Si–Cl bonds, respectively, while the discrepancy for the H2Si≡SiH2 double bond-breaking reaction is 6.6 (8.5)mhartree at $R=2(3)R_e$. CCL also predicts more accurate relative energies than the conventional CCSD and CCSD(T) approaches, and the predecessor of CR-CC(2,3) termed CR-CCSD(T).

Keywords
Chemical bonds, Hydrogen reactions, Hydrogen bonding, Nuclear reaction models, Chemical vapor deposition

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Breaking bonds with the left eigenstate completely renormalized coupled-cluster method

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The recently developed [P. Piecuch and M. Wloch, J. Chem. Phys. 123, 224105 (2005)] size-extensive left eigenstate completely renormalized (CR) coupled-cluster (CC) singles (S), doubles (D), and noniterative triples (T) approach, termed CR-CC(2,3) and abbreviated in this paper as CCL, is compared with the full configuration interaction (FCI) method for all possible types of single bond-breaking reactions between C, H, Si, and Cl (except H2) and the H2Si==SiH2 double bond-breaking reaction. The CCL method is in excellent agreement with FCI in the entire region R=1–3Re for all of the studied single bond-breaking reactions, where R and Re are the bond distance and the equilibrium bond length, respectively. The CCL method recovers the FCI results to within approximately 1 mhartree in the region R=1–3Re of the H–SiH3, H–Cl, H2Si–SiH3, Cl–CH3, H–CH3, and H3C–SiH3 bonds. The maximum errors are −2.1, 1.6, and 1.6 mhartree in the R=1–3Re region of the H3C–CH3, Cl–Cl, and H3Si–Cl bonds, respectively, while the discrepancy for the H2Si==SiH2 double bond-breaking reaction is 6.6 (8.5) mhartree at R =2(3)Re. CCL also predicts more accurate relative energies than the conventional CCSD and CCSD(T) approaches, and the predecessor of CR-CC(2,3) termed CR-CCSD(T). © 2007 American Institute of Physics. [DOI: 10.1063/1.2778419]

I. INTRODUCTION

Silicon carbide (SiC) has been used as a protective layer of nuclear energy pellets. A 114-reaction mechanism has been proposed to account for the gas-phase chemistry of the SiC chemical vapor deposition (CVD), which includes various bond-breaking reactions. It is important to have an easy-to-use, relatively inexpensive, size-extensive method that can quantitatively describe the potential energy surface (PES) of such reactions, in order to obtain the corresponding rate constants. The coupled-cluster singles, doubles, and noniterative triples [CCSD(T)] method has been widely used to obtain accurate relative energies for chemical reactions. However, it often fails for severely stretched bonds and biradicals. The completely renormalized (CR) CCSD(T) method developed by Kowalski and Piecuch performs much better than CCSD(T) for stretched bonds, but somewhat worse at near-equilibrium geometries. Recently, Piecuch and co-workers developed the size-extensive “left-eigenvalue (L)” CR-CCSD(T), or CR-CC(2,3) method (hereinafter called CCL), which belongs to a larger CR-CC(m,n) family based on the biorthogonal formulation of the method of moments coupled-cluster equations and which is expected to be as accurate as CCSD(T) for near-equilibrium geometries while outperforming CR-CCSD(T) in the bond-breaking region. CCL is a single-reference approach whose computational costs are on the same order as those of CCSD(T) calculations. Therefore, the CCL method, after being carefully tested, might be an ideal method for calculating the PES of bond-breaking reactions such as those involved in the SiC CVD. This paper explores the efficacy of the CCL method compared with full configuration interaction (FCI) for a modest basis set when applied to several bond-breaking reactions relevant to the SiC CVD. The performance of the CCL method is also compared with those of CCSD(T) and CR-CCSD(T). It is stressed that the focus of this work is on the comparison of the ability of these methods to break bonds, not on the prediction of highly accurate bond energies.

II. COMPUTATIONAL DETAILS

All of the studied structures were optimized at the FCI level of theory. Hessians (energy second derivatives) were determined by finite differentiation of the analytic FCI gradients. To follow bond-breaking reaction paths, FCI constrained optimizations were performed with the relevant bond length fixed at successively larger values. The MINI basis set was used to study the H–CH3, H–SiH3, H3C–CH3, H3Si–SiH3, H3C–SiH3, and H2Si==SiH2 bond-breaking reactions. The 6-31G basis set was used for HCl and Cl2. For the Cl–CH2 and Cl–SiH3 bond-breaking reactions, a mixed basis set was used: MINI on the two atoms of the breaking bond and 6-31G on H.

CCSD, CCSD(T), CR-CCSD(T), and CCL single point energies were obtained at the FCI geometries. A symmetry-adapted restricted Hartree-Fock (RHF) determinant was used as a reference in all of the CC calculations. To facilitate the proper convergence of CC calculations for Cl–CH3,
Cl–SiH₃, and H₂Si–=SiH₂. CCSD amplitudes and molecular orbitals (MOs) from a slightly tighter structure were used as initial guess in the calculation of the next structure. The MO interchange was restricted in the self-consistent field iterations in order to make valid use of the previous CCSD amplitudes.

All calculations were performed with the GAMESS suite of codes. In particular, the GAMESS CC routines exploited in this work are described in Refs. 5 (CCL) and 9 [CCSD, CCSD(T), and CR-CCSD(T)]. Core electrons were excluded from the correlation energy calculations. Molecular orbitals were visualized with the aid of the MACMOLPLT software.

III. RESULTS AND DISCUSSION

Figure 1 shows that the CCL PESs match the FCI ones in the region \( R = 1 - 3 \sigma \) of nine bond-breaking reactions between pairs of the atoms C, H, Si, and Cl. Figure 2 presents the absolute errors (in millihartrees) of the CCL, CCSD, CCSD(T), and CR-CCSD(T) methods at various bond distances, where the FCI energies are used as the reference. For better visualization of the amplitudes of the CC errors for the various studied reactions, all charts in Fig. 2, except for Cl–Cl and Cl–SiH₃, were drawn with the CC error axis

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**FIG. 1.** (Color online) CCL (blue) compared with FCI (red squares) energies at various bond distances for the nine single bond-breaking reactions.
scaled from (−8 to 8 mhartree). The Cl–Cl and Cl–SiH₃ charts have a wider −16 to 16 mhartree range to accommodate larger errors.

The CCL method recovers the FCI results to within less than 1 mhartree error in the region $R = 1−3R_e$ for the H–SiH₃, H–Cl, H₂Si–SiH₃, Cl–CH₃, H–CH₃, and H₃C–SiH₃ bonds; it has slightly larger but no more than 2 mhartree errors in the $R = 1−3R_e$ regions for the Cl–Cl, Cl–SiH₃, and H₃C–CH₃ bonds. The small absolute CCL errors quantitatively illustrate the excellent agreement between the CCL and FCI PES. For comparison, the CCSD(T) method predicts accurate energies at near-equilibrium bond distances, but it often gives significant negative errors when the bond is stretched to more than 2$R_e$. The CR-CCSD(T) method gives larger absolute errors than CCL for the H–SiH₃, H–Cl, H₂Si–SiH₃, Cl–Cl, and Cl–CH₃ bond-breaking reactions; it is comparable to CCL for H–CH₃, H₃C–SiH₃, and H₃C–CH₃ bond-breaking reactions; it is comparable to CCL for H–CH₃, H₃C–SiH₃, and H₃C–CH₃. These comparisons indicate that CCL exceeds the CCSD(T) and CR-CCSD(T) methods in accuracy relative to the FCI absolute energies. However, to obtain accurate relative energies of the structures on the bond-breaking reaction paths, how nearly a CC error curve is parallel to the zero-error axis is much more important than the absolute errors.

Figure 2 shows three types of shapes for the CCSD error curves. In the first type (e.g., H–SiH₃, H–Cl, H₂Si–SiH₃, Cl–Cl, H₃C–SiH₃, and Cl–SiH₃), the CCSD error increases with the bond length and then levels off. The second type (e.g., Cl–CH₃) is a bell shape, in which the CCSD error first increases with the stretching bond length and then decreases to nearly zero at $3R_e$. In the third type (e.g., H–CH₃ and H₃C–CH₃), the CCSD error increases with the bond length and then decreases to eventually become negative before the error levels off.

The CCSD(T) method predicts very accurate energies for the near-equilibrium structures. However, the CCSD(T) error curves drop significantly at longer bond distances, except for H–CH₃ and H₃C–CH₃, where the CCSD(T) error remains approximately constant even in the $R = 2−3R_e$ region. The CCL and CR-CCSD(T) error curves are much closer and more parallel to the zero-error axis than the CCSD and CCSD(T) ones in the $R = 1−3R_e$ regions. In most cases, the CR-CCSD(T) error curves are slightly above the CCL ones.

The standard deviations (in millihartrees) of the CCL, CCSD, CCSD(T), and CR-CCSD(T) absolute errors are given in Table I. The structures were sampled at every 0.2 Å, ranging from slightly tighter than $R_e$ to $R = 3R_e$ or to the bond distance where two consecutive structures have less than 0.1 mhartree FCI energy difference, whichever is larger. The bond-breaking reactions in the table are sorted in the order of increasing standard deviation of the CCL errors. Table I is a quantitative illustration that CCL performs better than the other CC methods used in this study. For the nine single bond-breaking reactions, the standard deviations of the CCL error curves are all less than 1 mhartree.

Unlike ethylene, H₂Si=SiH₂ adopts a nonplanar $C_{2v}$ structure. All of the structures on the H₂Si=SiH₂ bond-
breaking path were also optimized with \( C_{2h} \) symmetry. Figure 3 shows that CCL differs from FCI by 6.6 (8.5) millihartree at two (three) times the equilibrium \( \text{H}_2\text{Si} \equiv \text{SiH}_2 \) bond distance. In comparison, the CCSD(T) and CR-CCSD(T) errors are 10.5 (10.1) and 13.6 (15.3) millihartree. The last row of Table I shows that the standard deviations of the CCL, CCSD, CCSD(T), and CR-CCSD(T) errors for this reaction are 3.14, 6.56, 3.94, and 5.70 millihartree, so CCL predicts the most accurate relative energies among the CC methods used in this work.

The sharp changes on the CCSD error curve on the right hand side of Fig. 3 are due to a state crossing that originates from the mixing of the highest occupied molecular orbital (HOMO) and second lowest unoccupied molecular orbital (LUMO+1) during the \( C_{2h} \)-constrained \( \text{H}_2\text{Si} \equiv \text{SiH}_2 \) bond stretching. Figure 4 illustrates the HOMO−1, HOMO, LUMO, and LUMO+1 orbitals of \( \text{H}_2\text{Si} \equiv \text{SiH}_2 \) at \( R = 2.4 \)−4.2 Å. At \( R_e \) these orbitals correspond to \( \sigma_y, \pi_u, \pi_y^*, \) and \( \sigma_u^* \). HOMO and LUMO+1 both have \( B_u \) symmetry; as the bond length increases, they gradually mix with each other and eventually interchange. The CCSD \( T_2 \) amplitudes for the double excitation from HOMO to LUMO are shown in Fig. 5. The sharp bump in the region of 3.6−4.0 Å illustrates the existence of the crossing in this region between the RHF ground state and the \((\pi_u, \pi_u \rightarrow \sigma_u^*, \sigma_u^*)\) doubly excited state as the \( \text{H}_2\text{Si} \equiv \text{SiH}_2 \) bond is stretched. The correspond-
The occupation numbers of the 15th–18th natural orbitals as a function of Si–Si distance are shown in Fig. 6. The occupation numbers of the 15th–18th natural orbitals (σ_u, π_u, π_v*, and σ_v*-type orbitals in that order) are close to (2, 2, 0, 0) at the equilibrium structure and (1, 1, 1, 1) at R = 3R_e. The FCI NOON values at 3.6 and 4 Å are 1.74, 1.41, 0.60, 0.25 and 1.49, 1.17, 0.84, 0.51, respectively. The significant deviation from (2, 2, 0, 0) provides strong evidence for the multireference character of the stretched H_2Si=SiH_2 bond. Note that the CCSD NOON curves resemble the FCI ones very closely and are therefore not presented here. Finally, it is worth mentioning that the mixing of π_u and σ_v* is symme-

**TABLE I.** Standard deviation (in millihartrees) of the errors of the CCL, CCSD, CCSD(T), and CR-CCSD(T) methods.

<table>
<thead>
<tr>
<th>Breaking Bond</th>
<th>CCL</th>
<th>CCSD</th>
<th>CCSD(T)</th>
<th>CR-CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–SiH_2</td>
<td>0.04</td>
<td>1.00</td>
<td>0.75</td>
<td>0.24</td>
</tr>
<tr>
<td>H–Cl</td>
<td>0.08</td>
<td>1.66</td>
<td>2.95</td>
<td>0.39</td>
</tr>
<tr>
<td>HSi–SiH_2</td>
<td>0.14</td>
<td>1.94</td>
<td>1.37</td>
<td>0.51</td>
</tr>
<tr>
<td>Cl–Cl</td>
<td>0.26</td>
<td>2.47</td>
<td>3.49</td>
<td>0.54</td>
</tr>
<tr>
<td>Cl–CH_3</td>
<td>0.37</td>
<td>2.73</td>
<td>79.77</td>
<td>0.96</td>
</tr>
<tr>
<td>H–CH_4</td>
<td>0.41</td>
<td>0.51</td>
<td>0.45</td>
<td>0.42</td>
</tr>
<tr>
<td>H,C–SiH_2</td>
<td>0.52</td>
<td>0.65</td>
<td>1.81</td>
<td>0.39</td>
</tr>
<tr>
<td>Cl–SiH_3</td>
<td>0.63</td>
<td>1.82</td>
<td>6.04</td>
<td>0.69</td>
</tr>
<tr>
<td>H,C–CH_3</td>
<td>0.96</td>
<td>1.24</td>
<td>1.06</td>
<td>1.01</td>
</tr>
<tr>
<td>H_2Si=SiH_2</td>
<td>3.14</td>
<td>6.56</td>
<td>3.94</td>
<td>5.70</td>
</tr>
</tbody>
</table>

^aThe CR-CC(2,3) approach of Ref. 5.
IV. CONCLUSIONS

The recently developed\textsuperscript{5} single-reference CR-CC(2,3) method, abbreviated in this work as CCL, which is similar in the computational effort and ease of use to the conventional CCSD(T) approach, recovers the FCI results within 1–2 mhartree errors and predicts more accurate relative energies than the CCSD, CCSD(T), and CR-CCSD(T) methods for the studied single bond-breaking reactions. It also predicts a reasonably accurate PES for the H\textsubscript{2}Si脱位二硫化双键 at various \textit{Si}=\textit{Si} bond distances.

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