



Editor's choice

Basis set convergence of high-order coupled cluster methods up to CCSDTQ567 for a highly multireference molecule

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HIGHLIGHTS

- Study post-CCSD(T) contributions to the dissociation energy of $C_2(^1\Sigma_g^+)$.
- Examine contributions up to CCSDTQ567 in conjunction with basis sets up to cc-pV7Z.
- At the CBS limit, post-CCSD(T) contributions add up to $0.427 \text{ kcal mol}^{-1}$.
- Contributions up to CCSDTQ5(6) have to be obtained with relatively large basis sets.
- Contributions beyond CCSDTQ5(6) are smaller than $\sim 2 \text{ cm}^{-1}$.

ARTICLE INFO

Keywords:

CCSDT
CCSDTQ
CCSDTQ5
CCSDTQ56
Basis set limit
Basis set extrapolations

ABSTRACT

We examine the basis-set convergence of post-CCSD(T) contributions to the dissociation energy of the highly multireference $C_2(^1\Sigma_g^+)$ molecule. At the infinite basis set limit we obtain: CCSDT–CCSD(T)/cc-pV{6,7}Z = -2.268 , CCSDT(Q)–CCSDT/cc-pV{6,7}Z = 3.420 , CCSDTQ–CCSDT(Q)/cc-pV{5,6}Z = -1.151 , CCSDTQ(5)–CCSDTQ/cc-pV{Q,5}Z = 0.412 , CCSDTQ5–CCSDTQ(5)/cc-pV{T,Q}Z = -0.053 , CCSDTQ5(6)–CCSDTQ5/cc-pV{D,T}Z = 0.060 , CCSDTQ56–CCSDTQ5(6)/cc-pVTZ(1d) = 0.003 , CCSDTQ56(7)–CCSDTQ56/cc-pVTZ(1d) = 0.002 , and CCSDTQ567–CCSDTQ56(7)/cc-pVTZ(1d) = 0.001 kcal/mol . These post-CCSD(T) contributions add to 0.427 kcal/mol . Including the CCSD(T)/CBS energy, inner-shell, scalar relativistic, spin-orbit, DBOC, and ZPVE corrections from W4.3 theory results in a CCSDTQ567/CBS D_0 value of 144.08 kcal/mol , which agrees to within overlapping uncertainties with the experimental ATcT value of $144.006 \pm 0.06 \text{ kcal/mol}$.

1. Introduction

The ground electronic state ($^1\Sigma_g^+$) of the C_2 molecule has been extensively investigated both experimentally and theoretically [1–3]. Considerable high-level theoretical work over the past two decades has established C_2 as one of the most challenging targets in small molecule computational chemistry [4–38]. This is due to both pathological multireference character in the $^1\Sigma_g^+$ state and excessively slow basis set convergence of the higher-order correlation effects. Dicarbon is thus an important and challenging target in benchmarking and development of high-level standard and composite ab initio methods [15,20,22,26,27,29,32,39–42].

Over a decade ago, a number of high-level studies examined the basis set convergence of the frozen-core CCSD(T) bond dissociation energy close to the infinite basis set limit using correlation-consistent basis sets as large as aug-cc-pV7Z [20,22,26,27]. These studies have arrived at valence CCSD(T)/CBS bond dissociation energies ranging between 145.1 and $145.4 \text{ kcal mol}^{-1}$ (where CCSD(T)/CBS stands for coupled cluster with

single, double, and quasiperturbative triple excitations extrapolated to the complete basis set limit). More recently, in a tour de force study, Feller et al. explored the basis set convergence of the frozen-core CCSD(T) dissociation energy at (or very close to) the infinite basis set limit and arrived at an R/UCCSD(T)/aug-cc-pV{8,9}Z value of $145.37 \text{ kcal mol}^{-1}$ [15]. The post-CCSD(T) components of the C_2 dissociation energy, on the other hand, have been examined with smaller basis sets. For example, the same study by Feller et al. extrapolated the CCSDT–CCSD(T) and CCSDTQ–CCSDT components from the cc-pV{Q,5}Z and cc-pV{T,Q}Z basis set pairs, respectively, whilst CCSDTQ5 contributions were calculated in conjunction with a triple- ζ -quality basis set [15]. In earlier work, [20] which calculated the C_2 dissociation energy using W4.3 theory, [29] the post-CCSD(T) components were obtained at the following levels of theories: CCSDT–CCSD(T)/cc-pV{T,Q}Z, CCSDT(Q)–CCSDT/cc-pV{T,Q}Z, CCSDTQ–CCSDT(Q)/cc-pVTZ, CCSDTQ5/cc-pVDZ, and CCSDTQ5(6)/DZ, where DZ denotes the simple Dunning–Hay [43] valence double- ζ basis set.

In the present letter, we attempt to converge the post-CCSD(T)

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<https://doi.org/10.1016/j.cplett.2019.136810>

Received 20 August 2019; Received in revised form 26 September 2019; Accepted 28 September 2019

Available online 04 October 2019

0009-2614/© 2019 Published by Elsevier B.V.

components of the $C_2(^1\Sigma_g^+)$ dissociation energy to the infinite basis set limit. The largest basis sets and basis set extrapolations used are: CCSDT–CCSD(T)/cc-pV{6,7}Z, CCSDT(Q)–CCSDT/cc-pV{6,7}Z, CCSDTQ–CCSDT(Q)/cc-pV{5,6}Z, CCSDTQ(5)–CCSDTQ/cc-pV{Q,5}Z, CCSDTQ5–CCSDTQ(5)/cc-pV{T,Q}Z, CCSDTQ5(6)–CCSDTQ5/cc-pV{D,T}Z, CCSDTQ56–CCSDTQ5(6)/cc-pVTZ(1d), CCSDTQ567/cc-pVTZ(1d), where cc-pVTZ(1d) denotes a truncated version of the cc-pVTZ basis set.

2. Computational methods

All calculations were carried out using the MRCC program suite [44,45] with the standard correlation-consistent basis sets of Dunning and co-workers [46–48]. In the post-CCSDTQ5(6) calculations we also use a truncated version of the cc-pVTZ basis set in which the sp functions from the cc-pVTZ basis set are combined with the d functions from the cc-pVDZ basis set (denoted by cc-pVTZ(1d)). The post-CCSD(T) correlation components of the bond dissociation energies are extrapolated using the $E(L) = E_\infty + A/L^3$ two-point extrapolation formula (where L is the highest angular momentum represented in the basis set). Basis set extrapolations using the cc-pVnZ and cc-pV(n+1)Z basis sets are denoted by cc-pV{n,n+1}Z.

All calculations are nonrelativistic and are carried out within the frozen-core approximation, i.e., the 1s orbitals are constrained to be doubly occupied in all configurations. Thus, for the carbon atom CCSDTQ is equivalent to full configuration interaction (FCI). Coupled cluster calculations for the carbon atom are carried out within the restricted open-shell formalism. The equilibrium bond distance for $C_2(^1\Sigma_g^+)$ is taken from Ref. [20]. Finally, we note that some of the higher-order correlation calculations strained our computational resources to the absolute limit. For example, the iterative CCSDTQ/cc-pV6Z calculation involves ten billion amplitudes. This calculation required 21 iterations to converge to 10^{-8} Hartree. Each iteration ran for about 2.1 days on 20 cores of a dual Intel Xeon machine (E5-2683-v3 and 2.0 GHz) with 512 GB of RAM, with a total runtime of 46 days. Another big calculation was for the CCSDTQ5/cc-pVQZ energy, which involves six billion amplitudes, and ran for 47 days on an older machine (dual Intel Xeon E5-4650L, 2.60 GHz, 512 GB of RAM).

3. Results and discussion

In the present letter, we consider iterative and perturbative coupled cluster contributions up to connected septuples (CCSDTQ567). Table 1 gives an overview of the post-CCSD(T) coupled cluster terms that are discussed along with the abbreviations that are used.

Table 2 lists the post-CCSD(T) correlation components of the $C_2(^1\Sigma_g^+)$ dissociation energy. Fig. 1 shows the deviations within ± 0.15 kcal mol $^{-1}$ from our best basis set limit values. The T–(T) component converges fairly slowly to the CBS limit. For example, the

Table 1
Overview of the coupled cluster contributions considered in the present work.

Name	Definition	Abbreviation
Full-iterative connected triples	CCSDT–CCSD(T)	T–(T)
Noniterative connected quadruples	CCSDT(Q)–CCSDT	(Q)
Full-iterative connected quadruples	CCSDTQ–CCSDT(Q)	Q–(Q)
Connected quadruples as a whole	CCSDTQ–CCSDT	Q
Noniterative quintuples	CCSDTQ(5)–CCSDTQ	(5)
Full-iterative connected quintuples	CCSDTQ5–CCSDTQ(5)	5–(5)
Connected quintuples as a whole	CCSDTQ5–CCSDTQ	5
Noniterative sextuples	CCSDTQ5(6)–CCSDTQ5	(6)
Full-iterative connected sextuples	CCSDTQ56–CCSDTQ5(6)	6–(6)
Connected sextuples as a whole	CCSDTQ56–CCSDTQ5	6
Noniterative septuples	CCSDTQ56(7)–CCSDTQ56	(7)
Full-iterative connected septuples	CCSDTQ567–CCSDTQ56(7)	7–(7)
Connected septuples as a whole	CCSDTQ567–CCSDTQ56	7

difference between the cc-pV{5,6}Z and cc-pV{6,7}Z CBS limits is 0.011 kcal mol $^{-1}$ (or 3.8 cm $^{-1}$). The cc-pVnZ ($n = D, T, Q, 5, 6, 7$) basis sets converge smoothly to the CBS limit from above (Fig. 1). In particular, the deviations from the T–(T)/cc-pV{6,7}Z limit value are: 1.021 (cc-pVDZ), 0.358 (cc-pVTZ), 0.169 (cc-pVQZ), 0.083 (cc-pV5Z), 0.043 (cc-pV6Z), and 0.027 (cc-pV7Z) kcal mol $^{-1}$. The cc-pV{D,T}Z extrapolation achieves the same accuracy as the cc-pV5Z basis set and the cc-pV{T,Q}Z extrapolation achieves the same accuracy as the cc-pV7Z basis set.

The (Q) component of the dissociation energy converges faster to the CBS limit, such that the difference between the cc-pV{5,6}Z and cc-pV{6,7}Z CBS limits is merely 0.003 kcal mol $^{-1}$ (or just 1.0 cm $^{-1}$). The cc-pV{T,Q}Z extrapolation results in a deviation of 0.025 kcal mol $^{-1}$ from the (Q)/cc-pV{6,7}Z energy, whilst the cc-pV{D,T}Z extrapolation results in a deviation of 0.035 kcal mol $^{-1}$ from the (Q)/cc-pV{6,7}Z energy. The cc-pVnZ ($n = D, T, Q, 5, 6, 7$) basis sets converge smoothly to the CBS limit from below (Fig. 1). In particular, the deviations from the (Q)/cc-pV{6,7}Z limit value are: –0.765 (cc-pVDZ), –0.202 (cc-pVTZ), –0.070 (cc-pVQZ), –0.029 (cc-pV5Z), –0.015 (cc-pV6Z), and –0.010 (cc-pV7Z) kcal mol $^{-1}$. The cc-pV{D,T}Z extrapolation achieves a similar accuracy as the cc-pV5Z basis set.

For the higher-order quadruples, Q–(Q), component we were only able to obtain CBS limit values using the cc-pV{5,6}Z basis set extrapolation. Nevertheless, since the energy difference between the cc-pV{Q,5}Z and cc-pV{5,6}Z extrapolations is merely 0.001 kcal mol $^{-1}$ (or just 0.3 cm $^{-1}$), it is safe to assume that the Q–(Q)/cc-pV{5,6}Z value is fully converged to the CBS limit. Even the cc-pV{T,Q}Z extrapolation is merely 0.003 kcal mol $^{-1}$ (or 1.0 cm $^{-1}$) away from the cc-pV{5,6}Z CBS limit value. However, the cc-pV{D,T}Z extrapolation results in a deviation which is one order of magnitude larger, namely 0.033 kcal mol $^{-1}$. The cc-pVnZ ($n = D, T, Q, 5, 6, 7$) basis sets converge smoothly to the CBS limit from above. In particular, the deviations from the Q–(Q)/cc-pV{5,6}Z limit value are: 0.084 (cc-pVDZ), 0.048 (cc-pVTZ), 0.022 (cc-pVQZ), 0.011 (cc-pV5Z), and 0.006 (cc-pV6Z) kcal mol $^{-1}$.

It has been previously found, using smaller basis sets, that there is very effective cancellation between the higher-order triples, CCSDT–CCSD(T), and connected quadruples, CCSDTQ–CCSDT, contributions to the dissociation energy of $C_2(^1\Sigma_g^+)$ [15,20,26]. Here we show that at the CBS limit there is perfect cancellation between these two components, namely T–(T)/cc-pV{6,7}Z = –2.268 kcal mol $^{-1}$ and (Q)/cc-pV{6,7}Z + Q–(Q)/cc-pV{5,6}Z = +2.269 kcal mol $^{-1}$.

Our best value for the CCSDTQ(5)–CCSDTQ component is obtained from the cc-pV{Q,5}Z extrapolation. As pointed out in much earlier works which obtained this value with the cc-pVDZ basis set [20,26,29] its magnitude is still chemically significant. Specifically, at the (5)/cc-pV{Q,5}Z level we obtain a value of 0.412 kcal mol $^{-1}$ (Table 2). The cc-pV{T,Q}Z value of 0.420 kcal mol $^{-1}$ is only 0.008 kcal mol $^{-1}$ away from the cc-pV{Q,5}Z value (Table 2). Therefore, the cc-pV{Q,5}Z value is likely converged to the infinite basis set limit. Nevertheless, the (5)/cc-pV{D,T}Z components is clearly not fully converged, being as much as 0.041 kcal mol $^{-1}$ (or 14 cm $^{-1}$) away from the (5)/cc-pV{Q,5}Z value. As opposed to the perturbative, noniterative connected quadruple excitations, which converges fairly smoothly from below to the CBS limit (Fig. 1), the (5)/cc-pVnZ series exhibits oscillatory basis set convergence behaviour with the smaller basis sets. In particular, the deviations from the (5)/cc-pV{Q,5}Z CBS limit are: 0.053 (cc-pVDZ), –0.013 (cc-pVTZ), and –0.001 (cc-pVQZ and cc-pV5Z) kcal mol $^{-1}$.

We were able to extrapolate the higher-order quintuple excitations, 5–(5), from the cc-pV{T,Q}Z basis set pair. The 5–(5)/cc-pV{T,Q}Z value of –0.053 kcal mol $^{-1}$ is almost an order of magnitude smaller (in absolute value) than the (5)/cc-pV{Q,5}Z value (0.412 kcal mol $^{-1}$, Table 2). It is hard to estimate how far the 5–(5)/cc-pV{T,Q}Z value is from the true CBS limit, the difference between the 5–(5)/cc-pV{D,T}Z and 5–(5)/cc-pV{T,Q}Z values being 0.027 kcal mol $^{-1}$. As opposed to the higher-order triple and quadruple excitations (T–(T) and Q–(Q)),

Table 2

Post-CCSD(T) correlation contributions for the $C_2(^1\Sigma_g^+)$ dissociation energy calculated (and extrapolated to the CBS limit) with the cc-pVnZ basis sets ($n = D, T, Q, 5, 6,$ and 7).

Basis set	T-(T)	(Q)	Q-(Q)	(5)	5-(5)	(6)	6-(6)	(7)	7-(7)
cc-pVDZ	-1.246	2.655	-1.067	0.465	-0.146	0.061	-0.001	0.003	0.001
cc-pVTZ	-1.910	3.218	-1.103	0.399	-0.062	0.060	0.003 ^a	0.002 ^a	0.001 ^a
cc-pVQZ	-2.099	3.350	-1.129	0.411	-0.057				
cc-pV5Z	-2.185	3.391	-1.140	0.411					
cc-pV6Z	-2.224	3.405	-1.145						
cc-pV7Z	-2.240	3.410							
cc-pV{D,T}Z	-2.190	3.456	-1.118	0.371	-0.026	0.060			
cc-pV{T,Q}Z	-2.237	3.445	-1.148	0.420	-0.053				
cc-pV{Q,5}Z	-2.275	3.435	-1.152	0.412					
cc-pV{5,6}Z	-2.279	3.423	-1.151						
cc-pV{6,7}Z	-2.268	3.420							

^a Truncated version of the cc-pVTZ basis set denoted by cc-pVTZ(1d), see text.

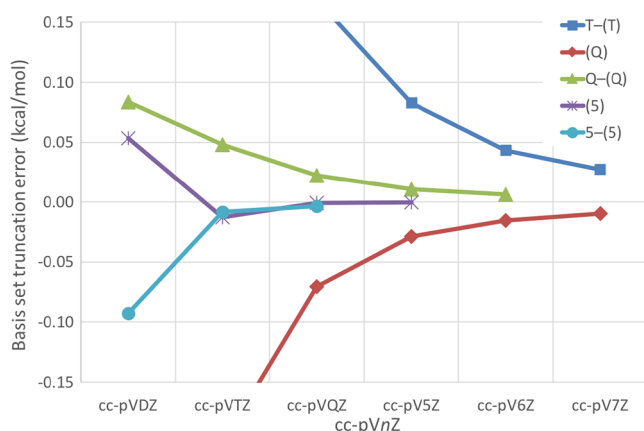


Fig. 1. Basis set truncation errors for the T-(T), (Q), Q-(Q), (5), and 5-(5) components of the $C_2(^1\Sigma_g^+)$ dissociation energy calculated in conjunction with the cc-pVnZ basis sets ($n = D, T, Q, 5, 6,$ and 7). Reference values are extrapolated from the following basis set pairs: T-(T)/cc-pV{6,7}Z, (Q)/cc-pV{6,7}Z, Q-(Q)/cc-pV{5,6}Z, (5)/cc-pV{Q,5}Z, and 5-(5)/cc-pV{T,Q}Z.

which converge smoothly from above to the CBS limit (Table 2 and Fig. 1), the 5-(5)/cc-pVnZ series converges fairly smoothly to the CBS limit from below. In particular, the deviations from the 5-(5)/cc-pV{T,Q}Z CBS limit value are: -0.093 (cc-pVDZ), -0.009 (cc-pVTZ), and -0.004 (cc-pVQZ) kcal mol⁻¹.

Our best perturbative, noniterative connected sextuple, CCSDTQ5(6)-CCSDTQ5, component is extrapolated from the cc-pV{D,T}Z basis set pair. The (6)/cc-pV{D,T}Z value (0.060 kcal mol⁻¹) is practically the same as the values obtained with the cc-pVTZ and cc-pVDZ basis sets, 0.060 and 0.061 kcal mol⁻¹, respectively. Thus it seems like the cc-pV{D,T}Z extrapolation is converged to the CBS limit. The (6)/cc-pV{D,T}Z component cancels out almost perfectly with our best 5-(5)/cc-pV{T,Q}Z component of -0.053 kcal mol⁻¹.

We were able to obtain excitations above CCSDTQ5(6) with a truncated version of the cc-pVTZ basis set in which the sp functions from the cc-pVTZ basis set are combined with the d functions from the cc-pVDZ basis set (denoted by cc-pVTZ(1d)). Importantly, all contributions to the binding energy beyond CCSDTQ5(6) are equal to or smaller than 1 cm⁻¹. In particular they are 0.003 (CCSDTQ56-CCSDTQ5(6)), 0.002 (CCSDTQ56(7)-CCSDTQ56), and 0.001 (CCSDTQ567-CCSDTQ56(7)) kcal mol⁻¹. Overall, the CCSDTQ567-CCSDTQ5(6) difference amounts to 0.006 kcal mol⁻¹ \approx 2 cm⁻¹, thus the n -particle limit has been reached at the CCSDTQ5(6) level.

Overall, our best basis set limit post-CCSD(T) contributions to the bond dissociation energy are: T-(T)/cc-pV{6,7}Z = -2.268, (Q)/cc-pV{6,7}Z = 3.420, Q-(Q)/cc-pV{5,6}Z = -1.151, (5)/cc-pV{Q,5}Z

Z = 0.412, 5-(5)/cc-pV{T,Q}Z = -0.053, (6)/cc-pV{D,T}Z = 0.060, 6-(6)/cc-pVTZ(1d) = 0.003, (7)/cc-pVTZ(1d) = 0.002, and 7-(7)/cc-pVTZ(1d) = 0.001 kcal mol⁻¹. Adding up these post-CCSD(T) corrections gives our best post-CCSD(T) value of 0.427 kcal mol⁻¹. Interestingly, this value is almost spot-on the post-CCSD(T) correction from Feller *et al.*¹⁵ (0.44 kcal mol⁻¹) and W4 theory (0.42 kcal mol⁻¹) [20,29]. Such good agreement is fortuitous and is due to error compensation between the approximated CCSDT-CCSD(T), CCSDTQ, and CCSDTQ5 terms in addition to the complete neglect of the CCSDTQ56 term. For comparison, the post-CCSD(T) correction from W4.3 theory is 0.50 kcal mol⁻¹. Combining our best post-CCSD(T) value of 0.427 kcal mol⁻¹ with the CCSD(T)/CBS energy (145.35), inner-shell correlation (1.25), scalar relativistic (-0.17), spin-orbit (-0.17), diagonal Born-Oppenheimer (0.03), and zero-point vibrational energy (2.64) corrections to the bond dissociation energy from W4.3 theory [20,29] results in a relativistic, all-electron, CCSDTQ567/CBS bond dissociation energy at 0 K of 144.08 kcal mol⁻¹. This value agrees to within overlapping uncertainties with the experimental value of 144.006 \pm 0.06 kcal mol⁻¹ from the Active Thermochemical Tables network of Ruscic and co-workers (ATcT, version 1.122e) [49]. We note that using the R/UCCSD(T)/aug-cc-pV{8,9}Z energy (145.37 kcal mol⁻¹) and inner-shell correction (1.29 kcal mol⁻¹) from ref. [15] instead of the above values from W4.3 theory would further increase the theoretical bond dissociation energy by 0.06 kcal mol⁻¹. The work presented here indicates that our best post-CCSD(T) correction (0.427 kcal mol⁻¹) is likely to be converged to about 0.01 kcal mol⁻¹, where the main sources of error are from the T-(T)/cc-pV{6,7}Z and 5-(5)/cc-pV{T,Q}Z contributions (*vide supra*).

4. Conclusions

We re-examine the magnitude and basis set convergence of the post-CCSD(T) correlation contributions (up to CCSDTQ567) to the dissociation energy of a pathologically multireference molecule - $C_2(^1\Sigma_g^+)$. At the infinite basis set limit we obtain the following contributions to the dissociation energy: T-(T)/cc-pV{6,7}Z = -2.268, (Q)/cc-pV{6,7}Z = 3.420, Q-(Q)/cc-pV{5,6}Z = -1.151, (5)/cc-pV{Q,5}Z = 0.412, 5-(5)/cc-pV{T,Q}Z = -0.053, (6)/cc-pV{D,T}Z = 0.060, 6-(6)/cc-pVTZ(1d) = 0.003, (7)/cc-pVTZ(1d) = 0.002, and 7-(7)/cc-pVTZ(1d) = 0.001 kcal mol⁻¹. Adding up these post-CCSD(T) corrections gives our best post-CCSD(T) value of 0.427 kcal mol⁻¹. Combining this post-CCSD(T) value with the CCSD(T)/CBS energy, inner-shell correlation, scalar relativistic, spin-orbit, diagonal Born-Oppenheimer, and zero-point vibrational energy corrections from W4.3 theory [20,29] results in a relativistic, all-electron, CCSDTQ567/CBS bond dissociation energy at 0 K of 144.08 kcal mol⁻¹, which agrees to within overlapping uncertainties with the experimental ATcT value of 144.006 \pm 0.06 kcal mol⁻¹.

The post-CCSD(T) correlation contributions to the dissociation

energy of this particularly challenging molecule are converged to within $\sim 10 \text{ cm}^{-1}$ using the following basis sets and basis set extrapolations: T-(T)/cc-pV{T,Q}Z, (Q)/cc-pV{T,Q}Z, Q-(Q)/cc-pV{D,T}Z, (5)/cc-pVTZ, 5-(5)/cc-pVTZ, and (6)/cc-pVDZ. The magnitude of higher-order correlation contributions (6-(6), (7), and 7-(7)) is smaller than $\sim 1 \text{ cm}^{-1}$ at the CBS limit. Overall, the CCSDTQ567-CCSDTQ5(6) difference amounts to $0.006 \text{ kcal mol}^{-1} \approx 2 \text{ cm}^{-1}$, thus the n -particle limit is practically reached at the CCSDTQ5(6) level.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We acknowledge system administration support provided by the Faculty of Science at the University of Western Australia to the Linux cluster of the Karton group. We gratefully acknowledge an Australian Research Council (ARC) Future Fellowship (FT170100373).

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