



How large are post-CCSD(T) contributions to the total atomization energies of medium-sized alkanes?



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ABSTRACT

The CCSD(T) method is often considered as the gold standard in quantum chemistry for single-reference systems. Using W4 and W4lite theories, we calculate post-CCSD(T) contributions to the total atomization energies (TAEs) of *n*-alkanes and show that they reach up to 0.65 kcal/mol for *n*-hexane. Furthermore, we find that post-CCSD(T) contributions increase linearly with the size of the *n*-alkane, indicating that they will reach ~ 1 kcal/mol for *n*-decane (C₁₀H₂₂) and ~ 2 kcal/mol for *n*-icosane (C₂₀H₄₂). These results are significant since today CCSD(T)/CBS-type methods are being applied to hydrocarbons of increasing size and are assumed to give TAEs with chemical accuracy for these systems.

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1. Introduction

Application of coupled cluster theory involves two approximations. The first is the use of a finite basis set to express the orbitals in the Hartree–Fock wavefunction (a.k.a. the one-particle truncation error). The second is the truncation of the cluster operator to include only *n*-tuple excitations (a.k.a. the *n*-particle truncation error) [1]. Including all possible excitations in the wavefunction and carrying out the calculation with an infinitely large basis set will result in the exact nonrelativistic electronic energy, which is equivalent to a complete-basis-set full-configuration-interaction (FCI/CBS) calculation. A number of composite approaches for approximating the FCI/CBS energy have been developed in the past two decades. Prominent examples of such methods include the Weizmann-4 (W4) [2–4], highly accurate extrapolated ab initio thermochemistry (HEAT) [5,6], focal point approximation (FPA) [7,8], and the Feller–Peterson–Dixon (FPD) [9–12] methods. These theories have been shown to afford total atomization energies with confident sub-kJ mol⁻¹ accuracy (i.e., 95% confidence intervals <1 kJ mol⁻¹, and maximal errors below ~ 1 kJ mol⁻¹ even for pathologically multireference systems such as ozone and halogen oxides) [4,10,11,13–15].

For systems dominated by a single reference determinant coupled cluster with singles, doubles, and quasiperturbative triple excitations (i.e., the CCSD(T) method) provides a very good approximation to the FCI energy at a significantly reduced computational

cost [16,17]. This is due to a systematic error cancellation between the higher-order connected triples, $T_3 - (T)$, correlation contribution and the connected quadruple and quintuple excitations ($T_4 + T_5$). These contributions are of similar orders of magnitude, but the $T_3 - (T)$ contribution tends to universally decrease the molecular binding energies, whereas the $T_4 + T_5$ contribution universally increases them. This error compensation has been shown to work remarkably well for relatively small systems dominated by a single-reference configuration [2–6,18–22]. The question that naturally arises, is how well this error compensation works for larger molecules? Or in other words, does the absolute magnitudes of the $T_3 - (T)$ and $T_4 + T_5$ contributions increase at the same rate as the size of the system grows? This is a timely question, since with the increase in computational power of modern supercomputers and important theoretical developments, CCSD(T)/CBS composite methods are being applied to increasingly larger systems. Recent examples include the application of the W1-F12 composite method to systems as large as dodecahedrane (C₂₀H₂₀) [23] and the application of the G4(MP2) method to Buckminsterfullerene (C₆₀) [24].

In the present letter, we will address this question for systems that are dominated by a single reference determinant, namely the homologous series of *n*-alkanes: methane, ethane, propane, butane, pentane, hexane, etc. We obtain the $T_3 - (T)$ and $T_4 + T_5$ contributions for *n*-alkanes of up to hexane using W4 and W4lite theories. We find that close to the basis-set limit the error compensation between these two components becomes less and less effective with the size of the *n*-alkane, making the CCSD(T)/CBS method less and less accurate. In addition, we find that there is a nearly perfect linear correlation between the magnitude of the post-CCSD(T) and CCSD(T) correlation contributions, with a squared correlation

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Table 1
Component breakdown of the W4 and W4lite valence, nonrelativistic atomization energies for *n*-alkanes of up to hexane (in kcal mol⁻¹).

	SCF ^a W4	CCSD ^a W4	(T) ^b W4	T ₃ – (T) ^c W4	T ₄ ^d W4lite	T ₄ ^e W4	T ₅ ^f W4	T ₄ + T ₅ ^g W4
CH ₄ ^h	331.546	84.737	2.890	–0.080	0.079	0.080	0.000	0.080
C ₂ H ₆ ^h	558.015	146.340	6.370	–0.350	0.219	0.230	0.010	0.240
C ₃ H ₈ ^h	785.335	209.050	10.120	–0.630	0.355	0.380	0.019 ⁱ	0.399
C ₄ H ₁₀	1012.593	271.812	13.883	–0.930	0.530	0.572	0.026 ⁱ	0.597
C ₅ H ₁₂	1239.834	334.541	17.654	–1.227	0.688	N/A	N/A	0.787 ^j
C ₆ H ₁₄	1467.005	397.384	21.441	–1.498 ^k	0.847	N/A	N/A	N/A
R ² ^l	1.0000	1.0000	0.9998	0.9997	0.9985	0.9961	0.9923	0.9974

^a The SCF and valence CCSD correlation components are extrapolated from the cc-pV5Z and cc-pV6Z basis sets.

^b The valence (T) correlation component is extrapolated from the cc-pVQZ and cc-pV5Z basis sets.

^c The valence CCSDT – CCSD(T) correlation component extrapolated from the cc-pVDZ and cc-pVTZ basis sets.

^d The T₄ component is taken as at the (Q)/cc-pVDZ correlation component.

^e The CCSDT(Q) – CCSDT component is calculated with the cc-pVTZ basis set, whilst the CCSDTQ – CCSDT(Q) component is calculated with the cc-pVDZ basis set (see Ref. [2] for further details).

^f The CCSDTQ5 – CCSDTQ component is calculated with the DZ basis set.

^g Sum of the T₄ + T₅ contributions from W4 theory.

^h Taken from Ref. [21].

ⁱ CCSDTQ(5) – CCSDTQ component calculated with the DZ basis set.

^j The T₄ + T₅ contribution is estimated assuming that the post-CCSD(T) contribution to the isodesmic reaction C₅H₁₂ + 3CH₄ → 4C₂H₆ are zero and taking the T₃ – (T) contribution from W4 theory.

^k The T₃ – (T) contribution is estimated assuming that the post-CCSD(T) contribution to the isodesmic reaction C₆H₁₄ + 4CH₄ → 5C₂H₆ are zero and taking the (Q) contribution from W4lite theory.

^l Squared correlation coefficient with the number of carbon atoms in the *n*-alkanes.

coefficient of $R^2 > 0.999$. We use this linear relationship to predict the post-CCSD(T) contributions for larger *n*-alkanes, and show that the post-CCSD(T) contribution is expected to exceed 1 kcal mol⁻¹ for systems larger than decane (C₁₀H₂₂).

2. Computational details

We obtain nonrelativistic total atomization energies (TAEs) for *n*-alkanes up to hexane using the W4lite and W4 composite procedures [2,4]. The reference geometries for these calculations were optimized at the CCSD(T)/cc-pVQZ level of theory as prescribed in the W4lite and W4 protocols. We note that throughout this work we use the so-called W4hlite and W4h versions of W4lite and W4 theories. The difference between the W_{nl}h and W_n protocols is that the diffuse functions are omitted from carbon in the SCF and valence CCSD(T) calculations [21,25]. For the hydrocarbon systems considered in the present work this approximation is of no thermochemical consequence, but computer resource requirements are substantially reduced. For the sake of simplicity, we will simply refer to these theories as W4lite and W4.

For the sake of making the article self-contained, we will briefly outline the various steps in the W4lite and W4 procedures (for further details see Refs. [2,21]). W4 theory represents a layered extrapolation to the CCSDTQ5 infinite basis-set-limit energy. The self-consistent field (SCF) energy is extrapolated from the cc-pV5Z and cc-pV6Z basis sets [26] using the Karton–Martin [27] modification of Jensen's extrapolation formula [28]. The CCSD valence correlation energy is calculated from these same basis sets. Following the suggestion of Klopper [29], the CCSD correlation energy is partitioned into singlet- and triplet-coupled pair energies, which are extrapolated separately to the infinite basis-set limit (see Ref. [2] for further details). The (T) valence correlation energy is extrapolated from the cc-pVQZ and cc-pV5Z basis sets. The higher-order connected triples, T₃ – (T), correlation contribution is extrapolated from the cc-pV_nZ basis sets (*n* = D and T). The parenthetical connected quadruple, (Q), and higher-order connected quadruple, T₄ – (Q), correlation contributions are calculated with the cc-pVTZ and cc-pVDZ basis sets, respectively. The connected quintuple, T₅, correlation contribution is calculated with the *sp* part of the cc-pVDZ basis set (denoted by DZ).

In W4lite theory, the post-CCSDT(Q) contributions are neglected altogether and the (Q) component is calculated in conjunction with the economical cc-pVDZ basis set. Nevertheless, for systems that are dominated by a single reference determinant, such as the hydrocarbons considered in the present work, W4lite gives very similar performance to W4 [4].

We also obtain the nonrelativistic TAEs for *n*-alkanes up to dodecane with the computationally efficient W1-F12 composite procedure [30]. W1-F12 theory represents a layered extrapolation to the CCSD(T)/CBS energy. The computational protocol of the W1-F12 method has been specified in Ref. [30]. In brief, the SCF energy is extrapolated from the cc-pVDZ-F12 and cc-pVTZ-F12 basis sets [31], which were developed for explicitly correlated calculations. The CCSD-F12 correlation energy is extrapolated from these same basis sets. The (T) valence correlation energy is obtained in the same way as in the original W1 theory [32], i.e., calculated with the standard CCSD(T) method and extrapolated to the basis-set limit from the aug'-cc-pVDZ and aug'-cc-pVTZ basis sets [33]. The reference geometries used in the W1-F12 calculations were optimized at the B3LYP-D3BJ/aug'-cc-pVTZ level of theory [34–37] as prescribed in the W1-F12 protocol [30].

All the CCSD(T) calculations were performed using the Molpro 2012.1 program suite [38,39]. All the post-CCSD(T) calculations were carried out with the MRCC program suite [40,41]. All the B3LYP-D3BJ geometry optimizations were carried out using the GAUSSIAN09 program suite [42].

3. Results and discussion

Table 1 gives a component breakdown of the W4 atomization energies for the homologous series of *n*-alkanes: methane, ethane, propane, butane, pentane, and hexane. As might be expected there is a high statistical correlations between the SCF, CCSD, and (T) components and the number of carbon atoms in the *n*-alkanes. For example, the squared correlation coefficients (R^2) are: 1.0000 (SCF), 1.0000 (CCSD), and 0.9998 ((T)). We note that high statistical correlations have also been observed for the SCF, CCSD, and (T) components of the TAEs in other homologous series. For example, the series of platonic hydrocarbon cages (tetrahedrane, triprismane, cubane, pentaprismane, octahedrane, and dodecahedrane) [23] and

Table 2
Component breakdown of the W1-F12 valence, nonrelativistic atomization energies for *n*-alkanes of up to dodecane (in kcal mol⁻¹).

	SCF ^a	CCSD ^a	(T) ^b	CCSD(T) ^c
CH ₄	331.51	84.58	2.92	87.51
C ₂ H ₆	557.95	146.20	6.42	152.63
C ₃ H ₈	785.30	208.83	10.16	218.98
C ₄ H ₁₀	1012.56	271.57	13.93	285.49
C ₅ H ₁₂	1239.77	334.33	17.70	352.03
C ₆ H ₁₄	1466.98	397.11	21.49	418.59
C ₇ H ₁₆	1694.20	459.89	25.27	485.16
C ₈ H ₁₈	1921.41	522.67	29.06	551.72
C ₉ H ₂₀	2148.62	585.45	32.84	618.29
C ₁₀ H ₂₂	2375.85	648.22	36.63	684.85
C ₁₁ H ₂₄	2603.07	711.00	40.41	751.41
C ₁₂ H ₂₆	2830.29	773.78	44.20	817.98
R ^{2d}	1.0000	1.0000	1.0000	1.0000

^a The SCF and valence CCSD-F12 correlation components are extrapolated from the cc-pVDZ-F12 and cc-pVDZ-F12 basis sets.

^b The valence (T) correlation component is extrapolated from the cc-pVDZ and cc-pVTZ basis sets.

^c Sum of the CCSD-F12 and (T) correlation components.

^d Squared correlation coefficient with the number of carbon atoms in the *n*-alkanes.

the series of linear polyacenes (benzene, naphthalene, anthracene, and naphthacene) [30].

What about the correlation between the SCF, CCSD, and (T) components of the TAEs and the number of carbon atoms in larger *n*-alkanes? We were able to obtain these components from W1-F12 for *n*-alkanes of up to dodecane. Table 2 lists these components of the TAEs along with the R² values. There is perfect linear correlation between these components and the number of carbons in the *n*-alkanes. Namely, for the SCF, CCSD, and (T) components we obtain R² = 1.0000.

In the present work we would like to explore the linear correlation between the post-CCSD(T) correlation components of the TAE and the number of carbon atoms in the *n*-alkanes. However, first a few comments are due on the magnitude of the post-CCSD(T) contributions. These results are shown in Table 1. The higher-order connected triple, T₃-(T), contributions universally reduce the atomization energies and range between -0.080 (CH₄) and -1.498 (C₆H₁₄) kcal mol⁻¹. The parenthetical connected quadruple contributions from W4lite theory universally increase the atomization energies and range between 0.079 (CH₄) and 0.847 (C₆H₁₄) kcal mol⁻¹. We were able to obtain the full quadruple contributions from W4 theory (i.e., including higher-order connected quadruple, T₄-(Q), contributions) for *n*-alkanes up to butane. There is reasonably good agreement between the (Q)/cc-pVDZ contributions from W4lite theory and the T₄ contributions from W4 theory (Table 1). Specifically, the T₄ values from W4lite underestimate those from W4 by 0.001 (CH₄), 0.011 (C₂H₆), 0.025 (C₃H₈), and 0.042 (C₄H₁₀) kcal mol⁻¹. It should be noted, however, that the connected quintuple, T₅, contributions further increase the gap between W4lite and W4 by 0.000 (CH₄), 0.010 (C₂H₆), 0.019 (C₃H₈), and 0.026 (C₄H₁₀) kcal mol⁻¹. Overall, W4lite theory underestimates the W4 post-CCSDT components by: 0.001 (CH₄), 0.021 (C₂H₆), 0.044 (C₃H₈), and 0.067 (C₄H₁₀) kcal mol⁻¹. Thus, it seems that these difference increase by ~0.02 kcal mol⁻¹ per each additional carbon atom in the *n*-alkane.

Let us now turn to the magnitude of the overall post-CCSD(T) contributions to the TAEs (i.e., the sum of the T₃-(T)+T₄+T₅ contributions). Table 3 lists these contributions from W4lite and W4 theories. Overall the post-CCSD(T) contributions tend to systematically decrease the TAEs. Let us begin with the W4 results. For methane there is a perfect cancelation between the T₃-(T) and T₄+T₅ components, such that the overall post-CCSD(T) contribution to the TAE is essentially zero. For ethane there is still

Table 3
Overall post-CCSD(T) contributions to the atomization energies of *n*-alkanes up to hexane from W4 and W4lite theories (in kcal mol⁻¹).

	W4lite ^a	W4 ^b
CH ₄	-0.001	0.000
C ₂ H ₆	-0.131	-0.110
C ₃ H ₈	-0.275	-0.231
C ₄ H ₁₀	-0.400	-0.332
C ₅ H ₁₂	-0.539	-0.440
C ₆ H ₁₄	-0.651	N/A
R ^{2c}	0.9991	0.9993

^a Sum of the T₃-(T)+T₄ contributions from W4lite theory.

^b Sum of the T₃-(T)+T₄+T₅ contributions from W4 theory.

^c Squared correlation coefficient with the number of carbon atoms in the *n*-alkane.

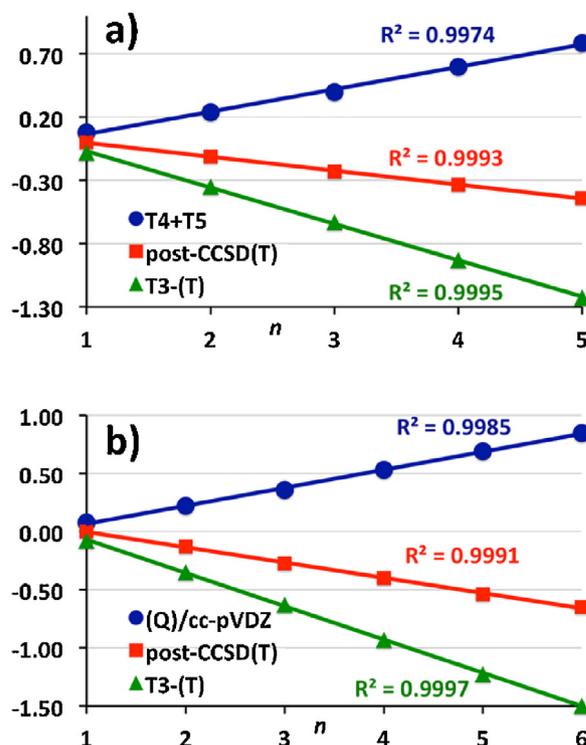


Figure 1. Linear correlation between the T₃-(T), post-CCSD(T), and post-CCSD(T) components to the TAEs (in kcal mol⁻¹) and the number of carbons in the C_nH_{2n+2} straight-chain alkanes from (a) W4 theory and (b) W4lite theory.

a very effective cancelation between the T₃-(T) and T₄+T₅ terms, namely the overall post-CCSD(T) contribution amounts to -0.110 kcal mol⁻¹. However, for propane the cancelation between the T₃-(T) and T₄+T₅ components is less effective with an overall post-CCSD(T) contribution of -0.231 kcal mol⁻¹, and this cancelation becomes less and less effective with the size of the system. The overall post-CCSD(T) contributions to the TAE are -0.332 (butane) and -0.440 (pentane) kcal mol⁻¹. In fact, there is a nearly perfect linear correlation between the magnitude of the post-CCSD(T) contributions and the number of carbon atoms in the *n*-alkane (R² = 0.9993, Table 3). This is a result of the fact that both the T₃-(T) and T₄+T₅ components correlate linearly with the number of carbon atoms (Table 1), however, the T₃-(T) contribution decreases at a faster rate than the T₄+T₅ contribution increases. This is illustrated in Figure 1a. Specifically, the overall post-CCSD(T) contribution to the TAE (in absolute value) increases by about 0.1 kcal mol⁻¹ per carbon atom.

We were able to obtain the post-CCSD(T) contributions to the TAEs from W4lite theory for *n*-alkanes of up to hexane (Table 3 and Fig. 1b). The W4lite results show that the CCSD(T)/CBS level of

Table 4

Post-CCSD(T) contributions to the atomization energies of *n*-alkanes up to dodecane estimated from the linear relationship between the CCSD(T) and post-CCSD(T) correlation components in W4lite and W4 theories (in kcal mol⁻¹).

	W4lite ^{a,c}	W4 ^{b,c}
CH ₄	-0.01	0.00
C ₂ H ₆	-0.13	-0.11
C ₃ H ₈	-0.27	-0.22
C ₄ H ₁₀	-0.40	-0.33
C ₅ H ₁₂	-0.53	-0.44
C ₆ H ₁₄	-0.66	-0.55
C ₇ H ₁₆	-0.79	-0.66
C ₈ H ₁₈	-0.92	-0.78
C ₉ H ₂₀	-1.06	-0.89
C ₁₀ H ₂₂	-1.19	-1.00
C ₁₁ H ₂₄	-1.32	-1.11
C ₁₂ H ₂₆	-1.45	-1.22

^a The linear relationship between the CCSD(T) and post-CCSD(T) correlation components is obtained from W4lite theory for *n*-alkanes up to hexane, specifically it is post-CCSD(T) = -0.00198 × CCSD(T)^{corr} + 0.16779 ($R^2 = 0.9990$).

^b The linear relationship between the CCSD(T) and post-CCSD(T) correlation components is obtained from W4 theory for *n*-alkanes up to pentane, specifically it is post-CCSD(T) = -0.00166 × CCSD(T)^{corr} + 0.14271 ($R^2 = 0.9992$).

^c The CCSD(T) correlation components used for obtaining the post-CCSD(T) correlation components for C_{*n*}H_{2*n*+2} (*n* = 1–12) are taken from W1-F12 theory (Table 2).

theory will have an error of 0.65 kcal mol⁻¹ for *n*-hexane due to the neglect of post-CCSD(T) correlation effects.

In the preceding paragraphs we have shown that the post-CCSD(T) contribution correlates linearly with the number of carbon atoms in *n*-alkanes up to hexane (Tables 1 and 3), and that the CCSD(T) correlation component correlates linearly with the number of carbon atoms in *n*-alkanes up to dodecane (Tables 1 and 2). It is instructive to see what is the correlation between the CCSD(T) and post-CCSD(T) correlation components. For *n*-alkanes up to pentane we obtain a squared correlation coefficient of $R^2 = 0.9992$ between the CCSD(T) and post-CCSD(T) correlation components from W4 theory. Whilst for *n*-alkanes up to hexane we obtain $R^2 = 0.9990$ between the CCSD(T) and post-CCSD(T) correlation components from W4lite theory. We can use these linear relationships to predict the post-CCSD(T) correlation contributions for larger *n*-alkanes using the CCSD(T) correlation component calculated from W1-F12 theory (Table 2). Table 4 gives these results for *n*-alkanes of up to dodecane (C₁₂H₂₆). We first note that, for the *n*-alkanes for which we have W4lite and W4 data, there is excellent agreement between the estimated and actual post-CCSD(T) contributions. In particular, the deviations are generally smaller than 0.01 kcal mol⁻¹ (Tables 3 and 4). We also note that the post-CCSD(T) contributions estimated from the W4lite data systematically overestimate those estimated from the W4 data (Table 4). This is consistent with the results from W4lite and W4 theories for the smaller *n*-alkanes (Table 3).

Perhaps the most striking result of Table 4 is that the overall post-CCSD(T) contribution to the TAE is expected to exceed the 1 kcal mol⁻¹ mark for systems larger than C₁₀H₂₂. According to our W4 and W1-F12 data it will reach 1.2 kcal mol⁻¹ for C₁₂H₂₆. In addition, we can estimate the magnitude of the post-CCSD(T) contribution for *n*-alkanes larger than C₁₂H₂₆ by exploiting the high statistical correlation ($R^2 = 0.9993$) between the post-CCSD(T) contribution and the number of carbons in the *n*-alkane (Table 3). From linear regression fits to the W4 data we estimate that the post-CCSD(T) contribution for icosane (C₂₀H₄₂) will exceed 2 kcal mol⁻¹.

4. Conclusions

We examine the post-CCSD(T) correlation contributions to the TAEs of straight-chain alkanes using the W4lite and W4 composite procedures. Using the more rigorous W4 theory we

obtain the following post-CCSD(T) contributions to the TAEs: 0.000 (CH₄), -0.110 (C₂H₆), -0.231 (C₃H₈), -0.332 (C₄H₁₀), and -0.440 (C₅H₁₂) kcal mol⁻¹. Whilst W4lite theory gives somewhat larger post-CCSD(T) contributions, namely: -0.001 (CH₄), -0.131 (C₂H₆), -0.275 (C₃H₈), -0.400 (C₄H₁₀), -0.539 (C₅H₁₂), and -0.651 (C₆H₁₄) kcal mol⁻¹. This gradual increase in the magnitude of the post-CCSD(T) correlation contribution is a result of a small but systematic imbalance in the rate at which the T₃ - (T) and T₄ + T₅ contributions increase with the size of the system. In particular, the T₃ - (T) contribution, which tends to decrease the TAE, increase faster with the size of the system than the T₄ + T₅ contributions, which tend to universally increase the TAE. Overall, the magnitude of the post-CCSD(T) contribution increases linearly with the size of the system, by about 0.1 kcal mol⁻¹ per each additional carbon atom. Small as this number may seem in relative terms, it means that the intrinsic error of the CCSD(T)/CBS atomization energy for decane (C₁₀H₂₂) is expected to approach ~1 kcal mol⁻¹, and ~2 kcal mol⁻¹ for icosane (C₂₀H₄₂). These results are surprising since *n*-alkanes are dominated by a single reference determinant and it is generally accepted that the CCSD(T)/CBS method should give atomization energies within chemical accuracy for these systems (i.e., with deviations below 1 kcal mol⁻¹ from FCI/CBS reference values).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cpl.2015.12.048.

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