PHYSICAL REVIEW A **86**, 022526 (2012)

Ab initio studies of electron correlation effects in heavier closed-shell atoms: Structure of the all-electron correlation energies of Zn^{2+} and Zn

Karol Jankowski
Faculty of Physics, Astronomy, and Informatics, Nicolaus Copernicus University, 87-100 Toruń, Poland

Kirk A. Peterson
Department of Chemistry, Washington State University, Pullman, Washington 99164-4630, USA

(Received 9 July 2012; published 31 August 2012)

To provide reliable reference results for various components of the electron correlation energies of Zn^{2+} and Zn, which play a similar role for $3d$-electron systems as Ne and Mg do for lighter atoms, we have performed extensive calculations of the all-electron correlation energy and of its various components with several state-of-the-art *ab initio* techniques. Two pairs of basis-set sequences that systematically converge to the complete basis set (CBS) limit have been employed in the calculations. One pair [cc-pVnZ and aug-cc-pVnZ (correlation consistent polarized valence n-zeta and augmented cc-pVnZ with $n =$ D, T, Q, 5, $6(-k)$)] is oriented towards the description of valence electron correlation. The second pair of sequences [cc-pCCVnZ and aug-cc-pCCVnZ (core core-valence n-zeta, with $n =$ D, T, Q, 5, $6(-k)$)] is developed for the description of all-electron correlation effects. The correlation energies have been determined with second-order Møller-Plesset perturbation theory (MP2) and several single-reference coupled-cluster (CC) methods. The present correlation energies represent accurate post-MP2 correlation energies for closed-shell atoms including $3d$ electrons both at the all-electron and subshell levels and should be useful benchmark results for various transitions. We have also employed the present results for assessments of the focal-point approximation (FPA), broadly used in approximations of difference correlation effects for molecular interaction problems, in applications aiming at estimating correlation effects in heavier atoms. Our results indicate that for the systems considered, the magnitudes of the MP2 correlation energies overestimate the magnitudes of the CC values for all electrons correlated as well as of their various subsets. For the all-electron correlation energies of the Zn atom, our result confirms the finding of S. P. McCarthy and A. J. Thakkar [J. Chem. Phys. **134**, 044102 (2011)] obtained by means of non–*ab initio* approaches for all heavy closed-shell atoms from Zn to Rn. We have shown that for both Zn^{2+} and Zn this overestimation is directly caused by the presence of the $3d^{10}$ electron configuration.

DOI: 10.1103/PhysRevA.86.022526 PACS number(s): 31.15.ve

I. INTRODUCTION

Within the Schrödinger formulation of quantum mechanics, the problem of accurately describing the electronic structure of the ground state of atomic systems (neutral and ionic) has always played an important methodological role. Let us just mention that beginning with the pioneering work of Hylleraas, most of the presently used categories of quantum chemistry *ab initio* methods have been developed and/or assessed in applications to those systems. This is especially true for methods accounting for *electron correlation effects*, i.e., yielding results of higher accuracy than the one-electron Hartree-Fock (HF) types. From the general methodological point of view, of special interest is the subset of closed-shell atomic systems. The theoretical description of those, being the simplest for the set of atoms of a similar size, might provide the possibility of discovering interesting features of the electronic structure that are hidden in open-shell atoms. Moreover, since the beginning of quantum theory, closed-shell atoms have been broadly used for testing new computational techniques.

One would expect that due to simplifications afforded by the spherical symmetry of atomic systems, very accurate, variational *ab initio* total nonrelativistic energies are available for relatively heavy atoms. Unfortunately, due to the barrier of computational costs and to the lack of efficient, atomic-oriented computer codes, the situation is far from being optimistic. Very accurate variational wave functions and energies, which provide upper bounds to the exact nonrelativistic energies, are available for atomic systems containing just up to four electrons (for details and references, see Refs. [1–3]). Recently, results of similar quality have also been obtained by Bunge and Carbó-Dorca for the Ne atom (see the last row in Table I of Ref. [4]). For larger systems, the accuracy of available variational energies drops rapidly as the number of electrons increases, e.g., for Mg and Ar the results represent 93.3% [5] and 90.9% of the exact correlation energy, respectively. Ar is largest system for which all-electron variational calculations based on a reasonably complete basis set have been performed. For closed-shell atoms containing up to 12 electrons, there have been several nonvariational studies carried out based on various versions of the coupled-cluster (CC) method (see, e.g., Ref. [6]). They resulted in benchmark results that are more accurate than the variational ones; e.g., for Ne Müller *et al*. [7] and Gdanitz [8] obtained about 99.7% of the correlation energy, whereas for Mg Malinowski *et al*. [9] obtained 98.9% of this quantity. For Ne Barnes *et al*. [10] have reached the complete basis set (CBS) limit at the coupled-cluster with single, double, and perturbative triple excitations [CCSD(T)] level of theory.

During the last 40 years, there have been several ingenious attempts to get information about the magnitude and structure of the electron correlation energies from atomic experimental data. The most extensive effort to estimate the "experimental" correlation energies has been undertaken by Davidson, Fischer, Chakravorty, and collaborators [11–13]. When using spectroscopic data corrected for relativistic effects, these authors extracted accurate correlation energies for atomic systems with 3 to 18 electrons for $3 \leqslant Z \leqslant 28$. It seems to us that, in the nearest future, obtaining such experimental correlation energies for atoms containing considerably more than 18 electrons, e.g., for transition metals (TM) containing $3d$ electrons, would be a very difficult if not impossible endeavor. This situation is caused not only by the lack of the enormous amount of relevant spectroscopic data required but also by the fact that for large nuclear charges the description of the innermost electron shells might require considering higher-order quantum electrodynamics (QED) terms (see, e.g., Ref. [14]).

Due to the lack of both *ab initio* and experimental correlation energies, the only way to facilitate some access to information about the structure of the electron correlation effects in atoms heavier than Ar is provided by second-order Møller-Plesset perturbation theory (MP2). In the last two decades, very accurate MP2 energies for closed-shell atoms, including the heaviest noble-gas atom Rn, have been obtained by Flores *et al.* by means of computations based on a p-version finite-element method (FEM) (for references, see Refs. [15–17]). This method combines the high reliability of the results in the radial sense with the use of virtual orbitals of very high angular momentum (up to $\ell_{\max} = 12$). Moreover, these results can be further refined by extrapolation methods based on asymptotic expansions whose leading terms take the form of simple integrals involving HF orbitals (for details, see Ref. [18]). Therefore, the MP2-FEM energies may be considered as practically basis-set independent. Mention should be made that for 10- and 18-electron systems, the MP2-FEM method furnishes all-electron correlation energies close to their experimental counterparts [13]; that is, for members of the Ne-isoelectronic series with $9 \leqslant Z \leqslant 28$, they agree to within 99.18% and 99.91% of the latter ones, whereas for Ar-like systems the agreement is between 98.24% and 100.56%.

For a long time the significance of the MP2 results as a useful hint for getting an idea about the magnitude of the all-electron correlation energies in heavy atoms has been further strengthened by the empirical finding that in all *ab initio* calculations for atoms and molecules, the magnitudes of the MP2 energies approach the exact energies from above. However, very recently, McCarthy and Thakkar, using arguments not based on systematic *ab initio* studies (for details, see Ref. [19]), have arrived at the conclusion that for heavy closed-shell atoms, from Zn to Rn, this empirical finding is no longer valid.

Since for closed-shell atoms heavier than Ar no *ab initio* or experimental benchmark correlation energies have been obtained so far, we are at a disadvantage in learning about the electronic structures of heavier atoms, especially in how they differ from those of the light atoms. Let us have a look at these differences for the Zn^{2+} and Zn systems, which are the objects of this study. One source of these differences is due to the increased number of electrons located in small regions and the strongly inhomogeneous charge distribution induced by the shell structure of the electron density. As indicated by Sarsa *et al.* [20], this complex electronic structure hinders for Zn and other TM systems obtaining, by means of quantum Monte Carlo (QMC) methods, energies of an accuracy similar to that attained for lighter atoms. Let us just mention that, for very small atoms, to obtain very accurate QMC energies, trial functions yielding about 99% of the correlation energy have been employed. Another source of the differences considered can be illustrated within the framework of the MP2 method. For atomic systems including up to 12 electrons, the MP2 energy can be represented as a sum of singlet and triplet spin-and-orbital symmetry-adapted pair energies, whose leading terms in the asymptotic expansions are proportional to $(\ell + 1/2)^{-4}$ and $(\ell + 1/2)^{-6}$, respectively. However, for heavier atoms we have, additionally, to consider the unnatural-parity singlet pairs identified by Kutzelnigg and Morgan [21] for the excited states of two-electron atoms. Their pair energies are small when compared with the former pairs, and the leading term in the asymptotic expansion of the pair energy is proportional to $(\ell + 1/2)^{-8}$ (for details, see Ref. [18]). Let us mention that in Ar and Zn we have to deal just with one and three such pairs, respectively. However, their number increases significantly when proceeding to heavier atoms.

TABLE I. Configurational MP2 pair energies for Ar, Zn^{2+}, Ca, and Zn [in millihartrees (mE_h), with signs reversed].

Configurational pair	Ar[a]	Zn^{2+}[b]	Ca[a]	Zn[a]
$3s^2$	10.95	6.22	11.14	6.07
$3s3p$	63.83	42.80	61.91	41.97
$3p^2$	179.79	78.92	199.89	79.03
Total	254.57	127.94	272.94	127.07

[a] From Ref. [16].
[b] From Ref. [26].

To finalize this discussion on the expected differences between the correlation effects in light and heavier atoms, let us have a look at the reconstruction of the correlation energies of the $3s^23p^6$ outer electrons of the "largest" light atoms, represented by Ar and Ca, caused by adding the $3d^{10}$ configuration present in the M shell of the "smallest" heavy atoms, represented by Zn^{2+} and Zn. Table I presents the MP2-FEM configurational pair energies for the atoms considered. The addition of the $3d^{10}$ set of electrons results in a dramatic reduction of the $3s^23p^6$ correlation energy compared to either Ar or Ca. This reduction is most pronounced for the $3p$ electrons, where it amounts to about 56% and 60% for Ar and Ca, respectively. These results are a clear demonstration of the large impact of the inclusion of the $3d^{10}$ electrons, which are present in all heavy closed-shell atoms. Let us just mention that a very similar impact of including the $4d^{10}$ can be observed when comparing the configurational pair energies for the $4s^24p^6$ configuration in Sr and Cd (see Table 13 in Ref. [16]).

We realize that for the heavier atoms, all-electron results obtained within the framework of the Schrödinger quantum mechanics are mainly of methodological significance. However, even at this theoretical level we have to deal with very interesting complex model systems containing many electrons in a spherical-symmetric volume. Efforts invested in a better understanding of these systems will certainly be rewarded in projects aiming to develop reliable broadly applicable many-electron theories, such as new formulations, as well as reliable approximate versions of the traditional quantum chemical *ab initio* techniques. Moreover, they may play a crucial role in the evaluation of new quasirelativistic, pseudopotential or density-functional methods. In addition to these applications the systems considered provide nontrivial testing opportunities for various extrapolation procedures, such as the CBS ones. It seems to us that the information gained in studies of heavier closed-shell atoms may contribute to overcoming some of the difficulties encountered by the rapidly developing QMC techniques, representing a potentially very powerful *ab initio*–type alternative to the traditional, orbital-based approaches.

In this study we are concerned with the ground states of the Zn^{2+} and Zn atoms, which may be considered the simplest elements of the series of heavy closed-shell atomic systems. This classification seems to be justified by the fact that they are the first elements to contain the $3d^{10}$ electron configuration. Like for the other members of the series, no *ab initio* or experimental benchmark correlation energies have been published so far. The reason why we consider the Zn^{2+} ion along with the Zn atom is that the former system has a perfectly closed electron configuration and is the first to have the closed *M* shell. Hence, from the methodological point of view, this ion may be considered as the heavy-atom counterpart of the Ne atom, which is the first to have a closed *L* shell. Due to the perfect closed-shell structure of the ground state of Zn^{2+}, the energies obtained for this system are not affected by quasidegeneracy effects.

The goal of this article is to present the results of post-MP2 *ab initio* studies of the structure of electron correlation energies in closed-shell atoms containing the $3d^{10}$ configuration. Although special attention is paid to the correlation effects for the valence electrons, we systematically proceed to the inner shells up to the *K* shell, i.e., to the case of the all-electron correlation. Accurate results for the correlation energies at all these levels provide guidance for the evaluation of the performance of various approximate methods. The energies are obtained by means of state-of-the-art *ab initio* methods, including the MP2, CC doubles (CCD), coupled-cluster theory with single and double excitations (CCSD), CCSD(T), CCSD with full iterative triples (CCSDT), CCSDT with perturbative quadruples [CCSDT(Q)], and CCSDT with full iterative quadruples (CCSDTQ) methods. The quality of the results is secured by the use of a series of extensive correlation-consistent basis sets optimized in this work that are capable of systematic convergence towards the CBS limits. We report both the directly computed and the extrapolated correlation energies, which might be useful for comparisons with the results of other types of methods.

The structure of this article is as follows: In Sec. II we restate for reference a cursory summary of the approaches used in this work. Section III is devoted to the presentation of the calculated and extrapolated correlation energies. We start with a discussion of these effects for the outermost electronic shells. Next, we correlate the *L*-shell electrons, and finally, we consider the all-electron correlation effects. Finally, in the last section we summarize the conclusions that can be drawn from this study.

II. METHODOLOGY

In order to provide systematic convergence towards the CBS limits for each method and correlation space, correlation-consistent basis sets were used throughout the present work. In

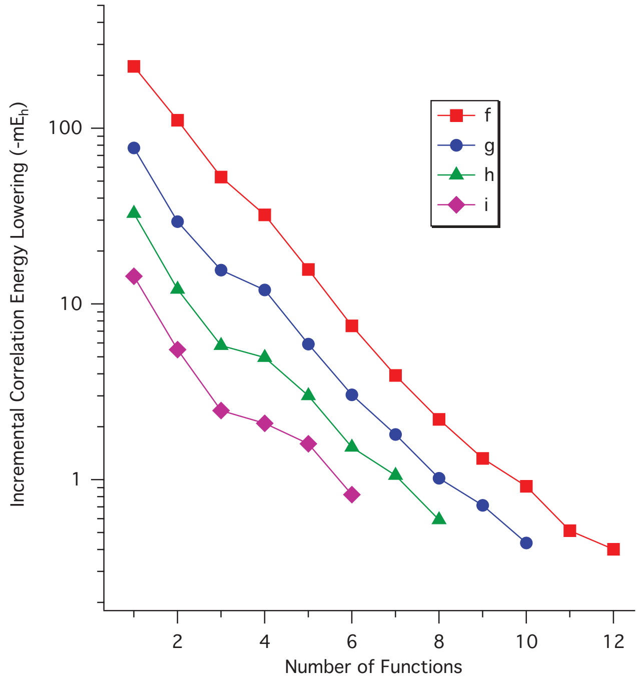

FIG. 1. (Color online) Incremental contributions of correlating functions to the all-electron MP2 correlation energy of the Zn atom.

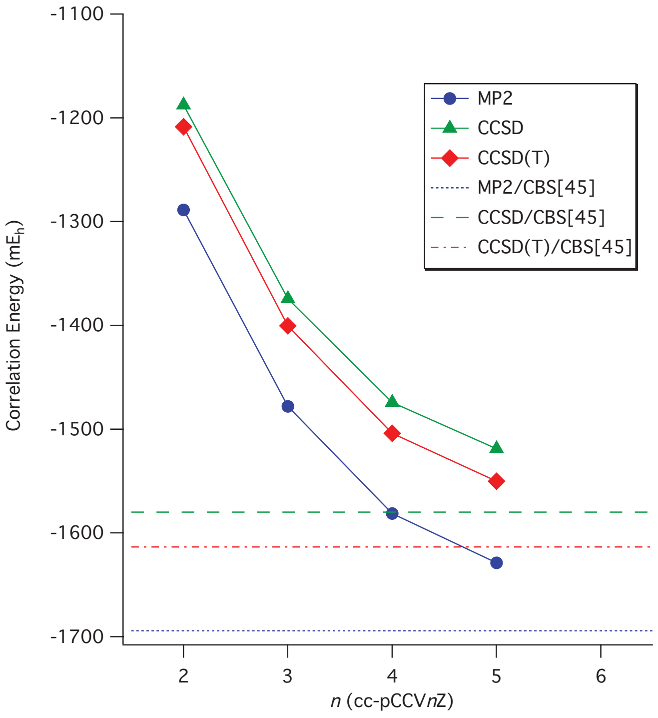

FIG. 2. (Color online) Convergence of the all-electron correlation energy of the Zn atom as a function of the cardinal number of the cc-pCCVnZ basis sets.

TABLE II. Calculated and extrapolated MP2, CCD, CCSD, and CCSD(T) valence correlation energies for the $3d^{10}$ configuration of Zn^{2+} (in millihartrees, with signs reversed).

	CBS	MP2		CCD		CCSD		CCSD(T)	
n	extrapolation	V*n*Z	CCV*n*Z	V*n*Z	CCV*n*Z	V*n*Z	CCV*n*Z	V*n*Z	CCV*n*Z
2		371.460	420.599	335.050	379.965	336.058	381.002	339.610	388.844
3		434.127	462.331	392.692	417.407	393.704	418.469	402.512	428.946
4		469.868	483.756	424.550	436.475	425.549	437.467	436.531	449.065
5		486.020	493.300	438.399	444.478	439.387	445.453	451.143	457.458
6(−*k*)		492.133	495.483	443.384	446.137	444.372	447.119	456.392	459.237
	CBS[3,4]	507.367	506.235	457.975	456.481	458.960	457.399	472.223	470.173
	CBS[4,5]	508.207	506.410	457.422	455.471	458.395	456.423	471.214	468.988
	CBS, est.[a]			456(2)		457(2)		470(2)	
	FPA[2]			470.608	466.384	471.616	467.421	475.168	475.263
	FPA[3]			465.583	462.094	466.595	463.156	475.403	473.633
	FPA[4]			461.700	459.737	462.699	460.729	473.681	472.327
	FPA[5]			459.397	458.196	460.385	459.171	472.141	471.176
	FPA[6]			458.269	457.672	459.257	458.654	471.277	470.772
aug-2		380.090	428.978	342.317	386.686	343.462	387.984	348.943	397.424
aug-3		443.841	466.765	400.707	420.813	401.857	421.996	412.089	433.276
aug-4		474.017	486.471	427.778	438.472	428.822	439.516	440.204	451.403
aug-5		488.004	494.722	439.827	445.411	440.829	446.410	452.712	458.528
aug-6(−*k*)		492.587	495.987	443.650	446.426	444.647	447.420	456.699	459.579
	CBS[3,4]	505.678	507.146	456.180	456.999	457.113	457.898	469.702	470.421
	CBS[4,5]	507.218	506.056	456.378	454.943	457.322	455.880	469.893	468.316
	CBS, est.[a]			456(2)		457(2)		469(2)	
	FPA[2]			469.245	464.726	470.390	466.024	475.871	475.464
	FPA[3]			463.884	461.066	465.034	462.249	475.266	473.529
	FPA[4]			460.779	459.019	461.823	460.063	473.205	471.950
	FPA[5]			458.841	457.707	459.843	458.706	471.726	470.824
	FPA[6]			458.081	457.457	459.078	458.451	471.130	470.610
Reference MP2[b]		507.037							

[a] Best estimates as the average of V*n*Z and CCV*n*Z CBS[4,5] results, with estimated uncertainties in the last digit given in parentheses.

[b] As reported in Ref. [26].

the case of frozen-core, valence electron correlation ($3d^{10}$ for Zn^{+2} and $3d^{10}4s^2$ for Zn) these included the standard cc-pV*n*Z and aug-cc-pV*n*Z (correlation consistent polarized valence *n*-zeta and augmented cc-pV*n*Z with $n = $ D, T, Q, 5) basis sets of Balabanov and Peterson [22,23]. For the correlation of the core electrons, however, these basis sets are not appropriate, and new sets of correlating functions were optimized for Zn based on the MP2 correlation energy with all electrons correlated. (It should be noted that the existing weighted core-valence cc-pwCV*n*Z basis sets are not designed to yield accurate total correlation energies even for the outer-core electrons since they are not well optimized for the intrashell, core-core correlation energy.) In order to determine the composition of these new basis sets, which will be denoted in this work by cc-pCCV*n*Z, the incremental correlation energy lowerings for Zn atom were determined at the MP2 level of theory as a function of adding sequences of optimized Gaussian functions with f, g, h, and i angular momenta. The *spd* part of the uncontracted cc-pVQZ basis set was used for these optimizations, and the exponents were constrained to follow an even-tempered prescription, i.e., for m exponents $\alpha_i = \alpha_1 \beta^{i-1}$ for $i = 1,m$. The results are shown in Fig. 1.

The convergence is fairly regular for each angular momentum; however, there is a noticeable change in convergence in each case when the fourth function is added. This is presumably just a byproduct of the even-tempered constraint as well as the general problem of optimizing a single set of exponents for the correlation of very spatially separated electron pairs, e.g., $1s^2$ and $4s^2$. Obviously, from the results shown in Fig. 1 there are a number of different schemes that could be used to construct a series of convergent basis sets. In the interest of keeping some of the flavor of the standard correlation-consistent basis sets, the following compositions were chosen for this work: (i) cc-pCCVDZ, uncontracted (*spd*) from cc-pVDZ + 2*f*; (ii) cc-pCCVTZ, uncontracted (*spd*) from cc-pVTZ + 4*f*2*g*; (iii) cc-pCCVQZ, uncontracted (*spd*) from cc-pVQZ + 6*f*4*g*2*h*; (iv) cc-pCCV5Z, uncontracted (*spd*) from cc-pV5Z + 8*f*6*g*4*h*2*i*; and (v) cc-pCCV6Z(-*k*), uncontracted (*spd*) from cc-pV5Z + 10*f*8*g*6*h*4*i*.

For the 6Z case the required *k*-type functions were not included since they are not supported in the MOLPRO program. In addition, a cc-pV6Z(−*k*) set was optimized using the Hartree-Fock *spd* primitives sets from cc-pV5Z, contracting these to [9*s*8*p*6*d*], and adding a set of

TABLE III. Calculated and extrapolated MP2, CCD, CCSD, and CCSD(T) valence correlation energies for the $3d^{10}4s^2$ configuration of Zn (in millihartrees, with signs reversed).

n	CBS extrapolated	MP2		CCSD		CCSD(T)	
		V*n*Z	CCV*n*Z	V*n*Z	CCV*n*Z	V*n*Z	CCV*n*Z
2		441.918	491.657	407.540	452.629	416.218	466.188
3		509.788	541.742	468.833	496.474	483.719	513.605
4		553.657	569.212	506.954	520.169	525.392	539.609
5		573.473	581.422	523.759	530.247	543.824	550.712
6(−*k*)		581.495		530.110		550.804	
	CBS[3,4]	599.683	598.033	546.950	545.029	569.116	566.892
	CBS[4,5]	600.693	598.194	546.843	544.090	569.142	565.963
	CBS, est.[a]			545(3)		568(3)	
	FPA[2]			564.95	560.29	573.62	573.85
	FPA[3]			558.36	554.05	573.25	571.18
	FPA[4]			552.62	550.28	571.06	569.72
	FPA[5]			549.61	548.15	569.67	568.61
	FPA[6]			547.94		568.63	
aug-2		461.923	513.511	424.223	470.385	436.461	487.358
aug-3		529.507	554.783	485.121	506.925	503.217	526.644
aug-4		562.793	576.201	514.216	525.442	534.155	546.053
aug-5		578.256	585.414	527.024	532.842	547.688	553.810
aug-6(−*k*)		583.591		531.184		552.093	
	CBS[3,4]	597.715	598.672	544.742	544.870	566.615	566.417
	CBS[4,5]	599.496	598.069	544.617	543.007	566.277	564.465
	CBS, est.[a]			544(2)		565(2)	
	FPA[2]			561.62	556.19	573.86	573.17
	FPA[3]			554.94	551.46	573.03	571.18
	FPA[4]			550.75	548.56	570.69	569.17
	FPA[5]			548.09	546.75	568.76	567.72
	FPA[6]			546.92		567.83	
Reference MP2[b]		599.32					

[a] Best estimates as the average of V*n*Z and CCV*n*Z CBS[4,5] results, with estimated uncertainties in the last digit given in parentheses.
[b] Reference [27].

optimized $5f4g3h2i$ correlating functions. Analogous to the standard cc-pV5Z set, the $5s5p5d$ set of correlating functions corresponded to atomic natural orbital (ANO) contractions from the singles and doubles configuration interaction (CISD) calculations.

In the valence correlation studies below, diffuse augmented versions of the cc-pCCV*n*Z sets were also used in which a single diffuse function in each angular momentum was added, with the exponent determined from the cc-pCCV*n*Z set by a simple even-tempered extension of the most diffuse exponent. In order to provide estimates of the CBS limits in each case, the correlation energies were extrapolated using the two-point formula of Helgaker *et al.* [24,25] as a function of the maximum angular momentum in each set ($\ell_{\max}$),

$$E^{\text{corr}}(\ell_{\max}) = E^{\text{corr}}_{\text{CBS}} + A\ell_{\max}^{-3}. \qquad (1)$$

The effectiveness of this CBS extrapolation formula will be assessed in the next section in part by comparing the MP2 limits obtained using TZ and QZ basis sets, CBS[3,4], as well as those from QZ and 5Z basis sets, CBS[4,5], to their very accurate MP2-FEM counterparts [26,27].

The convergence of the all-electron correlation energy in Zn atom towards the estimated CBS limit is shown in Fig. 2 as a function of the cardinal number (2–5) of the cc-pCCV*n*Z basis sets for the MP2, CCSD, and CCSD(T) levels of theory. Very regular convergence is observed in each case.

With the determination of CBS limits at the CCSD(T) level of theory, it is also of interest to investigate the utility of the focal-point analysis (FPA) of Allen *et al.* [28,29] to estimate the CCSD(T)-CBS limit correlation energies through combining MP2-CBS limits and finite basis set MP2 and CCSD(T) calculations, i.e.,

$$E^{\text{CBS}}_{\text{CCSD(T)}} \simeq E^{S\text{-basis}}_{\text{CCSD(T)}} + \left(E^{\text{CBS}}_{\text{MP2}} - E^{S\text{-basis}}_{\text{MP2}}\right), \qquad (2)$$

where *S*-basis denotes a particular cc-pV*n*Z or cc-pCCV*n*Z basis set and the benchmark MP2-FEM energies are used for $E^{\text{CBS}}_{\text{MP2}}$ in all cases. Generally, this approach is used to increase the accuracy of calculated differential correlation effects on various thermochemical predictions (see, e.g., Refs. [30–33]), so it is not *a priori* clear if it will perform well for total energies. All of the calculations of the present work utilized the MOLPRO suite of *ab initio* programs [34], except for coupled-cluster

TABLE IV. CCSD(T), CCSDT, CCSDT(Q), and CCSDTQ valence correlation energies for the $3d^{10}$ and $3d^{10}4s^2$ configurations of Zn^{2+} and Zn, respectively, calculated with cc-pV*n*Z basis sets together with their extrapolated CBS limits (in millihartrees, with signs reversed).

	CBS	CCSD(T)		CCSDT		CCSDT(Q)		CCSDTQ	
n	extrapolated	Zn^{2+}	Zn	Zn^{2+}	Zn	Zn^{2+}	Zn	Zn^{2+}	Zn
2		339.610	416.218	339.392	415.846	339.729	416.072	339.700	416.168
3		402.512	483.719	401.814	482.645	401.745	482.481	401.803	482.693
4		436.531	525.392	435.536	523.848	435.483	523.667	435.569	523.943
5		451.143	543.824	450.032	542.047	449.997	541.908		
6(−*k*)		456.392	550.804	455.226	548.920				
	CBS[3,4]	472.223	569.116	470.917	567.076	470.880	566.878	470.995	567.221
	CBS[4,5]	471.214	569.142	469.944	567.047	469.933	566.965		
aug-2		348.943	436.461	348.502	435.736	348.733	435.723	348.737	435.915
aug-3		412.089	503.217	411.197	501.784	411.113	501.508	411.193	501.799
aug-4		440.204	534.155	439.130	532.416	439.089	532.255		
aug-5		452.712	547.688	451.566	545.819	451.532	545.704		
aug-6(−*k*)		456.699	552.093	455.519	550.159				
	CBS[3,4]	469.702	566.615	468.438	564.555	468.441	564.515		
	CBS[4,5]	469.893	566.277	468.648	564.231	468.624	564.177		
	CBS, est.[a]	469(2)	565(2)						
	CBS	(T)		T−(T)		(Q)−T		Q−T	
n	extrapolated	Zn^{2+}	Zn	Zn^{2+}	Zn	Zn^{2+}	Zn	Zn^{2+}	Zn
2		3.552	8.678	−0.218	−0.372	0.338	0.226	0.308	0.322
3		8.808	14.885	−0.698	−1.073	−0.069	−0.164	−0.011	0.048
4		10.982	18.438	−0.995	−1.545	−0.053	−0.181	0.032	0.095
5		11.756	20.065	−1.111	−1.777	−0.035	−0.139		
6(−*k*)		12.020	20.694	−1.166	−1.884				
	CBS[3,4]	13.263	22.166	−1.306	−2.040	−0.037	−0.198	0.078	0.144
	CBS[4,5]	12.819	22.300	−1.271	−2.096	−0.011	−0.082		
aug-2		5.481	12.238	−0.441	−0.725	0.231	−0.013	0.235	0.178
aug-3		10.232	18.096	−0.892	−1.433	−0.083	−0.276	−0.004	0.016
aug-4		11.382	19.939	−1.074	−1.739	−0.041	−0.161		
aug-5		11.883	20.664	−1.146	−1.869	−0.034	−0.115		
aug-6(−*k*)		12.052	20.909	−1.180	−1.934				
	CBS[3,4]	12.589	21.873	−1.264	−2.060	0.003	−0.039		
	CBS[4,5]	12.571	21.660	−1.245	−2.046	−0.024	−0.053		
	CBS, est.[b]	12.6(3)	21.7(5)	−1.25(2)	−2.05(2)	−0.02(1)	−0.05(3)		

[a] Best estimates; see Table III.

[b] Best estimates obtained from CBS[4,5] using aug basis sets, with estimated uncertainties in the last digit given in parentheses.

calculations beyond CCSD(T), i.e., CCSDT, CCSDT(Q), and CCSDTQ, which employed the MRCC program [35,36] as interfaced with MOLPRO.

III. RESULTS AND DISCUSSION

The convergence of the valence correlation energy with respect to basis set is shown in Tables II and III for Zn^{+2} and Zn, respectively, for both MP2 and coupled-cluster methods. For the basis sets considered, the MP2 energies corresponding to the highest cardinal numbers X represent from 97.06% to 97.82% of the MP2-FEM reference energy, which is an indication of the rather good saturation of the bases employed. The differences between the use of the standard cc-pV*n*Z versus the more extensive cc-pCCV*n*Z sets are very similar for both atoms. At the DZ level the cc-pCCVDZ correlation energies are about 50 millihartrees (mE_h) lower than cc-pVDZ. At the 5Z level, however, this difference decreases to only about 6–7 mE_h. The resulting CBS limits differ by just 1–2 mE_h, with the cc-pV*n*Z series yielding lower correlation energies than cc-pCCV*n*Z. The lone exceptions are the CBS[3,4] results obtained from the diffuse augmented sequences of basis sets where the standard sets yield less negative CBS[3,4] values. Upon comparison of the MP2-CBS[4,5] limits to the accurate MP2-FEM values, the latter lies nearly midway between the cc-pV*n*Z and cc-pCCV*n*Z results and is within a few tenths of a mE_h of the CBS[4,5] value obtained using the aug-cc-pV*n*Z series of basis sets. The presence of diffuse functions tends to decrease the magnitude of the CBS[4,5] values obtained in the V*n*Z sequence by about a mE_h. The CCV*n*Z series is a little less sensitive to this. Overall, there is a bit more scatter between the CBS[3,4] values, but these are still generally within about 1 mE_h of the numerical limit. At least when looking at the CBS[4,5]

TABLE V. Calculated (for cc-pCCVnZ basis sets) and extrapolated MP2 and coupled-cluster correlation energies for the M, LM, and KLM shells of Zn^{2+} and the $M4s^2$, $LM4s^2$, and $KLM4s^2$ shells of Zn (in millihartrees, with signs reversed).

n	CBS extrapolated	MP2		CCD	CCSD		CCSD(T)	
		Zn^{2+}	Zn	Zn^{2+}	Zn^{2+}	Zn	Zn^{2+}	Zn
				M or $M4s^2$ shell ($3s3p3d4s$)				
2		802.469	878.571	711.604	714.683	787.281	727.348	806.737
3		917.282	1001.803	826.183	829.011	907.809	845.301	931.908
4		976.244	1066.955	883.805	886.358	969.953	904.630	997.350
5		1005.232	1098.670	910.841	913.255	998.968	932.332	1027.856
	CBS[3,4]	1038.106	1135.311	944.261	946.525	1035.153	966.876	1066.010
	CBS[4,5]	1045.051	1142.235	947.978	950.201	1038.824	970.384	1069.76
	CBS, est.[a]			950(3)	952(3)	1041(3)	972(3)	1072(3)
	FPA[2]			955.802	958.881	1053.14	971.546	1072.60
	FPA[3]			955.568	958.396	1050.44	974.686	1074.54
	FPA[4]			954.228	956.781	1047.43	975.053	1074.83
	FPA[5]			952.276	954.690	1044.73	−973.767	1073.62
Reference MP2[a]		1046.887	1144.43					
				LM or $LM4s^2$ shell ($2s2p3s3p3d4s$)				
2		1138.241	1214.378	1037.568	1040.853	1113.270	1054.749	1134.135
3		1317.904	1402.313	1217.015	1220.214	1298.604	1238.315	1324.720
4		1409.582	1500.134	1307.199	1310.187	1393.280	1330.504	1422.948
5		1452.307	1545.562	1347.610	1350.491	1435.654	1371.706	1466.913
	CBS[3,4]	1505.769	1602.766	1401.818	1404.585	1492.612	1427.227	1526.007
	CBS[4,5]	1510.995	1607.963	1403.120	1405.854	1493.860	1428.302	1527.304
	CBS, est.[a]			1404(3)	1407(3)	1495(3)	1430(3)	1529(3)
	FPA[2]			1411.289	1414.574	1508.42	1428.470	1529.29
	FPA[3]			1411.073	1414.272	1505.82	1432.373	1531.94
	FPA[4]			1409.579	1412.567	1502.68	1432.884	1532.34
	FPA[5]			1407.265	1410.146	1499.62	1431.361	1530.88
Reference MP2[a]		1512.241	1609.53					
				All-electron correlation ($1s2s2p3s3p3d4s$)				
2		1212.626	1288.747	1111.875	1115.169	1187.565	1129.124	1208.496
3		1393.715	1478.105	1292.734	1295.942	1374.309	1314.112	1400.500
4		1490.701	1581.236	1388.234	1391.234	1474.305	1411.627	1504.056
5		1535.580	1628.818	1430.785	1433.679	1518.820	1454.973	1550.166
	CBS[3,4]	1592.457	1689.439	1488.431	1491.212	1579.219	1513.937	1612.705
	CBS[4,5]	1597.227	1694.178	1489.234	1491.983	1579.967	1514.516	1613.504
	CBS, est.[b]			1492(4)	1495(4)	1583(4)	1517(4)	1617(4)
	FPA[2]			1499.152	1502.446	1596.28	1516.401	1617.21
	FPA[3]			1498.922	1502.130	1593.66	1520.300	1619.86
	FPA[4]			1497.436	1500.436	1590.53	1520.829	1620.28
	FPA[5]			1495.108	1498.002	1587.46	1519.296	1618.81
Reference MP2[c]		1600.187	1697.46					

[a] Best estimates calculated as CBS[4,5] plus the difference between MP2-CBS[4,5] and the reference MP2 values. Estimated uncertainties in the last digit are given in parentheses.

[b] Best estimates calculated as CBS[4,5] plus the difference between MP2-CBS[4,5] and the reference MP2 values. Estimated uncertainties in the last digit are given in parentheses.

[c] Zn^{2+}: Ref. [26]; Zn: Ref. [27].

values, the results for the coupled-cluster methods shown in Tables II and III mimic those at the MP2 level, although the effect of diffuse functions in the VnZ series is about twice as large as at the MP2 level in the neutral atom. Taken together, one can make somewhat conservative CCSD-CBS limit predictions of 457(2) and 544(2) mE_h for Zn^{+2} and Zn, respectively, and CCSD(T)-CBS limits of 469(2) and 565(2) mE_h for Zn^{+2} and Zn, respectively (estimated uncertainties in the last digit are given in parentheses). An excellent test of these results would be to employ large basis-set explicitly correlated F12 calculations (see, e.g., Ref. [37] and references therein) to these systems to obtain more definitive CBS limits. Unfortunately, for an atom with correlated d electrons, even a QZ quality orbital basis set would require k-type functions

TABLE VI. Calculated (for the cc-pCCVnZ basis set) and extrapolated MP2, CCSD, and CCSD(T) energies for correlating the $3s$ and $3p$ electrons of Zn^{2+} with the $3d$ electrons treated as core (in millihartrees, with signs reversed).

n	CBS extrapolated	MP2	CCSD	CCSD(T)
3		106.345	111.233	111.480
4		115.585	120.249	120.524
5		120.205	124.477	124.766
	CBS[3,4]	125.279	129.708	130.013
	CBS[4,5]	126.551	130.285	130.593
	CBS, est.[a]		132(2)	132(2)
	FPA[3]		132.828	133.075
	FPA[4]		132.604	132.879
	FPA[5]		132.212	132.501
	Reference MP2[b]	127.940		

[a] Best estimates calculated as CBS[4,5] plus the difference between MP2-CBS[4,5] and the reference MP2 value. Estimated uncertainties in the last digit are given in parentheses.

[b] Computed by Flores *et al.* [26].

in the auxiliary basis set for an accurate correlation energy, which is not possible with the present version of the MOLPRO program.

There are two other general trends that are apparent in the results shown in Tables II and III. One is that the MP2 correlation energy is clearly lower than either the CCSD or CCSD(T) correlation energies. In addition, comparison of the CCD and CCSD results for the Zn^{+2} atom indicates that the effect of single excitations is very small, just under 1 mE_h. From Table II one can see that proceeding from MP2 to the CCSD method reduces the magnitude of the CBS-extrapolated correlation energy of the $3d^{10}$ configuration by 9.59%. In turn, from Table III one finds that for the $3d^{10}4s^2$ configuration of Zn this reduction amounts to 8.75%. This reduction is certainly caused by the fact that in Zn the valence-electron configuration only consists of 83% of $3d$ electrons. Perusing Tables II and III, one can see that the reduction of the magnitude of the MP2 energy contributions takes place at every partial-wave level.

As shown in Tables II and III, the use of a FPA correction for the CCSD and CCSD(T) correlation energies leads to much improved values when only DZ or TZ coupled-cluster energies are utilized in Eq. (2), i.e., FPA[2] and FPA[3]. The series appears to be rather poorly convergent, however, for these systems, and the use of QZ basis sets, FPA[4], is already not competitive with the direct coupled-cluster CBS[3,4]-extrapolated values. Although not explicitly shown in this work, the FPA[3] results are, however, quite a bit closer to the true CBS limits than a CBS[23] extrapolation. Let us also notice that the FPA[n] values of the correlation energies obtained for the VnZ and CCVnZ bases are significantly closer than the values directly calculated for both bases.

Valence correlation energies for the $3d^{10}$ and $3d^{10}4s^2$ configurations of Zn^{2+} and Zn, respectively, calculated with the CCSD(T), CCSDT, CCSDT(Q), and CCSDTQ methods are shown in Table IV for the cc-pVnZ series of basis sets. Also shown are the corresponding incremental changes between CCSD(T) and CCSD, (T); CCSDT and CCSD(T), T$-$(T); CCSDT(Q) and CCSDT, (Q)$-$T; and CCSDTQ and CCSDT, Q$-$T. In terms of the basis-set convergence of the (T) contribution, it is converged to within 1 mE_h only at the 5Z level for both Zn^{+2} and Zn. From the iterative triples contributions obtained from CCSDT, it is apparent that the perturbative triples overshoot the actual effect of connected triples by $1-2$ mE_h. The T$-$(T) contribution is surprisingly slow to converge, although the QZ level is sufficient to reproduce the estimated CBS limits within a few tenths of a mE_h. In terms of connected quadruple excitations, the overall effect is quite small, only about 0.1 mE_h at the estimated CBS limit. Here again a perturbational estimate obtained via CCSDT(Q) overshoots this contribution and yields an incorrect sign for the effect of connected quadruples, -0.20 mE_h at the CBS[3,4] limit compared to $+0.14$ mE_h with CCSDTQ. In either case the convergence is not very monotonic, with the DZ result being somewhat too large in magnitude.

To get an idea about the all-electron correlation effects, we display in Table V the results for adding the K, L, and M electron shells to the correlation treatment for Zn^{+2} and Zn atoms using the cc-pCCVnZ series of basis sets partly optimized for the description for the correlation effects involving L- and K-shell electrons. Most of the trends are identical to those observed for the valence electron correlation shown in Table II and III. The MP2 correlation energy is again larger in magnitude than the coupled-cluster values, and the convergence with basis-set size in all cases appears to be monotonic. In terms of the extrapolated CBS limits, much more variability is observed between the CBS[3,4] and CBS[4,5] values, nearly 5–7 mE_h. Upon comparison to the reference MP2-FEM results, the CBS[4,5] limits are smaller in magnitude and grow from about 2 mE_h for the M or $M4s^2$ shell to just over 3 mE_h when all electrons are correlated. As discussed above, extrapolation of these basis sets for valence electron correlation results in an underestimate of the MP2 CBS limit by about 1 mE_h. Thus the CBS[4,5] values shown in Table V for the coupled-cluster methods are expected to be somewhat too small in magnitude but only by upwards of 3 mE_h or so. The final estimated CBS limits shown in Table V attempt to account for this difference by assuming the extrapolation error in the coupled-cluster correlation energies mimics those at the MP2 level of theory.

Last, Table VI displays results for the Zn^{+2} atom where the $3d$ electrons are treated within the frozen core approximation and only the $3s$ and $3p$ electrons were correlated. Hence, at the MP2 level, we obtain the energy presented in Table I. The present calculations utilized the cc-pCCVnZ sequence of basis sets. Without the involvement of the $3d$ electrons the magnitude of the MP2 correlation energy is smaller than either the CCSD or CCSD(T) values. Hence, we find the situation found in all calculations for lighter atoms. Similarly, as seen in the earlier tables and discussed above, the CBS[4,5] limit undershoots the MP2-FEM result by just a bit more than 1 mE_h. Here the FPA estimates for the coupled-cluster correlation energies perform much better than when the $3d$ electrons are correlated, showing little basis-set dependence and overshooting the CBS limits by only a mE_h or so (assuming the true CBS limits are slightly larger than the CBS[4,5] values).

IV. CONCLUSIONS

In this paper we report the results of extensive *ab initio* studies of electron correlation effects in Zn^{2+} and Zn. Accurate all-electron correlation energies and correlation energies for various subshells of electrons have been determined by several *ab initio* methods for systems that may be considered the simplest representatives of the heavier closed-shell atoms, for which no accurate experimental correlation energies [13] are available in the literature. Therefore, theoretical results based on reliable *ab initio* methods are the only source of information about the structure of these energies. The knowledge of details concerning the correlation effects in $3d$-electron systems plays a crucial role in the evaluation of new theoretical methods suitable for the rationalization of various physical properties of systems containing transition-metal atoms. Our results may also be used as a testing ground for DFT functionals, especially for the nonempirical ones. Let us mention that the Zn^{2+} system plays a similar role for $3d$-electron systems like Ne does for the second-row atoms.

To obtain results of benchmark quality we have applied several single-reference coupled-cluster methods [CCD, CCSD, CCSD(T), CCSDT, CCSDT(Q)] when using two pairs of basis-set sequences, yielding a systematic convergence to the CBS limit. These basis sets include both the standard cc-pVnZ and aug-cc-pVnZ sets of Balabanov and Peterson [22,23], as well as sets (cc-pCCVnZ) designed for all-electron correlation developed in the present work. As a result, the present correlation energies represent accurate post-MP2 correlation energies obtained for closed-shell atoms beyond Ar at both the all-electron and subshell levels.

Some attention has also been paid to systematic assessments of the performance of the focal-point approach of Allen *et al.* [28,29], which has gained increasing popularity in studies related to difference correlation effects present in molecular interaction problems, in estimations of correlation energies for single-TM systems. It turned out that for Zn^{2+} and Zn FPA yields correlation energies off by just 1%–3%.

At all levels of calculating the correlation energies for Zn^{2+} and Zn, we have found that the magnitudes of the MP2 energies overestimate the magnitudes of the CC correlation energies. Such a situation has not been found before in quantum chemical *ab initio* calculations for lighter atoms and molecules. However, in the case of the all-electron correlation energy for Zn, our result confirms the finding of McCarthy and Thakkar [19] obtained by means of non–*ab initio* approaches for all heavy closed-shell atoms from Zn to Rn. For the Zn^{2+} and Zn systems, we have demonstrated that this overestimation is a direct consequence of the significant increase of the MP2 energy caused by the presence of the $3d^{10}$ electron configuration.

ACKNOWLEDGMENTS

K.J. acknowledges the support from the Polish Committee for Scientific Research under Grant No. N204 560839, and K.A.P. acknowledges the support of the U.S. National Science Foundation (Grant No. CHE-0723997).

---

[1] J. Komasa, J. Rychlewski, and K. Jankowski, Phys. Rev. A **65**, 042507 (2002).

[2] C. Bunge, Theor. Chem. Acc. **126**, 139 (2010).

[3] S. Bubin, J. Komasa, M. Stanke, and L. Adamowicz, Phys. Rev. A **81**, 052504 (2010).

[4] C. Bunge and R. Carbó-Dorca, J. Chem. Phys. **125**, 014108 (2006).

[5] H. Meyer, T.Müller, and A. Schweig, Chem. Phys. Lett. **191**, 213 (1995).

[6] J. Paldus, in *Handbook of Molecular Physics and Quantum Chemistry*, edited by S.Wilson (Wiley, Chichester, UK, 2003), pp. 272–313.

[7] H. Müller, W. Kutzelnigg, and J. Noga, Mol. Phys. **92**, 535 (1997).

[8] R. J. Gdanitz, J. Chem. Phys. **109**, 9795 (1998).

[9] P. Malinowski, L. Meissner, and A. Nowaczyk, J. Chem. Phys. **116**, 7362 (2002).

[10] E. C. Barnes, G. A. Petersson, D. Feller, and K. A. Peterson, J. Chem. Phys. **129**, 194115 (2008).

[11] E. R. Davidson, S. A. Hagstrom, S. J. Chakravorty, V. M. Umar, and C. F. Fischer, Phys. Rev. A **44**, 7071 (1991).

[12] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. Fischer, Phys. Rev. A **47**, 3649 (1993).

[13] S. J. Chakravorty and E. R. Davidson, J. Phys. Chem. **100**, 6167 (1996).

[14] T. Stöhlker, A. Gumberidze, A. Kumar, R. Reuschl, and M. Trassinelli, Adv. Quantum Chem. **53**, 57 (2008).

[15] J. R. Flores, Chem. Phys. Lett. **195**, 377 (1992).

[16] J. R. Flores, K. Jankowski, and R. Słupski, Mol. Phys. **98**, 1125 (2000).

[17] J. R. Flores, R. Słupski, K. Jankowski, and P. Malinowski, J. Chem. Phys. **121**, 12334 (2004).

[18] K. Jankowski, R. Słupski, and J. R. Flores, Mol. Phys. **104**, 2213 (2006).

[19] V. McCarthy and A. J. Thakkar, J. Chem. Phys. **134**, 044102 (2011).

[20] A. Sarsa, E. Buendia, F. Gálvez, and P. Maldonado, J. Phys. Chem. **112**, 2074 (2008).

[21] W. Kutzelnigg and J. D. Morgan, III, J. Chem. Phys. **96**, 4484 (1992).

[22] N. B. Balabanov and K. A. Peterson, J. Chem. Phys. **123**, 064107 (2005).

[23] N. B. Balabanov and K. A. Peterson, J. Chem. Phys. **125**, 074110 (2006).

[24] T. Helgaker, W. Klopper, H. Koch, and J. Noga, J. Chem. Phys. **106**, 9639 (1997).

[25] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, Chem. Phys. Lett. **286**, 243 (1998).

[26] J. R. Flores, R. Słupski, and K. Jankowski, J. Chem. Phys. **124**, 104107 (2006).

[27] J. R. Flores and P. Redondo, Int. J. Quantum Chem. **45**, 563 (1993).

[28] A. East and W. D. Allen, J. Chem. Phys. **99**, 4638 (1993).

[29] A. G. Császár, W. D. Allen, and H. F. Schaefer III, J. Chem. Phys. **108**, 9751 (1998).

[30] P. Jurečka and P. Hobza, Chem. Phys. Lett. **365**, 89 (2002).

[31] C. D. Sherrill, T. Takatani, and E. G. Hohenstein, J. Phys. Chem. A **113**, 10146 (2009).

[32] N. J. DeYonker, T. Grimes, S. Yockel, A. Dinescu, B. Mintz, T. R. Cundari, and A. K. Wilson, J. Chem. Phys. **125**, 104111 (2006).

[33] T. H. Dunning, Jr., J. Phys. Chem. A **104**, 9062 (2000).

[34] H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, et al., MOLPRO, version 2010.1, University College Cardiff Consultants Limited, Cardiff, UK, 2011; see http://www.molpro.net.

[35] M. Kállay, MRCC, a string-based quantum chemical program, 2001, see, http://www.mrcc.hu.

[36] M. Kállay and P. R. Surján, J. Chem. Phys. **115**, 2945 (2001).

[37] J. G. Hill, K. A. Peterson, G. Knizia, and H. Werner, J. Chem. Phys. **131**, 194105 (2009).