Sub-meV accuracy in first-principles computations of the ionization potentials and electron affinities of the atoms H to Ne

Wim Klopper* and Rafał A. Bachorz
Center for Functional Nanostructures (CFN) and Institute of Physical Chemistry, Karlsruhe Institute of Technology, KIT Campus South, Kaiserstraße 12, D-76131 Karlsruhe, Germany

David P. Tew
School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom

Christof Hättig
Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany
(Received 22 September 2009; published 9 February 2010)

Recent advances in coupled-cluster methods for the treatment of electron correlation in atoms (and molecules) have now made possible the computation of the ionization potentials and electron affinities of the atoms H through Ne with a mean absolute deviation of 0.35 meV with respect to experimental data. In this article, coupled-cluster wave functions are parametrized using orbital and Slater-type geminal basis functions. Many-body electron interactions are accounted for through connected quintuple excitations, and relativistic effects (spin-orbit as well as scalar) and diagonal Born-Oppenheimer corrections are included.

DOI: 10.1103/PhysRevA.81.022503 PACS number(s): 31.15.ac, 31.15.bw, 31.15.ve, 31.30.jc

I. INTRODUCTION

For the light atoms H-Be, the numerical solution of the time-independent, nonrelativistic, clamped-nucleus Schrödinger equation can essentially be obtained with arbitrary prescribed precision, for example, by expanding the electronic wave function in exponentially correlated Gaussians (ECG) [1,2] or in many-electron functions of Hylleraas coordinates (Hylleraas-configuration interaction variational computations) [3–5]. By including non–Born-Oppenheimer, relativistic, and quantum electrodynamics (QED) corrections, energy levels of these atoms and their ions are obtained with an accuracy that rivals the best measurements. Hence, such high-precision computations allow for accurate QED tests and determinations of fundamental physical constants and/or atomic (nuclear) properties. However, in spite of the steady increase of computer power, no significant advances appear to have been made in the precise computation of nonrelativistic energies of five- and more-electron atoms since many years. The high complexity of the many-electron ECG and Hylleraas-configuration interaction computations creates an exponential wall that makes it impossible (at least at present) to push these computations beyond the four-electron limit.

Coupled-cluster methods commonly used in quantum chemistry are able to break through this exponential wall [6]. In this article, we report the accuracy that can be achieved for up to 10-electron atoms using coupled-cluster methods to expand the nonrelativistic wave function. Our approach can be used for high-precision computations of nonrelativistic wave functions of (atomic as well as molecular) systems with many more than five electrons and consists of two main components: (i) the use of cluster operators with up to connected quintuple excitations and (ii) the use of Slater-type geminals to form (in conjunction with spin-orbital pairs) a nearly complete space of double excitations.

II. COUPLED-CLUSTER THEORY

In many-electron coupled-cluster theory, the n-electron wave function is expressed in the exponentional form

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle, \tag{1}$$

where $|\mathrm{HF}\rangle$ is the Hartree-Fock determinant (Fermi vacuum) and $\hat{T}$ the cluster operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_n. \tag{2}$$

The $\hat{T}_m$ are m-excitation operators of the form

$$\hat{T}_1 = \sum_{ai} t_a^i a_a^\dagger a_i, \tag{3}$$

$$\hat{T}_2 = \frac{1}{4}\sum_{abij} t_{ab}^{ij} a_a^\dagger a_i a_b^\dagger a_j, \tag{4}$$

$$\hat{T}_3 = \frac{1}{36}\sum_{abcijk} t_{abc}^{ijk} a_a^\dagger a_i a_b^\dagger a_j a_c^\dagger a_k, \tag{5}$$

and so on. The $t_{abc\ldots}^{ijk\ldots}$ are associated cluster amplitudes and the operators $a_i, a_j, a_k, \ldots$ and $a_a^\dagger, a_b^\dagger, a_c^\dagger, \ldots$ are quasiparticle creation operators creating holes and particles, respectively, with respect to the Fermi vacuum. In practical computations, the number of quasiparticle states is finite and defined by the one-particle basis of spin orbitals $\varphi_p\sigma$ (p is a generic index).

When $\hat{T}$ is truncated after single ($\hat{T}_1$) and double ($\hat{T}_2$) excitations, the method is denoted CCSD (coupled-cluster with singles and doubles), when truncated after $\hat{T}_3$, the method is denoted CCSDT (coupled-cluster with singles, doubles, and triples), and so on. Recently, Kállay and Surján have developed a string-based coupled-cluster approach allowing for coupled-cluster computations up to essentially arbitrary

*klopper@kit.edu

 ©2010 The American Physical Society

levels of excitation [7]. Their approach has been implemented in the program MRCC [8]. Because the computational work involved in treating up to 10-electron systems is immense (with N representing the size of the system, the work scales as $O(N^{2m+2})$ when the operator $\hat{T}$ is truncated after the m-excitation operator $\hat{T}_m$), it is just possible to include up to quadruple excitations ($\hat{T}_4$) in a basis comprising 150 spin orbitals or up to quintuple excitations ($\hat{T}_5$) in a basis comprising 72 spin orbitals. Such computations, as performed in this article, represent the limits of what is currently technically feasible.

III. CCSD(F12) METHOD

With high excitations included, coupled-cluster theory soon provides an essentially exact solution to the Schrödinger equation in a given finite spin-orbital basis, but unfortunately, the error in the nonrelativistic energy of that solution is still unacceptably large due to the truncation of the one-particle spin-orbital basis.

This problem is solved by adding two-particle basis functions (geminals) to the coupled-cluster expansion. These are added via the operator $\hat{\mathcal{R}}$, for instance, at the CCSD level as [9,10]

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{\mathcal{R}}, \tag{6}$$

$$\hat{\mathcal{R}} = \frac{1}{8}\sum_{ij\mathbf{kl}} c_{\mathbf{kl}}^{ij} \sum_{\alpha\beta} \overline{w}_{\alpha\beta}^{\mathbf{kl}} a_\alpha^\dagger a_i a_\beta^\dagger a_j, \tag{7}$$

$$\overline{w}_{\alpha\beta}^{\mathbf{kl}} = \langle |\varphi_\alpha(1)\varphi_\beta(2)| |\hat{w}(12)| \chi_{\mathbf{kl}}(12)\rangle, \tag{8}$$

$$\hat{w}(12) = -\hat{Q}(12)\frac{1}{\gamma}\exp(-\gamma r_{12}). \tag{9}$$

$\hat{Q}(12)$ is an appropriate projection operator [11]. The crux here is that the formal indices $\alpha, \beta, \ldots$ refer to virtual spin orbitals that, together with the occupied spin orbitals, form a *complete basis set* (CBS) of spin orbitals. Another important point to note is that the bold indices **kl** refer to an occupied orbital pair function (two-electron determinant) of the type $|\varphi_k\sigma_\uparrow(1)\varphi_l\sigma_\uparrow(2)|$ for two spin-up orbitals and to $|\overline{\varphi}_k\sigma_\downarrow(1)\overline{\varphi}_l\sigma_\downarrow(2)|$ for two spin-down orbitals, but to

$$\chi_{\mathbf{kl}}(12) = \tfrac{3}{8}|\varphi_k\sigma_\uparrow(1)\overline{\varphi}_l\sigma_\downarrow(2)| + \tfrac{1}{8}|\overline{\varphi}_l\sigma_\uparrow(1)\varphi_k\sigma_\downarrow(2)| \tag{10}$$

for unlike spins, where φ_k is the spatial part of an occupied spin-up orbital and $\overline{\varphi}_l$ is the spatial part of an occupied spin-down orbital. The spin-flipped second term in Eq. (10) is required to satisfy the electron-electron cusp conditions in open-shell atoms [12–15]. The CCSD-F12 equations for the energy and the amplitudes are derived from the Eqs. (7)–(9) using the usual coupled-cluster projection techniques. The CCSD(F12) method [16,17] used in this article is an approximation to the full CCSD-F12 model obtained by partitioning the Hamiltonian into the Fock operator $\hat{F}$ and the fluctuation potential $\hat{\Phi}$ and discarding small $c_{\mathbf{kl}}^{ij}$ contributions higher than second order in $\hat{\Phi}$. We refer to Ref. [11] for a recent comprehensive review of the CCSD(F12) method.

The success of the nonrelativistic energy computations presented here is due to the ability to combine (assuming additivity) conventional coupled-cluster computations up to the level of quintuple excitations (CCSDTQ5) with CCSD(F12) computations in large basis sets (d-aug-cc-pwCV5Z, 434 spin orbitals for B-Ne, see Sec. V). The success is thus based on computational methods that have become available only very recently.

IV. RESULTS AND DISCUSSION

In this section, we shall discuss the main results of our work, and then, in Sec. V, we shall give the details of the individual computational steps involved. Still more details are given in the auxiliary material [18].

The ionization potentials (IP) and electron affinities (EA) of the atoms H-Ne computed at the CCSD level in the large d-aug-cc-pwCV5Z basis set are presented in the second column of Table I. Although this is a very large basis set, the basis set truncation error in these computations is significant. This error is removed by approaching the CBS limit of CCSD theory through CCSD(F12) computations. These change the computed values by up to ca. 35 meV (third column). Also the truncation of the $\hat{T}$ operator gives rise to large errors, but these errors are removed by including excitations beyond CCSD up to the level of quintuple excitations (CCSDTQ5). The corresponding "high level correction" (HLC) is given in the fourth column.

An analysis of this HLC correction to the IPs and EAs is presented in Table II. For the IPs, we observe a rapid convergence with respect to the order of excitation. None of the (Q) contributions are larger than ca. 2 meV and the CCSDT(Q) approximation appears to be an excellent approximation to the full CCSDTQ model [26]. The step from CCSDT(Q) to CCSDTQ [denoted as (Q) → Q] is about an order of magnitude smaller than the (Q) contribution itself. Concerning the IPs, quintuple excitations could have been neglected. To see this, one has to add the values in the "(5)" and "(5) → 5" columns. For example, the step from CCSDTQ to CCSDTQ5 adds only 0.02 meV to the IP of Ne. Note, however, that the (5) approximation appears to be a poor approximation to the full CCSDTQ5 model. This is even more pronounced for the EAs. While the CCSDT(Q) model is a useful approximation to CCSDTQ, the (5) approximation overestimates the CCSDTQ → CCSDTQ5 step by a factor 5–7. It was therefore important for the present work to push the coupled-cluster calculations all the way up to the full CCSDTQ5 model. While less important for the IPs, the effect of connected quintuples is significant for the accurate calculation of EAs. In particular for fluorine, the effect is −1.3 meV.

The sum of the values in the columns 2 through 4 of Table I (CCSD + F12 + HLC) basically represents the value that would be obtained from the exact solution of the nonrelativistic, clamped-nucleus n-electron Schrödinger equation. When adding relativistic and non–Born-Oppenheimer corrections, the values in the second last column are obtained, which agree to within a few tenths of a meV with the experimental values [19,22–25]. For the IPs and EAs, we find a mean deviation between theory and experiment of $\bar{\Delta} = 0.11$ and 0.13 meV, respectively. These are computations of unprecedented accuracy for systems with up to 10 electrons. Such high accuracy could be obtained only due to the very recent

TABLE I. Atomic ionization potentials and electron affinities (in eV).

	CCSD[a]	F12[b]	HLC[c]	Rel.[d]	SO[e]	DBOC[f]	Calc.	Expt.[g]
				Ionization potentials (IPs)				
H	13.60555	–	–	0.00015	–	−0.00741	13.59829	13.59843
He	24.57891	0.01269	–	−0.00024	–	−0.00396	24.58741	24.58739
Li	5.39000	0.00068	0.00117	0.00032	–	−0.00045	5.39172	5.39172
Be	9.30383	0.00176	0.01698	0.00085	–	−0.00058	9.32284	9.32270
B	8.24788	0.00663	0.04519	−0.00218	0.00126	0.00004	8.29881	8.29802
C	11.22422	0.00809	0.03430	−0.00403	−0.00157	−0.00001	11.26100	11.26030
N	14.51338	0.00969	0.02961	−0.00685	−0.01102	−0.00006	14.53475	14.5341
O	13.52111	0.03526	0.06138	−0.00962	0.00967	−0.00004	13.61776	13.61805
F	17.33527	0.03488	0.07071	−0.01410	−0.00414	−0.00008	17.42255	17.4228
Ne	21.50540	0.03490	0.07616	−0.02006	−0.03225	−0.00013	21.56401	21.56454
				Electron affinities (EAs)				
H	0.75167	0.00286	–	−0.00004	–	−0.00090	0.75360	0.75419
Li	0.60776	0.00028	0.00974	−0.00002	–	−0.00006	0.61770	0.61805
B	0.18801	0.00287	0.09092	−0.00112	−0.00055	0.00012	0.28027	0.27972
C	1.17297	0.00455	0.09141	−0.00267	−0.00367	0.00014	1.26273	1.26212
O	1.26544	0.01973	0.18398	−0.00589	−0.00235	0.00013	1.46104	1.46111
F	3.22762	0.02068	0.17930	−0.00973	−0.01670	0.00010	3.40127	3.40119

[a]Computed at the CCSD/d-aug-cc-pwCV5Z level.
[b]Computed at the CCSD(F12)/d-aug-cc-pwCV5Z level.
[c]High-level correction. See Table II.
[d]Scalar relativistic contribution. See Table III.
[e]Spin-orbit correction computed from the experimentally observed spin–orbit splitting. See Ref. [19]. Boron and oxygen negative-ion spin-orbit data from Ref. [20] and Ref. [21], respectively.
[f]Diagonal Born-Oppenheimer correction computed at the CCSD/d-aug-cc-pwCVQZ level.
[g]IPs from Ref. [19], EAs from Refs. [22–25].

developments in explicity correlated (F12) theory and high-order electronic coupled-cluster methods. Without the F12 correction for the basis set limit, the errors would have been two orders of magnitude larger. Similarly, without connected quadruple and quintuple excitations, errors of up to 15 meV would have resulted. Including both of these contributions, the IP mean absolute deviation is $|\bar{\Delta}| = 0.35$ meV and the maximum deviation is $\Delta_{\max} = 0.79$ meV (boron). For the EAs, we find mean absolute and maximum deviations of $|\bar{\Delta}| = 0.36$ meV and $\Delta_{\max} = 0.61$ meV (carbon).

TABLE II. High-level corrections (HLC) to atomic ionization potentials and electron affinities (in eV).

	(T)[a]	(T) → T[b]	(Q)[b]	(Q) → Q[c]	(5)[d]	(5) → 5[d]	HLC
				Ionization potentials (IPs)			
Li	0.00103	0.00013	–	–	–	–	0.00117
Be	0.01621	0.00060	0.00016	0.00001	–	–	0.01698
B	0.03401	0.01094	0.00023	0.00000	0.00000	0.00000	0.04519
C	0.02843	0.00440	0.00127	0.00020	0.00000	0.00000	0.03430
N	0.02848	0.00017	0.00098	−0.00003	−0.00001	0.00001	0.02961
O	0.05642	0.00326	0.00175	−0.00006	−0.00003	0.00004	0.06138
F	0.06901	−0.00031	0.00217	−0.00017	−0.00006	0.00008	0.07071
Ne	0.07882	−0.00466	0.00211	−0.00013	−0.00012	0.00014	0.07616
				Electron affinities (EAs)			
Li	0.00934	0.00025	0.00015	0.00000	–	–	0.00974
B	0.06974	0.01521	0.00538	0.00057	0.00002	0.00001	0.09092
C	0.07865	0.00694	0.00614	−0.00027	−0.00030	0.00026	0.09141
O	0.16842	0.00432	0.01581	−0.00374	−0.00483	0.00400	0.18398
F	0.18205	−0.01068	0.01174	−0.00249	−0.00706	0.00574	0.17930

[a]Computed in the d-aug-cc-pwCV5Z basis.
[b]Computed in the d-aug-cc-pwCVQZ basis.
[c]Computed in the d-aug-cc-pwCVTZ basis.
[d]Computed in the d-aug-cc-pwCVDZ basis.

TABLE III. Scalar relativistic contributions to atomic ionization potentials and electron affinities (in eV).

	MV[a]	D1[b]	D2[c]	Breit + QED[d]	Rel.[e]
			Ionization potentials (IPs)		
H	0.00088	−0.00070	–	−0.00003[f]	0.00015[f]
He	0.00483	−0.00469	0.00055	−0.00093[g]	−0.00024[g]
Li	0.00132	−0.00094	0.00005	−0.00011[h]	0.00032[h]
Be	0.00342	−0.00237	0.00036	−0.00056[i]	0.00085[i]
B	−0.00928	0.00719	−0.00018	0.00008	−0.00218
C	−0.01615	0.01243	−0.00025	−0.00006	−0.00403
N	−0.02602	0.01985	−0.00033	−0.00034	−0.00685
O	−0.03489	0.02594	0.00013	−0.00079	−0.00962
F	−0.04953	0.03676	0.00014	−0.00146	−0.01410
Ne	−0.06791	0.05030	0.00010	−0.00254	−0.02006
			Electron affinities (EAs)		
H	−0.00002	−0.00002	0.00002	−0.00001[j]	−0.00004[j]
Li	−0.00005	0.00003	0.00001	−0.00001[k]	−0.00002[k]
B	−0.00422	0.00301	−0.00009	0.00018	−0.00112
C	−0.00952	0.00676	−0.00018	0.00027	−0.00267
O	−0.01917	0.01310	−0.00009	0.00026	−0.00589
F	−0.03045	0.02084	−0.00018	0.00006	−0.00973

[a]Mass-velocity term, computed at the CCSD(T)/d-aug-cc-pwCV5Z level.

[b]One-electron Darwin term, computed at the CCSD(T)/d-aug-cc-pwCV5Z level.

[c]Two-electron Darwin term, computed at the CCSD(T)/d-aug-cc-pwCV5Z level.

[d]Breit and QED corrections. Unless otherwise noted, the Breit, vacuum polarization, and self-energy terms were computed at the Dirac-Fock level using the GRASP program [38].

[e]Rel. = MV + D1 + D2 + Breit + QED.

[f]From Ref. [34].

[g]From Ref. [4].

[h]From Ref. [5].

[i]From Ref. [1].

[j]From Ref. [3].

[k]From Ref. [2].

Details of the scalar relativistic contributions to the IPs and AEs are given in Table III. The scalar Breit and QED corrections to the IPs and EAs are small in magnitude (<1 meV) except for the IPs of F and Ne, which are reduced by 1.5 and 2.5 meV, respectively.

V. COMPUTATIONAL DETAILS

Let us now turn our attention to some of the details of the computations. We began our computations at the CCSD level. These computations were performed with the CFOUR program [27] in a d-aug-cc-pwCV5Z basis set [28,29]. Also the (T) correction for connected triple excitations was computed with CFOUR in this basis.

The MRCC program was used for computations beyond the CCSDT level. CCSDT(Q) computations [26] were performed in the d-aug-cc-pwCVQZ basis, coupled-cluster computations with full connected quadruples (CCSDTQ) in the d-aug-cc-pwCVTZ basis, and full connected quintuples (CCSDTQ5) were accounted for in the d-aug-cc-pwCVDZ basis. From all of the latter computations, increments are obtained that add up to the HLC. It is essential to include excitations as high as connected quintuple excitations to reach sub-meV accuracy in the IPs and EAs of the atoms H-Ne.

All coupled-cluster computations of this article were performed correlating all electrons and using an unrestricted Hartree-Fock (UHF) reference. At the CCSDT/d-aug-cc-pwCVQZ level, the effect on the IPs of B-Ne and on the EA of F, when using a restricted open-shell Hartree-Fock reference in place of a UHF reference, was less than 0.1 meV in magnitude. The effect is expected to be negligible at the CCSDTQ5 level.

All CCSD(F12) computations were performed with the Turbomole program [30], using a Slater-type geminal $\exp(-\gamma r_{12})$ with exponent $\gamma = 1.0\ a_0^{-1}$, expanded in six Gaussians [31]. The d-aug-cc-pwCV5Z basis was used as orbital basis, and the aug-cc-pV5Z exchange-fitting basis (jkbas) of Weigend [32], augmented with an extra set of diffuse functions for each angular momentum, was used as complementary auxiliary basis set. For the density-fitting approach, the aug-cc-pwCV5Z MP2-fitting basis (cbas) of Hättig [33] was used, augmented with three extra sets of diffuse functions for each angular momentum. Details on the basis sets are given in the auxiliary material [18]. The CCSD(F12) approach was applied using a UHF reference and correlating all electrons. The contributions in the column "F12" in Table I refer to the difference between the CCSD(F12)/d-aug-cc-pwCV5Z and CCSD/d-aug-cc-pwCV5Z energies, both computed with Turbomole.

Since our focus was on highly accurate nonrelativistic energies, scalar relativistic corrections were taken from the literature, where available (atoms H-Be) [1–5,34]. For the atoms B-Ne, we computed analytically [35] the mass-velocity and one-electron Darwin corrections at the CCSD(T)/d-aug-cc-pwCV5Z level with the CFOUR program. To these corrections, we added the two-electron Darwin term obtained from a finite-perturbation-theory approach at the CCSD(T)/d-aug-cc-pwCV5Z level using the DIRCCR12-OS program [36,37]. Furthermore, for the atoms B-Ne, Breit and QED corrections (i.e., the vacuum polarization and the self-energy terms that together comprise the Lamb shift) were taken into account as obtained from state-averaged Dirac-Fock computations with the GRASP program [38]. In these computations, the weighted average of all states obtained by distributing the valence electrons over the $2p$ orbitals (e.g., the average of the states $^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$, and $^1S_0$ for C) was optimized. The energy change of the weighted average of the ground-state levels (e.g., the average of the states $^3P_0$, $^3P_1$, and $^3P_2$ for C) due to the Breit and QED corrections was taken as *scalar* high-order relativistic correction.

As already mentioned, our focus was on highly accurate nonrelativistic energies. Therefore, spin-orbit (SO) corrections were not computed but derived from experimentally observed SO splittings. These were taken from Refs. [19–21]. For each atom and ion, the energy lowering due to SO coupling was computed as the difference between the lowest J term and the $(2J + 1)$-weighted average of the ground-state levels.

Diagonal Born-Oppenheimer corrections (DBOC) were computed at the CCSD/d-aug-cc-pwCVQZ level using the CFOUR program [27,39].

VI. CONCLUSIONS

Two recently developed numerical methods for solving the time-independent, nonrelativistic, clamped-nucleus Schrödinger equation have been combined to compute the IPs and EAs of the atoms H through Ne with high accuracy. These methods are, first, the string-based coupled-cluster method that allows for coupled-cluster computations up to essentially arbitrary level of excitation, and, second, the CCSD(F12) method that allows for coupled-cluster computations in the limit of a complete one-particle basis set.

Our computed data are about one order of magnitude more accurate than what can be accomplished with other modern approaches. At the level of Weizmann-3 (W3) theory, for example, which includes coupled-cluster theory with high levels of excitation and extrapolations to the CBS limit, the deviations (from the experimental values) of the computed IPs for the atoms B-Ne range between −4 and 5 meV [40]. At this same level, the errors in the EAs of B, C, O, and F are −5, 7, 3, and 6 meV, respectively [40]. In the present work, we have computed the IPs and EAs with a mean absolute deviation of only 0.35 meV with respect to experimental data.

Quantum Monte Carlo (QMC) approaches are able to compute the electron-correlation energy (defined as the difference between the exact clamped-nucleus, nonrelativistic energy and the restricted Hartree-Fock energy) with an accuracy of 98–99% for atoms such as O, F, and Ne [41]. However, since the electron-correlation contribution to the IPs and EAs of these atoms is of the order of 1.7–2.0 eV (see auxiliary material [18]), as much as 99.98% of this contribution should be recovered to obtain an agreement to within 0.34–0.4 meV.

In conclusion, we have shown that it is possible to compute the IPs and EAs of the atoms H-Ne accurately to within 0.35 meV by means of high-level coupled-cluster calculations in the limit of a complete one-particle basis set.

ACKNOWLEDGMENTS

This research has been supported by the Deutsche Forschungsgemeinschaft (DFG) through the Center for Functional Nanostructures (CFN, Project No. C3.3). It has been further supported by a grant from the Ministry of Science, Research and the Arts of Baden-Württemberg (Az: 7713.14-300). The research of D.P.T. has been supported by the DFG (TE 644/1) and the Royal Society. We thank Kirk A. Peterson (Washington State University) for providing us with the aug-cc-pwCVXZ basis sets for Li and Be prior to publication and Trond Saue (University of Strasbourg) for help with the GRASP program.

[1] K. Pachucki and J. Komasa, Phys. Rev. Lett. **92**, 213001 (2004).
[2] K. Pachucki and J. Komasa, J. Chem. Phys. **125**, 204304 (2006).
[3] G. W. F. Drake, Nucl. Instrum. Methods Phys. Res. B **31**, 7 (1988).
[4] G. W. F. Drake, Phys. Scr. **T95**, 22 (2001).
[5] Z.-C. Yan and G. W. F. Drake, Phys. Rev. Lett. **91**, 113004 (2003).
[6] P. Cársky, J. Paldus, and J. Pittner (Eds.), *Recent Progress in Coupled Cluster Methods: Theory and Applications* (Springer, Berlin, 2010).
[7] M. Kállay and P. R. Surján, J. Chem. Phys. **115**, 2945 (2001).
[8] MRCC, a string-based quantum chemical program suite written by M. Kállay. See http://www.mrcc.hu.
[9] J. Noga and W. Kutzelnigg, J. Chem. Phys. **101**, 7738 (1994).
[10] S. Ten-no, Chem. Phys. Lett. **398**, 56 (2004).
[11] D. P. Tew, C. Hättig, R. A. Bachorz, and W. Klopper. In: *Recent Progress in Coupled Cluster Methods: Theory and Applications*, edited by P. Cársky, J. Paldus, and J. Pittner (Springer, Berlin, 2010).
[12] D. P. Tew, J. Chem. Phys. **129**, 014104 (2008).
[13] D. Bokhan, S. Ten-no, and J. Noga, Phys. Chem. Chem. Phys. **10**, 3320 (2008).
[14] D. Bokhan, S. Bernadotte, and S. Ten-no, J. Chem. Phys. **131**, 084105 (2009).
[15] D. P. Tew and W. Klopper, Mol. Phys., first published on: 13 January 2010 (iFirst), doi:10.1080/00268970903449388.
[16] H. Fliegl, W. Klopper, and C. Hättig, J. Chem. Phys. **122**, 084107 (2005).
[17] D. P. Tew, W. Klopper, C. Neiss, and C. Hättig, Phys. Chem. Chem. Phys. **9**, 1921 (2007); **10**, 6325 (2008) (Erratum).
[18] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevA.81.022503 for details on basis sets and spin–orbit corrections.
[19] J. E. Sansonetti and W. C. Martin, J. Phys. Chem. Ref. Data **34**, 1559 (2005).
[20] M. Scheer, R. C. Bilodeau, and H. K. Haugen, Phys. Rev. Lett. **80**, 2562 (1998).
[21] D. M. Neumark, K. R. Lykke, T. Andersen, and W. C. Lineberger, Phys. Rev. A **32**, 1890 (1985).
[22] T. Andersen, H. K. Haugen, and H. Hotop, J. Phys. Chem. Ref. Data **28**, 1511 (1999).
[23] K. R. Lykke, K. K. Murray, and W. C. Lineberger, Phys. Rev. A **43**, 6104 (1991).
[24] C. Blondel, W. Chaibi, C. Delsart, C. Drag, F. Goldfarb, and S. Kröger, Eur. Phys. J. D **33**, 335 (2005).
[25] C. Blondel, C. Delsart, and F. Goldfarb, J. Phys. B **34**, L281 (2001); **34**, 2757 (2001) (Erratum).
[26] M. Kállay and J. Gauss, J. Chem. Phys. **123**, 214105 (2005).
[27] CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay, and others. For the current version, see http://www.cfour.de.
[28] K. A. Peterson and T. H. Dunning Jr., J. Chem. Phys. **117**, 10548 (2002). Downloaded from the Basis Set Exchange v1.2.2 (https://bse.pnl.gov/bse/portal). For H and He, the aug-cc-pwCVXZ basis refers to the aug-cc-pVXZ basis. All second sets of diffuse functions were downloaded as "d-aug-cc-pVXZ Diffuse."

[29] The aug-cc-pwCVXZ (X = D, T, Q, 5) basis sets for Li and Be were provided to us by K. A. Peterson in a private communication (June 2009). The second set of diffuse functions were constructed by geometric extrapolation.
[30] Turbomole v6.0, Turbomole GmbH, Karlsruhe, 2009. See http://www.turbomole.com.
[31] D. P. Tew and W. Klopper, J. Chem. Phys. **123**, 074101 (2005).
[32] F. Weigend, J. Comput. Chem. **29**, 167 (2007).
[33] C. Hättig, Phys. Chem. Chem. Phys. **7**, 59 (2005).
[34] J. Liu, E. J. Salumbides, U. Hollenstein, J. C. J. Koelemeij, K. S. E. Eikema, W. Ubachs, and F. Merkt, J. Chem. Phys. **130**, 174306 (2009).
[35] J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).
[36] DIRCCR12-OS, a direct CCSD(T)-R12 program (2003), written by J. Noga, W. Klopper, T. Helgaker, and P. Valiron.
[37] W. Klopper, J. Comput. Chem. **18**, 20 (1997).
[38] GRASP v1.0, a general-purpose relativistic atomic structure program written by A. Bar-Shalom, K. G. Dyall, I. P. Grant, C. T. Johnson, M. Klapisch, D. F. Mayers, B. J. McKenzie, P. H. Norrington, F. A. Parpia, E. P. Plummer, and N. C. Pyper, developed at Oxford and Monash, March 1988.
[39] J. Gauss, A. Tajti, M. Kállay, J. F. Stanton, and P. G. Szalay, J. Chem. Phys. **125**, 144111 (2006).
[40] A. D. Boese, M. Oren, O. Atasoylo, J. M. L. Martin, M. Kállay, and J. Gauss, J. Chem. Phys. **120**, 4129 (2004).
[41] M. D. Brown, J. R. Trail, P. López Ríos, and R. J. Needs, J. Chem. Phys. **126**, 224110 (2007).