Correlation energies for many-electron atoms with explicitly correlated Slater functions

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In this work we propose a composite method for accurate calculation of the energies of many-electron atoms. The dominant contribution to the energy (pair energies) are calculated by using explicitly correlated factorizable coupled cluster theory. Instead of the usual Gaussian-type geminals for the expansion of the pair functions, we employ a two-electron Hylleraas basis set and discuss the advantages of the latter approach, e.g., a small number of nonlinear parameters that need to be optimized. The remaining contributions to the energy are calculated within the algebraic approximation by using large one-electron basis sets composed of Slater-type orbitals. The method is tested for the beryllium atom where an accuracy better than 1 cm^{-1} is obtained. We discuss in detail possible sources of the error and estimate the uncertainty in each energy component. Finally, we consider possible strategies to improve the accuracy of the method by 1–2 orders of magnitude and apply it to larger atoms.

I. INTRODUCTION

Atomic spectroscopy remains an important and active field of modern physics. Many theoretical and experimental works concentrated on different aspects of atomic spectra touch upon the very fundamentals of the present scientific knowledge. Search for time-reversal symmetry violations [1], time dependence of fundamental physical constants [2–4], various empirical tests of the Standard Model, and quantum electrodynamics [5–10] are only a handful of prominent examples. Therefore, the need for development of accurate theoretical tools to predict the atomic spectra (and other relevant quantities) is easy to recognize.

If we restrict ourselves to light atoms, the most accurate theoretical results to date have been obtained with methods where all interparticle distances are explicitly incorporated into the trial wave function. This includes basis sets of Hylleraas-type functions [11–14], explicitly correlated Gaussians (ECG) [15,16], Hylleraas-CI expansions [17–19], and Slater geminals [20–23]. The common problem among these methods, however, is the exponential scaling of the computational costs with the number of particles in the system.

A different approach to the electronic structure is offered by the coupled cluster (CC) theory [24–27]. The total CC wave function is parametrized in terms of a cluster operator which can be truncated in a systematic way. As a result, the computational costs scale polynomially with increasing number of particles in the system. The most popular implementation of the CC theory relies on the algebraic approximation, i.e., expansion in a set of one-electron orbitals. Unfortunately, this leads to a relatively slow convergence of the results towards the complete basis set limit [28]—a manifestation of Kato's electron-electron cusp condition [29].

One possible remedy to this problem is to abandon the algebraic approximation entirely. To this end, various authors showed that a basis-set independent CC theory can be formulated in terms of the so-called pair functions [30–42]. The pair functions are two-electron objects and thus can be expanded in a basis set which overtly includes all coordinates of the given electron pair. This idea gave rise to the explicitly correlated CC theory.

One of the most difficult obstacles preventing straightforward application of this method is the presence of many-electron integrals. In the modern R12/F12 theory [43–48], this difficulty is avoided by proper insertions of the resolution of identity (RI) approximation. A different idea has been proposed by Szalewicz and collaborators [35–37], who imposed the strong-orthogonality (SO) requirement for the pair functions only in the complete basis set limit. This led to a family of weak-orthogonality (WO) functionals. At the second-order Møller-Plesset (MP2) level of theory [27], for example, this eliminates all four-electron integrals from the working equations, leaving only the relatively simple three-electron ones [35,36].

The WO functionals are typically combined with the Gaussian-type geminals (GTG) for expansion of the CC pair functions. The main advantage of such an approach is that the resulting three-electron integrals can be evaluated analytically in a closed form. Unfortunately, all GTG-based approaches require costly nonlinear optimizations of the GTG exponential parameters. For one-center systems an interesting alternative is to use Hylleraas basis set of the form

$$(4\pi)^{-1} r_1^u \, r_2^v \, r_{12}^t \, \exp(-a_i \, r_1 - a_j \, r_2), \tag{1}$$

where a_i, $a_j > 0$, and u, v, t are non-negative integers, for the expansion of the CC pair functions. As demonstrated further in the text, this basis set requires introduction of only a handful of nonlinear parameters per electron pair, making their optimization a straightforward task. Moreover, the basis

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set (1) can be systematically extended so that the basis set limits and the corresponding errors bars are easier to estimate.

The Hylleraas basis set has not found a significant use in CC theory thus far because of the resulting three-electron integrals. However, in the past two decades considerable progress has been achieved in attempts to evaluate them analytically and/or recursively. This started with the seminal paper of Fromm and Hill [49], who solved the simplest three-electron integral with inverse powers of all interparticle distances. Despite this success and subsequent works [50,51], the analytic formulas were lengthy and their evaluation (and differentiation) both expensive and prone to numerical instabilities.

Somewhat later, Pachucki and collaborators [52] proposed a set of recursive formulas connecting all three-electron integrals resulting from the basis set (1), thereby eliminating many problems shared by the previous approaches. This opens up a new avenue for application of the WO CC theory to many-electron atoms within the Hylleraas basis set. Since the three-electron integrals are no longer a bottleneck, the basis set is expected to be superior to the GTG expansion, both in terms of accuracy (satisfies the cusp condition) and computational efficiency (a small number of independent nonlinear parameters).

The purpose of this work is twofold. First, we consider calculation of explicitly correlated coupled cluster energies with the Hylleraas basis set used for expansion of the pair functions. We analyze the strengths and weaknesses of this approach and provide exemplary results for two- and four-electron closed-shell atomic systems. Second, we propose a composite method to calculate total energies of many-electron atoms comprising the aforementioned explicitly correlated techniques augmented with calculations based on one-electron basis sets. We discuss extensions of this method to heavier atoms, including the open-shell systems, and analyze the main sources of error.

II. THEORY AND IMPLEMENTATION

A. Explicitly correlated calculations

In the first-quantized formulation of the factorizable coupled cluster doubles theory (FCCD) [38] the electron correlation effects in an N-electron closed-shell system are expressed in terms of a set of $N^2/4$ spinless pair functions of well-defined permutational symmetry. There are $[N(N/2 + 1)]/4$ independent singlet pair functions $\tau_{\alpha\beta}^1(1,2)$ which are symmetric with respect to the exchange of electron coordinates and orbital indices α and β, and $[N(N/2 - 1)]/4$ triplet pair functions $\tau_{\alpha\beta}^3(1,2)$ which are antisymmetric under these operations, i.e., $\tau_{\alpha\beta}^s(1,2) = (2-s)\tau_{\alpha\beta}^s(2,1) = (2-s)\tau_{\beta\alpha}^s(1,2)$, $s = 1, 3$.

We assume that the reference Hartree-Fock determinant is constructed from canonical orbitals ϕ_α, $\alpha = 1, \ldots, N/2$ (corresponding to the lowest orbital energies ϵ_α) which are eigenfunctions of the standard closed-shell Fock operator f, i.e., $f\phi_\alpha = \epsilon_\alpha \phi_\alpha$. In this case, the individual pair functions $\tau_{\alpha\beta}^s(1,2)$ are solutions to the integrodifferential FCCD equations of the general form [38,53]

$$[f(1) + f(2) - \epsilon_\alpha - \epsilon_\beta]\tau_{\alpha\beta}^s(1,2) = R_{\alpha\beta}^s[\tau], \quad (2)$$

with an additional requirement that the pair functions must fulfill the SO condition

$$q_2(1,2)\tau_{\alpha\beta}^s(1,2) = \tau_{\alpha\beta}^s(1,2). \quad (3)$$

The exact two-electron SO projector q_2 in Eq. (3) is defined as

$$q_2(1,2) = [1 - p(1)][1 - p(2)], \quad (4)$$

where the action of a projector p on an arbitrary function χ is expressed in terms of the occupied orbitals ϕ_α as

$$p(1)\chi(1) = \sum_{\alpha=1}^{N/2} \phi_\alpha(1) \int \phi_\alpha^\star(3)\chi(3)\, d3. \quad (5)$$

Once the pair functions are known, the total FCCD correlation energy is computed as a sum of contributions from individual pairs,

$$E_{\text{FCCD}} = \sum_{\alpha=1}^{N/2} \epsilon_{\alpha\alpha}^1 + \sum_{\alpha<\beta}^{N/2} \left(\epsilon_{\alpha\beta}^1 + \epsilon_{\alpha\beta}^3 \right), \quad (6)$$

where the pair energies $\epsilon_{\alpha\beta}^s$ are defined by

$$\epsilon_{\alpha\beta}^s = \frac{s}{1 + \delta_{\alpha\beta}} \langle \phi_\alpha \phi_\beta | r_{12}^{-1} | \tau_{\alpha\beta}^s \rangle. \quad (7)$$

The right-hand-side term $R_{\alpha\beta}^s[\tau]$ in Eq. (2) depends explicitly on all pair functions (indicated by the bold symbol, τ). In the FCCD theory it consists of three contributions,

$$R_{\alpha\beta}^s[\tau] = -q_2(1,2)r_{12}^{-1}\phi_{\alpha\beta}^s(1,2) + L_{\alpha\beta}^s[\tau] + F_{\alpha\beta}^s[\tau], \quad (8)$$

where $\phi_{\alpha\beta}^s$ is a properly (anti-)symmetrized product of the occupied orbitals, i.e., $\phi_{\alpha\beta}^s(1,2) = \phi_\alpha(1)\phi_\beta(2) + (2 - s)\phi_\beta(1)\phi_\alpha(2)$, $L_{\alpha\beta}^s[\tau]$ collects all terms which are linear in the pair functions, and the so-called factorizable quadratic terms are included in $F_{\alpha\beta}^s[\tau]$. The detailed functional form of $L_{\alpha\beta}^s[\tau]$ and $F_{\alpha\beta}^s[\tau]$ is found in Refs. [38,53].

The coupled cluster equations are most conveniently solved iteratively. In the simplest approach (the straightforward iteration procedure of Ref. [38]), a sequence of consecutive approximations to the pair functions, $\tau^{[n]}$, is generated from an equation similar to Eq. (2) but with the right-hand-side term calculated using the pair functions from the previous iteration, $R_{\alpha\beta}^s[\tau^{[n-1]}]$.

The SO condition given by Eq. (3) must be fulfilled in each step of the iteration procedure. We adopt a method of solving the coupled cluster equations through an unconstrained minimization of a variational functional which imposes the SO condition approximately by means of a penalty term [35–37]. To this end, we employed the super-weak orthogonality (SWO) functional introduced in Ref. [54]. In the case of the FCCD theory it has the following form:

$$\begin{aligned} \mathcal{J}_{\alpha\beta}^s[\tilde\tau] = & \langle \tilde\tau | f(1) + f(2) - \epsilon_\alpha - \epsilon_\beta | \tilde\tau \rangle \\ & - 2\,\text{Re}\langle \tilde\tau | \bar{R}_{\alpha\beta}^s[\tau^{[n-1]}] \rangle + \Delta_1^{\alpha\beta}\langle \tilde\tau | p(1) + p(2) | \tilde\tau \rangle \\ & + \Delta_2^{\alpha\beta}\langle \tilde\tau | p_e(1) + p_e(2) | \tilde\tau \rangle + \Delta_3^{\alpha\beta}\langle \tilde\tau | p(1)p(2) | \tilde\tau \rangle, \end{aligned}$$

$$(9)$$

where the bar in $\bar{R}_{\alpha\beta}^s[\tau^{[n-1]}]$ indicates that the one-electron SO projectors appearing in the definition of $L_{\alpha\beta}^s$ in Eq. (8)

are omitted, and $p_e(1)$ is defined through Eq. (5) with orbital energies ϵ_α multiplying each $\phi_\alpha(1)$ term. No more than three-electron integrals are necessary within the SWO framework.

The last three terms in Eq. (9) constitute a penalty function which increases the value of the functional if any SO-violating components are present in the trial function. We adopt the formulas from Ref. [54] for the parameters $\Delta_i^{\alpha\beta}$:

$$\Delta_1^{\alpha\beta} = \epsilon_\alpha + \epsilon_\beta - \epsilon_{\mathrm{HO}} + \eta$$
$$\Delta_2^{\alpha\beta} = -1 \qquad (10)$$
$$\Delta_3^{\alpha\beta} = 2\epsilon_{\mathrm{HO}} - \epsilon_\alpha - \epsilon_\beta,$$

where ϵ_{HO} is the energy of the highest occupied reference orbital, and $\eta > 0$ is a parameter which allows us to control the strength of the SO forcing. The value of this parameter is irrelevant in the limit of the complete basis set but influences the results in any finite basis set.

The minimization of $\mathcal{J}_{\alpha\beta}^s[\tilde\tau]$, Eq. (9), is performed only with respect to the linear coefficients in the expansion of the trial function $\tilde\tau$ in terms of a set of fixed basis functions. Therefore, finding a minimum of the functional is equivalent to solving a set of linear equations. Additionally, after each step of the iteration procedure we perform an approximate projection of each pair function [39], where the strong-orthogonality projector is restricted to the space spanned by the geminal basis set (SWO with projection technique, SWOP).

All pair functions are expanded in a common set of primitive functions of the form (1). The proper permutational symmetry of the singlet and triplet pair functions is ensured by applying the (anti-)symmetrizer $\hat{A}_{12}^s = 1 + (2 - s)\hat{P}_{12}$, where $\hat{P}_{12}$ interchanges the electron coordinates. The positive exponents a_i and a_j, $i \leqslant j$, in Eq. (1) are all possible pairs (including repetitions) created out of an n_a-element set of pairwise distinct exponents. The powers u, v, t are all distinct triplets of non-negative integers subject to the condition $u + v + t \leqslant \Omega$. In the case when $i = j$, an additional constraint, $u \leqslant v$, is assumed. As a result, the set of primitive functions is completely specified by a set of n_a exponents and a single number Ω. The total number of symmetric basis functions used to expand the singlet pairs can be calculated from the formula

$$K(n_a, \Omega) = n_a \kappa_1(\Omega) + \frac{n_a(n_a - 1)}{2} \kappa_2(\Omega), \qquad (11)$$

with $\kappa_1(\Omega)$ and $\kappa_2(\Omega)$ defined as

$$\kappa_1(\Omega) = \lfloor (\Omega + 2)(\Omega + 4)(2\Omega + 3)/24 \rfloor,$$
$$\kappa_2(\Omega) = (\Omega + 1)(\Omega + 2)(\Omega + 3)/6, \qquad (12)$$

where $\lfloor x \rfloor$ denotes the floor function of x. The number of antisymmetric basis functions used for the expansion of the triplet pairs is expressed by a formula similar to Eq. (11) but with the term $n_a \kappa_1(\Omega)$ replaced by $n_a \kappa_1(\Omega - 1)$. This results from the fact that the primitive functions in Eq. (1) with $a_i = a_j$ and $u = v$ vanish after antisymmetrization.

The self-consistent field (SCF) orbitals of the beryllium atom used in the FCCD calculations were calculated with the basis set in the form

$$(4\pi)^{-1/2} r^s e^{-a_k r}, \qquad (13)$$

TABLE I. SCF energies of the beryllium atom calculated with SCF(n_a, ω) basis sets along with the optimized exponents (a_k) and the corresponding errors (ΔE_{SCF}) with respect to the reference value (see text). All values are given in atomic units.

	a_1	a_2	a_3	a_4	ΔE_{SCF}
SCF(2, 7)	1.139	6.377			2×10^{-10}
SCF(3, 3)	0.9089	3.000	8.918		9×10^{-10}
SCF(3, 5)	0.9276	3.032	10.05		2×10^{-14}
SCF(3, 7)	0.9562	3.544	11.88		5×10^{-17}
SCF(4, 5)	0.8859	2.476	5.658	16.05	7×10^{-18}

where $s = 0, \ldots, \omega$, and $k = 1, 2, \ldots, n_a$. This constitutes a set of approximations, denoted SCF(n_a, ω), to the exact SCF energy. The optimal exponents were found by variational minimization of the SCF energy for fixed n_a and ω. Several representative examples of the calculated SCF energies are given in Table I. The estimated limit ($E_{\mathrm{SCF}} = -14.573\,023\,168\,316\,399\,582\ E_{\mathrm{h}}$) comes from SCF(11, 7) calculations with fixed exponents, $\{a_k\} = \{1/2, 1, 2, \ldots, 10\}$, and we believe it to be accurate to more than 20 significant digits.

The nonlinear parameters of the Hylleraas basis set (1) were not optimized in subsequent explicitly correlated calculations. Instead, they are fixed as all possible combinations of nonlinear parameters from a given SCF(n_a, ω) wave function (subject to the conditions detailed earlier in the text).

Three-electron integrals that appear in some terms of Eqs. (6)–(9) have the following general form:

$$\int \frac{d\mathbf{r}_1}{4\pi} \int \frac{d\mathbf{r}_2}{4\pi} \int \frac{d\mathbf{r}_3}{4\pi} \, r_1^{n_1} r_2^{n_2} r_3^{n_3} r_{12}^{n_4} r_{13}^{n_5} r_{23}^{n_6} \, e^{-a\,r_1 - b\,r_2 - c\,r_3}. \qquad (14)$$

In the present work they were calculated with help of the method developed by Pachucki and collaborators [52] based on a family of recursive relations. However, let us mention that some combinations of the powers n_i are not required in the FCCD computations. In fact, in all terms of Eqs. (6)–(9), at least one of n_4, n_5, or n_6 is always either -1 or zero. This is advantageous, as it eliminates a significant portion of the integrals and reduces the size of the integral files. Calculations of the integral files were performed within the quad-double arithmetic precision (QD library [55], approximately 64 significant digits), while the explicitly correlated computations were accomplished in the standard FORTRAN quadruple arithmetic precision (approximately 32 significant digits).

B. Orbital calculations

For the purposes of this paper we separate the total energy of an atom into several contributions,

$$E_{\mathrm{tot}} = E_{\mathrm{SCF}} + E_{\mathrm{FCCD}} + \delta_{\mathrm{S}} + \delta_{\mathrm{NF}} + \delta_{\mathrm{FCI}}, \qquad (15)$$

TABLE II. Dependence of the calculated total FCCD correlation energy on the parameter η for selected values of Ω. The SCF basis set is SCF(3, 7), and S measures the deviation from the strong-orthogonality condition, see Eq. (18). The energies are given in mE$_h$.

η	$\tau_{\alpha\beta}^s$		$q_B \tau_{\alpha\beta}^s$		$q_2 \tau_{\alpha\beta}^s$
	E	$\log_{10} S$	E	$\log_{10} S$	E
			$\Omega = 2$		
10^6	−90.625 341 531	−6.1	−90.625 313 732	−6.1	−90.625 379 201
10^4	−92.021 944 336	−5.3	−92.018 869 225	−5.3	−92.020 366 249
10^2	−92.603 864 518	−3.9	−92.432 844 678	−5.1	−92.435 575 222
10^0	−94.168 577 256	−0.5	−92.463 225 833	−5.1	−92.464 729 391
10^{-2}	−91.743 645 183	−0.1	−92.486 653 218	−4.9	−92.487 865 631
0	7256.282 371 921	+0.3	−92.541 588 807	−4.9	−92.541 519 617
			$\Omega = 6$		
10^6	−92.988 784 177	−11.8	−92.988 766 087	−12.9	−92.988 766 089
10^4	−92.990 573 333	−7.8	−92.988 766 697	−11.9	−92.988 766 695
10^2	−93.151 221 033	−3.8	−92.988 766 726	−11.9	−92.988 766 717
10^0	−94.133 618 742	−0.4	−92.988 766 718	−11.9	−92.988 766 721
10^{-2}	−91.012 330 964	−0.1	−92.988 766 665	−11.8	−92.988 766 741
0	300619.748 845 206	+0.3	−92.988 766 961	−11.6	−92.988 766 607
			$\Omega = 10$		
10^6	−92.988 789 564	−11.8	−92.988 771 476	−17.6	−92.988 771 476
10^4	−92.990 578 115	−7.8	−92.988 771 476	−15.2	−92.988 771 476
10^2	−93.151 225 803	−3.8	−92.988 771 477	−14.0	−92.988 771 476
10^0	−94.133 624 138	−0.4	−92.988 771 477	−13.9	−92.988 771 476
10^{-2}	−91.012 337 221	−0.1	−92.988 771 477	−13.9	−92.988 771 476
0	359.724 711 204	+0.3	−92.988 771 477	−13.9	−92.988 771 476

where E_{SCF} is the reference Hartree-Fock energy, E_{FCCD} is the FCCD energy as described in the previous section, and

$$\delta_S = E_{\text{CCSD}} - E_{\text{CCD}}, \qquad (16)$$

$$\delta_{\text{NF}} = E_{\text{CCD}} - E_{\text{FCCD}}, \qquad (17)$$

where E_{CCD} denotes the energy of the coupled cluster method with double excitations, and E_{CCSD}—with single and double excitations [27]. Furthermore, δ_{FCI} denotes the remaining correlation energy due to triply and quadruply excited configurations. The rearrangements in Eq. (15) are formally exact and provide a convenient basis for a composite method. In fact, the first two terms (E_{SCF} and E_{FCCD}) are by far dominating in Eq. (15) and thus must be computed to very high absolute accuracy. The remaining terms are orders of magnitude smaller and can be calculated with the standard methods based on the algebraic approximation.

The orbital calculations of δ_S, δ_{NF}, and δ_{FCI} were performed in the basis set of the Slater-type orbitals (STOs) optimized specifically for the purpose of this work. Overall, their composition and preparation are similar to those of Refs. [56–58] but involve functions with the highest angular momentum ranging from $L = 2$ to $L = 7$. (Further details can be obtained from the authors upon request.)

The orbital coupled cluster calculations were performed with the GAMESS program package [59,60]. The CCD program of Piecuch and collaborators [61] was modified to exclude the nonfactorizable CCD terms and thus make the orbital calculations directly comparable with the explicitly correlated FCCD method described earlier. Full CI (FCI) calculations

were performed with the general FCI program HECTOR [62], written by one of us (M.P.).

III. NUMERICAL RESULTS

A. Explicitly correlated calculations

The remaining problem in calculation of the FCCD energy is the choice of the strong-orthogonality forcing parameter η [see Eqs. (9) and (10)]. In Table II we show results of FCCD calculations with a representative reference function SCF(3, 7). We consider three methods of calculating the final FCCD energy, where the pair energies are given by Eq. (7) with the following function in ket:

(1) $\tau_{\alpha\beta}^s$ – no projection,

(2) $q_B \tau_{\alpha\beta}^s$ – the approximate projection restricted to the given geminal basis, Ref. [39],

(3) $q_2 \tau_{\alpha\beta}^s$ – the exact strong-orthogonality projection.

According to Eq. (3), all three approaches should give the same value for exact pair functions in the complete basis set. Additionally, the deviations from the strong orthogonality are measured with help of the following quantity:

$$S = \max_{\alpha,\beta,s} \frac{\langle \tau_{\alpha\beta}^s | p(1) + p(2) | \tau_{\alpha\beta}^s \rangle}{\langle \tau_{\alpha\beta}^s | \tau_{\alpha\beta}^s \rangle}, \qquad (18)$$

which is obviously zero when $\tau_{\alpha\beta}^s$ is replaced by $q_2 \tau_{\alpha\beta}^s$.

From Table II one can see that the approach without any projection yields useful results only when very large η is used in the iterative procedure. However, even under this condition the stability of the method is poor and the results depend

TABLE III. Convergence of the MP2 and FCCD correlation energies with Ω for different SCF(n_a, ω) basis sets. Unless stated otherwise, the energies were obtained with $\eta = 0$. All values are given in mE$_h$.

Ω	SCF(2, 7)	SCF(3, 3)	SCF(3, 5)	SCF(3, 7)	SCF(4, 5)
			MP2		
4	−76.312 058 331	−76.354 429 971	−76.353 733 011	−76.354 112 775	−76.355 826 310
5	−76.353 482 469	−76.357 871 937	−76.357 822 897	−76.357 873 524	−76.358 023 944
6	−76.357 716 463	−76.358 208 177	−76.358 205 564	−76.358 209 133	−76.358 229 597
7	−76.358 163 297	−76.358 244 644	−76.358 244 549	−76.358 244 486	−76.358 247 719
8	−76.358 231 147	−76.358 248 823	−76.358 248 708	−76.358 248 682	−76.358 249 173
9	−76.358 242 659	−76.358 249 369	−76.358 249 184	−76.358 249 204	−76.358 249 279
10	−76.358 246 439	−76.358 249 473	−76.358 249 255	−76.358 249 272	−76.358 249 287
11	−76.358 247 892	−76.358 249 507	−76.358 249 272	−76.358 249 282	−76.358 249 287
12	−76.358 248 568	−76.358 249 521	−76.358 249 279	−76.358 249 285	−76.358 249 287
13	−76.358 248 915	−76.358 249 529	−76.358 249 283	−76.358 249 286	−76.358 249 287
14	−76.358 249 104	−76.358 249 533	−76.358 249 285	−76.358 249 287	−76.358 249 287
15	−76.358 249 212	−76.358 249 535	−76.358 249 286	−76.358 249 287	−76.358 249 287
			FCCD		
4	−92.963 174 714	−92.987 900 387	−92.987 651 796	−92.987 688 596	−92.988 687 929
5	−92.986 550 626	−92.988 732 196	−92.988 705 338	−92.988 697 147	−92.988 767 531
6	−92.988 565 205	−92.988 76 8763	−92.988 767 304[a]	−92.988 766 607	−92.988 771 278
7	−92.988 740 066	−92.988 771 250	−92.988 771 050	−92.988 771 149	−92.988 771 468
8	−92.988 760 589[a]	−92.988 771 646	−92.988 771 371	−92.988 771 438	−92.988 771 480
9	−92.988 766 686	−92.988 771 771	−92.988 771 435	−92.988 771 467	−92.988 771 481
10	−92.988 769 260	−92.988 771 822	−92.988 771 460	−92.988 771 476	−92.988 771 482[b]

[a]Calculated with $\eta = 10^{-2}$.
[b]Calculated with $\eta = 10^6$.

heavily on the adopted value of η. Therefore, this approach is not recommended even in large basis sets.

On the other hand, the approximate and exact projections give very similar results, with the difference diminishing with increasing Ω. Even more importantly, for larger Ω the results depend very weakly on the adopted η and it is reasonable to set $\eta = 0$. This confirms the earlier recommendations from Ref. [38].

In Table III we present results of MP2 and FCCD calculations with several SCF basis sets and with a systematic increase of Ω. This allows us to investigate the convergence of the results towards the complete basis set limit. In general, the convergence rate depends significantly on the value of n_a in the reference SCF wave function. The number of a_i, a_j pairs in the basis set (1), which is used to expand the pair functions, scales quadratically with n_a. This means that the flexibility of the trial wave function increases quickly with n_a, as illustrated in Table III. With the SCF(2, 7) reference wave function the results are not converged even with Ω as large as 15. If we employ $n_a = 3$, the convergence of the MP2 energy to 1 pE$_h$ is achieved with $\Omega = 15$, and with $n_a = 4$ it is sufficient to use $\Omega = 10$ in order to reach the same level. In the latter case the convergence rate is close to exponential, e.g., an increase of Ω by one unit allows recovery of one additional significant digit. Taking this into account, we assume that the values obtained with the SCF(4, 5) basis set and the largest Ω available are accurate to within all digits shown in Table III. This gives −76.358 249 287 mE$_h$ and −92.988 771 482 mE$_h$ as our best estimates of the MP2 and FCCD total pair-correlation energies in the beryllium atom. We believe that the error of both these values is no larger than 1 pE$_h$ (10^{-12} E$_h$).

It is also important to consider the adequacy of the SCF reference function when accessing the accuracy of the final results. In fact, the Hylleraas functional utilized in the present work is variational only with the exact reference function. As illustrated in Table III, smaller SCF basis sets tend to give pair-correlation energies which are below the exact limit. This can lead to a spurious overestimation of the final results. To avoid this we follow a general rule of thumb that the error in the SCF energy (which is much easier to control) must be at least an order of magnitude smaller than the desired accuracy in the pair energies. For example, the SCF(3, 3) energy is accurate to 0.9 nE$_h$, which causes the corresponding FCCD energy to overshoot by about 0.3 nE$_h$ below the estimated exact limit.

Finally, the convergence of the MP2 and FCCD correlation energies to the complete basis set limit is illustrated in Fig. 1. One can see that the convergence rate of the FCCD energy is slightly faster than of MP2. Another interesting phenomena is the pronounced change in the slope of the curve at around $\Omega = 8 - 10$. We do not have a well-justified explanation of this behavior, but it is probably due to the fact that the same nonlinear parameters were used in the SCF and Hylleraas pair functions (without reoptimization). Another possible contributing factor is the importance of the three-particle cusp condition (at the coalescence point of two electrons and the nucleus), which introduces logarithmic singularities [63,64] in the exact pair functions.

The final results of our explicitly correlated calculations are summarized in Table IV. The corresponding results for the helium atom and the lithium cation and anion are also provided, together with data from Refs. [65–67], which used to be the most accurate results available in the literature. The uncertainty of the present data ($\sim$1 pE$_h$) constitutes an
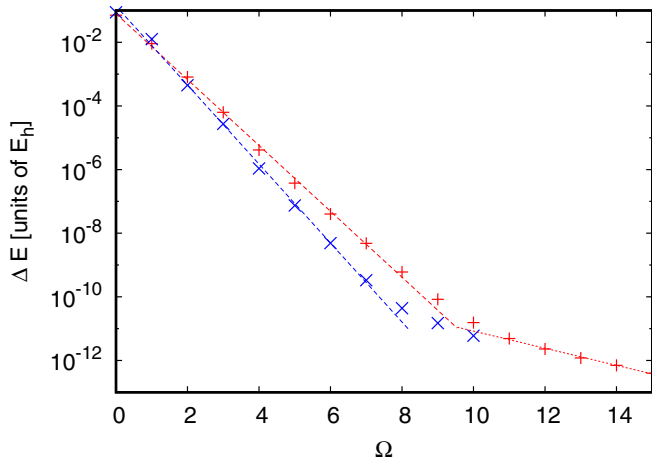
FIG. 1. Convergence of the MP2 (red pluses) and FCCD (blue crosses) correlation energy with Ω for the SCF(3, 7) basis set.

improvement of roughly 5 orders of magnitude compared with previous works. The only exception is the lithium anion, where the straightforward iteration procedure converges only for small values of Ω. For larger basis sets it becomes oscillatory and finally diverges. This change in the behavior usually occurred for n_a and Ω for which the number of basis functions exceeded 400 and prevented us from reducing the uncertainty below $0.01\,\mu E_h$.

B. Orbital calculations

In Table V we present results of the calculations of the δ_S, δ_{NF}, and δ_{FCI} corrections using Slater-type orbitals basis sets. The results were extrapolated to the complete basis set limit with help of the following three-point formula:

$$A + \frac{B}{(L+1)^3} + \frac{C}{(L+1)^5}, \qquad (19)$$

TABLE IV. Correlation energies (in mE_h) at different levels of theory for two- and four-electron atomic systems. The present results are shown in the first line while the best GTG results are collected in the second line.

	MP2	FCCD	CCD[a]
He	−37.377 474 518 9	−42.017 882 917	
	−37.377 474 52[b]	−42.017 71[c]	
Li⁺	−40.216 410 043 5	−43.490 592 055	
	−40.216 32[c]	−43.490 46[c]	
Li⁻	−60.473 978 826 7	−71.293 08	
	−60.473 971[d]	−71.293 022[e]	−71.266 072[e]
Be	−76.358 249 287 3	−92.988 771 482	
	−76.358 245[d]	−92.988 754[f]	−92.961 031[f]

[a]CCD and FCCD are equivalent for two-electron systems.
[b]600-term GTG expansion, Ref. [66].
[c]150-term GTG expansion, Ref. [65].
[d]400-term GTG expansion (optimized for MP2), Ref. [67].
[e]Reoptimized 400-term GTG expansion (infinite-order functional), Ref. [67].
[f]400-term GTG expansion (infinite-order functional), Ref. [67].

TABLE V. Corrections to the total correlation energy of the beryllium atom calculated within the STOs basis sets. The maximal angular momentum in each basis set is provided in the first column. All values are given in mE_h.

L	δ_S	δ_{NF}	δ_{FCI}
3	−0.680 857	0.028 117	−0.619 981
4	−0.692 823	0.027 932	−0.651 325
5	−0.693 542	0.027 843	−0.659 907
6	−0.695 871	0.027 793	−0.663 636
7	−0.697 089	0.027 768	−0.665 259
∞	−0.699 299	0.027 726	−0.667 195

which was found to perform best for the FCCD pair energies (in comparison with the corresponding explicitly correlated results). The quality of the extrapolation is illustrated in Fig. 2. One can see that the extrapolation formulas fit the results from $L = 4 - 7$ basis sets quite faithfully. The only exception is the basis set $L = 4$ for δ_S, which shows a considerable discrepancy, making the extrapolated result less reliable.

The extrapolated values of all corrections are given in Table V. In Table VI we provide a short summary of the results of the present paper and give the final estimation of the total energy of the beryllium atom. The errors of the respective components are estimated as twice the difference between the extrapolated results and the values in the largest basis set. The total error is about $5\,\mu E_h$ ($\sim 1\,cm^{-1}$) compared with the result of Puchalski *et al.* [68], which can be treated as a reference. This signifies that the present composite method is capable of reaching an accuracy comparable to many spectroscopic measurements. Further in the text we discuss the error in each component given in Table VI and attempt to isolate the dominant source of the discrepancy. As argued in the previous sections, the uncertainties in the SCF and FCCD energies are essentially negligible at this stage, as indicated in Table VI.
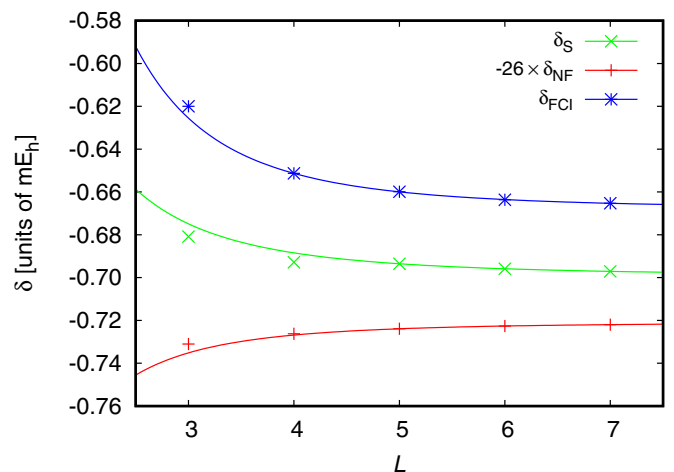

FIG. 2. Convergence of the δ_S, δ_{NF}, and δ_{FCI} corrections to the complete basis set limit. The correction δ_{NF} was multiplied by -26 to match the scale of the plot.

TABLE VI. Final prediction of the total energy of the beryllium atom. See the main text for details of the uncertainty estimation (shown in parentheses). The values without uncertainty estimation are accurate up to all digits quoted. The reference value is taken from Ref. [68]. All values are given in atomic units.

Contribution	Value
SCF	$-14.573\,023$
FCCD	$-0.092\,989$
δ_{NF}	$+0.000\,028$
δ_{S}	$-0.000\,699(4)$
Total CCSD	$-0.093\,660(4)$
δ_{FCI}	$-0.000\,667(4)$
Total energy	$-14.667\,351(6)$
Reference	$-14.667\,356$

The extrapolated value of the nonfactorizable doubles correction (δ_{NF}) agrees very well with the result from Table IV obtained independently with GTG expansions ($\delta_{NF} = 0.027\,723$ mE$_h$). The difference between these values is only about 3 nE$_h$, suggesting that both results are accurate to at least four significant digits. Moreover, as shown in Table V, the δ_{NF} correction stabilizes quickly with increasing basis set size. Therefore, we expect that in all practical applications it is sufficient to evaluate δ_{NF} with one-electron basis sets of a decent quality. In the present context, the uncertainty of δ_{NF} does not contribute significantly to the overall error, which is indicated in Table VI.

Unfortunately, the same cannot be said about the singles correction, δ_{S}. As mentioned earlier, the convergence of δ_{S} towards the complete basis set limit is less regular than for δ_{NF} or δ_{FCI}, and thus the related extrapolation is not as reliable. Therefore, we expect the extrapolated δ_{S} correction given in Table V to be accurate only to two significant digits. In fact, the present result differs by as much as 5 μE$_h$ from a more accurate value obtained in Ref. [65] using an explicitly correlated variant of the CCSD theory. We believe that this discrepancy dominates the error in the total energy of the beryllium atom given in Table VI. To confirm this we replace δ_{S} in Table VI by the value from Ref. [65] (-0.705 mE$_h$). The total error then drops to about ~ 0.1 cm^{-1}, which is an improvement by an order of magnitude. This shows clearly that the dominant error to the total result given in Table VI comes from inaccuracies in δ_{S}.

Finally, the correction for the higher-order excitations (δ_{FCI}) is of a similar magnitude as δ_{S} but exhibits a more regular convergence pattern towards the complete basis set limit. While we do not have any reliable result in the literature to compare with directly, a comparison with δ_{NF} allows us to claim that δ_{FCI} given in Table VI is accurate to three significant digits. In other words, the error in δ_{FCI} is of secondary concern in the present context.

IV. CONCLUSIONS

In this work we have reported the implementation and tests of a new composite method for accurate calculation of energies of many-electron atoms. The dominant contribution to the correlation energy has been calculated by using the explicitly correlated factorizable coupled cluster theory. To expand the pair functions we have employed the Hylleraas basis set and thus eliminated the need for optimization of the nonlinear parameters at the correlated level. This made it possible to compute pair-correlation energies of the beryllium atom with error smaller than 1 pE$_h$—an improvement of several orders of magnitude in comparison with the previous works—effectively removing the basis set incompleteness error in this component of the energy. The remaining contributions to the total energy have been calculated within the algebraic approximation employing large basis sets composed of Slater-type orbitals.

It is a natural and interesting question of how the present method can be used for heavier atoms, retaining or improving the current level of accuracy. In principle, the application of the theory to other closed-shell many-electron atoms is straightforward. However, the implementation is marred by difficulties related to proper treatment of angular factors originating from p, d, ... reference orbitals. Nonetheless, the Hylleraas basis set has been successfully applied to (high-l) excited states of the helium atom (see Ref. [69] and references therein), and we believe that similar extensions are feasible here.

The second problem is the extension of the present approach to open-shell reference states. The present state of the coupled cluster theory does not allow for routine treatment of all open-shell atoms, especially when quasidegenerate energy levels and partially occupied d or f shells are involved. Nevertheless, several possibilities have already been discussed in the literature and can be applied to s- and p-block atoms. The simplest solution is to build the wave function based on the restricted open-shell Hartree-Fock reference (ROHF) [70–74] whenever applicable. In some of the other cases various variants of the ionized or electron-attached equation-of-motion coupled cluster theories (IP-EOM or EA-EOM) can be employed [75–79]. Coupled cluster approaches of EOM or Fock-space [27] type are particularly attractive for applications in atomic spectroscopy as they enable simultaneous calculation of several electronic states with different characters (ionized, electron-attached, excited, etc.) [78,79]. Extension to open-shell cases requires solving technical questions specific for each open-shell formulation and will be reported in separate publications.

The present level of accuracy can be considerably improved if the correction due to single excitations (δ_{S}) is computed with smaller uncertainty. First-quantized expressions for the explicitly correlated CCSD model (where δ_{S} is included by construction) are well known [65]. Unfortunately, their implementation requires four-electron integrals which are, in general, not available in the Hylleraas basis set. Therefore, it is a considerable challenge to propose an approximate explicitly correlated CCSD model where the most problematic four-electron integrals can be eliminated. This is similar to the idea of Bukowski *et al.* [65], who proposed the factorizable quadratic CCSD model.

Another problem encountered for heavier atoms is calculation of energy contributions due to higher excitations from the reference determinant (pentuple, sextuple, etc.). With increasing number of electrons, the cost of the FCI method becomes prohibitively large. The most pragmatic approach to overcome

this problem is to employ a hierarchy of high-level orbital coupled cluster calculations [80]. With the aforementioned improvements we believe it will be possible to reach an accuracy of 0.1 cm^{-1} in calculation of the atomic energy differences. This will also require inclusion of the relativistic and quantum electrodynamics corrections, but as long as the atoms are not too heavy, these effects can be accounted for perturbatively. In this case the conventional calculations based on the algebraic approximation are probably sufficient to deliver the desired accuracy. This opens up a window for applications such as precision tests of the quantum electrodynamics [81]. Another

possible application is calculation of atomic properties such as polarizability (either by finite differences or analytically) which are used, e.g., in determination of the pressure and temperature standards [82].

[1] B. M. Roberts, V. A. Dzuba, and V. V. Flambaum, Annu. Rev. Nucl. Part. Sci. **65**, 63 (2015).

[2] T. Rosenband, D. B. Hume, P. O. Schmidt, C. W. Chou, A. Brusch, L. Lorini, W. H. Oskay, R. E. Drullinger, T. M. Fortier, J. E. Stalnaker, S. A. Diddams, W. C. Swann, N. R. Newbury, W. M. Itano, D. J. Wineland, and J. C. Bergquist, Science **319**, 1808 (2008).

[3] R. M. Godun, P. B. R. Nisbet-Jones, J. M. Jones, S. A. King, L. A. M. Johnson, H. S. Margolis, K. Szymaniec, S. N. Lea, K. Bongs, and P. Gill, Phys. Rev. Lett. **113**, 210801 (2014).

[4] N. Huntemann, B. Lipphardt, C. Tamm, V. Gerginov, S. Weyers, and E. Peik, Phys. Rev. Lett. **113**, 210802 (2014).

[5] K. S. E. Eikema, W. Ubachs, W. Vassen, and W. Hogervorst, Phys. Rev. A **55**, 1866 (1997).

[6] V. Korobov and A. Yelkhovsky, Phys. Rev. Lett. **87**, 193003 (2001).

[7] K. Pachucki, Phys. Rev. A **74**, 022512 (2006).

[8] B. Odom, D. Hanneke, B. D'Urso, and G. Gabrielse, Phys. Rev. Lett. **97**, 030801 (2006).

[9] G. Gabrielse, D. Hanneke, T. Kinoshita, M. Nio, and B. Odom, Phys. Rev. Lett. **97**, 030802 (2006).

[10] G. Gabrielse, D. Hanneke, T. Kinoshita, M. Nio, and B. Odom, Phys. Rev. Lett. **99**, 039902(E) (2007).

[11] E. A. Hylleraas, Z. Phys. **48**, 469 (1928).

[12] E. A. Hylleraas, Z. Phys. **54**, 347 (1929).

[13] G. W. F. Drake and Z.-C. Van, Chem. Phys. Lett. **229**, 486 (1994).

[14] M. Puchalski and K. Pachucki, Phys. Rev. A **73**, 022503 (2006).

[15] K. Szalewicz and B. Jeziorski, Mol. Phys. **108**, 3091 (2010).

[16] J. Mitroy, S. Bubin, W. Horiuchi, Y. Suzuki, L. Adamowicz, W. Cencek, K. Szalewicz, J. Komasa, D. Blume, and K. Varga, Rev. Mod. Phys. **85**, 693 (2013).

[17] J. S. Sims and S. A. Hagstrom, J. Chem. Phys. **55**, 4699 (1971).

[18] J. S. Sims and S. A. Hagstrom, J. Phys. B **37**, 1519 (2004).

[19] F. W. King, J. Chem. Phys. **99**, 3622 (1993).

[20] A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **15**, 1 (1977).

[21] A. M. Frolov and V. H. Smith, Jr., J. Phys. B **28**, L449 (1995).

[22] V. I. Korobov, Phys. Rev. A **66**, 024501 (2002).

[23] M. Puchalski and K. Pachucki, Phys. Rev. A **81**, 052505 (2010).

[24] F. Coester, Nucl. Phys. **7**, 421 (1958).

[25] F. Coester and H. Kümmel, Nucl. Phys. **17**, 477 (1960).

[26] J. Čížek, J. Chem. Phys. **45**, 4256 (1966).

[27] R. J. Bartlett and M. Musiał, Rev. Mod. Phys. **79**, 291 (2007).

[28] R. N. Hill, J. Chem. Phys. **83**, 1173 (1985).

[29] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[30] F. W. Byron and C. J. Joachain, Phys. Rev. **146**, 1 (1966).

[31] K. C. Pan and H. F. King, J. Chem. Phys. **53**, 4397 (1970).

[32] K. C. Pan and H. F. King, J. Chem. Phys. **56**, 4667 (1972).

[33] G. Chałasiński, B. Jeziorski, J. Andzelm, and K. Szalewicz, Mol. Phys. **33**, 971 (1977).

[34] K. Szalewicz and B. Jeziorski, Mol. Phys. **38**, 191 (1979).

[35] K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, Chem. Phys. Lett. **91**, 169 (1982).

[36] K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **78**, 1420 (1983).

[37] K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **79**, 5543 (1983).

[38] B. Jeziorski, H. J. Monkhorst, K. Szalewicz, and J. G. Zabolitzky, J. Chem. Phys. **81**, 368 (1984).

[39] K. Szalewicz, J. G. Zabolitzky, B. Jeziorski, and H. J. Monkhorst, J. Chem. Phys. **81**, 2723 (1984).

[40] L. Adamowicz and A. J. Sadlej, J. Chem. Phys. **67**, 4298 (1977).

[41] L. Adamowicz and A. J. Sadlej, J. Chem. Phys. **69**, 3992 (1978).

[42] L. Adamowicz, Int. J. Quantum Chem. **13**, 265 (1978).

[43] W. Kutzelnigg, Theor. Chim. Acta **68**, 445 (1985).

[44] W. Klopper and W. Kutzelnigg, Chem. Phys. Lett. **134**, 17 (1987).

[45] J. Noga, W. Kutzelnigg, and W. Klopper, Chem. Phys. Lett. **199**, 497 (1992).

[46] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, Chem. Rev. **112**, 4 (2012).

[47] L. Kong, F. A. Bischoff, and E. F. Valeev, Chem. Rev. **112**, 75 (2012).

[48] S. Ten-no, Theor. Chem. Acc. **131**, 1070 (2012).

[49] D. M. Fromm and R. N. Hill, Phys. Rev. A **36**, 1013 (1987).

[50] E. Remiddi, Phys. Rev. A **44**, 5492 (1991).

[51] F. E. Harris, Phys. Rev. A **55**, 1820 (1997).

[52] K. Pachucki, M. Puchalski, and E. Remiddi, Phys. Rev. A **70**, 032502 (2004).

[53] R. Bukowski, B. Jeziorski, and K. Szalewicz, in *Explicitly Correlated Wave Functions in Chemistry and Physics, Theory and Applications*, edited by J. Rychlewski (Kluwer, Dordrecht, 2003), pp. 185–248.

[54] K. B. Wenzel, J. G. Zabolitzky, K. Szalewicz, B. Jeziorski, and H. J. Monkhorst, J. Chem. Phys. **85**, 3964 (1986).

[55] Y. Hida, X. S. Li, and D. H. Bailey, "libqd: quad-double / double-double computation package", http://crd-legacy.lbl.gov/~dhbailey/mpdist/ (2012), version 2.3.20.

[56] M. Lesiuk and R. Moszynski, Phys. Rev. E **90**, 063318 (2014).

[57] M. Lesiuk and R. Moszynski, Phys. Rev. E **90**, 063319 (2014).

[58] M. Lesiuk, M. Przybytek, M. Musiał, B. Jeziorski, and R. Moszynski, Phys. Rev. A **91**, 012510 (2015).

[59] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).

[60] M. S. Gordon and M. W. Schmidt, in *Theory and Applications of Computational Chemistry. The First Forty Years*, edited by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria (Elsevier, Amsterdam, 2005), pp. 1167–1189.

[61] P. Piecuch, S. A. Kucharski, K. Kowalski, and M. Musiał, Comput. Phys. Commun. **149**, 71 (2002).

[62] M. Przybytek, FCI program HECTOR (unpublished).

[63] V. A. Fock, Izv. Akad. Nauk SSSR, Ser. Fiz. **18**, 161 (1954).

[64] J. D. Morgan III, Theor. Chim. Acta **69**, 181 (1986).

[65] R. Bukowski, B. Jeziorski, and K. Szalewicz, J. Chem. Phys. **110**, 4165 (1999).

[66] K. Patkowski, W. Cencek, M. Jeziorska, B. Jeziorski, and K. Szalewicz, J. Phys. Chem. A **111**, 7611 (2007).

[67] M. Przybytek, B. Jeziorski, and K. Szalewicz, Int. J. Quantum Chem. **109**, 2872 (2009).

[68] M. Puchalski, J. Komasa, and K. Pachucki, Phys. Rev. A **87**, 030502 (2013).

[69] G. W. F. Drake, in *Springer Handbook of Atomic, Molecular, and Optical Physics*, edited by G. W. F. Drake (Springer, New York, 2006), pp. 199–219.

[70] M. Rittby and R. J. Bartlett, J. Phys. Chem. **92**, 3033 (1988).

[71] C. L. Janssen and H. F. Schaefer, Theor. Chem. Acc. **79**, 1 (1991).

[72] W. J. Lauderdale, J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, J. Chem. Phys. **97**, 6606 (1992).

[73] P. J. Knowles, C. Hampel, and H. Werner, J. Chem. Phys. **99**, 5219 (1993).

[74] B. Jeziorski, J. Paldus, and P. Jankowski, Int. J. Quantum Chem. **56**, 129 (1995).

[75] J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993).

[76] M. Nooijen and R. J. Bartlett, J. Chem. Phys. **102**, 3629 (1995).

[77] A. I. Krylov, Annu. Rev. Phys. Chem. **59**, 433 (2008).

[78] M. Musiał, A. Perera, and R. J. Bartlett, J. Chem. Phys. **134**, 114108 (2011).

[79] M. Musiał, M. Olszówka, D. I. Lyakh, and R. J. Bartlett, J. Chem. Phys. **137**, 174102 (2012).

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

[81] K. Pachucki and J. Komasa, Phys. Rev. Lett. **92**, 213001 (2004).

[82] C. Gaiser and B. Fellmuth, Phys. Rev. Lett. **120**, 123203 (2018).