Relativistic coupled-cluster single-double method applied to alkali-metal atoms

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A relativistic version of the coupled-cluster single-double (CCSD) method is developed for atoms with a single valence electron. In earlier work, a linearized version of the CCSD method (with extensions to include a dominant class of triple excitations) led to accurate predictions for energies, transition amplitudes, hyperfine constants, and other properties of monovalent atoms. Further progress in high-precision atomic structure calculations for heavy atoms calls for improvement of the linearized coupled-cluster methodology. In the present work, equations for the single and double excitation coefficients of the Dirac-Fock wave function, including all nonlinear coupled-cluster terms that contribute at the single-double level, are worked out. Contributions of the nonlinear terms to energies, electric-dipole matrix elements, and hyperfine constants of low-lying states in alkali-metal atoms from Li to Cs are evaluated and the results are compared with other calculations and with precise experiments.

I. INTRODUCTION

A relativistic version of the coupled-cluster single-double (CCSD) approximation for monovalent atoms is developed. In this approximation, single and double excitations of the (frozen-core) Dirac-Fock wave function for an atom with one valence electron are included to all orders in perturbation theory. The relativistic CCSD is an extension of an earlier relativistic single-double (SD) approximation, in which all nonlinear coupled-cluster terms were omitted. The relativistic SD approximation provides a method closely related to the configuration-interaction method for including classes of correlation corrections to Dirac-Fock wave functions to all orders in perturbation theory. When modified to include the dominant triple excitations, the SD method led to accurate predictions for energies, transition matrix elements, lifetimes, hyperfine constants, and polarizabilities in alkali-metal atoms (see, for example, Refs. [1–6]). Owing to recent improvements in the precision of atomic experiments, it is important to go beyond the relativistic SD approximation and include the nonlinear coupled-cluster terms.

The coupled-cluster method is an all-order extension of many-body perturbation theory introduced into nuclear physics by Coester and Kümmel [7,8] and adapted to atomic and molecular physics by Čížek and Paldus [9–11]. A comprehensive review of the coupled-cluster method and its applications in quantum chemistry is given in Ref. [12]. Relativistic CCSD calculations for monovalent atoms have been carried out previously by Ynnerman *et al.* [13] for transition energies in Li-like U, by Eliav *et al.* [14] for ionization and excitation energies of alkali-metal atoms, by Lim *et al.* [15]

for polarizabilities of alkali-metal atoms from Li to element 119, by Mårtensson-Pendrill [16] for charge radii of francium isotopes, by Landau *et al.* [17] for electron affinities in alkali-metal atoms Na to element 119, by Chaudhuri *et al.* [18] for ionization and excitation energies in Rb and Cs, by Porsev and Derevianko [19] for properties of Na, by Derevianko and Porsev [20] for properties of Cs, and by Sahoo *et al.* [21] for parity nonconservation in Cs and Ba$^+$. Among the nonrelativistic applications of the CCSD method to alkali-metal atoms, we mention those of Lindgren [22] who calculated energies and hyperfine constants of $2s$ and $2p$ states in Li and Salomonson and Ynnerman [23] who evaluated energies and hyperfine constants of $3s$ and $3p$ states in Na.

The relativistic SD method for alkali-metal atoms was introduced in Ref. [24], where it was used to obtain energy levels, fine-structure intervals, hyperfine constants, and electric-dipole matrix elements in Li and Be$^+$. Later, the SD method was applied successfully to study properties of heavier alkali-metal atoms and monovalent ions [1–6]. Despite the success of the SD all-order method (and its extension to include important triples) in predicting many properties of monovalent systems, there are various instances where it fails to produce accurate results. For example, the magnetic-dipole hyperfine constant for the $7d_{5/2}$ state of Fr calculated using the SD method significantly disagrees with the experimental value [25]. The $nd_{5/2}$ hyperfine constants in Cs provide other such examples [26]. This issue is not limited to the hyperfine constants; correlation corrections to electric-dipole $6d_j−6p_{j'}$ matrix elements in Rb are so large that they change the sign of the matrix elements [4]. The large differences between third-order and all-order values

noted in Ref. [4] lead to the conclusion that the omitted higher-order contributions are significant. Cases where correlation corrections are extremely large lead to poor accuracy for the SD method, which is generally of high precision; in such cases, a more accurate treatment of correlations is mandatory.

Another motivation for further development of the relativistic SD method is the study of parity nonconservation (PNC) in heavy atoms. One goal of PNC studies is to provide atomic-physics tests of the standard model of the electroweak interactions through determination of the weak charge Q_W; another is to extract nuclear anapole moments from PNC measurements. A precise calculation of the PNC amplitude (together with an uncertainty estimate of the calculation) is necessary to derive a value of the weak charge Q_W from experimental measurements. The accuracy of the most advanced experimental study of PNC (which was carried out in Cs) is 0.3% [27], while the accuracy of the corresponding theoretical calculations is about 0.5% (see [28] and references therein). The difference between the value of Q_W extracted from experiment and the value inferred from the standard model stands at 1σ [20]. More accurate experiments, coupled with improvements in the calculation of PNC amplitude, will lead to a more accurate determination of Q_W and a more stringent test of the standard model.

Recently, a rather complete treatment of a class of triple excitations that included the valence electron and two core electrons was carried out in Refs. [19,20] for Na and Cs, respectively. Contributions of quadratic valence nonlinear terms were also calculated and found to be relatively large. As a result, further development of the all-order method must include a complete treatment of the nonlinear terms at the SD level.

In this work, we include all valence and core nonlinear coupled-cluster corrections to the SD equations, leading to a complete set of CCSD equations, and we study their effects on various atomic properties of alkali-metal atoms. In particular, we calculate ionization energies and hyperfine constants for the ground ns states and the $np_{1/2}$, $np_{3/2}$ excited states of Li, Na, K, Rb, and Cs. Reduced electric-dipole matrix elements for the $ns-np_{1/2}$ and $ns-np_{3/2}$ transitions are also calculated. We give a detailed breakdown of various nonlinear contributions in order to identify the most important effects and to measure the influence of core nonlinear terms. Comparison of our calculations with other theoretical calculations and with experimental results is presented.

II. COUPLED-CLUSTER METHOD

In coupled-cluster theory, the wave function of an atom with one valence electron in a state v is written as

$$|\Psi_v\rangle = \exp(S)|\Phi_v\rangle, \tag{1}$$

where $|\Phi_v\rangle$ is the lowest-order atomic wave function for atomic state v, which is taken to be a frozen-core Dirac-Fock (DF) wave function, and where the wave operator (the operator that maps the DF wave function onto the exact wave function) is expressed in exponential form $\exp(S)$. The exponential function in Eq. (1) can be expanded to give

$$|\Psi_v\rangle = (1 + S + \tfrac{1}{2}S^2 + \cdots)|\Phi_v\rangle. \tag{2}$$

The cluster operator S is expressed as a sum of n-particle excitations S_n of the lowest-order wave function

$$S = S_1 + S_2 + \cdots. \tag{3}$$

As the number of excitations increases, the complexity of the wave function increases. The computational complexity rises dramatically beyond the double excitation term S_2. Retaining only single and double excitations, Eq. (2) may be written

$$|\Psi_v\rangle = (1 + S_1 + S_2 + \tfrac{1}{2}S_1^2 + S_1 S_2 + \tfrac{1}{6}S_1^3 + \tfrac{1}{2}S_2^2 + \tfrac{1}{2}S_1^2 S_2$$
$$+ \tfrac{1}{24}S_1^4 + \cdots)|\Phi_v\rangle. \tag{4}$$

The one-electron excitation S_1 may be either an excitation of a core electron or an excitation of the valence electron. Correspondingly, the single core and valence excitations are given by

$$S_{1c} = \sum_{ma} \rho_{ma} a_m^\dagger a_a,$$

$$S_{1v} = \sum_{m \neq v} \rho_{mv} a_m^\dagger a_v. \tag{5}$$

Similarly, for double core and valence excitations

$$S_{2c} = \frac{1}{2} \sum_{mnab} \rho_{mnab} a_m^\dagger a_n^\dagger a_b a_a,$$

$$S_{2v} = \sum_{mnb} \rho_{mnvb} a_m^\dagger a_n^\dagger a_b a_v. \tag{6}$$

The expansion coefficients ρ_{ma} and ρ_{mv} are referred to later as single core and valence excitation coefficients, while ρ_{mnab} and ρ_{mnva} are referred to as double core and valence excitation coefficients, respectively. In Eqs. (5) and (6), $a_i^\dagger$ and a_i are creation and annihilation operators for an electron state i. Here and in subsequent formulas, the indices from the beginning of the alphabet $a, b, \ldots$ designate core states, indices from the middle of the alphabet $m, n, \ldots$ designate excited states, the index v labels the valence state, and indices i, j, k, and l designate arbitrary states.

In the SD method, only terms linear in the excitation coefficients are retained, and all remaining terms are omitted. Substituting Eqs. (5) and (6) into Eq. (4) and retaining the terms linear in the excitation coefficients yields the single-double (SD) all-order wave function

$$|\Psi_v\rangle = \left[1 + \sum_{ma} \rho_{ma} a_m^\dagger a_a + \frac{1}{2} \sum_{mnab} \rho_{mnab} a_m^\dagger a_n^\dagger a_b a_a \right.$$
$$\left. + \sum_{m \neq v} \rho_{mv} a_m^\dagger a_v + \sum_{mnb} \rho_{mnvb} a_m^\dagger a_n^\dagger a_b a_v \right] |\Phi_v\rangle. \tag{7}$$

To derive the equations for the excitation coefficients (see Ref. [24] for details), the SD all-order wave function (7) is substituted into the many-body Schrödinger equation

$$H|\Psi_v\rangle = E|\Psi_v\rangle, \tag{8}$$

where the Hamiltonian H is the relativistic *no-pair* Hamil-

tonian [29], which can be written in second-quantized form as $H = H_0 + V$, where

$$H_0 = \sum_i \epsilon_i [a_i^\dagger a_i], \qquad (9)$$

$$V = \frac{1}{2} \sum_{ijkl} g_{ijkl} [a_i^\dagger a_j^\dagger a_l a_k] + \sum_{ij} (V_{\rm DF} - U)_{ij} [a_i^\dagger a_j]$$

$$+ \frac{1}{2} \sum_a (V_{\rm DF} - 2U)_{aa}. \qquad (10)$$

In the *no-pair* Hamiltonian, contributions from negative-energy (positron) states are omitted. Products of operators enclosed in brackets, such as $[a_i^\dagger a_j^\dagger a_l a_k]$, designate normal products with respect to a closed core. The quantity U in Eq. (10) is the model potential used in the Dirac equation defining single-particle orbitals. In this work, U_{ij} is taken to be frozen-core Dirac-Fock potential

$$U_{ij} = (V_{\rm DF})_{ij} = \sum_a (g_{iaja} - g_{iaaj}). $$

Such a choice of the potential significantly simplifies calculation since the second term in Eq. (10) disappears. The quantities g_{ijkl} are two-body Coulomb matrix elements:

$$g_{ijkl} = \int d^3r \int d^3r' \, \psi_i^\dagger(\mathbf{r}) \psi_j^\dagger(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_k(\mathbf{r}) \psi_l(\mathbf{r}'),$$

and the quantity ϵ_i in Eq. (9) is the eigenvalue of the Dirac equation. The third term in Eq. (10) is a *c*-number and provides an additive constant to the energy of the atom.

The all-order SD wave function given by Eq. (7) includes only terms that are linear in the excitation coefficients. In the present work, we take into account all nonlinear terms that arise from the single and double excitations. Out of all possible nonlinear terms, only six terms, $\frac{1}{2}S_1^2$, $S_1 S_2$, $\frac{1}{6}S_1^3$, $\frac{1}{2}S_2^2$, $\frac{1}{2}S_1^2 S_2$, and $\frac{1}{24}S_1^4$, contribute to the single-double equations. Explicitly, the nonlinear terms contributing to the core single-double equations are $\frac{1}{2}S_{1c}^2$, $S_{1c}S_{2c}$, $\frac{1}{6}S_{1c}^3$, $\frac{1}{2}S_{2c}^2$, $\frac{1}{2}S_{1c}^2 S_{2c}$, and $\frac{1}{24}S_{1c}^4$ and the nonlinear terms contributing to the valence single-double equations are $S_{1c}S_{1v}$, $\{S_{1v}S_{2c}, S_{1c}S_{2v}\}$, $\frac{1}{2}S_{1c}^2 S_{1v}$, $S_{2c}S_{2v}$, $\{S_{1v}S_{1c}S_{2c}, \frac{1}{2}S_{1c}^2 S_{2v}\}$, and $\frac{1}{6}S_{1c}^3 S_{1v}$.

First, we consider the contributions from the nonlinear core terms. The first three nonlinear core terms,

$$T_1 = \frac{1}{2}S_{1c}^2 = \frac{1}{2} \sum_{rscd} \rho_{rc}\rho_{sd} a_r^\dagger a_s^\dagger a_d a_c, \qquad (11)$$

$$T_2 = S_{1c}S_{2c} = \frac{1}{2} \sum_{rstcde} \rho_{te}\rho_{rscd} a_r^\dagger a_s^\dagger a_t^\dagger a_e a_d a_c, \qquad (12)$$

$$T_3 = \frac{1}{6}S_{1c}^3 = \frac{1}{6} \sum_{rstcde} \rho_{te}\rho_{rc}\rho_{sd} a_r^\dagger a_s^\dagger a_t^\dagger a_e a_d a_c, \qquad (13)$$

contribute to equations for both single- and double-excitation coefficients, while the last three terms,

$$T_4 = \frac{1}{2}S_{2c}^2 = \frac{1}{8} \sum_{rstucdef} \rho_{rscd}\rho_{tuef} a_r^\dagger a_s^\dagger a_t^\dagger a_u^\dagger a_f a_e a_d a_c, \qquad (14)$$

$$T_5 = \frac{1}{2}S_{1c}^2 S_{2c} = \frac{1}{4} \sum_{rstucdef} \rho_{te}\rho_{uf}\rho_{rscd} a_r^\dagger a_s^\dagger a_t^\dagger a_u^\dagger a_f a_e a_d a_c, \qquad (15)$$

$$T_6 = \frac{1}{24}S_{1c}^4 = \frac{1}{24} \sum_{rstucdef} \rho_{rc}\rho_{sd}\rho_{te}\rho_{uf} a_r^\dagger a_s^\dagger a_t^\dagger a_u^\dagger a_f a_e a_d a_c, \qquad (16)$$

contribute to the equation for the double-excitation coefficients only.

The right-hand side of the single-double equations is obtained by operating on the nonlinear terms above with the two-particle interaction operator

$$G = \frac{1}{2} \sum_{ijkl} g_{ijkl} [a_i^\dagger a_j^\dagger a_l a_k] \qquad (17)$$

according to Eq. (10).

To derive the equation for the core single-excitation coefficients, we extract those terms in GT_k ($k = 1, 2, 3$) that are proportional to $a_m^\dagger a_a a_v^\dagger$. To derive the equation for the core double-excitation coefficients, we extract the terms in GT_k ($k = 1, \ldots, 6$) that are proportional to $\frac{1}{2}a_m^\dagger a_n^\dagger a_b a_a a_v^\dagger$. In all cases, we drop terms corresponding to disconnected diagrams. Below, we use the notations GT_k^s and GT_k^d to designate contribution of the corresponding terms to the single- or double-excitation equations, respectively. For clarity, we give the contributions from all terms separately.

The equation for the core single-excitation coefficients becomes

$$(\epsilon_a - \epsilon_m)\rho_{ma} = X_{\rm SD} + GT_1^s + GT_2^s + GT_3^s, \qquad (18)$$

where ϵ_i is the one-body DF energy for the state i, $X_{\rm SD}$ is the contribution from the linear coupled-cluster terms given in [24], and the contributions of the nonlinear terms are

$$GT_1^s = \sum_{drs} \widetilde{g}_{mdrs}\rho_{ra}\rho_{sd} - \sum_{cds} \widetilde{g}_{cdas}\rho_{mc}\rho_{sd}, \qquad (19)$$

$$GT_2^s = -\sum_{cdrs} \widetilde{g}_{cdsr}\rho_{rsda}\rho_{mc} - \sum_{cdrs} \widetilde{g}_{cdsr}\rho_{smcd}\rho_{ra}$$

$$+ \sum_{cdrs} \widetilde{g}_{cdrs}\widetilde{\rho}_{rmca}\rho_{sd}, \qquad (20)$$

$$GT_3^s = -\sum_{cdrs} \widetilde{g}_{cdsr}\rho_{mc}\rho_{rd}\rho_{sa}. \qquad (21)$$

We used the notations $\widetilde{g}_{mnab} = g_{mnab} - g_{mnba}$ and $\widetilde{\rho}_{mnab} = \rho_{mnab} - \rho_{mnba}$ in the above formulas.

The equation for the core double-excitation coefficients is

$$(\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n)\rho_{mnab}$$
$$= X_{\mathrm{SD}} + GT_1^d + GT_2^d + GT_3^d + GT_4^d + GT_5^d + GT_6^d, \tag{22}$$

where

$$GT_1^d = \sum_{rs} g_{mnrs}\rho_{ra}\rho_{sb} + \sum_{cd} g_{cdab}\rho_{mc}\rho_{nd}$$
$$- \left[\sum_{dr} \widetilde{g}_{mdar}\rho_{rb}\rho_{nd} + \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix} \right], \tag{23}$$

$$GT_2^d = \left[-\sum_{cdr} \widetilde{g}_{cdrb}\rho_{nd}\widetilde{\rho}_{rmca} - \sum_{cdr} \widetilde{g}_{cdar}\rho_{rd}\rho_{mncb} \right.$$
$$+ \sum_{cdr} g_{cdra}\rho_{rb}\rho_{nmcd} + \sum_{crs} \widetilde{g}_{ncrs}\rho_{rb}\widetilde{\rho}_{smca}$$
$$\left. + \sum_{crs} \widetilde{g}_{ncrs}\rho_{sc}\rho_{mrab} - \sum_{crs} g_{ncrs}\rho_{mc}\rho_{srab} + \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix} \right], \tag{24}$$

$$GT_3^d = \left[\sum_{cdr} g_{cdar}\rho_{nd}\rho_{mc}\rho_{rb} - \sum_{crs} g_{mcrs}\rho_{nc}\rho_{ra}\rho_{sb} + \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix} \right], \tag{25}$$

$$GT_4^d = \sum_{cdtu} g_{cdtu}\rho_{tuab}\rho_{mncd} + \sum_{cdtu} \widetilde{g}_{cdtu}\widetilde{\rho}_{mtac}\widetilde{\rho}_{undb}$$
$$- \left[\sum_{cdtu} \widetilde{g}_{cdtu}(\rho_{tubd}\rho_{mnac} + \rho_{mucd}\rho_{ntba}) + \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix} \right], \tag{26}$$

$$GT_5^d = \sum_{cdtu} g_{cdtu}(\rho_{ta}\rho_{ub}\rho_{mncd} + \rho_{mc}\rho_{nd}\rho_{tuab})$$
$$- \left[\sum_{cdtu} \widetilde{g}_{cdut}\rho_{tb}\rho_{uc}\rho_{mnad} + \sum_{cdtu} \widetilde{g}_{cdtu}\rho_{tc}\rho_{nd}\rho_{muab} \right.$$
$$\left. + \sum_{cdtu} \widetilde{g}_{cdtu}\rho_{tb}\rho_{nc}\widetilde{\rho}_{muad} + \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix} \right], \tag{27}$$

$$GT_6^d = \sum_{cdtu} g_{cdtu}\rho_{ta}\rho_{ub}\rho_{mc}\rho_{nd}. \tag{28}$$

All nonlinear contributions to double-excitation coefficients are symmetrized to preserve the property $\rho_{mnab} = \rho_{nmba}$.

Only one nonlinear term, $GT_1 = \frac{1}{2}GS_{1c}^2$, contributes to the equation for the core correlation energy:

$$\delta E_c = \delta E_c^{\mathrm{SD}} + \sum_{abmn} \frac{1}{2}\widetilde{g}_{abmn}\rho_{ma}\rho_{nb}, \tag{29}$$

where δE_c^{SD} is the core correlation energy obtained with linearized SD wave function (7):

$$\delta E_c^{\mathrm{SD}} = \frac{1}{2} \sum_{mnab} g_{abmn}\widetilde{\rho}_{mnab}.$$

We note that the summation over each index, for example i, involves summing over the principal quantum number n_i, the relativistic angular momentum quantum number κ_i, and the magnetic quantum number m_i. The sum over the magnetic quantum numbers is carried out analytically and the final formulas are given in the Appendix.

The equations for the valence excitation coefficients ρ_{mv} and ρ_{mnvb} are identical to the core equations given by Eqs. (18)–(28) with replacement of index a by index v and addition of the valence correlation energy δE_v into the parentheses on the left-hand side of both equations, i.e.,

$$(\epsilon_v - \epsilon_m + \delta E_v)\rho_{mv} = X_{\mathrm{SD}} + (GT_1^s + GT_2^s + GT_3^s)_{a\to v}, \tag{30}$$

$$(\epsilon_v + \epsilon_b - \epsilon_m - \epsilon_n + \delta E_v)\rho_{mnvb}$$
$$= X_{\mathrm{SD}} + (GT_1^d + GT_2^d + GT_3^d + GT_4^d + GT_5^d + GT_6^d)_{a\to v}. \tag{31}$$

The valence correlation energy δE_v is given by

$$\delta E_v = \delta E_v^{\mathrm{SD}} - \sum_{cdt} \widetilde{g}_{cdvt}\rho_{td}\rho_{vc} + \sum_{dtu} \widetilde{g}_{vdtu}\rho_{tv}\rho_{ud}$$
$$- \sum_{cdtu} \widetilde{g}_{cdut}\rho_{vc}\rho_{utvd} - \sum_{cdtu} \widetilde{g}_{cdut}\rho_{tv}\rho_{uvcd}$$
$$+ \sum_{cdtu} \widetilde{g}_{cdtu}\widetilde{\rho}_{vtvc}\rho_{ud} - \sum_{cdtu} \widetilde{g}_{cdut}\rho_{td}\rho_{uv}\rho_{vc}. \tag{32}$$

The term δE_v^{SD} represents the expression for the valence correlation energy without the nonlinear terms [24]:

$$\delta E_v^{\mathrm{SD}} = \sum_{ma} \widetilde{g}_{vavm}\rho_{ma} + \sum_{mab} g_{abvm}\widetilde{\rho}_{mvab} + \sum_{mnb} g_{vbmn}\widetilde{\rho}_{mnvb}.$$

The nonlinear contributions to the valence correlation energy arise from the $S_{1c}S_{1v}$, $\{S_{1v}S_{2c}, S_{1c}S_{2v}\}$, and $\frac{1}{2}S_{1c}^2S_{1v}$ terms.

We solve the SD equations using a finite basis set. Each orbital wave function is represented as a linear combination of the B splines. We consider a radial grid of 250 points within a sphere of radius 100 a.u. We include 35 out of 40 basis orbitals for each angular momentum and include all partial waves with $l \le 6$ in our calculations. A detailed description of the B-spline method is given in Ref. [30]. We treat the nonlinear terms on the same footing with the linear terms, i.e., all the linear and nonlinear terms are iterated together. First, the equations for the single core and double core excitation coefficients are iterated until the core correlation energy given by Eq. (29) converges to relative accuracy $\epsilon = 10^{-5}$. Then, the valence equations are iterated until the valence correlation energy given by Eq. (32) converges to the relative accuracy ϵ. Atomic properties can be evaluated once the values of the excitation coefficients are known, as briefly described below.

Matrix elements of a one-body operator $Z = \sum_{ij} Z_{ij}a_i^\dagger a_j$ are determined using the formula

$$Z_{wv} = \frac{\langle \Psi_w | Z | \Psi_v \rangle}{\sqrt{\langle \Psi_v | \Psi_v \rangle \langle \Psi_w | \Psi_w \rangle}}. \tag{33}$$

Substituting the expression for the wave function from Eq. (7) in the above equation and simplifying, one finds

$$Z_{wv} = \delta_{wv} Z_{\text{core}} + \frac{Z_{\text{val}}}{\sqrt{(1 + N_v)(1 + N_w)}}, \tag{34}$$

where Z_{core}, Z_{val}, N_v, and N_w are linear or quadratic functions of the single- and double-excitation coefficients written out in Refs. [1,24].

In general, the nonlinear terms coming from expanding the exponent in the CC wave function also contribute to the expressions to matrix elements. Even at the CCSD truncation level, one encounters an infinite number of such contributions. A rigorous method of partial summation (dressing) of the resulting series was devised in Ref. [31]. The method is built upon expanding a product of cluster amplitudes into a sum of n-body insertions. Although in the present paper we do not include these direct nonlinear contributions to matrix elements, calculations [20] show that dressing may contribute as much as a few 0.1% to hyperfine constants in Cs.

III. RESULTS AND DISCUSSION

A. Energies

Table I shows a detailed breakdown of contributions from nonlinear terms to the removal energies of the alkali-metal atoms Li, Na, K, Rb, and Cs. To illustrate the relative importance of the various terms, we conducted five separate calculations for each atom. Each subsequent calculation includes all terms in the previous calculation together with additional terms, the effect of which is being determined. For clarity, we describe each of the calculations below.

(1) Linearized SD calculation, with all nonlinear terms omitted. The results of this calculation are listed in the rows labeled "SD."

(2) All nonlinear terms are included in the core equations only, all nonlinear valence terms are omitted. The differences of those values and the SD results are listed in rows labeled "Core NL terms."

(3) All nonlinear terms are included in the core equations and the quadratic term $S_{2c}S_{2v}$ is included in the valence equations. The differences with the calculation (2) give the contributions from the nonlinear valence term $S_{2c}S_{2v}$ and are listed in the rows labeled accordingly.

(4) All nonlinear terms are included in the core equations, and all remaining quadratic terms are included in the valence equations. The differences between those values and the results of the calculation (3) give the contributions of the $S_{1c}S_{1v}$ and $\{S_{1v}S_{2c}, S_{1c}S_{2v}\}$ quadratic valence terms.

(5) Final calculation: all nonlinear terms are included in the core and valence equations. The results of this calculation are listed in the rows labeled "Total." The differences between those values and the results of the calculation (4) give the contributions of the cubic and quartic nonlinear terms that are listed in rows labeled "Other valence NL SD terms."

In all of the cases considered here, the addition of the nonlinear terms results in a decrease in the correlation con-

TABLE I. Contributions of the nonlinear (NL) terms to removal energies for Li, Na, K, Rb, and Cs. A detailed description of all contributions is given in text. SD designates the correlation corrections to the energies calculated using the SD method. All results are in cm^{-1}.

Li	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$
SD	406.0	352.1	352.0
Core NL terms	0.9	0.1	0.1
$S_{2c}S_{2v}$	−5.1	−4.2	−4.2
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	−2.6	−0.9	−0.9
Other valence NL SD terms	0.0	0.0	0.0
Total	399.2	347.1	347.0
Na	$3s_{1/2}$	$3p_{1/2}$	$3p_{3/2}$
SD	1483.3	462.0	459.8
Core NL terms	0.5	2.6	2.5
$S_{2c}S_{2v}$	−44.3	−15.3	−15.3
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	−23.8	−10.2	−10.1
Other valence NL SD terms	0.0	0.0	0.0
Total	1415.6	439.1	436.9
K	$4s_{1/2}$	$4p_{1/2}$	$4p_{3/2}$
SD	2869.7	1114.3	1100.5
Core NL terms	26.8	11.3	11.2
$S_{2c}S_{2v}$	−142.5	−59.1	−58.5
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	−62.9	−34.4	−34.3
Other valence NL SD terms	0.1	0.1	0.1
Total	2691.2	1032.2	1019.1
Rb	$5s_{1/2}$	$5p_{1/2}$	$5p_{3/2}$
SD	3423.2	1301.1	1236.3
Core NL terms	31.7	13.5	13.1
$S_{2c}S_{2v}$	−185.4	−76.7	−73.2
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	−105.0	−47.9	−46.3
Other valence NL SD terms	0.3	0.1	0.1
Total	3164.8	1190.1	1130.0
Cs	$6s_{1/2}$	$6p_{1/2}$	$6p_{3/2}$
SD	3881.5	1618.7	1442.3
Core NL terms	44.3	18.1	16.8
$S_{2c}S_{2v}$	−224.4	−107.3	−96.3
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	−162.4	−74.6	−68.3
Other valence NL SD terms	0.9	0.4	0.4
Total	3539.9	1455.3	1294.9

tributions to the removal energies. From Table I, we see that while the contribution of the core nonlinear terms to the removal energies is negligible compared to contribution of the valence nonlinear terms for the ground states of Na, it becomes significant (over 10% of the total NL contribution and about 1% of the total correlation energy) for all states of K, Rb, and Cs considered here. Furthermore, the contribution

from core NL terms is opposite in sign to that from the valence nonlinear contribution.

The $S_{2c}S_{2v}$ term gives the dominant nonlinear contribution, as expected. More than half of the contribution from nonlinear terms to the removal energy arises from this term. However, contributions from other quadratic terms, $S_{1c}S_{1v}$ and $\{S_{1v}S_{2c}, S_{1c}S_{2v}\}$, are also significant. Finally, the contributions from terms $\frac{1}{2}S_{1c}^2 S_{1v}$, $\{S_{1v}S_{1c}S_{2c}, \frac{1}{2}S_{1c}^2 S_{2v}\}$, and $\frac{1}{6}S_{1c}^3 S_{1v}$, i.e., terms that are cubic or quartic in the excitation coefficients, are negligible. For Li and Na, contributions from these terms are essentially zero; for K, Rb, and Cs, the contributions are less than 0.5% of the total from all nonlinear terms. The breakdown of contributions from the valence NL terms is essentially identical for all states of Na, K, Rb, and Cs under consideration. The total contribution of the NL terms to the correlation energies of the lowest three states of Na, K, Rb, and Cs is remarkably large; it is about 1.5% of the linear SD correlation energy for Li, 5% for Na, and 9% for Cs.

In Table II, we compare our results for the correlation with the linearized all-order calculations of Ref. [2] that partially include triple excitations, CCSD calculations of Ref. [14], the CCSD(T) calculations of Ref. [18], and with the experimental energies [32]. The values in the rows labeled "SD" are the sum of lowest-order (DF) energies, the SD contributions given in Table I, and the extrapolated contributions of the higher partial waves (E_{extrap}); the values in the rows labeled "CCSD" are the sums of the DF, SD, nonlinear contributions, and E_{extrap}. The CCSD values should agree with the calculation of Ref. [14] within the numerical uncertainties of the calculations. Significant differences between all-order SD results and CCSD results were noted earlier in Ref. [2], indicating that NL terms may be large. In this work, we find a good agreement between our CCSD values and the results of Ref. [14]. The remaining discrepancies can be explained by the differences in some numerical details of the calculations. In our calculations, we truncated the number of partial waves included in all sums over excited states at $l_{\text{max}} = 6$. Contributions from partial waves with $l > 6$ are extrapolated in second order (see [3] for details of the extrapolation procedure). The resulting correction increase for heavier alkali-metal atoms and is about 0.1% of the total energy of the $6s$ state in Cs. The differences between our values and those of Ref. [14] are of the same order of magnitude as the E_{extrap} contributions.

The SD approximation omits contributions to energies of third order in perturbation theory that arise from triple excitations. These missing third-order terms were included in the calculation of Ref. [2]. The size of these terms is approximately given by the differences between values listed in rows "SD" and "SD [2]." The calculation of Ref. [14] omits these terms entirely. Interestingly, these terms are of nearly the same magnitude as the NL terms and of the same sign. As a result, both calculation of Ref. [2], that omitted NL terms, and of Ref. [14], that omitted missing third-order terms, were in quite good agreement with experiment. It was shown in [19,20] that actual iterated triple contribution significantly differs from the third-order values. For this reason, and to make a clear comparison with previous CCSD results, we

TABLE II. Comparison of the all-order removal energies with the theoretical results obtained by the coupled-cluster method [14,18] and experiment. All the values are in cm^{-1}.

Li	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$
SD	43494	28586	28585
CCSD	43488	28581	28580
Expt. [32]	43487	28584	28583
Na	$3s_{1/2}$	$3p_{1/2}$	$3p_{3/2}$
SD	41444	24495	24476
CCSD	41376	24472	24453
SD [2]	41447	24494	24477
CCSD [14]	41352	24465	24447
Expt. [32]	41449	24493	24476
K	$4s_{1/2}$	$4p_{1/2}$	$4p_{3/2}$
SD	35258	22219	22066
CCSD	35080	22044	21984
SD [2]	34962	22023	21966
CCSD [14]	35028	22016	21957
Expt. [32]	35010	22025	21967
Rb	$5s_{1/2}$	$5p_{1/2}$	$5p_{3/2}$
SD	34021	21241	20994
CCSD	33762	21130	20888
SD [2]	33649	21111	20875
CCSD [14]	33721	21117	20877
CCSD [18]	33603	21080	20831
Expt. [32]	33691	21112	20874
Cs	$6s_{1/2}$	$6p_{1/2}$	$6p_{3/2}$
SD	31871	20421	19842
CCSD	31529	20258	19695
SD [2]	31262	20204	19652
CCSD [14]	31443	20217	19669
CCSD [18]	31250	20137	19574
Expt. [32]	31407	20228	19674

omit all triple contributions in this calculation. For Rb and Cs, we also list values from the CCSD(T) calculations of Ref. [18] in the rows labeled "CCSD [18]" that include contributions from triple excitations, but omit the odd-parity channels.

B. Reduced electric-dipole matrix elements

Table III gives the detailed breakdown of the contributions of the nonlinear terms to the reduced electric-dipole matrix elements for Li, Na, K, Rb, and Cs. This table is structured in exactly the same way as Table I; the only exception is that we added lowest-order DF values to the linearized SD values in rows labeled "SD." The breakdown of the nonlinear terms is identical to the breakdown for corre-

TABLE III. Contributions of the nonlinear terms to the $ns_{1/2}-np_{1/2}$ and $ns_{1/2}-np_{3/2}$ reduced electric-dipole matrix elements for Li, Na, K, Rb, and Cs. The final values are compared with experimental results. All values are given in atomic units (ea_0, where a_0 is the Bohr radius).

Li	$2s_{1/2}-2p_{1/2}$	$2s_{1/2}-2p_{3/2}$
SD	3.31654	4.69033
Core NL terms	−0.00007	−0.00008
$S_{2c}S_{2v}$	0.00063	0.00088
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	0.00020	0.00028
Other valence NL SD terms	0.00000	0.00000
Total	3.31730	4.69141
Expt. [33]	3.317(4)	4.689(5)
Na	$3s_{1/2}-3p_{1/2}$	$3s_{1/2}-3p_{3/2}$
SD	3.53099	4.99314
Core NL terms	0.00005	0.00006
$S_{2c}S_{2v}$	0.00487	0.00690
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	0.00211	0.00297
Other valence NL SD terms	0.00000	0.00000
Total	3.53802	5.00307
Expt. [33]	3.5246(23)	4.9838(34)
K	$4s_{1/2}-4p_{1/2}$	$4s_{1/2}-4p_{3/2}$
SD	4.09820	5.79392
Core NL terms	−0.00474	−0.00669
$S_{2c}S_{2v}$	0.02261	0.03198
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	0.00873	0.01231
Other valence NL SD terms	−0.00002	−0.00003
Total	4.12478	5.83149
Expt. [33]	4.102(5)	5.800(8)
Rb	$5s_{1/2}-5p_{1/2}$	$5s_{1/2}-5p_{3/2}$
SD	4.22005	5.95527
Core NL terms	−0.00649	−0.00913
$S_{2c}S_{2v}$	0.03230	0.04564
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	0.01533	0.02156
Other valence NL SD terms	−0.00004	−0.00006
Total	4.26115	6.01328
Expt. [33]	4.231(3)	5.977(4)
Cs	$6s_{1/2}-6p_{1/2}$	$6s_{1/2}-6p_{3/2}$
SD	4.48157	6.30391
Core NL terms	−0.01057	−0.01482
$S_{2c}S_{2v}$	0.04585	0.06437
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	0.02762	0.03865
Other valence NL SD terms	−0.00015	−0.00021
Total	4.54432	6.39190
Expt. [34]	4.4890(65)	6.3238(73)

TABLE IV. Values of the Fermi half-density c (fm) parameter used for magnetization distribution and gyromagnetic ratio g_I (in units of the nuclear magneton) which were used to calculate hyperfine constants.

Atom	c	g_I
^{7}Li	1.7995	2.17093
^{23}Na	2.8853	1.4784
^{39}K	3.6108	0.260993
^{85}Rb	4.8708	0.54136
^{133}Cs	5.6748	0.737886

lation energies. The major contribution comes from the term $S_{2c}S_{2v}$ as in the case of the removal energies. Also, there is almost no contribution from terms which are cubic or quartic in the excitation coefficients. The core nonlinear terms and the cubic and quartic valence nonlinear terms decrease the $E1$ reduced matrix elements, while the quadratic valence nonlinear terms increase these values. The only exception to the statement above is the contribution of the core nonlinear terms for Na which behaves in the opposite manner. Since the contribution of the quadratic valence nonlinear terms outweighs the contribution of all the other terms, the ultimate effect is an increase in values of the reduced electric-dipole matrix elements. As in the case of the correlation energies, the contribution of the NL terms is rather large, especially for heavy alkali metals where it reaches 1.5%. The comparison of our results with the experiment [33,34] is also given in Table III. Addition of nonlinear terms results in a deterioration of the agreement with experimental values as expected from [19,20] owing to significant cancellation between the valence NL and valence triple terms. A very interesting finding of this work is relatively large contribution of the core nonlinear terms for heavy alkali-metal atoms. While the core nonlinear term is entirely negligible for Na, it is found to be 0.2% for Cs.

C. Hyperfine constants

We calculate the magnetic-dipole hyperfine constants A for the $ns_{1/2}$ ground states and the $np_{1/2}$, $np_{3/2}$ excited states of Li, Na, K, Rb, and Cs. The nuclear magnetization density is described by a Fermi distribution with half-density radius c and 90%–10% falloff thickness $t=2.3$ fm. Table IV lists values of the parameter c (fm) used for magnetization distribution and the gyromagnetic ratio g_I for each of the alkali-metal atoms. The nuclear magnetic moments were taken from Ref. [35] and weighted averages were considered when more than one value was present.

Contributions of the various nonlinear terms to the hyperfine constants are given in Table V. The comparison of our results with experiment [36–43] is also given. The structure of Table V is identical to that of Table III. The "SD" values are the sum of the lowest-order DF values and correlation correction calculated in the absence of the NL terms. Addition of the nonlinear terms resulted in a decrease in the values of the hyperfine constants in comparison to the linearized

TABLE V. Contributions of nonlinear terms to the magnetic-dipole hyperfine constants A (MHz) of Li, Na, K, Rb, and Cs and comparison with experimental results. The experimental values are from Ref. [36] unless noted otherwise.

Li	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$
SD	395.232	45.176	−2.291
Core NL terms	−0.025	−0.005	0.006
$S_{2c}S_{2v}$	−1.439	−0.212	0.167
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	−0.183	−0.002	−0.011
Other valence NL SD terms	0.000	0.000	0.000
Total	393.585	44.957	−2.129
Expt.	401.75[a]	46.17(35)[b]	−3.07(13)[c]
Na	$3s_{1/2}$	$3p_{1/2}$	$3p_{3/2}$
SD	888.286	95.050	18.854
Core NL terms	−0.663	−0.242	−0.057
$S_{2c}S_{2v}$	−2.645	−1.022	−0.193
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	−4.878	−0.696	−0.174
Other valence NL SD terms	0.001	0.000	0.001
Total	880.101	93.090	18.431
Expt.	885.8	94.44(13)[d]	18.534(15)[e]
K	$4s_{1/2}$	$4p_{1/2}$	$4p_{3/2}$
SD	237.159	28.696	6.214
Core NL terms	0.457	0.138	0.032
$S_{2c}S_{2v}$	−2.783	−0.798	−0.123
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	−3.208	−0.489	−0.145
Other valence NL SD terms	0.007	0.002	0.001
Total	231.632	27.549	5.979
Expt.	230.85	28.85(30)	6.09(4)
Rb	$5s_{1/2}$	$5s_{1/2}$	$5p_{3/2}$
SD	1051.554	125.624	25.560
Core NL terms	5.319	0.710	0.155
$S_{2c}S_{2v}$	−14.198	−4.091	−0.577
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	−22.636	−3.058	−0.816
Other valence NL SD terms	0.047	0.007	0.002
Total	1020.086	119.192	24.324
Expt.	1011.9	120.7(1)	25.029(16)
Cs	$6s_{1/2}$	$6p_{1/2}$	$6p_{3/2}$
SD	2439.053	311.138	51.900
Core NL terms	20.455	2.604	0.475
$S_{2c}S_{2v}$	−39.441	−12.871	−1.137
$S_{1c}S_{1v}, \{S_{1v}S_{2c}, S_{1c}S_{2v}\}$	−80.300	−11.259	−2.489
Other valence NL SD terms	0.321	0.043	0.015
Total	2340.088	289.655	48.764
Expt.	2298.2	291.89(8)[f]	50.275(3)[g]

[a]Reference [37].
[b]Reference [38].
[c]Reference [39].
[d]Reference [40].
[e]Reference [41].
[f]Reference [42].
[g]Reference [43].

SD values. The NL core terms and the cubic and quartic valence nonlinear terms contribute with a positive sign to the hyperfine constants, while the quadratic valence nonlinear terms contribute with negative sign for K, Rb, and Cs. For Na and Li, all core and valence nonlinear terms contribute with the same sign. The most significant difference between the NL contributions to the hyperfine constants and to the removal energies and $E1$ matrix elements is that the contribution of the $S_{2c}S_{2v}$ terms is smaller than the contribution of the other three quadratic valence nonlinear terms $S_{1c}S_{1v}$, $\{S_{1v}S_{2c}, S_{1c}S_{2v}\}$ for the ground states of Na, K, Rb, and Cs. The breakdown is also different for the ns, $np_{1/2}$, and $np_{3/2}$ hyperfine constants while it is very uniform for all energies and $E1$ matrix elements considered here. The contributions of the core NL terms are particularly large for the hyperfine constants, almost 1% of the total values for Cs.

IV. CONCLUSION

We have extended the relativistic SD method to include all nonlinear terms at the SD level. The effect of the nonlinear terms on the removal energies, hyperfine constants, and electric-dipole matrix elements of the alkali-metal atoms from Li to Cs was systematically investigated. In particular, five different calculations were carried out to establish the importance of the various contributions for each alkali-metal atom. The effect of the core nonlinear terms was found to be not negligible for heavier alkali metals, reaching nearly 1% of the total values of the Cs hyperfine constants. Among other terms, the S_2^2 term was found to be dominant for removal energies and electric-dipole matrix elements with other quadratic terms being also significant. In the case of the hyperfine constants, the contributions of the other quadratic terms exceeded that of the S_2^2 term for most cases. The contribution of the cubic and quartic terms was found to be negligible in all cases considered in the present work. Inclusion of nonlinear terms in the single-double all-order method is a significant step toward further development of high-precision methodologies for the calculation of the atomic properties.

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APPENDIX: ANGULAR REDUCTION

1. Designations and definitions

The Coulomb interaction g_{mnab} is decomposed into the product of a term $J_k(mnab)$,

$$J_k(mmab) = \sum_q (-1)^{j_m - m_m + j_n - m_n + k - q}$$

$$\times \begin{pmatrix} j_m & k & j_a \\ -m_m & -q & m_a \end{pmatrix} \begin{pmatrix} j_n & k & j_b \\ -m_n & q & m_b \end{pmatrix},$$

(A1)

depending on only the angular momentum quantum numbers j_i and m_i of the four states (m, n, a, b), and a term $X_k(mnab)$ depending only on the principal quantum numbers n_i and angular quantum numbers κ_i of the states:

$$g_{mnab} = \sum_k J_k(mnab) X_k(mnab). \qquad (A2)$$

Here

$$X_k(mnab) = (-1)^k \langle \kappa_m \| C^k \| \kappa_a \rangle \langle \kappa_n \| C^k \| \kappa_b \rangle R_k(mnab).$$

(A3)

The quantities $R_k(mnab)$ are (relativistic) Slater integrals and $\langle \kappa_m \| C^k \| \kappa_a \rangle$ is a reduced matrix element of a normalized spherical harmonic. The quantities $Z_k(mnab)$ are given by

$$Z_k(mnab) = X_k(mnab) + \sum_{k'} [k] \begin{Bmatrix} j_m & j_a & k \\ j_n & j_b & k' \end{Bmatrix} X_{k'}(mnba),$$

where $[k] = 2k+1$. Double excitation coefficients have the same angular structure as Coulomb matrix elements:

$$\rho_{mnab} = \sum_k J_k(mnab) S_k(mnab)$$

and the quantities $\tilde{S}_k(mnab)$ are defined in the same way as $Z_k(mnab)$. The angular reductions for the single-excitation coefficients are defined as follows:

$$\rho_{ma} = \delta_{\kappa_m \kappa_a} \delta_{m_m m_a} S(ma),$$

$$\rho_{mv} = \delta_{\kappa_m \kappa_v} \delta_{m_m m_v} S(mv), \qquad (A4)$$

where κ is the relativistic angular momentum quantum number defined as

$$\kappa = \mp (j + 1/2) \quad \text{for } j = l \pm 1/2.$$

2. Angular decomposition of terms contributing to the equation for core single-excitation coefficients

$$GT_1^s = \sum_{drs} \sqrt{\frac{[j_d]}{[j_a]}} Z_0(mdrs) S(ra) S(sd)$$

$$- \sum_{cds} \sqrt{\frac{[j_d]}{[j_a]}} Z_0(cdas) S(mc) S(sd),$$

$$GT_1^s = -\sum_{cdrsl} \frac{(-1)^{r+s-a-d}}{[l][j_a]} Z_l(cdsr) S_l(rsda) S(mc)$$

$$- \sum_{cdrsl} \frac{(-1)^{c+s-a-d}}{[l][j_a]} Z_l(cdsr) S_l(smcd) S(ra)$$

$$+ \sum_{cdrs} \sqrt{\frac{[j_d]}{[j_a]}} \delta_{j_r j_c} Z_0(cdrs) \tilde{S}_0(rmca) S(sd),$$

$$GT_3^s = -\sum_{cdrs} \sqrt{\frac{[j_d]}{[j_a]}} Z_0(cdsr) S(mc) S(rd) S(sa).$$

3. Angular decomposition of the terms contributing to the equation for core double-excitation coefficients

$$GT_1^d = \sum_{rs} X_l(mnrs) S(ra) S(sb) + \sum_{cd} X_l(cdab) S(mc) S(nd) - \left[\sum_{dr} Z_l(mdar) S(rb) S(nd) + \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix} \right],$$

$$GT_2^d = \sum_{cdr} \frac{(-1)^{c+r+l}}{[l]} Z_l(cdrb) \tilde{S}_l(rmca) S(nd) - \sum_{cdr} \sqrt{\frac{[j_r]}{[j_a]}} \delta_{j_c j_a} Z_0(cdar) S_l(mncb) S(rd) + \sum_{cdrjk} (-1)^{n+m+a+b} [l] \begin{Bmatrix} k & l & j \\ j_a & j_d & j_m \end{Bmatrix}$$

$$\times \begin{Bmatrix} k & l & j \\ j_b & j_c & j_n \end{Bmatrix} X_j(cdra) S_k(nmcd) S(rb) - \sum_{crs} \frac{(-1)^{l+c+s}}{[l]} Z_l(ncrs) \tilde{S}_l(smca) S(rb) + \sum_{crs} \sqrt{\frac{[j_c]}{[j_n]}} \delta_{j_r j_n} Z_0(ncrs) S_l(mrab) S(sc)$$

$$- \sum_{crsjk} (-1)^{n+m+a+b} [l] \begin{Bmatrix} k & l & j \\ j_n & j_s & j_b \end{Bmatrix} \begin{Bmatrix} k & l & j \\ j_m & j_r & j_a \end{Bmatrix} X_j(ncrs) S_k(srab) S(mc) + \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix},$$

$$GT_3^d = \sum_{cdr} X_l(cdar) S(nd) S(mc) S(rb) - \sum_{crs} X_l(mcrs) S(nc) S(ra) S(sb) + \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix},$$

$$GT_4^d = \sum_{cdtu} \sum_{k_1 k_2 k_3 k} (-1)^{a+b+t+u} [l][k] \begin{Bmatrix} k_1 & k_3 & k \\ j_m & j_t & j_c \end{Bmatrix} \begin{Bmatrix} k_1 & k_3 & k \\ j_n & j_u & j_d \end{Bmatrix} \begin{Bmatrix} k_2 & k & l \\ j_m & j_a & j_t \end{Bmatrix} \begin{Bmatrix} k_2 & k & l \\ j_n & j_b & j_u \end{Bmatrix} X_{k_1}(cdtu) S_{k_2}(tuab) S_{k_3}(mncd)$$

$$+ \sum_{cdtu} \frac{(-1)^{c+d+t+u}}{[l]^2} Z_l(cdtu) \widetilde{S}_l(mtac) \widetilde{S}_l(undb) - \left[\sum_{cdtuk} \frac{(-1)^{c+d+t+u}}{[l][j_b]} \delta_{j_b j_c} Z_k(cdtu) S_k(tubd) S_l(mnac) \right.$$

$$+ \sum_{cdtuk} \frac{(-1)^{c+d+t+u}}{[l][j_m]} \delta_{j_t j_m} Z_k(cdtu) S_k(mucd) S_l(ntba) + \left. \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix} \right],$$

$$GT_5^d = \sum_{cdtujk} (-1)^{n+m+a+b} [l] \begin{Bmatrix} k & l & j \\ j_b & j_d & j_n \end{Bmatrix} \begin{Bmatrix} k & l & j \\ j_a & j_c & j_m \end{Bmatrix} X_j(cdtu) S_k(mncd) S(ta) S(ub) + \sum_{cdtujk} (-1)^{n+m+a+b} [l] \begin{Bmatrix} k & l & j \\ j_n & j_u & j_b \end{Bmatrix}$$

$$\times \begin{Bmatrix} k & l & j \\ j_m & j_t & j_a \end{Bmatrix} X_j(cdtu) S_k(tuab) S(mc) S(nd) - \left[\sum_{cdtu} \sqrt{\frac{[j_c]}{[j_b]}} \delta_{j_d j_b} Z_0(cdut) S_l(mnad) S(tb) S(uc) \right.$$

$$+ \sum_{cdtu} \sqrt{\frac{[j_c]}{[j_n]}} \delta_{j_n j_u} Z_0(cdtu) S_l(muab) S(tc) S(nd) + \sum_{cdtu} \frac{(-1)^{u-d+l}}{[l]} Z_l(cdtu) \widetilde{S}_l(muad) S(tb) S(nc) + \left. \begin{pmatrix} a \leftrightarrow b \\ m \leftrightarrow n \end{pmatrix} \right],$$

$$GT_6^d = \sum_{cdtu} X_l(cdtu) S(ta) S(ub) S(mc) S(nd).$$

4. Angular decomposition of terms contributing to the core and valence energies

$$\delta E_c^{NL} = \frac{1}{2} \sqrt{[j_a][j_b]} Z_0(abmn) S(ma) S(nb),$$

$$\delta E_v^{NL} = -\sum_{cdt} \sqrt{\frac{[j_d]}{[j_v]}} Z_0(cdvt) S(td) S(vc) + \sum_{dtu} \sqrt{\frac{[j_d]}{[j_v]}} Z_0(vdtu) S(tv) S(ud) - \sum_{cdutk} \frac{1}{[k][j_v]} Z_k(cdut) S_k(utvd) S(vc)$$

$$- \sum_{cdutk} \frac{1}{[k][j_v]} Z_k(cdut) S_k(uvcd) S(tv) + \sum_{cdtu} \sqrt{\frac{[j_d]}{[j_v]}} Z_0(cdtu) S_0(vtvc) S(ud) + \sum_{cdtu} \sqrt{\frac{[j_d]}{[j_v]}} Z_0(cdut) S(td) S(uv) S(vc).$$

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