

Third-order isotope-shift constants for alkali-metal atoms and ions

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We derive expressions for third-order matrix elements of one- and two-particle operators within the framework of relativistic many-body perturbation theory and use these formulas to evaluate specific-mass isotope shifts and isotope field shifts in atoms and ions with one valence electron. Third-order corrections to isotope-shift constants for $3s$, $3p$, and $3d$ levels in sodium and sodiumlike ions with $Z=12-18$ and $Z=26$ are given. Applications to $4s$, $4p$, $3d$, and $4d$ levels in K and $4s$, $4p$, and $3d$ levels in Ca^+ are also given. Comparisons are made with previous calculations and with experiment. Including third-order corrections improves the agreement between theoretical and experimental values of the specific-mass isotope-shift constants for the cases considered.

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I. INTRODUCTION

Isotope shifts of atomic transition frequencies consist of two parts, one arising from nuclear recoil and the other from the finite size of the nuclear charge distribution [1]. The nuclear recoil contribution is subdivided into a normal-mass shift (NMS) associated with the operator $-(1/2M)\sum_i p_i^2$, which can be accurately evaluated in terms of the transition frequency, and a specific-mass shift (SMS), contributed by the operator $(1/M)\sum_{i<j} \mathbf{p}_i \cdot \mathbf{p}_j$, which is difficult to evaluate accurately. The part of the isotope shift caused by the finite size of the nuclear charge distribution, referred to as the field shift (FS), is obtained from matrix elements of the operator $\delta V/\delta\langle r^2\rangle$, where V is the nuclear potential and $\langle r^2\rangle$ is the mean-square radius of the nucleus.

The Hartree-Fock (HF) method was used by Bauche [2] to evaluate the SMS in alkali-metal atoms and in a few atoms with two and three valence electrons. Bauche and Champau point out in their review of the theory of isotope shifts [3] that the HF value of the SMS of the D_1 line in Na does not agree at all with the experimental value [4]. Reasonable values of the SMS were obtained, starting from the HF theory and including higher-order corrections from many-body perturbation theory (MBPT), by Mårtensson and Salomonson [5] for Li and K, and by Lindroth and Mårtensson-Pendrill [6] for Na. Subsequently, Hörbäck *et al.* [7], Lindroth *et al.* [8], Mårtensson-Pendrill *et al.* [9,11,12], Hartley and Mårtensson-Pendrill [10], and Kurth *et al.* [13] carried out extensive MBPT calculations of the SMS and the field shifts for various atoms and ions. Theoretical values of the SMS have also been obtained using third-order MBPT by Veseth [14], and using multiconfiguration HF methods by Froese Fischer and coworkers [15].

In this paper, we develop formulas for diagonal third-order matrix elements of one- and two-particle operators, including angular reduction, within the framework of relativistic MBPT and use these formulas to evaluate third-order matrix elements of the one-particle field-shift operator and the two-particle SMS operator for atoms with one valence electron. With the aid of these third-order matrix elements, we obtain isotope shifts for $3s$, $3p$, and $3d$ levels in sodium and sodiumlike ions with $Z=12-18$ and $Z=26$; for $4s$, $4p$,

$3d$, and $4d$ levels in K; and $4s$, $4p$, and $3d$ levels in Ca^+ . Accurate values of the isotope shifts for sodiumlike ions are of importance currently in connection with the search for time variation of the fine-structure constant in alkali doublet absorption lines from quasars [16].

II. MATRIX ELEMENT

A. Specific-mass shift

We restrict our attention to an atom or ion with one valence electron and suppose that it is described to lowest order in the “frozen-core” HF approximation, where the core electrons satisfy closed-shell HF equations and the valence electron satisfies the HF equation in the fixed potential of the core. We express the SMS operator $P=\sum_{i<j} \mathbf{p}_i \cdot \mathbf{p}_j$ in second quantization as the sum of a normally ordered two-particle operator T and a normally ordered one-particle operator S

$$P=T+S, \quad (2.1)$$

$$T=\sum_{ijkl} t_{ijkl} : a_i^\dagger a_j^\dagger a_l a_k :, \quad (2.2)$$

$$S=\sum_{ij} t_{ij} : a_i^\dagger a_j :, \quad (2.3)$$

where $t_{ijkl}=\langle ij|\mathbf{p}_1 \cdot \mathbf{p}_2|kl\rangle$ and $t_{ij}=-\sum_a t_{iaaj}$, a being a core orbital. In the above equation, the notation $:\dots:$ designates normal ordering with respect to the core. The matrix element of P is referred to as the specific-mass shift constant; it is designated by K^{SMS} in Refs. [5–13,17].

We expand the state vector of the atom in powers of the residual Coulomb interaction and use it to obtain an order-by-order expansion of matrix elements of the operators S and T . As discussed by Bauche and Champau [3], formulas for matrix elements of P can be easily inferred from the corresponding formulas for the energy. In the relativistic case, the energy expansion for atoms with one valence electron is carried out explicitly through third order, for example, in [18]. To obtain formulas for the first-, second-, and third-order matrix elements of S and T , one simply replaces the Cou-

lomb matrix element $g_{ijkl} = \langle ij | 1/r_{12} | kl \rangle$ by $g_{ijkl} + t_{ijkl}$ and $(V_{\text{HF}} - U)_{ij}$ by $(V_{\text{HF}} - U)_{ij} + t_{ij}$ in expressions for the first-, second-, and third-order energy in [18] and linearizes in t_{ijkl} and t_{ij} , respectively. In this way, we find, for example,

$$S_{vv}^{(1)} = t_{vv} \equiv - \sum_a t_{avva}, \quad (2.5)$$

$$T_{vv}^{(1)} = 0. \quad (2.6)$$

Detailed expressions for first-, second-, and third-order matrix elements of S and T after angular reduction are written out in the Appendix.

Our calculation of $S^{(2)}$ is modified to include all third- and higher-order corrections from the random-phase approximation (RPA). This is done by replacing the “bare” matrix elements t_{ij} in Eq. (A4) by “dressed” RPA matrix elements t_{ij}^{RPA} obtained by solving the core RPA Eqs. (A9). The corresponding third-order RPA contributions are, of course, excluded from $S^{(3)}$. We also include important higher-order corrections in the remaining part of $S^{(3)}$, given in Eqs. (A10–A26), by replacing bare matrix elements of t_{ij} by their RPA counterparts t_{ij}^{RPA} . This generalization of third-order matrix elements is precisely the one required to make electric-dipole transition matrix elements gauge independent through third order, as shown in Ref. [19]. Second- and third-order electric-dipole matrix elements, modified as described above, led to amplitudes for dipole transitions in alkali-metal atoms that were accurate to better than 1% for all cases where precise comparison values were available.

To improve our calculations of S , we also carry out calculations using singles-doubles (SD) wave functions. These wave functions include single and double excitations of the lowest-order HF wave function to all orders in perturbation theory. The evaluation of one-particle matrix elements using SD wave functions is discussed in Refs. [20,21] and complete formulas, after summation over angular-momentum projection quantum numbers, are given in Ref. [22]. The SD wave functions used here also include the subset of triple excitations needed to reproduce all third-order corrections to valence energies as described in Refs. [21,22]. The relative importance of triple excitations in calculations of SMS matrix elements will be discussed later. We use the notation $S^{(\text{SD})}$ to designate corrections to one-particle SMS matrix elements evaluated using all-order SD wave functions. It should be noted that the matrix elements $S^{(\text{SD})}$ are complete through third order in MBPT. The two methods used here to calculate matrix elements of the operator S lead to values that include different subsets of the fourth- and higher-order corrections. We present results of both calculations in our tabulations of SMS values but, based on studies of the SD matrix elements reported in [20], we recommend $S^{(\text{SD})}$ as the more accurate alternative.

Two-particle contributions T to the specific-mass shift are calculated only through third order. Expressions for second- and third-order matrix elements of T are given in Eqs. (A7)–(A8) and (A27)–(A62) of the Appendix. These formulas are obtained from the corresponding expressions for the second- and third-order energy. The formulas are given for an arbitrary

TABLE I. Summary of contributions to the third-order two-particle matrix element of the specific-mass shift $T^{(3)}$ for the $3s$ state of Na in GHz amu.

	Term	Contr.	Term	Contr.	Term	Contr.
<i>I</i>	A27	247.72	A28	1.60	A29	247.72
<i>J</i>	A30	-247.17	A31	-1.34	A32	-247.17
<i>K</i>	A33	-6.36	A34	4.96	A35	-4.08
<i>L</i>	A36	-3.56	A37	-33.84	A38	6.46
<i>C</i>	A39	-43.41	A40	0.71	A41	-1.32
<i>A</i>	A42	7.20	A43	43.98	A44	7.20
<i>D</i>	A45	2.02	A46	0.33	A47	-1.31
<i>B</i>	A48	0.31	A49	-0.27	A50	0.31
<i>H</i>	A51	3.12	A52	-0.16	A53	-0.67
<i>G</i>	A54	-0.21	A55	1.45	A56	0.14
<i>F</i>	A57	-0.28	A58	0.04	A59	-0.28
<i>E</i>	A60	-0.61	A61	-6.97	A62	-0.61
	Total	-41.24		10.49		6.38

two-body operator and, therefore, can be used to calculate other quantities besides the specific-mass shift. Because of the complexity of calculations of matrix elements of two-body operators, we did not include corrections beyond third order. The expression for the third-order energy contains 56 terms associated with 56 distinct Brueckner-Goldstone diagrams. Substituting $g_{ijkl} + t_{ijkl}$ into the third-order energy and linearizing as described above, leads to $3 \times 56 = 168$ terms for the $T^{(3)}$. These terms can be regrouped and reduced to 36 terms by combining direct and exchange integrals. We give the breakdown of $T^{(3)}$ for the $3s$ state of Na in Table I. Before discussing this table, we briefly describe the numerical implementation of the many-body calculations.

To evaluate the formulas for one- and two-particle matrix elements in the Appendix, we use a one-particle basis set formed from linear combinations of B splines [23]. The one-particle basis orbitals are given on a nonlinear radial grid constrained to a large spherical cavity. The radius of the cavity is chosen to be 50 a.u. for neutral atoms and scaled down appropriately for ions. One-particle states with orbital angular momentum $l \leq 6$ are included in the basis, which consists of 40 radial wave functions represented as linear combinations of B splines of order 7, for each value of l .

In Table I, we list contributions from each of the 36 terms in Eqs. (A27)–(A62) for the $3s$ state of Na in GHz amu. We include the corresponding labels from Eqs. (A27)–(A62) for each term in columns headed “Term.” The three terms arising from a single third-order energy term $E^{(3)}$ in Ref. [24] are listed in the same rows for convenience; the labels of the corresponding energy diagrams from [24] are given in the first column of Table I. As we see from the table, seven terms, namely, A27, A29, A30, A32, A37, A39, and A43 are 5 to 35 times larger than any other term. It is easily seen from Eqs. (A27) and (A29) that the terms A27 and A29 are identical as are the terms A30 and A32, therefore, we omit terms A29 and A32 from further discussion.

We present the Goldstone diagrams for terms A27 and A30 in Fig. 1. In the figure, we designate the Coulomb in-

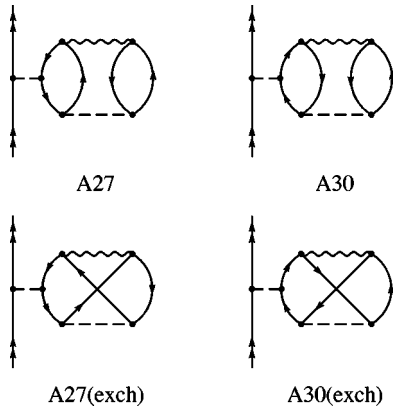


FIG. 1. Goldstone diagrams for the large third-order terms in $T^{(3)}$: Eqs. (A27) and (A30). These diagrams cancel almost completely.

teraction g_{ijkl} using a dashed line and the two-particle matrix element t_{ijkl} using a wavy line. We note that each of these two terms actually consists of four diagrams; however, only the one direct and one exchange diagram shown in Fig. 1 contributes significantly. The exchange diagrams presented in the second row of Fig. 1 are five times smaller than the direct terms and contribute with an opposite sign. In Fig. 1, each diagram on the left cancels each diagram on the right almost exactly and the remainder, after summing the terms A27 and A30, is only 0.2% of the individual terms. As shown in Table I, these diagrams correspond to third-order energy diagrams I and J from Ref. [24]. The cancellation of the I and J energy diagrams was discussed in Ref. [24]. We note that the terms A28 and A31 are very small since the Coulomb matrix element g_{vcvb} is replaced by t_{vcvb} , which vanishes because of selection rules. Therefore, only two small contributions containing t_{vcvb} survive for these two terms.

In Fig. 2, we present Goldstone diagrams for the other three large terms: A37, A39, and A43. These terms are represented by 20 Goldstone diagrams; however, only one diagram for each term gives the dominant contribution. The corresponding diagrams are shown in Fig. 2. As seen from Table I, terms A37 and A39 contribute with negative signs while term A43 contributes with a positive sign. The sum of all three diagrams is the dominant contribution to the total $T^{(3)}$ value for the $3s$ state of Na. Several other terms also give significant contributions to $T^{(3)}$ for the $3s$ state of Na. The largest of these is the sum of terms A42 and A44, which are equivalent as seen from the corresponding equations. These terms are dominated by the diagrams shown in Fig. 3.

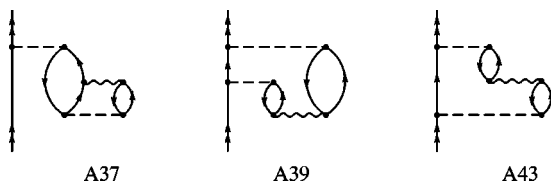


FIG. 2. Goldstone diagrams for the dominant residual terms in $T^{(3)}$ from Eqs. (A37), (A39), and (A43) for the $3s$ state of Na.

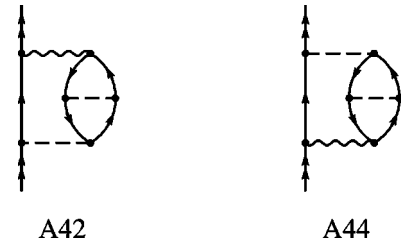


FIG. 3. Goldstone diagrams for the next-to-leading terms in $T^{(3)}$ from Eqs. (A42) and (A44) for the $3s$ state of Na.

For all of the cases considered, the terms A27, A29, A30, and A32 are the largest and strongly cancel, leading to an insignificant remainder. For $3s$ states of Na-like ions with $Z > 11$, the three terms A37, A39, and A43 remain dominant while A42 and A44 become relatively smaller with increasing nuclear charge. The terms A37, A39, and A43 are large for the $3p$ states of Na and Na-like ions, but A42 and A44 are small for these cases. For the $3d$ states, terms A39 and A43 are the largest but contribute with opposite signs. The term A37 becomes relatively more important for $3d$ states of Na-like ions as the nuclear charge increases. We note that the relative contribution from other diagrams also increases with the nuclear charge for all five states of Na-like ions considered here. For the $4s$ and $4p$ states of K and Ca^+ , as well as for the $3d$ states of K, the three terms A37, A39, and A43 are dominant with the term A37 being the smallest. For the case of the $3d$ states of Ca^+ , numerous other terms are large.

The relative importance of the third-order contributions to SMS constants is illustrated in Table II, where we give a breakdown for the $n=3$ states in Na. We list lowest-order (HF) values $P^{(1)}$, one-particle corrections $S^{(2)}$, $S^{(3)}$, and $S^{(2)}+S^{(3)}$; all-order corrections $S^{(\text{SD})}$; second- and third-order two-particle corrections $T^{(2)}$, $T^{(3)}$, and $T^{(2)}+T^{(3)}$; and the final theoretical SMS constants P_{tot} . The final values are sums of the $P^{(1)}$, $S^{(\text{SD})}$, and $T^{(2)}+T^{(3)}$. As we see from the table, the correlation correction is largest for the $3s$ state; the lowest-order value $P^{(1)}$ for the $3s$ state has the same order of magnitude as $S^{(2)}$, but has an opposite sign. The all-order result $S^{(\text{SD})}$ differs from the MBPT result $S^{(2)}+S^{(3)}$ by about 5% for $3s$ and $3p$ states. For $3d$ states, higher-order corrections are very important; second- and third-order corrections have the same order of magnitude and the all-order values

TABLE II. Contributions to specific-mass isotope-shift constants (GHz amu) in Na.

	$3s$	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
$P^{(1)}$	-222.00	-115.55	-115.46	-4.84	-4.87
$S^{(2)}$	167.93	48.35	48.28	0.96	0.97
$S^{(3)}$	28.11	1.20	1.20	0.95	0.95
$S^{(2)}+S^{(3)}$	196.04	49.55	49.48	1.92	1.92
$S^{(\text{SD})}$	205.26	51.57	51.48	2.79	2.79
$T^{(2)}$	95.04	28.16	28.11	-0.42	-0.42
$T^{(3)}$	-24.37	-7.54	-7.52	-0.48	-0.49
$T^{(2)}+T^{(3)}$	70.68	20.62	20.59	-0.90	-0.90
P_{tot}	53.94	-43.36	-43.39	-2.95	-2.99

TABLE III. Contributions to specific-mass isotope-shift constants (GHz amu) in K.

	$4s$	$4p_{1/2}$	$4p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$	$4d_{3/2}$	$4d_{5/2}$
$P^{(1)}$	-387.9	-118.7	-117.7	-113.8	-114.5	-74.8	-75.2
$S^{(2)}$	192.3	59.1	58.7	43.5	43.6	29.4	29.4
$S^{(3)}$	-2.2	0.1	0.2	-46.0	-46.2	-31.9	-31.9
$S^{(2)}+S^{(3)}$	190.1	59.2	59.0	-2.5	-2.5	-2.5	-2.5
$S^{(SD)}$	202.9	66.3	66.0	-26.9	-26.8	-19.2	-18.9
$T^{(2)}$	143.2	35.8	35.5	19.0	19.1	14.3	14.4
$T^{(3)}$	-32.9	-8.2	-8.1	-13.3	-13.4	-8.9	-8.9
$T^{(2)}+T^{(3)}$	110.3	27.7	27.4	5.7	5.7	5.5	5.5
P_{tot}	-74.7	-24.7	-24.3	-135.0	-135.6	-88.5	-88.6

are 30% higher than $S^{(2)}+S^{(3)}$. By evaluating the matrix elements of $S^{(SD)}$ using all-order wave functions with and without triple excitations, we found that triple-excitation corrections were negligible for all five states of Na. Two-particle contributions $T^{(2)}+T^{(3)}$ are two to three times smaller than one-particle contributions $S^{(2)}+S^{(3)}$ or $S^{(SD)}$ for all five states considered.

We find good agreement between our *second-order* values and the results of [6], which were also evaluated in second-order MBPT. Our final value of the specific-mass shift constant of the $3p-3s$ transition -97.3 GHz amu differs by 12% from the experimental value -110 GHz amu, which was obtained by subtracting the NMS and FS from the measured isotope shift [25]. It is in fair agreement with the multiconfiguration Hartree-Fock result of Froese Fischer *et al.* [15] and the MBPT result of Veseth [14], both of which are in close agreement with experiment.

In Tables III and IV, we present contributions to the SMS constants for $4s$, $4p$, $3d$, and $4d$ states of K, and for $4s$, $4p$, and $3d$ states of Ca^+ , respectively. The designations for various contributions are the same as in Table II. Lowest-order values $P^{(1)}$ for the $4s$ states of K and Ca^+ have the same sign as the final values; however, the HF approximation overestimates the size of P by a factor of five for K and a factor of three for Ca^+ . As in the case of sodium, third-order contributions, both one-particle and two-particle, are largest

TABLE IV. Contributions to specific-mass isotope-shift constants (GHz amu) in Ca^+ .

	$4s$	$4p_{1/2}$	$4p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
$P^{(1)}$	-927	-497	-491	-4308	-4296
$S^{(2)}$	421	207	205	1802	1794
$S^{(3)}$	5	-17	-16	-530	-526
$S^{(2)}+S^{(3)}$	426	190	189	1272	1268
$S^{(SD)}$	432	198	197	1299	1294
$T^{(2)}$	303	127	125	861	858
$T^{(3)}$	-67	-32	-32	-454	-452
$T^{(2)}+T^{(3)}$	236	95	93	408	407
P_{tot}	-259	-204	-200	-2601	-2595

for the d states. For K, the one-particle terms $S^{(2)}$ and $S^{(3)}$ nearly cancel for $3d$ and $4d$ states, enhancing contributions from fourth- and higher-order corrections. One, therefore, expects that the final theoretical values of P for $3d$ and $4d$ states of K will be less accurate than those for $3d$ states of Ca^+ . In Ca^+ , the third-order one-particle contribution $S^{(3)}$ is smaller than $S^{(2)}$ by a factor of three or more and the two-particle third-order contribution $T^{(3)}$ is about half of $T^{(2)}$. Therefore, the relative size of the correlation correction is smaller for Ca^+ than for K. The all-order one-particle values $S^{(SD)}$ are in good agreement with MBPT values $S^{(2)}+S^{(3)}$ for both K and Ca^+ , with the exception of the d states in K. However, as mentioned above, fourth- and higher-order corrections for these states are enhanced. This could explain differences for d states, given that MBPT and SD calculations take into account different subsets of fourth- and higher-order terms. The effect of partial inclusion of triple excitations in $S^{(SD)}$ is found to be negligible for all states of Na and is below 5% of $S^{(SD)}$ for all states of K and Ca^+ , except for d states of K.

In Ref. [9], the specific-mass shift constant for the $4p_{1/2}-4s$ transition was obtained from the experimental values for the $4p_{1/2}-4s$ level shifts in the $^{38-47}\text{K}$ chain [5]. The field shift was separated using the theoretical value for the field-shift constant calculated in [9] and the muonic value $\delta\langle r^{-2} \rangle^{41,39} = 0.117(40) \text{ fm}^2$ from Ref. [26]. The resulting value of the SMS constant, $15.4(3.8)$ GHz amu, [9] is much smaller than our value, 50 GHz amu. As we discussed above, there is a strong cancellation between the lowest-order and second-order values; consequently, fourth- and higher-order corrections, which are only in part included in our calculation of the one-particle contribution and are omitted from the two-particle contribution, become relatively more important.

Our final values for SMS constants of the $3d-4s$ and $3d-4p$ transitions in Ca^+ are in good agreement with experiment (7–11%). The agreement between our results and experimental values from Refs. [11,13,27] is worse for $4p-4s$ than for $3d-nl$ transitions; however, the experimental values for these transitions have large uncertainties and significant differences are found between values from different experiments [11,13,27]. We also compare our results with the many-body theoretical calculations for the $4s$ and $4p$ SMS constants from Ref. [8] and find good agreement. The many-body result for the SMS constant of the $3d$ state from Ref. [13] agrees with our second-order value. As we noted above, the second-order calculation underestimates the $3d$ SMS constant in Ca^+ by a factor of two. The present value of the SMS constant for the $3d$ state in Ca^+ , $P_{\text{tot}} = 2600$ GHz amu, is in good agreement with the value 2400 GHz amu inferred from experiment in Ref. [13].

We give our SMS constants for the $3s$, $3p$, and $3d$ states of Na-like ions with $Z=12-18$ and $Z=26$ in Table V. Triple excitations were found to be negligible for all of the states of Na considered here and they are, therefore, omitted in $S^{(SD)}$ calculations for Na-like ions. As expected, the relative importance of correlation decreases with increasing ionic charge. We found that $S^{(SD)}$ is relatively large for the $3s$ states of Na-like ions as it was for Na. For $3p$ and $3d$ states,

TABLE V. Specific-mass isotope-shift constants (GHz amu) for $n=3$ states of Na-like ions.

Ion	$3s$	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
Na I	54	-43	-43	-3	-3
Mg II	38	-324	-323	-105	-106
Al III	-34	-871	-869	-511	-514
Si IV	-152	-1678	-1672	-1326	-1333
P V	-312	-2737	-2726	-2558	-2570
S VI	-511	-4043	-4026	-4183	-4202
Cl VII	-748	-5594	-5569	-6177	-6204
Ar VIII	-1023	-7386	-7351	-8522	-8560
Fe XVI	-4587	-30 249	-30 028	-39 038	-39 246

contributions from $S^{(SD)}$ are several times smaller than $P^{(1)}$ for all values of Z considered. The two-particle contribution $T^{(2)}+T^{(3)}$ is also important, but it is two to three times smaller than $S^{(SD)}$ for most of the cases considered in Table V. Only limited comparison data is available for ions. Our value for the $3s$ specific-mass shift in Mg^+ , $\delta\nu_{\text{SMS}}^{26,24} = -120.4$ MHz, differs from the result of Ref. [14] by 6%.

We emphasize that third-order two-particle contributions are important for SMS constants in all of the cases considered here, not only because of the relatively large size of this contribution but also because of the strong cancellation between other MBPT terms.

B. Field shift

Following Lindroth and Mårtensson-Pendrill [6], we assume that the nuclear charge distribution can be well approximated as a uniformly charged ball of radius R . Using the fact that $\langle r^2 \rangle = (3/5)R^2$ for a uniform distribution, it follows that the operator describing the field shift is

$$f(r) \stackrel{\text{def}}{=} -\frac{\delta V(r,R)}{\delta \langle r^2 \rangle} = -\frac{5Z}{4R^3} \left[1 - \frac{r^2}{R^2} \right], \quad r < R$$

$$= 0, \quad r \geq R. \quad (2.7)$$

If we define the many-body field-shift operator F by

$$F = \sum_{ij} f_{ij} : a_i^\dagger a_j : + \sum_a f_{aa}, \quad (2.8)$$

then the change in energy of a state δE_F associated with a change in mean-square nuclear radius $\delta \langle r^2 \rangle$ in a valence state v is

$$\delta E_F = -\langle \Psi_v | F | \Psi_v \rangle \delta \langle r^2 \rangle. \quad (2.9)$$

The MBPT expressions for first-, second-, and third-order contributions to the field shift F are precisely the same as those for the one-particle part of the specific-mass shift S . Thus, for example, the lowest-order contribution to the field shift is

$$F_{vv}^{(1)} = f_{vv}, \quad (2.10)$$

TABLE VI. Contributions to field-shift constants F (MHz/fm²) in Na, K, and Ca⁺, $n=3$ for Na and $n=4$ for K and Ca⁺.

		ns	$np_{1/2}$	$np_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
Na	$F^{(1)}$	-29.70	-0.01	0.00	0.00	0.00
	$F^{(2)}$	-1.88	1.65	1.65	-0.01	-0.01
	$F^{(3)}$	-5.25	-0.04	-0.04	-0.06	-0.06
	F_{tot}	-36.83	1.60	1.60	-0.06	-0.06
K	$F^{(1)}$	-73.03	-0.08	0.00	0.00	0.00
	$F^{(2)}$	-6.52	4.43	4.42	0.82	0.81
	$F^{(3)}$	-27.18	-0.54	-0.52	0.06	0.06
	F_{tot}	-106.72	3.81	3.90	0.89	0.87
Ca ⁺	$F^{(1)}$	-215.5	-0.4	0.0	0.0	0.0
	$F^{(2)}$	-9.5	19.4	19.2	84.6	84.0
	$F^{(3)}$	-41.6	0.6	0.7	27.3	27.1
	F_{tot}	-266.6	19.6	19.9	111.8	111.2

where we have ignored the core contribution $\sum_a f_{aa}$ that cancels for transitions. Numerical calculations of the field shift require a refined radial grid. In the present calculations, we use a 1000 point radial grid with about 100 points inside the nucleus to evaluate the field shift.

In Table VI, we list first-, second-, and third-order contributions to the field-shift constants $F^{(1)}$, $F^{(2)}$, and $F^{(3)}$, respectively, in Na, K, and Ca⁺. The total field-shift contributions are given in rows labeled F_{tot} . It should be recalled that third- and higher-order RPA corrections are grouped together with the second-order RPA terms $F^{(2)}$. The contributions $F^{(3)}$ are obtained using Eqs. (A10)–(A26) of the Appendix with “dressed” matrix elements f_{ij}^{RPA} . As we see from Table VI, third-order contributions $F^{(3)}$ are very important for the ground states of Na, K, and Ca⁺, where they give 17–36% of F_{tot} . For $p_{3/2}$ and d states, the entire field shift arises from correlation, since $F^{(1)}$ vanishes. We note that terms $F^{(1)}$, $F^{(2)}$, and $F^{(3)}$ add coherently for most of the states; thus, we do not observe the severe cancellation between first-, second-, and third-order contributions found for the SMS constants. Field-shift constants for $3s$, $3p$, and $3d$ states of Na-like ions with $Z=12$ –18 and $Z=26$ are presented in Table VII.

Our values of $F^{(1)}+F^{(2)}$ for Na agree well with the corresponding values from Ref. [6]. Our final value F_{tot} for the $3p$ - $3s$ transition in Na 38.4 MHz/fm² is, however, in poor agreement with the third-order MBPT result 44.3 MHz/fm² from [14].

The field-shift constants for K were calculated in Ref. [9] using a nonrelativistic coupled-cluster singles-doubles method (CCSD) and corrected for relativistic effects. The final value for the $4s$ state of K given in [9] was obtained by modifying the *ab initio* CCSD value by 2.5%, based on a comparison of the theoretical $4s$ hyperfine constant with experiment. Our result for the $4s$ field-shift constant -106.7 MHz/fm² agrees with the final value -105 MHz/fm² Ref. [9] to 1.5%. Our value of F for the $4p$ - $4s$ transition agrees with that from [9] $-110(3)$ MHz/fm² within its uncertainty. The field-shift constant F for the $4p$ - $4s$ transition was also calculated by

TABLE VII. Field-shift constants (MHz/fm²) for $n=3$ states of Na-like ions.

	$3s$	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
Na I	-36.825	1.597	1.603	-0.062	-0.062
Mg II	-116.01	9.800	9.811	-0.083	-0.085
Al III	-243.36	25.029	25.057	1.477	1.470
Si IV	-433.42	47.568	47.652	6.538	6.517
P V	-703.15	78.040	78.280	16.389	16.334
S VI	-1072.3	117.33	117.86	31.874	31.755
Cl VII	-1563.4	166.34	167.44	53.683	53.458
Ar VIII	-2200.5	225.96	228.03	82.475	82.082
Fe XVI	-16 891	1223.9	1288.5	673.64	666.05

MBPT in Ref. [14] giving a result that is 34% below our value and that of Ref. [9].

Our values of F for the $4s$, $4p$, and $3d$ states of Ca^+ are in excellent agreement with the many-body calculation of Mårtensson-Pendrill *et al.* [11]. In Ref. [17], the values for the $3d$ - $4p$ field-shift constants were obtained from a King plot analysis of the experimental isotope shifts for the corresponding transitions. These experimental values differ from our calculation by 15%; however, uncertainties in the values from Ref. [17] range from 5 to 15%.

III. RESULTS AND COMPARISONS

In Table VIII, we compare our values of the isotope shifts $\delta\nu^{22,23}$ of $n=3$ states in Na with experimental data from Refs. [4,25,28]. The one-particle data for the SMS in the second column of the Table VIII is calculated in the SD approximation. We also list data for the field shift calculated using the field-shift constants from Table VI and the value $\delta\langle r^2 \rangle^{22,23} = -0.205(3) \text{ fm}^2$ obtained from the fit $\sqrt{\langle r^2 \rangle} = 0.836A^{1/3} + 0.570 \pm 0.05 \text{ fm}$ given in Ref. [29]. Our data for the total isotope shift for $3p$ - $3s$ transitions agree with experiment at the 3% level.

In Table IX, we present results for the total isotope shifts $\delta\nu^{41,39}$ of $4s$, $4p$, $3d$, and $4d$ states and $4p$ - $4s$, $3d$ - $4s$, and $4d$ - $4s$ transitions in K. The designations in Table IX follow those used in Table VIII. The field shifts are obtained using

TABLE VIII. Isotope shifts $\delta\nu^{22,23}$ (MHz) for $n=3$ states of Na.

	NMS+SMS	FS	Total IS	Expt.
$3s$	1448.8	-7.5	1441.3	
$3p_{1/2}$	707.9	0.3	708.2	
$3p_{3/2}$	707.3	0.3	707.6	
$3d_{3/2}$	391.8	0.0	391.8	
$3d_{5/2}$	391.8	0.0	391.8	
$3p_{3/2}$ - $3s$	-740.9	7.9	-733.0	-758.5(7) ^a -756.9(1.9) ^b
$3p_{5/2}$ - $3s$	-741.5	7.9	-733.6	-757.72(24) ^c

^aPescht *et al.* [4].^bHuber *et al.* [28].^cGangrsky *et al.* [25].TABLE IX. Isotope shifts $\delta\nu^{41,39}$ (MHz) in K.

	NMS+SMS	FS	Total IS	Expt.
$4s$	-627.6	12.5	-615.1	
$4p_{1/2}$	-422.7	-0.5	-423.2	
$4p_{3/2}$	-422.1	-0.5	-422.6	
$3d_{3/2}$	-108.5	-0.1	-109.6	
$3d_{5/2}$	-107.8	-0.1	-107.9	
$4d_{3/2}$	-46.0	-0.1	-46.1	
$4d_{5/2}$	-45.8	-0.1	-45.9	
$4p_{1/2}$ - $4s$	204.9	-12.9	192.0	235.25(75) ^a
$4p_{3/2}$ - $4s$	205.5	-12.9	192.6	
$3d_{3/2}$ - $4s$	519.1	-12.6	506.5	
$3d_{5/2}$ - $4s$	519.8	-12.6	507.2	
$4d_{3/2}$ - $4s$	581.6	-12.6	569.0	585(9) ^b
$4d_{5/2}$ - $4s$	581.8	-12.6	569.2	

^aTouchard *et al.* [30].^bHörbäck *et al.* [7].

field-shift constants from Table VI and the muonic atom value $\delta\langle r^2 \rangle^{41,39} = 0.117(40) \text{ fm}^2$ from Ref. [26]. Our value for the isotope shift for the $4p_{1/2}$ - $4s$ transition differs from the experimental value from Ref. [30] by 18%. The agreement is much better for the $4d_{1/2}$ - $4s$ transition where the difference is only 3%.

In Table X, we summarize results for the total isotope shifts $\delta\nu^{43,40}$ for $4s$, $4p$, and $3d$ states and $4p$ - $4s$, $3d$ - $4s$, and $3d$ - $4p$ transitions in Ca^+ and compare our results with

TABLE X. Isotope shifts $\delta\nu^{43,40}$ (MHz) in Ca^+ .

	NMS+SMS	FS	Total IS	Expt.
$4s$	-2298	33	-2265	
$4p_{1/2}$	-1670	-2	-1672	
$4p_{3/2}$	-1670	-2	-1672	
$3d_{3/2}$	2185	-14	2171	
$3d_{5/2}$	2175	-14	2161	
$4p_{1/2}$ - $4s$	627	-36	591	706(42) ^a 672(9) ^b 685(36) ^c
$4p_{3/2}$ - $4s$	628	-36	592	713(31) ^a 677(19) ^b 685(36) ^c
$3d_{3/2}$ - $4s$	4482	-47	4435	4180(48) ^a
$3d_{5/2}$ - $4s$	4473	-47	4426	4129(10) ^a
$3d_{3/2}$ - $4p_{1/2}$	3855	-12	3843	3464.3(3.0) ^d 3483(40) ^a
$3d_{3/2}$ - $4p_{3/2}$	3855	-11	3844	3462.4(2.6) ^d 3446(20) ^a
$3d_{5/2}$ - $4p_{3/2}$	3846	-11	3835	3465.4(3.7) ^d 3427(33) ^a

^aKurth *et al.* [13].^bMårtensson-Pendrill *et al.* [11].^cMaleki and Goble [27].^dNötherhäser *et al.* [17].

experiment from Refs. [11,13,17,27]. We use the same designations as in Table IX. To obtain the field-shift values listed in column FS, we use the value $\delta\langle r^{-2} \rangle^{43,40} = 0.1254(32) \text{ fm}^2$ from Ref. [31] and the field-shift constants listed in Table VI. The present values for the total isotope shifts are in agreement with experiment to 6% for the $3d-4s$ transitions, to 11% for the $3d-4p$ transitions and 15% for the $4p-4s$ transitions.

IV. CONCLUSION

In summary, we derived a set of formulas to evaluate diagonal matrix elements of one- and two-particle operators through third order for atoms with one valence electron. We used these formulas to determine specific-mass shift constants and field-shift constants in $3s$, $3p$, and $3d$ states of Na and Na-like ions with $Z=12-18$, and $Z=26$; $4s$, $4p$, $3d$, and $4d$ states of K, and $4s$, $4p$, and $3d$ states of Ca^+ . We found strong cancellation between lowest-order and second-order contributions to the specific-mass shift constants for Na, K, and Ca^+ . Because of these cancellations, it was necessary to conduct complete third-order calculations of both one-particle and two-particle contributions for the specific-mass shift constants. Since the one-particle contributions are dominant for all of the cases considered here, we also included subsets of fourth- and higher-order corrections to the one-particle part of the SMS. We also calculated the one-particle part of the SMS using the all-order SD method, including the subset of triple excitations. We found that one-particle contributions calculated in third-order MBPT were in good agreement with SD values for most of the cases considered here. We emphasize that even though the one-particle contribution is dominant for the states considered, the third-order two-particle contribution $T^{(3)}$ is very significant because of strong cancellation between lower-order MBPT terms. We presented a detailed breakdown of two-particle third-order SMS matrix elements to illustrate the relative importance of the various contributions to $T^{(3)}$.

Our values of the SMS constants for $3p-3s$ transitions in Na and $4p-3d$ and $3d-4s$ transitions in Ca^+ are in agreement with experiment to 7–11% [13,17,25]. The agreement is worse for K owing to strong cancellations between lowest-order and second-order values that enhances the role of fourth- and higher-order corrections. We calculated FS constants in third-order MBPT including subsets of fourth- and higher-order terms; good agreement between our calculations and other theoretical [6,9,11] and experimental [17] data was obtained.

We used our results for the SMS and FS constants to calculate total isotope shifts $\delta\nu^{(22,23)}$ in Na, $\delta\nu^{(41,39)}$ in K, and $\delta\nu^{(43,40)}$ in Ca^+ , and compared these results with other theoretical and experimental values. Our values for the isotope shifts for $3p-3s$ transitions in Na and $4d-4s$ transitions in K agree with experimental values [7,25] at the 3% level. The differences between our values and experiment [17] for $3d-4s$ and $3d-4p$ transitions in Ca^+ are 6 and 11%, respectively. The agreement between our results and experiment for $4s-4p$ transitions in K and Ca^+ is worse (15–18%). This can

be explained by strong cancellation of various MBPT contributions for these cases.

Including third-order two-particle matrix elements in calculations of specific-mass isotope shifts improves the agreement between theoretical and experimental values of isotope shifts for the cases considered. Further improvements along the lines of MBPT await a detailed study of fourth- and higher-order terms.

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APPENDIX: MATRIX ELEMENTS OF TWO-PARTICLE OPERATORS

To obtain formulas for the first-, second-, and third-order matrix elements of two-particle operators such as the specific-mass isotope shift operator, one simply replaces the Coulomb matrix element $g_{ijkl} = \langle ij | 1/r_{12} | kl \rangle$ by $g_{ijkl} + t_{ijkl}$ and $(V_{\text{HF}} - U)_{ij}$ by $(V_{\text{HF}} - U)_{ij} + t_{ij}$ in expressions for the first-, second-, and third-order energy in [18] and linearizes in t_{ijkl} and t_{ij} , respectively. In this way, we obtain the expressions for the diagonal contributions to the matrix element in the valence state v .

The first-order reduced matrix elements are

$$S^{(1)} = - \sum_a \frac{(-1)^{j_a - j_v + J}}{\sqrt{[j_v]}} T_J(vaav), \quad (\text{A1})$$

$$T^{(1)} = 0. \quad (\text{A2})$$

Here, and in the sequel, we designate core orbitals using indices a, b, c, d ; excited orbitals using indices m, n, r, s, t ; the valence orbital using the index v ; and arbitrary orbitals using indices i, j, k, l . For the case of the specific-mass shift, J has the value 1, and $T_1(ijkl)$ is given by

$$T_1(ijkl) = - \langle \kappa_i || C_1 || \kappa_k \rangle \langle \kappa_j || C_1 || \kappa_l \rangle P(ik)P(jl), \quad (\text{A3})$$

where $P(ij)$ are radial matrix elements of the momentum operator. The quantities $\langle \kappa_v || C^k || \kappa_a \rangle$ are reduced matrix elements of a normalized spherical harmonic,

$$\langle \kappa_v || C_k || \kappa_a \rangle = (-1)^{j_v + 1/2} \sqrt{[j_v][j_a]} \\ \times \begin{pmatrix} j_v & j_a & k \\ -1/2 & 1/2 & 0 \end{pmatrix} \Pi(l_v + l_a + k),$$

$$\Pi(l) = \begin{cases} 1, & \text{if } l \text{ is even} \\ 0, & \text{if } l \text{ is odd} \end{cases} \quad [k] = 2k + 1.$$

The second-order one-particle reduced matrix element $S^{(2)}$ is given by

$$S^{(2)} = \sum_{an} \frac{(-1)^{j_a - j_n + J}}{[J]} \frac{t(an)Z_J(vnva)}{\epsilon_a - \epsilon_n} + \sum_{an} \frac{(-1)^{j_a - j_n + J}}{[J]} \frac{Z_J(vavn)t(na)}{\epsilon_a - \epsilon_n}, \quad (\text{A4})$$

where ϵ_i is the one-body Dirac-Hartree-Fock energy for the state i , and the quantity $Z_L(ijkl)$ is defined as

$$Z_L(ijkl) = X_L(ijkl) + \sum_{L'} [L] \begin{Bmatrix} j_i & j_k & L \\ j_j & j_l & L' \end{Bmatrix} X_{L'}(ijlk),$$

where $X_L(ijkl)$ is expressed in terms of reduced matrix elements of unit tensors $C_L(\hat{r})$ and Slater integrals $R_L(ijkl)$ by

$$X_L(ijkl) = (-1)^L \langle \kappa_i || C_L || \kappa_k \rangle \langle \kappa_j || C_L || \kappa_l \rangle R_L(ijkl). \quad (\text{A5})$$

The quantities $t(ij)$ are defined as

$$t(ij) = \delta_{\kappa_i \kappa_j} \sum_a \frac{(-1)^{j_a - j_i}}{\sqrt{[j_i]}} T_J(iaaj). \quad (\text{A6})$$

The second-order two-particle matrix elements are given by

$$T^{(2)} = -2 \sum_{mab} \frac{1}{[j_v][J]} \frac{T_J(mvab)Z_J(mvab)}{\epsilon_{ab} - \epsilon_{mv}} \quad (\text{A7})$$

$$+ 2 \sum_{amn} \frac{1}{[j_v][J]} \frac{T_J(mnva)Z_J(mnva)}{\epsilon_{va} - \epsilon_{mn}}, \quad (\text{A8})$$

where $\epsilon_{ij} \equiv \epsilon_i + \epsilon_j$.

Before writing out the expression for the third-order one-particle matrix elements, we define the one-particle matrix elements in random-phase approximation (RPA):

$$t^{\text{RPA}}(ij) = t(ij) + \sum_{bm} \frac{(-1)^{j_b - j_m + J}}{[J]} \frac{t^{\text{RPA}}(bm)Z_J(imjb)}{\epsilon_b - \epsilon_m} + \sum_{bm} \frac{(-1)^{j_b - j_m + J}}{[J]} \frac{Z_J(ibjm)t^{\text{RPA}}(mb)}{\epsilon_b - \epsilon_m}. \quad (\text{A9})$$

The third-order RPA contribution to the one-particle matrix elements $S_{\text{RPA}}^{(3)}$ is obtained by replacing $t(an)$ and $t(na)$ in Eq. (A4) by the first term in the iterative solution of the RPA equations for $t^{\text{RPA}}(an)$ and $t^{\text{RPA}}(na)$. The ‘‘full’’ RPA contribution to the one-particle matrix elements is obtained by replacing $t(an)$ and $t(na)$ in Eq. (A4) by the fully converged $t^{\text{RPA}}(an)$ and $t^{\text{RPA}}(na)$ matrix elements. The angular reduction of the third-order one-particle matrix elements has been carried out in Ref. [32].

The remaining third-order contribution is given by

$$\bar{S}^{(3)} = \sum_{i \neq v} \sum_{abm} \sum_k \delta_{\kappa_i \kappa_v} \frac{1}{[k][j_v]} \frac{t(vi)X_k(imab)Z_k(vmab)}{(\epsilon_v - \epsilon_i)(\epsilon_{vm} - \epsilon_{ab})} \quad (\text{A10})$$

$$+ \sum_{i \neq v} \sum_{abm} \sum_k \delta_{\kappa_i \kappa_v} \frac{1}{[k][j_v]} \frac{t(iv)X_k(imab)Z_k(vmab)}{(\epsilon_v - \epsilon_i)(\epsilon_{vm} - \epsilon_{ab})} \quad (\text{A11})$$

$$- \sum_{i \neq v} \sum_{amn} \sum_k \delta_{\kappa_i \kappa_v} \frac{1}{[k][j_v]} \frac{t(vi)X_k(ianm)Z_k(vanm)}{(\epsilon_v - \epsilon_i)(\epsilon_{nm} - \epsilon_{av})} \quad (\text{A12})$$

$$- \sum_{i \neq v} \sum_{amn} \sum_k \delta_{\kappa_i \kappa_v} \frac{1}{[k][j_v]} \frac{t(iv)X_k(ianm)Z_k(vanm)}{(\epsilon_v - \epsilon_i)(\epsilon_{nm} - \epsilon_{av})} \quad (\text{A13})$$

$$+ \sum_{abcr} \sum_{kk'} (-1)^J \begin{Bmatrix} j_v & j_v & J \\ k & k' & j_b \end{Bmatrix} \begin{Bmatrix} j_r & j_c & J \\ k' & k & j_a \end{Bmatrix} \frac{t(cr)Z_k(vrba)X_{k'}(bavc)}{(\epsilon_r - \epsilon_c)(\epsilon_{rv} - \epsilon_{ab})} \quad (\text{A14})$$

$$+ \sum_{abcr} \sum_{kk'} (-1)^J \begin{Bmatrix} j_v & j_v & J \\ k & k' & j_b \end{Bmatrix} \begin{Bmatrix} j_r & j_c & J \\ k' & k & j_a \end{Bmatrix} \frac{t(rc)Z_k(bavr)X_{k'}(vcba)}{(\epsilon_r - \epsilon_c)(\epsilon_{rv} - \epsilon_{ab})} \quad (\text{A15})$$

$$+ \sum_{cmnr} \sum_{kk'} (-1)^J \begin{Bmatrix} j_v & j_v & J \\ k & k' & j_n \end{Bmatrix} \begin{Bmatrix} j_r & j_c & J \\ k' & k & j_m \end{Bmatrix} \frac{t(cr)X_k(vrnm)Z_{k'}(nmvc)}{(\epsilon_r - \epsilon_c)(\epsilon_{nm} - \epsilon_{cv})} \quad (\text{A16})$$

$$+ \sum_{cmnr} \sum_{kk'} (-1)^J \begin{Bmatrix} j_v & j_v & J \\ k & k' & j_n \end{Bmatrix} \begin{Bmatrix} j_r & j_c & J \\ k' & k & j_m \end{Bmatrix} \frac{t(rc)X_k(nmvr)Z_{k'}(vcnm)}{(\epsilon_r - \epsilon_c)(\epsilon_{nm} - \epsilon_{cv})} \quad (\text{A17})$$

$$+ \sum_{acnr} \sum_k \frac{(-1)^{j_r - j_c + j_a - j_n + k + J}}{[k]} \begin{Bmatrix} j_v & j_v & J \\ j_c & j_r & k \end{Bmatrix} \frac{t(rc)Z_k(ncav)Z_k(avnr)}{(\varepsilon_r - \varepsilon_c)(\varepsilon_{rn} - \varepsilon_{av})} \quad (\text{A18})$$

$$+ \sum_{acnr} \sum_k \frac{(-1)^{j_r - j_c + j_a - j_n + k + J}}{[k]} \begin{Bmatrix} j_v & j_v & J \\ j_c & j_r & k \end{Bmatrix} \frac{t(cr)Z_k(avnc)Z_k(nrav)}{(\varepsilon_r - \varepsilon_c)(\varepsilon_{rn} - \varepsilon_{av})} \quad (\text{A19})$$

$$+ \sum_{acnr} \sum_k \frac{(-1)^{j_r - j_c + j_a - j_n + k + J}}{[k]} \begin{Bmatrix} j_v & j_v & J \\ j_c & j_r & k \end{Bmatrix} \frac{t(cr)Z_k(nvac)Z_k(arnv)}{(\varepsilon_r - \varepsilon_c)(\varepsilon_{nv} - \varepsilon_{ac})} \quad (\text{A20})$$

$$+ \sum_{acnr} \sum_k \frac{(-1)^{j_r - j_c + j_a - j_n + k + J}}{[k]} \begin{Bmatrix} j_v & j_v & J \\ j_c & j_r & k \end{Bmatrix} \frac{t(rc)Z_k(acnv)Z_k(nvar)}{(\varepsilon_r - \varepsilon_c)(\varepsilon_{nv} - \varepsilon_{ac})} \quad (\text{A21})$$

$$- \sum_{abcn} \sum_k \frac{(-1)^{j_b - j_n + k + J}}{[k]} \begin{Bmatrix} j_v & j_v & J \\ j_c & j_a & k \end{Bmatrix} \frac{t(ca)Z_k(vnab)Z_k(bcnu)}{(\varepsilon_{nv} - \varepsilon_{bc})(\varepsilon_{nv} - \varepsilon_{ab})} \quad (\text{A22})$$

$$- \sum_{amnr} \sum_k \frac{(-1)^{j_a - j_n + k + J}}{[k]} \begin{Bmatrix} j_v & j_v & J \\ j_m & j_r & k \end{Bmatrix} \frac{t(mr)Z_k(avnr)Z_k(mnva)}{(\varepsilon_{mn} - \varepsilon_{av})(\varepsilon_{rn} - \varepsilon_{av})} \quad (\text{A23})$$

$$- \sum_{abmn} \sum_{kk'} (-1)^J \begin{Bmatrix} j_v & j_v & J \\ k & k' & j_n \end{Bmatrix} \begin{Bmatrix} j_a & j_b & J \\ k' & k & j_m \end{Bmatrix} \frac{t(ab)X_k(mnav)Z_{k'}(bvmm)}{(\varepsilon_{mn} - \varepsilon_{bv})(\varepsilon_{nm} - \varepsilon_{av})} \quad (\text{A24})$$

$$- \sum_{abmn} \sum_{kk'} (-1)^J \begin{Bmatrix} j_v & j_v & J \\ k & k' & j_a \end{Bmatrix} \begin{Bmatrix} j_n & j_m & J \\ k' & k & j_b \end{Bmatrix} \frac{t(nm)X_k(abvn)Z_{k'}(mvba)}{(\varepsilon_{nv} - \varepsilon_{ab})(\varepsilon_{mv} - \varepsilon_{ba})} \quad (\text{A25})$$

$$- t(vv) \sum_{abm} \sum_k \frac{1}{[k][j_v]} \left\{ \frac{X_k(vmab)Z_k(vmab)}{(\varepsilon_{vm} - \varepsilon_{ab})^2} + \frac{X_k(vanm)Z_k(vanm)}{(\varepsilon_{nm} - \varepsilon_{av})^2} \right\}. \quad (\text{A26})$$

The total third-order contribution is

$$S^{(3)} = S_{\text{RPA}}^{(3)} + \bar{S}^{(3)}.$$

In our calculation, we replace $t(ij)$ in Eqs. (A10–A26) by $t^{\text{RPA}}(ij)$ given by Eq. (A9).

The third-order two-particle matrix elements are given by

$$T^{(3)} = \sum_{mnabc} \sum_{kk'} \delta_{\kappa_c \kappa_b} \frac{(-1)^{j_m + j_n + j_a + j_v + k'}}{[k][j_c][j_v]} \frac{T_k(abmn)Z_{k'}(cvvb)Z_k(mnac)}{(\varepsilon_{ab} - \varepsilon_{mn})(\varepsilon_{ac} - \varepsilon_{mn})} \quad (\text{A27})$$

$$+ \sum_{mnabc} \sum_{kk'} \delta_{\kappa_c \kappa_b} \frac{(-1)^{j_m + j_n + j_a + j_v + k'}}{[k][j_c][j_v]} \frac{X_k(abmn)\tilde{T}_{k'}(cvvb)Z_k(mnac)}{(\varepsilon_{ab} - \varepsilon_{mn})(\varepsilon_{ac} - \varepsilon_{mn})} \quad (\text{A28})$$

$$+ \sum_{mnabc} \sum_{kk'} \delta_{\kappa_c \kappa_b} \frac{(-1)^{j_m + j_n + j_a + j_v + k'}}{[k][j_c][j_v]} \frac{X_k(abmn)Z_{k'}(cvvb)\tilde{T}_k(mnac)}{(\varepsilon_{ab} - \varepsilon_{mn})(\varepsilon_{ac} - \varepsilon_{mn})} \quad (\text{A29})$$

$$- \sum_{mnabs} \sum_{kk'} \delta_{\kappa_m \kappa_s} \frac{(-1)^{j_b + j_n + j_a + j_v + k'}}{[k][j_s][j_v]} \frac{T_k(abmn)Z_{k'}(mvvs)Z_k(nsba)}{(\varepsilon_{ab} - \varepsilon_{mn})(\varepsilon_{ba} - \varepsilon_{ns})} \quad (\text{A30})$$

$$- \sum_{mnabs} \sum_{kk'} \delta_{\kappa_m \kappa_s} \frac{(-1)^{j_b + j_n + j_a + j_v + k'}}{[k][j_s][j_v]} \frac{X_k(abmn)\tilde{T}_{k'}(mvvs)Z_k(nsba)}{(\varepsilon_{ab} - \varepsilon_{mn})(\varepsilon_{ba} - \varepsilon_{ns})} \quad (\text{A31})$$

$$- \sum_{mnabs} \sum_{kk'} \delta_{\kappa_m \kappa_s} \frac{(-1)^{j_b + j_n + j_a + j_v + k'}}{[k][j_s][j_v]} \frac{X_k(abmn)Z_{k'}(mvvs)\tilde{T}_k(nsba)}{(\varepsilon_{ab} - \varepsilon_{mn})(\varepsilon_{ba} - \varepsilon_{ns})} \quad (\text{A32})$$

$$+2 \sum_{mnabc} \sum_{kk'} \delta_{\kappa_c \kappa_n} \frac{(-1)^{j_b+j_m+j_a+j_v+k'}}{[k][j_c][j_v]} \frac{\tilde{T}_k(abmn)X_k(cmba)Z_{k'}(vncv)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{cv}-\varepsilon_{nv})} \quad (\text{A33})$$

$$+2 \sum_{mnabc} \sum_{kk'} \delta_{\kappa_c \kappa_n} \frac{(-1)^{j_b+j_m+j_a+j_v+k'}}{[k][j_c][j_v]} \frac{Z_k(abmn)T_k(cmba)Z_{k'}(vncv)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{cv}-\varepsilon_{nv})} \quad (\text{A34})$$

$$+2 \sum_{mnabc} \sum_{kk'} \delta_{\kappa_c \kappa_n} \frac{(-1)^{j_b+j_m+j_a+j_v+k'}}{[k][j_c][j_v]} \frac{Z_k(abmn)X_k(cmba)\tilde{T}_{k'}(vncv)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{cv}-\varepsilon_{nv})} \quad (\text{A35})$$

$$-2 \sum_{mnabs} \sum_{kk'} \delta_{\kappa_b \kappa_s} \frac{(-1)^{j_n+j_m+j_a+j_v+k'}}{[k][j_b][j_v]} \frac{\tilde{T}_k(abmn)X_k(mnas)Z_{k'}(vsbv)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{bv}-\varepsilon_{vs})} \quad (\text{A36})$$

$$-2 \sum_{mnabs} \sum_{kk'} \delta_{\kappa_b \kappa_s} \frac{(-1)^{j_n+j_m+j_a+j_v+k'}}{[k][j_b][j_v]} \frac{Z_k(abmn)T_k(mnas)Z_{k'}(vsbv)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{bv}-\varepsilon_{vs})} \quad (\text{A37})$$

$$-2 \sum_{mnabs} \sum_{kk'} \delta_{\kappa_b \kappa_s} \frac{(-1)^{j_n+j_m+j_a+j_v+k'}}{[k][j_b][j_v]} \frac{Z_k(abmn)X_k(mnas)\tilde{T}_{k'}(vsbv)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{bv}-\varepsilon_{vs})} \quad (\text{A38})$$

$$-2 \sum_{mnabs} \sum_k \frac{(-1)^{j_m+j_n+j_a+j_b+j_v+j_s+k}}{[k]^2[j_v]} \frac{\tilde{T}_k(bamn)Z_k(nvas)Z_k(msbv)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{bv}-\varepsilon_{ms})} \quad (\text{A39})$$

$$-2 \sum_{mnabs} \sum_k \frac{(-1)^{j_m+j_n+j_a+j_b+j_v+j_s+k}}{[k]^2[j_v]} \frac{Z_k(bamn)\tilde{T}_k(nvas)Z_k(msbv)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{bv}-\varepsilon_{ms})} \quad (\text{A40})$$

$$-2 \sum_{mnabs} \sum_k \frac{(-1)^{j_m+j_n+j_a+j_b+j_v+j_s+k}}{[k]^2[j_v]} \frac{Z_k(bamn)Z_k(nvas)\tilde{T}_k(msbv)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{bv}-\varepsilon_{ms})} \quad (\text{A41})$$

$$- \sum_{mnarc} \sum_k \frac{(-1)^{j_c+j_r+k}}{[k]^2[j_v]} \frac{\tilde{T}_k(mnva)Z_k(cnra)Z_k(mrv c)}{(\varepsilon_{va}-\varepsilon_{mn})(\varepsilon_{vc}-\varepsilon_{mr})} \quad (\text{A42})$$

$$- \sum_{mnarc} \sum_k \frac{(-1)^{j_c+j_r+k}}{[k]^2[j_v]} \frac{Z_k(mnva)\tilde{T}_k(cnra)Z_k(mrv c)}{(\varepsilon_{va}-\varepsilon_{mn})(\varepsilon_{vc}-\varepsilon_{mr})} \quad (\text{A43})$$

$$- \sum_{mnarc} \sum_k \frac{(-1)^{j_c+j_r+k}}{[k]^2[j_v]} \frac{Z_k(mnva)Z_k(cnra)\tilde{T}_k(mrv c)}{(\varepsilon_{va}-\varepsilon_{mn})(\varepsilon_{vc}-\varepsilon_{mr})} \quad (\text{A44})$$

$$+2 \sum_{mnabc} \sum_k \frac{(-1)^{j_m+j_n+j_a+j_b+j_v+j_c+k}}{[k]^2[j_v]} \frac{\tilde{T}_k(abmn)Z_k(cmva)Z_k(nvbc)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{bc}-\varepsilon_{nv})} \quad (\text{A45})$$

$$+2 \sum_{mnabc} \sum_k \frac{(-1)^{j_m+j_n+j_a+j_b+j_v+j_c+k}}{[k]^2[j_v]} \frac{Z_k(abmn)\tilde{T}_k(cmva)Z_k(nvbc)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{bc}-\varepsilon_{nv})} \quad (\text{A46})$$

$$+2 \sum_{mnabc} \sum_k \frac{(-1)^{j_m+j_n+j_a+j_b+j_v+j_c+k}}{[k]^2[j_v]} \frac{Z_k(abmn)Z_k(cmva)\tilde{T}_k(nvbc)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{bc}-\varepsilon_{nv})} \quad (\text{A47})$$

$$+ \sum_{mabrc} \sum_k \frac{(-1)^{j_c+j_r+k}}{[k]^2[j_v]} \frac{\tilde{T}_k(mvab)Z_k(cmra)Z_k(vrbc)}{(\varepsilon_{ab}-\varepsilon_{mv})(\varepsilon_{bc}-\varepsilon_{vr})} \quad (\text{A48})$$

$$+ \sum_{mabrc} \sum_k \frac{(-1)^{j_c+j_r+k}}{[k]^2[j_v]} \frac{Z_k(mvab)\tilde{T}_k(cmra)Z_k(vrbc)}{(\varepsilon_{ab}-\varepsilon_{mv})(\varepsilon_{bc}-\varepsilon_{vr})} \quad (\text{A49})$$

$$+ \sum_{mabrc} \sum_k \frac{(-1)^{j_c+j_r+k}}{[k]^2[j_v]} \frac{Z_k(mvab)Z_k(cmra)\tilde{T}_k(vrbc)}{(\varepsilon_{ab}-\varepsilon_{mv})(\varepsilon_{bc}-\varepsilon_{vr})} \quad (\text{A50})$$

$$+ 2 \sum_{mncab} \sum_{kk'k''} \frac{1}{[j_v]} \left\{ \begin{matrix} k & k' & k'' \\ j_c & j_n & j_b \end{matrix} \right\} \left\{ \begin{matrix} k & k' & k'' \\ j_v & j_m & j_a \end{matrix} \right\} \frac{\tilde{T}_k(abmn)X_{k'}(cvba)X_{k''}(mnvc)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{vc}-\varepsilon_{mn})} \quad (\text{A51})$$

$$+ 2 \sum_{mncab} \sum_{kk'k''} \frac{1}{[j_v]} \left\{ \begin{matrix} k & k' & k'' \\ j_c & j_n & j_b \end{matrix} \right\} \left\{ \begin{matrix} k & k' & k'' \\ j_v & j_m & j_a \end{matrix} \right\} \frac{Z_k(abmn)T_{k'}(cvba)X_{k''}(mnvc)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{vc}-\varepsilon_{mn})} \quad (\text{A52})$$

$$+ 2 \sum_{mncab} \sum_{kk'k''} \frac{1}{[j_v]} \left\{ \begin{matrix} k & k' & k'' \\ j_c & j_n & j_b \end{matrix} \right\} \left\{ \begin{matrix} k & k' & k'' \\ j_v & j_m & j_a \end{matrix} \right\} \frac{Z_k(abmn)X_{k'}(cvba)T_{k''}(mnvc)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{vc}-\varepsilon_{mn})} \quad (\text{A53})$$

$$- 2 \sum_{mnsab} \sum_{kk'k''} \frac{1}{[j_v]} \left\{ \begin{matrix} k & k' & k'' \\ j_v & j_b & j_m \end{matrix} \right\} \left\{ \begin{matrix} k & k' & k'' \\ j_s & j_a & j_n \end{matrix} \right\} \frac{\tilde{T}_k(abnm)X_{k'}(mnvs)X_{k''}(vsba)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{ba}-\varepsilon_{vs})} \quad (\text{A54})$$

$$- 2 \sum_{mnsab} \sum_{kk'k''} \frac{1}{[j_v]} \left\{ \begin{matrix} k & k' & k'' \\ j_v & j_b & j_m \end{matrix} \right\} \left\{ \begin{matrix} k & k' & k'' \\ j_s & j_a & j_n \end{matrix} \right\} \frac{Z_k(abnm)T_{k'}(mnvs)X_{k''}(vsba)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{ba}-\varepsilon_{vs})} \quad (\text{A55})$$

$$- 2 \sum_{mnsab} \sum_{kk'k''} \frac{1}{[j_v]} \left\{ \begin{matrix} k & k' & k'' \\ j_v & j_b & j_m \end{matrix} \right\} \left\{ \begin{matrix} k & k' & k'' \\ j_s & j_a & j_n \end{matrix} \right\} \frac{Z_k(abnm)X_{k'}(mnvs)T_{k''}(vsba)}{(\varepsilon_{ab}-\varepsilon_{mn})(\varepsilon_{ba}-\varepsilon_{vs})} \quad (\text{A56})$$

$$- \sum_{mabcd} \sum_{lkk'} \frac{(-1)^{j_m+j_v+j_a+j_b}}{[j_v]} \left\{ \begin{matrix} j_m & j_a & k \\ l & k' & j_c \end{matrix} \right\} \left\{ \begin{matrix} j_v & j_b & k \\ l & k' & j_d \end{matrix} \right\} \frac{\tilde{T}_k(mvab)X_l(cdab)X_{k'}(mvcd)}{(\varepsilon_{ab}-\varepsilon_{mv})(\varepsilon_{cd}-\varepsilon_{mv})} \quad (\text{A57})$$

$$- \sum_{mabcd} \sum_{lkk'} \frac{(-1)^{j_m+j_v+j_a+j_b}}{[j_v]} \left\{ \begin{matrix} j_m & j_a & k \\ l & k' & j_c \end{matrix} \right\} \left\{ \begin{matrix} j_v & j_b & k \\ l & k' & j_d \end{matrix} \right\} \frac{Z_k(mvab)T_l(cdab)X_{k'}(mvcd)}{(\varepsilon_{ab}-\varepsilon_{mv})(\varepsilon_{cd}-\varepsilon_{mv})} \quad (\text{A58})$$

$$- \sum_{mabcd} \sum_{lkk'} \frac{(-1)^{j_m+j_v+j_a+j_b}}{[j_v]} \left\{ \begin{matrix} j_m & j_a & k \\ l & k' & j_c \end{matrix} \right\} \left\{ \begin{matrix} j_v & j_b & k \\ l & k' & j_d \end{matrix} \right\} \frac{Z_k(mvab)X_l(cdab)T_{k'}(mvcd)}{(\varepsilon_{ab}-\varepsilon_{mv})(\varepsilon_{cd}-\varepsilon_{mv})} \quad (\text{A59})$$

$$+ \sum_{mnars} \sum_{lkk'} \frac{(-1)^{j_m+j_n+j_v+j_a}}{[j_v]} \left\{ \begin{matrix} j_m & j_v & k \\ k' & l & j_r \end{matrix} \right\} \left\{ \begin{matrix} j_n & j_a & k \\ k' & l & j_s \end{matrix} \right\} \frac{\tilde{T}_k(mnva)X_l(mnrs)X_{k'}(rsva)}{(\varepsilon_{va}-\varepsilon_{mn})(\varepsilon_{va}-\varepsilon_{rs})} \quad (\text{A60})$$

$$+ \sum_{mnars} \sum_{lkk'} \frac{(-1)^{j_m+j_n+j_v+j_a}}{[j_v]} \left\{ \begin{matrix} j_m & j_v & k \\ k' & l & j_r \end{matrix} \right\} \left\{ \begin{matrix} j_n & j_a & k \\ k' & l & j_s \end{matrix} \right\} \frac{Z_k(mnva)T_l(mnrs)X_{k'}(rsva)}{(\varepsilon_{va}-\varepsilon_{mn})(\varepsilon_{va}-\varepsilon_{rs})} \quad (\text{A61})$$

$$+ \sum_{mnars} \sum_{lkk'} \frac{(-1)^{j_m+j_n+j_v+j_a}}{[j_v]} \left\{ \begin{matrix} j_m & j_v & k \\ k' & l & j_r \end{matrix} \right\} \left\{ \begin{matrix} j_n & j_a & k \\ k' & l & j_s \end{matrix} \right\} \frac{Z_k(mnva)X_l(mnrs)T_{k'}(rsva)}{(\varepsilon_{va}-\varepsilon_{mn})(\varepsilon_{va}-\varepsilon_{rs})}. \quad (\text{A62})$$

In Eqs. (A27)–(A62), the quantities $\tilde{T}_L(abcd)$ are defined as

$$\tilde{T}_L(abcd) = T_L(abcd) + \sum_{L'} [L] \left\{ \begin{matrix} j_a & j_c & L \\ j_b & j_d & L' \end{matrix} \right\} T_{L'}(abdc).$$

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