

Relativistic all-order calculations of In I and Sn II atomic properties

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We use all-order relativistic many-body perturbation theory to study $5s^2nl$ configurations of In I and Sn II. Energies, $E1$ amplitudes, and hyperfine constants are calculated using all-order method, which accounts for single and double excitations of the Dirac-Fock wave functions. A comprehensive review of experimental and theoretical studies of In I and Sn II properties is given. Our results are compared with other studies were available.

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I. INTRODUCTION

In this work, we present a systematic calculation of various In I and Sn II atomic properties and study the importance of the high-order correlation corrections to those properties using relativistic all-order method. Previously these atoms have been studied in a number of experimental and theoretical papers. First theoretical studies were published 30 years ago by Migdalek [1]. They used relativistic semiempirical method including exchange to calculate the oscillator strengths in In I for the $5s^25p_j-5s^2ns_{1/2}$, $5s^26p_j-5s^2ns_{1/2}$, $5s^25p_j-5s^2nd_j$, and $5s^26s_{1/2}-5s^2np_j$ transitions.

Later, the oscillator strengths determined from single-configuration relativistic Hartree-Fock (RHF) calculations were reported by Migdalek and Baylis [2] for the lowest $5s^25p_j-5s^26s_{1/2}$ and $5s^25p_j-5s^25d_j$ transitions. A quantum defect theory was used by Gruzdev and Afanaseva [3] to calculate oscillator strengths f averaged over j in neutral indium. Configuration interaction gf values for transitions between the $5s^26s_{1/2}$, $5s^2nd_j$, and $5s^2np_j$ (with $n=5,6$) states were reported for the indium isoelectronic sequence up to Ba VIII in Ref. [4]. A self-consistent-field method was used to generate one-electron orbitals. The method used in Ref. [4] included relativistic effects albeit in an approximate way, and the configuration interaction scheme accounts for correlation effects [4]. Hartree-Fock calculations including relativistic corrections and configuration interaction in an intermediate coupling scheme were carried out in Ref. [5] to analyze the spectrum of Sn II. Transition probabilities for 36 lines of Sn II arising from the $5s^2ns$, $5s^2np$, $5s^2nd$, $5s^2nf$, and $5s5p^2$ configurations of Sn II were evaluated in Ref. [5] using the Cowan code. Radiative transition probabilities and oscillator strengths for 164 lines arising from the $5s^2ns$, $5s^2np$, $5s^2nd$, $5s^2nf$, $5s^2ng$, and $5s5p^2$ configurations of Sn II were calculated recently by Alonso-Medina *et al.* in Ref. [6]. These

values were obtained in intermediate coupling (IC) using *ab initio* relativistic Hartree-Fock (HFR) calculations. The standard method of least square fitting of experimental energy levels by means of computer codes from Cowan was used [6] to calculate IC transition rates. Recently, energies of the $5s^25p_j$, $5s5p^2$, $5s^26s_{1/2}$, $5s^25d_j$, and $5s^26p_j$ states in Sn II were evaluated by Dzuba and Flambaum in Ref. [7] using many-body perturbation theory (MBPT). It was underlined that correlations and relativistic corrections were important. The screening of the Coulomb interaction and hole-particle interaction was included in all orders of the MBPT [7].

The experimental study of atomic lifetimes in gallium, indium, and thallium was carried by Andersen and Sørensen [8] using beam-foil technique. Results for the $5s^26s$ and $5s^2nd$ ($n=5-7$) levels in In I were given in Ref. [8]. Lifetimes of the $5s^2ns$ and $5s^2nd$ ($n \leq 20$) states in indium measured using pulsed laser excitation of an atomic beam were reported by Jönsson *et al.* in Ref. [9]. Determination of radiative lifetimes of the $5s^26p$, $5s^2ns$, and $5s^2nd$ ($n \leq 10$) levels in In I using a pulsed laser was presented in Refs. [10,11]. The atoms were excited in an atomic beam, with a nitrogen-laser-pumped dye laser. The fluorescence decay from the atoms was observed by a fast photomultiplier [10,11]. The optical emission from a laser produced plasma generated by 1064 nm irradiation of Sn-Pb alloy targets at a flux of 2×10^{10} W cm⁻² was recorded and analyzed between 200 and 700 nm [5]. Experimental transition probabilities for 36 lines of Sn II arising from the $5s^2ns$, $5s^2np$, $5s^2nd$, $5s^2nf$, and $5s5p^2$ configurations of Sn II were determined by Alonso-Medina *et al.* in Ref. [5]. Lifetime measurements for levels arising from the $5s^25d$ and $5s^24f$ configurations in Sn II were presented by Schectman *et al.* in Ref. [12]. These measurements utilized the University of Toledo Heavy Ion Accelerator Beam Foil Facility. The results were discussed in the context of interpreting vacuum ultraviolet absorption spectra observed with the Goddard High Resolution Spectrograph on board the Hubble Space Telescope [12].

Hyperfine structure of the $5s^25p_j$ states of In¹¹⁵ and In¹¹³ were measured by the magnetic-resonance method [13,14].

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An atomic beam irradiated by a narrow band dye laser was used in Ref. [15] to observe resonance fluorescence in free indium atom. From the resonance frequencies, values for the hyperfine structure of the $5s^26s$ level in In^{115} and In^{113} were derived by Neijzen and Dönszelmann in Ref. [15]. The spin-forbidden $5s^25p^2P-5s5p^2^4P$ In^{115} transition was analyzed and absolute wavelengths, hyperfine constants A and B , as well as improved energy level values were reported by Karlsson and Litzén in Ref. [16].

A high-resolution study of the $\lambda=451.1$ nm transition in In I using CW dye laser was reported by Zaal *et al.* in Ref. [17]. The blue dye laser setup was tested on the $5s^25p_{3/2}-5s^26s_{1/2}$ $\lambda=451.1$ nm transition in natural indium [17]. Proposal for laser on self-terminating transition in blue spectral range on indium atom transition at 451.1 nm was presented recently by Riyves *et al.* in Ref. [18]. The spectroscopy of dense In vapor was studied recently via resonant pulsed laser excitation at $\lambda=410.13$ nm (the $5s^25p_{1/2}-5s^26s_{1/2}$ transition) [19].

In this paper, we conduct both relativistic many-body perturbation theory (RMBPT) and all-order single-double (SD) calculations of In I and Sn II properties. Such calculations permit one to investigate convergence of perturbation theory and estimate the uncertainty of theoretical predictions. We evaluate reduced matrix elements, oscillator strengths, and transition rates for possible $5s^2nl-5s^2n'l'$ electric-dipole transitions in In I and Sn II and calculate the lifetimes of the corresponding levels. Our results are compared with theoretical results from Refs. [1,3,2,4–6] and with measurements from Refs. [8,9,11,10] in In I and Refs. [5,12] in Sn II . We also calculate hyperfine constants A for the $5s^2np_j$ ($n=5-8$), $5s^2ns_{1/2}$ ($n=6-9$), and $5s^2nd_j$ ($n=5-8$) states in ^{115}In using the relativistic MBPT and SD all-order methods. Where possible, we compare our results with the measurements from Refs. [13–15].

We consider the three-electron system $[\text{Ni}]4s^24p^64d^{10}5s^2nl$ in In I and Sn II as a one-electron nl system with $[\text{Ni}]4s^24p^64d^{10}5s^2$ core. Recently, the relativistic all-order method was used to evaluate the excitation energies, oscillator strengths, transition rates, and lifetimes in Ga I [20] as well as in Tl I and Tl -like Pb [21]. The $[\text{Ni}]4s^2nl$ states in Ga I were treated in Ref. [20] as the nl one-electron system with $[\text{Ni}]4s^2$ core and $[\text{Xe}]4f^{14}5d^{10}6s^2nl$ states in Tl I and Pb II were evaluated in Ref. [21] as the nl one-electron system with $[\text{Xe}]4f^{14}5d^{10}6s^2$ core.

To summarize, this work presents both a systematic calculation of various properties of In I and Sn II , and a study of the importance of the high-order correlation corrections to these properties. We conclude that all-order SD method, in general, produce more accurate values than the third-order MBPT and can be used for the accurate calculation of In and Sn^+ properties. By comparing the all-order and third-order MBPT results, we were able to study the relative importance of the correlation corrections for different properties and single out the cases where the treatment of In as a three-particle system may be important, i.e., the cases where significant discrepancies between theory and experiment persist even for the all-order calculations. The development of the all-order approach that is capable to fully treat In or Sn^+ as a

three-particle system is a difficult problem [22–24], and the initial studies of the applicability of the all-order method to such systems may be useful. We find that the all-order SD method works relatively well for In I even without explicit consideration of the three-particle states. For Sn II , the convergence of MBPT expansion is worse than for In , particularly for d wave, where SD equations diverge. That is caused by the strong interaction between $5s^2nd$ configurations and low-lying $5s5p^2$ configuration, which corresponds to the excitation from the core.

In the next section, we briefly review the RMBPT theory and all-order SD method for the calculation of atomic properties of the atoms with one unpaired electron. The energies are given in Table I. Extension of the theory to one-electron matrix elements is discussed in Sec. III. Our results for $E1$ transitions are listed in Tables II–V. Calculated and experimental lifetimes for In are given in Table VI. Magnetic hyperfine structure of In s discussed in Sec. IV and results are summarized in Table VII.

II. ENERGIES OF In I AND Sn II

We start from the “no-pair” Hamiltonian [26] in the second quantization form

$$H = H_0 + V_I, \quad (1)$$

$$H_0 = \sum_i \varepsilon_i a_i^\dagger a_i, \quad (2)$$

$$V_I = \sum_{ijkl} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k, \quad (3)$$

where negative energy (positron) states are excluded from the sums; ε_i are eigenvalues of the one-electron DF equations with a frozen core, and g_{ijkl} is the Coulomb two-particle matrix element.

Considering neutral In as a one-electron system we use V^{N-1} DF potential $[\text{Ni}]4s^24p^64d^{10}5s^2$ to calculate DF orbitals and energies ε_i . There are a number of advantages associated with this potential, including a greatly reduced number of the Goldstone diagrams [27], which leads to important simplifications in calculation. For example, when considering the total energy of different valence states of a one-electron atom, that energy can be written as

$$E = E_v + E_{\text{core}}, \quad (4)$$

where E_{core} is the same for all valence states v . The first-order correlation correction to valence removal energies vanishes for a V^{N-1} DF potential and the first nonvanishing corrections appear in the second order [28]:

$$E_v^{(2)} = \sum_{mn} \sum_a \frac{g_{avmn}(g_{mnav} - g_{mnva})}{\varepsilon_a + \varepsilon_v - \varepsilon_n - \varepsilon_m} + \sum_n \sum_{ab} \frac{g_{nvba}(g_{abnv} - g_{abvn})}{\varepsilon_a + \varepsilon_b - \varepsilon_n - \varepsilon_v}. \quad (5)$$

We use indexes a and b to label core states and m and n to designate any excited states. The second-order Coulomb-

TABLE I. Valence energies in different approximations for In I and Sn II in cm^{-1} . We calculate zeroth-order (DF), single-double Coulomb correction E^{SD} , and the part of third-order $E_{\text{extra}}^{(3)}$ which is not included in the E^{SD} . Breit corrections $B^{(n)}$ are calculated in first and second orders. The sum of these five terms $E_{\text{tot}}^{\text{SD}}$ is compared with experimental energies E_{NIST} [25], $\delta E^{\text{SD}} = E_{\text{tot}}^{\text{SD}} - E_{\text{NIST}}$. The differences $\delta E^{(2)}$ and $\delta E^{(3)}$ between total energies ($E_{\text{tot}}^{(2)} = E^{(0)} + E^{(2)} + B^{(1)} + B^{(2)}$, $E_{\text{tot}}^{(3)} = E_{\text{tot}}^{(2)} + E^{(3)}$) and experimental energies E_{NIST} [25] are given for comparison.

nlj	E^{DF}	E^{SD}	$E_{\text{extra}}^{(3)}$	$B^{(1)}$	$B^{(2)}$	$E_{\text{tot}}^{\text{SD}}$	E_{NIST}	$\delta E^{(2)}$	$\delta E^{(3)}$	δE^{SD}
In I										
$5p_{1/2}$	-41 507	-5554	913	105	-146	-46 189	-46 670	-2163	547	481
$5p_{3/2}$	-39 506	-5378	912	73	-132	-44 031	-44 457	-2040	557	426
$5d_{3/2}$	-12 390	-1350	161	2	-4	-13 581	-13 778	256	493	197
$5d_{5/2}$	-12 374	-1337	160	1	-4	-13 554	-13 755	260	493	201
$6s_{1/2}$	-20 572	-2096	232	12	-18	-22 442	-22 297	-237	249	-145
$6p_{1/2}$	-13 979	-964	113	13	-16	-14 833	-14 853	-150	122	20
$6p_{3/2}$	-13 719	-919	112	10	-16	-14 532	-14 555	-155	115	23
$6d_{3/2}$	-6955	-558	69	1	-2	-7445	-7809	375	479	364
$6d_{5/2}$	-6946	-554	68	1	-2	-7433	-7697	277	379	264
$7s_{1/2}$	-9867	-584	72	4	-6	-10 381	-10 368	-95	64	-13
$7p_{1/2}$	-7488	-349	41	5	-6	-7797	-7809	-56	45	12
$7p_{3/2}$	-7388	-335	41	4	-6	-7684	-7697	-58	42	13
$8s_{1/2}$	-5816	-251	32	2	-3	-6036	-6033	-45	27	-3
$4f_{5/2}$	-6863	-118	14	0	0	-6967	-6963	-4	9	-4
$4f_{7/2}$	-6863	-118	14	0	0	-6967	-6962	-5	8	-5
$5f_{5/2}$	-4393	-67	8	0	0	-4452	-4450	-3	5	-2
$5f_{7/2}$	-4393	-67	8	0	0	-4452	-4450	-3	5	-2
$7d_{3/2}$	-4441	-285	35	0	-1	-4692	-4834	148	201	142
$7d_{5/2}$	-4436	-283	35	0	-1	-4685	-4808	129	181	123
$8p_{1/2}$	-4687	-168	20	2	-3	-4836	-4843	-28	21	7
$8p_{3/2}$	-4638	-162	20	2	-3	-4781	-4789	-28	21	8
$8d_{3/2}$	-3078	-171	21	0	-1	-3229	-3334	112	144	105
$8d_{5/2}$	-3075	-170	21	0	-1	-3225	-3315	98	129	90
$9s_{1/2}$	-3837	-132	17	1	0	-3951	-3951	-24	15	0
Sn II										
$5p_{1/2}$	-111 452	-6848	1014	206	-233	-117 313	-118 017	-2578	712	704
$5p_{3/2}$	-107 358	-6719	1032	146	-216	-113 115	-113 766	-2459	736	651
$6s_{1/2}$	-57 995	-3597	467	35	-44	-61 134	-61 131	-641	435	-3
$6p_{1/2}$	-44 483	-2244	271	39	-38	-46 455	-46 523	-316	314	68
$6p_{3/2}$	-43 691	-2133	258	28	-37	-45 575	-45 640	-297	300	65
$7s_{1/2}$	-30 735	-1230	172	14	-17	-31 796	-31 737	-343	55	-59
$4f_{5/2}$	-27 689	-1189	147	0	-1	-28 732	-28 731	-24	206	-1
$4f_{7/2}$	-27 691	-1193	147	0	-1	-28 738	-28 725	-34	196	-13
$7p_{1/2}$	-25 253	-930	115	16	-16	-26 068	-26 114	-107	153	46
$7p_{3/2}$	-24 917	-895	109	12	-15	-25 706	-25 751	-94	152	45
$8s_{1/2}$	-19 133	-629	84	7	-9	-19 680	-19 615	-162	26	-65
$5f_{5/2}$	-17 759	-670	85	0	-1	-18 345	-18 358	-13	131	13
$5f_{7/2}$	-17 761	-674	86	0	-1	-18 350	-18 352	-22	121	2
$8p_{1/2}$	-16 354	-487	60	8	-8	-16 781	-16 821	-31	102	40
$8p_{3/2}$	-16 179	-472	57	6	-8	-16 596	-16 630	-29	97	34
$9s_{1/2}$	-13 070	-301	47	4	0	-13 320	-13 337	-88	13	17

TABLE II. Wavelengths λ (Å), transition rates A_r (s^{-1}), oscillator strengths (f), and line strengths S (a.u.) for transitions in In I calculated in all-order perturbation theory. Numbers in brackets represent powers of 10.

Transition	λ	A_r	f	S	Transition	λ	A_r	f	S
$5p_{1/2} 6s_{1/2}$	4153	5.15[7]	1.33[-1]	3.64[0]	$4f_{5/2} 8d_{5/2}$	26 532	3.32[5]	3.51[-2]	1.84[1]
$5p_{1/2} 5d_{3/2}$	3045	1.30[8]	3.61[-1]	7.24[0]	$4f_{7/2} 7d_{5/2}$	42 937	1.65[5]	3.42[-2]	3.86[1]
$5p_{1/2} 7s_{1/2}$	2792	1.37[7]	1.60[-2]	2.93[-1]	$4f_{7/2} 8d_{5/2}$	26 532	6.65[4]	5.26[-3]	3.68[0]
$5p_{1/2} 6d_{3/2}$	2578	3.63[7]	7.24[-2]	1.23[0]	$8p_{1/2} 7d_{3/2}$	529 101	4.67[3]	3.92[-1]	1.37[3]
$5p_{1/2} 8s_{1/2}$	2493	5.81[6]	5.41[-3]	8.88[-2]	$8p_{1/2} 8d_{3/2}$	61 275	3.79[5]	4.27[-1]	1.72[2]
$5p_{1/2} 7d_{3/2}$	2410	1.47[7]	2.56[-2]	4.06[-1]	$8p_{3/2} 7d_{3/2}$	740 741	3.40[2]	2.80[-2]	2.73[2]
$5p_{1/2} 8d_{3/2}$	2329	7.49[6]	1.22[-2]	1.87[-1]	$8p_{3/2} 7d_{5/2}$	704 225	2.38[3]	2.66[-1]	2.47[3]
$5p_{3/2} 6s_{1/2}$	4576	9.05[7]	1.42[-1]	8.56[0]	$8p_{3/2} 8d_{3/2}$	63 371	8.38[4]	5.05[-2]	4.21[1]
$5p_{3/2} 5d_{3/2}$	3266	2.49[7]	3.98[-2]	1.71[0]	$8p_{3/2} 8d_{5/2}$	63 211	4.95[5]	4.44[-1]	3.70[2]
$5p_{3/2} 5d_{5/2}$	3264	1.47[8]	3.53[-1]	1.52[1]	$5f_{5/2} 8d_{3/2}$	79 681	1.22[5]	7.75[-2]	1.22[2]
$5p_{3/2} 7s_{1/2}$	2977	2.31[7]	1.53[-2]	6.02[-1]	$5f_{5/2} 8d_{5/2}$	79 428	5.70[3]	5.39[-3]	8.46[0]
$5p_{3/2} 6d_{3/2}$	2734	6.88[6]	7.71[-3]	2.78[-1]	$5f_{7/2} 8d_{5/2}$	79 428	1.14[5]	8.09[-2]	1.69[2]
$5p_{3/2} 6d_{5/2}$	2734	4.05[7]	6.81[-2]	2.45[0]	$6s_{1/2} 6p_{1/2}$	13 669	1.43[7]	4.02[-1]	3.61[1]
$5p_{3/2} 8s_{1/2}$	2639	9.72[6]	5.07[-3]	1.76[-1]	$6s_{1/2} 6p_{3/2}$	13 146	1.57[7]	8.13[-1]	7.03[1]
$5p_{3/2} 7d_{3/2}$	2547	2.79[6]	2.71[-3]	9.08[-2]	$6s_{1/2} 7p_{1/2}$	7002	1.40[6]	1.03[-2]	4.75[-1]
$5p_{3/2} 7d_{5/2}$	2546	1.63[7]	2.38[-2]	7.97[-1]	$6s_{1/2} 7p_{3/2}$	6949	1.96[6]	2.84[-2]	1.30[0]
$5p_{3/2} 8d_{3/2}$	2456	1.43[6]	1.29[-3]	4.18[-2]	$6s_{1/2} 8p_{1/2}$	5806	4.07[5]	2.06[-3]	7.86[-2]
$5p_{3/2} 8d_{5/2}$	2456	8.32[6]	1.13[-2]	3.65[-1]	$6s_{1/2} 8p_{3/2}$	5787	6.40[5]	6.42[-3]	2.45[-1]
$6p_{1/2} 5d_{3/2}$	69 156	1.57[5]	2.25[-1]	1.03[2]	$5d_{3/2} 7p_{1/2}$	18 116	7.58[5]	1.86[-2]	4.45[0]
$6p_{1/2} 7s_{1/2}$	22 594	3.48[6]	2.66[-1]	3.96[1]	$5d_{3/2} 7p_{3/2}$	17 765	6.13[4]	2.90[-3]	6.78[-1]
$6p_{1/2} 6d_{3/2}$	13 512	7.35[6]	4.02[-1]	3.58[1]	$5d_{3/2} 4f_{5/2}$	15 798	1.32[7]	7.43[-1]	1.55[2]
$6p_{1/2} 8s_{1/2}$	11 463	1.13[6]	2.22[-2]	1.68[0]	$5d_{3/2} 8p_{1/2}$	11 816	3.07[5]	3.21[-3]	5.00[-1]
$6p_{1/2} 7d_{3/2}$	9903	3.79[6]	1.12[-1]	7.27[0]	$5d_{3/2} 8p_{3/2}$	11 741	2.46[4]	5.09[-4]	7.87[-2]
$6p_{1/2} 8d_{3/2}$	8665	2.19[6]	4.92[-2]	2.81[0]	$5d_{3/2} 5f_{5/2}$	11 312	5.54[6]	1.59[-1]	2.37[1]
$6p_{3/2} 5d_{3/2}$	86 580	1.60[4]	1.80[-2]	2.05[1]	$5d_{5/2} 7p_{3/2}$	17 838	5.67[5]	1.80[-2]	6.36[0]
$6p_{3/2} 5d_{5/2}$	84 890	1.03[5]	1.66[-1]	1.86[2]	$5d_{5/2} 4f_{5/2}$	15 855	9.46[5]	3.56[-2]	1.12[1]
$6p_{3/2} 7s_{1/2}$	24 184	6.36[6]	2.79[-1]	8.88[1]	$5d_{5/2} 4f_{7/2}$	15 855	1.42[7]	7.13[-1]	2.23[2]
$6p_{3/2} 6d_{3/2}$	14 065	1.54[6]	4.56[-2]	8.45[0]	$5d_{5/2} 8p_{3/2}$	11 773	2.29[5]	3.17[-3]	7.36[-1]
$6p_{3/2} 6d_{5/2}$	14 043	9.12[6]	4.04[-1]	7.48[1]	$5d_{5/2} 5f_{5/2}$	11 342	3.93[5]	7.59[-3]	1.70[0]
$6p_{3/2} 8s_{1/2}$	11 858	1.96[6]	2.06[-2]	3.22[0]	$5d_{5/2} 5f_{7/2}$	11 342	5.90[6]	1.52[-1]	3.40[1]
$6p_{3/2} 7d_{3/2}$	10 197	7.61[5]	1.19[-2]	1.59[0]	$7s_{1/2} 7p_{1/2}$	39 370	2.42[6]	5.62[-1]	1.46[2]
$6p_{3/2} 7d_{5/2}$	10 190	4.54[6]	1.06[-1]	1.42[1]	$7s_{1/2} 7p_{3/2}$	37 750	2.63[6]	1.12[0]	2.79[2]
$6p_{3/2} 8d_{3/2}$	8889	4.31[5]	5.11[-3]	5.98[-1]	$7s_{1/2} 8p_{1/2}$	18 238	3.95[5]	1.97[-2]	2.37[0]
$6p_{3/2} 8d_{5/2}$	8886	2.58[6]	4.58[-2]	5.36[0]	$7s_{1/2} 8p_{3/2}$	18 060	5.16[5]	5.04[-2]	6.00[0]
$7p_{1/2} 6d_{3/2}$	229 885	2.00[4]	3.17[-1]	4.80[2]	$6d_{3/2} 4f_{5/2}$	266 667	1.11[4]	1.77[-1]	6.23[2]
$7p_{1/2} 8s_{1/2}$	56 883	8.36[5]	4.06[-1]	1.52[2]	$6d_{3/2} 8p_{1/2}$	39 872	3.44[5]	4.10[-2]	2.15[1]
$7p_{1/2} 7d_{3/2}$	31 928	1.33[6]	4.05[-1]	8.51[1]	$6d_{3/2} 8p_{3/2}$	39 032	2.82[4]	6.44[-3]	3.31[0]
$7p_{1/2} 8d_{3/2}$	21 858	8.39[5]	1.20[-1]	1.73[1]	$6d_{3/2} 5f_{5/2}$	34 662	1.94[6]	5.24[-1]	2.39[2]
$7p_{3/2} 6d_{3/2}$	306 748	1.68[3]	2.37[-2]	9.59[1]	$6d_{5/2} 4f_{5/2}$	274 725	7.24[2]	8.19[-3]	4.45[1]
$7p_{3/2} 6d_{5/2}$	296 736	1.12[4]	2.22[-1]	8.67[2]	$6d_{5/2} 4f_{7/2}$	274 725	1.09[4]	1.64[-1]	8.89[2]
$7p_{3/2} 8s_{1/2}$	60 643	1.53[6]	4.20[-1]	3.36[2]	$6d_{5/2} 8p_{3/2}$	39 200	2.61[5]	4.01[-2]	3.10[1]
$7p_{3/2} 7d_{3/2}$	33 080	2.87[5]	4.72[-2]	2.05[1]	$6d_{5/2} 5f_{5/2}$	34 795	1.40[5]	2.54[-2]	1.74[1]
$7p_{3/2} 7d_{5/2}$	33 003	1.70[6]	4.16[-1]	1.81[2]	$6d_{5/2} 5f_{7/2}$	34 795	2.10[6]	5.07[-1]	3.49[2]
$7p_{3/2} 8d_{3/2}$	22 391	1.75[5]	1.31[-2]	3.87[0]	$8s_{1/2} 8p_{1/2}$	84 388	6.59[5]	7.04[-1]	3.91[2]
$7p_{3/2} 8d_{5/2}$	22 371	1.04[6]	1.17[-1]	3.44[1]	$8s_{1/2} 8p_{3/2}$	80 710	7.18[5]	1.40[0]	7.45[2]
$4f_{5/2} 7d_{3/2}$	43 066	1.77[5]	3.28[-2]	2.79[1]	$7d_{3/2} 5f_{5/2}$	531 915	4.89[3]	3.11[-1]	2.18[3]
$4f_{5/2} 7d_{5/2}$	42 937	8.24[3]	2.28[-3]	1.93[0]	$7d_{5/2} 5f_{5/2}$	552 486	3.12[2]	1.43[-2]	1.56[2]
$4f_{5/2} 8d_{3/2}$	26 560	7.12[4]	5.02[-3]	2.63[0]	$7d_{5/2} 5f_{7/2}$	552 486	4.68[3]	2.85[-1]	3.11[3]

TABLE III. Wavelengths λ (Å), transition rates A_r (cm^{-1}), oscillator strengths (f), and line strengths S (a.u.) for transitions in Sn II calculated using all-order method.

Transition	λ	A_r	f	S	
$5p_{1/2}$	$6s_{1/2}$	1780	3.17[8]	1.47[-1]	1.70[0]
$5p_{1/2}$	$7s_{1/2}$	1170	8.18[7]	1.65[-2]	1.26[-1]
$5p_{1/2}$	$8s_{1/2}$	1024	7.29[6]	1.13[-3]	7.55[-3]
$5p_{3/2}$	$6s_{1/2}$	1924	5.76[8]	1.56[-1]	3.90[0]
$5p_{3/2}$	$7s_{1/2}$	1231	1.35[8]	1.50[-2]	2.41[-1]
$5p_{3/2}$	$8s_{1/2}$	1070	1.73[7]	1.46[-3]	2.04[-2]
$6p_{1/2}$	$7s_{1/2}$	6859	3.87[7]	2.65[-1]	1.18[1]
$6p_{1/2}$	$8s_{1/2}$	3735	1.45[7]	3.00[-2]	7.34[-1]
$6p_{3/2}$	$7s_{1/2}$	7300	7.38[7]	2.86[-1]	2.71[1]
$6p_{3/2}$	$8s_{1/2}$	3862	2.66[7]	2.94[-2]	1.49[0]
$7p_{1/2}$	$8s_{1/2}$	15 654	1.07[7]	3.79[-1]	3.84[1]
$7p_{3/2}$	$8s_{1/2}$	16 592	2.04[7]	4.06[-1]	8.72[1]
$6s_{1/2}$	$6p_{1/2}$	6813	5.89[7]	4.14[-1]	1.86[1]
$6s_{1/2}$	$6p_{3/2}$	6428	6.91[7]	8.63[-1]	3.67[1]
$6s_{1/2}$	$7p_{1/2}$	2852	1.76[5]	2.15[-4]	4.05[-3]
$6s_{1/2}$	$7p_{3/2}$	2823	1.30[6]	3.11[-3]	5.78[-2]
$6s_{1/2}$	$8p_{1/2}$	2255	2.52[5]	1.93[-4]	2.86[-3]
$6s_{1/2}$	$8p_{3/2}$	2245	1.38[1]	2.08[-8]	3.08[-7]
$7s_{1/2}$	$7p_{1/2}$	17 218	1.21[7]	5.71[-1]	6.69[1]
$7s_{1/2}$	$7p_{3/2}$	16 210	1.41[7]	1.18[0]	1.30[2]
$7s_{1/2}$	$8p_{1/2}$	6625	4.04[5]	2.72[-3]	1.20[-1]
$7s_{1/2}$	$8p_{3/2}$	6545	9.67[5]	1.27[-2]	5.54[-1]
$8s_{1/2}$	$8p_{1/2}$	34 495	3.62[6]	6.95[-1]	1.64[2]
$8s_{1/2}$	$8p_{3/2}$	32 425	4.26[6]	1.43[0]	3.16[2]

Breit contribution $B_v^{(2)}$ is obtained from the $E_v^{(2)}$ expression (5) by changing $g_{ijkl} \rightarrow g_{ijkl} + b_{ijkl}$ and keeping only terms that are linear in b_{ijkl} that is a two-particle matrix element of the Breit interaction [29]:

$$B = -\frac{\alpha}{r_{12}} \left\{ \alpha_1 \alpha_2 - \frac{1}{2} [\alpha_1 \alpha_2 - (\alpha_1 \hat{\mathbf{r}}_{12})(\alpha_2 \hat{\mathbf{r}}_{12})] \right\}, \quad (6)$$

where α_1 is the Dirac matrix, $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/r_{12}$, and α is the fine-structure constant. The first-order Breit correction is $B_v^{(1)} = \sum_a [b_{vava} - b_{vaav}] = -\sum_a b_{vaav}$, where direct term vanishes after summing over closed shells.

Even though the number of Goldstone diagrams for the V^{N-1} DF potential is much smaller than in general case, the third-order expression for energy correction still includes 52 terms. The corresponding formula for $E_v^{(3)}$ was presented by Blundell *et al.* in Ref. [30], where 52 terms were combined into 12 groups with distinct energy denominators:

$$E_v^{(3)} = E_A^{(3)} + \dots + E_L^{(3)}. \quad (7)$$

Expression (7) includes terms with one-, two-, three-, and four-particle sums over virtual states in addition to sums over core states.

The all-order SD method was discussed previously in Refs. [21,31–36]. Briefly, we represent the wave function Ψ_v

TABLE IV. Oscillator strengths f and wavelengths λ (Å) in In I. The SD data (f^{SD}) are compared with semiempirical calculations (f^{SE}) from Ref. [1] and experimental data (f^{expt}) from Ref. [56].

Lower	Upper	λ^{SD}	f^{SD}	f^{SE}		
$5p_{1/2}$	$6s_{1/2}$	4153	4102	0.133	0.137	0.14
$5p_{3/2}$	$6s_{1/2}$	4576	4511	0.142	0.153	0.15
$5p_{1/2}$	$7s_{1/2}$	2792	2754	0.016	0.0158	0.017
$5p_{3/2}$	$7s_{1/2}$	2977	2933	0.015	0.161	0.017
$5p_{1/2}$	$8s_{1/2}$	2493	2460	0.0054	0.00541	0.006
$5p_{3/2}$	$8s_{1/2}$	2639	2602	0.0051	0.00539	0.006
$5p_{1/2}$	$9s_{1/2}$	2370	2340	0.0025	0.00256	0.0029
$5p_{3/2}$	$9s_{1/2}$	2502	2468	0.0024	0.00254	0.0026
$5p_{1/2}$	$5d_{3/2}$	3045	3039	0.361	0.51	0.36
$5p_{3/2}$	$5d_{3/2}$	3266	3259	0.040	0.056	0.06
$5p_{3/2}$	$5d_{5/2}$	3264	3256	0.353	0.49	0.37
$5p_{1/2}$	$6d_{3/2}$	2578	2560	0.072	0.11	0.043
$5p_{3/2}$	$6d_{3/2}$	2734	2713	0.0077	0.011	0.006
$5p_{3/2}$	$6d_{5/2}$	2734	2710	0.068	0.10	0.052
$5p_{1/2}$	$7d_{3/2}$	2410	2388	0.026	0.039	0.006
$5p_{3/2}$	$7d_{3/2}$	2547	2523	0.0027	0.0033	0.0014
$5p_{3/2}$	$7d_{5/2}$	2546	2521	0.024	0.035	0.009
$5p_{1/2}$	$8d_{3/2}$	2329	2306	0.012	0.017	0.0003
$5p_{3/2}$	$8d_{3/2}$	2456	2432	0.0013	0.0016	
$5p_{3/2}$	$8d_{5/2}$	2456	2439	0.011	0.016	0.0013
$6p_{1/2}$	$7s_{1/2}$	22 594		0.266	0.274	
$6p_{3/2}$	$7s_{1/2}$	24 184		0.279	0.287	
$6p_{1/2}$	$8s_{1/2}$	11 463		0.0222	0.233	
$6p_{3/2}$	$8s_{1/2}$	11 858		0.0207	0.218	
$6p_{1/2}$	$9s_{1/2}$	9264		0.00729	0.00764	
$6p_{3/2}$	$9s_{1/2}$	9520		0.00664	0.00702	
$6s_{1/2}$	$6p_{1/2}$	13 669		0.402	0.467	
$6s_{1/2}$	$6p_{3/2}$	13 146		0.813	0.944	
$6s_{1/2}$	$7p_{1/2}$	7002		0.0103	0.0110	
$6s_{1/2}$	$7p_{3/2}$	6949		0.0284	0.0207	
$6s_{1/2}$	$8p_{1/2}$	5806		0.00206	0.00223	
$6s_{1/2}$	$8p_{3/2}$	5787		0.00642	0.00704	

of the atom with one valence electron as $\Psi_v \equiv \Psi_v^{\text{SD}}$:

TABLE V. Transition probabilities A (in 10^7 s^{-1}) and wavelengths λ (Å) in Sn II. Our SD results are compared with experimental data from Ref. [5].

Lower	Upper	λ^{SD}	λ^{expt}	A^{SD}	A^{expt}
$6s_{1/2}$	$6p_{1/2}$	6813	6844	5.89	5.8 ± 1.1
$6p_{1/2}$	$7s_{1/2}$	6859	6761	3.87	4.2 ± 0.1
$6s_{1/2}$	$6p_{3/2}$	6428	6453	6.91	5.2 ± 1.0
$6p_{3/2}$	$8s_{1/2}$	3862	3841	2.66	2.5 ± 0.5
$6p_{1/2}$	$8s_{1/2}$	3735	3715	1.45	1.8 ± 0.3

TABLE VI. Lifetimes τ in ns for the nl levels in indium. The SD data are compared with experimental results.

Level	τ^{SD}	τ^{expt}	Level	τ^{SD}
$6s_{1/2}$	7.04	$7.5 \pm 0.7^{\text{a}}$	$6p_{1/2}$	69.7
$7s_{1/2}$	21.5	$19.5 \pm 1.5;^{\text{c}} 19.5 \pm 1.5;^{\text{d}} 27 \pm 6^{\text{b}}$	$7p_{1/2}$	219
$8s_{1/2}$	47.7	$53 \pm 5;^{\text{c}} 55 \pm 6^{\text{b}}$	$7p_{3/2}$	192
$9s_{1/2}$	89.4	$118 \pm 10;^{\text{c}} 104 \pm 12^{\text{b}}$	$8p_{1/2}$	473
$5d_{3/2}$	6.45	$6.3 \pm 0.5^{\text{a}}$	$8p_{3/2}$	414
$5d_{5/2}$	6.78	$7.6 \pm 0.5^{\text{a}}$	$4f_{5/2}$	70.4
$6d_{3/2}$	19.2	$21 \pm 3^{\text{a}}$	$4f_{7/2}$	70.4
$6d_{5/2}$	20.1	$22 \pm 3;^{\text{a}} 18.6 \pm 1.5;^{\text{c}} 18.6 \pm 1.5^{\text{d}}$	$5f_{5/2}$	125
$7d_{3/2}$	42.0	$50 \pm 5;^{\text{a}} 200 \pm 4^{\text{b}}$	$5f_{7/2}$	125
$7d_{5/2}$	44.0	$50 \pm 5;^{\text{a}} 154 \pm 10;^{\text{c}} 147 \pm 10^{\text{b}}$		
$8d_{3/2}$	75.7	$317 \pm 22^{\text{c}}$		
$8d_{5/2}$	77.2	$300 \pm 60;^{\text{c}} 238 \pm 20^{\text{b}}$		
$6p_{3/2}$	63.7	$55.0 \pm 4^{\text{d}}$		

^aReference [8].^bReference [9].^cReference [11].^dReference [10].

$$\Psi_v^{\text{SD}} = \left[1 + \sum_{ma} \rho_{ma} a_m^\dagger a_a + \frac{1}{2} \sum_{mnab} \rho_{mnab} a_m^\dagger a_n^\dagger a_b a_a + \sum_{m \neq v} \rho_{mv} a_m^\dagger a_v + \frac{1}{2} \sum_{mna} \rho_{mnva} a_m^\dagger a_n^\dagger a_a a_v \right] \Phi_v, \quad (8)$$

where Φ_v is the lowest-order atomic wave function, which is taken to be the frozen-core DF wave function of a state v . The coupled equations for the single- (ρ_{mv} and ρ_{ma}) and double-excitation coefficients ρ_{mnva} and ρ_{mnab} are obtained

TABLE VII. Hyperfine constants, A (in MHz) for ^{115}In ($I = 9/2$, $\mu = 5.5408$ [57]). Dirac-Fock (DF) and all-order (SD) calculations are compared to experimental values.

Level	DF	SD	Expt.	Level	DF	SD
$6s_{1/2}$	983.0	1812	1685^{a}	$5d_{3/2}$	4.365	-11.48
$7s_{1/2}$	335.6	544.5		$6d_{3/2}$	2.305	-11.20
$8s_{1/2}$	153.6	240.8		$7d_{3/2}$	1.275	-7.692
$9s_{1/2}$	83.10	128.1		$8d_{3/2}$	0.805	-5.385
$5p_{1/2}$	1780	2306	2282^{b}	$5d_{5/2}$	1.862	47.83
$6p_{1/2}$	222.7	263.2		$6d_{5/2}$	0.981	30.81
$7p_{1/2}$	85.15	95.61		$7d_{5/2}$	0.543	18.95
$8p_{1/2}$	41.90	45.97		$8d_{5/2}$	0.342	12.59
$5p_{3/2}$	267.8	262.4	242.2^{c}	$4f_{5/2}$	0.0611	0.1871
$6p_{3/2}$	35.69	77.82		$5f_{5/2}$	0.0316	0.1055
$7p_{3/2}$	13.71	30.83		$4f_{7/2}$	0.0339	0.2293
$8p_{3/2}$	6.767	15.42		$5f_{7/2}$	0.0176	0.1658

^aReference [15].^bReference [13].^cReference [14].

by substituting the wave function Ψ_v^{SD} into the many-body Schrödinger equation, with Hamiltonian given by Eqs. (1)–(3). Note that we again start from V^{N-1} DF potential. The coupled equations for the excitation coefficients are solved iteratively. In the following sections, the resulting excitation coefficients are used to evaluate hyperfine constants and transition matrix elements.

The valence energy E_v^{SD} is given by

$$E_v^{\text{SD}} = \sum_{ma} \tilde{g}_{vavm} \rho_{ma} + \sum_{mab} g_{abvm} \tilde{\rho}_{mvab} + \sum_{mna} g_{vamn} \tilde{\rho}_{mnva}. \quad (9)$$

This expression does not include a certain part of the third-order MBPT contribution. This part of the third-order contribution $E_{v,\text{extra}}^{(3)}$ is given in Ref. [34] and has to be calculated separately. We use our third-order energy code to separate out $E_{v,\text{extra}}^{(3)}$ and add it to the E_v^{SD} . We drop the index v in the $E_v^{(2)}$, $E_v^{(3)}$, and E_v^{SD} designations in the text and tables below.

We use B-splines [37] to generate a basis set of DF wave functions for the calculations of MBPT and all-order expressions. Typically, we use 40 or 50 splines of order $k=7$ or 9, respectively, for each partial wave (see below for more details). Basis orbitals for In I and Sn II are constrained to cavities of radii $R=95$ and 85 a.u., respectively. The cavity radii are chosen large enough to accommodate all orbitals considered in this paper and small enough for 50 splines to approximate inner-shell DF wave functions with good precision.

Results of our all-order SD calculations of energies for the lowest states of neutral In and In-like Sn ion are given in Table I. Our final answer $E_{\text{tot}}^{\text{SD}}$ also includes the part of the third-order energies omitted in the SD calculation $E_{\text{extra}}^{(3)}$, as well as the first-order Breit correction $B^{(1)}$ and the second-order Coulomb-Breit $B^{(2)}$ correction. Theoretical values are compared with the recommended values E_{NIST} from the National Institute of Standards and Technology database [25], $\delta E^{\text{SD}} = E_{\text{tot}}^{\text{SD}} - E_{\text{NIST}}$. For comparison, we also give the differences between the second-order and third-order MBPT calculations and experimental values in columns labeled $\delta E^{(2)}$ and $\delta E^{(3)}$. In Sn II the all-order SD equations for d -wave do not converge and we exclude d orbitals of Sn II from Table I.

The largest correlation contribution to the valence energy comes from the second-order term $E^{(2)}$. As we have discussed above, this term is simple to calculate in comparison with $E^{(3)}$ and E^{SD} terms. Thus, we calculate $E^{(2)}$ with better accuracy than $E^{(3)}$ and E^{SD} . To increase the accuracy of the $E^{(2)}$ calculations, we use 50 splines of order $k=9$ for each partial wave and include partial waves up to $l_{\text{max}}=10$. Then, the final value is extrapolated to account for contributions from higher partial waves (see, for example, Refs. [38,39]). We estimate the numerical uncertainty of $E^{(2)}$ caused by incompleteness of the basis set to be approximately 10 cm^{-1} or less, depending on the valence state.

Owing to the numerical complexity of the E^{SD} calculation, we use $l_{\text{max}}=6$ and 40 splines of order $k=7$. As we noted above, the second-order $E^{(2)}$ is included in the E^{SD} value. Therefore, we use our high-precision calculation of $E^{(2)}$ described above to account for the contributions of the

higher partial waves by replacing $E^{(2)}[l_{\max}=6]$ value with the final high-precision second-order value $E_{\text{final}}^{(2)}$:

$$E_{\text{final}}^{\text{SD}} = E^{\text{SD}} + E_{\text{final}}^{(2)} - E^{(2)}[l_{\max}=6].$$

The size of this correction varies from $\sim 200 \text{ cm}^{-1}$ for the lowest valence states to $\sim 1-20 \text{ cm}^{-1}$ for other valence states considered in this work.

A lower number of partial waves, $l_{\max}=6$, is used also in the third-order calculation. Since the asymptotic l dependence of the second- and third-order energies are similar (both fall off as l^{-4}), we use the second-order remainder to estimate the numerical uncertainties in the third-order and in all-order corrections.

In our calculations of the Breit contribution, we use the whole operator (6) in the first-order correction $B^{(1)}$, while the second-order Coulomb-Breit energies $B^{(2)}$ are evaluated using the unretarded Breit operator, also known as Gaunt [it is described by the first term in Eq. (6)]. Usually Gaunt part strongly dominates in the Breit corrections to the valence energies [40]. Table I shows that there is strong cancelation between first and second order corrections. It is in agreement with the well known observation that Breit interaction for valence electrons is screened by the core [41,42].

We have also estimated Lamb shift correction to valence energies. The vacuum-polarization was calculated in the Uehling approximation. The self-energy contribution is estimated for the s , $p_{1/2}$, and $p_{3/2}$ orbitals by interpolating the values obtained by [43–45] using Coulomb wave functions. We found, as expected, that Lamb shift correction is very small ($E_{\text{LS}} \leq 3 \text{ cm}^{-1}$ for In I and $E_{\text{LS}} \leq 10 \text{ cm}^{-1}$ for Sn II). This is well below the accuracy of the present theory, and we neglect this contribution in Table I.

Comparison of the differences $\delta E^{(2)} = E_{\text{tot}}^{(2)} - E_{\text{NIST}}$ and $\delta E^{(3)} = E_{\text{tot}}^{(3)} - E_{\text{NIST}}$ given in Table I shows that convergence of MBPT series is not very good for both In and Sn^+ . In particular, the second-order results for d -wave in In and f -wave in Sn^+ are even better than the third-order ones. All-order results are more accurate than the third-order ones, but the difference is not very large. For p -waves, SD calculation without the third-order correction overestimates valence binding energies and underestimates it when this correction is included. For the d -wave, both variants lead to underestimation of the binding energy and term $E_{\text{extra}}^{(3)}$ worsens the agreement with the experiment.

We conclude that all-order calculation is generally more accurate than the third-order MBPT calculation. Account of the missing third-order terms does not lead to improvement of the accuracy. On the other hand, this term is generally on the order of our final difference with experiment and can serve as an estimate of the latter. For most levels, our final accuracy is better than 1%, but the accuracy for the d -wave of In is noticeably worse. That can be explained by the existence of the low-lying configuration $5s5p^2$ which strongly interacts with configurations $5s^2nd$. To account for this interaction effectively, one needs to consider In as a three electron atom [46]. The same reason explains mentioned above divergence of the SD equations for the d -wave of Sn II. Interaction between configurations $5s5p^2$ and $5s^2ns$ is weaker and SD

equations for s -wave converge for both atoms considered here. In the opposite parity there is no such a low-lying excitation of the $5s$ shell, so MBPT works better and no problems with convergence occur.

In order to study the relative role of the valence correlations we have performed the second-order RMBPT calculations of atomic properties of In I and Sn II considering these atoms as three-electron systems. Corresponding variant of RMBPT was developed in Ref. [47–51]. The energies of the $[\text{He}]2s^22p$, $[\text{He}]2s2p^2$, and $[\text{He}]2p^3$ states of B-like systems were presented in Ref. [47]. The second-order RMBPT was used by Johnson *et al.* [52] to calculate $[\text{Ne}]3s^23l$ and $[\text{Ne}]3p^23s$ states in Al I and $[\text{Xe}]4f^{14}5d^{10}6s^26pl$ and $[\text{Xe}]4f^{14}5d^{10}6s6p^2$ states in Tl I. Comparing results obtained for neutral B I, Al I, and Tl I, we find that the discrepancy between RMBPT and experimental results increases significantly from B I to Tl I. For example, the RMBPT and NIST values of the ns^2np [$^2P_{3/2}$ - $^2P_{1/2}$] splitting in cm^{-1} for $n=2$ are equal to 17 and 15; for $n=3$ corresponding values are 123 and 112; finally, for $n=6$ we get 6710 and 7793, respectively. It is evident that for a light system, such as B I, the second-order three-electron RMBPT treatment works much better than for a heavy system, such as Tl I. For the latter case it is more appropriate to consider Tl I as one-electron system with $[\text{Xe}]4f^{14}5d^{10}6s^2$ core but treat correlation more completely. It was found in Ref. [21] that in such approach the discrepancy between the SD and NIST values of the $6s^26p$ [$^2P_{3/2}$ - $^2P_{1/2}$] splitting is only 41 cm^{-1} instead of 1083 cm^{-1} obtained in Ref. [52]. Alternatively, one can use CI+MBPT method [23], where the discrepancy is 43 cm^{-1} [46].

The main difference between configurations $[\text{Ni}]4s^24p^64d^{10}5s^2nl$ of In-like ions and $[\text{Ne}]3s^2nl$ configurations of Al-like ions is the necessary size of the model space for valence electrons. For $5l$ electrons in In-like ions, we could not construct sufficiently complete three-electron model space as we did for $3l$ electrons. Additionally, in In-like ions the $n=4$ core shell is not filled. Obviously, we cannot expect the same accuracy as in the case of Al-like ions [50,52].

We tried two model spaces to evaluate energies of In-like ions. Firstly we constructed the model space including $5s$, $5p$, and $5d$ electrons, $[spd]$ model space. Secondly, the odd-parity model space was $[5s^25p+5p^3]$ and even-parity model space was $[5s^25d+5s5p^2]$. We found that in the second case the RMBPT energies were in better agreement with NIST data [25] than in the case of more complete $[spd]$ model space. Theoretical values of the $5s^25p$ [$^2P_{3/2}$ - $^2P_{1/2}$] splitting were equal to 2669 and 4889 cm^{-1} in In I and Sn II, respectively. Comparison of these values with the $E_{\text{tot}}^{\text{SD}}$ values from Table I (2158 cm^{-1} in In I and 4198 cm^{-1} in Sn II) shows that the one-electron representation with all-order treatment of correlation correction gives the results that are in substantially better agreement with experiment than the three-electron model space theory. Because of that, we decided not include three-electron results in the present paper.

III. ELECTRIC-DIPOLE MATRIX ELEMENTS, OSCILLATOR STRENGTHS, TRANSITION RATES, AND LIFETIMES IN In I AND Sn II

The one-body matrix element of the operator Z is given by [31]

$$Z_{wv} = \frac{\langle \Psi_w | Z | \Psi_v \rangle}{\sqrt{\langle \Psi_v | \Psi_v \rangle \langle \Psi_w | \Psi_w \rangle}}, \quad (10)$$

where $\Psi_{v,w}$ are exact wave functions for the many-body “no-pair” Hamiltonian H

$$H|\Psi_v\rangle = E|\Psi_v\rangle. \quad (11)$$

In MBPT, we expand the many-electron function Ψ_v in powers of V_I as

$$|\Psi_v\rangle = |\Psi_v^{(0)}\rangle + |\Psi_v^{(1)}\rangle + |\Psi_v^{(2)}\rangle + |\Psi_v^{(3)}\rangle + \dots \quad (12)$$

The denominator in Eq. (10) arises from the normalization condition that starts to contribute in the third order [53]. In the lowest order, we find

$$Z_{wv}^{(1)} = \langle \Psi_w^{(0)} | Z | \Psi_v^{(0)} \rangle = z_{wv}, \quad (13)$$

where z_{wv} is the corresponding one-electron matrix element. Since $\Psi_w^{(0)}$ is a DF function, we use Z^{DF} designation instead of $Z^{(1)}$ below.

The second-order Coulomb correction to the transition matrix element in the case of V^{N-1} DF potential is given by [54]

$$Z_{wv}^{(2)} = \sum_{na} \frac{z_{an}(g_{wnva} - g_{wnav})}{\varepsilon_a + \varepsilon_v - \varepsilon_n - \varepsilon_w} + \sum_{na} \frac{(g_{wavn} - g_{wanv})z_{na}}{\varepsilon_a + \varepsilon_w - \varepsilon_n - \varepsilon_v}. \quad (14)$$

The second-order Breit corrections are obtained from Eq. (14) by changing g_{ijkl} to b_{ijkl} [29]. The third-order Coulomb correction is obtained from Eqs. (10) and (12) as

$$Z_{wv}^{(3)} = \langle \Psi_w^{(2)} | Z | \Psi_v^{(0)} \rangle + \langle \Psi_w^{(0)} | Z | \Psi_v^{(2)} \rangle + \langle \Psi_w^{(1)} | Z | \Psi_v^{(1)} \rangle - \frac{Z_{wv}^{(1)}}{2} [\langle \Psi_v^{(1)} | \Psi_v^{(1)} \rangle + \langle \Psi_w^{(1)} | \Psi_w^{(1)} \rangle], \quad (15)$$

where the last term arises from the normalization condition. In Ref. [53], contributions to $Z_{wv}^{(3)}$ were presented in a following form:

$$Z_{wv}^{(3)} = Z^{\text{RPA}} + Z^{\text{BO}} + Z^{\text{SR}} + Z^{\text{norm}}. \quad (16)$$

The first term here corresponds to the well known random phase approximation (RPA). Though RPA corresponds to the summation of certain MBPT terms to all orders, it is possible to include it here using the procedure described in Ref. [53]. Next term Z^{BO} corresponds to the correction which arise from substituting DF orbitals with Brueckner ones. The last two terms in Eq. (16) describe structural radiation Z^{SR} and normalization Z^{norm} corrections.

In the all-order SD calculation, we substitute the all-order SD wave function Ψ_v^{SD} into the matrix element expression given by Eq. (10) [31]:

$$Z_{wv}^{\text{SD}} = \frac{z_{wv} + Z^{(a)} + \dots + Z^{(t)}}{\sqrt{(1 + N_w)(1 + N_v)}}, \quad (17)$$

where z_{wv} is the DF matrix element (13) and the terms $Z^{(k)}$, $k = a \dots t$ are linear or quadratic function of the excitation coefficients introduced in Eq. (8). Normalization terms $N_{v,w}$ are quadratic functions of the excitation coefficients. This

expression completely incorporates $Z^{(3)}$ and certain sets of MBPT terms are summed to all orders [31]. The part of the fourth-order correction that is not included in the SD matrix element (17) was recently discussed by [55], but we do not include it here.

In Tables II and III, we present theoretical transition rates A_r , oscillator strengths f , and line strengths S for $E1$ transitions between low-lying states of In I and Sn II, respectively. These results are obtained by combining all-order $E1$ amplitudes (17) in the length gauge and theoretical energies $E_{\text{tot}}^{\text{SD}}$ from Table I using well-known expressions (see, for example, Ref. [25]).

Calculation of the transition amplitudes provides another test of the quality of atomic-structure calculations and another measure of the size of the correlation corrections. In Tables IV and V, we compare our results with available experimental data. For convenience, we also present theoretical and experimental wavelengths for all transitions. There is good agreement with experimental results for the strongest lines of In. For Sn II, agreement is also good with exception of the $6s-6p_{3/2}$ transition where experimental value is much smaller than the calculated one. Note that the theory and experiment are in good agreement for the $6s-6p_{1/2}$ transition.

We also use $E1$ transition rates to calculate the lifetimes of low-lying levels of In I and Sn II. We compare these lifetimes $\tau^{(\text{SD})}$ with available experimental measurements in Table VI. For $7d_j$ levels, the measurements from Refs. [8,9,11] gave rather different lifetimes. Our calculations support the shorter times obtained in Ref. [8].

IV. HYPERFINE CONSTANTS FOR INDIUM

Calculations of hyperfine constants follow the same pattern as calculations of $E1$ amplitudes, described in the previous section. The value of the nuclear magnetic moment for ^{115}In used here is taken from Ref. [57]. Hyperfine constants for another odd isotope ^{113}In can be obtained using the scaling factor 0.99785, which is indistinguishable from unity within the accuracy of the present theory. In contrast with dipole amplitudes considered above, the hyperfine structure is sensitive to the wave function at short distances and to very different types of correlation corrections.

Table VII shows that SD method significantly improves DF values of the hyperfine constants of the lowermost levels. It is rather unusual that correlation correction to the hyperfine structure constant of $5p_{3/2}$ level is so small. For other $p_{3/2}$ levels, correlation corrections are comparable to the initial DF contribution. This situation is more typical for other atoms with $ns^2np_{3/2}$ configuration, such as Tl [46,58].

V. CONCLUSION

Summarizing results of the previous sections, we can make several conclusions. We have seen that all-order SD calculations, when converge, provide an improvement to the third-order MBPT calculation. Convergence of the SD equations is hampered by the existence of low-lying excitations from the uppermost core shell $5s$. The lowest such excitation corresponds to configuration $5s5p^2$ that has positive parity

and primarily affects SD equations for the valence d -wave. Because of that, we were not able to solve these equations for Sn II. To avoid this problem one has to exclude 5s electrons from the core and consider In I and Sn II as three-electron systems. However, our attempt to treat In I and Sn II as three-electron systems within second-order RMBPT for the valence model space, as suggested in Refs. [47], resulted in rather poor agreement with experimental spectra. We conclude that valence correlations for atoms in question cannot be accurately accounted within model space approach. It would be interesting to perform CI+MBPT calculations [23], but it goes beyond the scope of the present paper.

Another interesting observation concerns the addition of the missing part of the third-order term $E_{\text{extra}}^{(3)}$ to the SD results. It was suggested in Ref. [34] to add this term, so that all third-order terms are accounted for. For heavy alkali-

metal atoms omission of this term leads to significant discrepancies of the all-order values with experiment. One can see from Table I, that for atoms considered here this term does not improve agreement with experimental energies. We have also found that first- and second-order Breit corrections tend to cancel each other in agreement with Ref. [42]; final Breit corrections are small and can be neglected within present accuracy of the theory.

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