All-ORDER CALCULATIONS OF THE ENERGY LEVELS
OF HEAVY ELEMENTS INDIUM (In) AND TIN (Sn)

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ABSTRACT

The energy levels of the heavy elements In, Sn^+ and Sn are presented in this article. Dominating corrections beyond the relativistic Hartree-Fock method are included to all orders in the Coulomb interaction using the Feynman diagram technique and the correlation potential method. The configuration interaction technique is combined with the many-body perturbation theory to construct the many-electron wave function for valence electrons and to include core-valence correlations. The good agreement of the results of our calculation with experiment data illustrates the power of the method.

Keywords: energy levels, relativistic Hartree-Fock, configuration interaction.

TÓM TẮT

Tính toán trong gần đúng tất cả các bậc nguyên tố nặng Indi (In) và Thiếc (Sn)

Trong bài báo này, chúng tôi trình bày phổ năng lượng của các nguyên tố nặng Indi (In), ion Thiếc (Sn^+) và Thiếc (Sn) với độ chính xác khá cao. Phương pháp Hartree-Fock tương đối tính được kết hợp với những hiệu chỉnh trong tất cả các bậc của tương tác Coulomb sử dụng giản đồ Feynman và phương pháp thế. Bên cạnh đó, phương pháp lí thuyết nhiễu loạn cho hệ nhiều hạt được kết hợp với tương tác cấu hình để xây dựng hàm sóng nhiều electron cho những electron ngoài vỏ và bao gồm sự tương quan lõi-vỏ. Sự sai lệch rất ít của kết quả với dữ liệu thực nghiệm chứng tỏ được sức mạnh của phương pháp.

Từ khóa: phổ năng lượng, phương pháp Hartree-Fock tương đối tính, tương tác cấu hình.

1.   Introduction

Apart from huge activity in the theoretical and experimental nuclear physics there are also many theoretical works in atomic physics and quantum chemistry with attempts to predict the chemical properties of the heavy elements In and Sn, their electron structure and the spectra [1-3]. Accurate atomic calculations are very important for a number of applications, such as the search for prediction of the properties of atoms and their ions, especially in calculation of the spectra of the elements.

The best results for atoms with one external electron above a closed-shell core are achieved by the use of all-order techniques based on different versions of the correlation-

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potential (CP) method [4,5]. For heavy atoms with several valence electrons the highest accurate methods include the multiconfigurational Hartree-Fock method (MCHF) [6] and different versions of the configuration-interaction (CI) techniques. Here, we apply this method to calculate In and Sn+ which have one external electron above a closed-shell core.

The many-body perturbation theory (MBPT) combined with the CI method to include core-valence correlations (the MBPT + CI [7]) turned out to be a very effective tool for accurate calculations for many-electron atoms having two or three valence electrons [8-10]. In this method, an effective CI Hamiltonian included core-valence correlations in second order of the MBPT. The Sn atom have two valence electrons is applied to control the accuracy of this method.

In the present paper, we perform relativistic calculations for the energy levels of the heavy element In, the singly-ionized Sn and the neutral Sn applying the same approach as our earlier works for superheavy elements E119 and E120+ [11], E113 and E114 [10], E120 [8] and E112 [9].

2.   Method of calculations and results for In and Sn+

We have performed the calculations with the use of the method which has been described in detail in the previous works [10,11]. Here we repeat its main points with the focus on the details specific for current calculations.

Calculations are done in the V^{N-1} approximation, which means that the self-consistent potential are formed by the $N-1$ electrons in the core (V^{N-1} potential). A complete set of single-electron orbitals is obtained in this way. The orbitals satisfy the equation

$$\hat{h}_o \psi_o = \varepsilon_o \psi_o, \tag{1}$$

where $\hat{h}_o$ is the relativistic Hartree-Fock Hamiltonian

$$\hat{h}_o = c\boldsymbol{\alpha}.\mathbf{p} + (\boldsymbol{\beta} - 1)mc^2 - \frac{Ze^2}{r} + V^{N-1}. \tag{2}$$

2.1. Correlations

Calculations start from the relativistic Hartree-Fock (RHF) method in the V^{N-1} approximation. States of valence electron are calculated with the use of the correction potential $\hat{\Sigma}$:

$$(\hat{h}_o + \hat{\Sigma})\psi_a = \varepsilon_a \psi_a. \tag{3}$$

The correlation potential operator $\hat{\Sigma}$ is constructed in such a way that its average value for the valence electron coincides with the correlation correction to the energy $\delta\varepsilon = \langle a|\hat{\Sigma}|a\rangle$. Here, $\hat{\Sigma}$ is non-local operator. The many-body perturbation theory expansion for $\hat{\Sigma}$ starts in second order in the Coulomb interaction. There are direct and exchange contributions to the correlation potential.

The calculations may be improved by including three dominating higher-order diagrams into the second-order correlation potential [4]. These are (i) screening of the Coulomb interaction, (ii) the hole-particle interaction in the polarization operator, and (iii) chaining of the correlation potential $\hat{\Sigma}$.

In particular, (i) and (ii) are included into the direct diagrams of $\hat{\Sigma}$ using the Feynman diagram technique. For the exchange diagrams, we use factors in the second-order $\hat{\Sigma}$ to imitate the effects of screening. These factors are $f_0 = 0,62$, $f_1 = 0,60$, $f_2 = 0,85$, $f_3 = 0,89$, $f_4 = 0,95$, $f_5 = 0,97$, $f_6 = 1$; the subscript denotes the multipolarity of the Coulomb interaction.

2.2. Breit interaction

The Breit interaction is included to claim high accuracy of the calculations [11]. The Breit operator in the zero-energy-transfer approximation has the form

$$h^B = -\frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + (\boldsymbol{\alpha}_1 \cdot \mathbf{n})(\boldsymbol{\alpha}_2 \cdot \mathbf{n})}{2r}, \tag{4}$$

where $\mathbf{r} = \mathbf{n}.r$, r is the distance between electrons, and $\boldsymbol{\alpha}$ is the Dirac matrix.

Similar way to the Coulomb interaction, we determine the self-consistent Hartree-Fock contribution arising from Breit. Other words, Breit interaction is included into self-consistent Hartree-Fock procedure. This is found by solving Eq. (2) in the potential

$$V^{N-1} = V^C + V^B, \tag{5}$$

here V^C is the Coulomb potential, V^B is the Breit potential.

2.3. QED corrections

We use the radiative potential method introduced in Ref. [11] to include quantum electrodynamics radiative corrections to the energies. The radiative potential has the form

$$V_{rad}(r) = V_U(r) + V_g(r) + V_e(r), \tag{6}$$

where V_U is the Uehling potential, V_g is the potential arising from the magnetic formfactor and V_e is the potential arising from the electric formfactor.

As for the case of Breit interaction, this potential is added to the Hartree-Fock potential,

$$V^{N-1} \equiv V^{N-1} + V_{rad}. \tag{7}$$

We included it in the self-consistent solution of the core Hartree-Fock states. Core relaxation, demonstrated to be important for the energies of valence *p*-states, is therefore taken into account.

2.4. Results for In and Sn+

The removal energies for the low-lying states *s*, $p_{1/2}$, and $p_{3/2}$ have been calculated. The results are presented in Table 1 in different approximations. The "RHF" column

obtained by solving Eq. (3) without $\hat{\Sigma}$ presents Hartree-Fock energies. The "$\hat{\Sigma}^{(2)}$" column obtained by solving Eq. (3) with second-order correlation potential $\hat{\Sigma}^{(2)}$ presents Brueckner energies and the column "$\hat{\Sigma}^{(\infty)}$" listed the *ab initio* results of the energy levels obtained by solving Eq. (3) with all-order $\hat{\Sigma}$. Moreover, the Breit corrections are also calculated in the self-consistent Breit-Hartree-Fock potential with the results are presented in the "Breit" column. The "QED" column present the results for quantum electrodynamics (QED) radiative corrections. They are calculated at the Hartree-Fock level, with correlation corrections included. The Breit and QED corrections are relatively small. Thus, our results should only be considered estimates, to give an idea of the size of these corrections. However, adding them generally leads to better agreement with the experiment in some case for In (for example, 6*s*, 7*s*, 5*p₁/₂*, 5*p₃/₂* states).

The results for In and Sn⁺ are present in Table 1 and compared with the experiment. It is clear by looking at the "$\hat{\Sigma}^{(\infty)}$" column, the differences in all cases are small, up to 0.8%. This is consistent with the estimate of the accuracy based on similar method for E113 [10].

Table 1. *Energy levels of In and Sn⁺ (units cm $^{-1}$) in different approximations together with Breit and QED corrections and experimental data.* $\Delta = 100(E_{total} - E_{exp\,t})/E_{exp\,t.}$

Atom	State	*RHF*	$\hat{\Sigma}^{(2)}$	$\hat{\Sigma}^{(\infty)}$	Breit	QED	Total	$\Delta(\%)$	Expt.
In	6s	20.572	22.749	22.424	-7	-9	22.408	0,5	22.297
	7s	9867	10.459	10.390	-2	-3	10.385	0,2	10.368
	8s	5816	6066	6035	-1	-1	6033	0,0	6033
	5p₁/₂	41.507	48.839	46.982	-57	25	46.950	0,6	46.670
	6p₁/₂	13.979	14.892	14.779	-8	2	14.773	0,5	14.853
	7p₁/₂	7488	7809	7768	-3	1	7766	0,6	7809
	5p₃/₂	39.506	46.503	44.819	-25	18	44.812	0,8	44.457
	6p₃/₂	13.719	14.598	14.491	-4	1	14.488	0,5	14.555
	7p₃/₂	7388	7699	7660	-2	0	7658	0,5	7697
Sn⁺	6s	57.995	61.971	60.663	-22	-27	60.614	0,8	61.131
	7s	30.735	31.967	31.536	-8	-9	31.519	0,7	31.737
	8s	19.133	19.692	19.492	-4	-4	19.484	0,7	19.615
	5p₁/₂	111.452	120.411	117.545	-117	30	117.458	0,5	11.8017
	6p₁/₂	44.483	46.383	46.349	-25	3	46327	0,4	46523
	7p₁/₂	25.253	25.979	25.955	-10	1	25946	0,6	26114
	5p₃/₂	107.358	116.018	113.736	-57	22	113701	0,1	113766
	6p₃/₂	43.691	45.499	45.465	-14	2	45453	0,4	45640
	7p₃/₂	24.917	25.613	25.590	-6	1	25585	0,6	25751

3. Method of calculations and results for Sn

3.1. Method of calculations

We performed the calculations with a method that combines the configuration interaction (CI) technique with many-body perturbation theory (MBPT).

Calculations are carried out in the V^{N-2} approximation [12]. This means that the initial Hartree-Fock procedure is performed for the doubly ionized ion, with the two valence electrons removed. This approach has many advantages. It simplifies the inclusion of the core-valence correlations by avoiding the so-called *subtraction* diagrams [7,12]. This in turn allows one to go beyond second order in many-body perturbation theory in the treatment of core-valence correlations. Inclusion of the higher-order core-valence correlations significantly improves the accuracy of the results [2,12].

We use the effective CI Hamiltonian for an atom with two valence electrons,

$$\hat{H}^{eff} = \hat{h}_1(r_1) + \hat{h}_1(r_2) + \hat{h}_2(r_1, r_2) \tag{8}$$

The single-electron Hamiltonian for a valence electron has the form

$$\hat{h}_1 = \hat{h}_0 + \hat{\Sigma}_1 , \tag{9}$$

where $\hat{h}_o$ is the relativistic Hartree-Fock Hamiltonian,

$$\hat{h}_o = c\boldsymbol{\alpha}.\mathbf{p} + (\boldsymbol{\beta}-1)mc^2 - \frac{Ze^2}{r} + V^{N-2} , \tag{10}$$

and $\hat{\Sigma}_1$ is the correlation potential operator, which represents the correlation interaction of a valence electron with the core.

The interaction between valence electrons is given by the sum of the Coulomb interaction and the correlation correction operator $\hat{\Sigma}_2$,

$$\hat{h}_2 = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \hat{\Sigma}_2(r_1, r_2) . \tag{11}$$

The operator $\hat{\Sigma}_2$ represents screening of the Coulomb interaction between valence electrons by core electrons.

The two-electron wave function for the valence electrons ψ can be expressed as an expansion over single-determinant wave functions,

$$\psi = \sum_i c_i \Phi_i(r_1, r_2) . \tag{12}$$

Where Φ_i are constructed from the single-electron valence basis states calculated in the V^{N-2} potential,

$$\Phi_i(r_1, r_2) = \frac{1}{\sqrt{2}} \left[\psi_a(r_1)\psi_b(r_2) - \psi_b(r_1)\psi_a(r_2) \right] , \tag{13}$$

The coefficients c_i and two-electron energies are found by solving the matrix eigenvalue problem

$$\left(H^{\text{eff}} - E \right) X = 0, \tag{14}$$

where $H_{\text{ij}}^{\text{eff}} = \left\langle \Phi_i \left| \hat{H}^{\text{eff}} \right| \Phi_j \right\rangle$ và $X = \{c_1, c_2, \ldots\ldots, c_n\}$.

Calculation of the correlation correction operators $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$ is the most complicated part. Here, we use MBPT and the Feynman diagram technique to do the calculations. The MBPT expansion for $\hat{\Sigma}$ starts from the second order in the Coulomb interaction. Inclusion of the second-order operators $\hat{\Sigma}_1^{(2)}$ and $\hat{\Sigma}_2^{(2)}$ into the effective Hamiltonian (8) accounts for most of the core-valence correlations. However, further improvement is achieved if higher-order correlations are included into $\hat{\Sigma}_1$ and $\hat{\Sigma}_2$.

Where, the higher orders are included into $\hat{\Sigma}_1$ in the same way as for a single-valence electron atom [4]. Two dominating classes of higher-order diagrams are included by applying the Feynman diagram technique to the part of $\hat{\Sigma}_1$ that corresponds to the direct Coulomb interaction. These two classes correspond to (a) screening of the Coulomb interaction between valence and core electrons by other core electrons and (b) the interaction between an electron excited from the core and the hole in the core created by this excitation [4].

Table 2. *Screening factors f_k for inclusion of higher-order correlations into the exchange part of $\hat{\Sigma}_1$ and into $\hat{\Sigma}_2$ as functions of the multipolarity k of the Coulomb interaction.*

k	0	1	2	3	4	5	6
$\hat{\Sigma}_1^{exch}$	0,62	0,60	0,85	0,89	0,95	0,97	1,00
$\hat{\Sigma}_2$	0,90	0,72	0,98	1,00	1,02	1,02	1,02

The screening factors f_k (see Table 2) is introduced to approximate the effect of Coulomb interaction by the core electrons in the exchange diagrams. We assume that screening factors f_k depend only on the multipolarity of the Coulomb interaction k. The screening factors were calculated in our early work [4] and then used in a number of later works. It turns out that screening factors have very close values for atoms with similar electron structure. The screening factors for $\hat{\Sigma}_1^{exch}$ were found by calculating the direct part of $\hat{\Sigma}_1$ with and without screening.

We also use a similar way of approximate inclusion of higher-order correlations via screening factors for $\hat{\Sigma}_2$. The values of the factors, however, are different (see Table 2). These factors were found by comparing $\hat{\Sigma}_1$ in second order and in all orders with both screening and hole-particle interaction included.

A complete set of single-electron states is needed to calculate $\hat{\Sigma}$ and to construct the two-electron basis states (13) for the CI calculations. We use the same basis in both cases. It is constructed using the *B*-spline technique [11]. We use 40 *B*-splines of order 9 in a cavity of radius $R_{max} = 40$ a_B, where a_B is Bohr's radius. The upper and lower radial components $R_a^{u,l}(r)$ of the Dirac spinors for single-electron basis orbitals ψ_a in each partial wave are constructed as linear combinations of 40 *B* splines,

$$R_a^{u,l}(r) = \sum_{i=1}^{40} b_{ai}^{u,l} B_i(r). \tag{15}$$

The coefficients $b_{ai}^{u,l}$ are found from the condition that ψ_a is an eigenstate of the Hartree-Fock Hamiltonian $\hat{h}_0$ (10).

3.2. Results for Sn

The results of our calculations for Sn are presented in Table 3. The column "$\hat{\Sigma}^{(\infty)}$" listed the *ab initio* results of the energy levels of the element. Results of calculations with second-orders correlation potential appear in the column "$\hat{\Sigma}^{(2)}$"; and without correlation potential in the columns "*CI*". In the column "Δ" present the percentage deviation from experiment and other calculations. Experimental numbers are taken from [13].

It is seen from Table 3 that the deviation from experiment for the *ab initio* results are ranges between 0,1% and 1,0% with the exception of the larger deviation for the $5p^2$ (J=2) configuration of 1,2% and the largest deviation for the 5p6p (J=2) configuration of 1,5%. Our final results do not include either Breit or radiative corrections. The reason is that from our results for In and Sn$^+$ (see Table 1) the contribution are relatively small. As can be seen, the reaults of only few state are better with a small fraction of a percent. This results for Sn is the same level as the accuracy for Pb and E114 [10]

Table 3. *Energy levels of Sn (units cm^{-1}).* $\Delta = 100(E_{total} - E_{expt})/E_{expt.}$

Config.	Term	J	CI	$\hat{\Sigma}^{(2)}$	$\hat{\Sigma}^{(\infty)}$	$\Delta(\%)$	Expt.
$5p^2$	^3P	0	0	0	0	0	0
$5p^2$	^3P	1	1560	1717	1691	0,1	1692
$5p^2$	^3P	2	3292	3588	3469	1,2	3428
$5p^2$	^1D	2	8519	8762	8698	1,0	8612

5p^2	^1D	0	16.365	18.464	17.316	0,9	17.162
6s5p	^3P	0	30.970	36.064	34.814	0,5	34.641
6s5p	^3P	1	31.243	36369	35.193	0,8	34.914
6s5p	^3P	2	34.827	40.192	38.938	0,8	38.629
6s5p	^1P	1	38.298	40.519	39.835	0,2	39.257
5p6p	^3D	1	40.375	43.634	42.553	0,5	42.342
5p6p	^3D	2	41.042	44.560	43.864	1,0	43.430
5p6p	^3D	3	45.305	48.209	47.242	0,5	47.007
5p6p	^3P	1	37.874	44.120	43.456	0,2	43.369
5p6p	^3P	0	39.186	45.446	43.930	0,3	43.799
5p6p	^3P	2	46.756	48.427	47.943	1,5	47.235
5p6d	^3F	2	42.432	45.569	44.119	1,0	43.683
5p6d	^3F	3	43.450	45.270	44.754	0,4	44.576
5p6d	^3F	4	47.013	49.200	48.491	0,8	48.107
5p6p	^3D	2	42.923	45.172	44.320	0,4	44.144
5p6p	^3D	1	42.904	45.577	44.687	0,4	44.509
5p6p	^3D	3	46.317	48.822	47.725	0,5	47.488

4.   Conclusion

The energy levels of low-lying s and p states of the heavy elements In, Sn$^+$ and Sn have been performed. The accuracy of our calculations is estimated within one percent. The results were compared with the experiment for further tests of the accuracy.

REFERENCES

[1]   J. B. Sanders, "Spectroscopic calculation of energy levels of some Tin isotopes," *Nuc. Phys.* **23**, pp. 305-311, 1961.

[2]   V. A. Dzuba, "Calculation of the energy levels of Ge, Sn, Pb, and their ions in the V^{N-4} approximation," *Phys. Rev. A* **71**, 6, pp. 062501-062507, 2005.

[3]   H. Shin, J. B. KIM, "Ground state energy levels of Indium arsenide quantum dots calculated by a single band effective mass model using representative strained input properties," *Mod. Phys. Lett. B* **27**, 16, pp. 1350120-1350130, 2013.

[4]   V. A. Dzuba, V. V. Flambaum, and O.P. Sushkov, "Summation of the perturpation theory high order contributions to the correlation correction for the energy levels of the Caesium atom," *Phys. Lett. A* **140**, 9, pp. 493-497, 1989.

[5]   V. A. Dzuba, "Correlation potential and ladder diagrams," *Phys. Rev. A* **78**, 4, 042502-042509, 2008.

[6]   Y. Zou and C. F. Fischer, "Resonance transition energies and oscillator strengths in Lutetium and Lawrencium," *Phys. Rev. Lett.* **88**, 18, pp. 183001-183004, 2002.

[7]   V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, "Combination of the many-body perturbation theory with the configuration-interaction method," *Phys. Rev. A* **54**, 5, pp. 3948-3959, 1996.

[8]   T. H. Dinh, V. A. Dzuba, V. V. Flambaum and J. S. M. Ginges, *"*Calculation of the spectrum of the superheavy element Z=120*," Phys. Rev. A* **78**, 5, pp. 054501-054504, 2008.

[9]   T. H. Dinh, V. A. Dzuba and V. V. Flambaum, "Calculation of the spectra for the superheavy element Z=112,*" Phys. Rev. A* **78**, 6, pp. 062502-062506, 2008.

[10]   T. H. Dinh, and V. A. Dzuba, "All-order calculations of the spectra of superheavy elements 113 and 114," *Phys. Rev. A* **94**, 5, pp. 052501-052504, 2016.

[11]   T. H. Dinh, V. A. Dzuba, V. V. Flambaum and J. S. M. Ginges, "Calculations of the spectra of superheavy elements Z=119 and Z=120$^+$,*" Phys. Rev. A* **78**, 2, pp. 022507-022513, 2008.

[12]   V. A. Dzuba, "V^{N-M} approximation for atomic calculations," *Phys. Rev. A* **71**, 3, pp. 032512-032517, 2005.

[13]   C. E. Moore, "Atomic Energy Levels," *Natl. Bur. Stand. (U.S.) Circ.* No. 467, U.S. GPO, Washington, D.C., 1958.