ATOMIC
SPECTROSCOPY

Higher Orders in Residual Two-Electron Interaction

M. G. Kozlov

Institute of Nuclear Physics, Russian Academy of Sciences, Gatchina, 188300 Russia
e-mail: mgk@MF1309.spb.edu
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Abstract—Precise methods of calculations of many-electron atoms are under intensive development. In such calculations, higher orders of the perturbation theory in regard to residual interaction of electrons should be taken into account. In this study, a model of an atom with two electrons in its core and two valence electrons is considered. In terms of this model, expansion with respect to residual interaction is analyzed for two initial approximations based on the potentials $V^{(2)}$ and $V^{(4)}$. It turns out that the higher order corrections are nearly the same in both cases. At the same time, the potential $V^{(2)}$ has a number of advantages. © *2003 MAIK "Nauka/Interperiodica".*

INTRODUCTION

Completely accounting for electron correlations is possible only for atoms with a very small number of electrons. In the general case, calculations of atomic structure are only possible in terms of some approximate methods. Presently, there are several approaches to calculation of many-electron atoms (see, for example, [1, 2]). Generally, some variant of a mean field is used as an initial approximation. Most often, it is a Hartree–Fock field for one of the electronic configurations. For atoms with one valence electron above occupied shells of the core, it is reasonable to use a Hartree–Fock core potential. In the case of two or more valence electrons, it seems reasonable to construct an initial approximation with complete or partial allowance made for the field of valence electrons. The many-body perturbation theory (MBPT), which is based on such an initial approximation, is more intricate, since it contains a large class of additional diagrams. It is customary to call them subtraction diagrams.

The possibility of partially taking into account the field of valence electrons is provided for in the method of the effective Hamiltonian for valence electrons [3–5]. For example, calculations for the Hg and Ba atoms [6] were carried out for the potential $V^{(N)}$, where N is the total number of electrons in the atom, including the two valence electrons. In this case, the correlation corrections turn out to be significantly smaller than in the case when the initial approximation is constructed on the basis of the core potential $V^{(N-2)}$. Thus, one might expect to obtain higher accuracy in the calculations based on the $V^{(N)}$ approximation. In this study, we analyze higher order corrections for the potentials $V^{(N-2)}$ and $V^{(N)}$ on the example of a simple model.

A completely satisfactory theory for taking into account electron correlations in atoms has not yet been developed, in particular, due to the absence of an adequate smallness parameter. Even when the correlation corrections are small, this parameter cannot be distinguished explicitly. This makes it difficult to estimate ignored terms and the accuracy of calculations. Therefore, even rough estimates of the effective smallness parameter are of interest.

We suggest a simple estimation of the accuracy of the method of the effective Hamiltonian for valence electrons [3–5]. In this method, the valence correlations are rigorously taken into account and the core–valence correlations are considered in the second order of the MBPT. The contribution of the latter correlations to the energy can be roughly estimated as

$$\delta E_{cv} = \frac{\langle V' \rangle^2}{\Delta_{cv}}, \qquad (1)$$

where V' is the energy of residual interaction and Δ_{cv} is the excitation energy of the core. Let us introduce the parameter

$$\lambda_{\text{eff}} = \frac{\langle V' \rangle}{\Delta_{cv}}, \qquad (2)$$

which characterizes the magnitude of the residual interaction, and express this parameter from (1):

$$\lambda_{\text{eff}} = \sqrt{\frac{\delta E_{cv}}{\Delta_{cv}}}. \qquad (3)$$

The latter equation allows us to relate λ_{eff} to well-known quantities. The results of calculations in the second order of the MBPT can be used to obtain a correlation correction to the energy. Then, the terms ignored are of the third order with respect to the residual interaction and, consequently,

$$\text{error} \sim \frac{\langle V' \rangle^3}{\Delta_{cv}^2} = \lambda_{\text{eff}} \delta E_{cv}. \qquad (4)$$

In order to verify the above estimates, some exactly solvable model with an explicit parameter λ should be considered and the dependence of the calculation error on this parameter should be determined.

MODEL

An evident requirement of the model is that it must take into account the valence–core correlations as rigorously as possible; i.e., complete configuration interaction (CI) should be possible. For this purpose, it is sufficient to consider an atom with a small core and use a small basis of one-electron orbitals. Calculations based on a small basis do not allow us to adequately describe the actual spectrum of the atom, but this is not the point of our consideration. Since no less than two valence electrons are required for a valuable verification of the method (for a one-electron atom, there are no two-electron screen diagrams, which are imperative for many-electron systems), an atom or an ion having two electrons in its core and two valence electrons may serve as the simplest model system. Thus, we are speaking of an atom with the core configuration $[1s^2]$ and two valence electrons n_1l_1 and n_2l_2. A larger number of electrons makes it impossible to solve the problem exactly even using a very small basis. For definiteness, we chose the C^{++} ion ($Z = 6$), which turned out to be convenient from the computational point of view.

In the model system suggested, the core excitation energy $\Delta_{cv} \sim 10$ au. According to estimate (3), one might expect that the parameter $\lambda_{\text{eff}} \ll 1$ and the higher order effects are quite small. At the same time, this circumstance makes it possible to calculate a large number of levels while remaining in the domain of applicability of the effective Hamiltonian method (the effective Hamiltonian has poles above the core excitation energy).

Let us write the Hamiltonian for the initial approximation H_0 in the form [6]

$$H_0 = PHP + QH_{DF}Q, \qquad (5a)$$

$$H_{DF} = E_{\text{core}} + \varepsilon_i a_i^\dagger a_i - \varepsilon_n b_n^\dagger b_n, \qquad (5b)$$

where $a_i^\dagger$ and $b_n^\dagger$ are the creation operators for valence electrons and core holes, respectively, and P is the projector onto the valence subspace ($Q = 1 - P$). The creation and annihilation operators in formula (5b) are constructed in terms of the Dirac–Fock approximation for the potentials $V^{(2)}$ and $V^{(4)}$. Thus, we obtain two variants of the model.

Let us represent the complete Hamiltonian of the model system in the form

$$H^\lambda = H_0 + \lambda(H - H_0). \qquad (6)$$

The introduction of the parameter λ in an explicit form allows us to control the magnitude of the residual

Fig. 1. Diagrams describing a second-order correction to the core energy. The wavy lines correspond to the Coulomb interaction.

interaction and to obtain the expansion of the eigenvalues of the operator H^λ in the form

$$E_i^\lambda = E_i^{(0)} + a_i\lambda^2 + b_i\lambda^3 + c_i\lambda^4 + \dots . \qquad (7)$$

At $\lambda = 1$, the Hamiltonian H^λ coincides with the initial Hamiltonian H and $E_i^\lambda\big|_{\lambda = 1} = E_i$. The coefficient a_i is equal to the second-order correction in respect to the residual interaction $V' \equiv H - H_0$ for the Hamiltonian H. It can be found both by direct diagonalization of Hamiltonian (6) with different values of λ and by the use of the method of the effective Hamiltonian, which can be written in our model as

$$H_{\text{ef}}(E) = PHP + \lambda^2 PV'QR_{DF}(E)QV'P, \qquad (8a)$$

$$R_{DF}(E) = (E - QH_{DF}Q)^{-1}. \qquad (8b)$$

Thus, the model suggested makes it possible to

(i) verify the effective Hamiltonian method;

(ii) find the higher order corrections in respect to the residual interaction and verify estimates (3) and (4); and

(iii) compare the two initial approximations based on the potentials $V^{(2)}$ and $V^{(4)}$.

Comparing the results of calculations in terms of complete CI and by the method of the two-electron effective Hamiltonian, one should bear in mind that the latter procedure makes it possible to determine the correlation corrections to the valence energy rather than the total energy. In this case, the correlation correction to the core energy E_{core} is disregarded. This correction is the same for all levels and does not change the valence spectrum of the atom. Therefore, one should compare the differences $a_i - a_1$ rather than the coefficients a_i.

At the same time, the second-order correction to the core energy can be calculated in terms of the conventional MBPT and, thus, not only the differences $a_i - a_1$ but also the coefficients a_i can be compared. For the potential $V^{(N_{\text{core}})}$, the second-order correction to the energy E_{core} is described by the two diagrams shown in Fig. 1. In the general case, subtraction diagrams are added to these diagrams. Both diagrams in Fig. 1 and all subtraction diagrams can be obtained by summation with respect to the external line of the diagrams shown
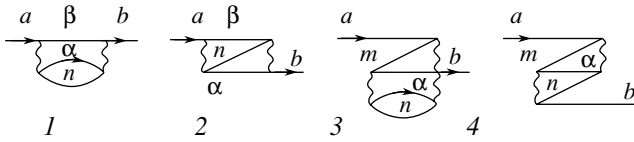
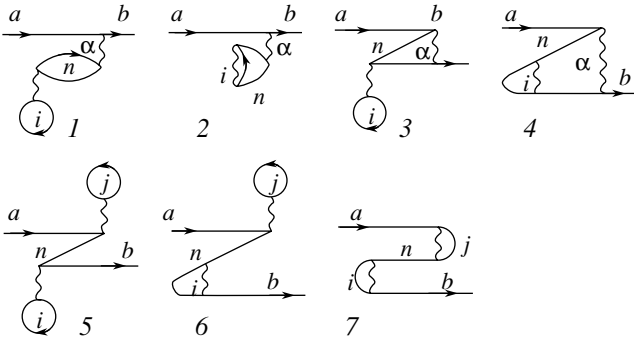**Fig. 2.** Basic second-order diagrams for the self-energy.

Fig. 3. Second-order subtraction diagrams for the self-energy. Summation over the indices i and j is performed over the valence orbitals included in the zero-approximation potential. These diagrams are set to zero for the potential $V^{(N_{core})}$.

in Figs. 2 and 3, which describe the one-particle second-order correlation correction (called the self-energy correction). In particular, the two diagrams in Fig. 1 are obtained from diagrams *3* and *4* in Fig. 2. The general expression for the correlation correction to E_{core} has the form

$$\delta E_{core} = -\sum_a (2j_a + 1)\Big[\frac{1}{2}D(\text{Fig. 2, }3)$$
$$+ \frac{1}{2}D(\text{Fig. 2, }4) + D(\text{Fig. 3, }5) \quad (9)$$
$$+ 2D(\text{Fig. 3, }6) + D(\text{Fig. 3, }7)\Big],$$

where all diagrams on the right-hand side are calculated for $b = a$. The numerical factors before the diagrams in Eq. (9) account for their symmetry, and the common factor is equal to the statistical weight of the orbital.

NUMERICAL RESULTS

As was noted above, the calculation of the physical spectrum of the C^{++} ion is beyond our consideration. Instead, we want to compare the results of complete CI with the effective Hamiltonian method. Therefore, we will use a very small basis composed of 14 orbitals $1 - 4s_{1/2}$, $2 - 4p_j$, $3, 4d_j$. For this basis, the complete CI for four electrons can be performed using a personal com-

puter. However, even in this case, the dimension of the Hamiltonian matrix is about 14 000, and complete diagonalization is not possible. Therefore, we restrict ourselves to the calculation of only the first 11 levels of the configurations $2s^2$, $2s2p$, $2p^2$, and $2s3s$.

In the calculations, we used programs based on the Dirac equation with allowance made for the Coulomb interaction. In this case, many-electron basis functions are written in the form of Slater determinants. The latter have a certain value of the component J_z of the total momentum of electrons, but no certain value of the quantum number J. This number arises due to the diagonalization of the Hamiltonian matrix. In the case of heavy atoms, for which fine splitting between levels with different J is rather large, such a method is generally quite adequate. However, here, we consider a light atom, for which the fine splitting of the electronic structure is small and the levels of the same multiplet are almost degenerate. In such cases, the numerical diagonalization may result in mixing of nearby levels, due to which the values of the quantum number J differ only slightly from integers.

For eigenenergies, the corresponding numerical errors are negligible, but they may be appreciable in calculation of other observables. Therefore, instead of the Hamiltonian matrix, we diagonalize numerically the matrix

$$H^g = H + g\mathbf{J}^2, \quad (10)$$

where $\mathbf{J}$ is the operator of the angular momentum of the electrons and the parameter g is chosen arbitrarily. The matrices H and H^g have a common set of eigenvectors, and the eigenvalues are related as follows:

$$E_n = E_n^g - gJ_n(J_n + 1). \quad (11)$$

Equations (10) and (11) make it possible to diagonalize the matrix H instead of H^g and, hence, to avoid quasi-degeneration of levels. We verified that such a method allows one to significantly improve the quality of diagonalization of nearby levels.

In order to determine the expansion coefficients (7), the calculations based on complete CI were performed for five values of the parameter λ: 0, ± 0.5, and ± 1. This makes it possible to find the expansion coefficients (7) with an accuracy up to the fifth order. However, in our model, the last coefficient is about 10^{-6} au and is appreciably affected by the round-off errors. Therefore, we neglect this coefficient in the further consideration. When the effective Hamiltonian method is used, expansion (7) contains only even powers of λ; therefore, it is sufficient to perform calculations for $\lambda = 0, 0.5$, and 1.

As can be seen from formulas (8), the effective Hamiltonian depends on the energy. Accounting exactly for this dependence would make the above method absolutely inefficient, since one would have to calculate all diagrams by the MBPT method anew for each energy. Instead of this, it was suggested in [4–6] to

Table 1. Four-electron calculation for the C^{++} ion using the potential $V^{(2)} = V[1s^2]$. ($E^{(0)}$ corresponds to the calculation with the frozen core $[1s^2]$, and a, b, and c are the expansion coefficients in (7), atomic units are used)

Level	$E^{(0)}$	a	b	c
$^1S_0[2s^2]$	36.497727	0.007132	0.000348	0.000041
$^3P_0^o[2s2p]$	36.257342	0.008002	0.000483	0.000048
$^3P_1^o[2s2p]$	36.257189	0.008002	0.000483	0.000047
$^3P_2^o[2s2p]$	36.256883	0.007998	0.000484	0.000049
$^1P_1^o[2s2p]$	36.015509	0.010743	0.000643	0.000075
$^3P_0[2p^2]$	35.862936	0.011272	0.000786	0.000088
$^3P_1[2p^2]$	35.862786	0.011273	0.000786	0.000086
$^3P_2[2p^2]$	35.862489	0.011268	0.000786	0.000087
$^1D_2[2p^2]$	35.820411	0.010012	0.000622	0.000064
$^1S_0[2p^2]$	35.643836	0.010744	0.000558	0.000065
$^3S_1[2s3s]$	35.404971	0.007397	0.000440	0.000046

take the energy dependence of the effective Hamiltonian into account approximately. In this case, each coupled diagram (similar to those shown in Figs. 2 and 3) is calculated only once for some energy value. Simultaneously, its derivative with respect to the energy is calculated, which does not require any appreciable additional computational resources. In construction of an effective Hamiltonian, the energy, for which the values of MBPT corrections should be known, is determined for each matrix element and the corresponding extrapolation is carried out. In this case, the smoothness and

asymptotic behavior of the MBPT corrections are taken into account (for more details, see [7]).

POTENTIAL $V^{(2)} = V[1s^2]$

The results of calculations for the potential $V^{(2)}$ are listed in Tables 1 and 2 (we give the values of positive binding energies in au everywhere). In Table 1, the coefficients of expansion of the eigenvalues of Hamiltonian (6) in terms of λ are listed. In Table 2, the complete four-electron calculation is compared with three variants of two-electron calculation by the effective-potential method. In the first two variants, the energy dependence of the effective Hamiltonian is disregarded. Notably, in variant 1, the diagrams are calculated at the corresponding Hartree–Fock energies, while, in variant 2, they are calculated at the lowest Hartree–Fock energy for the corresponding partial wave (e.g., all one-particle diagrams for the ns orbitals are calculated at the energy ε_{2s}, and so on). In the third variant, all MBPT corrections are extrapolated to the correct energy, as described above. In this case, it turns out to be of little importance which of the two previous variants is used as a basis for extrapolation.

In the calculation of the coefficient a_1 by the effective-potential method, the second-order correction to the core energy (9) is taken into account. The value of this correction is

$$\delta E_{\text{core}} = 0.006051. \tag{12}$$

Table 2. Coefficients a_1 and differences $a_i - a_1$ for the four-electron calculation by the complete CI method and for three variants of two-electron calculation by the effective Hamiltonian method. (The last column contains the magnitudes of differences between the results of the four-electron calculation and the last variant of the two-electron calculation Δ)

Level	4 e	2 e			Δ
		variant 1	variant 2	variant 3	
$^1S_0[2s^2]$	0.007132	0.006970	0.006986	0.007019	0.000113
$^3P_0^o[2s2p]$	0.000870	0.000836	0.000825	0.000868	0.000002
$^3P_1^o[2s2p]$	0.000870	0.000837	0.000821	0.000863	0.000007
$^3P_2^o[2s2p]$	0.000866	0.000832	0.000816	0.000863	0.000003
$^1P_1^o[2s2p]$	0.003611	0.003355	0.003352	0.003575	0.000036
$^3P_0[2p^2]$	0.004140	0.003930	0.003919	0.004123	0.000017
$^3P_1[2p^2]$	0.004141	0.003931	0.003922	0.004118	0.000023
$^3P_2[2p^2]$	0.004136	0.003932	0.003919	0.004119	0.000017
$^1D_2[2p^2]$	0.002880	0.002699	0.002687	0.002858	0.000022
$^1S_0[2p^2]$	0.003612	0.003299	0.003250	0.003554	0.000058
$^3S_1[2s3s]$	0.000265	0.000308	0.000310	0.000307	0.000042

Table 3. Coefficients a, b, and c for the four-electron calculation with the potential $V^{(4)}$

Level	$E^{(0)}$	a_i	b_i	c_i
$^1S_0[2s^2]$	36.495774	0.003259	0.000258	0.000044
$^3P_0^o[2s2p]$	36.253274	0.003494	0.000352	0.000064
$^3P_1^o[2s2p]$	36.253120	0.003494	0.000352	0.000063
$^3P_2^o[2s2p]$	36.252811	0.003492	0.000357	0.000064
$^1P_1^o[2s2p]$	35.993803	0.005176	0.000621	0.000120
$^3P_0[2p^2]$	35.859712	0.005178	0.000745	0.000153
$^3P_1[2p^2]$	35.859563	0.005178	0.000745	0.000153
$^3P_2[2p^2]$	35.859266	0.005176	0.000740	0.000152
$^1D_2[2p^2]$	35.798718	0.004476	0.000539	0.000098
$^1S_0[2p^2]$	35.623666	0.005076	0.000591	0.000105
$^3S_1[2s3s]$	35.387470	0.003535	0.000269	0.000053

Equation (3) allows one to estimate the effective smallness parameter for the MBPT:

$$\lambda_{\text{eff}} \approx \sqrt{\frac{0.0075}{12}} \approx 0.03. \tag{13}$$

It can be seen from Table 1 that the characteristic value of the higher order corrections to the correlation energy is ~0.0005, whereas formula (4) with parameter (13) yields

$$\text{error} \sim 0.0002. \tag{14}$$

A comparison of the parameters a, b, and c from Table 1 with each other shows that, actually, $\lambda_{\text{eff}} \approx 0.08$. This difference from (13) may be considered as fairly reasonable, bearing in mind the simplicity of estimate (3).

Let us consider the difference between the coefficients a obtained in the complete four-electron calculation and in the calculations by the effective Hamiltonian method. For the coefficient a_1, this difference is about 1×10^{-4}, which is three times smaller than the correction of the next-order smallness b_1. Moreover, as was noted above, this difference may be partially attributed to correction (12), which does not affect the valence spectrum of the atom. Therefore, it is of greater importance to analyze the differences $a_i - a_1$. In this case, the largest difference is about two times smaller and the average difference is only 2×10^{-5}. As can be seen from Table 1, this value is significantly smaller than the fourth-order coefficient c and is comparable with the average value of $|c_i - c_1|$.

Thus, for the potential $V^{(2)}$, the effective Hamiltonian method reproduces the differences $a_i - a_1$ fairly well. The deviations from the complete four-electron calculation are of the order of λ^4. Note that accounting for the energy dependence of the effective Hamiltonian turns out to be essential. If this dependence is disregarded, the error becomes comparable with the coefficient b, i.e., is of the order of λ^3.

POTENTIAL $V^{(4)} = V[1s^2, 2s^2]$

Let us now consider the same model system with the use of the potential $V^{(4)} = V[1s^2, 2s^2]$. For this purpose, we will reconstruct the basis in such a way as to make the orbitals eigenfunctions of the new Dirac–Fock operator. From the point of view of four-electron calculation, there is no difference with the previous case. However, the two-electron calculation is distinguished by the appearance of a new class of so-called subtraction diagrams in the effective Hamiltonian [4]. One-electron subtraction diagrams are shown in Fig. 3.

Table 4. Coefficients a_1 and differences $a_i - a_1$ for the potential $V^{(4)}$ (The notation is the same as in Table 2)

Level	4e	2e			Δ
		variant 1	variant 2	variant 3	
$^1S_0[2s^2]$	0.003259	0.003408	0.003413	0.003376	0.000117
$^3P_0^o[2s2p]$	0.000235	0.000317	0.000312	0.000301	0.000066
$^3P_1^o[2s2p]$	0.000235	0.000317	0.000312	0.000295	0.000060
$^3P_2^o[2s2p]$	0.000233	0.000317	0.000312	0.000296	0.000063
$^1P_1^o[2s2p]$	0.001917	0.002105	0.002100	0.001953	0.000036
$^3P_0[2p^2]$	0.001919	0.002308	0.002295	0.002032	0.000113
$^3P_1[2p^2]$	0.001919	0.002299	0.002291	0.002032	0.000113
$^3P_2[2p^2]$	0.001917	0.002304	0.002291	0.002032	0.000115
$^1D_2[2p^2]$	0.001217	0.001485	0.001497	0.001328	0.000111
$^1S_0[2p^2]$	0.001817	0.001992	0.002015	0.001900	0.000083
$^3S_1[2s3s]$	0.000276	0.000305	0.000296	0.000297	0.000021

From the computational point of view, these diagrams are significantly simpler than the diagrams in Fig. 2, and their introduction does not increase the calculation time. They are also significantly smaller in magnitude, but the total value of the correlation corrections may change significantly due to the fact that there are a large number of subtraction diagrams and different contributions become significantly reduced (see below).

The results of calculations for the potential $V^{(4)}$ are listed in Tables 3 and 4. The second-order correlation correction to the core energy (9) is introduced into the calculations of the coefficient a_1 by the effective Hamiltonian method (Table 4). The numerical value of this correction is

$$\delta E_{\text{core}} = 0.003377. \qquad (15)$$

According to formula (3),

$$\lambda_{\text{eff}} \approx \sqrt{\frac{0.0034}{11}} \approx 0.02. \qquad (16)$$

Equation (4) yields for the expected error the estimate

$$\text{error} \sim 0.00006, \qquad (17)$$

which is three times smaller than in the previous example (14). However, as one can see from Table 3, the actual error is approximately the same as for the potential $V^{(2)}$, i.e., ~0.0005.

A comparison of the parameters a, b, and c from Table 2 with each other yields the value of $\lambda_{\text{eff}} \approx 0.14$, which is larger than the value in (16) by almost an order of magnitude. Thus, one can see that estimates (3) and (4) are much poorer in this case.

Let us now consider the coefficients a_i from Table 3. A comparison of these coefficients obtained in different calculation schemes shows that, for the potential $V^{(4)}$, the difference between the four- and two-electron calculations is considerably larger than for the potential $V^{(2)}$. The allowance made for the energy dependence of the effective Hamiltonian improves the agreement between the two- and four-electron calculations by nearly threefold, but leaves the average error for the quantities $|a_i - a_1|$ at a level of 8×10^{-5}, which is four times larger than in the case of calculation with the potential $V^{(2)}$.

As was noted above, in the MBPT based on the potential $V^{(N)}$, there are significant reductions between different second-order corrections. For example, the summed diagrams from Figs. 2 and 3 for the orbitals $2s$ and $2p_j$ are listed in Table 5. It can be seen that the subtraction diagrams amount to about 50% of the self-energy and have the opposite sign. On the one hand, this circumstance leads to reduction of the second-order correlation corrections, but, on the other hand, it may increase errors related to the extrapolation of the diagrams to the required energy. Apparently, for higher orders of the MBPT, such a reduction of the contributions as that for the second order does not take place.

Table 5. Summed diagrams

Orbital	Fig. 2	Fig. 3	Sum
$2s_{1/2}$	−0.000517	+0.000160	−0.000357
$2p_{1/2}$	−0.001001	+0.000307	−0.000694
$2p_{3/2}$	−0.000997	+0.000305	−0.000692

This is because the coefficients b and c from Tables 2 and 4 have close values.

HYPERFINE STRUCTURE

The model considered makes it possible to compare not only the spectra, but also other observable parameters. The core–valence correlations affect most strongly those observables that depend on the electron wave function at small distances from the nucleus. As an example, we chose the constants of magnetic hyperfine structure (HFS), whose theory was developed in [8]. Complete analysis is hindered here by the fact that the effective HFS operator partially includes higher MBPT orders; hence, it is impossible to perform expansion in terms of the parameter λ. Therefore, we restricted our calculations to the case of $\lambda = 1$; the results of the calculations are summarized in Table 6.

One can see that the corrections to the HFS constants for different levels differ strongly from each other. For the levels $^3P^{\circ}_{1,2}$ the method of effective operators significantly overestimates the correlation correction to A, whereas, for other levels, there is good agreement with calculations based on the use of a complete set of electrons. An analysis of various MBPT corrections shows that, for triplet levels $^3P^{\circ}_{1,2}$ of the configuration $2s2p$, the main contribution is from the two-particle corrections to the HFS operator, which are shown in Fig. 4. For the other levels listed in Table 6, including the singlet level $^1P^{\circ}_1$ of the same configuration, the two-particle corrections are smaller, by at least an order of magnitude.

The large values of the two-particle corrections for the triplet levels of the configuration $2s2p$ are due to the fact that the direct and exchange diagrams for these levels enhance each other, whereas, for the other levels, they cancel each other. This can be explained both by the spin selection rules and by the fact that the $2s$ and $3s$ orbitals are orthogonal to the $1s$ core orbital.
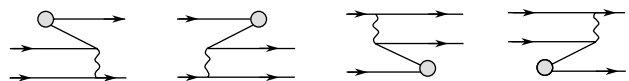

Fig. 4. Two-particle corrections to the effective HFS operator. Circles denote the matrix elements of the HFS operator in the random-phase approximation.

Table 6. Magnetic HFS constants A for the potentials $V^{(2)}$ and $V^{(4)}$ in arbitrary units ($A^{(0)}$ corresponds to the calculations with the frozen core $[1s^2]$; $\Delta A(4e)$ and $\Delta A(2e)$ are the corrections to these values obtained in the four-electron and two-electron calculations, respectively)

Level	$V^{(2)}$			$V^{(4)}$		
	$A^{(0)}$	$\Delta A(4e)$	$\Delta A(2e)$	$A^{(0)}$	$\Delta A(4e)$	$\Delta A(2e)$
$^3P_1^o[2s2p]$	986.4	38.7	108.7	1054.4	19.5	63.6
$^3P_2^o[2s2p]$	827.2	37.4	106.6	883.6	19.0	62.9
$^1P_1^o[2s2p]$	247.9	1.5	1.1	257.1	0.7	0.5
$^3P_1[2p^2]$	−0.4	−108.4	−107.1	−0.5	−97.8	−95.1
$^3P_2[2p^2]$	153.8	−107.1	−106.0	163.7	−97.3	−94.7
$^1D_2[2p^2]$	239.8	1.3	2.0	255.5	0.6	0.7
$^3S_1[2s3s]$	2018.7	161.6	161.0	2206.1	96.4	94.6

It can be seen from Table 6 that the correlation corrections to the HFS constants are large for most of the levels considered. However, except for the levels $^3P_{1,2}^\circ$, large contributions correspond to the one-particle corrections of the random-phase method (for more details, see [8]). As is known, this method is equivalent to summation over an infinite chain of MBPT diagrams. Thus, when the corrections of the random-phase method are dominant, one can expect that the main higher order MBPT corrections are taken into account. When the two-particle contributions, which are taken into account only in the lower order of the MBPT, are dominant, one cannot expect the calculation to be of high accuracy.

CONCLUSIONS

On the example of a simple model, we compared calculations of the low-energy part of the atomic spectrum by the effective Hamiltonian method with the calculation based on the complete set of electrons. The results of these calculations allow us to draw some conclusions about the effective Hamiltonian method and the properties of two variants of the perturbation theory based on the potentials $V^{(2)}$ and $V^{(4)}$.

(1) For both potentials, the error of the effective Hamiltonian method for the frequencies of valence transitions is of the third order with respect to the residual interaction between the core and valence electrons.

(2) The allowance made for the energy dependence of the effective Hamiltonian does not reduce the total error of the method, but does make it possible to significantly increase the accuracy of calculation of the second-order coefficients of the residual interaction a_i. For the potential $V^{(2)}$, the accuracy of calculations of the coefficients a_i is several times higher than for the potential $V^{(4)}$. This circumstance may be associated with significant mutual reductions of different contributions in the perturbation theory based on the potential $V^{(4)}$.

(3) The second-order correlation corrections for the potential $V^{(4)}$ are two times smaller than those for the potential $V^{(2)}$, but the higher order corrections are comparable. Therefore, the convergence of the perturbation theory for the potential $V^{(4)}$ is no better than for the potential $V^{(2)}$.

(4) The estimate of the accuracy of calculations based on the effective smallness parameter $\lambda_{\text{eff}} = \sqrt{\delta E_{cv}/\Delta_{cv}}$ yields the correct order of the error for the potential $V^{(2)}$, but cannot be applied to the potential $V^{(4)}$.

(5) For the magnetic HFS constants, the correlation corrections are significantly larger than for the valence energies. Nevertheless, the method of effective operators for valence electrons is adequate when one-particle corrections are dominant.

Summing up the abovesaid, we can state that, if the higher order corrections with respect to the residual interaction are disregarded, calculations of the valence spectrum by the effective Hamiltonian method with the potentials $V^{(2)}$ and $V^{(4)}$ yield similar accuracy. In this case, there is no point in taking into account the energy dependence of the effective Hamiltonian, since the corresponding corrections have a higher order of smallness with respect to the residual interaction. In developing methods that take into account higher orders in the residual interaction, the potential $V^{(2)}$ seems to be preferable.

We think that the model system investigated by us represents, to some extent, general properties of atoms with two valence electrons. If this holds true, it is preferable to use the potential $V^{(N-2)}$ for constructing an initial approximation in analyzing higher MBPT orders for other atoms with two valence electrons.

REFERENCES

1. I. Lindgren and J. Morrison, *Atomic Many-Body Theory* (Springer, Berlin, 1982), Springer Ser. Chem. Phys., Vol. 13.

2. M. G. Veselov and L. N. Labzovskiĭ, *Theory of Atom. Structure of Electron Shells* (Nauka, Moscow, 1986).

3. V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Pis'ma Zh. Éksp. Teor. Fiz. **63**, 844 (1996) [JETP Lett. **63**, 882 (1996)].

4. V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **54**, 3948 (1996).

5. M. G. Kozlov and S. G. Porsev, Zh. Éksp. Teor. Fiz. **111**, 838 (1997) [JETP **84**, 461 (1997)].

6. M. G. Kozlov and S. G. Porsev, Opt. Spektrosk. **87**, 384 (1999) [Opt. Spectrosc. **87**, 352 (1999)].

7. M. G. Kozlov, Doctoral Dissertation (St. Petersburg Inst. of Nuclear Physics, Russian Academy of Sciences, 2002); http://www.qchem.pnpi.spb.ru/kozlov.

8. V. A. Dzyuba, M. G. Kozlov, S. G. Porsev, and V. V. Flambaum, Zh. Éksp. Teor. Fiz. **114**, 1636 (1998) [JETP **87**, 885 (1998)].

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