

Correlation Effects for $1s^23l3l'$ and $1s^23l4l'$ States

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Abstract

The Feynman diagram technique was used to calculate the non-relativistic part of the energy of $1s^23l3l'$ and $1s^23l4l'$ states. The Hartree–Fock part of the energy was calculated by the Z -expansion method. The correlation part of the energy was obtained as the difference between these two energies represented in form of $1/Z$ series. The resulting data were compared with theoretical data obtained for the identification of electron spectra ($1s^23l3l' - 1s^22l$ transitions).

1. Introduction

Perturbation theory is now of typical use in quantum calculations for multielectron systems. There are various perturbational procedures, in which some appropriate quantity plays the principal part and other atomic characteristics are to be derived from it. Perturbation theory expansion for that basic quantity is usually obtained employing some technique aimed to the minimization of the perturbation. Many-body Green functions and scattering matrix are likely to be the most popular object to start from, as well as scattering wave functions. Various ionization and recombination processes, radiative transitions between atomic levels and non-radiative rearrangements in atoms or ions can be described in terms of either of these quantities, though they are convenient for different calculations. In these lines, the S-matrix approach has its evident advantages. The field formulation of the theory admits large uniformity in describing systems with any number of electrons involving any sort of interaction between them. All expressions can easily be made gauge invariant, relativistic effects are introduced in a straightforward way. The theory can be adapted to describe any kind of atomic processes and permits a number of simplifications. The S-matrix is immediately related to transition amplitudes, which makes it convenient in multichannel scattering calculations. Finally, R-matrices and Green functions can be simply expressed through S-matrices.

Since early 60-s S-matrix perturbation theory in secondary quantization representation is widely used in atomic calculations. The energies of the ground and some lowest excited states of a large number of ions have been calculated up to the third-order contributions (see, for example [1–3]). The expansion in powers of $1/Z$ have been constructed for the corrections due to Coulomb as well as to the relativistic Breit interactions between atomic levels [4, 5]. Explicit Z -dependence implies that the energy of a stationary level is calculated only once for the whole isoelectronic sequence.

The same procedure was used for an autoionizing level [6]. In the above-mentioned papers the $1s^k2s^m2p^n$ ($0 \leq k \leq 2$, $0 \leq m \leq 2$, $0 \leq n \leq 6$) states were considered.

Some years ago were obtained experimental data for more excited states as $3l3l'$ and $1s^23l3l'$ [7–12]. The spectra of $1s^23l3l'$ states were the most interesting to study since the ejected electron spectra for these states consist of rare lines which can be well resolved.

Theoretical data for these states were calculated by Vaeck and Hansen [13], Chen and Lin [14], Bauchau *et al.* [15], van der Hart and Hansen [16]. The energy of the single and triplet $1s^23l3l'$ states were calculated by using Cowan's code in the paper [13]. All data were shifted to about 1 eV for $C^{2+} - Ne^{6+}$ ions. It was explained by these authors that data computed by the Cowan program are obtained using the Hartree–Fock approximation, without taking into account the correlation effects which are very important for $1s^23l3l'$ states. The estimation of these effects (1 eV for ions with $0 \leq Z \leq 10$) was also given. The same data obtained by the conventional configuration–interaction method were presented by Chen and Lin [14]. One fitting parameter for the model potential which was obtained from $1s^2nl$ data was used. A model potential was used by Bauchau *et al.* [15] but the fitting parameter was given in the analytical form without taking into account any experimental data. A very large number of eigenfunctions (3s–8s, 3p–8p, 3d–8d, 4f–8f, 5g–8g, 6h–8h, 7i–8i) was involved in this configuration–interaction method. The data for the single and triplet $1s^23lnl'$ states with $3 \leq n \leq 7$ were obtained in this paper. The energies of $1s^23lnl'$ states with $3 \leq n \leq 5$ single terms were calculated by van der Hart and Hansen [16] by using a B-spline basis set. This basis set consists of two-electron functions, which are products of the one-electron functions which are B-spline solution of the O^{5+} system.

In the present paper we used the perturbation theory method in order to make *ab initio* calculations of energies of $1s^23l3l'$ and $1s^23l4l'$ states and to obtain a direct contribution of the correlation part of the energy. The application of the perturbation theory method by using the S-matrix approach has some serious limitations. Computational difficulties do in most cases not allow the evaluation of higher than third order, or even than second order terms. The correct treatment of the singularities arising at calculating energies of autoionizing states requires partial summation of the perturbation series [6, 17], which lead to loosening the explicitness of the Z -dependence characteristics of non-stationary levels. Relativistic effects are accounted for rather incompletely and not always consistently up to now [4, 5, 18]. Together with these difficulties the clear realization of the basic principle of the approach is required. But their

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formulation is scattered and incomplete. Most of the references concerning the original formulation of the theory are hardly available [1, 17]. Years of practical use have resulted in many additions, corrections and recomprehension of some sentences [19–23]. So the present paper is intended to start a general review of the S-matrix approach, a brief summary of its significant features and the most illustrative results (1s²3l3l' and 1s²3l4l' states). Such a review should cover both non-relativistic and relativistic calculations of energies, radiative and non-radiative transition probabilities. The first step of this program is the description of non-relativistic energy calculations. It is mostly based on Ref. [1, 17] with regard to some other papers [19–23]. The formulae are revised and rewritten in a more concise form, the computer programs are written by using a new algorithm, the old numerical results are checked and corrected in some cases and new results are presented in this paper.

2. Diagram perturbation theory

We could not consider the problem in any detail. A reasonable compromise seems to be achieved when our account deals with the practical application of the formalism, just noting the basic facts constituting its theoretical foundations. That is why we have dropped any details concerning the development of the adiabatic S-matrix formalism and the theory of the secular operator [1, 17, 19].

In the adiabatic formalism of Gell–Mann and Low [24] the energy shift of a level due to interelectronic interaction is given by

$$\Delta E = \lim_{\gamma \rightarrow \infty} i\gamma g \frac{\partial}{\partial g} \log \langle S_\gamma(0, -\infty) \rangle |_{g=1}. \tag{1}$$

Using the expansion

$$S_\gamma(0, -\infty) = 1 + gS_\gamma^{(1)}(0, -\infty) + g^2S_\gamma^{(2)}(0, -\infty) + \dots \tag{2}$$

one can derive from eq. (1)

$$\begin{aligned} \Delta E = \lim_{\gamma \rightarrow 0} \{ & \langle S_\gamma^{(1)}(0, -\infty) \rangle \\ & + [2\langle S_\gamma^{(2)}(0, -\infty) \rangle - \langle S_\gamma^{(1)}(0, -\infty) \rangle^2] \\ & + 3\langle S_\gamma^{(3)}(0, -\infty) \rangle - 3\langle S_\gamma^{(2)}(0, -\infty) \rangle \\ & \times \langle S_\gamma^{(1)}(0, -\infty) \rangle + \langle S_\gamma^{(1)}(0, -\infty) \rangle^3 + \dots \}. \end{aligned} \tag{3}$$

The *n*-order term of the S-matrix, eq. (2), reads

$$\begin{aligned} S_\gamma^{(n)}(0, -\infty) = \frac{1}{n!} \int_{-\infty}^0 dt_1 e^{\gamma t_1} \dots \int_{-\infty}^0 dt_n e^{\gamma t_n} \\ \times T\{H_{\text{int}}(t_1) \dots H_{\text{int}}(t_n)\}. \end{aligned} \tag{4}$$

Now let relativistic interactions be small corrections, so that their effect could be evaluated on a non-relativistic basis. In the case of pure Coulomb interaction

$$\begin{aligned} H_{\text{int}}(t) = \frac{1}{2} \sum_{j_1 j_2 j_3 j_4} V_{j_1 j_2; j_4 j_3} \\ \times a_{j_1}^+(t+0) a_{j_2}^+(t+0) a_{j_4}(t) a_{j_3}(t) \end{aligned} \tag{5}$$

where

$$\begin{aligned} V_{j_1 j_2; j_4 j_3} = \sum_{\delta_1 \delta_2} \int d\mathbf{r}_1 r_2 \frac{1}{r_{12}} \psi_{j_1}^*(\mathbf{r}_1, \sigma_1) \\ \times \psi_{j_2}^*(\mathbf{r}_2, \sigma_2) \psi_{j_4}(\mathbf{r}_2, \sigma_2) \psi_{j_3}(\mathbf{r}_1, \sigma_1) \end{aligned} \tag{6}$$

and $\Psi_j(\mathbf{r}, \sigma) = R_{nl}(r)Y_{lm}(\theta, \varphi)\delta(m_s, \sigma)$ is a hydrogenic function. An interaction Hamiltonian in the form (5) maximally accounts for the symmetries of the corresponding, combination of the creation and annihilation operators a_j^+ and a_j , which greatly simplify further diagrammatization.

Equation (1) assumes averaging the S-matrix over a state with the non-perturbed energy $E^{(0)}$ and is formally valid for degenerated states, though one would have to sum terms not cancelling in each order and the energy shift is obtained using proper linear combinations of the zero order states belonging to the subspace of the degenerate levels. We confine ourselves, in this paper, to the case of *n* electrons in open shells:

$$\Phi_n^Q = \frac{1}{n!} \sum_{\alpha_1 \dots \alpha_n} C_{\alpha_1 \dots \alpha_n}^Q a_{\alpha_1}^+ \dots a_{\alpha_n}^+ \Phi_0 \tag{7}$$

with Φ_0 denoting the state of the core and *Q* means quantum numbers of the atomic system: *L, S, M, M_s*. To provide orthonormality of the wave function (7) the anti-symmetric in all indexes coefficients C^Q must obey

$$\sum_{\alpha_1 \dots \alpha_n} C_{\alpha_1 \dots \alpha_n}^{*Q} \dots C_{\alpha_1 \dots \alpha_n}^{Q'} = n! \delta(Q, Q'). \tag{8}$$

The normal product of operators a_j and a_j^+ is defined so that it would vanish when averaged over the vacuum state Φ_0 . Then it follows from the conventional relation for the time-ordered product

$$T[a_j(t)a_j^+(t')] = \overline{a_j(t)a_j^+(t')} + N[a_j(t)a_j^+(t')] \tag{9}$$

and the anticommutation relations for $a_j(t) = a_j \exp(-iE_j t)$ and $a_j^+(t) = a_j^+ \exp(iE_j t)$ that

$$\begin{aligned} \overline{a_j(t)a_j^+(t')} = \delta(j, j')G_j(t-t') = \langle T a_j(t)a_j^+(t') \rangle \\ = \delta(j, j') \exp(-iE_j[t-t']) \\ \times (1-n_j)\theta(t-t') - n_j\theta(t'-t) \end{aligned} \tag{10}$$

where $n_j = 1$ for closed shells and $n_j = 0$ for open or vacant shells. According to the Wick's theorem [25], the *T*-product of any number of field operators can be expanded into a sum of *N*-products with all possible pairing sets, including the term without any pairings. Then with use of the equation

$$\begin{aligned} \langle \Phi_n^Q | N[a_{j_1} \dots a_{j_m} a_{j_m}^+ \dots a_{j_1}^+] | \Phi_n^{Q'} \rangle \\ = \frac{(-1)^m}{(n-m)!} \sum_{\alpha_1 \dots \alpha_n} \sum_{\alpha'_1 \dots \alpha'_m} C_{\alpha_1 \dots \alpha_n}^{*Q} C_{\alpha'_1 \dots \alpha'_m \alpha_{m+1} \dots \alpha_n}^{Q'} \\ \times \delta(\alpha_1, j'_1) \dots \delta(\alpha_m, j'_m) \delta(\alpha'_1, j_1) \dots \delta(\alpha'_m, j_m) \end{aligned} \tag{11}$$

one can obtain the explicit expressions for the matrix elements $\langle \Phi_n^Q | S_\alpha^N(0, -\infty) | \Phi_n^{Q'} \rangle$ and therefore formulate the rules for their graphic representations.

The diagram as a whole implies the factor

$$\begin{aligned} \frac{(-1)^l}{(n-m)! \Gamma} \sum_{\alpha'_1 \dots \alpha'_m} \sum_{\alpha_1 \dots \alpha_n} C_{\alpha_1 \dots \alpha_n}^{*Q} C_{\alpha'_1 \dots \alpha'_m \alpha_{m+1} \dots \alpha_n}^{Q'} \\ \times \int_{-\infty}^0 dt_1 e^{\gamma t_1} \dots \int_{-\infty}^0 dt_N e^{\gamma t_N} \end{aligned} \tag{12}$$

where *N* is the number of vertices, *m* is the number of incoming (or outgoing) lines, *l* is the number of loops. The symmetry number Γ is the number of topology conserving permutations of lines and vertices, which do not change the view of the diagram. The indexes α' and α correspond to the

incoming and outgoing lines belonging to the same vertex or connected with an electronic line. All indexes at the internal lines should be summed over. Let us notice that the same rules apply for atomic states with n holes in a closed shell, with the only addition that $2m$ -tailed diagrams should be multiplied by a factor of $(-1)^m$.

All Feynman diagrams can be divided into "vacuum" diagrams, diagrams for one and more electrons above the core. Examples of these diagrams are given on Fig. 1. To decrease the number of diagrams (46 diagrams for the second order) we decided to draw a point instead of a vertical line. In these cases we join direct and exchanging parts ($V_{j_1 j_2, j_4 j_3}$ and $V_{j_1 j_2, j_3 j_4}$) of each contribution. This will give 3 first order diagrams (instead of 5) and 10 second order diagrams (instead of 42). These diagrams are shown in Fig. 2 and Fig. 3. All diagram contributions include the radial integral:

$$R_k(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) = \int_0^\infty r_2^2 dr_2 \int_0^\infty dr_1 \delta r_1^2 \frac{r_1^k}{r_1^{k+1}} \times R_{n_1 l_1}(r_1) R_{n_2 l_2}(r_2) R_{n_4 l_4}(r_2) R_{n_3 l_3}(r_1) \quad (13)$$

with radial hydrogen functions $R_n(r)$. It is useful to define some expressions with these radial integrals:

$$P_k(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) = R_k(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) \times \begin{pmatrix} l_1 & l_3 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l_4 & k \\ 0 & 0 & 0 \end{pmatrix} (-1)^{k+(l_1+l_2+l_3+l_4)/2}, \quad (14)$$

$$X(n_1 l_1 n_2 l_2; n_2 l_2 n_1 l_1) = 2R_0(n_1 l_1 n_2 l_2; n_2 l_2 n_1 l_1) - \sum_k P_k(n_1 l_1 n_2 l_2; n_1 l_1 n_2 l_2), \quad (15)$$

$$Y(n_1 l_1; n_3 l_1) = \sum_{n_2 l_2 \in f_0} (2l_2 + 1) X(n_1 l_1 n_2 l_2; n_2 l_2 n_1 l_1) \quad (16)$$

where f_0 includes the core orbitals and sum over g_0 means the sum over excited states. The core is $1s^2$ for the configurations considered here. Sum over $nl \in g_0$ is sum over l and n where n includes sum over discrete and continuous hydro-

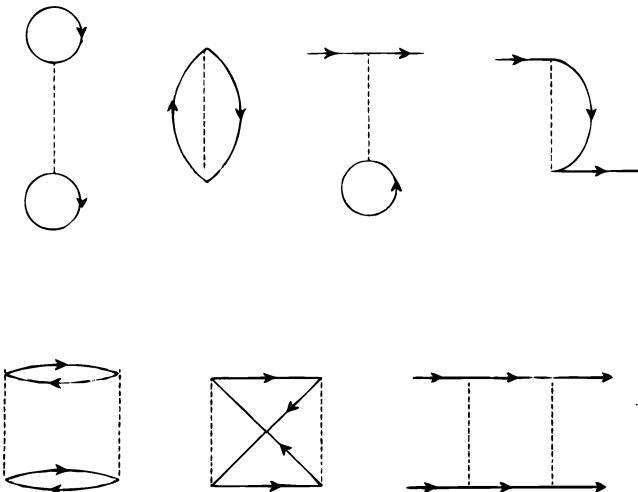


Fig. 1. Direct and exchanging Feynman diagrams.

gen spectra (with core $1s^2$ ($n = 1$) being excluded):

$$\sum_n f(n) = \sum_{n=2}^{\infty} f(n) + \int_0^{\infty} dk f(k). \quad (17)$$

Below we represent contributions from the diagrams given in Fig. 2 and Fig. 3. We divided all diagrams into "vacuum" diagrams (1A, 2A, 2E), diagrams for one valence electron $n_\alpha l_\alpha$ (2B, 2C, 2H-c, 2H-d) and diagrams for two valence electrons $n_1 l_1 n_2 l_2$ (2D, 2F, 2R-c, 2R-d).

2.1. Contribution of "vacuum" diagrams:

$$E(1A) = \sum_{n_1 l_1 \in f_0} (2l_1 + 1) Y(n_1 l_1; n_1 l_1), \quad (18)$$

$$E(2A) = \sum_{n_2 l_2 \in g_0} \sum_{n_4 l_4 \in f_0} (2l_4 + 1) \delta(l_2, l_4) \times Y^2(n_2 l_2; n_4 l_2) \frac{1}{E_{n_2} - E_{n_4}}, \quad (19)$$

$$E(2E) = - \sum_{n_1 l_1 \in g_0} \sum_{n_2 l_2 \in g_0} \sum_{n_3 l_3 \in f_0} \sum_{n_4 l_4 \in f_0} \times \frac{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)(2l_4 + 1)}{E_{n_1} + E_{n_2} + E_{n_3} + E_{n_4}} \times \sum_k \left[\frac{2}{(2k + 1)} P_k^2(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) - \sum_{k'} \begin{Bmatrix} l_1 & l_3 & k \\ l_2 & l_4 & k' \end{Bmatrix} P_k(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) \times P_{k'}(n_1 l_1 n_2 l_2; n_3 l_3 n_4 l_4) \right]. \quad (20)$$

2.2. Contributions of diagrams with one electron $n_\alpha l_\alpha$ above the core:

$$C(n_\alpha l_\alpha) = Y(n_\alpha l_\alpha), \quad (21)$$

$$2B(n_\alpha l_\alpha) = - \sum_{n_2 l_2 \in g_0} \sum_{n_4 l_4 \in f_0} (2l_4 + 1) \delta(l_2, l_4) \frac{1}{E_{n_2} - E_{n_4}} \times Y(n_2 l_2; n_4 l_2) X(n_2 l_4 n_\alpha l_\alpha; n_\alpha l_\alpha n_2 l_2), \quad (22)$$

$$2C(n_\alpha l_\alpha) = - \sum_{n_2 \neq n_\alpha} \frac{1}{E_{n_2} - E_{n_\alpha}} Y^2(n_2 l_\alpha; n_\alpha l_\alpha), \quad (23)$$

$$2H_c(n_\alpha l_\alpha) = - \sum_{n_1 l_1 \in g_0} \sum_{n_2 l_2 \in g_0} \sum_{n_4 l_4 \in f_0} \times \frac{(2l_1 + 1)(2l_2 + 1)(2l_4 + 1)}{E_{n_1} + E_{n_2} - E_{n_\alpha} - E_{n_4}} \times \sum_k \left[\frac{2}{(2k + 1)} P_k^2(n_1 l_1 n_2 l_2; n_4 l_4 n_\alpha l_\alpha) - \sum_{k'} \begin{Bmatrix} l_1 & l_\alpha & k \\ l_2 & l_4 & k' \end{Bmatrix} P_k(n_1 l_1 n_2 l_2; n_4 l_4 n_\alpha l_\alpha) \times P_{k'}(n_1 l_1 n_2 l_2; n_\alpha l_\alpha n_4 l_4) \right]. \quad (24)$$

We can use eq. (24) with g_0 exchanged to f_0 in the sum over $n_1 l_1$, $n_2 l_2$ and f_0 exchanged to g_0 in the sum over $n_4 l_4$ for the contribution of $2H_d(n_\alpha l_\alpha)$ diagram. As a result we obtain

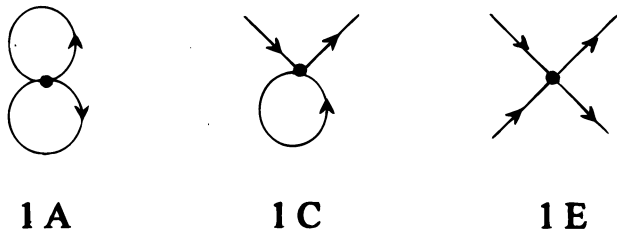


Fig. 2. First order diagrams.

an expression with one sum over all hydrogen spectra and two sums over closed shells which give only one term in the sum over $n_1 l_1$ and $n_2 l_2$ (1s).

2.3. Contribution of diagrams with two electrons $n_1 l_1, n_2 l_2$ above the core.

These contributions must include the LS momentum of this two electron system. In this case we obtain diagonal and non-diagonal elements since only the parity of the two-electron system and LS (in non-relativistic approximation) can be exact quantum numbers. As a result we must consider two-electron states with the same momentum and parity together. For example, there are three states of even parity for the $1s^2 3l 3l'$ 1S configurations: $1s^2 3s^2$, $1s^2 3p^2$ and $1s^2 3d^2$. This is the reason why we must consider diagonal and non-diagonal elements for these diagrams together. Let us note that only two-electron diagrams give contributions for non-diagonal elements. The second point which is necessary to underline is that the contribution of each of any order two-electron diagram (Q) has the same dependence on

LS which can be written in the form:

$$E^Q(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3, LS) = (-1)^{(l_1+l_3-l_2-l_4)/2} \sqrt{(2l_1+1)(2l_2+1)(2l_3+1)(2l_4+1)} \times \sum_k (-1)^k \left[(-1)^L S_k^Q(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) \begin{Bmatrix} l_1 & l_2 & L \\ l_4 & l_3 & k \end{Bmatrix} + (-1)^S S_k^Q(n_1 l_1 n_2 l_2; n_3 l_3 n_4 n_4) \begin{Bmatrix} l_1 & l_2 & L \\ l_3 & l_4 & k \end{Bmatrix} \right] \quad (25)$$

We can now write an expression for $S^Q(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3)$ which does not depend on momentum LS . The expression for the first order diagram ($Q = 1E$) becomes in this case very simple:

$$S_k^{1E}(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) = P_k(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) \quad (26)$$

where P_k is given by eq. (14). We can take into account the symmetry of the initial and final states for diagrams of the second order which means that P_k can be represented by two terms:

$$S_k^Q(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) = \frac{1}{2} T_k^Q(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) + \frac{1}{2} T_k^Q(n_3 l_3 n_4 l_4; n_2 l_2 n_1 l_1). \quad (27)$$

We can now write an expression for T_k^Q where $Q = 2D, 2F, 2R-c$ and $2R-d$.

$$T_k^{2D}(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) = -4 \sum_{n \neq n_1} \frac{1}{E_n - E_{n_1}} Y(n l_1; n_1 l_1) P_k(n l_1 n_2 l_2; n_4 l_4 n_3 l_3), \quad (28)$$

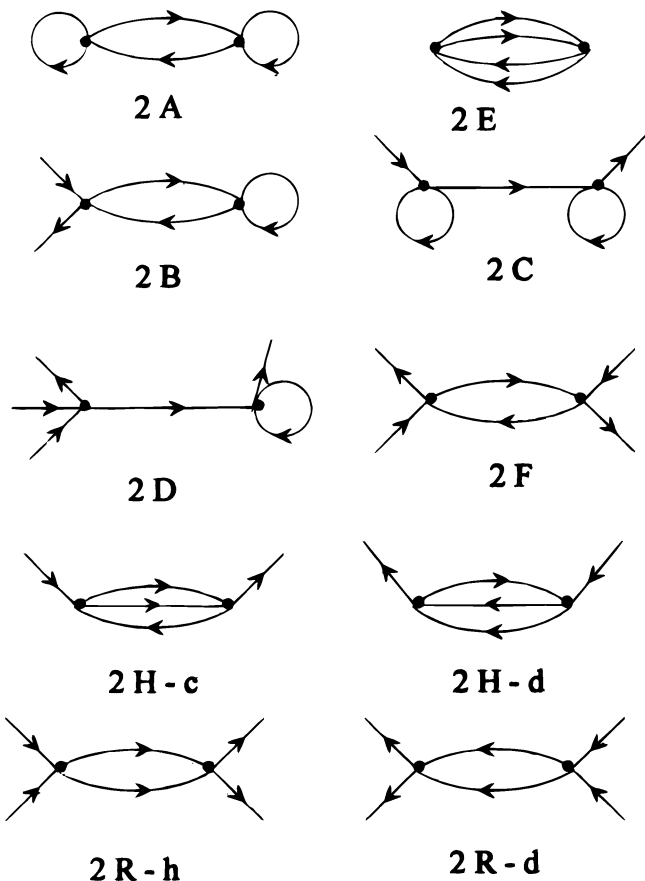


Fig. 3. Second order diagrams.

$$T_k^{2F}(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) = - \sum_{n_5 l_5 \in g_0} \sum_{n_6 l_6 \in f_0} \frac{(2l_5+1)(2l_6+1)}{E_{n_5} + E_{n_3} - E_{n_1} - E_{n_6}} \times \left[\frac{2}{(2k+1)} P_k(n_5 l_5 n_3 l_3; n_1 l_1 n_6 l_6) \times P_k(n_5 l_5 n_2 l_2; n_4 l_4 n_6 l_6) - 2 \sum_{k'} \begin{Bmatrix} l_3 & l_1 & k \\ l_5 & l_6 & k' \end{Bmatrix} \times P_{k'}(n_5 l_5 n_3 l_3; n_6 l_6 n_1 l_1) P_{k'}(n_5 l_5 n_2 l_2; n_4 l_4 n_6 l_6) - (2k+1) \sum_{k'} \sum_{k''} (-1)^{k'-k''+k} \begin{Bmatrix} k'' & k' & k \\ l_4 & l_2 & l_6 \end{Bmatrix} \times \begin{Bmatrix} k'' & k' & k \\ l_1 & l_3 & l_5 \end{Bmatrix} P_{k'}(n_5 l_5 n_4 l_4; n_6 l_6 n_1 l_1) \times P_{k''}(n_5 l_5 n_2 l_2; n_6 l_6 n_3 l_3) \right], \quad (29)$$

$$T_k^{2R-c}(n_1 l_1 n_2 l_2; n_4 l_4 n_3 l_3) = - \sum_{n_5 l_5 \in g_0} \sum_{n_6 l_6 \in g_0} \frac{(2l_5+1)(2l_6+1)(2k+1)}{E_{n_5} + E_{n_6} - E_{n_1} - E_{n_2}} \times \sum_{k'} \sum_{k''} (-1)^{k'-k''+l_1+l_2} \begin{Bmatrix} k'' & k' & k \\ l_2 & l_4 & l_6 \end{Bmatrix} \begin{Bmatrix} k'' & k' & k \\ l_1 & l_3 & l_5 \end{Bmatrix} \times P_{k'}(n_5 l_5 n_5 l_6; n_2 l_2 n_1 l_1) \times P_{k''}(n_5 l_5 n_5 l_6; n_4 l_4 n_3 l_3). \quad (30)$$

Table I. Diagrams for one electron in open shell nl and core $1s^2$

nl	1C	2B	2C	2H-c	2H-d	sum
2 0	0.397805	-0.007744	-0.235553	-0.009669	0.002467	-0.250498
2 1	0.468526	-0.025406	-0.331308	-0.015593	0.001402	-0.370905
3 0	0.193206	-0.002518	-0.141970	-0.002704	0.000628	-0.146566
3 1	0.213120	-0.006205	-0.176810	-0.003837	0.000368	-0.186484
3 2	0.221799	-0.000732	-0.218048	-0.001628	0.000003	-0.220405
4 0	0.112927	-0.001088	-0.090564	-0.001123	0.000251	-0.092524
4 1	0.121188	-0.002476	-0.106294	-0.001535	0.000148	-0.110157
4 2	0.124768	-0.000382	-0.122780	-0.000708	0.000002	-0.123868
4 3	0.124997	-0.000009	-0.124946	-0.000191	0.000000	-0.125146

The expression for the contribution of the 2R-d diagram looks exactly as the one for the 2R-c diagram (see eq. (30)) but g_0 must be exchanged to f_0 in the sum over $n_5 l_5$ and $n_6 l_6$ indexes. There will be only one term in this sum in the case which is considered here ($1s^2$ core, so $n_5 = n_6 = 1$, $l_5, l_6 = 0$). The contributions of these diagrams were computed for $1s^23l3l'$ states and the results of the calculations are given in Tables I and II.

3. Numerical calculation of diagram contributions for $1s^23l3l'$ and $1s^23l4l'$ states

Table I lists the data for the contributions of the diagrams with one electron outside the $1s^2$ core. We included the results for $1s^22l$ states also since the data for these states are necessary for an identification of electron spectra. The last column of Table I, "sum", gives the contribution of the second order diagrams. Table II lists the data for contributions of diagrams with two electrons $3l, 3l'$ and $3l, 4l'$ outside the $1s^2$ core. We included also the results for $2l, 2l'$ electrons outside the $1s^2$ core. Both diagonal and non-diagonal elements were calculated. Contributions of "vacuum" diagrams for $1s^2$ were given by many authors and we can repeat their result (see for example, Ivanova and Safronova [19]):

$$E(1A) = 0.625, \quad E(2A) = -0.111003, \quad E(2E) = -0.046662. \quad (31)$$

The sums of these diagrams are given in Table III. Following our dividing system to core and electron outside the core we represent the energy of $1s^2nl n'l'$ in this form:

$$\begin{aligned} E(1s^2n_1l_1n_2l_2 - 1s^2n_1l_1n_2l_2, LS) \\ = E(1s^2) + E(n_1l_1n_2l_2, LS), \\ E(1s^2n_1l_1n_2l_2 - 1s^2n_3l_3n_4l_4; LS) \\ = E(n_1l_1n_2l_2 - n_3l_3n_4l_4; LS). \end{aligned} \quad (32)$$

As we said before "vacuum" diagrams and diagrams with one electron outside the core do not contribute to non-diagonal matrix elements. We did not write the same designations twice for diagonal elements (see Table III). As a result Z -expansion for diagonal and non-diagonal elements can be presented in the following form ($E_3(1s^2)$ was taken from [18]):

$$\begin{aligned} E(n_1l_1n_2l_2, LS) &= -Z^2 \left(\frac{1}{2n_1^2} + \frac{1}{2n_2^2} \right) + E_1Z + E_2, \\ E(1s^2) &= -Z^2 + 0.625Z - 0.157665 + 0.00869/Z, \\ E(n_1l_1n_2l_2 - n_3l_3n_4l_4; LS) &= E_1Z + E_2. \end{aligned} \quad (33)$$

According to the perturbation theory for degenerate states

(Safronova and Senashenko [18]) contributions of each order can be recalculated by using eigenvectors obtained after diagonalization of the first order matrix. It is simple to explain. Diagonalization of the first order matrix removes the degeneracy of the states and these eigenvectors play the role of zero order functions, so we can recalculate each order with these functions since each order is a perturbation of zero order. We made such a diagonalization and the recalculation of the second order. The results for $1s^23l3l'$ and $1s^23l4l'$ states are given in Table IV.

We can use these data for the comparison with other theoretical data and for the discussion of experimental data given by electron spectra.

For ejected-electron spectra we can calculate the energy counted from the energies of $1s^22l$ states. We represent these energies in the same form as the one for $1s^23l3l'$ states:

$$E(1s^22l, ^2l) = E(1s^2) + E(2l, ^2l) \quad (34)$$

where

$$E(2s, ^2S) = -\frac{Z^2}{8} + 0.397805Z - 0.250498 - 0.037/Z, \quad (35)$$

$$E(2p, ^2P) = -\frac{Z^2}{8} + 0.468526Z - 0.370905 - 0.067/Z. \quad (36)$$

We should mention that E_3 coefficients were calculated numerically for two-electron systems only. The values of E_3 for three-electron systems were estimated by comparison with experimental data (see for detail Safronova & Senashenko [18]). These coefficients were not calculated for four-electron systems.

4. Discussion of results

By using the Z -expansion formula for binding energy:

$$\begin{aligned} E(1s^23l3l', LS) - E(1s^2) &= -Z^2/9 + E_1Z + E_2, \\ E(1s^23l4l', LS) - E(1s^2) &= -25Z^2/288 + E_1Z + E_2 \end{aligned} \quad (37)$$

with coefficients E_1 and E_2 given by Table IV we can obtain data for this energy at least for ions with $7 \leq Z \leq 10$ since relativistic corrections and third order diagram's contribution are small for these ions. Tables V and VI give these data for O^{4+} . We compare our results with data given in papers [13–16] for $O^{4+}(1s^23l3l')$ and with data from [15] for $O^{4+}(1s^23l4l')$. Let us discuss data given by Vaeck and Hansen [13] more in detail. These data were obtained in the Hartree–Fock approximation and shifted with 1.2 eV (0.044 a.u.) to account for correlation effects. By perturbation theory it is possible to present the energy obtained in the Hartree–Fock approximation (E^{HF}) in a form of a series

Table II *Diagrams for two electrons in open shell n_1l_1, n_2l_2 with core $1s^2$*

$n_1l_1n_2l_2$	$n_3l_3n_4l_4$	LS	1E	2D	2F	2R-c	2R-d
2020	2020	0 0	0.150390635	-0.187261	0.001861	-0.038107	-0.000642
2021	2021	1 0	0.191406250	-0.245530	-0.004968	-0.096307	
2021	2021	1 1	0.132812500	-0.206857	0.004103	-0.029433	
2121	2121	0 0	0.216796875	-0.366026	0.003450	-0.116373	-0.001166
2121	2121	1 1	0.164062500	-0.273731	-0.003126	-0.039386	
2121	2121	2 0	0.185156250	-0.310649	-0.001078	-0.087334	
2020	2121	0 0	-0.050743676	0.033491	0.006331	-0.029813	0.000865
3030	3030	0 0	0.0664062500	-0.099281	0.000118	-0.018074	-0.000037
3031	3031	1 0	0.0828993056	-0.128984	-0.000403	-0.041466	
3031	3031	1 1	0.0546875000	-0.095956	0.000323	-0.008440	
3032	3032	2 0	0.0776909722	-0.122837	-0.000026	-0.043000	
3032	3032	2 1	0.0685763889	-0.118773	-0.000003	-0.029027	
3131	3131	0 0	0.0862630208	-0.157284	0.000117	-0.046933	-0.000069
3131	3131	1 1	0.0646701389	-0.117714	-0.000165	-0.012561	
3131	3131	2 0	0.0733072917	-0.133542	-0.000099	-0.032719	
3132	3132	1 0	0.0926215278	-0.171508	0.000034	-0.066511	
3132	3132	1 1	0.0756944444	-0.144547	0.000020	-0.025410	
3132	3132	2 0	0.0649305556	-0.124857	-0.000016	-0.014289	
3132	3132	2 1	0.0744791667	-0.138984	-0.000051	-0.022283	
3132	3132	3 0	0.0929625496	-0.169983	-0.000008	-0.065753	
3132	3132	3 1	0.0650297619	-0.127425	0.000055	-0.019894	
3232	3232	0 0	0.1074869792	-0.196773	-0.000012	-0.050836	2.2-7
3232	3232	1 1	0.0868923611	-0.183840	-0.000018	-0.042716	
3232	3232	2 0	0.0856832837	-0.165363	0.000005	-0.029959	
3232	3232	3 1	0.0780257937	-0.156125	0.000008	-0.023605	
3232	3232	4 0	0.0898210152	-0.178297	-0.000006	-0.050410	
3030	3131	0 0	-0.0244321403	0.028603	0.000550	0.020163	0.000051
3030	3232	0 0	0.0101904140	-0.004544	-0.000008	-0.009482	0.000004
3032	3131	2 0	0.0186050653	-0.023950	-0.000123	-0.026908	
3032	3232	2 0	-0.0082359150	0.001663	-0.000009	-0.016454	
3131	3232	0 0	-0.0256349809	0.039782	0.000021	0.025348	0.000005
3131	3232	1 1	-0.0106756718	0.015794	0.000053	0.003475	
3131	3232	2 0	-0.0117917219	0.018073	0.000017	0.015005	
3031	3132	1 0	-0.0242628904	0.028223	0.000144	0.033962	
3031	3132	1 1	-0.0097051562	0.015504	0.000107	0.004582	
3040	3040	0 0	0.0486804	-0.078015	0.000094	-0.018094	-0.021627
3040	3040	0 1	0.0411308	-0.065305	0.000000	-0.008455	
3041	3041	1 0	0.0479345	-0.085567	-0.000074	-0.024342	
3041	3041	1 1	0.0450885	-0.079911	0.000046	-0.011018	
3042	3042	2 0	0.0515064	-0.099897	-0.000015	-0.030677	
3042	3042	2 1	0.0482339	-0.085712	0.000001	-0.016204	
3043	3043	3 0	0.0589976	-0.109291	0.000000	-0.042235	
3043	3043	3 1	0.0529136	-0.096086	0.000000	-0.022746	
3140	3140	1 0	0.0473538	-0.078947	-0.000114	-0.020408	
3140	3140	1 1	0.0440375	-0.073274	0.000074	-0.011532	
3141	3141	0 0	0.0606227	-0.112968	0.000082	-0.047903	-0.000410
3141	3141	0 1	0.0475237	-0.088791	0.000002	-0.016067	
3141	3141	1 0	0.0408356	-0.075941	0.000000	-0.007334	
3141	3141	1 1	0.0475699	-0.088228	-0.000131	-0.013652	
3141	3141	2 0	0.0527910	-0.098124	-0.000084	-0.029598	
3141	3141	2 1	0.0435109	-0.081081	0.000001	-0.011608	
3142	3142	1 0	0.0564604	-0.111703	0.000017	-0.041830	
3142	3142	1 1	0.0527143	-0.102065	0.000004	-0.021800	
3142	3142	2 0	0.0463802	-0.088924	-0.000011	-0.010968	
3142	3142	2 1	0.0479199	-0.093697	-0.000024	-0.016436	
3142	3142	3 0	0.0545100	-0.108681	0.000000	-0.040708	
3142	3142	3 1	0.0493524	-0.093963	0.000021	-0.016448	
3143	3143	2 0	0.0652550	-0.121561	0.000003	-0.038889	
3143	3143	2 1	0.0579002	-0.119752	0.000004	-0.037597	
3143	3143	3 0	0.0502040	-0.095556	0.000000	-0.012900	
3143	3143	3 1	0.0528447	-0.104601	-0.000001	-0.022594	
3143	3143	4 0	0.0654607	-0.128888	0.000002	-0.064769	
3143	3143	4 1	0.0524817	-0.101755	0.000005	-0.022754	
3240	3240	2 0	0.0480012	-0.080684	-0.000010	-0.021518	
3240	3240	2 1	0.0463318	-0.078617	-0.000001	-0.015834	
3241	3241	1 0	0.0536396	-0.101257	0.000011	-0.034543	
3241	3241	1 1	0.0505560	-0.095741	0.000005	-0.021449	
3241	3241	2 0	0.0456384	-0.086814	-0.000010	-0.012678	
3241	3241	2 1	0.0466655	-0.088664	-0.000014	-0.014440	
3241	3241	3 0	0.0518825	-0.098081	0.000004	-0.028679	

Table II *continued*

$n_1l_1n_2l_2$	$n_3l_3n_4l_4$	LS	1E	2D	2F	2R-c	2R-d
3241	3241	3 1	0.0480660	-0.091232	0.000011	-0.018343	
3242	3242	0 0	0.0701015	-0.130563	-0.000005	-0.052379	0.000007
3242	3242	0 1	0.0521779	-0.101800	-0.000003	-0.019996	
3242	3242	1 0	0.0489259	-0.098713	-0.000002	-0.017646	
3242	3242	1 1	0.0592084	-0.123397	-0.000014	-0.041558	
3242	3242	2 0	0.0582336	-0.113159	0.000003	-0.027171	
3242	3242	2 1	0.0476965	-0.094302	0.000000	-0.014267	
3242	3242	3 0	0.0462277	-0.092097	0.000001	-0.013012	
3242	3242	3 1	0.0540995	-0.108041	0.000003	-0.021832	
3242	3242	4 0	0.0606178	-0.120326	-0.000004	-0.039726	
3242	3242	4 1	0.0489556	-0.097389	-0.000001	-0.019870	
3243	3243	1 0	0.0709863	-0.134241	-0.000013	-0.036523	
3243	3243	1 1	0.0622041	-0.126298	0.000005	-0.027097	
3243	3243	2 0	0.0555388	-0.112721	0.000026	-0.019625	
3243	3243	2 1	0.0618631	-0.130403	-0.000029	-0.039092	
3243	3243	3 0	0.0640398	-0.124362	-0.000053	-0.035039	
3243	3243	3 1	0.0523184	-0.102313	0.000056	-0.013843	
3243	3243	4 0	0.0496807	-0.099858	0.000093	-0.012899	
3243	3243	4 1	0.0609501	-0.122947	-0.000089	-0.035874	
3243	3243	5 0	0.0736151	-0.147216	-0.000138	-0.091934	
3243	3243	5 1	0.0501193	-0.099778	0.000135	-0.015392	
3040	3141	0 0	0.0157511	0.017069	0.000332	0.019609	0.000032
3040	3141	0 1	-0.0112582	0.017221	0.000133	0.007444	
3141	3042	2 0	0.0089803	-0.016760	-0.000004	-0.019861	
3141	3042	2 1	0.0066069	-0.008355	-0.000074	-0.004086	
3143	3240	2 0	0.0032725	-0.014324	-0.000116	-0.000961	
3143	3240	2 1	-0.0026220	0.008578	0.000117	0.002060	
3143	3242	2 0	0.0041759	-0.010400	-0.000008	-0.014904	
3143	3242	2 1	0.0010353	-0.000768	0.000011	-0.000997	
3143	3242	3 0	0.0011415	-0.000531	0.000026	0.001012	
3143	3242	3 1	0.0040356	-0.009467	-0.000028	-0.007900	
3143	3242	4 0	0.0090306	-0.021704	-0.000043	-0.031663	
3143	3242	4 1	0.0024289	-0.001377	0.000044	-0.001293	
3240	3242	2 0	-0.0025397	-0.003073	-0.000005	0.006056	
3240	3242	2 1	-0.0014965	-0.000055	-0.000001	0.002352	
3041	3140	1 0	0.0118012	-0.016509	-0.000169	-0.017163	
3041	3140	1 1	0.0037926	-0.003288	-0.000134	-0.002509	
3041	3142	1 0	-0.0107543	0.016918	0.000067	0.018602	
3041	3142	1 1	-0.0093686	0.015506	0.000049	0.006799	
3142	3140	1 0	-0.0034819	-0.003280	0.000038	0.013428	
3142	3140	1 1	-0.0026218	0.004285	0.000057	0.002243	
3043	3241	3 0	0.0004666	-0.007152	0.000074	-0.009302	
3043	3241	3 1	0.0008943	0.004096	-0.000075	0.001413	
3043	3243	3 0	-0.0079431	0.012161	-0.000001	0.020926	
3043	3243	3 1	-0.0022391	0.001750	-0.000001	0.004096	
3241	3243	1 0	0.0044747	-0.010005	-0.000036	-0.004256	
3241	3243	1 1	-0.0033456	0.009083	0.000032	0.003914	
3241	3243	2 0	-0.0019899	0.003275	0.000024	0.000662	
3241	3243	2 1	0.0017328	-0.005534	-0.000026	-0.001537	
3241	3243	3 0	0.0022515	-0.006581	-0.000021	-0.002655	
3241	3243	3 1	-0.0019286	0.003623	0.000016	0.001434	
3040	3242	0 0	0.0045605	0.003455	-0.000008	-0.008006	-0.000038
3040	3242	0 1	0.0038107	-0.004035	0.000001	-0.004476	
3042	3143	2 0	-0.0091031	0.022207	0.000003	0.012838	
3042	3143	2 1	-0.0063435	0.012557	0.000002	0.004309	
3042	3240	2 0	0.0057624	-0.005877	-0.000012	-0.014457	
3042	3240	2 1	-0.0020187	0.005618	0.000001	0.002697	
3141	3242	0 0	-0.0138917	0.018771	-0.000015	0.024248	0.000005
3141	3242	0 1	-0.0105361	0.018263	0.000035	0.010214	
3141	3242	1 0	-0.0063902	0.010830	0.000029	0.003286	
3141	3242	1 1	-0.0065964	0.008758	0.000019	0.003274	
3141	3242	2 0	-0.0066275	0.008910	-0.000004	0.010850	
3141	3242	2 1	-0.0054327	0.009345	0.000020	0.004887	
3042	3242	2 0	-0.0037942	0.004458	-0.000007	-0.008006	
3042	3242	2 1	-0.0024169	0.003163	0.000002	-0.004476	
3141	3143	2 0	-0.0006369	0.000086	-0.000004	0.005036	
3141	3143	2 1	-0.0014976	0.002139	0.000000	0.001827	
3141	3240	2 0	0.0084792	-0.011102	-0.000050	-0.014473	
3141	3240	2 1	0.0054553	-0.005916	-0.000026	-0.005124	

Table II *continued*

$n_1 l_1 n_2 l_2$	$n_3 l_3 n_4 l_4$	LS	1E	2D	2F	2R-c	2R-d
3041	3241	1 0	-0.0048060	0.004345	0.000019	0.013806	
3041	3241	1 1	-0.0018973	0.003563	-0.000007	0.003059	
3041	3243	1 0	0.0003943	-0.001755	-0.000001	-0.000074	
3041	3243	1 1	0.0016846	-0.002912	0.000000	-0.001127	
3043	3142	3 0	0.0089407	-0.024331	-0.000004	-0.021115	
3043	3142	3 1	0.0041141	-0.005050	0.000000	-0.003195	
3140	3241	1 0	-0.0099328	0.011391	0.000061	0.014306	
3140	3241	1 1	-0.0080566	0.010579	0.000047	0.006734	
3140	3243	1 0	-0.0023586	0.010027	-0.000001	0.001153	
3140	3243	1 1	0.0015188	-0.002610	0.000001	-0.001407	
3142	3241	1 0	0.0087584	-0.014842	0.000012	-0.025560	
3142	3241	1 1	-0.0019517	0.004478	-0.000006	0.002831	
3142	3241	2 0	-0.0005055	0.002022	0.000008	0.001350	
3142	3241	2 1	0.0063133	-0.010782	-0.000023	-0.007193	
3142	3241	3 0	0.0120336	-0.019649	-0.000006	-0.022972	
3142	3241	3 1	0.0027132	-0.002657	-0.000023	-0.002070	
3142	3243	1 0	-0.0080607	0.015735	-0.000002	0.005187	
3142	3243	1 1	-0.0069729	0.014984	0.000002	0.005827	
3142	3243	2 0	-0.0042718	0.007445	0.000003	0.001255	
3142	3243	2 1	-0.0043912	0.009285	0.000000	0.001274	
3142	3243	3 0	-0.0043738	0.009415	-0.000003	0.006333	
3142	3243	3 1	-0.0036620	0.007005	0.000003	0.003191	

of $1/Z$ (see [18, 19])

$$E^{\text{HF}}(1s^2 3l3l', LS) = E^{\text{HF}}(1s^2) + E^{\text{HF}}(3l3l', LS) \quad (38)$$

where

Table III. *Z-expansion for diagonal and non-diagonal elements for $1s^2 3l3l'$ states*

$$E(1s^2 3l_1 3l_2 - 1s^2 3l_1 3l_2, LS) = E(1s^2) + E(3l_1 3l_2, LS),$$

$$E(1s^2 3l_1 3l_2 - 1s^2 3l_3 3l_4; LS) = E(3l_1 3l_2 - 3l_3 3l_4; LS),$$

$$E(3l_1 3l_2, LS) = -\frac{Z^2}{9} + E_1 Z + E_2,$$

$$E^{\text{HF}}(3l_1 3l_2, LS) = -\frac{Z^2}{9} + E_1 Z + E_2^{\text{HF}}, \quad E(3l_1 3l_2 - 3l_3 3l_4; LS) = E_1 Z + E_2.$$

$n_1 l_1 n_2 l_2 - n_3 l_3 n_4 l_4$	LS	E_1	E_2	E_2^{HF}	E_2^{CORR}
$3s^2$	1S	0.452818	-0.410406	-0.396532	-0.013874
$3s3p$	1P	0.489225	-0.503903	-0.469569	-0.034334
$3s3p$	3P	0.461013	-0.437123	-0.430276	-0.006847
$3s3d$	1D	0.492696	-0.532834	-0.498967	-0.033867
$3s3d$	3D	0.483581	-0.506474	-0.492842	-0.013632
$3p^2$	1S	0.512503	-0.577137	-0.539403	-0.037734
$3p^2$	3P	0.490910	-0.503408	-0.493192	-0.010216
$3p^2$	1D	0.499547	-0.539328	-0.511445	-0.027883
$3p3d$	1P	0.527540	-0.644874	-0.582638	-0.062236
$3p3d$	3P	0.510613	-0.576826	-0.550829	-0.021997
$3p3d$	1D	0.499850	-0.546051	-0.546839	0.000788
$3p3d$	3D	0.509398	-0.568207	-0.562110	-0.006097
$3p3d$	1F	0.527881	-0.642633	-0.587044	-0.055589
$3p3d$	3F	0.499949	-0.554153	-0.538890	-0.015263
$3d^2$	1S	0.551085	-0.688431	-0.682941	-0.005490
$3d^2$	3P	0.530490	-0.667384	-0.629008	-0.038376
$3d^2$	1D	0.529281	-0.636127	-0.626225	-0.009902
$3d^2$	3F	0.521624	-0.620532	-0.607284	-0.013248
$3d^2$	1G	0.533419	-0.669523	-0.636561	-0.032926
$3s^2$	$3p^2$	1S	-0.0244321	0.049367	
$3s^2$	$3d^2$	1S	0.0101904	-0.014034	
$3s3d$	$3p^2$	1D	0.0186051	-0.050981	
$3s3d$	$3d^2$	1D	-0.0082359	0.018108	
$3p^2$	$3d^2$	1S	-0.0256350	0.065156	
$3p^2$	$3d^2$	3P	-0.0106757	0.019322	
$3p^2$	$3d^2$	1D	-0.0117917	0.033095	
$3s3p$	$3p3d$	1P	-0.0242629	0.062329	
$3s3p$	$3p3d$	3P	-0.0097052	0.020193	

Table IV. Z -expansion for energy of Be-like systems
$$E(1s^2n_1l_1n_2l_2, LS) = E(1s^2) + E(n_1l_1n_2l_2, LS), \quad 1l_1n_2l_2, LS) = -Z^2\left(\frac{1}{2n_1^2} + \frac{1}{2n_2^2}\right) + E_1Z + E_2.$$

$n_1l_1n_2l_2$	LS	E_1	E_2	$n_1l_1n_2l_2$	LS	E_1	E_2
2s ²	¹ S	0.934274	-0.719751	3p4d	¹ F	0.383248	-0.421123
2s2p	¹ P	1.057737	-0.968209	3d4s	³ D	0.383016	-0.409605
2s2p	³ P	0.999143	-0.853591	3p4d	¹ D	0.383146	-0.409171
2p ²	¹ S	1.165576	-1.227321	3p4d	¹ P	0.385268	-0.421082
2p ²	³ P	1.101114	-1.058053	3p4d	³ F	0.385930	-0.421584
2p ²	¹ D	1.122208	-1.140871	3p4f	³ G	0.389603	-0.439765
3s ²	¹ S	0.444083	-0.398090	3d4p	¹ D	0.388562	-0.430559
3s3p	¹ P	0.477468	-0.481791	3p4p	¹ D	0.392695	-0.457977
3s3p	³ P	0.459182	-0.434568	3p4f	¹ F	0.388046	-0.421917
3s3d	¹ D	0.477172	-0.484951	3p4p	¹ S	0.391787	-0.447821
3s3d	³ D	0.483581	-0.506474	3p4f	³ F	0.389503	-0.431785
3p ²	¹ S	0.504810	-0.557460	3d4p	³ F	0.391248	-0.437468
3p ²	³ P	0.488214	-0.504810	3d4d	³ D	0.394634	-0.458978
3p ²	¹ D	0.506171	-0.567689	3p4d	³ P	0.390479	-0.429421
3p3d	¹ P	0.539297	-0.666987	3d4d	¹ F	0.393069	-0.447550
3p3d	³ P	0.512444	-0.579381	3d4p	³ D	0.394237	-0.447539
3p3d	¹ D	0.499850	-0.546051	3d4f	¹ G	0.396477	-0.458215
3p3d	³ D	0.509398	-0.568207	3d4d	³ G	0.396519	-0.457902
3p3d	¹ F	0.527881	-0.642633	3d4f	³ H	0.396915	-0.460586
3p3d	³ F	0.499949	-0.554153	3d4d	¹ P	0.397333	-0.461975
3d ²	¹ S	0.567514	-0.720424	3d4p	³ P	0.396077	-0.451502
3d ²	³ P	0.533186	-0.666728	3d4f	¹ H	0.420411	-0.584839
3d ²	¹ D	0.538181	-0.655649	3d4d	¹ G	0.407398	-0.528294
3d ²	³ F	0.521624	-0.620532	3p4f	³ D	0.400099	-0.468529
3d ²	¹ G	0.533419	-0.669523	3d4d	³ F	0.402126	-0.481184
3s4s	³ S	0.343912	-0.306499	3d4f	¹ F	0.414681	-0.529765
3s4s	¹ S	0.349367	-0.344585	3d4p	¹ F	0.405918	-0.503375
3s4p	¹ P	0.353334	-0.335017	3p4f	¹ G	0.403365	-0.481320
3s4p	³ P	0.356221	-0.341183	3d4f	³ F	0.401281	-0.465592
3s4d	³ D	0.361412	-0.360280	3d4d	³ P	0.407475	-0.508180
3s4d	¹ D	0.363415	-0.369362	3d4f	¹ D	0.403520	-0.478460
3s4f	³ F	0.370064	-0.388418	3d4f	³ G	0.407746	-0.504461
3s4f	¹ F	0.371458	-0.391039	3d4f	³ D	0.409491	-0.512359
3p4s	³ P	0.367426	-0.360590	3p4f	¹ D	0.402659	-0.464063
3p4s	¹ P	0.374325	-0.390330	3d4p	¹ P	0.410932	-0.520821
3p4p	¹ P	0.373304	-0.378575	3d4d	³ S	0.405047	-0.477456
3d4s	¹ D	0.375747	-0.391003	3d4d	¹ D	0.412962	-0.514883
3p4p	³ D	0.376205	-0.393484	3d4f	³ P	0.412510	-0.507550
3p4d	³ D	0.380393	-0.409366	3d4f	¹ P	0.420626	-0.524481
3p4p	³ S	0.378881	-0.396464	3d4d	¹ S	0.425259	-0.549379
3p4p	³ P	0.380178	-0.399714				

$$E^{\text{HF}}(1s^2) = -Z^2 + 0.625Z - 0.111003 - 0.00106/Z,$$

$$E^{\text{HF}}(3l3l', LS) = -\frac{Z^2}{9} + E_1Z + E_2^{\text{HF}}. \quad (39)$$

We do not discuss calculations of E_2^{HF} further since the space of the paper is limited. Data for E_2^{HF} were calculated (see for detail [18, 19] and given in Table III. The contribution of correlation effects to the energy (E^{CORR}) can be defined as the difference between the total energy E and E^{HF} . As we can see from the comparison of eqs (33) and eqs 38, 39) the first contribution to E^{CORR} gives the second order term of perturbation theory:

$$E^{\text{CORR}}(1s^2) = -0.046662 + 0.00975/Z,$$

$$E^{\text{CORR}}(3l3l', LS) = E_2^{\text{CORR}}. \quad (40)$$

The value of E_2^{CORR} are given in the last column of Table III. We can see that this value is negative for almost all terms. It will be exactly the leading term for E^{CORR} of the binding

energies. We can say that correlation contributions for binding energy are in the range of 0.0008–0.062 a.u. But this contribution was estimated as a positive value which is equal to 0.044 a.u. in paper [13]. We can explain this value by different representation of data since in this paper the energy which was counted from the $1s^2$ state is given. We can guess that the exact value for this energy was subtracted from the total energy of $1s^23l3l'$ states obtained in the Hartree–Fock approximation. In this case $E^{\text{CORR}}(1s^2)$ can be subtracted from $E^{\text{CORR}}(3l3l', LS)$ given by eq. (40). In the result the range of the correlation contribution can be estimated in the range 0.047–0.016 a.u. and in the middle it is possible to think that it will be 0.044 a.u. which was given for this contribution by Vaeck and Hansen [13]. Let us return to the discussion about the difference in the theoretical data given in Table V.

There are rather large differences between our data and data from [14] and much better agreement with data in [15, 16]. It is not possible to estimate the correlation contribution from these data sine a model potential was used. We

Table V. $1s^2 3l3l'$ states for *OV*. Energy (a.u.) counted from $1s^2$

Conf.	Level	P.T.	[13]	[14]	[15]	[16]
$1s^2 3s^2$	1S	-3.9565	-3.9468	-3.9817	-3.9654	-3.9620
$1s^2 3s3p$	3P	-3.8722	-3.8660	-3.8891	-3.8841	
$1s^2 3s3p$	1P	-3.7732	-3.7594	-3.7991	-3.7823	-3.7794
$1s^2 3s3d$	1D	-3.7787	-3.7667	-3.7917	-3.7900	-3.7850
$1s^2 3s3d$	3D	-3.7489	-3.7300	-3.7638	-3.7558	
$1s^2 3p^2$	3P	-3.7095	-3.7006	-3.7160	-3.7225	
$1s^2 3p^2$	3P	-3.7095	-3.7006	-3.7160	-3.7225	
$1s^2 3p3d$	3F	-3.6657	-3.6491	-3.6664	-3.6730	
$1s^2 3p3d$	1D	-3.6584	-3.6455	-3.6620	-3.6663	-3.6646
$1s^2 3p^2$	1S	-3.6301	-3.6197	-3.6385	-3.6445	-3.6442
$1s^2 3p^2$	1D	-3.6294	-3.6087	-3.6322	-3.6336	-3.6344
$1s^2 3p3d$	3D	-3.6041	-3.5903	-3.6091	-3.6118	
$1s^2 3p3d$	3P	-3.5909	-3.5756	-3.5951	-3.5997	
$1s^2 3d^2$	3F	-3.5587	-3.5389	-3.5565	-3.5582	
$1s^2 3p3d$	1F	-3.5307	-3.4838	-3.5304	-3.5356	-3.5370
$1s^2 3d^2$	1G	-3.5133	-3.4727	-3.5110	-3.5154	-3.5134
$1s^2 3d^2$	3P	-3.5123	-3.4696	-3.4896	-3.4922	
$1s^2 3d^2$	1D	-3.4613	-3.4139	-3.4749	-3.4737	-3.4720
$1s^2 3p3d$	1P	-3.4637	-3.4176	-3.4683	-3.4661	-3.4680
$1s^2 3d^2$	1S	-3.2914	-3.2486	-3.3195	-3.3231	-3.3222
$1s^2 2p$	2P	-4.6311			-4.6367	-4.6378
$1s^2 2s$	2S	-5.0681			-5.0758	-5.0689

think that by using a model potential and taking into account a very large number of configurations correlation effects were computed at least in the frame of the second order (or a little less) in [15]. On the other hand the third order contribution will be negative and preliminary equal to $(-0.1-0.2)/Z$. (see eqs (35, 36) and Table III, IV). In this case it can give us an additional $-0.01-0.025$ a.u. for the binding energy of O^{4+} . We can see that T.P. data and data from [15] disagree in this limit.

Let us note that data for electron spectra can be obtained as the difference between the $E(3l3l', LS)$ and $E(2l, ^2l)$ data. In order to know the contribution of the correlation effects to these values we can find the difference between E_2^{CORR} given in Table III and of $E_2^{\text{CORR}}(2p, ^2P)$ which is equal to -0.012446 a.u. We can see that this difference is almost equal to zero for some terms ($3s3p\ ^1P$, $3s3d\ ^1D$, $3s3d\ ^3D$, $3p^2\ ^3P$, $3p3d\ ^3F$, $3d^2\ ^3F$). It is very interesting that in the result we obtain zero effect by subtractions of two equal contributions. We did not compare our data with experimental data (see for example [12]) because this could not be a direct comparison. It is necessary to take into account post-collision interaction (PCI) by which experimental data can be shifted for some levels on $0.02-0.048$ a.u. [12]. We hope to estimate this contribution more accurately in the future. Also the resolution of spectra does sometimes not allow us to measure the energy very accurately in order to be a referee for theoretical approaches.

5. Conclusion

We reviewed some features of non-relativistic energy calculations in S-matrix perturbation theory. One of the most appealing advantages is profound explicitness. We calculated $1/Z$ expansion coefficients for highly excited states which were discovered by new experimental techniques. Our theoretical data can be used for the identification of electron spectra and also for the prediction of new experimental results.

Table VI. $1s^2 3l4l'$ states for *OV*. Energy (a.u.) counted from $1s^2$

Conf.	Level	P.T.	[15]
$3s4s$	3S	-3.1108	-3.1189
$3s4s$	1S	-3.1052	-3.0907
$3s4p$	1P	-3.0639	-3.0697
$3s4p$	3P	-3.0470	-3.0554
$3s4d$	3D	-3.0245	-3.0301
$3s4d$	1D	-3.0176	-3.0224
$3s4f$	3F	-2.9835	-2.9877
$3s4f$	1F	-2.9749	-2.9780
$3p4s$	3P	-2.9767	-2.9856
$3p4s$	1P	-2.9513	-2.9553
$3p4p$	1P	-2.9477	-2.9568
$3d4s$	1D	-2.9406	-2.9464
$3p4p$	3D	-2.9394	-2.9452
$3p4d$	3D	-2.9218	-2.9243
$3p4p$	3S	-2.9210	-2.9295
$3p4p$	3P	-2.9138	-2.9211
$3p4d$	1F	-2.9107	-2.9127
$3d4s$	3D	-2.9010	-2.9054
$3p4d$	1D	-2.8996	-2.9061
$3p4d$	1P	-2.8945	-2.8986
$3p4d$	3F	-2.8897	-2.8959
$3p4f$	3G	-2.8785	-2.8844
$3d4p$	1D	-2.8776	-2.8808
$3p4p$	1D	-2.8720	-2.8648
$3p4f$	1F	-2.8731	-2.8838
$3p4p$	1S	-2.8691	-2.8715
$3p4f$	3F	-2.8713	-2.8732
$3d4p$	3F	-2.8630	-2.8664
$3d4d$	3D	-2.8575	-2.8439
$3p4d$	3P	-2.8611	-2.8719
$3d4d$	1F	-2.8586	-2.8591
$3d4p$	3D	-2.8492	-2.8520
$3d4f$	1G	-2.8420	-2.8418
$3d4d$	3G	-2.8413	-2.8439
$3d4f$	3H	-2.8408	
$3d4d$	1P	-2.8395	-2.8375
$3d4p$	3P	-2.8384	-2.8430
$3d4f$	1H	-2.7771	
$3d4d$	1G	-2.8247	-2.7853
$3p4f$	3D	-2.8233	-2.8226
$3d4d$	3F	-2.8197	-2.8176
$3d4f$	1F	-2.7679	-2.8719
$3d4p$	1F	-2.8116	-2.8113
$3p4f$	1G	-2.8110	-2.8466
$3d4f$	3F	-2.8109	-2.8164
$3d4d$	3P	-2.8039	-2.7891
$3d4f$	1D	-2.8059	-2.8042
$3d4f$	3G	-2.7980	-2.7950
$3d4f$	3D	-2.7920	-2.7794
$3p4f$	1D	-2.7983	-2.8131
$3d4p$	1P	-2.7889	-2.7910
$3d4d$	3S	-2.7926	-2.8014
$3d4d$	1D	-2.7667	-2.7799
$3d4f$	3P	-2.7630	-2.7629
$3d4f$	1P	-2.7150	-2.7104
$3d4d$	1S	-2.7029	-2.7130

It is useful to calculate correlation energies leaving only correlation diagrams. It is correct, unfortunately, only for closed shell ($1s^2$, for example) and the correlation energy for the states with two electrons above the core was obtained as the difference between two series of $1/Z$ expansion. Another approach assumes the basic of Hartree-Fock functions in place of Coulomb ones, which reduces the theory to non-degenerate case, but drops the convenient explicitly of Z -dependence. Moreover, the Hartree-Fock basis does not

improve the rapidity of the convergence of the $1/Z$ expansion.

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