EQUATIONS FOR DETERMINATION OF VECTOR COUPLING COEFFICIENTS IN SYSTEMS WITH TWO OPEN SHELLS. IONS OF TRANSITION METALS WITH $p^M d^N$ CONFIGURATION

B. N. Plakhutin and A. V. Arbuznikov

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An analysis is made of the necessary conditions that must be satisfied by vector coupling coefficients (VCCs) a_{mn} and b_{mn} characterizing individual L,S-multiplets in atomic configurations $p^M d^N$ and $s^1 d^N$ ($1 \leqslant N \leqslant 9$, $1 \leqslant M \leqslant 5$). It is shown that in the systems with two open shells, the sought VCCs satisfy not only the known limitations that follow from spherical symmetry, but also a certain supplementary equation that is introduced in the present work in the form of a postulate. These VCCs obtained in the present work have been used in ab initio calculations, by the single coupling operator method, of atoms and ions of titanium and vanadium with configurations $3d^1 4p^1$, $3p^4 3d^3$, and $3p^5 3d^3$.

INTRODUCTION

The inner electronic levels in molecules that are detected upon ionization are known to be very nearly purely atomic levels [1]; therefore, in quantum-chemical interpretation of the corresponding experimental data (x-ray, photoelectron, Auger, and other spectra), both the molecule in question and the corresponding isolated atom (or their ions) are commonly calculated. In the Hartree–Fock (HF) method, the atomic states are calculated by the use of a specially written atomic program [2, 3], since in the general Hartree–Fock theory of open shells – the unified coupling operator (UCO) method [4-8] – the problem of calculating ionized atoms is not completely solved. In particular, difficulty is recognized in using the UCO method to calculate ions in states with two degenerate open shells [9, 10].

In this article we are presenting a solution of this problem for atoms (or ions) with electronic configuration $p^{N_p} d^{N_d}$ ($1 \leqslant N_p \leqslant 5$, $1 \leqslant N_d \leqslant 9$). The calculation of such states is of interest (for example) in interpreting Auger spectra of transition-metal compounds [1].

The main interest in this problem, however, is in its theoretical aspect. As is known, when calculating systems with degenerate open shells using the single-configuration (Hartree–Fock) approach, special measures are required for matching of the symmetry of (a) the nuclear core and one-electron orbitals and (b) the nuclear core and many-electron fucntions of state.

Problem a was solved in general form by Roothaan [11], who proposed that the mean energy of the term should be used as the energy functional in the Hartree–Fock method.

The second problem b arises in systems with a certain symmetry – in cubic, tetragonal, and icosahedral point groups – and also in atoms with open d-shells in certain ("non-Roothaan" [12]) spectroscopic states of the atoms. A solution of this problem was given in [10, 12-14] for systems with a single degenerate open shell (electronic configuration γ^N). For more complicated systems that have two or more degenerate open shells, such as transition-metal ions with configuration $p^{N_p} d^{N_d}$, solution of this problem, as suggested in [9], is impossible in principle.

The salient feature of the solution found in the present work is that, in determining vector coupling coefficients a_{mn} and b_{mn} that are sought in the UCO method, a new equation is introduced in the form of a postulate (this is in addition to the equations proposed previously in [10]). The validity of the postulated equation has been justified by comparing the results of a calculation with data obtained within the framework of the atomic theory [2]. However, we have not been successful in clarifying the physical condition expressed by this equation.

Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk.
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POSSIBLE STATES AND ENERGY OF ATOM (OR ION) WITH $p^{N_p}d^{N_d}$ CONFIGURATION

The possible states of existence of an atom with electronic configuration $p^{N_d}d^{N_d}$ ($1 \leqslant N_p \leqslant 5$, $1 \leqslant N_d \leqslant 9$) are determined by general rules [15], starting with the corresponding states in configurations p^{N_p} and d^{N_d}. If L_p and S_p are the values of the orbital and spin moments for a system with the electronic configuration p^{N_p}, and L_d and S_d are the analogous values for the configuration d^{N_d}, then the possible values of the total moments L and S for an atom with the electronic configuration $p^{N_p}d^{N_d}$ will be given by the following (here and subsequently, we are assuming a Russell–Saunders L,S-bond [15]):

$$\begin{aligned} L &= L_p + L_d,\ L_p + L_d - 1,\ \ldots,\ |L_p - L_d|; \\ S &= S_p + S_d,\ S_p + S_d - 1,\ \ldots,\ |S_p - S_d|. \end{aligned} \tag{1}$$

Configurations of the $p^{N_p}d^{N_d}$ type give rise to a large number of terms (L,S-multiplets), many of which are multiple. For example, in the p^4d^3 configuration that is examined in the following material, the following states are possible:

$$\begin{aligned} p^4d^3 \rightarrow\ & {}^6G,\ {}^6F,\ {}^6D(2),\ {}^6P,\ {}^6S, \\ & {}^4I,\ {}^4H(3),\ {}^4G(5),\ {}^4F(8),\ {}^4D(8),\ {}^4P(7),\ {}^4S(2), \\ & {}^2K,\ {}^2I(3),\ {}^2H(6),\ {}^2G(10),\ {}^2F(12),\ {}^2D(13),\ {}^2P(9),\ {}^2S(4), \end{aligned}$$

where the numbers in the parentheses denote the number of terms with the given symmetry. The same as in the simpler case of atoms with d^N configuration, a formally correct calculation of multiple terms (from the standpoint of the variational principle) requires going beyond the framework of the Hartree–Fock method [15].

The energy of the term (L, S, $p^{N_p}d^{N_d}$) can be represented as a sum of components from individual shells

$$E(L,\ S,\ p^{N_p}d^{N_d}) = E' + E_{pp} + E_{dd} + E_{pd}, \tag{2}$$

where E_{pp} is the energy of interelectron interaction within the open p-shell; E_{dd} is the analogous energy for the d-shell; E_{pd} is the energy of interaction of open p- and d-shells; E' is the remainder of the energy of the term, which is identical for all states of the configuration $p^{N_p}d^{N_d}$.

If the particular L,S-multiplet in configuration $p^{N_p}d^{N_d}$ is singular (not multiple), it is not difficult to show that

$$\begin{aligned} E_{pp} &= E_{pp}(L,\ S,\ p^{N_p}d^{N_d}) = E_{pp}(L_p,\ S_p,\ p^{N_p}), \\ E_{dd} &= E_{dd}(L,\ S,\ p^{N_p}d^{N_d}) = E_{dd}(L_d,\ S_d,\ d^{N_d}), \end{aligned} \tag{3}$$

i.e., for nonmultiple terms, the values of L_p, S_p, L_d, and S_d are still "good" quantum numbers. [In other words, if two different nonmultiple L,S-multiplets correspond to exactly the same set $\{L_p, S_p, L_d, S_d\}$, then the energies (2) of these multiplets will differ only in the term E_{pd}.] Only such states will be considered in the following discussion.

In the theory of atomic multiplets [15], the individual terms in Eq. (2) are expressed through Slater–Condon parameters

$$E_{pp} = c_{pp}^{(0)}F_{pp}^0 + c_{pp}^{(2)}F_{pp}^2, \tag{4}$$

$$E_{dd} = c_{dd}^{(0)}F_{dd}^0 + c_{dd}^{(2)}F_{dd}^2 + c_{dd}^{(4)}F_{dd}^4, \tag{5}$$

$$E_{pd} = c_{pd}^{(0)}F_{pd}^0 + c_{pd}^{(2)}F_{pd}^2 + c_{pd}^{(1)}G_{pd}^1 + c_{pd}^{(3)}G_{pd}^3, \tag{6}$$

where numerical values of the coefficients $c^{(0)}$, $c^{(1)}$,..., characterizing the L,S-multiplet and configuration that are being calculated, have been given in Slater's monograph [15, Vol. II]; but the term E', which includes the kinetic energy of the electrons, the energy of their interaction with the core, etc. [see below, Eq. (8)], is not detailed in the theory of [15].

EQUATIONS FOR DETERMINATION OF VECTOR COUPLING COEFFICIENTS

In the unified coupling operator (UCO) method [4-8, 16], the energy of an atom with electronic configuration $p^{N_p}d^{N_d}$ in a state described by quantum numbers L and S has the form

$$E(L,\ S,\ p^{N_p}d^{N_d}) = E' + \sum_m \sum_n f_m f_n (2a_{mn}J_{mn} - b_{mn}K_{mn}), \tag{7}$$

where the summation covers all p- and d-orbitals of the open shell: $\{m\} = \{n\} = \{p\} \oplus \{d\}$; and

$$E' = 2\sum_k H_{kk} + \sum_k \sum_l (2J_{kl} - K_{kl}) + 2\sum_m f_m \left(H_{mm} + \sum_k (2J_{km} - K_{km}) \right). \quad (8)$$

The subscripts k and ℓ number the orbitals of the closed shell; f_m is the occupation number of the open shell, which in the present problem assumes one of two possible values: $f_p = N_p/2n_p = N_p/6$ or $f_d = N_d/2n_d = N_d/10$.

The coefficients a_{mn} and b_{mn}, which are termed vector coupling coefficients (VCCs), in the UCO method assign the electronic configuration and state of the system [8, 16]. In transition-metal atoms and ions, which have an unfilled d-shell, these coefficients, generally speaking, are not constants but rather depend on the specific selection of the basis set of degenerate orbits of the open shell [10]. In the subsequent analysis it will be assumed that the basis set of p- and d-orbitals has been assigned (fixed) as follows:

$$\sigma = d_{z^2}, \quad \pi = d_{xz}, \quad \pi' = d_{yz}, \quad \delta = d_{x^2-y^2}, \quad \delta' = d_{xy}, \quad x = p_x, \quad y = p_y, \quad z = p_z. \quad (9)$$

In the interest of simplifying the subsequent formulas, we will introduce the notation

$$Q_{mn} = 2a_{mn}J_{mn} - b_{mn}K_{mn}. \quad (10)$$

Then,

$$E(L, S, p^{N_p}d^{N_d}) = E' + \sum_m \sum_n f_m f_n Q_{mn}. \quad (11)$$

Thus, for the calculation of atoms and ions with the $p^{N_p}d^{N_d}$ configuration, it is necessary to determine a set of coefficients a_{mn} and b_{mn} of Eq. (7) for each state. Considering the dimensionality of the p- and d-shells ($n_p = 3$ and $n_d = 5$), in calculating an ion with electronic configuration $p^{N_p}d^{N_d}$ it is necessary to determine $2 \times (n_p + n_d)^2 = 128$ unknown coefficients a_{mn} and b_{mn}, forming a matrix of the type

$$\| a_{mn} \| = \left| \begin{array}{c|c} a_{pp'} & a_{pd} \\ \hline a_{dp} & a_{dd'} \end{array} \right| \quad (12)$$

where p, p' = x, y, z; d, d' = σ, π, π', δ, δ'.

A general approach to the problem of finding the coefficients a_{mn} and b_{mn} for atoms with an open d-shell was proposed in [10]. With certain extensions, the results of [10] can also be used in the case under consideration, with two open shells.

The first equation for determining the sought VCCs a_{mn} and b_{mn}, an equation that follows from [10], expresses physically the condition that the energy of the L,S-multiplet must be identical in the two different versions of Hartree–Fock theorem, i.e., in the atomic theory of [15] and in the SCO method [4-8]. Omitting the term E' in Eqs. (2) and (11), we have

$$\sum_m \sum_n f_m f_n Q_{mn} = f_p^2 \sum_p \sum_{p'} Q_{pp'} + f_d^2 \sum_d \sum_{d'} Q_{dd'} + f_p f_d \sum_p \sum_d (Q_{pd} + Q_{dp}) = E_{pp} + E_{dd} + E_{pd}, \quad (13)$$

where E_{pp}, E_{dd}, and E_{pd} are determined in Eqs. (4)-(6). After substituting Eqs. (10) and (4)-(6) into Eq. (13), the resulting equation establishes the relationship between the unknown VCCs a_{mn} and k_{mn} and the known coefficients $c^{(0)}$, $c^{(1)}$, ...

The second equation for the determination of VCCs that was proposed in [10] expresses the condition of degeneracy of an open shell. In the $p^{N_p}d^{N_d}$ configuration there are two degenerate open shells, i.e.,

$$\varepsilon_p = \varepsilon_{\underline{p}}; \quad (p, \underline{p} = x, y, z), \quad (14)$$

$$\varepsilon_d = \varepsilon_{\underline{d}}; \quad (d, \underline{d} = \sigma, \pi, \pi', \delta, \delta'), \quad (15)$$

where ε_p and ε_d are the one-electron energies.

In the Hartree–Fock method for open shells, the one-electron energies are the eigenvalues of the single coupling operator R

$$R\varphi_m = \varphi_m \varepsilon_m. \quad (16)$$

Using a general expression for R that was obtained by Hirao, specifically Eq. (3.8) in [7], we have

$$\varepsilon_m = \langle \varphi_m | R | \varphi_m \rangle = \langle \varphi_m | F_m | \varphi_m \rangle = f_m \{ H_{mm} + \sum_k (2J_{km} - K_{km}) + \sum_n f_n Q_{mn} \}, \tag{17}$$

where F_m is the Fock operator for the orbital φ_m [7, Eq. (2.1)]. After substituting (17) into (14) and (15) and performing the required transformations [10], we obtain

$$f_p \sum_{p'} Q_{pp'} + f_d \sum_d Q_{pd} = f_p \sum_{p'} Q_{\underline{p}p'} + f_d \sum_d Q_{\underline{p}d}$$
$$(\varepsilon_p = \varepsilon_{\underline{p}};\ p, \underline{p}, p' = x, y, z), \tag{18}$$

$$f_p \sum_p Q_{dp} + f_d \sum_{d'} Q_{dd'} = f_p \sum_p Q_{\underline{d}p} + f_d \sum_{d'} Q_{\underline{d}d'}$$
$$(\varepsilon_d = \varepsilon_{\underline{d}};\ d, \underline{d}, d' = \sigma, \pi, \pi', \delta, \delta'), \tag{19}$$

where the notations in parentheses of the type ($\varepsilon_p = \varepsilon_{\underline{p}}$ and p, $\underline{p}$, p' = x, y, z) point out the origin of the equation – from the condition of degeneracy (14) or (15).

Thus, within the framework of the approach of [10], in calculating the VCCs a_{mn} and b_{mn} in the $p^N pd^N d$ configuration, we have three basic relationships: (13), (18), and (19). Equation (18) is broken up into two independent equations ($\varepsilon_x = \varepsilon_y$ and $\varepsilon_x = \varepsilon_z$); and analogously, Eq. (19) is broken up into four equations. [The number of independent equations in Eqs. (18) and (19) is determined by the inequalities p < $\underline{p}$ and d < $\underline{d}$, respectively.] With an element-by-element writing (see below), each of these seven equations, in turn, is broken up into several linear equations.

FACTORIZATION OF EQUATIONS {(13), (18), (19)}

In order to obtain from Eqs. (13), (18), and (19), an equation in explicit form relating the unknown VCCs a_{mn} and b_{mn} to the known coefficients $c^{(0)}$, $c^{(1)}$,..., the integrals J_{mn} and K_{mn} in Eq. (10) must be expressed in terms of Slater–Condon parameters [15].

Corresponding expressions are given in the monograph [15] for the case of complex AOs and in the monograph [17] for real AOs (integrals of the type of $J_{pp'}$, K_{pp}, $J_{dd'}$, and $K_{dd'}$, and also four-index integrals $\langle d\underline{d} | d'\underline{d}' \rangle$). Analogous expressions in real AOs for integrals $J_{pd} = \langle pp | dd \rangle$ and $K_{pd} = \langle pd | pd \rangle$ were obtained in [18] and are given below. (For simplification of the formulas, we have used the notation $F^0 = F^0_{pd}$, $F^2 = F^2_{pd}$,...)

$$\begin{aligned}
&J_{x\sigma} = J_{y\sigma} = F^0 - \frac{2}{35} F^2, \\
&J_{z\sigma} = F^0 + \frac{4}{35} F^2, \\
&J_{x\pi} = J_{y\pi'} = J_{z\pi} = J_{z\pi'} = J_{x\delta} = J_{x\delta'} = J_{y\delta} = J_{y\delta'} = F^0 + \frac{2}{35} F^2, \\
&J_{x\pi'} = J_{y\pi} = J_{z\delta} = J_{z\delta'} = F^0 - \frac{4}{35} F^2; \\
&K_{x\sigma} = K_{y\sigma} = \frac{1}{15} G^1 + \frac{18}{245} G^3, \\
&K_{z\sigma} = \frac{4}{15} G^1 + \frac{27}{245} G^3, \\
&K_{x\pi} = K_{y\pi'} = K_{z\pi} = K_{z\pi'} = K_{x\delta} = K_{x\delta'} = K_{y\delta} = K_{y\delta'} = \frac{3}{15} G^1 + \frac{24}{245} G^3, \\
&K_{x\pi'} = K_{y\pi} = K_{z\delta} = K_{z\delta'} = \frac{15}{245} G^3.
\end{aligned} \tag{20}$$

After substituting into Eq. (13) the values of Q_{pd} from Eqs. (10) and (20) and values of $Q_{pp'}$ and $Q_{dd'}$ from [17], and equating individually the coefficients of F^0_{pp}, F^2_{pp}, F^0_{dd},..., G^3_{pd} in the left and righ sides, we obtain 9 linear inhomogeneous equations for the determination of 128 unknowns a_{mn} and b_{mn}.

An analogous substitution of values of Q_{mn} into the two equations (18) and into the four equations (19) gives (respectively) 2 × 6 = 12 and 4 × 7 = 28 homogeneous linear equations. [In Eqs. (13), (18), and (19), after the indicated substitution, we find that there are (respectively) 9, 6, and 7 Slater–Condon parameters.] Thus, in all we have 9 inhomogeneous and 40 homogeneous linear equations for the determination of the 128 unknowns a_{mn} and b_{mn}.

The system of equations thus obtained is broken up (factorized) into three groups of equations, each of which contains unknowns from only one block of the matrix (12): $\{a_{pp'}; b_{pp'}\}$, $\{a_{dd'}; b_{dd'}\}$, $\{a_{dp}, b_{dp}; a_{pd}, b_{pd}\}$.

Equations for Determination of Coefficients $a_{dd'}$ and $b_{dd'}$

The set of equations containing the unknowns $a_{dd'}$ and $b_{dd'}$ includes three inhomogeneous equations obtained from Eq. (13). These three equations can be written in the form of a single equation that follows directly from (13),

$$f_d^2 \sum_d \sum_{d'} Q_{dd'} = c_{dd}^{(0)} F_{dd}^{(0)} + c_{dd}^{(2)} F_{dd}^2 + c_{dd}^{(4)} F_{dd}^4. \tag{21}$$

After substituting the Slater–Condon parameters into the formula for $Q_{dd'}$ (10) and equating individually the coefficients of F_{dd}^0, F_{dd}^2, and F_{dd}^4 in the left and right sides of Eq. (21), we obtain three inhomogeneous linear equations relating the unknowns $a_{dd'}$ and $b_{dd'}$ to the known quantities $c_{dd}^{(0)}$, $c_{dd}^{(2)}$, and $c_{dd}^{(4)}$.

The correponding homogeneous equations for the determination of $a_{dd'}$ and $b_{dd'}$ are obtained from the condition of degeneracy of an open d-shell (19). The 28 equations obtained above from Eq. (19) can be written in the form of two general equations, one of which contains the unknowns $a_{dd'}$ and $b_{dd'}$ (and does not contain any other unknowns)

$$\sum_{d'} Q_{dd'} = \sum_{d'} Q_{\underline{d}d'}, \quad (\varepsilon_d = \varepsilon_{\underline{d}}, \ d < \underline{d}), \tag{22}$$

where the notations in the parentheses indicate, the same as previously, the origin of this equation – see Eqs. (18) and (19). The second equation obtained from (19), containing the unknowns $\{a_{dp}, b_{dp}\}$, is given below – see Eq. (27).

Transferring all terms in Eq. (22) to the left side and performing the transformations described above, we obtain $3 \times (n_d - 1) = 12$ homogeneous linear equations. Thus, when we take (21) into account, we obtain a total of $3 \times n_d = 15$ equations for the determination of $2 \times n_d \times n_d = 50$ unknowns $a_{dd'}$ and $b_{dd'}$.

Through a direct comparison, we are convinced that the equations (21) and (22) that we have obtained do coincide exactly with Eqs. (9) and (16) from [10], which were obtained from the vector coupling coefficients (VCCs) in an atom with the d^N configuration. This result means that the VCCs $a_{dd'}$ and $b_{dd'}$ that are calculated for the multiplet (L_d, S_d, d^N) remain the same for all nonmultiple (not double) multiplets $(L, S, p^N p d^N d)$ if $N_d = N$, and the quantum numbers L, S, L_d and S_d are related to the equations (1).

It can be shown analogously that the coefficients $a_{pp'}$ and $b_{pp'}$ can also be taken as identical for the multiplets $(L_p, S_p, p^N p)$ and $(L, S, p^N p d^N d)$. The corresponding equations obtained from Eqs. (13) and (18) are given below without any detailed commentary.

Equations for Determination of Coefficients $a_{pp'}$ and $b_{pp'}$

$$f_p^2 \sum_p \sum_{p'} Q_{pp'} = c_{pp}^{(0)} F_{pp}^0 + c_{pp}^{(2)} F_{pp}^2, \tag{23}$$

$$\sum_{p'} Q_{pp'} = \sum_{p'} Q_{\underline{p}p'}, \quad (\varepsilon_p = \varepsilon_{\underline{p}}, \ p < \underline{p}). \tag{24}$$

After substituting the Slater–Condon parameters into the formula for $Q_{pp'}$ (10) and equating individually the coefficients of F_{pp}^0 and F_{pp}^2 in the left and right sides of both equations, we obtain 6 equations for the determination of 18 unknowns $a_{pp'}$ and $b_{pp'}$.

Equations for Determination of Coefficients a_{dp}, b_{dp}, a_{pd}, and b_{pd}

Subtracting Eqs. (21) and (23) from Eq. (13), we obtain an inhomogeneous equation for the determination of the VCCs a_{dp}, b_{dp}, a_{pd}, and b_{pd} that appear in the off-diagonal blocks of the matrix (12):

$$f_p f_d \sum_p \sum_d (Q_{pd} + Q_{dp}) = c_{pd}^{(0)} F_{pd}^0 + c_{pd}^{(2)} F_{pd}^2 + c_{pd}^{(1)} G_{pd}^1 + c_{pd}^{(3)} G_{pd}^3. \tag{25}$$

An analogous procedure of subtracting Eqs. (24) and (22) from Eqs. (18) and (19), respectively, leads to two homogeneous equations

$$\sum_d Q_{pd} = \sum_d Q_{\underline{p}d} \quad (\varepsilon_p = \varepsilon_{\underline{p}}, \ p < \underline{p}), \tag{26}$$

$$\sum_p Q_{dp} = \sum_p Q_{\underline{d}p} \quad (\varepsilon_d = \varepsilon_{\underline{d}},\ d < \underline{d}). \tag{27}$$

The relationships that have been obtained, Eqs. (25)-(27), permit further simplification. By applying to Eq. (25) the above-described transformations [see Eq. (21) and subsequent text], we obtain a system of inhomogeneous linear equations in the form

$$\sum_{j=1}^{M_x} \lambda_{ij} x_j = c_{pd}^{(i-1)}/f_p f_d, \quad i = 1, 2, \ldots, M_{SCP}, \tag{28}$$

where x_j are the unknowns a_{dp}, a_{pd}, b_{dp}, and b_{pd}, ordered in a certain manner; M_x is the number of unknowns; λ_{ij} are numerical coefficients; M_{SCP} is the number of Slater–Condon parameters (SCPs) in Eq. (25). (In the present case, $M_x = 2 \times 2 \times n_p \times n_d = 60$, and $M_{SCP} = 4$.)

Analogous transformations in Eqs. (26) and (27) lead to the set of homogeneous equations (29)

$$\sum_{j=1}^{M_x} \lambda_{ij} x_j = 0, \quad i = M_{SCP} + 1,\ M_{SCP} + 2, \ldots, M_t, \tag{29}$$

where M_t is the total number of linear equations (28)-(29), $M_t = M_{SCP} \times \{1 + (n_p - 1) + (n_d - 1)\} = 28$. [The numbers of homogeneous equations obtained individually from Eqs. (26) and (27) are $M_{SCP} \times (n_p - 1)$ and $M_{SCP} \times (n_d - 1)$, respectively.]

Thus, for the determination of 60 unknown VCCs a_{dp}, b_{dp}, a_{pd}, and b_{pd}', we have 4 inhomogeneous and 24 homogeneous linear equations; i.e., there is a certain arbitrariness in the selection of these VCCs. As will be shown subsequently, this circumstance is very important; and hence we will examine in more detail this system of equations and its solutions for various configurations.

1. The system of homogeneous equations (29) does not contain the coefficients $c^{(0)}$, $c^{(2)}, \ldots$, characterizing the state of the system an the electronic configuration; and it is identical for all atoms (or ions) with the configuration $p^N pd^N d$ with all possible N_p and N_d. In view of the rationality of the coefficients λ_{ij} [which follows from the rationality of the coefficients and the equations (20)], this system can be solved in integers, thus avoiding rounding-off errors in computerized calculations. In the present work, we are using a special procedure given in [10] for the analytical solution of the system of homogeneous equations (29) with integral rectangular matrices λ_{ij}.

2. Equations of the type of (28)-(29) for finding VCCs were examined for the first time in [10] in application to atoms with the d^N configuration, for which a problem also arises in the arbitrariness in selecting the VCCs $a_{dd'}$ and $b_{dd'}$ [in the latter case, $M_{SCP} = 3$, $M_t = 15$, and $M_x = 50$ – see Eqs. (21)-(22)]. As was shown in [10], such freedom in selecting the VCCs does not affect the physically significant results: The total energy of the atom, the matrix density, and so on, remain unchanged in the quantum-chemical calculation, as they should.

The VCC matrices $\|a_{dd'}\|$ and $\|b_{dd'}\|$ that were obtained in [10] for various (nonmultiple) terms in the d^N configuration, on the basis of their characteristics, are divided into two groups in accordance with the known division of terms into "Roothaan" and "non-Roothaan" terms [12-14]. In the case of non-Roothaan terms, corresponding to $c_{dd}^{(2)} \neq c_{dd}^{(4)}$ [10], at least one of the above-indicated matrices is (must be) asymmetric: $\|a_{dd'}\| \neq \|a_{dd'}\|^T$ and/or $\|b_{dd'}\| \neq \|b_{dd'}\|^T$, in spite of the great arbitrariness in selecting the VCCs ($M_x - M_t = 35$).

At the same time, for terms of the Roothaan type, which in the d^N configuration correspond to $c_{dd}^{(2)} = c_{dd}^{(4)}$ [10], from Eqs. (28)-(29) [with numerical values of the parameters M_x, M_t,... obtained from Eqs. (21)-(22)], there are no consequent limitations on the form of the matrices $\|a_{dd'}\|$ and $\|b_{dd'}\|$. In particular, the corresponding VCCs can be assigned in the standard Roothaan form [11]: $a_{dd'} = a$ and $b_{dd'} = b$, where $a = [-7c_{dd}^{(2)} + N(N-1)]/100f_d^2$ and $b = -7c_{dd}^{(2)}/10f_d^{(2)}$ (see [10]).

3. A similar analysis of Eqs. (28)-(29) for the p^N configuration shows that the existing arbitrariness in selecting the VCCs $a_{pp'}$ and $b_{pp'}$, [$M_x - M_t = 12$, see Eqs. (23)-(24)] similarly does not affect the results obtained in the calculation of physical characteristics. In the subsequent development, we will use the values of these VCCs that were obtained by Roothaan [11].

4. A completely different situation is found in the case of the VCCs a_{dp}, b_{dp}, a_{pd}, and b_{pd}. The general solution of Eqs. (28)-(29) for this case contains $M_x - M_t = 32$ arbitrary parameters; and when these parameters are changed, it is possible to obtain different sets of the sought VCCs.

Using these VCCs, we carried out ab initio calculations of the titanium atom and vanadium ions, which have the electronic configurations $3d^14p^1$ and $3p^53d^3$, $3p^43d^3$, respectively. The details of the calculation scheme and a list of the states calculated will be given subsequently.

In these calculations, we found that the results from the calculation of such characteristics as the energy of the atom, the coefficients in the expansion of AOs in a basis set of Gaussian functions, and the one-electron energies ε_p, ε_d, and so on, are dependent on the selection of the arbitrary parameters with an accuracy within that of the determination of the VCCs a_{dp}, b_{dp}, a_{pd}, and b_{pd}. Let us remember that the VCCs ($a_{dd'}$) and ($a_{pp'}$, $b_{pp'}$) were taken unchanged from [10, 11], respectively.

Here it is important to note that the symmetric characteristics of electron distribution that are obtained from the calculation, characteristics such as the regular degeneracy of the p- and d-shells (14)-(15), and also the relationships (20) and (17) between the integrals of interelectron interaction, were obtained correctly in all cases and were independent of the selection of arbitrary parameters.

5. An analysis of the results that have been set forth has led to the conclusion that the system of equations {(13), (18), (19)} for determining the VCCs a_{mn} and b_{mn} in an atom with the p^Npd^Nd configuration is necessary but not sufficient, and certain supplementary equations are required.

SUPPLEMENTARY EQUATION FOR DETERMINATION OF COEFFICIENTS a_{dp}, b_{dp}, a_{pd}, b_{pd}

In view of the above discussion, a supplementary equation is required only for the calculation of VCCs appearing in the off-diagonal blocks of the matrices (12). The sought equation has the following form:

$$\sum_{p'}\sum_{d} Q_{pd} = \sum_{p}\sum_{d} Q_{dp}, \tag{30}$$

where matrice elements Q_{pd} and Q_{dp} generally speaking do not equal each other.

The validity of Eq. (30) is justified in [19] (see the next article in the present issue of the journal) by an examination of the results of a quantum-chemical calculation by the UCO method using the values obtained for the VCCs a_{mn} and b_{mn}, in comparison with analogous data obtained within the framework of the Roothaan–Hartree–Fock atomic theory [2]. However, there has not yet been any rigorous theoretical justification of this formula, and it can be regarded only as a certain postulate (see also the following discussion).

By the method described above, Eq. (30) is transformed to a system of four homogeneous equations. Thus, for the determination of 60 unknown VCCs a_{dp}, b_{dp}, a_{pd}, and b_{pd}, we finally have 28 inhomogeneous and 28 homogeneous linear equations {(25)-(27), (30)}; therefore, in finding the VCCs we can use 28 supplementary, arbitrary relationships.

The basic difference from the situation described in the preceding section of this article is that the energy of the atom and other physical characteristics calculated with an accounting for Eq. (30) do not depend on the selection of the 28 arbitrary parameters, as should be the case. In all instances, the newly obtained values for the energies of atoms and ions with the p^Npd^Nd configuration (see Table 4) proved to be lower than the corresponding values obtained in the preceding section of this article.

In order to represent the values obtained for the VCCs a_{dp} and a_{pd} in a form that is suitable for practical application, we have used "natural" supplementary relationships among them

$$a_{\sigma x} = a_{\sigma y}, \quad a_{\pi x} = a_{\pi z}, \quad a_{\pi' y} = a_{\pi' z}, \quad a_{\delta x} = a_{\delta y}, \quad a_{\delta' x} = a_{\delta' y}, \tag{31}$$

$$a_{x\pi} = a_{x\delta} = a_{x\delta'}, \quad a_{y\pi'} = a_{y\delta} = a_{y\delta'}, \quad a_{z\pi} = a_{z\pi'}, \quad a_{z\delta} = a_{z\delta'} \tag{32}$$

and analogous relationships for the coefficients b_{dp} and b_{pd} ($b_{\sigma x} = b_{\sigma y}; \ldots; b_{z\delta} = b_{z\delta'}$). These relationships follow naturally from Eqs. (25)-(27) and (30): The unknowns ($a_{\sigma x}$, $a_{\sigma y}$) and ($a_{\pi x}$, $a_{\pi z}$) appear in Eqs. (25)-(27) and (30) with equal coefficients; therefore, the sup-

plementary relationships (31) and (32) do not change the number of linearly independent equations (a total of 32 equations), but they do reduce the number of unknowns from 60 to 38.

Of these 38 VCCs, only 4 are physically independent, corresponding to the number of independent coefficients in Eq. (25). (See the discussion of this question in [10].) As independent VCCs we selected

$$a_{\sigma x} = (4c^{(0)} - 35c^{(2)})/240f_p f_d, \quad a_{\sigma z} = (4c^{(0)} + 70c^{(2)})/240f_p f_d, \tag{33}$$

$$b_{\sigma x} = (27 \times 15c^{(1)} - 4 \times 245c^{(3)})/900f_p f_d, \quad b_{\sigma z} = (-36 \times 15c^{(1)} + 2 \times 245c^{(3)})/900f_p f_d, \tag{34}$$

where $c^{(0)} = c_{pd}^{(0)} = N_p \times N_d$, $c^{(2)} = c_{pd}^{(2)}, \ldots$. The other coefficients of the type of a_{dp} and a_{pd} satisfying Eqs. (25)-(27) and (30) are expressed in terms of independent coefficients (33)

$$\begin{aligned} a_{\pi x} &= a_{\pi' y} = a_{\delta x} = a_{\delta' x} = (a_{\sigma x} + 2a_{\sigma z})/3, \\ a_{\pi y} &= a_{\pi' x} = a_{\delta z} = a_{\delta' z} = (4a_{\sigma x} - a_{\sigma z})/3, \\ a_{x\sigma} &= (5a_{\pi y} - 3A_1)/2, \\ a_{x\pi} &= (5a_{\sigma z} + A_1)/6, \\ a_{x\pi'} &= A_1, \end{aligned} \tag{35}$$

$$\begin{aligned} a_{y\sigma} &= 10a_{\pi x} - 9A_2, \\ a_{y\pi} &= -5a_{\sigma z} + 6A_2, \\ a_{y\pi'} &= A_2, \\ a_{z\sigma} &= -5a_{\pi y} + 6A_3, \\ a_{z\pi} &= 5a_{\sigma x} - 4A_3, \\ a_{z\delta} &= A_3, \end{aligned} \tag{36}$$

where A_1, A_2, and A_3 are certain arbitrary numbers. Analogous expressions for the coefficients b_{dp} amd b_{pd} are obtained from Eqs. (35) and (36) by simultaneous replacement of all coefficients a_{ik} by corresponding coefficients b_{ik} (by replacing $a_{\pi x}$ by $b_{\pi x}$, $a_{\pi' y}$ by $b_{\pi' y}$, and so on), and also by replacement of the arbitrary parameters A_1, A_2, and A_3 by analogous arbitrary quantities B_1, B_2, and B_3.

VECTOR COUPLING COEFFICIENTS FOR s^1d^N CONFIGURATION

The approach that we have set forth in the foregoing material can also be used to determine VCCs in transition-metal atoms (or ions) with the s^1d^N configuration s^1d^N $(1 \leqslant N \leqslant 9)$. The sought coefficients a_{ds}, b_{ds}, a_{sd}, and b_{sd} are determined from the equations

$$f_s f_d \sum_{\underline{d}} (Q_{sd} + Q_{ds}) = c_{sd}^{(0)} F_{sd}^{(0)} + c_{sd}^{(2)} F_{sd}^{(2)}, \tag{37}$$

$$Q_{ds} = Q_{\underline{d}s}; \quad (\varepsilon_d = \varepsilon_{\underline{d}}, \ d < \underline{d}), \tag{38}$$

$$\sum_{\underline{d}} Q_{s\underline{d}} = \sum_{d} Q_{ds}, \tag{39}$$

which are analogous to Eqs. (25), (27), and (30), respectively. [The coefficients a_{ss} and b_{ss} from the corresponding diagonal block of the matrix (12) are equal to zero: $a_{ss} = b_{ss} = 0$.] Further considering that $J_{sd} = F_{sd}^0$ and $K_{sd} = (1/5)F_{sd}^2$ [15] and omitting the intermediate elementary computations, we obtained the following solution of Eqs. (37)-(39)

$$a_{\sigma s} = a_{\pi s} = a_{\pi' s} = a_{\delta s} = a_{\delta' s} = a, \quad b_{\sigma s} = b_{\pi s} = b_{\pi' s} = b_{\delta s} = b_{\delta' s} = b, \tag{40}$$

$$\sum_{d} a_{sd} = 5a, \quad \sum_{d} b_{sd} = 5b, \tag{41}$$

where $a = c_{sd}^{(0)}/20f_s f_d = 1$; $b = -c_{sd}^{(2)}/f_d$.

Thus, in the s^1d^N configuration, coefficients of the type of a_{ds} and b_{ds} ($d = \sigma, \pi, \pi', \delta, \delta'$) are determined uniquely for each term by (40); and the coefficients a_{sd} and b_{sd} are determined with an accuracy within certain arbitrary relationships [there are only 2 equations of (41) for the determination of 10 coefficients]. In particular, we can set $a_{ds} = a$ and $b_{sd} = b$.

TABLE 1. Coefficients $c_{pd}^{(k)}$ in Expression for Energy E_{pd}; See Eqs. (6) and (25)

Configuration, term	F_{pd}^0	F_{pd}^2	G_{pd}^1	G_{pd}^3
p^3d^3, ^5G	15	1/35	—18/15	—189/245
^3I	15	—3/35	—18/15	—144/245
^1I	15	—3/35	—18/15	—84/245
p^4d^3, ^6G	12	—1/35	—18/15	—189/245
^6F	12	3/35	—18/15	—189/245
^4I	12	3/35	—18/15	—129/245
^2K	12	—6/35	—18/15	—69/245
p^1d^1, ^3F	1	2/35	—6/15	—3/245

TABLE 2. General Form of Matrices $\|a_{pd}\|$ and $\|b_{pd}\|$ Satisfying Eqs. (25)-(27) and (30) and Supplementary Relationships (31)-(32),* for Nonmultiple Terms in Configuration $p^N p d^N d$

	x	y	z
	Matrix $\|\|a_{pd}\|\|^t$		
σ	$(5a_{\pi y} - 3A_1)/2$	$10a_{\pi x} - 9A_2$	$-5a_{\pi y} + 6A_3$
π	$(5a_{\sigma z} + A_1)/6$	$-5a_{\sigma z} + 6A_2$	$5a_{\sigma x} - 4A_3$
π'	A_1	A_2	$5a_{\sigma x} - 4A_3$
δ	$(5a_{\sigma z} + A_1)/6$	A_2	A_3
δ'	$(5a_{\sigma z} + A_1)/6$	A_2**	A_3
	Matrix $\|\|b_{pd}\|\|^t$		
σ	$(5b_{\pi y} - 3B_1)/2$	$10b_{\pi x} - 9B_2$	$-5b_{\pi y} + 6B_3$
π	$(5b_{\sigma z} + B_1)/6$	$-5b_{\sigma z} + 6B_2$	$5b_{\sigma x} - 4B_3$
π'	B_1	B_2	$5b_{\sigma x} - 4B_3$
δ	$(5b_{\sigma z} + B_1)/6$	B_2	B_3
δ'	$(5b_{\sigma z} + B_1)/6$	B_2**	B_3

*See footnotes to Table 3.
**A_1, A_2, A_3, and B_1, B_2, B_3, are arbitrary numbers.

TABLE 3. General Form of Matrices $\|a_{dp}\|$ and $\|b_{dp}\|$ Satisfying Eqs. (25)-(27) and (30), and Supplementary Relationships (31)-(32),* for Nonmultiple Terms in Configuration $p^N p d^N d$

	σ	π	π'	δ	δ'
	Matrix $\|\|a_{dp}\|\|^t$				
x	$a_{\sigma x}$	$a_{\pi x}$	$a_{\pi y}$	$a_{\pi x}$	$a_{\pi x}$
y	$a_{\sigma x}$**	$a_{\pi y}$	$a_{\pi x}$	$a_{\pi x}$	$a_{\pi x}$
z	$a_{\sigma z}$	$a_{\pi x}$	$a_{\pi x}$	$a_{\pi y}$	$a_{\pi y}$
	Matrix $\|\|b_{dp}\|\|^t$				
x	$b_{\sigma x}$	$b_{\pi x}$	$b_{\pi y}$	$b_{\pi x}$	$b_{\pi x}$
y	$b_{\sigma x}$**	$b_{\pi y}$	$b_{\pi x}$	$b_{\pi x}$	$b_{\pi x}$
z	$b_{\sigma z}$	$b_{\pi x}$	$b_{\pi x}$	$b_{\pi y}$	$b_{\pi y}$

*Transposes $\|a_{dp}\|^t$, $\|b_{dp}\|^t$, $\|a_{pd}\|^t$, and $\|b_{pd}\|^t$ are given in Tables 2 and 3. [The determination of the corresponding original matrices $\|a_{pd}\|$, $\|b_{dp}\|$,... is given in Eq. (12).] Let us emphasize that $\|a_{dp}\|^t \neq \|a_{pd}\|$, $\|b_{dp}\|^t \neq \|b_{pd}\|$, etc; see Table 2.
**The coefficients $a_{\sigma y}$, $a_{\sigma z}$, $a_{\pi x}$, $a_{\pi y}$ and the analogous coefficients of the b-type are determined in Eqs. (33)-(35).

TABLE 4. Hartree–Fock Energies of Atoms and Ions of Vanadium and Titanium*

Atom (or ion)	Configuration, term	Origin of term (L_d, S_d, L_p, S_p)	Total energy, au
V	$3d^3$, ^4F	—	—942.837196
	^2H	—	—942.749087
V^+	$3p^53d^3$, ^5G	$^4F(d^3)$; $^2P(p^5)$	—941.072849
	^3I	$^2H(d^3)$ $^2P(p^5)$	—940.971360
	^1I	$^2H(d^3)$; $^2P(p^5)$	—940.900879
V^{2+}	$3p^43d^3$, ^6G	$^4F(d^3)$: $^3P(p^4)$	—938.748763
	^6F	$^4F(d^3)$: $^3P(p^4)$	—938.702954
	^4I	$^2H(d^3)$; $^3P(p^4)$	—938.531404
	^2K	$^2H(d^3)$; $^1D(p^4)$	—938.450883
Ti	$3d^2$, ^3F	—	—848.367900
	$3d^14p^1$, ^3F	$^2D(d^1)$; $^2P(p^1)$	—845.342161

*Exactly the same HF basis set was used in calculating the vanadium atom and ions; see basis set (14s9p5d)/[8s4p2d] with contraction scheme 3 for vanadium atom in [21]. Exactly the same HF basis set was used in calculating the ground and excited states of the titanium atom; see the basis set for the titanium atom in [21].

RESULTS AND DISCUSSION

Using Eqs. (31)-(36), we calculated the VCCs a_{dp}, b_{dp}, a_{pd}, and b_{pd} for a number of atomic states in the configurations p^5d^3, p^4d^3, and p^1d^1; a list of these states is given in Table 1, along with the coefficients $c^{(0)}$, $c^{(1)}$,... that are needed for the calculation.

In Tables 2 and 3 we show the general form of the VCC matrices $\|a_{pd}\|$, $\|b_{dp}\|$, $\|a_{pd}\|$, and $\|b_{pd}\|$ satisfying Eqs. (25)-(27) and (30), and also the supplementary relationships (31)-(32) for nonmultiple terms, in the $p^Np^Nd^Nd$ configuration.

In Table 4 we present results from ab initio calculations of atoms and ions of titanium and vanadium, calculations performed using the VCCs obtained in this work. In the calculations we used the MONSTERGAUSS-81 program [20]; details of the calculation scheme have been reported previously [10]. (See also the footnotes to Table 4.)

A comparison of the results presented in Table 4 with analogous data [19] obtained within the framework of the Roothaan–Hartree–Fock atomic theory "expansion method") [2] demonstrates that the results are completely identical, as they should be.

Such agreement is obviously not accidental and hence can be regarded as proof of the validity of Eq. (30). With this in view, let us examine the line of reasoning we used in deriving this equation. We should emphasize that the line of reasoning does not pretend to any mathematical rigor, but serves only as an indication of the origin of the equation.

Earlier in this article, it was stated that the one-electron energies ε_p and ε_d, as well as the total energy of the system, depend on the selection of the arbitrary parameters. In the light of the analysis that we performed, it appeared natural to impose an additional condition on the VCCs in such a manner that the one-electron energies ε_p and ε_d would be independent of the selection of the arbitrary parameters. Using Eq. (17), we can represent ε_p and ε_d as follows:

$$\varepsilon_p = f_p H_{pp} + \varepsilon_p(\text{closed}) + \varepsilon_p(p') + \varepsilon_p(d),$$
$$\varepsilon_d = f_d H_{dd} + \varepsilon_d(\text{closed}) + \varepsilon_d(d') + \varepsilon_d(p). \quad (42)$$

When Eqs. (25)-(27) are taken into account, it can be shown that the requirement that ε_p and ε_d be independent of the selection of the arbitrary parameters can be reduced to the condition

$$\sum_p \varepsilon_p(d) = \sum_d \varepsilon_d(p), \quad (30a)$$

from which Eq. (30) follows directly.*

*After this article was ready for press, the authors were able to obtain an analytical proof of Eq. (30a); this will be published subsequently [22]. From the proof it follows that equations of the type of (30a) have an extremely general character and that they follow from the variational principle.

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