STRUCTURE OF MATTER
AND QUANTUM CHEMISTRY

Symmetric Vector Coupling Coefficients
for Atomic Non-Roothaan States in the d^N Configuration

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Received May 13, 1992

Abstract – The set of equations suggested by the authors earlier for determining the vector coupling coefficients (VCC) a_{mn} and b_{mn} in atoms with the d^N configuration is revised. It is shown that in the basis of complex d orbitals, the equations obtained earlier permitted a symmetric solution, $a_{mn} = a_{nm}$ and $b_{mn} = b_{nm}$. This is not true for real d orbitals considered earlier. The ensuing contradiction between the formal requirement that VCC be symmetric and the physical equivalence of various VCC sets for non-Roothaan terms (nonsymmetric VCC in the basis of real d orbitals and symmetric VCC in the basis of complex d orbitals) is discussed.

As shown earlier, calculating open-shell systems by the restricted Hartree–Fock (RHF) method [1 - 6] requires the determination of vector coupling coefficients (VCC) a_{ij} and b_{ij} entering into the energy functional

$$E_{RHF} = 2\sum_i f_i H_{ii}$$

$$+ \sum_i \sum_j f_i f_j (2a_{ij} J_{ij} - b_{ij} K_{ij}) , \tag{1}$$

where f_i are the occupation numbers of one-electron orbitals, and H_{ii}, J_{ij}, and K_{ij} are the core, Coulomb, and exchange integrals, respectively. The coefficients that we seek, a_{ij} and b_{ij}, are nonvariational quantities in the RHF method. They characterize the state (term) and the configuration of the system [1, 5]. For most frequently occurring open shells, these coefficients are tabulated in [5 - 7]. With more complex systems such as high-symmetry systems in certain (non-Roothaan) states, calculating VCC involves problems discussed in [8 - 12].

The determination of VCC for the most symmetric systems is of special interest, viz. atoms and atomic ions in states arising from the d^N electronic configuration [7, 12 - 14]. In [12], we obtained a set of equations for calculating the corresponding VCC. It follows from [12] that non-Roothaan terms of the d^N configuration can only be described by nonsymmetric VCC matrices: $\|a_{ij}\| \neq \|a_{ij}\|^t$ and/or $|b_{ij}\| \neq \|b_{ij}\|^t$.

Here we treat the set of equations from [12] in more detail, including complex d orbitals in our study. The central result of our analysis is the conclusion that with complex d-orbitals, as opposed to real ones [12], the set of equations from [12] permits both nonsymmetric and symmetric solutions for non-Roothaan terms. The most important inferences from this result are discussed briefly.

VECTOR COUPLING COEFFICIENTS
IN THE BASIS OF COMPLEX d ORBITALS

The set of equations derived in [12] for determining VCC in transition metal atoms and ions with the d^N configuration has the form

$$f^2 \sum_m \sum_n (2a_{mn} J_{mn} - b_{mn} K_{mn})$$

$$= c^{(0)} F^0 + c^{(2)} F^2 + c^{(4)} F^4 , \tag{2}$$

$$\sum_n (2a_{mn} J_{mn} - b_{mn} K_{mn})$$

$$= \sum_n (2a_{\underline{m}n} J_{\underline{m}n} - b_{\underline{m}n} K_{\underline{m}n}) , \tag{3}$$

where the indices m, $\underline{m}$ and n are the numbers of open d shell orbitals ($\underline{m} > m$) with occupation number $f = N/10$; $F^k = F^k(d, d)$ are the Slater–Condon parameters [15]; and $c^{(k)}$ are some numerical coefficients characterizing particular L, S multiplets [15].

Physically, equation (2) establishes equality between atomic energies in two versions of the restricted Hartree–Fock method [12]; these are the atomic theory [15] and the most general version equally applicable to atoms and molecules, the generalized coupling operator (GCO) method [1 - 6]. More explicitly, both the left- and right-hand sides of (2) represent the energy of interelectronic interactions in an open d shell, which is the sole concern of the Slater–Condon theory of atomic multiplets [15].

Equation (3) follows from the condition of equality of one-electron energies $\{\varepsilon_m\}$ for degenerate d orbitals:

$$\varepsilon_m = \varepsilon_{\underline{m}}; \quad (\underline{m} > m). \tag{4}$$

In the GCO method, one-electron energies $\{\varepsilon_m\}$ are the eigenvalues of the general coupling operator $\hat{R}$ [4, equation (3.8)]:

$$\varepsilon_m = \langle \phi_m | \hat{R} | \phi_m \rangle = \langle \phi_m | \hat{F}_m | \phi_m \rangle / f_m, \quad (5)$$

where $\hat{F}_m$ is the Fock operator for orbital ϕ_m. We write $\hat{F}_m$ in the form [4, equation (2.1)] (see also [5, equations (22) through (11)])

$$\hat{F}_m = f_m \left[\hat{H} + \sum_k (2\hat{J}_k - \hat{K}_k) \right.$$
$$\left. + \sum_n f_n (2a_{mn}\hat{J}_n - b_{mn}\hat{K}_n) \right], \quad (6)$$

where the index k numbers the closed-shell orbitals. Using (6) and bearing in mind that $H_{mn} = H_{\underline{mn}}$ and $\sum_{(k)} (2J_{km} - K_{km}) = \sum_{(k)} (2J_{k\underline{m}} - K_{k\underline{m}})$ [1], we obtain (3) directly from equations (4) through (6).

An important point in calculating vector coupling coefficients a_{mn} and b_{mn} for atoms with the d^N configuration is that these coefficients are not defined unambiguously [12]. They depend on the choice of the basis of degenerate d orbitals generally defined with an accuracy to some unitary transformation u. Therefore, if necessary, we will use the denotations $a_{mn}^{(u)}$ and $b_{mn}^{(u)}$, and also $a_{mn}^{(C)}$ and $b_{mn}^{(C)}$, and $a_{mn}^{(R)}$ and $b_{mn}^{(R)}$, where the coefficients with the indices C (complex) and R (real) refer to the complex (7) and real (8) basis sets of d orbitals, respectively:

$$\{ d_0; d_{+1}; d_{-1}; d_{+2}; d_{-2} \}, \quad (7)$$

$$\{ d_{z^2}; d_{xz}; d_{yz}; d_{x^2-y^2}; d_{xy} \}. \quad (8)$$

To determine the unknown VCC $a_{mn}^{(C)}$ and $b_{mn}^{(C)}$ corresponding to a certain L, S multiplet characterized by the coefficients $c^{(0)}$, $c^{(2)}$, and $c^{(4)}$ from (2) and (3), we must express the integrals J_{mn} and K_{mn} for complex d orbitals through the Slater–Condon parameters F^0, F^2, and F^4 [15]:

$$J_{0,0} = F^0 + (36F^2 + 36F^4)/441,$$

$$J_{1,1} = J_{-1,-1} = J_{1,-1} = F^0 + (9F^2 + 16F^4)/441,$$

$$J_{2,2} = J_{-2,-2} = J_{2,-2} = F^0 + (36F^2 + F^4)/441,$$

$$J_{0,1} = J_{0,-1} = F^0 + (18F^2 - 24F^4)/441,$$

$$J_{0,2} = J_{0,-2} = F^0 + (-36F^2 + 6F^4)/441, \quad (9)$$

$$J_{1,2} = J_{1,-2} = J_{-1,2}' = J_{-1,-2}$$
$$= F^0 + (-18F^2 - 4F^4)/441;$$

$$K_{0,1} = K_{0,-1} = (9F^2 + 30F^4)/441,$$

$$K_{0,2} = K_{0,-2} = (36F^2 + 15F^4)/441,$$

$$K_{1,-1} = (54F^2 + 40F^4)/441,$$

$$K_{1,2} = K_{-1,-2} = (54F^2 + 5F^4)/441,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad (9)$$
$$K_{1,-2} = K_{-1,2} = 35F^4/441,$$

$$K_{2,-2} = 70F^4/441.$$

Substituting (9) into (2) and (3) and equating the coefficients of F^0, F^2, and F^4 on the right- and left-hand sides yields two sets of linear equations in 50 ($= 2 \times 5 \times 5$) unknown coefficients $a_{mn}^{(C)}$ and $b_{mn}^{(C)}$:

$$\sum_{j=1}^{50} \lambda_{ij} x_j = c^{(2(i-1))}/f^2, \quad i = 1, 2, 3, \quad (2a)$$

$$\sum_{j=1}^{50} \lambda_{ij} x_j = 0, \quad i = 4, 5, ..., 15, \quad (3a)$$

where x_j are the unknowns that we seek, and $a_{mn}^{(C)}$ and $b_{mn}^{(C)}$, ordered in a certain way ($x_1 = a_{0,0}$, $x_2 = a_{0,1}$, ..., $x_5 = a_{0,-2}$, $x_6 = a_{1,0}$, ..., $x_{25} = a_{-2,-2}$, $x_{26} = b_{0,0}$, ..., $x_{50} = b_{-2,-2}$), and λ_{ij} are the corresponding (real) coefficients.

The set (2a), (3a) comprises 15 linear equations in 50 unknowns, and therefore, there is a certain arbitrariness in determining the VCC. This is typical of VCC calculations on systems with degenerate open shells [7, 9 - 12]. According to [9, 10, and 12], this arbitrariness has no effect on physically meaningful results. Quantum chemical calculations with various VCC sets give the same total energy of the system, density matrix, etc., as required.

The set (2a), (3a) can conveniently be solved in two stages [12]: 1) Equations (3a) are solved to find 12 chosen variables. 2) The obtained 12 variables expressed in terms of the remaining 38 are substituted into three equations (2a). The undefined 35 variables may be required to meet arbitrary additional relations (see below).

The λ_{ij} coefficients are rational, and the set (3a) can therefore be solved in integer numbers; that is, the exact solution can be obtained. In [12], we developed the corresponding procedure as a special integral computer program, and used this program to analyze equations (2a) and (3a) in the basis of real d orbitals ($\lambda_{ij} = \lambda_{ij}^{(R)}$). Here we apply a similar procedure to complex d orbitals (7).

A comparison of the results obtained in [12] and in this work reveals a qualitative difference between general solutions of the sets (2a), (3a) for non-Roothaan terms. These terms in the d^N configuration are characterized by the inequality $c^{(2)} \neq c^{(4)}$ [12]. In basis (8) of real orbitals, the set (2a), (3a) is consistent if and only if one of the matrices of the VCC that we seek is nonsymmetric, that is, $\|a_{mn}\| \neq \|a_{mn}\|'$ and/or $\|b_{mn}\| \neq \|b_{mn}\|'$, in spite of the arbitrariness in the choice of the VCC (15 equations in 50 unknowns) [12]. In basis (7) of complex d orbitals, there arise no restrictions on the a_{mn} and b_{mn} we seek for non-Roothaan terms, and they can be obtained in an arbitrary form, either symmetric or nonsymmetric (depending on various additional relations, see above).

For Roothaan terms (that is, when $c^{(2)} = c^{(4)}$ [12]), neither of the basis sets leads to restrictions on the VCC. Thus we can use the standard Roothaan form [1], $a_{mn} = a$ and $b_{mn} = b$, which also makes the VCC independent of the choice of the basis of degenerate d orbitals [12].

On the other hand, as shown in [16], the VCC a_{mn} and b_{mn} for all states should meet the symmetry condition

$$a_{mn} = a_{nm}, \quad b_{mn} = b_{nm} \tag{10}$$

(see discussion in the next section). Therefore, we consider symmetric solutions in the basis of complex d orbitals in more detail.

To represent the VCC a_{mn} and b_{mn}, which are solutions of (2a), (3a), and (10), in a form convenient for practical use, let us introduce the additional relation

$$a_{mn} = a, \tag{11}$$

which leaves the set (2a), (3a), (10) consistent. (With the relation $b_{mn} = b$ [9 - 12, 17] instead of (11), the set (2a), (3a), (10) is inconsistent when $c^{(2)} \neq c^{(4)}$.)

With relations (10) and (11), we have 16 unknowns to be determined from 15 equations (2a) and (3a). Solving them yields the following expressions for the coefficients a and $b_{mn}^{(C)}$:

$$a = c^{(0)}/50f^2 + \beta/10,$$

$$b_{0,1} = -7\,(-5c^{(2)} + 12c^{(4)})/50f^2 - 4\beta/10, \tag{12}$$

$$b_{1,2} = -7\,(5c^{(2)} + 2c^{(4)})/50f^2 - 4\beta/10;$$

$$b_{0,-1} = b_{1,-2} = b_{-1,2} = b_{0,1},$$

$$b_{-1,-2} = b_{1,2},$$

$$b_{0,2} = (-b_{0,1} + 3b_{1,2})/2,$$

$$b_{0,-2} = (-b_{0,1} + 3b_{1,2})/2, \tag{13}$$

$$b_{1,-1} = (-b_{0,1} + 2b_{1,2})/2 + \beta/2,$$

$$b_{2,-2} = (b_{0,1} + b_{1,2})/4 + \beta/2,$$

$$b_{mm} = \beta; \quad (m = 0, +1, -1, +2, -2),$$

where β is some arbitrary parameter.

For Roothaan terms (that is, when $c^{(2)} = c^{(4)}$), we may introduce yet another relation, $b_{mn} = b$. This gives $b = \beta = -7c^{(2)}/10f^2$, and $a = (2c^{(0)} - 7c^{(2)})/100f^2$. These VCC values coincide with those obtained earlier using the basis set of real d orbitals [12, equation (11)].

DISCUSSION

For proof of the validity of the suggested procedure for calculating the VCC, we refer to a detailed comparison [12, 18] of calculations on transition metal atoms performed using two versions of the restricted Hartree–Fock method and the same basis of real Gauss functions $(14s9p5d)$ / $[8s4p2d]$ from [19]. The results obtained from the generalized coupling operator method [1 - 4] with the VCC from [12] and from the

method based on the Roothaan–Hartree–Fock atomic theory [20] were compared.

In more detail, the comparison procedure was as follows. For each particular L, S multiplet with the d^N configuration, several ab initio GCO calculations with various sets of VCC (symmetric and nonsymmetric for Roothaan terms and various sets of nonsymmetric VCC for non-Roothaan terms) were performed. The results (the total energy, the coefficients of expansion of AOs in the basis (Gauss) functions, etc.) were identical to each other for all terms and coincided completely with the corresponding data [18, 19] obtained using the atomic theory [20].

Considering the last circumstance leads us to conclude that clearly enough, similar GCO calculations on transition metal atoms with complex d orbitals and symmetric VCC, (12) and (13), should give the same results [12, 13, and 14] because the initial equations (2) and (3) for calculating VCC were derived for an arbitrary basis of d orbitals. Therefore various VCC sets for non-Roothaan terms (nonsymmetric [12] in the basis of real d orbitals and symmetric (12) and (13) in the basis of complex orbitals) are physically equivalent to each other.

On the other hand, it follows from [16] that for all states, the VCC a_{mn} and b_{mn} should be symmetric (10). The authors of [16] revised the variational procedure in the RHF method with energy functional (1) to obtain the Fock operator in the form

$$\hat{F}_m = f_m \left[\hat{H} + \sum_k (2\hat{J}_k - \hat{K}_k) \right. $$

$$\left. + \sum_n f_n (2A_{mn}\hat{J}_n - B_{mn}\hat{K}_n) \right], \tag{14a}$$

$$A_{mn} = (a_{mn} + a_{nm})/2, \quad B_{mn} = (b_{mn} + b_{nm})/2. \tag{14b}$$

The coefficients of the Coulomb and exchange operators are different here from those in the usual expression (6).

According to (14), (3) should include the new coefficients A_{mn} and B_{mn} (14b) rather than the VCC a_{mn} and b_{mn}:

$$\sum_n (2A_{mn}J_{mn} - B_{mn}K_{mn})$$

$$= \sum_n (2A_{\underline{m}n}J_{\underline{m}n} - B_{\underline{m}n}K_{\underline{m}n}). \tag{3'}$$

A comparison of the two sets used to determine the VCC, {(2), (3)} and {(2), (3')}, readily shows [16] that they become equivalent (but not identical) if the latter is augmented by (10).

It follows that according to [16], for non-Roothaan terms in the d^N configuration, all the necessary requirements are met only by symmetric VCC (12) and (13) determined using the basis set of complex d orbitals. Similarly, for Roothaan terms, the criterion of [16] selects only symmetric VCC as permitted sets although

both symmetric and nonsymmetric VCC lead to the same SCF solution [12].[1]

We conclude that there is a certain contradiction between the formal requirement that the VCC be symmetric [16] and physical equivalence of various VCC sets in systems with open shells. This contradiction has not yet been resolved (the problem is discussed in more detail in [16, 18, and 21]). It is, however, important that our finding of the symmetric solution ((12) and (13)) for the VCC proves in principle that it is possible to calculate atomic non-Roothaan states in the d^N configuration using the general coupling operator approach [2 - 6] with energy functional (1). Earlier, this possibility was only suggested for states separable by multiplicity [7] (that is, for the Roothaan $^2D(d^1, d^9)$, $^5D(d^4, d^6)$, and $^6S(d^5)$ states).

REFERENCES

1. Roothaan, C.C.J., *Rev. Mod. Phys.*, 1960, vol. 32, no. 2, p. 179.
2. Dyadyusha, G.G. and Kuprievich, V.A., *Teor. Eksp. Khim.*, 1965, vol. 1, no. 3, p. 406.
3. Hirao, K. and Nakatsuji, H., *J. Chem. Phys.*, 1973, vol. 59, no. 3, p. 1457.
4. Hirao, K., *J. Chem. Phys.*, 1974, vol. 60, no. 8, p. 3215.
5. Carbo, R. and Riera, J.M., *A General SCF Theory* (Lecture Notes in Chemistry, vol. 5), Springer-Verlag, Berlin, 1978.
6. Edwards, W.D. and Zerner, M.C., *Theor. Chim. Acta*, 1987, vol. 72, no. 5/6, p. 347.

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[1] We observed a similar identity of Hartree–Fock calculation results obtained using symmetric and nonsymmetric VCC for molecular systems with degenerate open shells [21].

7. Domingo, L.I. and Burgos, J.I., *Studies in Phys. and Theor. Chem.*, 1989, vol. 62, p. 103.
8. Plakhutin, B.N. and Zhidomirov, G.M., *Zh. Strukt. Khim.*, 1986, vol. 27, no. 2, p. 3.
9. Plakhutin, B.N., Klimko, G.T., Mestechkin, M.M., and Zhidomirov, G.M., *Teor. Eksp. Khim.*, 1987, vol. 23, no. 2, p. 129.
10. Klimko, G.T., Mestechkin, M.M., Plakhutin, B.N., et al., *Int. J. Quantum Chem.*, 1990, vol. 37, no. 1, p. 35.
11. Plakhutin, B.N. and Zhidomirov, G.M., *Zh. Fiz. Khim.*, 1988, vol. 62, no. 7, p. 1724.
12. Plakhutin, B.N., Zhidomirov, G.M., and Arbuznikov, A.V., *Int. J. Quantum Chem.*, 1992, vol. 41, no. 2, p. 311.
13. Guest, M.F. and Saunders, V.R., *Mol. Phys.*, 1974, vol. 28, no. 3, p. 819.
14. Poirier, R., Kari, R., and Csizmadia, I., *Handbook of Gaussian Basis Sets* (Physical Sciences Data, vol. 24), Elsevier, Amsterdam, 1985.
15. Slater, J.C., *Quantum Theory of Atomic Structure*, McGraw Hill, New York, Toronto, London, 1960, vols. I, II.
16. Arbuznikov, A.V. and Plakhutin, B.N., *Dokl. Ros. Akad. Nauk* (in press).
17. Evarestov, R.A., *Teor. Eksp. Khim.*, 1982, vol. 18, no. 5, p. 515.
18. Plakhutin, B.N. and Trofimov, A.B., *Zh. Strukt. Khim.*, 1992, vol. 33, no. 6, p. 21.
19. Wachters, A.J.H., *J. Chem. Phys.*, 1970, vol. 52, no. 3, p. 1033.
20. Roothaan, C.C.J. and Bagus, P.S., *Methods in Computational Physics*, 1963, vol. 2, p. 47.
21. Plakhutin, B.N. and Arbuznikov, A.V., *Chem. Phys. Lett.* (in press).