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On the Calculation of $10Dq$

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Abstract: Previous theoretical frameworks for the calculation of $10Dq$ are investigated, and two new such frameworks are proposed. One is based on the ordinary Roothaan formalism for low-spin d^6 octahedral complexes, which have a closed t_{2g} shell, while the other is based on the average-of-configuration Roothaan open-shell formalism. Both methods are applied to the calculation of $10Dq$ for CrF_6^{3-} , FeF_6^{3-} , and NiF_6^{4-} , and reasonable agreement with experiment is found. The Roothaan open-shell formalism is compared with semiempirical methods of calculation, and some close connections are established.

The quantity $10Dq$, or Δ , occurring in ligand-field theory, is difficult to calculate. Even the simplest transition metal complexes, such as MF_6^{3-} , contain 79 or more electrons, and clearly fairly gross approximations or simplifications of some sort are necessary to the calculation. However, the present paper is not so much concerned with the nature of these approximations as with the definition of $10Dq$ itself, and the way in which the precise theoretical definition can affect the calculated value. There is in the literature a partially resolved controversy between two different ways of calculating $10Dq$, that of Sugano and Shulman¹ (SS), whose work on NiF_6^{4-} produced results in excellent agreement with experiment, and that of Watson and Freeman² (WF), whose calculations, although presumably more theoretically rigorous, produced results in rather poor agreement with experiment. The phrase "partially resolved" is used because Sugano himself, in conjunction with Tanabe,³ has taken the WF point of view, as has the present author in a previous publication.⁴

The definition of $10Dq$ is really a simple matter, at least in certain systems. In compounds containing one or nine d electrons, it is the difference in energy between the ground state (${}^2T_{2g}$ or 2E_g) and the first excited state (2E_g or ${}^2T_{2g}$) of the octahedrally symmetric molecule.

Similarly, in systems with two, three, or eight d electrons, $10Dq$ is very close to the energy of the lowest d-d excitation, and this is true for high-spin d^4 , d^6 , and d^7 systems as well. Exact definitions are not possible in the other cases (d^5 , and low-spin d^4 , d^6 , and d^7), but there is no real difficulty in obtaining an *experimental* value of $10Dq$ which gives the best fit to the observed spectrum. The problem arises in deciding which quantity to compare with calculations.

Any definition of $10Dq$ based on state energy differences cannot cover all possible complexes, and thus lacks coherence. A more useful definition can be given in the framework of the orbital picture, which is of course not rigorous, however. It is usual to say that $10Dq$ is the difference in orbital energy between the e_g and t_{2g} molecular orbitals which are largely localized on the transition metal. However, this definition is not true unless, as we shall see, the orbital energy is defined in a very special way. The problem of orbital energy definition is best illustrated if we consider the crude crystal-field model, in which the relevant quantities are e_g and t_{2g} atomic d orbitals.

Let us define the energy of the i th orbital as

$$\epsilon_i = H_i + \sum_j (J_{ij}' - K_{ij}') \quad (1)$$

where the sum over j extends over all singly occupied spin orbitals, and where K_{ij}' is zero unless orbitals i and j contain electrons of the same spin. H_i is the usual

- (1) S. Sugano and R. G. Shulman, *Phys. Rev.*, **130**, 517 (1963).
- (2) R. E. Watson and A. J. Freeman, *ibid.*, **134**, 1526 (1964).
- (3) S. Sugano and Y. Tanabe, *J. Phys. Soc. Japan*, **20**, 1155 (1965).
- (4) P. O'D. Offenhardt, *J. Chem. Phys.*, **47**, 2951 (1967).

one-electron operator consisting of kinetic and nuclear potential energies, while J_{ij}' and K_{ij}' are respectively Coulomb and exchange integrals over the orbitals. This equation can give rise to up to ten different values of ϵ_i , one for each possible spin orbital in the d shell. For example, consider the d^8 configuration of Ni^{2+} . It is not difficult to show that

$$\begin{aligned}\epsilon_t^{f+} &= U + 7A - 14B + 5C = -1.414 \\ \epsilon_t^{f-} &= U + 7A - 10B + 7C = -1.275 \\ \epsilon_e^{f+} &= U + 7A - 14B + 3C = -1.503 \\ \epsilon_e^{e-} &= U + 8A - 6B + 7C = -0.381\end{aligned}\quad (2)$$

as first noted by Watson and Freeman.² Here subscripts t and e refer to t_{2g} and e_g orbitals, while superscripts f and e denote whether the orbital in question is full or empty. Similarly, plus and minus superscripts indicate spin. Calculations of ϵ carried out in this way are valid only within the context of a particular state and component; for Ni^{2+} this was taken as the $M_S = 3/2$ component of the ${}^3A_{2g}$ ground state of the $t_{2g}^6 e_g^2$ configuration. Different orbital energies would obtain if we calculated them for a different state, such as the first excited state ${}^3T_{2g}$. (In eq 2, A , B , and C are the usual Racah parameters,⁵ while U represents the kinetic energy and core potential.)

For a free metal ion it is true that the t_{2g} and e_g orbitals are degenerate in the absence of any interelectronic repulsions among the d orbitals. This is because the inner shells are spherically symmetric. Hence, in crystal field theory, $10Dq$ may be defined as the difference in t_{2g} and e_g orbital energies in the absence of any interelectronic repulsions among the d orbitals. Finally, in ligand field theory, that is, the molecular orbital version of crystal field theory, we may define $10Dq$ as the difference in t_{2g} and e_g orbital energies (for t_{2g} and e_g orbitals largely localized on the metal) in the absence of interelectronic repulsions among these same molecular orbitals. Thus

$$10Dq = \epsilon_t - \epsilon_e - \sum_d (J_{td}' - K_{td}') + \sum_d (J_{ed}' - K_{ed}') \equiv \epsilon_t^0 - \epsilon_e^0 \quad (3)$$

where ϵ_t and ϵ_e are defined as in eq 1. The sums extend over singly occupied spin orbitals of maximum d orbital character.

Part of the difficulty which arises in producing a satisfactory definition of $10Dq$ has its origin in the fact that such a definition invariably involves an open-shell system. The definition of orbital energy given in eq 1 is really satisfactory only for closed-shell systems, and definitions of orbital energy for open-shell systems are usually formulated in such a way as to preserve the degeneracy of a set of orbitals belonging to the same irreducible representation. Such definitions are considered in a following section of the present paper.

Comparisons among Computational Frameworks

The most straightforward way of calculating $10Dq$ is to calculate the total energy of two suitable states, such as the ${}^3A_{2g}$ and ${}^3T_{2g}$ states of the d^8 system. There is no

(5) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, England, 1961, p 83.

possible theoretical objection to this method, since, as noted, it is completely rigorous and does not require one to use the molecular orbital method. Thus, Simanek and Stroubek⁶ have obtained $10Dq$ by this method for MnF_6^{4-} using a function constructed from a superposition of several configurations, and de Laat⁷ has treated TiF_6^{3-} via an unrestricted Hartree-Fock calculation on the ground and excited states. However, there are two disadvantages to this scheme. First, it cannot be used with approximate methods in which total energies are not obtainable. Secondly, the scheme suffers in not being based on orbitals, since it is an orbital picture which is in turn most completely compatible with ligand field theory itself.

Within molecular orbital theory there are several other possible points of view on the proper method of calculating $10Dq$ in addition to that expressed at the beginning of this paper. We consider first the point of view of Watson and Freeman.² They begin by considering the mixing of the d orbitals with the symmetry orbitals of the ligands. For example, the bonding t_{2g} orbitals, largely localized on the ligands, can be written as

$$\psi_t^b = N_t(\chi_t + \gamma_t \varphi_t) \quad (4)$$

where χ_t is itself a linear combination of ligand $2p_\pi$ atomic orbitals (see ref 1 for details). In addition, φ_t is a d orbital of t_{2g} symmetry, N_t a normalizing factor, and γ_t a small number known as the covalency parameter. In the crystal-field limit, $\gamma_t = 0$. Similarly, the antibonding t_{2g} orbitals of fundamental interest may be written as

$$\psi_t^a = N_t'(\varphi_t - \lambda_t \chi_t) \quad (5)$$

Since ψ_t^a and ψ_t^b are orthogonal, γ and λ are not independent, and in fact

$$\lambda = \frac{\gamma + S}{1 + \gamma S} \quad (6)$$

$$S = \langle \varphi_t | \chi_t \rangle$$

In a system in which ψ_t^a and ψ_t^b are both occupied, the total energy of the system no longer depends on γ (or λ). This is because the mixing of filled shells is irrelevant to any physical property. Since the orbital energies of ψ_t^a and ψ_t^b depend on γ , they can have any values although their values are related to each other. Watson and Freeman therefore calculate a value of γ appropriate to an orbital ψ_t^b whose antibonding counterpart ψ_t^a is empty. In this way the formalism of the restricted Hartree-Fock method is preserved, and all orbitals ψ_t^b have the same value of γ . Since this choice of γ determines λ , it determines the orbital energy of ψ_t^a , and thus the value of $10Dq$. The values thus calculated are in poor agreement with experiment. Furthermore, $10Dq$ is obtained as a difference in the orbital energy of unoccupied orbitals, a somewhat peculiar point of view physically speaking.

The argument of Watson and Freeman does not apply if additional orbitals are added to the basis set. Thus, once $3p_\pi$ ligand orbitals or metal 4d are added, such that

$$\psi_t^a = N_t'(\varphi_t - \lambda \chi_t - \lambda' \chi_t' + k \varphi_t') \quad (7)$$

then λ is no longer completely determined by γ , pro-

(6) E. Simanek and Z. Stroubek, *Phys. Status Solidi*, **4**, 251 (1964).

(7) F. L. M. A. H. de Laat, Thesis, Eindhoven, 1968.

vided of course that the number of electrons in the orbitals is not increased along with the size of the basis. The approach of Watson and Freeman is thus unsatisfactory if the basis set is enlarged. An additional argument to be brought against the scheme of Watson and Freeman is that, in practice, orbital energies do not much depend on the size of the basis. Thus, although the orbitals they employ may satisfy the requirements of restricted Hartree-Fock theory, they probably do not correspond to the orbital energies to be found using a larger basis, nor would their method retain its rigor in such a basis.

Another different point of view is that of the conventional molecular orbital theory for closed shells. Technically, this scheme can be applied only to the configuration t_{2g}^6 , but a heuristic extension to open shells is not difficult. Consider the t_{2g}^6 case. The total energy of the ground state ${}^1A_{1g}$ is

$$E({}^1A_{1g}) = 2\sum_i H_i + \sum_i \sum_j (2J_{ij} - K_{ij}) = \sum_i (H_i + \epsilon_i) \\ \epsilon_i = H_i + \sum_j (2J_{ij} - K_{ij}) \quad (8)$$

Here the sums extend over doubly occupied spatial orbitals; $K_{ii} = J_{ii}$. The energy of the excited state ${}^1T_{2g}$, produced by exciting an electron from the d_{xy} -type molecular orbital to the d_{z^2} , is⁸

$$E({}^1T_{2g}) = E({}^1A_{1g}) + H(\theta) - H(\zeta) + \sum_i (2J_{i\theta} - K_{i\theta}) - \\ \sum_i (2J_{i\zeta} - K_{i\zeta}) - J_{i\theta} + 2K_{i\theta} \quad (9)$$

Therefore

$$E({}^1T_{2g}) - E({}^1A_{1g}) = \epsilon_\theta - \epsilon_\zeta - J_{\zeta\theta} + 2K_{\zeta\theta} \quad (10)$$

All orbital energies and related integrals are calculated with the operators and wave functions appropriate to the ground state.

Unfortunately, the states ${}^1T_{2g}$ and ${}^1A_{1g}$ do not differ merely by $10Dq$. In fact, even in the absence of a ligand field

$$E^0({}^1T_{2g}) - E^0({}^1A_{1g}) = 2J_{\theta\xi} + 2J_{\theta\eta} + 2J_{\theta\zeta} - \\ K_{\theta\xi} - K_{\theta\eta} - K_{\theta\zeta} - 2J_{\zeta\xi} - 2J_{\zeta\eta} - \\ J_{\zeta\zeta} + K_{\zeta\xi} + K_{\zeta\eta} \quad (11)$$

Since the energy difference in the presence of a ligand field is greater than the energy difference in the absence of a ligand field by $10Dq$, we obtain

$$10Dq = \epsilon_\theta - \epsilon_\zeta - 2J_{\theta\xi} - 2J_{\theta\eta} - 2J_{\theta\zeta} + 2J_{\zeta\xi} + \\ 2J_{\zeta\eta} + 2J_{\zeta\zeta} + K_{\theta\xi} + K_{\theta\eta} + K_{\theta\zeta} - \\ K_{\zeta\xi} - K_{\zeta\eta} - K_{\zeta\zeta} \quad (12)$$

This expression, however, is identical with eq 3. We have thus proved that the conventional molecular orbital method of calculating excited state energies, *i.e.*, eq 10, is essentially identical with the method developed at the beginning of the present paper. Since the latter method is readily generalized to any system with either closed or open shells, we can always follow the formalism of eq 3.

There is one ambiguity inherent in the use of eq 3. It is possible to choose the orbitals φ_t and φ_e in many

(8) We employ the usual abbreviations $\xi = yz$, $\eta = xz$, $\zeta = xy$, $\theta = z^2$, and $\epsilon = x^2 - y^2$.

ways: in the selected component of the ground state they may both be filled, both empty, or one filled and one empty. It is easy to show that these choices will give rise to different values of $10Dq$ unless all orbitals have the same value of γ . Since this condition is not always satisfied when dealing with open shells, the ambiguity remains. The solution is to always take a *filled* orbital for φ_t but an *empty* orbital for φ_e . In this way the analogy with the t_{2g}^6 case is fully preserved.

Two additional points are worth noting. First, the calculation of Sugano and Shulman¹ is incorrect, although their method at first may seem similar to eq 3. Their error lies partially in using a *filled* orbital for φ_e . They also left an electron out of their Hamiltonian. Secondly, the remarks of Watson and Freeman are correct insofar as they apply to the calculation of spin densities. Thus, a second defect of the calculation of Sugano and Shulman is that their spin densities are incorrectly obtained.

Open-Shell, Average-of-Configuration Framework

The definitions given thus far lack physical appeal since $10Dq$ is not expressed simply as a difference of orbital energies and since orbitals belonging to a given irreducible representation are not necessarily degenerate. These difficulties are avoided in the Roothaan⁹ open-shell method, which guarantees that the Fock operator belongs to the totally symmetric representation of the applicable symmetry group, here octahedral. Roothaan-Fock operators can be defined for each state, although in fact the simple Roothaan formalism cannot be applied to all states of d^n systems. (A more complicated formalism¹⁰ can be used, however.) For the sake of simplicity, and in order to bring out the explicit relationships among $10Dq$ values for systems with differing numbers of d electrons, we will use the operator appropriate to no particular state, but valid instead for the average state¹¹ of a configuration. Even this choice of state is not unambiguous, since in ligand-field theory we deal with more than one configuration, $t_{2g}^p e_g^q$ and $t_{2g}^{p-1} e_g^{q+1}$, for example. We therefore take the operator appropriate to the average state of the entire d^n configuration. This is fully in the spirit of ligand-field theory, which ordinarily recognizes but a single value of $10Dq$ for all possible states. In the same way, the average-of-configuration Roothaan formalism recognizes a single $10Dq$ and a single set of molecular orbitals for all possible ligand-field states.

In the language of the original paper by Roothaan, the fractional occupancy of the d shell is

$$f = n/10 \quad (13)$$

Furthermore, for the average-of-configuration, the constants a and b are given as

$$a = b = 10(n-1)/9n \quad (14)$$

Values of α and β are readily derived since

$$\alpha = \beta = (1-a)/(1-f) = 10/9n \quad (15)$$

The open-shell Fock operator may therefore be written

(9) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).
 (10) C. C. J. Roothaan and P. S. Bagus in "Methods in Computational Physics," Vol. IV, B. Alder, Ed., Academic Press, New York, N. Y., 1963, p 47 ff.
 (11) J. C. Slater, "Quantum Theory of Atomic Structure," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 27.

in the form

$$\mathfrak{F}_O = \mathbf{H} + \sum_i (2\mathbf{J}_i - \mathbf{K}_i) + \frac{(n-1)}{9} \times \sum_d (2\mathbf{J}_d - \mathbf{K}_d) + 2\alpha\mathbf{L}_C - \beta\mathbf{M}_C \quad (16)$$

The sum over i extends over all closed shells, while the sum over d extends over all antibonding molecular orbitals of predominant d character, regardless of occupancy. \mathbf{H} , \mathbf{J} , and \mathbf{K} are one-electron, Coulomb, and exchange operators, respectively, while \mathbf{L}_C and \mathbf{M}_C are the Roothaan coulomb and exchange coupling operators. The Fock operator appropriate to the closed shells, although not used in the present paper, is

$$\mathfrak{F}_C = \mathbf{H} + \sum_i (2\mathbf{J}_i - \mathbf{K}_i) + f \sum_d (2\mathbf{J}_d - \mathbf{K}_d) + 2\alpha\mathbf{L}_O - \beta\mathbf{M}_O \quad (17)$$

The two Fock operators satisfy eigenvalue equations of the form

$$\begin{aligned} \mathfrak{F}_C \psi_i &= \epsilon_i \psi_i \\ \mathfrak{F}_O \psi_d &= \epsilon_d \psi_d \end{aligned} \quad (18)$$

where ψ_i and ψ_d are closed-shell and open-shell molecular orbitals, respectively. Furthermore, the total average-of-configuration energy is given as

$$E = \sum_i (H_i + \epsilon_i) + f \sum_d (H_d + \epsilon_d) \quad (19)$$

All the sums over d can be further broken down into sums over t_{2g} and e_g orbitals, and, for example, the total energy can be written in the form

$$\bar{E} = \sum_i (H_i + \epsilon_i) + f \sum_t (H_t + \epsilon_t) + f \sum_e (H_e + \epsilon_e) \quad (20)$$

By symmetry, all t_{2g} and e_g orbitals have the same energy, so

$$\bar{E} = \sum_i (H_i + \epsilon_i) + 3f(H_t + \epsilon_t) + 2f(H_e + \epsilon_e) \quad (21)$$

It is easy to prove that ϵ_t and ϵ_e are equal for the free metal ion. Proving that $10Dq$ is their difference in a ligand field is more difficult. According to Roothaan⁹

$$E = 2 \sum_i H_i + \sum_i \sum_j (2J_{ij} - K_{ij}) + f \left[2 \sum_d H_d + f \sum_d \sum_{d'} (2aJ_{dd'} - bK_{dd'}) + 2 \sum_i \sum_d (2J_{id} - K_{id}) \right] \quad (22)$$

The sums over i and j extend over doubly occupied closed-shell orbitals, while the sums over d and d' extend over the open t_{2g} and e_g shells. Consider the d^1 configuration, in which $a = b = 0, f = 1/10$. There are two ligand field states, and it is easy to show that their energies are

$$\begin{aligned} E(^2T_{2g}) &= 2 \sum_i H_i + \sum_i \sum_j (2J_{ij} - K_{ij}) + H_t + \sum_i (2J_{it} - K_{it}) \\ E(^2E_g) &= 2 \sum_i H_i + \sum_i \sum_j (2J_{ij} - K_{ij}) + H_e + \sum_i (2J_{ie} - K_{ie}) \end{aligned} \quad (23)$$

In terms of \bar{E} we obtain

$$E(^2T_{2g}) = \bar{E} + \frac{2}{5}(H_t - H_e) + \frac{2}{5} \sum_i (2J_{it} - K_{it}) - \frac{2}{5} \sum_i (2J_{ie} - K_{ie}) \quad (24)$$

$$E(^2E_g) = \bar{E} - \frac{3}{5}(H_t - H_e) - \frac{3}{5} \sum_i (2J_{it} - K_{it}) + \frac{3}{5} \sum_i (2J_{ie} - K_{ie})$$

Thus

$$E(^2E_g) - E(^2T_{2g}) = \epsilon_e - \epsilon_t \quad (25)$$

Note that the coupling operators \mathbf{L}_C and \mathbf{M}_C give no contribution to ϵ .

We have verified that

$$10Dq = \epsilon_e - \epsilon_t \quad (26)$$

for the d^1 configuration. Similar proofs can presumably be given for any other configuration, although this would be tedious. Alternatively, eq 26 may be regarded as the open-shell definition of $10Dq$, since in fact it satisfies all criteria for a suitable definition within an orbital picture. Note that here ϵ is given by eq 18, and not by eq 1.

Matrix Elements in the Open-Shell Framework

In the next section we will consider specific calculations of $10Dq$ on CrF_6^{3-} , FeF_6^{3-} , and NiF_6^{4-} , using both the "closed-shell" formalism of eq 3 (with ϵ determined by eq 1) and the "open-shell" formalism of eq 26 (with ϵ determined by eq 18). First we must develop the method of evaluating the matrix elements necessary to the calculations. In the closed-shell formalism the evaluation of matrix elements closely follows the method given previously⁴ for the WF formalism. We therefore do not consider the details. The open-shell formalism is quite different from that of Watson and Freeman, however, and so we outline the numerical methods involved.

First of all, there is a problem involving the coupling operators \mathbf{L}_C and \mathbf{M}_C . If the basis set is restricted to the Hartree-Fock orbitals of the free ligands and the metal ion, the basis will be insufficiently large to treat the coupling operators in an entirely rigorous way. Since, for this basis, γ determines λ (see eq 6), all integrals involving \mathbf{L}_C and \mathbf{M}_C will vanish on account of the fixed orthogonality of the bonding and antibonding molecular orbitals. This inconsistency is due to an excess of constraints in the Roothaan open-shell equations and cannot be removed without enlarging the basis. However, we may hope that omitting the coupling operators entirely will not prove too drastic an approximation, and will lead to results not too different from those which would be obtained by employing a larger basis and keeping the coupling operators.

We next consider the matrix elements of \mathfrak{F}_O using the "ionic approximation" in which S and γ are assumed to be zero. Then we can divide the potential energy into a part originating on the metal and a part due to the ligands

$$\mathfrak{F}_O^0 = -1/2\nabla^2 + V_M + \sum_i V_{L_i} \quad (27)$$

Table I. Matrix Elements of the Self-Consistent Open-Shell Roothaan-Fock Operator \mathcal{F}_0 for NiF_6^{4-} ^a

| t_{2g} | χ_r | φ_d | e_g | χ_s | χ_p | φ_d |
|----------|----------|-------------|--------|----------|----------|-------------|
| 0.124 | -0.044 | -0.785 | 0.040 | -0.078 | | |
| -0.044 | 0.303 | 0.040 | 0.084 | -0.110 | | |
| | | -0.078 | -0.110 | 0.258 | | |

^a All matrix elements and orbital energies in these tables are in atomic units.

Table II. Orbital Coefficients and Energies Using the Open-Shell Roothaan-Fock operator \mathcal{F}_0

| | e_g | χ_s | χ_p | φ_d | ϵ | t_{2g} | χ_r | φ_d | ϵ |
|---------------------|---------|----------|----------|-------------|------------|----------|----------|-------------|------------|
| NiF_6^{4-} | 0.9989 | 0.0008 | 0.0132 | -0.785 | 0.9490 | 0.2542 | 0.110 | | |
| | 0.0021 | 0.8586 | 0.4226 | 0.028 | -0.3238 | 0.9699 | 0.326 | | |
| | -0.1132 | -0.5294 | 0.9180 | 0.359 | | | | | |
| CrF_6^{3-} | 0.9907 | 0.1140 | 0.0531 | -1.213 | 0.9369 | 0.2703 | -0.322 | | |
| | -0.1273 | 0.8824 | 0.3366 | -0.450 | -0.3650 | 0.9682 | 0.316 | | |
| | -0.1436 | -0.4870 | 0.9612 | 0.400 | | | | | |
| FeF_6^{3-} | 0.9926 | 0.1172 | 0.0524 | -1.154 | 0.9137 | 0.3402 | -0.270 | | |
| | -0.1222 | 0.8626 | 0.3904 | -0.393 | -0.4141 | 0.9438 | 0.201 | | |
| | -0.1138 | -0.5131 | 0.9336 | 0.264 | | | | | |

Table III. Matrix Elements of the Self-Consistent Closed-Shell Formalism (Eq 3) for NiF_6^{4-} ^a

| t_{2g} | χ_r | φ_d | e_g | χ_s | χ_p | φ_d |
|----------|----------|-------------|--------|----------|----------|-------------|
| 0.193 | -0.030 | -0.662 | 0.040 | -0.081 | | |
| -0.030 | 0.219 | 0.040 | 0.056 | -0.068 | | |
| | | -0.082 | -0.068 | 1.098 | | |

^a Corrections to diagonal elements are not included.

Table IV. Orbital Coefficients and Energies Using the "Closed-Shell" Formalism of Eq 3

| | e_g | χ_s | χ_p | φ_d | ϵ | t_{2g} | χ_r | φ_d | ϵ |
|---------------------|---------|----------|----------|-------------|------------|----------|----------|-------------|------------|
| NiF_6^{4-} | 0.9991 | -0.0080 | 0.0036 | -0.662 | 0.7795 | 0.5725 | 0.162 | | |
| | 0.0472 | 0.9884 | 0.0954 | 0.049 | -0.6306 | 0.8231 | 0.257 | | |
| | -0.1305 | -0.1830 | 1.0062 | 1.160 | | | | | |
| FeF_6^{3-} | 0.9966 | 0.0699 | 0.0397 | -0.996 | 0.1131 | 0.9846 | -0.458 | | |
| | -0.0465 | 0.9527 | 0.1977 | -0.196 | 0.9968 | -0.1919 | -0.061 | | |
| | -0.1330 | -0.3296 | 0.9930 | 0.824 | | | | | |
| CrF_6^{3-} | 0.9967 | 0.0617 | 0.0315 | -0.997 | 0.2340 | 0.9493 | -0.302 | | |
| | -0.0502 | 0.9399 | 0.2205 | -0.203 | 0.9773 | -0.3298 | -0.052 | | |
| | -0.1494 | -0.3761 | 0.9952 | 0.694 | | | | | |

If we choose the metal d orbitals as solutions to the atomic average-of-configuration problem

$$(-\frac{1}{2}\nabla^2 + V_M)|\varphi_d\rangle = \epsilon_d|\varphi_d\rangle \quad (28)$$

It is therefore easily proved that

$$\langle\varphi_d|\mathcal{F}_0^0|\varphi_d\rangle = \epsilon_d + \sum_{i=1}^6\langle\varphi_d|V_{L_i}|\varphi_d\rangle$$

$$\langle\chi_k|\mathcal{F}_0^0|\chi_k\rangle = \epsilon_k + \sum_{i=2}^6\langle\varphi_{k1}|V_{L_i}|\varphi_{k1}\rangle + \langle\chi_k|V_M|\chi_k\rangle \quad k = 2p \text{ or } 2s \quad (29)$$

$$\langle\chi_k|\mathcal{F}_0^0|\varphi_d\rangle = S(\epsilon_d + \epsilon_k) + \langle\chi_k|\frac{1}{2}\nabla^2|\varphi_d\rangle + \sum_{i=2}^6\langle\varphi_{k1}|V_{L_i}|\varphi_d\rangle$$

The third equation given is especially simple, since it involves only one-electron integrals plus an easily approximated⁴ three-center integral. Note that eq 29 is related to various semiempirical and/or approximate

methods of matrix element evaluation, such as those of Schreiner and Brown¹² and of Caulton and Fenske.¹³

The zero-order "ionic Hamiltonian" matrix elements cannot be used as is, and corrections must be made for self-consistency. These are easily done using the techniques of the previous paper.⁴ Since there are no fully occupied or empty antibonding orbitals, one must calculate the population of each atomic orbital at every iterative stage and in this way obtain the corrections to the matrix elements of \mathcal{F}_0^0 .

Self-consistent Hamiltonian matrix elements in the open-shell formalism are reported in Table I for NiF_6^{4-} . (The overlap matrices have been given previously.) Resulting orbitals and orbital energies for CrF_6^{3-} , FeF_6^{3-} , and NiF_6^{4-} are given in Table II. Similar data for the closed-shell formalism are reported in Table III and Table IV. Table V gives calculated values of $10Dq$.

Discussion

By and large, the agreement between experimental and theoretically calculated values of $10Dq$ is gratifying. The one exception occurs in the "closed-shell" calculation on NiF_6^{4-} , in which, due to heavy metal-ligand mixing, it is difficult to determine which t_{2g} orbital is the one of greatest d character.

It is of interest to break down a typical open-shell calculation of $10Dq$ into its component stages. This is done in Figure 1 and in Table V. At the first level we can consider the difference between $\langle\varphi_e|V_L|\varphi_e\rangle$ and $\langle\varphi_t|V_L|\varphi_t\rangle$. This is the crystal-field value of $10Dq$, and, as noted in the literature, it is negative. At the second stage, we have the difference between the matrix elements $\langle\varphi_e|\mathcal{F}_0|\varphi_e\rangle$ and $\langle\varphi_t|\mathcal{F}_0|\varphi_t\rangle$. This difference is even more negative, due to the unequal influence of covalent donation of charge to the metal on φ_e and φ_t . Finally, when mixing of metal and ligand orbitals is considered explicitly, the difference between $\langle\psi_e^a|\mathcal{F}_0|\psi_e^a\rangle$ and

(12) A. F. Schreiner and T. L. Brown, *J. Am. Chem. Soc.*, **90**, 3366 (1968).

(13) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968).

Table V. Comparison of Calculated and Experimental Values of $10Dq^a$

| | | NiF ₆ ⁴⁻ | FeF ₆ ³⁻ | CrF ₆ ³⁻ |
|------------------------|---|--------------------------------|--------------------------------|--------------------------------|
| Closed-shell formalism | $10Dq$ | 0.0833 (18,300) | 0.0498 (10,950) | 0.0578 (12,700) |
| Open-shell formalism | $\langle \varphi_e \mathcal{F}_0^0 \varphi_e \rangle - \langle \varphi_t \mathcal{F}_0^0 \varphi_t \rangle$ | -0.0163 | -0.0220 | -0.0327 |
| | $\langle \varphi_e \mathcal{F}_0^0 \varphi_e \rangle - \langle \varphi_t \mathcal{F}_0^0 \varphi_t \rangle$ | -0.0449 | -0.0488 | -0.0639 |
| | $10Dq$ | 0.0331 (7250) | 0.0634 (13,900) | 0.0841 (18,450) |
| | $10Dq$, exptl, cm ⁻¹ | 7250 | 14,000 | 15,300 |

^a For simplicity, the sum in eq 3 has been evaluated using *atomic* orbitals. Values in parentheses in cm⁻¹.

$\langle \psi_t^a | \mathcal{F}_0 | \psi_t^a \rangle$ is correctly positive. It is to be noted that the usual semiempirical and/or approximate schemes do not take the first two effects into account.

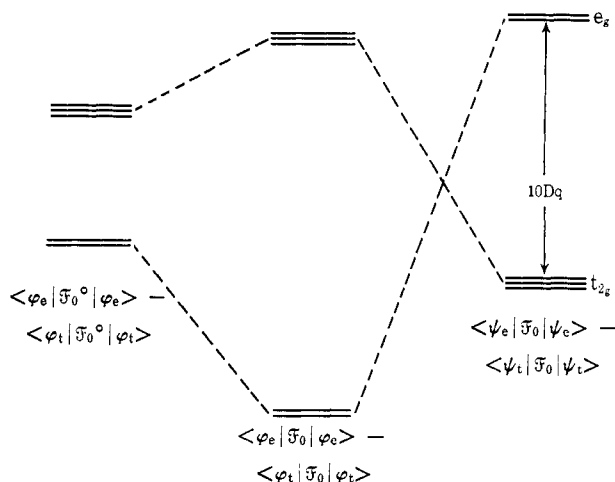


Figure 1. Stages in the open-shell calculation of $10Dq$ for NiF₆⁴⁻. Note that $10Dq$ is negative until the final stage of the calculation.

The information given for the closed-shell formalism is insufficient to obtain spin densities at the fluoride nuclei except in the case of NiF₆⁴⁻. For this molecule the results are substantially the same as the (rather poor) results obtained in the WF formalism given in the previous paper. It appears, therefore, that the basis is insufficiently flexible to give good spin densities. On the other hand, it is easy to show that the data given in Table II (for the open-shell formalism) predict excessively large spin densities. However, it is not clear in the first place that spin densities, which are valid only

in the ground state, *should* be correctly calculated in the average-of-configuration formalism. Alternatively, the disagreement may depend on the neglect of the coupling operators. In any case, the WF formalism, which refers to a particular state of a particular configuration, is more rigorously applicable to the calculation of spin densities than any average-of-configuration (*dⁿ* average) method. An improved and more rigorous formalism for spin densities would involve the average of a $t_{2g}^2 e_g^2$ configuration, rather than the average of all possible states in the *dⁿ* system.

Conclusions

One purpose of this paper has been to provide a framework for the calculation of $10Dq$ which is compatible with the conventional ligand-field picture. This has been done with the open-shell, average-of-configuration formalism. The quantity $10Dq$ is expressed as the simple difference of orbital energies, and the matrix elements involved show a close resemblance to certain approximate schemes. A second purpose has been to attempt to provide numerical techniques for estimating $10Dq$ and determining the relative importance of different physical influences on its value. This second task has been approached from two independent viewpoints, closed-shell as well as open-shell Hartree-Fock theory. One may thus have some confidence that the present methods of calculation can be extended to other metal-ligand systems.

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