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On the Calculation of 10*Dq*. II. Approximations in the Open-Shell Treatment

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Abstract: A systematic set of approximations is developed for the calculation of matrix elements in the Roothaan open-shell formalism for the calculation of 10*Dq* as previously formulated by the present author. The approximations are applied to NiF_6^{4-}, and good agreement with the author's previous, less approximate calculation is obtained. Both calculations, which are strictly nonempirical, yield values of 10*Dq* in reasonable agreement with experiment.

We have previously shown[1] that the quantity 10*Dq*, occurring in ligand-field theory, cannot be regarded as a simple orbital energy difference unless the Fock operator determining the e_g and t_{2g} energies is defined in a rather special way. Specifically, if we take as our Fock operator the average-of-configuration Roothaan open-shell operator, then indeed

$$10Dq = \epsilon_e - \epsilon_t \qquad (1)$$

The averaging is done over all states of the d^n system; hence 10*Dq* as defined is valid for all possible ligand-field states, and a single set of molecular orbitals is generated. The molecular orbital forms and their energies are determined by solving pseudo-eigenvalue equations of the form

$$\mathfrak{F}_O\psi_i = \epsilon_i\psi_i \qquad (2)$$

for $i = t_{2g}$ and e_g. The open-shell Fock operator is defined as

$$\mathfrak{F}_O = \mathbf{H} + \sum_i(2\mathbf{J}_i - K_i) + \left(\frac{n-1}{9}\right)\sum_d(2\mathbf{J}_d - \mathbf{K}_d) + 2\alpha\mathbf{L}_C - \beta\mathbf{M}_C \qquad (3)$$

where **H** is the usual one-electron operator; **J** and **K** are coulomb and exchange operators, respectively, and $\mathbf{L}_C$ and $\mathbf{M}_C$ the Roothaan coulomb and exchange coupling operators. The sum over *i* extends over all closed shells in the molecule, while the sum over d extends over all antibonding molecular orbitals of predominantly d character, regardless of occupancy.

The author is indebted to an alert referee for pointing out that eq 1 is not entirely consistent with the usual definition of 10*Dq* as given by eq 3 of paper I. (He has also pointed out that eq 3 contains a rather obvious and astonishing sign error!) The expression $\epsilon_e - \epsilon_t$ contains the term

$$\frac{n-1}{9}\sum_d(\langle\psi_e|2\mathbf{J}_d - \mathbf{K}_d|\psi_e\rangle - \langle\psi_t|2\mathbf{J}_d - \mathbf{K}_d|\psi_t\rangle) \qquad (4)$$

which vanishes only if $n = 1$ or if ψ_e and ψ_t have the same radial dependence. Nevertheless, *either* definition is suitable, although they are not completely consistent with each other. The possibility of ambiguity arises from the fact that interelectronic repulsions among the t_{2g} and e_g orbitals can be described by three independent parameters (*A*, *B*, and *C*) when these orbitals are d orbitals, while up to ten parameters may be necessary in general.[2] As noted by Griffith,[2a] one consequence is that the free-ion ground state may be split even when 10*Dq*, as defined by either of the above definitions, is zero. In practice, the numerical differences among the different kinds of 10*Dq* will be small as long

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[1] Part I: P. O. Offenhartz, *J. Amer. Chem. Soc.*, **91**, 5699 (1969).

[2] J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, 1961, p 230; (a) p 192; (b) p 409.

as the ψ_i's are close in form to the d orbitals. That this is indeed a good assumption is shown by the well-known observation that a *single* value of $10Dq$ will fit *several* bands in the spectrum of a transition metal complex. However, the first sentence following eq 26 of paper I is incorrect. Not all definitions of $10Dq$ are equivalent!

The molecular orbitals ψ_i are expressed as linear combinations of atomic orbitals centered on the metal and the ligands. The treatment is simplified somewhat if we employ from the start linear combinations of ligand orbitals, χ, having the appropriate symmetry properties ("symmetry orbitals"); the explicit forms of the χ are given in texts on ligand-field theory and in ref 3. We write[3]

$$\psi_t^{b} = N_t(\chi_t + \gamma_t \varphi_t) \qquad (5)$$

for the bonding t_{2g} orbital largely localized on the ligand $2p_\pi$ orbitals. The quantity γ_t is the covalency parameter, equal to zero in the crystal-field limit, while φ_t is a d orbital of t_{2g} symmetry. The corresponding antibonding orbital

$$\psi_t^{a} = N_t'(\varphi_t - \lambda_t \chi_t) \qquad (6)$$

is largely localized on the metal, and it is the energy of this molecular orbital, and the e_g orbital ψ_e^{a}, in which we are fundamentally interested. However, γ and λ are not independent, since ψ_t^{a} and ψ_t^{b} are orthogonal, and

$$\begin{aligned} \lambda_t &= (\gamma_t + S_t)/(1 + \gamma_t S_t) \\ S_t &= \langle \varphi_t | \chi_t \rangle \end{aligned} \qquad (7)$$

In order to evaluate ϵ_e and ϵ_t we need to calculate the matrix elements $\langle \varphi_t | \mathcal{F}_O | \varphi_t \rangle$, $\langle \varphi_t | \mathcal{F}_O | \chi_t \rangle$, and so forth. In part I we have done this nonempirically for NiF_6^{4-}, FeF_6^{3-}, and CrF_6^{3-}, and have determined values of $10Dq$ in reasonable agreement with experiment (worst case error ~20%). What we wish to show in the present paper is that these results can be repeated without the necessity of detailed evaluation of difficult many-centered integrals, and that, in a reasonably simple numerical scheme, equally good results may be obtained. We do this by considering the matrix elements for NiF_6^{4-} alone.

Integral Approximations

As usual, we break up the integral evaluation problem into two parts, the first being the matrix elements of $\mathcal{F}_O$ in the "ionic approximation" and the second being the corrections to this. We begin by dividing the potential energy into a part originating on the metal and a part due to the ligands

$$\mathcal{F}_O^{0} = -{}^1/_2\nabla^2 + V_M + \sum_i V_{Li} \qquad (8)$$

As shown in part I (note that we rather arbitrarily[1] neglect the coupling operators $\mathbf{L}_C$ and $\mathbf{M}_C$)

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

$$\langle \chi_k | \mathcal{F}_O^{0} | \chi_k \rangle = \epsilon_k + \sum_{i=2}^{6} \langle \varphi_{k1} | V_{Li} | \varphi_{k1} \rangle + \langle \chi_k | V_M | \chi_k \rangle \qquad k = 2p \text{ or } 2s \qquad (9)$$

$$\langle \chi_k | \mathcal{F}_O^{0} | \varphi_d \rangle = S(\epsilon_d + \epsilon_k) + \langle \chi_k | {}^1/_2\nabla^2 | \varphi_d \rangle + \sum_{i=2} \langle \varphi_{k1} | V_{Li} | \varphi_d \rangle$$

We next introduce the following approximations (all integrals and distances in atomic units).

$$\begin{aligned} \langle \varphi_d | V_{Li} | \varphi_d \rangle &= 1/R_{ML} \\ \langle \varphi_{k1} | V_{Li} | \varphi_{k1} \rangle &= 1/R_{L1Li} \\ \sum_{i=2}^{6} \langle \varphi_{k1} | V_{Li} | \varphi_{k1} \rangle &= (2\sqrt{2} + {}^1/_2)/R_{ML} \sim 3.328/R_{ML} \qquad (10) \\ \langle \chi_k | V_M | \chi_k \rangle &= -C/R_{ML} \\ \sum_{i=2}^{6} \langle \varphi_{k1} | V_{Li} | \varphi_d \rangle &= \langle \chi_k | \varphi_d \rangle (8/\sqrt{5} + {}^2/_3)/R_{ML} \sim 4.244 \langle \chi_k | \varphi_d \rangle / R_{ML} \end{aligned}$$

The R's are the internuclear distances between the nuclei indicated by subscripts. The constant C is determined by the net charge on the metal and the number of d electrons, but is *not* precisely equal to the net charge on the metal as might be expected. Because of the form of Roothaan open-shell operator in eq 3, the d electrons in the ionic approximation are counted in an unusual way. Thus, the ligands see the coulomb field of $10(n-1)/9$ d electrons, in addition to the field of the metal core. In general, for a metal of *net* charge Z, $C = Z + n - 10 \cdot (n-1)/9$. For Ni^{2+}, $n = 8$ and $Z = 2$, and we find $C = 20/9$. For the method of determining the constant in the last line of eq 10, see eq A61 of ref 3. Values of the matrix elements of eq 9 calculated using the approximations of eq 10 are compared in Table I with the more carefully evaluated matrix elements of part I.

Table I. Matrix Elements of $\mathcal{F}_O^{0}$ as Calculated with (A) and without (B) the Approximations of Equation 10 for NiF_6^{4-}

A			B		
χ_s	χ_σ	φ_d	χ_s	χ_σ	φ_d
−0.785	0.00	−0.117	−0.786[a]	0.040	−0.114
b	0.110	−0.116	0.040	0.056[a]	−0.124
−0.117	−0.116	0.1714	−0.114	−0.124	0.1308

A		B	
χ_π	φ_d	χ_π	φ_d
0.110	−0.047	0.120[a]	−0.049
−0.047	0.1877	−0.049	0.1471

[a] These elements differ somewhat from those in part I primarily because a more accurate method of treating V_M^{core} has been used in the present paper. [b] Taken as zero for convenience; see Table II.

One small but extremely important correction has been made to the elements $\langle \varphi_d | \mathcal{F}_O^{0} | \varphi_d \rangle$, which according to eq 10 are the same for t_{2g} and e_g orbitals. We have corrected them for the amount of "crystal-field" splitting obtained by Sugano and Shulman,[3] so that the e_g matrix element lies *below* the t_{2g} element by 0.0163 au (3580 cm⁻¹). (We have arbitrarily kept the center of gravity constant.) The calculation of this splitting involves the evaluation of many coulomb and exchange integrals which are not readily approximated; we may hope that when evaluations for many complexes have been carried out, a simple approximation, perhaps involving proportionality to metal–ligand overlap integrals, will be found.

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(3) S. Sugano and R. G. Shulman, *Phys. Rev.*, 130, 517 (1963).

Table II. Matrix Elements of the Self-Consistent Open-Shell Operator $\mathfrak{F}_O$

A			B		
χ_s	χ_σ	φ_d	χ_s	χ_σ	φ_d
−0.785	0.00	−0.079	−0.786	0.040	−0.078
^{a}	0.110	−0.102	0.040	0.056	−0.108
−0.079	−0.102	0.2741	−0.078	−0.108	0.2533
χ_π	φ_d		χ_π	φ_d	
0.110	−0.035		0.120	−0.044	
−0.035	0.3232		−0.044	0.2937	

^{a} Taken as zero for convenience; 10*Dq* increases by ~900 cm^{-1} when this element is 0.040 au.

Table III. Orbital Coefficients and Energies for the Matrix Elements of Table II, with Overlap Integrals from Ref 6

A				B			
χ_s	χ_σ	φ_d	ϵ	χ_s	χ_σ	φ_d	ϵ
1.0000	0.0454	0.0141	−0.787	0.9989	0.0009	0.0128	−0.786
−0.0383	0.8609	0.4164	0.057	0.0061	0.8763	0.3908	0.008
−0.0956	−0.5237	0.9209	0.3676	−0.1128	−0.4995	0.9321	0.3456
χ_π	φ_d		ϵ	χ_π	φ_d		ϵ
0.9693	0.1869		0.102	0.9465	0.2614		0.106
−0.2577	0.9854		0.3389	−0.3308	0.9680		0.3167
10*Dq* = 0.0287 au, 6300 cm^{-1}				10*Dq* = 0.0288 au, 6320 cm^{-1}			
10*Dq* (exptl) = 7250 cm^{-1}							

We consider next the corrections to the matrix elements involved in the replacement of $\mathfrak{F}_O{}^0$ by $\mathfrak{F}_O$ in eq 9. These corrections arise in the fact that the self-consistent charge distribution in the complex is not precisely Ni^{2+} and six F^- ligands, but includes some partial transfer of electrons from the fluoride ions to the empty d orbitals of the metal. The corrections to the elements $\langle\chi_{k'}|\mathfrak{F}_O{}^0|\chi_k\rangle$ are least important to the correct calculation of 10*Dq* and in any event can be shown to be rather small in the case of the $NiF_6{}^{4-}$ calculation. We therefore neglect this correction. Corrections to the elements $\langle\varphi_d|\mathfrak{F}_O{}^0|\varphi_d\rangle$ may be made *via* a population analysis. We decrease these matrix elements by $1/R_{ML}$ for each unit *change* in the net charge on the ligands, and correspondingly increase the elements by $2P_O/R_{ML}$ to compensate for the effect of the overlap population P_O. These two effects do not cause any further splitting of the e_g and t_{2g} elements. However, increase in the populations of the e_g and t_{2g} d orbitals does cause an additional splitting. In Ni^{2+}, the populations of the e_g and t_{2g} orbitals are $^{16}/_5$ and $^{24}/_5$, respectively. Using an elementary crystal-field approach to the increases in e_g and t_{2g} d-orbital populations, *i.e.*, employing Griffith's[2b] Table A26 for the evaluation of d–d coulomb and exchange integrals in terms of Racah parameters *A*, *B*, and *C*, we finally obtain

$$\begin{aligned}\langle\varphi_e|\mathfrak{F}_O|\varphi_e\rangle &= \langle\varphi_e|\mathfrak{F}_O{}^0|\varphi_e\rangle + (P_L - 14)/R_{ML} + \\ &\quad 2P_O/R_{ML} + (^3/_4)(P_e - {}^{16}/_5)(A - 8B/3 + 4C/3) + \\ &\quad (P_t - {}^{24}/_5)(A - B + C/2) \\ \langle\varphi_t|\mathfrak{F}_O|\varphi_t\rangle &= \langle\varphi_t|\mathfrak{F}_O{}^0|\varphi_t\rangle + (P_L - 14)/R_{ML} + \\ &\quad 2P_O/R_{ML} + (P_e - {}^{16}/_5)(A - B + C/2) + \\ &\quad (^5/_6)(P_t - {}^{24}/_5)(A - 2B + C)\end{aligned} \tag{11}$$

The indicated populations are P_L, the total number of t_{2g} and e_g electrons assigned to the ligands, P_O, the overlap population, and P_e and P_t, the metal population assigned to e_g and t_{2g} orbitals. Note that $P_L + P_O + P_e + P_t = 14 + n$. For Ni^{2+} average of configuration,[4] $A = 0.8462$, $B = 0.0121$, and $C = 0.0448$ au.

Finally, we consider the corrections to the elements $\langle\chi_k|\mathfrak{F}_O{}^0|\varphi_d\rangle$. These are, as noted by Watson and Freeman,[5] rather large, but are given at least roughly by the relation

$$\langle\chi_k|\mathfrak{F}_O|\varphi_d\rangle = \langle\chi_k|\mathfrak{F}_O{}^0|\varphi_d\rangle - P_{kd}/(S_{kd}R_{ML}) \tag{12}$$

The population factor P_{kd} represents the population in a *single* spin orbital between χ_k and φ_d, and is defined such that $P_O = 6P_{tt} + 4P_{\sigma e} + 4P_{se}$.

Self-consistent matrix elements of $\mathfrak{F}_O$ are listed in Table II. Two sets of values are given, those obtained using eq 10 and those obtained without using these approximations. In both sets the approximations of eq 11 and 12 have been used to take the corrections to $\mathfrak{F}_O{}^0$ into account. The results of the diagonalizations of these matrices are given in Table III (the overlap integrals necessary for the diagonalization have been given previously[6]). As can be seen, the orbital coefficients do not change greatly in going over to the crude approximations of eq 10. The orbital energies do change considerably, but the difference in antibonding t_{2g} and e_g orbital energies is nearly unchanged, and 10*Dq* is calculated with little loss in accuracy.

The coefficients of Table III are not in even qualitative agreement with the results of recent calculations by Richardson, *et al.*[7] For example, the coefficient of χ_σ in $\psi_e{}^a$ is about −0.5 here, but is −0.2396 in their calculation. The results for the t_{2g} orbitals are in even poorer agreement. This is traceable to a difference in the open-shell formalisms used. Here we employ, for convenience, and for conceptual simplicity in the definition of 10*Dq*, the *average-of-configuration* open-shell method. Richardson, *et al.*, make a separate open-shell calculation for each state, and do not calculate 10*Dq per se* but subtract total energies to get the excitation energies directly. This has the disadvantage that, in effect, a separate 10*Dq* is defined for each state, contrary to the spirit of traditional ligand-field theory. On the other hand, Richardson's method is the proper one for obtaining ground-state properties such as spin densities. In fact, it has certain similarities to the so-called "closed-shell" formalism introduced previously,[1] and Richardson's coefficients for $\psi_e{}^a$ for $NiF_6{}^{4-}$ and

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(4) R. E. Watson, *Phys. Rev.*, **118**, 1039 (1960).

(5) R. E. Watson and A. J. Freeman, *ibid.*, **134**, 1526 (1964).

(6) P. O. Offenhartz, *J. Chem. Phys.*, **47**, 2951 (1967).

(7) J. W. Richardson, D. M. Vaught, T. F. Soules, and R. R. Powell, *ibid.*, **50**, 3633 (1969).

CrF_6^{3-} are in qualitative agreement with those of Table IV of part I. On the other hand, the coefficients for ψ_t^a for CrF_6^{3-} do not agree, nor should they, due to differences in the way ψ_t^a is defined. It would be of great interest to see a direct comparison of the present approximate average-of-configuration calculation with a more accurate open-shell average-of-configuration using Richardson's programs. Agreement would confirm that $10Dq$ can be obtained accurately as a difference in orbital energies.

It is also of interest to note in passing that the NEMO method of Newton, Boer, and Lipscomb[8] cannot be used to approximate the off-diagonal matrix elements in these calculations. Presumably their method fails because we are dealing with ions and not neutral molecules.

Conclusion

The approximations given by eq 10 are sufficiently accurate for the open-shell calculation of $10Dq$ when dealing with highly ionic systems in which $\mathcal{F}_O^0$ is at least a rough approximation to $\mathcal{F}_O$. The restriction to highly ionic systems is quite important. A recent attempt by the present author to calculate the ligand-field splitting parameters in the gaseous linear molecule NiF_2 failed owing to the very large covalency of the d orbitals. The field of two negative ions is not sufficient to raise the d-orbital diagonal elements to the point where the d orbitals are antibonding.

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(8) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2353 (1966).

Thermodynamics of Lithium Chloride in Dimethylformamide

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Abstract: Potential measurements of the cell Tl(1.01 mol % in Hg)|TlCl(s)|Li^+,Cl^-,DMF|Li(1.06 mol % in Hg) have been carried out in an argon atmosphere as a function of time over a range of temperatures from 13.45 to 46.40°, and LiCl concentrations from 0.001 to 2.0 *m*. From these data were calculated standard potentials, free energies, enthalpies, and entropies for the reactions $Li^+ + Cl^- + Tl(s) \rightarrow Li(s) + TlCl(s)$ and $Li^+ + Tl(s) \rightarrow Li(s) + Tl^+$, as well as activity coefficients for LiCl in DMF. Water concentrations between 0.002 and 0.013 *m* have negligible effect on these measurements. Ion pairing between Li^+ and Cl^- is found to be weak, and the Guggenheim equation gives the most accurate empirical description of the activity coefficients. Free energies, enthalpies, and entropies of transfer for LiCl from water to DMF solvents are calculated from EMF, solubility, and calorimetric measurements.

Recent interest in thermodynamics of nonaqueous electrolytes has prompted a number of potentiometric studies of activity coefficients for LiCl in dimethyl sulfoxide (DMSO)[1,2] propylene carbonate (PC),[3] and N-methylformamide (NMF).[4,5] Although enthalpy of solution data for LiCl in N,N-dimethylformamide (DMF) are available,[6,7] there is some question regarding the extent of ion pairing in this electrolyte, and neither free energy of solution nor activity coefficient data are available.

In DMSO[1,2] and propylene carbonate,[3] the cell

$$Tl(Hg)|TiCl(s)|Li^+,Cl^-,solvent|Li(Hg) \text{ or } Li(s)$$

has proved to be stable and reversible, and has yielded accurate values of activity coefficients and thermodynamic potentials. Our preliminary work[8,9] showed that both the Tl(Hg) and the Li(Hg) electrodes were reversible in DMF solutions, and that the solubility of TlCl in excess chloride was small enough that liquid junction potentials could be neglected. This paper reports the results of an extensive investigation using this cell. In addition, we have critically evaluated a number of related studies in the literature, and have compared the potentiometric data with calorimetric and solubility data where these are available.

Experimental Section

Amalgams were prepared by weight from thallium rod (American Smelting and Refining Co., 99.999%), lithium rod (Foote Mineral Co., 99.97%), and mercury (Doe and Ingalls, triple-distilled). In all measurements, the thallium amalgam was 1.01 mol % (1.02 wt %) and the lithium amalgam was 1.06 mol % (0.0372 wt %). These were unsaturated and were stirred during preparation and just prior to use in the cells. Solutions of lithium chloride (Anderson Physics Laboratories, ultrapure grade) in N,N-dimethylformamide (Matheson Coleman and Bell, spectroquality) were also prepared by weight.

The DMF used in one set of measurements was dried using Linde 4A molecular sieves, which were dried before use by heating in a quartz tube under a stream of argon at 375° for 24 hr. They were

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(1) D. R. Cogley and J. N. Butler, *J. Electrochem. Soc.*, **113**, 1074 (1966); G. Holleck, D. R. Cogley, and J. N. Butler, *ibid.*, **116**, 952 (1969).

(2) W. H. Smyrl and C. W. Tobias, *ibid.*, **115**, 33 (1968).

(3) M. Salomon, *J. Phys. Chem.*, 73, 3299 (1969); *J. Electrochem. Soc.*, **116**, 1392 (1969).

(4) R. P. Held and C. M. Criss, *J. Phys. Chem.*, **69**, 2611 (1965).

(5) E. Luksha and C. M. Criss, *ibid.*, 70, 1496 (1966).

(6) R. P. Held and C. M. Criss, *ibid.*, **71**, 2487 (1967).

(7) L. Weeda and G. Somsen, *Rec. Trav. Chim. Pays-Bas.*, **86**, 893 (1967).

(8) J. C. Synnott and J. N. Butler, *Anal. Chem.*, **41**, 1890 (1969).

(9) J. N. Butler, *Advan. Electrochem. Electrochem. Eng.*, **7**, 77 (1970).