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Orthonormal Interelectronic Repulsion Operators in the Parametrical d^q Model. Application of the Model to Gaseous Ions

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The atomic energy levels of 37 3d^q, one 4d^2, and one 5d^2 transition-metal atoms and ions have been parametrized by using a new formulation of the Slater–Condon–Shortley model. This formulation has two remarkable features. First, it introduces two orthonormal symmetry operators $\hat{Q}_D$ and $\hat{Q}_E$, associated with the empirical parameters D and E, where D is the well-known spin-pairing energy parameter that is found to account for 70% of the nd^q repulsion splitting. Second, it allows this splitting to be parametrized by using one parameter $\rho = (D^2 + E^2)^{1/2}$ for each atomic species. This parameter is associated with the empirically weighted operator $\rho^{-1}(D\hat{Q}_D + E\hat{Q}_E)$, which is found to be very close to $(3.25)^{-1/2}(1.50\hat{Q}_D + \hat{Q}_E)$ for all 39 atomic species studied. The formalism also allows the interelectronic repulsion to be quantitatively compared with the spin–orbit coupling, and it is found that while V^{3+} and Nb^{3+} can be described as having 99.8% and 97.1% Russell–Saunders coupling, this percentage is 71.6% for Ta^{3+}, which means that this ion is 28.4% on the way toward *jj* coupling. Finally, the d^q repulsion data have for fixed q been used to express the (fractional) charge z on the metal ion as a function of the interelectronic repulsion parameter ρ. These expressions for the different values of q form the empirical basis for the interpretation of nephelauxetism in ligand-field theory.

1. Introduction

The parametrical d^q model is a concept covering a particular quantitative version of ligand-field theory. This model embodies the interelectronic repulsion within the d shell as well as the ligand field and the spin–orbit coupling. All these Hamiltonian terms are described by empirical parameters whose coefficients in an energy matrix are quantitatively calculated within the model. In actual fact these calculated coefficients are completely determined by symmetry, and the parametrical d^q model is in this sense a symmetry model. It is also a semiempirical model because it has a theoretical part, the coefficients, and an empirical one, the parameters.

When the parametrical d^q model is applied to gaseous atoms and ions, one has the usual Slater–Condon–Shortley model. This model parametrizes the energies of the Russell–Saunders multiplet terms $^{2S+1}$L, which arise from the interelectronic repulsion operator acting on the q-electron functions of the d^q configuration (the d^q space). The present paper is primarily concerned with a new parametrization of this model, based upon an orthonormal set of operators.[1] However, the observables of the atomic spectra are not the $^{2S+1}$L terms themselves but their fine-structure J levels, which arise from the action of the spin–orbit coupling operator upon the d^q space. This paper is therefore secondarily concerned with the spin–orbit coupling.

The use of orthonormal operators for expressing a model Hamiltonian has been shown in connection with ligand-field Hamiltonians to allow a quantitative comparison of the magnitudes of the different symmetry components of the field.[2,3] By the introduction here of an orthonormal operator description of the interelectronic repulsion model Hamiltonian, the same kind of comparisons will be possible between the symmetry-independent terms of the repulsion Hamiltonian. Furthermore, since it will be shown that a general normalization of one- and two-electron operators is not possible, this paper will describe the method by which comparison of Hamiltonian terms described by orthogonal, but nonnormalized, operators must be made. Thereby the relative magnitudes of the interelectronic repulsion and the spin–orbit coupling Hamiltonian terms can be expressed quantitatively. Although the ligand field is not discussed here, it can, since it is represented by one-electron operators, be handled in quantitative comparisons in exactly the same way as the spin–orbit coupling.

The paper is structured as follows. Section 2 reviews the present situation with regard to parametrizations of interelectronic repulsion. Section 3 discusses the concepts of the parametrical Hamiltonian, the average interelectronic repulsion energy of a d^q configuration, and the trace of an operator. Section 4 exemplifies the orthogonality of operators and overlap between operators. Section 5 introduces normalized operators and their use in a quantitative comparison of Hamiltonian terms. It further defines this paper's new orthonormal set of repulsion operators $\hat{Q}_D$ and $\hat{Q}_E$ and tabulates the energies of all $^{2S+1}$L terms of all d^q configurations in terms of the parameters D and E. Section 6 presents the results of a nonlinear least-squares parameter fitting of repulsion and spin–orbit coupling parameters to the experimentally determined energy levels of 37 3d^q gaseous atoms and ions. Section 7 compares the contributions from the two symmetry-independent, orthonormal operators $\hat{Q}_D$ and $\hat{Q}_E$ to the total interelectronic repulsion splitting of the d^q configurations. It further discusses how the spin–orbit coupling operator can be included in the comparison of Hamiltonian terms without renormalizing it and illustrates this inclusion by means of an example. Finally, section 8 introduces a single empirically based operator $\hat{Q}_R$ and its associated parameter R, which is able to account for the energies of the $^{2S+1}$L terms of the d^q configurations studied in section 6 almost as well as the two symmetry-based operators $\hat{Q}_D$ and $\hat{Q}_E$ with their two associated parameters D and E.

2. Interelectronic Repulsion Parametrizations

In 1929 Slater showed[4] that it is possible to describe the interelectronic repulsion interaction between the electrons of a d^q configuration (q = 2–8) in terms of only three radial integrals: F^0, F^2, and F^4. When Slater's theory is applied to the analysis of experimental atomic spectra, these integrals play the role of the empirical parameters by which the energies of the multiplet terms of the configuration are expressed. In order to avoid fractional coefficients to the parameters in the energy expressions for the terms, Condon and Shortley[5] introduced k-subscript parameters that are fractions of the corresponding Slater parameters: $F_2 = (1/49)F^2$ and $F_4 = (1/441)F^4$. Laporte and Platt noticed[6] that for $F_4/F_2 = 1/5$, high accidental degeneracies of the multiplet terms occur within the d^q configurations, a fact that was used by Racah[7] to reparametrize the repulsion. Racah introduced the parameters A, B, and C (eq 1–3), which have several advantages

$$A = F_0 - 49F_4 \tag{1}$$

$$B = F_2 - 5F_4 \tag{2}$$

$$C = 35F_4 \tag{3}$$

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(1) Schäffer, C. E. *Physica A (Amsterdam)* **1982**, *114A*, 28–49.

(2) Brorson, M.; Damhus, T.; Schäffer, C. E. *Comments Inorg. Chem.* **1983**, *3*, 1–34.

(3) Schäffer, C. E. In *Understanding Molecular Properties*; Avery, J., Dahl, J. P., Hansen, A. E., Eds.; Reidel: Dordrecht, The Netherlands 1987; pp 143–175.

(4) Slater, J. C. *Phys. Rev.* **1929**, *34*, 1293–1322.

(5) Condon, E. U.; Shortley, G. H. *The Theory of Atomic Spectra*; Cambridge University Press: Cambridge, England, 1935.

(6) Laporte, O.; Platt, J. R. *Phys. Rev.* **1942**, *61*, 305–308.

(7) Racah, G. *Phys. Rev.* **1942**, *62*, 438–462.

0020-1669/88/1327-2522$01.50/0

relative to the F_k parameters. The high degeneracies just mentioned now occur for the situation $B = 0$, which, although physically unrealistic, is a useful situation to consider in the analysis of the parametrical model. Seen from a practical point of view, the most important advantage of the Racah parametrization probably is that the energy differences between terms of maximum spin multiplicity are independent of C.

Recently the advantages of using orthogonal operators in parametric models have been emphasized[8-10] and a reparametrization of the interelectronic repulsion in the f shell based on such orthogonal operators has been introduced.[11] We shall here do this for the d shell. However, the operators to be used by us are not only mutually orthogonal but also normalized.[1] Our orthonormal parametrization has all the attractive properties of the traditional Racah parametrization, but in addition to this, its parameters can be given simpler conceptual interpretations. Thus, one of its parameters is identical to Jørgensen's spin-pairing energy parameter.[12]

3. Parametrical Repulsion Hamiltonians and Their Barycenters

The parametrical (or effective) Hamiltonian which describes the interelectronic repulsion interaction between the q electrons of a d^q configuration may in the Racah parametrization be written as (4). This operator expression is an abstract, basis-independent

$$\hat{H}_{\text{rep}} = \hat{Q}_A A + \hat{Q}_B B + \hat{Q}_C C \tag{4}$$

way of expressing the information[7] that is present in the interelectronic repulsion energy matrices for the various d^q configurations. It is therefore not necessary to worry about the explicit forms of the three $\hat{Q}$ operators that carry their associated parameters as subscripts.

The term $\hat{Q}_A A$, which in a loose sense is thought to be much larger than the other two, gives the same destabilization of all the multiplet terms of a d^q configuration. This is the same as stating that the matrices of $\hat{Q}_A$ are diagonal and their diagonal elements are all identical for a given value of q. However, this does not mean that the term $\hat{Q}_A A$ of the Racah parametrization (or the term $\hat{Q}_{F_0} F_0$ of the Slater–Condon–Shortley parametrization) represents the average interelectronic repulsion interaction energy within the d^q configuration in question.[13] The parametrizations need small modifications in order to obtain this convenient[14,15] property and in (6)–(8) the operators of such a modified (primed) Racah parametrization (5) are given. In

$$\hat{H}_{\text{rep}} = \hat{Q}_{A'} A' + \hat{Q}_{B'} B' + \hat{Q}_{C'} C' \tag{5}$$

$$\hat{Q}_{A'} = \hat{Q}_A = \binom{q}{2}\hat{1} \tag{6}$$

$$\hat{Q}_{B'} = \hat{Q}_B + (14/9)\binom{q}{2}\hat{1} \tag{7}$$

$$\hat{Q}_{C'} = \hat{Q}_C - (7/9)\binom{q}{2}\hat{1} \tag{8}$$

(6)–(8) $\hat{1}$ represents the identity operator on the d^q space and the binomial coefficient $\binom{q}{2}$ is the number of individual pair interactions between the q electrons. The parameters of the primed parametrization are, as far as the parameters B' and C' are concerned, equal to the parameters of the traditional Racah parametrization, i.e.

$$B' = B \tag{9}$$

$$C' = C \tag{10}$$

while relation 11 applies to A'. Since A' expresses the average

$$A' = A - (14/9)B + (7/9)C \tag{11}$$

interelectronic repulsion interaction energy per electron pair, it is identical with Av(nd,nd) of Condon and Odabasi (ref 15, p 221). The parameter A' is furthermore identical with A_* of Jørgensen who also finds relation 11 (eq 19.14 of ref 16).

Whereas the values of the two parameters B' and C' can be determined on the basis of transitions between different d^q multiplet terms, the parameter A' cannot be determined on the basis of experiments. Determination of A' would require that one was able to switch off the interelectronic repulsion within the d shell and observe the absolute increase in the average energy of the d^q configuration when the repulsion was turned back on. It is important to realize that the average interelectronic repulsion energy of a d^q configuration is not the same as the average energy E_{av} of the configuration. The latter can be determined experimentally and will be discussed in section 6.

The modification of (4), which led us to (5) through (6)–(8), may be elucidated by using the concepts of the operator trace and barycentration of Hamiltonian terms. The trace of an operator

$$\text{Tr}(\hat{A}) = \text{Tr}(\mathbf{A}) = \sum_i A_{ii} \tag{12}$$

is the sum of the diagonal elements of one of its matrix representations (sometimes called representatives). The trace is independent of the basis. The operators $\hat{Q}_{B'}$ and $\hat{Q}_{C'}$ have traces that are equal to zero, and they are therefore said to be traceless. The operator $\hat{Q}_{A'}$ has a non-vanishing trace as have all of the unprimed operators $\hat{Q}_A$, $\hat{Q}_B$, and $\hat{Q}_C$. Equations 7 and 8 transform the operators $\hat{Q}_B$ and $\hat{Q}_C$ into their traceless associates $\hat{Q}_{B'}$ and $\hat{Q}_{C'}$, respectively. Thereby a transformation of Hamiltonian 4 into (5) takes place, and the new primed parameters B' and C' emerge. The tracelessness of $\hat{Q}_{B'}$ and $\hat{Q}_{C'}$ within the d^q space has the consequence[1] that the barycenter rule applies within d^q to those parts of the energy which depend on these operators' associated parameters B' and C'. In the formulation (eq 5) of the model Hamiltonian, tracelessness of a symmetry operator reflects the possibility for experimental determination of its associated energy parameter. The energy differences between the multiplet terms of a d^q configuration can be expressed in terms of the full set of parameters of this kind. By being nontraceless the operator $\hat{Q}_{A'}$ is of a different kind than $\hat{Q}_{B'}$ and $\hat{Q}_{C'}$, and its parameter A' cannot be determined from intraconfigurational transitions or, in fact, as discussed above, cannot be determined empirically at all.

4. Orthogonal Repulsion Operators

It is well-known nowadays among chemists how the concepts of orthogonality and orthonormality of vectors can be generalized to functions. It is much less well-known that analogous concepts can be applied to operators with very convenient consequences from a conceptual as well as from an applicational point of view.[1]

Two operators $\hat{A}$ and $\hat{B}$ are defined to be orthogonal if their scalar product or operator overlap, defined by (13), vanishes.[1] Here the last equality is valid when the matrices are real.

$$\langle \hat{A} | \hat{B} \rangle = \text{Tr}(\mathbf{A}^\dagger \mathbf{B}) = \sum_{ij} A^\dagger_{ij} B_{ji} = \sum_{ij} A_{ij} B_{ij} \tag{13}$$

Calculation of the operator overlap between $\hat{Q}_{B'}$ and $\hat{Q}_{C'}$ shows that these operators are not orthogonal while they are both orthogonal to $\hat{Q}_{A'}$. It is not difficult to construct three new (double primed) operators that span the same operator space as $\hat{Q}_{A'}$, $\hat{Q}_{B'}$, and $\hat{Q}_{C'}$ but are mutually orthogonal. This can be done in infinitely many ways. We here choose to conserve the operators $\hat{Q}_{A'}$ and $\hat{Q}_{C'}$, so that we have

$$\hat{Q}_{A''} = \hat{Q}_{A'} \tag{14}$$

$$\hat{Q}_{C''} = \hat{Q}_{C'} \tag{15}$$

This choice has the advantage of conserving the Racah parametrization property of having the same coefficient to one of the

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(8) Newman, D. J. *J. Phys. A: Math. Gen.* **1981**, *14*, L429–L431.

(9) Judd, B. R.; Hansen, J. E.; Raassen, A. J. J. *J. Phys. B* **1982**, *15*, 1457–1472.

(10) Newman, D. J. *Phys. Lett. A* **1982**, *92A*, 167–169.

(11) Judd, B. R.; Crosswhite, H. *J. Optical Soc. Am. B: Opt. Phys.* **1984**, *1*, 255–260.

(12) Jørgensen, C. K. *Orbitals in Atoms and Molecules*; Academic: London, New York, 1962; p 22.

(13) Shortley, G. H. *Phys. Rev.* **1936**, *50*, 1072–1075.

(14) Slater, J. C. *Quantum Theory of Atomic Structure*; McGraw-Hill: New York, Toronto, London, 1960; Vol. 1, section 14-2.

(15) Condon, E. U.; Odabasi, H. *Atomic Structure*; Cambridge University Press: Cambridge, England, 1980.

(16) Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*; North-Holland: Amsterdam, 1971.

Table I. Matrix Elements of the Interelectronic Repulsion in d^q Configurations Expressed in Terms of the Parameters D and E of the Orthonormal Parametrization[a]

d^2

	ν	$\hat{Q}_B$	$\hat{Q}_C$	$\hat{Q}_{B'}$	$\hat{Q}_{C'}$	$21\hat{Q}_D$	$21\hat{Q}_E$
^{3}P	2	7	0	77/9	-7/9	-14	42
^{3}F	2	-8	0	-58/9	-7/9	-14	-18
^{1}S	0	14	7	140/9	56/9	112	0
^{1}D	2	-3	2	-13/9	11/9	22	-18
^{1}G	2	4	2	50/9	11/9	22	10

d^3

	ν	$21\hat{Q}_D$	$21\hat{Q}_E$		ν	$21\hat{Q}_D$	$21\hat{Q}_E$
^{4}P	3	-42	42	^{2}F	3	12	48
^{4}F	3	-42	-18	^{2}G	3	12	-32
^{2}P	3	12	-12	^{2}H	3	12	-12
^{2}D1	1	84	0	^{2}D1, ^{2}D2		0	$12(21)^{1/2}$
^{2}D2	3	12	24				

d^4

	ν	$21\hat{Q}_D$	$21\hat{Q}_E$		ν	$21\hat{Q}_D$	$21\hat{Q}_E$
^{5}D	4	-84	0	^{1}D2	4	24	36
^{3}P1	2	42	-14	^{1}F	4	24	24
^{3}P2	4	-12	32	^{1}G1	2	78	-30
^{3}D	4	-12	24	^{1}G2	4	24	8
^{3}F1	2	42	6	^{1}I	4	24	-36
^{3}F2	4	-12	12	^{3}P1, ^{3}P2		0	$16(14)^{1/2}$
^{3}G	4	-12	-4	^{3}F1, ^{3}F2		0	48
^{3}H	4	-12	-24	^{1}S1, ^{1}S2		0	$24(21)^{1/2}$
^{1}S1	0	168	0	^{1}D1, ^{1}D2		0	$48(2)^{1/2}$
^{1}S2	4	24	48	^{1}G1, ^{1}G2		0	$16(11)^{1/2}$
^{1}D1	2	78	54				

d^5

	ν	$21\hat{Q}_D$	$21\hat{Q}_E$		ν	$21\hat{Q}_D$	$21\hat{Q}_E$
^{6}S	5	-140	0	^{2}F2	5	4	24
^{4}P	3	-14	-42	^{2}G1	3	40	52
^{4}D	5	-50	18	^{2}G2	5	4	8
^{4}F	3	-14	18	^{2}H	3	40	-48
^{4}G	5	-50	-10	^{2}I	5	4	-36
^{2}S	5	4	48	^{2}D1, ^{2}D2		0	0
^{2}P	3	40	120	^{2}D1, ^{2}D3		0	$24(14)^{1/2}$
^{2}D1	1	112	0	^{2}D2, ^{2}D3		0	0
^{2}D2	3	40	24	^{2}F1, ^{2}F2		0	0
^{2}D3	5	4	36	^{2}G1, ^{2}G2		0	0
^{2}F1	3	40	-60				

[a] Term designations are made according to Nielson and Koster.[38] For comparison the matrix elements given by Racah[7] in terms of the parameters B and C are included for the d^2 configuration. Also the d^2 elements of the barycentered Racah parametrization (primed parametrization, section 3) are given. ν is the seniority quantum number.

parameters in the energy expressions for all the terms of maximum spin multiplicity. The new operator $\hat{Q}_{B''}$ of (16) can then by

$$\hat{Q}_{B''} = \hat{Q}_{B'} - \frac{\langle \hat{Q}_{B'} | \hat{Q}_{C'} \rangle}{\langle \hat{Q}_{C'} | \hat{Q}_{C'} \rangle} \hat{Q}_{C'} \quad (16)$$

analogy with functions be constructed by a Schmidt orthogonalization as the part of $\hat{Q}_{B'}$ that is orthogonal to $\hat{Q}_{C'}$.

We illustrate the operator overlap concept by calculating the coefficient to $\hat{Q}_{C'}$ using the d^2 configuration as our example. This configuration embodies $\binom{10}{2} = 45$ states, sometimes called microstates. In Russell–Saunders coupling these states are classified as multiplet terms $^{2S+1}$L, each having a degeneracy (Russell–Saunders weight) of $(2S + 1)(2L + 1)$. This classification is a symmetry property. The d^2 configuration gives rise to the terms ^{3}P, ^{3}F, ^{1}S, ^{1}D, and ^{1}G whose degeneracies are 9, 21, 1, 5, and 9, respectively, adding up to 45 and thereby comprising all the states of d^2. The relevant operators act on this 45-dimensional two-electron space and the dummy indices i and j of (13) both run over the 45 functions. The matrices of $\hat{Q}_B$ and $\hat{Q}_C$ of (4) are both diagonal in d^2 and consist of elements that are integers. These numbers define the operators and are given in Table I in the Russell–Saunders basis so that the energies of the multiplet terms are in units of the Racah parameters B and C, which have the dimension of energy. The matrices of the traceless operators $\hat{Q}_{B'}$ and $\hat{Q}_{C'}$ of (5) are also given. In this case the energies are in units of the parameters B' and C' of the barycentered parametrization (eq 5; see eq 9 and 10 though). Let us now find the value of the coefficient to $\hat{Q}_{C'}$ in (16).

First we look at the denominator $\langle \hat{Q}_{C'} | \hat{Q}_{C'} \rangle$, which is the squared "length" of $\hat{Q}_{C'}$ or the overlap of this operator with itself.[1] This overlap is found from Table I as

$$\langle \hat{Q}_{C'} | \hat{Q}_{C'} \rangle = 9(-7/9)^2 + 21(-7/9)^2 + (56/9)^2 + 5(11/9)^2 + 9(11/9)^2 = 6300/81 \quad (17)$$

where the coefficients to the squared matrix elements are the Russell–Saunders weights required to form the scalar product in the 45-dimensional function space.

Second we look at the numerator $\langle \hat{Q}_{B'} | \hat{Q}_{C'} \rangle$, which is the operator overlap between $\hat{Q}_{B'}$ and $\hat{Q}_{C'}$. This is found analogously to (17) as

$$\langle \hat{Q}_{B'} | \hat{Q}_{C'} \rangle = 9(77/9)(-7/9) + 21(-58/9)(-7/9) + (140/9)(56/9) + 5(-13/9)(11/9) + 9(50/9)(11/9) = 15750/81 \quad (18)$$

Taking the ratio between the numbers of (18) and (17), one obtains 5/2, which is minus one times the coefficient to $\hat{Q}_{C'}$ of (16). This coefficient is the same for all d^q configurations, and $\hat{Q}_{B''}$ can therefore quite generally be rewritten as

$$\hat{Q}_{B''} = \hat{Q}_{B'} - (5/2)\hat{Q}_{C'} \tag{19}$$

The invariance of this coefficient can be induced from the general rule[11] that two traceless operators that are orthogonal when acting on the space of the d^q configuration are also orthogonal when acting on the d^{q+1} configuration.

The operators $\hat{Q}_{A''}$, $\hat{Q}_{B''}$, and $\hat{Q}_{C''}$ represent with their associated parameters a third way (eq 20) of expressing $\hat{H}_{rep}$ of (4) and (5).

$$\hat{H}_{rep} = \hat{Q}_{A''}A'' + \hat{Q}_{B''}B'' + \hat{Q}_{C''}C'' \tag{20}$$

Quite generally the parametrical Hamiltonian consists of terms that are products of symmetry operators and their associated parameters. It is illustrative of the formalism to derive relations between the parameters of the different parametrizations. The right-hand sides of (5) and (20) have to be equal for all values of the parameters. Equating these right-hand sides while using (14), (15), and (19) to insert the single primed operators in (20), we obtain

$$\hat{Q}_{A'}A' + \hat{Q}_{B'}B' + \hat{Q}_{C'}C' = \hat{Q}_{A'}A'' + (\hat{Q}_{B'} - (5/2)\hat{Q}_{C'})B'' + \hat{Q}_{C'}C'' \tag{21}$$

which can be rearranged to give (22). Since the coefficients to

$$\hat{Q}_{A'}A' + \hat{Q}_{B'}B' + \hat{Q}_{C'}C' = \hat{Q}_{A'}A'' + \hat{Q}_{B'}B'' + \hat{Q}_{C'}(C'' - (5/2)B'') \tag{22}$$

the operators must be the same on both sides of the equality sign in (22) we thus have

$$A'' = A' = A - (14/9)B + (7/9)C \tag{23}$$

$$B'' = B' = B \tag{24}$$

$$C'' = (5/2)B' + C' = (5/2)B + C \tag{25}$$

where the relations to the traditional Racah parameters are also given (cf. (9)–(11)). Notice that while in operator space $\hat{Q}_{C''} = \hat{Q}_{C'}$ (eq 15) and $\hat{Q}_{B''} \neq \hat{Q}_{B'}$ (eq 19), the corresponding relationships in parameter space are the reverse, $C'' \neq C'$ and $B'' = B'$. Apart from two different constants of proportionality (see section 5) B'' and C'' are the parameters proposed in the present paper for measuring the multiplet separations in d^q systems. The parameter C'' happens to be equal to the average exchange integral K_{av} of the usual real d functions.

In a rarely cited paper[17] Racah presented a parametrization of the repulsion in the d shell based on E^k parameters. This parametrization was, contrary to the A, B, and C parametrization, constructed on the basis of group-theoretical considerations. Racah's E^k parameters are extremely similar to ours, even though ours have been constructed by the orthogonalization procedure just discussed. However, contrary to our parametrization, Racah's E^k parametrization is not orthogonal. These similarities and differences will be discussed further in the Appendix.

5. Normalization, Comparison of Hamiltonian Terms, and Spin-Pairing Energy

An orthogonal set of operators is said to be normalized if the operator lengths, defined for $\hat{A}$ in (26), are equal. The advantage

$$\text{length}(\hat{A}) = +(\langle\hat{A}|\hat{A}\rangle)^{1/2} \tag{26}$$

of using normalized operators[1-3] in connection with parametrical Hamiltonians lies in the fact that the relative magnitudes of the Hamiltonian terms thereby are directly reflected in the relative magnitudes of their parameters. The magnitude of a Hamiltonian term is here not to be understood in the usual absolute sense, i.e. as the term's contribution to the total energy of the system. Rather, since the d^q model is not concerned with absolute energies but with energy differences within the d^q configuration, the relative magnitude of a Hamiltonian term is its contribution to the *total splitting* of this configuration. The square of this total splitting is defined as the sum of the squared energy deviations of all the states of the configuration from its barycenter, and this squared sum is in an orthonormal parametrization proportional to the sum of the squared parameters.[1-3] Since the nontraceless operator $\hat{Q}_{A''}$ does not describe a splitting of the d^q configuration and since its parameter cannot be experimentally determined in the d^q model we shall here only discuss the normalization of the traceless repulsion operators $\hat{Q}_{B''}$ and $\hat{Q}_{C''}$.

Jørgensen[12] has defined a so-called spin-pairing energy parameter D (eq 27), which is a measure of the average spin-pairing energy of a d^q configuration. The energy difference between the

$$D = (7/6)[(5/2)B + C] \tag{27}$$

barycenter of the terms with spin S and the barycenter of the terms with spin $(S - 1)$ is equal to $2SD$.[18] The particular linear combination of the traditional Racah parameters B and C that occurs in (27) is, apart from the factor (7/6), identical with that of our parameter C'' (eq 25). Since the parameter D is already in the literature and since it can be given the simple interpretation mentioned, we choose to use it in our orthonormal operator formalism and the operator $\hat{Q}_D$ of (28) is therefore chosen to be one

$$\hat{Q}_D = (6/7)\hat{Q}_{C''} = (6/7)\hat{Q}_{C'} \tag{28}$$

of the operators of the orthonormal set so that $\hat{Q}_D D = \hat{Q}_{C''}C''$. The length of $\hat{Q}_D$ varies with the d^q space on which the operator acts. When the dimension of the d^q space is increased together with q (up till $q = 5$), the length is also increased. This increase is described by (29) and (30).

$$\langle\hat{Q}_D|\hat{Q}_D\rangle_{l^q} = \langle\hat{Q}_D|\hat{Q}_D\rangle_{l^2}\binom{4l-2}{q-2} \tag{29}$$

$$\langle\hat{Q}_D|\hat{Q}_D\rangle_{d^2} = 400/7 \tag{30}$$

Equation 29 is a general formula that applies not only to $\hat{Q}_D$ but to all traceless two-electron operators acting on l^q configuration spaces.[19] Since our orthogonal repulsion operators are both two-electron operators, a common normalization for one particular d^q configuration will thus hold for any other one. Having fixed the standard of normalization by the definition of $\hat{Q}_D$ (eq 28), we can therefore normalize the other operator, $\hat{Q}_{B''}$, so as to give it the same length as $\hat{Q}_D$. By a procedure analogous to that of (17), the operator (eq 31) and its associated parameter (eq 32) are

$$\hat{Q}_E = (4/21)\hat{Q}_{B''} = (4/21)[\hat{Q}_{B'} - (5/2)\hat{Q}_{C'}] \tag{31}$$

$$E = (21/4)B \tag{32}$$

obtained. In Table I the parameters D and E of our new orthonormal operators $\hat{Q}_D$ and $\hat{Q}_E$ have been used to parametrize the energies of all the multiplet terms of all relevant d^q configurations. The parametrization is identical for d^q and d^{10-q}.

The parameter E measures the energy separation between the terms of the highest spin multiplicity for the configurations that contain more terms of this kind. This is the case for d^2, d^3, d^7, and d^8 configurations, which each give rise to a P and an F term whose energy difference is $(20/7)E$. The spin-pairing energy parameter D is a measure of the energy differences between the barycenters of the different spin multiplicities of a configuration.

6. Least-Squares Fits of Parameters to Atomic Energy Levels

Hitherto we have been concerned with what was called in the introduction the theoretical or symmetry-determined part of the parametrical d^q model for atoms. We shall now confront the model with experimental data and thereby obtain a collection of empirical values for the repulsion parameters associated with our orthonormal set of symmetry operators.

Experimental atomic energy levels are determined on the basis of atomic spectra and are traditionally found in the tables of Moore.[20] For the metals of the first transition period an updated and revised set of tables has been published in the course of the seventies by Sugar and Corliss. These tables, which comprise Sc,[21] Ti,[22] V,[23] Cr,[24] Mn,[25] Fe,[26] Co,[27] and Ni,[28] are much more complete

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[17] Racah, G. *Bull. Res. Counc. Isr.* **1953**, *3*, 290–298.

[18] Notice the similarity in form with the Landé interval rule: If S is replaced by J and $2D$ by λ, this rule is obtained.

[19] Judd, B. R.; Leavitt, R. C. *J. Phys. B* **1986**, *19*, 485–499.

[20] Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards: Washington, DC, 1949, 1952, 1958; Vol. 1–3.

[21] Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1980**, *9*, 473–511.

[22] Corliss, C.; Sugar, J. *J. Phys. Chem. Ref. Data* **1979**, *8*, 1–62.

[23] Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1978**, *7*, 1191–1262.

than the Moore tables: Highly ionized atoms are included, and for a given atomic species usually all but a few terms of its d^q configuration have been observed. With regard to the second and third transition period, the data in ref 20 seldom comprise more than very incomplete d^q configurations for the neutral and singly ionized atoms. We have therefore here focused mainly on the $3d^q$ configurations.

In the atomic energy level tables the multiplet terms ${}^{2S+1}L$ appear with fine structures due to spin–orbit coupling, which splits the terms into J levels. The levels of a particular ${}^{2S+1}L$ multiplet term are associated with J quantum numbers which extend from $|L - S|$ to $L + S$ with intervals of unity. Since S is always an integer for q even and half an odd integer for q odd, it follows that J follows S as far as these qualitative properties are concerned. Since it is J levels (of degeneracy $2J + 1$)) rather than the ${}^{2S+1}L$ Russell–Saunders terms that are the observed quantities, fitting of the repulsion parameters to the experimental energy levels of an atom or an ion must necessarily involve a codetermination of the spin–orbit coupling parameter ζ.

In the least-squares fitting we have also included the parameter E_{av}, which measures the average energy of the d^q configuration relative to the ground level of the atomic species examined. This ground level may belong to the d^q configuration itself or to another configuration (e.g. $3d^{q-1}4s$). The parameter E_{av} is included in order to account for the fact that it is the ground level and not the d^q configuration barycenter that defines the zero point of energy in the atomic energy tables. It is customary among atomic spectroscopists to include E_{av} in the fitting, but contrary to e.g. ref 9, which weights all J levels equally, our E_{av} expresses a true d^q configuration barycenter since we weight the J levels by ($2J + 1$) (see below).

According to this discussion the parametrical Hamiltonian which we have used is that of eq 33.

$$\hat{H} = \hat{1}E_{av} + \hat{Q}_D D + \hat{Q}_E E + \hat{Q}_\zeta \zeta \qquad (33)$$

The use of orthogonal operators in parametrical Hamiltonians like (33) has besides the advantages mentioned above also the statistical advantage that the relative errors of the fitted parameters are smaller than those of parameters associated with nonorthogonal operators.[8-11,29] The fact that $\hat{Q}_D$ and $\hat{Q}_E$ are orthogonal both to each other and to the spin–orbit coupling operator $\hat{Q}_\zeta$ only when the weight factors of the J levels are $2J + 1$, dictates this weighting and at the same time sees to it that our fitted parameters obtain minimal errors within the d^q model. It is consistent with this discussion that the purpose of using the least-squares procedure here is to confront the model with experiment, not in order to test the model in light of the experimental uncertainty but in order to determine the best model parameters, given the particular experiments. Thus, the use of the least-squares regression analysis does not involve an assumption about the data being distributed normally; the experimental errors are in fact small enough to require that the model be rejected. When the model is used anyway, its justification lies in the fact that it is used as a data reduction model for series of independent experiments. This is frequently the situation in chemistry.[30]

The quality of the fit may be described by the weighted mean deviation (eq 34). The summations here run over all J levels that

$$\sigma'_w = \{\sum_i (2J_i + 1)[E_i^{\text{calcd}} - E_i^{\text{exptl}}]^2 / \sum_i (2J_i + 1)\}^{1/2} \qquad (34)$$

belong to the d^q configuration in question and whose energies are listed in the tables of Sugar and Corliss. It should be noted that the weighting used in (34) is equivalent to weighting Russell–Saunders multiplet terms ${}^{2S+1}L$ by $(2S + 1)(2L + 1)$.

The results of the least-squares fittings are given in Table II. We point out several regularities in the variation of the parameters together with their usual d^q model explanations. For a given element the magnitude of the total interelectronic repulsion may be measured by the accumulative parameter ρ (ρ = Greek r, r for repulsion) defined in (35). The parameter ρ decreases with

$$\rho = (D^2 + E^2)^{1/2} \qquad (35)$$

decreasing ionic charge, indirectly due to the concomitant expansion of the d shell. By this expansion the average distance between the d electrons is increased while the average reciprocal distance, which directly reflects the repulsion, is decreased. This is nephelauxetism,[31,32] which will be discussed quantitatively below. Similarly, and for the same reason, ρ increases (decreases) with increasing (decreasing) atomic number Z when the number q of d electrons is kept constant. Keeping the ionic charge constant and moving across the transition period, i.e. toward higher atomic numbers, an increase of ρ is observed. This increase is accounted for by the incomplete mutual screening ability of the d electrons, which brings about a contraction of the d shell, when the nuclear charge Z is increased by one simultaneously with an increase in the number q of d electrons, also by one.

Let us now briefly discuss the empirical basis for the interpretation of nephelauxetism: if K is the number of electrons so that $q = K - 18$ for the $3d^q$ configurations, then the charge of the ion is $z = Z - K$. Table II shows that ρ decreases almost linearly with decreasing z (or with Z) for constant q (or K). This is, as mentioned above, nephelauxetism qualitatively. The polynomials[33] shown in (36)–(41) express the quantitative relationships

$$3d^2{:}\quad z = 1.87\rho^2 + 2.92\rho - 0.61 \qquad (36)$$

$$3d^3{:}\quad z = 0.73\rho^2 + 4.84\rho - 1.65 \qquad (37)$$

$$3d^4{:}\quad z = 2.11\rho^2 + 2.40\rho - 0.93 \qquad (38)$$

$$3d^5{:}\quad z = 2.50\rho^2 + 1.53\rho - 0.83 \qquad (39)$$

$$3d^6{:}\quad z = 2.13\rho^2 + 2.11\rho - 1.36 \qquad (40)$$

$$3d^7{:}\quad z = 5.17\rho^2 - 3.48\rho + 0.73 \qquad (41)$$

between ρ and z and allows an empirical ρ value for a metal complex to be associated with a (fractional) z value. This is the parametrical d^q model's wonderful demonstration of the concept of the prepondenant d^q configuration (q integer), which determines the number and types of energy levels whose relative positions depend on the value of z, which in general is fractional.

A new striking regularity in Table II is the constancy of the ratio between the repulsion parameters D and E. If the few atomic species that have the 4s shell populated in their ground state or low-lying excited states and for which configuration interaction may thus be assumed to be large are disregarded, the ratio D/E is always very close to 1.50. It is not possible by a simple criterion

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(24) Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1977**, *6*, 317–383.

(25) Corliss, C.; Sugar, J. *J. Phys. Chem. Ref. Data* **1977**, *6*, 1253–1329.

(26) Corliss, C.; Sugar, J. *J. Phys. Chem. Ref. Data* **1982**, *11*, 135–241.

(27) Sugar, J. Corliss, C. *J. Phys. Chem. Ref. Data* **1981**, *10*, 1097–1174.

(28) Corliss, C.; Sugar, J. *J. Phys. Chem. Ref. Data* **1981**, *10*, 197–289.

(29) If the same data and the same data weighting are used for two regression analyses, based upon operators spanning the same space, for example, $\{\hat{Q}_B\ \hat{Q}_C\}$ or $\{\hat{Q}_E\ \hat{Q}_D\}$, then the results of the fitting procedure will be identical. However, the parameters expressing the data reduction will have smaller relative errors if the parameters belong to orthogonal operators. A simple numerical example can illustrate this. For Ni^{2+} the fitted values of the traditional Racah parameters are $B = 0.104 \pm 0.005\ \mu m^{-1}$ and $C = 0.459 \pm 0.031\ \mu m^{-1}$. A similar fit using the orthonormal parameters gives the values $E = 0.547 \pm 0.027\ \mu m^{-1}$ and $D = 0.841 \pm 0.026\ \mu m^{-1}$. As far as B and E are concerned, their relative errors are the same (5.0%) since the parameters only differ by a constant of proportionality (eq 32). However, D has a relative error of 3.0%, which is less than half that of C (6.8%).

(30) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399–1407.

(31) Schäffer, C. E.; Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **1958**, *8*, 143–148.

(32) Jørgensen, C. K. *Prog. Inorg. Chem.* **1962**, *4*, 73–124.

(33) These polynomials that express the relations between z and ρ for the different $3d^q$ configurations have been found by polynomial regressions using the ρ values of Table II. The ρ value of Table II for Sc^0 does not agree with the ρ value one can obtain by a reasonable nonlinear extrapolation from the other $3d^3$ species, and Sc^0 was therefore not included in the fit that produced eq 37. The other five polynomials are based upon all the atomic species of the particular configuration. For the $3d^8$ configuration, which is represented by only two atomic species in Table II, no polynomial can be given. Equations 36–41 have no theoretical content but simply express the empirical relation between z and ρ in a convenient way.

to point out the atomic species with large configuration interactions, but in Table II the atoms/ions that have non-d^q ground terms have been marked by a dagger. This may give some indication of where the configuration interaction is likely to be large. The empirical value $D/E \approx 1.50$ generally found corresponds to a Racah C/B ratio of 4.25. Section 8 is concerned with the operator corresponding to the parameter ρ of (35) and with an operator corresponding to the generally found empirical D/E ratio.

Although the data on which Table II is based are plentiful, the model Hamiltonian (eq 33) is not good enough to define the value of the spin–orbit coupling parameter ζ satisfactorily. Accordingly a discussion of the variation of ζ with q and with ionic charge is apparently not justified here even though the expected trends can be observed in the ζ values of Table II. In a forthcoming paper[34] we shall show that addition of two extra orthonormal symmetry operators to our effective Hamiltonian allows a much better determination of ζ, at least for d^2 systems.[35]

7. Comparison of the Magnitudes of Hamiltonian Terms Including Terms Containing Nonnormalized Operators

As mentioned in section 5, one of the advantages of an orthonormal parametrization is that the values of the empirical parameters directly reflect the importance of the Hamiltonian terms to which they are associated. The fact that $D/E \approx 1.50$ for most first transition period ions can be used to make general statements about the relative splitting effects of $\hat{Q}_D$ and $\hat{Q}_E$. Since $\hat{Q}_D$ and $\hat{Q}_E$ are orthogonal, the squared length of the traceless part of the repulsion operator is equal to the sum of the squared lengths of the two terms $\hat{Q}_D D$ and $\hat{Q}_E E$. The normalization implies that the lengths of the symmetry operators $\hat{Q}_D$ and $\hat{Q}_E$ are equal, so that it is the squared parameters which are to be compared. For $D/E \approx 1.50$, the contribution of the spin-pairing term $\hat{Q}_D D$ to the squared splitting of a d^q configuration can be calculated by (42)

$$x(D) = D^2/(D^2 + E^2) = [1 + (D/E)^{-2}]^{-1} \approx 70\% \quad (42)$$

to be approximately 70% of the total squared splitting of the configuration. The remaining 30% of the total squared splitting is due to the $\hat{Q}_E E$ term.

Comparison of the relative d^q configuration splitting effects of the interelectronic repulsion and the spin–orbit coupling is also possible since $\hat{Q}_\zeta$ is orthogonal to $\hat{Q}_D$ and $\hat{Q}_E$. However, $\hat{Q}_\zeta$ and the repulsion operators do not have the same length. A renormalization of the spin–orbit coupling operator $\hat{Q}_\zeta$ so as to give it the same length as the repulsion operators cannot be done simultaneously for all d^q configurations. The reason for this is that $\hat{Q}_\zeta$ is a one-electron operator whereas the repulsion operators are two-electron operators. The squared length of a two-electron operator acting on an l^q configuration was given in (29). For traceless one-electron operators (43), here exemplified by using

$$\langle \hat{Q}_\zeta | \hat{Q}_\zeta \rangle_{l^q} = \langle \hat{Q}_\zeta | \hat{Q}_\zeta \rangle_{l^1} \binom{4l}{q-1} \quad (43)$$

$\hat{Q}_\zeta$, is generally valid.[19] The squared length of the spin–orbit coupling symmetry operator $\hat{Q}_\zeta$ on the l^1 spin–orbital space is given by (44). Since the lengths of one- and two-electron operators

$$\langle \hat{Q}_\zeta | \hat{Q}_\zeta \rangle_{l^1} = (2l + 1)[l(l + 1)/2] \quad (44)$$

do not increase in the same way with the number of electrons q in the l shell, a q-independent normalization of the two kinds of operators is not possible. A comparison of the repulsion and the spin–orbit coupling terms will therefore be made by inclusion of the squared lengths of the symmetry operators for the configuration in question.

For V^{3+} as an example, the contribution $x(\zeta)$ of the spin–orbit coupling term in the Hamiltonian (eq 33) to the total squared splitting of the d^2 configuration may, by using (30), (43), and (44), be calculated by (45) to be 0.2%. It is interesting to compare

$$x(\zeta) = \frac{120\zeta^2}{(400/7)[D^2 + E^2] + 120\zeta^2} \quad (45)$$

this value of $x(\zeta)$ with those of the heavier analogues of V^{3+}: i.e. Nb^{3+} and Ta^{3+}. Although energy level data are usually scarce for atoms and ions of the second and third transition period, complete sets of energy levels exist[36,37] for these two ions. On the basis of the fitted parameters of Table III and (45) one obtains $x(\zeta) = 2.9\%$ and $x(\zeta) = 28.4\%$ for Nb^{3+} and Ta^{3+}, respectively. The dramatic increase in the importance of the spin–orbit coupling with increasing nuclear charge Z is qualitatively well-known, but the present analysis expresses this quantitatively probably for the first time.

The parametrical Hamiltonian (eq 33) embodies only two perturbations, the repulsion, summarized by the parameter ρ (eq 35) and the spin–orbit coupling, parametrized by ζ. The contributions from ζ of 0.2%, 2.9%, and 28.4% therefore implies ρ contributions $x(\rho)$ of 99.8%, 97.1%, and 71.6%, respectively, in agreement with the obvious definition

$$x(\rho) = \frac{(400/7)(D^2 + E^2)}{(400/7)(D^2 + E^2) + 120\zeta^2} \quad (46)$$

so that $x(\rho) + x(\zeta) = 1$. This means that gaseous V^{3+} and Nb^{3+} are quite close to Russell–Saunders coupling ($x(\zeta) = 0$) while Ta^{3+} is nearly one-third on the way toward *jj* coupling ($x(\rho) = 0$).

8. One Empirically Based Repulsion Operator and One Empirical Parameter

In Table II the empirical values of the repulsion parameters are given in two alternative ways for each spectrum, first as the parameters D and E of the orthonormal symmetry operators $\hat{Q}_D$ and $\hat{Q}_E$ and second as the "root square sum" repulsion parameter $\rho = (D^2 + E^2)^{1/2}$ and the ratio D/E of the two positive parameters. ρ is an invariant of the operator space in the sense that every set of two orthonormal linear combinations of $\hat{Q}_D$ and $\hat{Q}_E$ will be associated with parameters whose square sum is ρ^2. If

$$\alpha\hat{Q}_D + \beta\hat{Q}_E \quad (47)$$

$$\beta\hat{Q}_D - \alpha\hat{Q}_E \quad (48)$$

are two such orthonormal operators ($\alpha^2 + \beta^2 = 1$), it is a property of the orthonormal operators' formalism[1-3] that their associated parameters are

$$\alpha D + \beta E \quad (49)$$

$$\beta D - \alpha E \quad (50)$$

respectively. This makes it possible to construct an operator whose associated parameter is ρ and whose orthogonal operator counterpart obtains a vanishing associated parameter. These two operators are

$$\hat{Q}_\rho = \rho^{-1}(D\hat{Q}_D + E\hat{Q}_E) \quad (51)$$

$$\hat{Q}_\rho{}^\perp = \rho^{-1}(E\hat{Q}_D - D\hat{Q}_E) \quad (52)$$

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(34) Brorson, M.; Schäffer, C. E., to be submitted for publication.

(35) The high relative standard deviation on ζ is mainly caused by insufficiencies in that part of the parametrical model that describes the energy differences between multiplet terms, unsplit by spin–orbit coupling. These differences are here described by the interelectronic repulsion parameters D and E, but the description may be improved by including so-called effective parameters in order to account for all observed energy differences between Russell–Saunders terms. If, for example, a four-parameter model is used to describe the four term energy differences within the d^2 system V^{3+}, ζ turns out to have a relative error of only 1%.

(36) Meinders, E.; Meijer, F. G.; Remijn, L. *Phys. Scr.* **1982**, *25*, 527–535.

(37) Meijer, F. H.; Metsch, B. C. *Physica B+C (Amsterdam)* **1978**, *94B+C*, 259–269.

(38) Nielson, C. W.; Koster, G. F. *Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations*; MIT Press: Cambridge, MA, 1963.

(39) In the atomic energy level table[26] for Fe^{3+} an error of assignment, not present in the original source, seems to have been introduced. The upper one of the two ^2F d^5 terms is denoted $^2F1$ while the lower one is denoted $^2F2$. As far as the Slater model is concerned these labels should be interchanged since $^2F1$ is below $^2F2$ for $D/E < 7/3$ (cf. Table I). However, these two ^2F d^5 terms form the only set of repeated d^q terms for which the energies of the terms do not increase with decreasing seniority for all reasonable D/E ratios.

Table II. Collection of Parameters of Interelectronic Repulsion and Spin–Orbit Coupling for the Metals of the First Transition Period[a]

	d^2	d^3	d^4	d^5	d^6	d^7	d^8
Sc	[9/9]† σ'_w = 0.0276 E_{av} = 0.940 (5), ζ = 0.005 (5) D = 0.345 (6), E = 0.253 (5) D/E = 1.36 (4), ρ = 0.428 (5)	[19/19]† σ'_w = 0.0897 E_{av} = 3.773 (23), ζ = −0.010 (25) D = 0.138 (16), E = 0.082 (17) D/E = 1.69 (44), ρ = 0.160 (15)					
Ti	[9/9] σ'_w = 0.0417 E_{av} = 0.689 (13), ζ = 0.012 (13) D = 0.519 (15), E = 0.375 (13) D/E = 1.38 (7), ρ = 0.641 (13)	[17/19]† σ'_w = 0.0597 E_{av} = 1.167 (14), ζ = 0.021 (17) D = 0.402 (11), E = 0.306 (10) D/E = 1.31 (5), ρ = 0.505 (11)	[11/34]† σ'_w = 0.0011 E_{av} = 3.7800 (7), ζ = 0.0080 (5) D = 0.2230 (3), E = 0.2038 (8) D/E = 1.094 (4), ρ = 0.3020 (6)				
V	[9/9] σ'_w = 0.0471 E_{av} = 0.882 (16), ζ = 0.023 (15) D = 0.669 (19), E = 0.465 (17) D/E = 1.44 (8), ρ = 0.815 (16)	[19/19] σ'_w = 0.0574 E_{av} = 1.520 (15), ζ = 0.013 (20) D = 0.561 (10), E = 0.399 (11) D/E = 1.41 (5), ρ = 0.689 (9)	[33/34]† σ'_w = 0.0926 E_{av} = 1.821 (16), ζ = 0.005 (33) D = 0.454 (9), E = 0.307 (11) D/E = 1.48 (6), ρ = 0.548 (9)	[9/37]† σ'_w = 0.0688 E_{av} = 3.765 (36), ζ = 0.039 (31) D = 0.251 (15), E = 0.229 (29) D/E = 1.09 (11), ρ = 0.340 (28)			
Cr	[9/9] σ'_w = 0.0545 E_{av} = 1.061 (19), ζ = 0.034 (18) D = 0.801 (23), E = 0.545 (21) D/E = 1.47 (8), ρ = 0.969 (19)	[19/19] σ'_w = 0.0683 E_{av} = 1.903 (18), ζ = 0.026 (25) D = 0.705 (12), E = 0.490 (13) D/E = 1.44 (5), ρ = 0.858 (11)	[33/34] σ'_w = 0.0676 E_{av} = 2.517 (12), ζ = 0.023 (23) D = 0.617 (7), E = 0.418 (8) D/E = 1.48 (4), ρ = 0.745 (7)	[33/37] σ'_w = 0.0803 E_{av} = 3.401 (15), ζ = 0.034 (21) D = 0.503 (8), E = 0.344 (10) D/E = 1.46 (5), ρ = 0.610 (9)	too few data		
Mn	[8/9] σ'_w = 0.0508 E_{av} = 1.239 (24), ζ = 0.052 (22) D = 0.935 (33), E = 0.617 (28) D/E = 1.51 (10), ρ = 1.120 (25)	[19/19] σ'_w = 0.0793 E_{av} = 2.255 (21), ζ = 0.042 (29) D = 0.832 (14), E = 0.571 (15) D/E = 1.46 (5), ρ = 1.010 (13)	[23/34] σ'_w = 0.0677 E_{av} = 3.090 (16), ζ = 0.044 (23) D = 0.757 (10), E = 0.499 (13) D/E = 1.52 (5), ρ = 0.907 (9)	[32/37] σ'_w = 0.0784 E_{av} = 4.456 (15), ζ = 0.049 (21) D = 0.662 (8), E = 0.451 (10) D/E = 1.47 (4), ρ = 0.801 (9)	[32/34]† σ'_w = 0.0870 E_{av} = 3.773 (15), ζ = 0.058 (22) D = 0.564 (9), E = 0.357 (11) D/E = 1.58 (6), ρ = 0.668 (9)	too few data	
Fe	[9/9] σ'_w = 0.0799 E_{av} = 1.417 (26), ζ = 0.069 (24) D = 1.039 (33), E = 0.694 (31) D/E = 1.50 (10), ρ = 1.249 (26)	[19/19] σ'_w = 0.0892 E_{av} = 2.596 (23), ζ = 0.062 (32) D = 0.952 (16), E = 0.648 (17) D/E = 1.47 (5), ρ = 1.152 (15)	[34/34] σ'_w = 0.0947 E_{av} = 3.628 (17), ζ = 0.044 (30) D = 0.882 (10), E = 0.589 (11) D/E = 1.50 (4), ρ = 1.061 (9)	[37/37] σ'_w = 0.0855 E_{av} = 5.363 (14), ζ = 0.061 (21) D = 0.798 (8), E = 0.540 (9) D/E = 1.48 (3), ρ = 0.964 (8)	[32/34] σ'_w = 0.0790 E_{av} = 2.937 (13), ζ = 0.061 (21) D = 0.714 (8), E = 0.471 (9) D/E = 1.51 (4), ρ = 0.855 (8)	[19/19]† σ'_w = 0.0614 E_{av} = 1.864 (14), ζ = 0.041 (16) D = 0.628 (10), E = 0.401 (11) D/E = 1.57 (5), ρ = 0.745 (9)	too few data
Co	[9/9] σ'_w = 0.0793 E_{av} = 1.602 (27), ζ = 0.093 (24) D = 1.157 (36), E = 0.763 (34)	[13/19] σ'_w = 0.1582 E_{av} = 3.016 (69), ζ = 0.064 (61) D = 1.107 (39), E = 0.749 (60)	[34/34] σ'_w = 0.1062 E_{av} = 4.137 (18), ζ = 0.060 (32) D = 1.001 (11), E = 0.665 (12)	[37/37] σ'_w = 0.0957 E_{av} = 6.195 (16), ζ = 0.076 (23) D = 0.923 (9), E = 0.622 (10)	[33/34] σ'_w = 0.0906 E_{av} = 3.488 (15), ζ = 0.077 (24) D = 0.847 (9), E = 0.567 (10)	[17/19] σ'_w = 0.0638 E_{av} = 2.093 (15), ζ = 0.057 (16) D = 0.780 (12), E = 0.519 (12)	[8/9] σ'_w = 0.0292 E_{av} = 0.923 (12), ζ = 0.047 (11) D = 0.744 (19), E = 0.419 (16)

	D/E = 1.52 (10), ρ = 1.385 (27)	D/E = 1.48 (11), ρ = 1.337 (55)	D/E = 1.50 (4), ρ = 1.202 (10)	D/E = 1.48 (3), ρ = 1.113 (9)	D/E = 1.49 (3), ρ = 1.019 (9)	D/E = 1.50 (4), ρ = 0.937 (12)	D/E = 1.78 (10), ρ = 0.854 (14)
Ni	uncertain data	[13/19] σ'_w = 0.1737 E_{av} = 3.339 (75), ζ = 0.084 (66) D = 1.209 (43), E = 0.812 (65) D/E = 1.49 (11), ρ = 1.457 (60)	[17/34] σ'_w = 0.0993 E_{av} = 4.635 (80), ζ = 0.091 (38) D = 1.113 (26), E = 0.736 (71) D/E = 1.51 (12), ρ = 1.334 (57)	[37/37] σ'_w = 0.1052 E_{av} = 6.984 (18), ζ = 0.095 (24) D = 1.041 (10), E = 0.699 (11) D/E = 1.49 (3), ρ = 1.254 (9)	[33/34] σ'_w = 0.1010 E_{av} = 4.004 (16), ζ = 0.098 (26) D = 0.969 (10), E = 0.650 (11) D/E = 1.49 (3), ρ = 1.167 (10)	[19/19] σ'_w = 0.0723 E_{av} = 2.456 (16), ζ = 0.081 (18) D = 0.898 (12), E = 0.603 (12) D/E = 1.49 (4), ρ = 1.081 (11)	[9/9] σ'_w = 0.0644 E_{av} = 1.132 (18), ζ = 0.072 (17) D = 0.841 (26), E = 0.547 (27) D/E = 1.54 (11), ρ = 1.003 (18)

[a] All values of parameters and weighted mean deviations (eq 34) are in units of μm^{-1} (1 μm^{-1} = 10 000 cm^{-1}). Standard deviations of the parameters are given in parentheses. On the basis of the parameter values obtained in the least-squares fit, D/E and $\rho = (D^2 + E^2)^{1/2}$ have been calculated with standard deviations (covariances taken into account). The number of d^q levels which for a particular atomic species has been observed[21-28] and thus included in the least-squares fit is given in square brackets as a fraction of the total number of levels of the configuration. Atomic species that have ground terms not belonging to their d^q configuration have been marked with a dagger. For some species, especially neutral atoms, only one term has been observed, and a determination of the repulsion parameters is therefore impossible. The energy levels of Ni^{8+} are uncertain. We have not attempted to be critical about the atomic energy level data (except for the case mentioned in footnote 39). With the results at hand a few comments can be made. Atoms for which configuration interaction is expected to be important have comparatively large σ'_w values (Sc^0, V^0, V$^+$, Mn$^+$). In this connection the good results for Ti^0 and Sc$^+$ are very surprising. The very large σ'_w values for Co^{6+} and Ni^{7+} may indicate incorrect assignments of the experimental data. In both cases the $^3_2$D terms are responsible for a large part of the weighted mean error.

Table III. Interelectronic Repulsion and Spin–Orbit Coupling Parameters[a] for the Heavy-Transition-Metal Ions Nb^{3+} and Ta^{3+}

	4d^2		5d^2
Nb^{3+}	[9/9] σ'_w = 0.0231 E_{av} = 0.720 (9), ζ = 0.067 (8) D = 0.466 (13), E = 0.317 (13) D/E = 1.47 (9), ρ = 0.564 (9)	Ta^{3+}	[9/9] σ'_w = 0.0522 E_{av} = 1.118 (18), ζ = 0.234 (16) D = 0.449 (30), E = 0.295 (29) D/E = 1.52 (22), ρ = 0.537 (21)

[a] The parameters are found by least-squares fittings to the energy level data of ref 36 and 37. Notice (cf. Table II) that while $\rho(\mathrm{V}^{3+}) \gg \rho(\mathrm{Nb}^{3+})$ the lanthanide contraction makes $\rho(\mathrm{Nb}^{3+}) \approx \rho(\mathrm{Ta}^{3+})$. All energy parameters are given in units of μm^{-1}.

which according to (47)–(50) have the associated parameters in (53) and (54), respectively. The operators $\hat{Q}_\rho$ and $\hat{Q}_\rho{}^\perp$ are

$$\rho = \rho^{-1}(D^2 + E^2) \qquad (53)$$

$$\rho^\perp = \rho^{-1}(ED - DE) = 0 \qquad (54)$$

empirical operators since they depend on the empirical parameters D and E. However, since the lengths of the operators are fixed by the normalization, their content of $\hat{Q}_D$ and $\hat{Q}_E$ does not depend on the magnitudes of D and E but only on their ratio D/E.

This whole discussion would have been only a formal exercise, had it not been for the fact that, as discussed in sections 6 and 7, the ratio D/E is close to 1.50 for the vast majority of 3d^q transition-metal ions. In (55) and (56) the $\hat{Q}_\rho$ and $\hat{Q}_\rho{}^\perp$ operators

$$\hat{Q}_R = (3.25)^{-1/2}[1.50\hat{Q}_D + \hat{Q}_E] \qquad (55)$$

$$\hat{Q}_R{}^\perp = (3.25)^{-1/2}[\hat{Q}_D - 1.50\hat{Q}_E] \qquad (56)$$

corresponding to D/E = 1.50 are given. These two operators, which we have called $\hat{Q}_R$ and $\hat{Q}_R{}^\perp$ (R for repulsion), give identically the same description of the d^q term energies as any other orthonormal linear combination of $\hat{Q}_D$ and $\hat{Q}_E$. For the atomic species where the D/E ratio has been found empirically to be exactly 1.50 the parameter R will be equal to ρ and $R^\perp$ will be zero. What makes the operators 55 and 56 interesting is that it will always be exactly true that $\rho^2 = R^2 + (R^\perp)^2$ so the ratio $(R\perp)^2/\rho^2$ will therefore be a quantitative measure of the fraction of the squared splitting that is not accounted for by the operator $\hat{Q}_R$. This fraction turns out to be very small for almost all the atomic species analyzed here.

We take the gaseous d^2 ion V^{3+} as an example. Here D = 0.669 μm^{-1}, E = 0.465 μm^{-1}, ρ = 0.815 μm^{-1}, and D/E = 1.44. Using now (49), (50), (55), and (56), i.e. $\alpha = (1.50)/(3.25)^{1/2}$ and $\beta = 1/(3.25)^{1/2}$, we obtain

$$R = [1.50/(3.25)^{1/2}]0.669 + [1/(3.25)^{1/2}]0.465 = 0.815\ \mu\mathrm{m}^{-1} \qquad (57)$$

$$R^\perp = [1/(3.25)^{1/2}]0.669 - [1.50/(3.25)^{1/2}]0.465 = -0.016\ \mu\mathrm{m}^{-1} \qquad (58)$$

Whenever the best fit yields D/E less than 1.50, $R^\perp$ will come out negative, as here. Equations 57 and 58 imply that only $100(R^\perp)^2/\rho^2\%$ = 0.04% of the total squared splitting has in this case not been accounted for by $\hat{Q}_R$. The worst case among the d^q ground level examples, that of the d^8 ion Co$^+$ with D/E = 1.78, gives R = 0.851 μm^{-1}, and even here, $R^\perp$ = 0.064 μm^{-1} is only 0.6% of ρ (in the squares). This suggests that one can base the repulsion description on the operator $\hat{Q}_R$ alone and leave out $\hat{Q}_R{}^\perp$ altogether.

Such a single-operator repulsion description turns out to be surprisingly good. Whereas thus a least-squares description of the repulsion of V^{3+} using the parameters R and $R^\perp$ (or, equivalently, D and E) gives σ'_w = 0.0471 μm^{-1}, a description based on the parameter R alone gives σ'_w = 0.0535 μm^{-1}, i.e. only a slight increase in the mean deviation. The reason for this good repulsion description by means of $\hat{Q}_R$ alone is that R is very close to the parameter ρ expressing the total interelectronic repulsion. Only for the atomic species where the D/E ratio deviates markedly from

1.50 will the one-parameter repulsion description not be good. These atomic species are, however, also those where configuration interaction is important and where the use of the d^q model is questionable anyway. This may actually be the reason for the D/E ratios being far from 1.50 in many of these cases. The two 4d and 5d transition metal ions of Table III have $D/E \approx 1.50$, which may indicate that the operator $\hat{Q}_R$ may be applied equally well for the heavy transition elements.

9. Conclusion

The Slater–Condon–Shortley model for the interelectronic repulsion within d^q configurations has been reparametrized by using the two parameters D and E to describe the energy differences between the terms. The parameter D is the average spin-pairing energy parameter because the energy difference between the mean energy of all terms with spin S and the mean energy of all terms with spin $(S - 1)$ is equal to $2SD$. Least-squares fittings of D, E, and ζ to the experimental energy levels of all first transition period atoms and ions (Sc–Ni), whose d^q configurations have been observed, were presented. It was found empirically that D/E always is close to 1.50. This fact made it possible to fix the D/E ratio and parametrize the $3d^q$ interelectronic repulsion almost equally well by using only one parameter $R \approx (D^2 + E^2)^{1/2}$. Since D and E are associated with orthonormal operators, their magnitudes directly reflect the importance of their Hamiltonian terms. Using the above mentioned empirical result for the D/E ratio, we may say that close to 70% of the squared splitting of each of the d^q configurations studied is due to the D term of the model Hamiltonian while the remaining 30% is due to the E term. Comparison of the splitting effects of the spin–orbit coupling and the interelectronic repulsion can also be made, and we find that the contribution of the spin–orbit coupling to the squared splitting of the d^2 configurations amounts to 0.2%, 2.9%, and 28.4% for V^{3+}, Nb^{3+}, and Ta^{3+}, respectively. Monotonic relationships between the accumulative repulsion parameter ρ and the metal ion charge z were obtained for different $3d^q$ configurations. These relationships allow interpolation between integer z values and form the basis for the empirical interpretation of nephelauxetism in ligand-field theory.

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Appendix

The interelectronic repulsion Hamiltonian of the parametrical d^q model can be expressed in terms of Racah's E^k parameters,[17] which, though rarely used for d electrons, have dominated the parametrization of the f shell repulsion.

$$\hat{H}_{\text{rep}} = \hat{Q}_{E^0}E^0 + \hat{Q}_{E^1}E^1 + \hat{Q}_{E^2}E^2 \qquad (59)$$

Racah[17] gives the following relations between the parameters of his two d shell parametrizations.

$$E^0 = A - (7/2)B \qquad (60)$$

$$E^1 = C + (5/2)B \qquad (61)$$

$$E^2 = (1/2)B \qquad (62)$$

By translating these relations into our double primed Racah parameters (eq 23–25) and by equating the Racah Hamiltonian (eq 59) with our Hamiltonian (eq 20), one obtains the operator equations (63)–(65). Since our double primed operators form

$$\hat{Q}_{E^0} = \hat{Q}_{A''} \qquad (63)$$

$$\hat{Q}_{E^1} = (7/9)\hat{Q}_{A''} + \hat{Q}_{C''} \qquad (64)$$

$$\hat{Q}_{E^2} = 2\hat{Q}_{B''} \qquad (65)$$

an orthogonal set, (63)–(65) reveal that the Racah E^k operators are mutually orthogonal apart from $\langle \hat{Q}_{E^0}|\hat{Q}_{E^1}\rangle = (7/9)\langle \hat{Q}_{A''}|\hat{Q}_{A''}\rangle$. However, if $\hat{Q}_{E^1}$ is made traceless by subtraction of $(7/9)\hat{Q}_{A''}$, a new orthogonal set spanning the same operator space is obtained and this set consists of members that are identical with ours apart from a factor of 2 in the case of $\hat{Q}_{B''}$.

For the f^q configurations Racah's E^k parametrization is the basis for the orthogonal f shell operators of Judd and Crosswhite.[11] They found that the E^k parametrization scheme is close to being an orthogonal one since the only nonvanishing operator overlap is $\langle \hat{Q}_{E^0}|\hat{Q}_{E^1}\rangle$. The f shell E^k parametrization is thus in this respect similar to the d shell parametrization.

Furthermore, for the f^q configurations the spin-pairing energy parameter is given[12] by the expression $D = (9/8)E^1$. Since for the d shell $D = (7/6)E^1$, it would seem that the spin-pairing parameter for an l shell generally is $[(2l + 3)/(2l + 2)]E^1$ when expressed in terms of the E^k parametrization for the l shell in question (cf. also ref 12, pp 22–23).

Registry No. Sc, 7440-20-2; Sc^+, 14336-93-7; Ti^{2+}, 15969-58-1; Ti^+, 14067-04-0; Ti, 7440-32-6; V^{3+}, 22541-77-1; V^{2+}, 15121-26-3; V^+, 14782-33-3; V, 7440-62-2; Cr^{4+}, 15723-28-1; Cr^{3+}, 16065-83-1; Cr^{2+}, 22541-79-3; Cr^+, 14067-03-9; Mn^{5+}, 20574-97-4; Mn^{4+}, 19768-33-3; Mn^{3+}, 14546-48-6; Mn^{2+}, 16397-91-4; Mn^+, 14127-69-6; Fe^{6+}, 14127-55-0; Fe^{5+}, 14127-54-9; Fe^{4+}, 14127-53-8; Fe^{3+}, 20074-52-6; Fe^{2+}, 15438-31-0; Fe^+, 14067-02-8; Co^{7+}, 20508-39-8; Co^{6+}, 20499-81-4; Co^{5+}, 20499-80-3; Co^{4+}, 20499-79-0; Co^{3+}, 22541-63-5; Co^{2+}, 22541-53-3; Co^+, 16610-75-6; Ni^{7+}, 49587-47-5; Ni^{6+}, 20508-37-6; Ni^{5+}, 21595-54-0; Ni^{4+}, 21595-53-9; Ni^{3+}, 22541-64-6; Ni^{2+}, 14701-22-5; Ni^+, 14903-34-5.