2838 *Inorg. Chem.* **1993,** *32,* 2838-2849

Accurate Empirical Spin-Orbit Coupling Parameters ζ_{nd} for Gaseous nd^q Transition Metal Ions. The Parametrical Multiplet Term Model

Jesper Bendix,[†] Michael Brorson,[‡] and Claus E. Schäffer*,[†]

Department of Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark, and Chemistry Department A, Building 207, The Technical University of Denmark, DK-2800 Lyngby, Denmark

Received January 24, 1992

A comprehensive and up-to-date tabulation of one-electron spin-orbit coupling parameters ζ_{nd} for atomic nd^q systems of chemical relevance is provided. The results are obtained from an effective-operator analysis that projects out of the empirical nd^q data a complete parametrization as far as eigenvalues and eigenstates of the configuration's multiplet terms are concerned. The only additional parameter is ζ_{nd}. In the language of the literature we have made the Coulomb analysis mathematically complete for the experimentally sufficiently known d^3, d^4, d^5, d^6, and d^7 systems. This was done 40 years ago for d^2 and d^8, while an extension to other d^q systems has been approached many times ever since. Although the method is not in a simple way related to first principles, it is not merely a data-reduction machinery using a well-defined procedure. Thus, the model parameters for a given nd^q system are interpretable as the multiplet-term energies and ζ_{nd}. Therefore, not only do the procedure's parametric results serve as a guide to academic overviews over the periodic table but its parameter values may also serve as reference values in ligand-field and magnetism contexts. The present method has an advantage in its straightforward relationship with current methods for obtaining ζ_{nd} values, *viz.* the use of the Landé interval rule or of the Slater-Condon-Shortley model. The paper includes a discussion of the present model in relation to the Slater-Condon-Shortley framework, which no longer can be considered a conventional physical model but still can be used pragmatically with considerable success. Sets of mutually orthogonal operators have served our analyses both as a conceptual and a practical tool. It is, however, demonstrated that the use of orthogonal sets of operators does not imply that their associated parameters will be uncorrelated, but it makes the correlation analysis more transparent. The general conclusion is that all nd^q systems of chemical relevance are parametrizable, quite accurately and in a chemically useful way.

1. Introduction

In an assessment of the role of spin-orbit coupling in the analysis of experimentally found magnetic susceptibilities and ESR spectra for metal complexes, a knowledge of the spin-orbit coupling parameters of the corresponding gaseous metal ions is important. Two essentially different methods for empirical determination of the one-electron operator spin-orbit coupling parameter ζ_{nl} (l = p, d, f, ...) are in current use. The first method involves the application of the Landé interval rule (cf. eq 6). This rule has a *local focus* within the l^q configuration in question by being applied to the energy levels of individual, observed multiplet terms ^{2S+1}L. Therefore, this method has the advantage of being to first order (splitting of ^{2S+1}L into J levels; cf. Table I) completely independent of two-electron operator energy sources, such as, *e.g.*, interelectronic repulsion, but the disadvantage of embodying (in the exact J level energies), to second order, systematic errors from these same sources. While the Landé-rule method thus allows each multiplet term to provide its own, local bid to the value for ζ_{nl}, the second method, application[1] of the Slater-Condon-Shortley model,[2] has a *global focus* within l^q. While the global focus is philosophically advantageous, it suffers from the entanglement of the spin-orbit-coupling and a multiplet-term description that is far from perfect.

A recent paper,[1] concerned with a new parametrization of the interelectronic repulsion in free ion d^q configurations within the Slater-Condon-Shortley (SCS) model, gave global values for ζ_{nd} as a byproduct. For first transition period d^q ions, the ζ_{nd} values ($n = 3$) were found to vary with the number q of electrons and with the external ionic charge z, quite regularly and just as expected, irrespective of the fact that the *errors* associated with the ζ_{nd} parameters were in many cases as large as the parameters themselves.

In the present paper we discuss these findings and introduce a method of parametrization based on multiplet term energy parameters, the so-called parametrical multiplet term (PMT) model. Contrary to the Slater-Condon-Shortley (SCS) model, the PMT model is mathematically free of shortcommings as far as the multiplet-term energy description within d^q is concerned. It therefore allows the determination of well-defined global values for ζ_{nd} in the model denoted by PMTζ. The analogous Slater-Condon-Shortley model (*e.g.*, ref 1) thus becomes the SCSζ model. It is an essential property of the PMTζ model that the operators associated with its term energy parameters are mutually orthogonal[3-8] and, in addition, orthogonal to the operator describing the spin-orbit coupling.

We have previously used sets of orthonormal operators in pure symmetry contexts[5] as well as in contexts where parametrical Hamiltonians were the issue, be it for the description of ligand fields,[6,7] of atomic energy levels,[1] or of the combination of both, known as quantitative ligand-field theory.[8] Along with our contributions to exemplifying the use of sets of mutually orthogonal operators, this issue has been illuminated[3,4] in complementary ways by the atomic spectroscopic community.

[†] University of Copenhagen.

[‡] The Technical University of Denmark.

(1) Brorson, M.; Schäffer, C. E. *Inorg. Chem.* **1988**, *27*, 2522-2530.

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

(3) Judd, B. R.; Hansen, J. E.; Raassen, A. J. J. *J. Phys. B: At. Mol. Phys.* **1982**, *15*, 1457-1472.

(4) Judd, B. R.; Leavitt, R. C. *J. Phys. B: At. Mol. Phys.* **1986**, *19*, 485-499.

(5) Schäffer, C. E. *Physica A (Amsterdam)* **1982**, *114A*, 28-49.

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

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

(8) Bendix, J.; Schäffer, C. E.; Brorson, M. *Coord. Chem. Rev.* **1989**, *94*, 181-241.

0020-1669/93/1332-2838$04.00/0

Thus, a model, equivalent to our present PMT model, has been derived[4] but never applied in full to experiments before.

In the derivation of this previous form of the PMT model,[4] its operators were labeled by irreducible representations of a hierarchy of Lie groups (the first three stages of eq 1), thus securing

$$U(10) \supset Sp(10) \supset SO_S(3) \otimes SO(5) \supset SO_S(3) \otimes SO_L(3) \qquad (1)$$

that the operators formed a complete orthogonal set and, what is more important, seeing to it that the operators were pure-*n*-electron operators. However, neither do the Lie groups used, at least at this time, belong to the vocabulary of chemistry, nor do the group labels of the operators seem to be revealing as far as conceptual connection with d^q spectra is concerned.

In this paper the PMT model has been derived by using the previous work on basis functions[9–11] and basic operators[5,12–14] and by referring only to the lowest member of the group hierarchy (1), *i.e.*, the three-dimensional rotation double group, which is already well-known in chemistry (section 5). By doing this, the parameters associated with our effective operators have interpretations that are directly related to the general symmetry conception of d^q spectra. Moreover, we have added spin–orbit coupling to the PMT model to obtain our PMTζ model (section 7). This is the obvious thing to do and the conventional thing for the Slater–Condon–Shortley model.

From a chemical point of view, the PMTζ model for d^q represents a most interesting stage of refinement in the analysis of atomic spectra because of its mathematical completeness with regard to multiplet term separation. Besides this atomic, intraconfigurational term separation, which carries over into chemistry through the area of ligand-field spectra (cf. here also the concept of nephelauxetism[15,16]), the PMTζ model embodies also spin–orbit coupling, which is the only remaining d^q atomic phenomenon, which has an acknowledged importance in chemistry.

The PMTζ model can be extended with fine-structure operators and parameters[17,18] to become complete also as far as J level separation is concerned. However, this extension, which for $3d^q$ and $4d^q$ systems involves eigenenergy changes only of the order of magnitude of 10 cm^{-1} (0.0010 μm^{-1}), are, at least at this stage, rarely of chemical interest. Fine-structure interactions beyond spin–orbit coupling will therefore from a practical point of view not be further discussed in this paper although their inclusion will be used in the formal discussion concerning the mathematically complete, so-called parametrical J level (PJL) model (cf. section 6 and, in particular, eq 21).

This paper begins by recording the degradation of the Slater–Condon–Shortley model as a physical model and in the same breath to argue that its symmetry-based qualitative success and its energy-based quantitative success justify its revival as two different members SCS and SCSζ of a hierarchy of mathematical parametrization models (section 2 and eqs 2 and 3). These models are formulated in terms of semiempirical Hamiltonians embodying effective, parametrical operators. The nonparametrical part is purely symmetry-based and is developed here in terms of sets of mutually orthogonal operators whose matrix elements are coefficients to the parameters in the energy expressions. The paper gradually builds up the conceptual framework whose summit is the PJL model, which is parametrically complete but impractical because it contains too many parameters compared with the number of observed J levels (section 6).

During the building-up process, the stage designated the parametrical multiplet term (PMT) model is reached (section 5). Its Hamiltonian, $\hat{H}_{PMT}$, being parametrically complete regarding both multiplet term eigenvalues and eigenstates, would not have been practical had it not been because of the existence of spin–orbit coupling. When this is included, this paper's final choice of parametrical Hamiltonian $\hat{H}_{PMT\zeta}$ appears. This is the intermediate-stage operator (cf. eqs 2 and 3), which is extremely

$$\hat{H}_{PJL} \supset \hat{H}_{PMT\zeta} \supset \hat{H}_{SCS\zeta} \supset \hat{H}_{SCS} \qquad (2)$$

$$\hat{H}_{PJL} \supset \hat{H}_{PMT\zeta} \supset \hat{H}_{PMT} \supset \hat{H}_{SCS} \qquad (3)$$

useful for conceptual as well as practical reasons. At this stage all fine-structure operators but the spin–orbit coupling operator have been left out. The situation may be illustrated by the two truncation hierarchies of eqs 2 and 3, which are *not* group hierarchies. Here the point is to keep the spin–orbit coupling not only as the only fine-structure operator but also as the *only* effective *one-electron* operator. By that, the PMTζ formalism attains the property of not differing in any essential way from the well-known SCSζ formalism. Thus, $\hat{H}_{PMT\zeta}$ allows a continuous passage from the Russell–Saunders limit of $\hat{H}_{PMT}$ through intermediate coupling to the jj-coupling limit. Similarly, the matrix representative of $\hat{H}_{PMT\zeta}$ in an SL basis may be transformed into a jj-coupling basis by rediagonalization[14,19,20] with respect to ζ_{nd}.

The paper provides a few relevant illustrations of its formalism's ability to quantitatively compare its parametric expansion terms (cf. Table I), but the paper's main result is the comprehensive compilation of least-squares fitted ζ_{nd} values for gaseous nd^q ions. The regular variation of the ζ_{nd} values with *n*, *q*, *z* (ionic charge), and *Z* (atomic number) is commented on (section 10).

2. Breakdown of the Slater–Condon–Shortley Framework as a Physical Theory and Its Revival as a Pragmatically Used Parametrical Model

Slater–Condon–Shortley (SCS) theory came into chemistry mainly through its association with ligand-field theory. The concept of a ligand field is in a strict sense concerned with l^q systems having $q = 1$. However, by ligand-field theory being combined with the SCS framework for atoms and atomic ions, the basis for parametric ligand-field theory, valid for all *q* values, was established from the beginning.[21] This was how the parametrical SCS model obtained its placement in transition metal chemistry.

The SCS framework was originally introduced as a physical theory of interelectronic repulsion[2] whose radial parameters F^k could in principle be calculated if the radial functions of the l orbitals were known. However, this was not so in the first 30 years of the existence of the theory and during this time SCS theory established itself by its superb applicability as a semiempirical, *i.e.*, parametrical model, in particular for f^q and d^q atomic spectra.

Around 1960 the first Hartree–Fock estimates of F^k parameters for d^q systems were made. They invariably came out high,[22,23]

---

(9) Harnung, S. E.; Schäffer, C. E. *Struct. Bonding (Berlin)* **1972**, *12*, 201–255.

(10) Harnung, S. E.; Schäffer, C. E. *Struct. Bonding (Berlin)* **1972**, *12*, 257–295.

(11) Damhus, T.; Harnung, S. E.; Schäffer, C. E. *Theoret. Chim. Acta (Berlin)* **1984**, *65*, 317–447 (6 consecutive papers).

(12) Schäffer, C. E. *Int. J. Quantum Chem.* **1971**, *5*, 379–390.

(13) Schäffer, C. E. *Struct. Bonding (Berlin)* **1973**, *14*, 69–110.

(14) Schäffer, C. E. *Wave Mechanics—The First Fifty Years.* Price, W. C., Chissick, S. S., Ravensdale, T., Eds.; Butterworths: London, 1973; pp 174–192.

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

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

(17) Hansen, J. E.; Judd, B. R. *J. Phys. B: At. Mol. Phys.* **1985**, *18*, 2327–2338.

(18) Hansen, J. E.; Raassen, A. J. J; Uylings, P. H. M.; Lister, G. M. S. *Nucl. Instrum. Methods Phys. Res. (Amsterdam)* **1988**, *B31*, 134–138.

(19) Schäffer, C. E. *Proc. R. Soc. (London), Ser. A* **1967**, *A297*, 96–133.

(20) Brorson, M.; Jensen, G. S.; Schäffer, C. E. *J. Chem. Educ.* **1986**, *63*, 387–391.

(21) Orgel, L. E. *J. Chem. Soc.* **1952**, 4756–4761.

(22) Watson, R. E. *Solid-state and Molecular Group Theory, Technical Report No. 12*; MIT: Cambridge, MA, 1959.

10-20%, relative to the empirically determined values. This did not, however, seriously make people loose confidence in SCS theory. Later, it was pointed out[24] that SCS theory violated the virial theorem and that the multiplet term *energy differences* were sometimes dominantly caused by nuclear attraction rather than interelectronic repulsion. Recently, detailed computational analysis at the Hartree–Fock level further discredited SCS theory by quantifying the importance of the inner shells[25] in determining the energy differences[26–28] between the l^q multiplet terms, which the parametrical application of SCS theory had associated with pure configurations.[29] Thus, the link between SCS theory and first principles of physics has been irreversibly broken. This situation must be realized as a fact.

With SCS theory having been realized as unsound in this sense, there is another fact, which, at least in chemistry, is equally important to remember: the series of experimentally established levels previously classified as components of the multiplet terms of pure d^q configurations are still there, observable as ever. In other words, the J levels of the multiplet terms whose number and kind are predictable on the basis of d^q configurations are in fact to be found by the analysis of atomic spectra. Moreover, the amazingly good quantitative accomplishments of the pragmatically used SCSζ model in parametrizing energy level differences within f^q and d^q remain.

In a previous paper[1] we let these accomplishments justify an attempt at a revival of SCS theory as a parametrical model. We reformulated the SCS model in terms of a set of mutually orthogonal operators that are effective operators acting on d^q. However, we observed that the numerical results obtained for the one-electron spin–orbit coupling parameters had extremely large relative standard deviations. This observation was the original background for the present work.

3. Configurations, Multiplet Terms, and Levels: Structure and Fine Structure

It is necessary at the outset briefly to discuss the concept of an l^q configuration (l = s, p, d, f). Actually, the symbol l^q may be used in two different ways: in a pure symmetry sense and in a chemical or classificatory sense. In both cases the symbol l^q carries its group-theoretical contents including the Pauli principle restrictions on equivalent electrons. In real, atomic systems, pure l^q configurations are *never* found since they are *always* to a greater or lesser extent mixed with other configurations.[29] Moreover, different radial functions apply to different multiplet terms of an l^q configuration. This fuzzyness of the l^q concept has, however, no effect on the qualitative features of the observed energy levels, and this is why the concept of an l^q configuration is so highly useful for classification purposes. For gaseous V^{3+}, for example, the experimental fact that the ground level is $^3F_2$ may be associated with the classificatory statement that this ion is a d^2 system. This statement is analogous to the chemical statement that vanadium of oxidation number +3 in compounds is a $3d^2$ system though the d orbitals of this expression are in fact molecular orbitals and the actual net charge on V may be about +1 rather than +3. Besides the d parentage, the important point is that the superscript in $3d^2$ is an *integer*[70] while the net charge is not.

A bridge may be built between a genuine l^q configuration that is split up into terms and levels and mixed with other configurations by genuine, quantum mechanical, one- and two-electron operators and a classificatory l^q configuration that remains unmixed but is acted upon by effective operators modeling or imaging the experimentally found energy levels that are classified as l^q levels. These effective operators may be *n*-electron operators ($n \leq q$).

The $\binom{4l+2}{q}$ states that make up an l^q configuration form energetically separated groups of states, known as Russell–Saunders terms ^{2S+1}L. Each such term contains $(2S + 1)(2L + 1)$ states. The degeneracy of the states within the terms is partially lifted by spin–orbit coupling which splits some terms into subgroups of states, known as levels or sometimes J levels. The levels are labeled by their total angular momentum quantum number *J* and by a Russell–Saunders term parentage so that the full symmetry labeling of a level within a given l^q is written either SLJ or $^{2S+1}L_J$. As a secondary consequence of the spin–orbit

---

(23) Watson, R. E. *Phys. Rev.* **1960**, *118*, 1036–1045.
(24) Katriel, J.; Pauncz, R. *Adv. Quantum Chem.* **1977**, *10*, 143–185.
(25) (a) Vanquickenborne, L. G.; Hoet, P.; Pierloot, K. *Inorg. Chem.* **1986**, *25*, 4228–4233. (b) Vanquickenborne, L. G.; Pierloot, K.; Görller-Walrand, C. *Inorg. Chim. Acta* **1986**, *120*, 209–213.
(26) Jørgensen, C. K. *Quim. Nova* **1988**, *11*, 10–19.
(27) Jørgensen, C. K. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 139–142.
(28) Jørgensen, C. K. *J. Less-Common Met.* **1989**, *148*, 147–150.
(29) The effect of configuration interaction[30] upon the multiplet term energy differences of d^q is still not known. However, this effect on the total energy of the ground state is now super-computer estimatable. For He, Ne, Ar, Zn^{2+}, and Kr these values are[31] in units of μm^{-1} 0.82, 8.52, 15.5, 35.1, and 41.6, respectively. The last number is also exactly obtained by Jørgensen's formula,[32] $E_{corr} = (0.7\ \text{eV})Z^{1.2}$, for closed-shell atoms. If E_{corr} for Zn^{2+} is compared with the energy differences of Table I, it is almost a must that configuration interaction contributes to these.
(30) Nesbet, R. K. *J. Phys. Chem.* **1990**, *94*, 5444–5448.
(31) Termath, V.; Klopper, W.; Kutzelnigg, W. *J. Chem. Phys.* **1991**, *94*, 2002–2019.
(32) Jørgensen, C. K. *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Ed.; North-Holland Publishing Co.: Amsterdam, The Netherlands, 1988; Vol. 11, pp 197–292.
(33) Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1980**, *9*, 473–511.
(34) Corliss, C.; Sugar, J. *J. Phys. Chem. Ref. Data* **1979**, *8*, 1–62.
(35) Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1978**, *7*, 1191–1262.
(36) Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1977**, *6*, 317–383.
(37) Corliss, C.; Sugar, J. *J. Phys. Chem. Ref. Data* **1977**, *6*, 1253–1329.
(38) Corliss, C.; Sugar, J. *J. Phys. Chem. Ref. Data* **1982**, *11*, 135–241.
(39) Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1981**, *10*, 1097–1174.
(40) Corliss, C.; Sugar, J. *J. Phys. Chem. Ref. Data* **1981**, *10*, 197–289.
(41) Sugar, J.; Musgrove, A. *J. Phys. Chem. Ref. Data* **1990**, *19*, 527–616.
(42) Reference 37 and ^1S energy from: Ryabtsev, A. N. *Opt. Spectrosc. (USSR)* **1982**, *53*, 13–15.
(43) Ekberg, J. O. *Phys. Scr.* **1981**, *23*, 7–20.
(44) Tchang-Brillet, W.-Ü. L.; Artru, M.-C., Wyart, J.-F. *Phys. Scr.* **1986**, *33*, 390–400.
(45) Reference 38 and ${}^{1}_{2}D$ at 7.7044 μm^{-1} according to J. O. Ekberg (private communication cited in ref 86).
(46) Raassen, A. J. J.; Orti Ortin, S. *Physica C (Amsterdam)* **1984**, *123C*, 353–369.
(47) Epstein, G. L.; Reader, J. *J. Opt. Soc. Am.* **1975**, *65*, 310–314.
(48) Acquista, N.; Reader, J. *J. Opt. Soc. Am.* **1980**, *70*, 789–792.
(49) Shujauddin, Q.; Mushtaq, A.; Chaghtai, M. S. Z. *Phys. Scr.* **1982**, *25*, 924–928.
(50) Sugar, J.; Musgrove, A. *J. Phys. Chem. Ref. Data* **1988**, *17*, 155–239.
(51) Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards: Washington, DC, 1952, 1958; Vols. 2–3.
(52) Khan, Z. A.; Chaghtai, M. S. Z.; Rahimullah, K. *Phys. Scr.* **1981**, *23*, 29–37.
(53) Meinders, E.; Meijer, F. G.; Remijn, L. *Phys. Scr.* **1982**, *25*, 527–535.
(54) Raassen, A. J. J.; van Kleef, Th. A. M. *Physica C (Amsterdam)* **1987**, *146C*, 423–437.
(55) Raassen, A. J. J.; van Kleef, Th. A. M. *Physica C (Amsterdam)* **1986**, *142C*, 359–374.
(56) Joshi, Y. N.; Raassen, A. J. J.; van Kleef, Th. A. M.; van der Valk, A. A. *Phys. Scr.* **1988**, *38*, 677–698.
(57) Barakat, M. M.; van Kleef, Th. A. M.; Raassen, A. J. J. *Physica C (Amsterdam)* **1985**, *132C*, 240–250.
(58) Barakat, M. M.; van Kleef, Th. A. M.; Raassen, A. J. J. *Physica C (Amsterdam)* **1985**, *132C*, 111–118.
(59) van Kleef, Th. A. M.; Joshi, Y. N. *Can. J. Phys.* **1981**, *59*, 1930–1939.
(60) Benschop, H.; Joshi, Y. N.; van Kleef, Th. A. M. *Can. J. Phys.* **1975**, *53*, 498–503.
(61) Klinkenberg, P. F. A.; van Kleef, Th. A. M.; Noorman, P. E. *Physica (Amsterdam)* **1961**, *27*, 1177–1188.
(62) Meijer, F. G.; Klinkenberg, P. F. A. *Physica (Amsterdam)* **1973**, *69*, 111–118.
(63) Meijer, F. G. *Physica (Amsterdam)* **1974**, *73*, 415–420.
(64) Meijer, F. G. *Physica C (Amsterdam)* **1976**, *81C*, 189–192.
(65) Meijer, F. G.; Metsch, B. C. *Physica C (Amsterdam)* **1978**, *94C*, 259–269.
(66) Meijer, F. G. *Physica C (Amsterdam)* **1986**, *141C*, 230–236.
(67) Iglesias, L.; Kaufman, V.; Garcia-Riquelme, O.; Rico, F. R. *Phys. Scr.* **1985**, *31*, 173–183.
(68) Gluck, G. G.; Bordarier, Y.; Bauche, J.; van Kleef, Th. A. M. *Physica (Amsterdam)* **1964**, *30*, 2068–2104.
(69) van Kleef, Th. A. M.; Metsch, B. C. *Physica C (Amsterdam)* **1978**, *95C*, 251–265.
(70) Jørgensen, C. K. *Oxidation Numbers and Oxidation States*; Springer-Verlag: Berlin, Heidelberg, New York, 1969.

coupling, ${}^{2S+1}L_J$ levels of different S and L but of the same J may mix. This mixing of fractions of multiplet terms makes fuzzy the term part of ${}^{2S+1}L_J$ while J remains a valid symmetry symbol and J a good quantum number. Consequently we shall sometimes use the symbol $\{{}^{2S+1}L\}_J$ for J levels that do not necessarily have a pure term parentage (cf. Table I).

The bookkeeping based upon the number of states N_s for a complete l^q configuration can be written as in eq 4, where the

$$N_s = \binom{4l+2}{q} = \sum_h (2S_h + 1)(2L_h + 1) = \sum_i (2J_i + 1) \qquad (4)$$

dummy indices h and i comprise all the terms and all the levels of l^q, respectively, *i.e.*, all the terms and levels allowed by the Pauli principle for the system of q equivalent l electrons. It should be noted that S_h and L_h do not vary independently because of this antisymmetry restriction.

In the cases where an l^q configuration contains more than one Russell–Saunders term with the same S and L, an unambiguous labeling of the terms requires an additional quantum number, which is usually chosen as the seniority number[71,72] v. The full label for a term is then vSL or ${}^{2S+1}_{v}L$. For all terms of d^2 and for most terms of the other d^q, the seniority label is redundant. For these terms the three-dimensional rotation double group in the form $SO_S(3) \otimes SO_L(3)$ suffices for an unambiguous double-representation labeling of multiplet terms.

In view of the problems concerning the fundamental physics (cf. section 2), we shall, as regards the splitting of l^q into multiplet terms, talk about the *structure* of l^q and, as regards its further splitting into J levels, talk about its *fine structure*.

4. Spin–Orbit Coupling Operator on l^q Multiplet Terms

The fine structure is for chemically relevant oxidation numbers of $3d^q$ and $4d^q$ metal ions much smaller[1] than the structure. Even for the heavier $5d^q$ systems the structure dominates the fine structure[1] for normal, chemical oxidation numbers, z. Because of these facts, it is useful to consider the effect of the spin–orbit coupling part of the Hamiltonian from the viewpoint of the multiplet terms ${}^{2S+1}L$, *i.e.*, to use an SL basis. By so doing, it is possible mathematically to divide the energy contributions of the spin–orbit coupling into two parts: the first-order contribution, linear in ζ_{nl}, and the rest of the contributions, which is the sum of all higher order terms caused by all the nondiagonal matrix elements within l^q. The first-order contribution gives rise to the *true splitting* of ${}^{2S+1}L$ into ${}^{2S+1}L_J$ while the rest causes a mixing of different ${}^{2S+1}L_J$ levels having the same J value, thus resulting in a mixing that is restricted to involve a fraction of the ${}^{2S+1}L$ terms. Up to and including the first-order spin–orbit contribution, it is a symmetry property that the energies $h(l^q,\mathrm{vSLJ})$ of the levels associated with a particular l^q multiplet term ${}^{2S+1}_{v}L$ can be written as in eq 5. The Landé interval rule of eq 6 derives from eq 5 and applies *exactly* to the energy level differences within the *pure* term.[73] In eq 5 the symbol $<J(J + 1)>$ denotes the average value of $J(J + 1)$ among the states of ${}^{2S+1}_{v}L$. This value is

$$\begin{aligned} h(l^q,\mathrm{vSLJ}) &= h(l^q,\mathrm{vSL}) + \\ &\quad {}^1/_2\lambda(l^q,\mathrm{vSL})\,[J(J+1) - S(S+1) - L(L+1)] \\ &= h(l^q,\mathrm{vSL}) + {}^1/_2\lambda(l^q,\mathrm{vSL})[J(J+1) - \langle J(J+1)\rangle] \\ &\equiv h(J) \end{aligned} \qquad (5)$$

$$h(J) - h(J-1) = \lambda(l^q,\mathrm{vSL})J \equiv \lambda J \qquad (6)$$

independent of v. Equation 5 implies that the J levels ${}^{2S+1}_{v}L_J$ are barycentered around the energy $h(l^q,\mathrm{vSL})$ of the unsplit term.[74]

The expressions of eq 5 are based upon the symmetry of l^q for fixed q. They apply to an effective spin–orbit coupling operator $\lambda\hat{S}\cdot\hat{L}$ acting within a ${}^{2S+1}_{v}L$ term. By using the additional symmetry assumption of the connection with a varying number q of l electrons, the empirical parameter, $\lambda(l^q,\mathrm{vSL})$, may be expressed by the one-electron spin–orbit coupling parameter, ζ_{nl}.

$$\lambda(l^q,\mathrm{vSL}) = k(l^q,\mathrm{vSL})\ \zeta_{nl} \qquad (0 < q < 4l + 2) \qquad (7)$$

The constant of proportionality, $k(l^q,\mathrm{vSL})$, is then a number purely determined by symmetry. For $q = 1$ its value is unity and the one-electron parameter, ζ_{nl}, is the λ of the l^1 configuration (cf. eq 6):

$$h(l_{l+1/2}) - h(l_{l-1/2}) = \zeta_{nl}[(2l + 1)/2] \qquad (8)$$

There exists a one to one relationship (eq 9) between pairs of

$$k(l^q,\mathrm{vSL}) = -k(l^{4l+2-q},\mathrm{vSL}) \qquad (9)$$

levels l^q,vSLJ and l^{4l+2-q},vSLJ, *i.e.*, corresponding levels of complementary configurations. This relationship is valid for ground multiplet terms as well as for excited terms. A consequence of eq 9 is that half-full-shell systems have no first-order spin–orbit splitting of their multiplet terms,[75] *i.e.*, for $q = 2l + 1$, $k(l^q,\mathrm{vSL}) = 0$ and thus $\lambda(l^q,\mathrm{vSL}) = 0$. This means, on the other hand, that the full effect of the spin–orbit coupling operator, which is function basis independent, lies *off* the diagonal in a Russell–Saunders basis, $|l^{2l+1},\mathrm{vSL}\}$.

Finally, it should be remarked that the symmetry relationship of eq 7, which provides k, only gives a formal connection between the l^q parameter λ and the l^1 parameter ζ_{nl}. In practice the value of either λ or ζ_{nl} is empirically determined for one particular system, that is, for n, q, and z fixed, and the value of the remaining parameter then obtained from eq 7. However, the variation of ζ_{nl} with n, q, and z is in an effective operator model a matter of empiricism rather than theory (cf. section 10).

5. Parametrical Multiplet Term Model for nd^q Systems

This section will be concerned with the complete set of eigenstates of the classifying d^q configuration. The energies of these eigenstates will be modeled as the eigenvalues of effective operators on d^q. These operators can be subdivided into three

---

[71] Racah, G. *Phys. Rev.* **1943**, *63*, 367–382. The seniority v is an additional symmetry-based label but, in principle, never a good quantum number when it is nontrivial. It has the symmetry basis that $l^p,{}^{2S+1}L$ gives $l^{p+2},{}^{2S+1}L$ when $l^2,{}^1S$ is added to it. For example, $d^5,{}^2_1D$ is the term formed by adding $d^2,{}^1S$ twice to $d^1,{}^2D$. The intermediate term $d^3,{}^2_1D$ has a partner, labeled $d^3,{}^2_3D$, which is orthogonal to ${}^2_1D$. This partner gives birth to $d^5,{}^2_3D$ when $d^2,{}^1S$ is added to it. ${}^2_5D$ is the remaining ${}^2D$ of d^5, orthogonal to ${}^2_1D$ and ${}^2_3D$ of d^5.

[72] Racah, G. *Phys. Rev.* **1952**, *85*, 381–382.

[73] The Landé interval rule was originally found experimentally. When it is compared directly with experimental splittings of multiplet terms into levels, these splittings are not true splittings but involve also term mixing. Therefore, the Landé rule is often found not to apply particularly well (cf. here the distinction between $\{{}^{2S+1}L\}$ and ${}^{2S+1}L$ in Table I).

[74] The energies of the levels with maximum and minimum J values within a term can be found from the following expressions:

$$\begin{aligned} h(J_{max}) &= h(l^q,\mathrm{vSL}) + \lambda SL \\ h(J_{min}) &= \begin{cases} h(l^q,\mathrm{vSL}) - \lambda S(L+1) & \text{for } S \le L \\ h(l^q,\mathrm{vSL}) - \lambda(S+1)L & \text{for } S \ge L \end{cases} \end{aligned}$$

The expression for $h(J_{min})$ depends on whether the spin multiplicity of the term is fully developed[2] or not.

[75] In our vocabulary the apparent term splitting caused by higher order effects of spin–orbit coupling is strictly speaking *not* referred to as a *splitting*. Rather it is conceived as a consequence of the *mixing* of J levels belonging to different terms but having the same J value (cf. Table I).

classes so that the effective Hamiltonian on d^q embodies three main terms.

$$\hat{H} = \hat{H}_{av} + \hat{K} + \hat{K}^* = \hat{I} E_{av} + \hat{K} + \hat{K}^* \qquad (10)$$

In eq 10, $\hat{I}$ is the number-operator whose norm square[1,5-8] is equal to the number of states, $\binom{10}{q}$, of d^q (cf. also eq 4). E_{av} is the associated energy parameter which, with any arbitrarily chosen zero point for the energy, expresses the average energy of all the states of d^q.

$\hat{K}$ is an operator splitting the configuration into multiplet terms and mixing terms of the same S and L but different seniority. Its symmetry is that of the scalar representation of the group K (= R_3 = $SO_L(3)$), which is the three-dimensional rotation group (Kugelgruppe (German)). This operator, which is barycentered over d^q, will also be named the *structure operator* on d^q. $\hat{K}$ is the subject of this section.

$\hat{K}^*$ is similarly an operator splitting the multiplet terms into levels and mixing fractions of the terms and thus making fuzzy the S and L quantum numbers. Its symmetry is that of the scalar representation of the corresponding double group K^* (=R_3^* = SU_2 = $SO_S(3) \otimes SO_L(3)$ = $SO_J(3)$). The operator $\hat{K}^*$ will be named the *fine-structure operator*, so that $\hat{K}$ and $\hat{K}^*$, taken *together*, account for the *total structure* of d^q. This total structure will be the subject of section 6.

The semiempiricism of the effective Hamiltonian approach finds its expression in the fact that $\hat{K}$ and $\hat{K}^*$ may be expressed in terms of energy parameters to be determined by bringing the model energy levels as closely as possible into coincidence with the observed energy levels. From a *model-theory* point of view, the component parameters of $\hat{K}$ and $\hat{K}^*$ thus determined belong to a single observation set, *i.e.*, a set for which Z, z, and thus q are fixed. However, from a *chemical* point of view, comparison of the component parameters of $\hat{K}$ and $\hat{K}^*$ for a series of observation sets, *i.e.*, for sets with varying Z, z, and q, may be the major chemical value of the model work.

In the SCS model, $\hat{K}$ may be expressed in terms of the spin-pairing energy[1] parameter, D, and the Racah parameter, B, while $\hat{K}^*$ is expressed in terms of the one-electron spin–orbit coupling parameter, ζ_{nd}. We may thus write[1]

$$\hat{K}_{SCS} = \hat{Q}_D D + \hat{Q}_B B \qquad (11)$$

$$\hat{K}^*_{SCS} = \hat{Q}_\zeta \zeta \qquad (12)$$

where we note that the number of structure parameters, $N_p(\hat{K}_{SCS})$, is equal to two, independently of q. The practical SCS model operator is that of eq 13.

$$\hat{H}_{SCS\zeta} \equiv \hat{H}_{SCS} + \hat{K}^*_{SCS} = \hat{H}_{av} + \hat{K}_{SCS} + \hat{K}^*_{SCS} = \hat{I} E_{av} + \hat{Q}_D D + \hat{Q}_B B + \hat{Q}_\zeta \zeta \qquad (13)$$

The SCS and SCSζ models may be extended to the PMT and PMTζ models, all applied to d^2, as shown in eqs 14 and 15. In

$$\hat{H}_{PMT}[d^2] = \hat{H}_{av}[d^2] + \hat{K}_{PMT}[d^2] = \hat{I} E_{av} + \hat{Q}_D D + \hat{Q}_B B + \hat{Q}_{D\perp}(D\perp) + \hat{Q}_{B\perp}(B\perp) \qquad (14)$$

$$\hat{H}_{PMT\zeta}[d^2] = \hat{H}_{PMT}[d^2] + \hat{K}^*_{SCS} \qquad (15)$$

eq 14 the operator, $\hat{K}_{PMT}[d^2]$, is a complete structure operator on d^2 and its four component operators are mutually orthogonal and all effective two-electron operators. $\hat{H}_{av}$ is a zero-electron operator. Thus $\hat{H}_{PMT}[d^2]$ of eq 14 is a linear combination of five mutually orthogonal operators. Actually, it is a different form of $\hat{H}_{PMT}[d^2]$ which accounts for the naming, the parametrical multiplet term model on d^2. This configuration embodies the five multiplet terms ^1S, ^3P, ^1D, ^3F, and ^1G. In eq 16, the energies,

$$\hat{H}_{PMT}[d^2] = \hat{Q}(^1S)h(^1S) + \hat{Q}(^3P)h(^3P) + \hat{Q}(^1D)h(^1D) + \hat{Q}(^3F)h(^3F) + \hat{Q}(^1G)h(^1G) \qquad (16)$$

$h(^{2S+1}L)$, of these multiplet terms are the empirical parameters. Apart from a change in formalism, eq 16 is due to Uylings.[76] $\hat{H}_{PMT}[d^2]$ may be imaged as a fixed vector $\mathbf{\hat{H}}_{PMT}[d^2]$ in a five-dimensional, orthogonal vector space. This space is spanned by either of the two sets of basis vectors $\{\hat{Q}(E_{av}) = \hat{I}, \hat{Q}_D, \hat{Q}_B, \hat{Q}_{D\perp}, \hat{Q}_{B\perp}\}$ or $\{\hat{Q}(^1S), \hat{Q}(^3P), \hat{Q}(^1D), \hat{Q}(^3F), \hat{Q}(^1G)\}$, where the latter set that embodies operators of mixed zero-electron and two-electron character consists of the operators, which (within d^2) act non-trivially only on the states of one, single multiplet term. Going from eq 14 to eq 16 corresponds to a specific rotation of the basis frame (coordinate system) of the five-dimensional vector space that contains the vector image $\mathbf{\hat{H}}_{PMT}[d^2]$ of $\hat{H}_{PMT}[d^2]$.[77] It should be noted that $\hat{H}_{PMT}[d^2]$, like $\hat{H}_{SCS}$, may act on any relevant d^q, *i.e.*, $2 \le q \le 8$.

With the background now given, the parametric multiplet term model Hamiltonian $\hat{H}_{PMT}[d^q]$ for general q may be explained almost completely by analyzing the example of $q = 3$ (or 7). For the d^3 configuration, we have eq 17. Alternatively, we may write

$$\hat{H}_{PMT}[d^3] = \hat{Q}(^4P)h(^4P) + \hat{Q}(^4F)h(^4F) + \hat{Q}(^2P)h(^2P) + \hat{Q}(^2F)h(^2F) + \hat{Q}(^2G)h(^2G) + \hat{Q}(^2H)h(^2H) + \hat{Q}(^2_1D)h(^2_1D) + \hat{Q}(^2_3D)h(^2_3D) + \hat{Q}(^2_1D,^2_3D)h(^2_1D,^2_3D) \qquad (17)$$

it as eq 18, where in the last expression the first three terms equal

$$\hat{H}_{PMT}[d^3] = \hat{I} E_{av} + \hat{Q}_D D + \hat{Q}_B B + \hat{Q}_{D\perp}(D\perp) + \hat{Q}_{B\perp}(B\perp) + p_1{}^t \hat{t}_1 + p_2{}^t \hat{t}_2 + p_3{}^t \hat{t}_3 + p_4{}^t \hat{t}_4 \qquad (18)$$

$\hat{H}_{SCS}[d^q]$ and the first five terms $\hat{H}_{PMT}[d^2]$ for which $N_p(\hat{K})$ is 2 and 4, respectively. The four $\hat{t}$ operators are the coefficient operators additionally required for d^3 for which $N_p(\hat{K}) = 8$. They make up the complete set of effective three-electron structure operators on d^q with the p set as the associated energy parameters. The $\hat{t}$ operators have been given by Judd and Leavitt[4] together with the 12 four-electron operators $\hat{f}_i$ (i = 1, 2, ..., 12) which apply to situations where q = 4, 5, or 6. $N_p(\hat{K}) = 20$ in all these cases (cf. eq 19). Our SCS operators, $\hat{Q}_D$ and $\hat{Q}_B$, and their

$$\hat{H}_{av} + \hat{K}_{complete}[d^q] = \hat{H}_{av} + \hat{K}_{PMT}[d^q] = \sum_{i=0}^{4} p_i^e \hat{e}_i + \sum_{i=1}^{4} p_i^t \hat{t}_i + \sum_{i=1}^{12} p_i^f \hat{f}_i \qquad (19)$$

respective orthogonal complements, $\hat{Q}_{D\perp}$ and $\hat{Q}_{B\perp}$, span the same operator space as the Judd-Leavitt set of effective two-electron operators $\{\hat{e}_1, \hat{e}_2, \hat{e}_3, \hat{e}_4\}$. Similarly, our operator $\hat{I}$ of eq 10 is identical to the Judd-Leavitt operator $\hat{e}_0$. We may thus use the

---

(76) Uylings, P. H. M. *J. Phys. B: At. Mol. Phys.* **1984**, *17*, 2375–2392.

(77) The model described by $\hat{H}_{PMT}[d^q]$ is, when $q = 2$, from a purely mathematical point of view—and, therefore, also from a data-fitting and data-reduction point of view—equal to the Racah–Trees model.[72,78] This model has been used for a long time by the atomic spectroscopists using the Racah parameters A, B, and C (or the Slater parameters F^0, F^2, F^4 or E_{av}, F^2, and F^4) supplemented by the Racah–Trees parameters α and β.[79] Therefore, from a neat data-reduction point of view $\hat{H}_{PMT}[d^q]$ is only new when $q \neq 2$ or 8. However, the Racah–Trees formulation of $\hat{H}_{PMT}[d^2]$ corresponds to referring its vector image to a basis-vector coordinate system with skew axes. This means that the norm square of $\hat{H}_{PMT}[d^2]$ cannot in this formulation be divided in parts referring to the individual parameters, since part of this norm square will lie in the overlap region between the nonorthogonal operators.

(78) Trees, R. E. *Phys. Rev.* **1951**, *83*, 756–760.

(79) The operator associated with α is $\hat{L}^2$; the one associated with β is Racah's seniority operator.[72]

results of these authors to write a general expression containing the *complete* structure operator $\hat{K}$ acting on d^q (eq 19).

Alternatively, we may formulate the expression analogously to those of eqs 16 and 17

$$\hat{H}_{av} + \hat{K}_{complete}[\mathrm{d}^q] = \hat{H}_{av} + \hat{K}_{PMT}[\mathrm{d}^q] = \sum_{v,S,L} \hat{Q}({}^{2S+1}_{v}\mathrm{L})h({}^{2S+1}_{v}\mathrm{L}) + \sum_{v \neq v'} \hat{Q}({}^{2S+1}_{v}\mathrm{L}, {}^{2S+1}_{v'}\mathrm{L})\, h({}^{2S+1}_{v}\mathrm{L}, {}^{2S+1}_{v'}\mathrm{L}) \qquad (20)$$

and, as we shall see in section 7, when the SCS spin–orbit coupling operator $\hat{Q}_\zeta \zeta$ representing $\hat{K}^*$ is added to either of these expressions, we obtain this paper's PMTζ model for the total structure of d^q.

We finish this section with a few clarifying remarks. In the d^3-eq 17, as compared with the d^2-eq 16, there is the new feature that a few of the energy parameters have been given additional specifications. These are caused by the occurrence of repeated ${}^{2S+1}\mathrm{L}$ terms in d^3, distinguished by seniority numbers (see the end of section 3). Thus $h({}^{2}_{1}\mathrm{D})$ is for instance the energy of ${}^{2}_{1}\mathrm{D}$ (seniority one), while $h({}^{2}_{1}\mathrm{D}, {}^{2}_{3}\mathrm{D})$ is the nondiagonal element connecting ${}^{2}_{1}\mathrm{D}$ and ${}^{2}_{3}\mathrm{D}$. Because of this nondiagonal element, the operator acting on d^3 is *more than complete* as far as energies of multiplet terms are concerned, but the complete structure model's nondiagonal element also involves the *nontrivial* eigenvector that contains information about the extent to which the two seniorities are mixed in the eigenstates.[80]

We find it conceptually clarifying to generally think about this paper's PMT model as consisting of *energy-completing* in-space[5] (diagonal) operators and *eigenvector-completing* cross-space[5] (nondiagonal) operators. With these latter ones included, the PMT model applied to d^q for $3 \leq q \leq 7$ is *structure complete* but *energy overcomplete* and by that essentially different from the Trees-Racah model[77] for d^2 and d^8 since these configurations do not give rise to such cross-space operators.

6. Parametrical J Level Model, a Mathematically Complete d^q Model

In the previous section we saw that the assumption of spin-free energy operators acting on a classificatory $n\mathrm{d}^q$ configuration, restricted only by the symmetries of the configuration's multiplet terms, led to the parametrical multiplet term model Hamiltonian, $\hat{H}_{PMT}[\mathrm{d}^q]$, which from hereon will be abbreviated as $\hat{H}_{PMT}$. This operator is structure complete in that $\hat{H}_{PMT} = \hat{H}_{av} + \hat{K}_{complete}$. As a premise for arriving at this result, it was used that the eigenstates of $\hat{H}_{PMT}$ can be classified as multiplet terms embodying degenerate function sets $|\mathrm{d}^q, v\mathrm{SL}\}$.

Analogous arguments using the premise that the eigenstates must be further specified and classifiable as J levels embodying the complete basis of degenerate sets $|\mathrm{d}^q, v\mathrm{SLJ}\}$ lead to the mathematically complete parametrical J level model. Its Hamiltonian of eq 21 completely accounts for the total structure of d^q.

$$\hat{H}_{PJL} = \hat{H}_{complete} = \hat{H}_{av} + \hat{K}_{complete} + \hat{K}^*_{complete} \qquad (21)$$

$\hat{H}_{PJL}$ acting on d^q may be obtained in terms of a linear combination of mutually orthogonal sets of basic coefficient operators $|\mathrm{d}^q, v\mathrm{SLJ}\}\{\mathrm{d}^q, v'\mathrm{S'L'J'}|$ with energy parameters as coefficients. We illustrate the idea in eq 22 by taking d^2 (and d^8) as our example.

$$\begin{aligned}\hat{H}_{PJL}[\mathrm{d}^2] \equiv\ & \hat{Q}({}^1\mathrm{S}_0)h({}^1\mathrm{S}_0) + \hat{Q}({}^3\mathrm{P}_0)h({}^3\mathrm{P}_0) + \hat{Q}({}^3\mathrm{P}_1)h({}^3\mathrm{P}_1) + \\ & \hat{Q}({}^3\mathrm{P}_2)h({}^3\mathrm{P}_2) + \hat{Q}({}^1\mathrm{D}_2)h({}^1\mathrm{D}_2) + \hat{Q}({}^3\mathrm{F}_2)h({}^3\mathrm{F}_2) + \\ & \hat{Q}({}^3\mathrm{F}_3)h({}^3\mathrm{F}_3) + \hat{Q}({}^3\mathrm{F}_4)h({}^3\mathrm{F}_4) + \hat{Q}({}^1\mathrm{G}_4)h({}^1\mathrm{G}_4) + \\ & \hat{Q}({}^1\mathrm{S}_0,{}^3\mathrm{P}_0)h({}^1\mathrm{S}_0,{}^3\mathrm{P}_0) + \hat{Q}({}^3\mathrm{P}_2,{}^1\mathrm{D}_2)h({}^3\mathrm{P}_2,{}^1\mathrm{D}_2) + \\ & \hat{Q}({}^3\mathrm{P}_2,{}^3\mathrm{F}_2)h({}^3\mathrm{P}_2,{}^3\mathrm{F}_2) + \hat{Q}({}^1\mathrm{D}_2,{}^3\mathrm{F}_2)h({}^1\mathrm{D}_2,{}^3\mathrm{F}_2) + \\ & \hat{Q}({}^3\mathrm{F}_4,{}^1\mathrm{G}_4)h({}^3\mathrm{F}_4,{}^1\mathrm{G}_4) \qquad (22)\end{aligned}$$

Here we have $J = 0$ and 4 (both occurring twice), $J = 1$ and 3 (once), and $J = 2$ (three times). This gives for instance for $J = 4$ the energy parameters associated with the operator sets $|{}^1\mathrm{G}_4\}\{{}^1\mathrm{G}_4|$, $|{}^3\mathrm{F}_4\}\{{}^3\mathrm{F}_4|$, $|{}^3\mathrm{F}_4\}\{{}^1\mathrm{G}_4|$, and $|{}^1\mathrm{G}_4\}\{{}^3\mathrm{F}_4|$, where the last two sets are associated with the same parameter.[5] $J = 0$ also gives three energy parameters. $J = 2$ gives six energy parameters and $J = 1$ and 3 give one energy parameter for each of them. All together $\hat{H}_{PJL}[\mathrm{d}^2]$ embodies 14 energy parameters, whose operator sets were counted here in a manner that counts the energy parameters of the total structure of d^2 plus the average energy of the configuration without separating the three classes of operators as in eq 21. From the previous section we know, however, that $\hat{H}_{PJL}[\mathrm{d}^2]$ consists of $\hat{H}_{PMT}[\mathrm{d}^2]$ and $\hat{K}^*{}_{complete}[\mathrm{d}^2]$, and since the former contains five parameters, the latter must contain nine.

A set of orthogonal coefficient operators spanning $\hat{K}^*{}_{complete}[\mathrm{d}^2]$ was found by Hansen and Judd[17] by using a symmetry method based on Lie groups. Their operators fall into three classes: the spin–orbit coupling operator $\hat{Q}_\zeta$ (a one-electron operator), denoted by z_v, five other operators with the same form in the rotation double group R_3*, *i.e.*, vectors in both spin space and orbital space (all two-electron operators), and finally three operators of rank 2 in both spin and orbital space (also two-electron operators).[81]

Parallel to what was found for the PMT model, the 5 + 9 = 14 Lie-group operators (cf. refs 4 and 17, respectively) and our 14 basic J-level operators of eq 22 span the complete operator space on d^2, namely, that of $\hat{H}_{av}$ plus that of the total structure. They do this in terms of two sets of mutually orthogonal operators whose normalized basis operators are related to each other by an orthogonal transformation in operator space. The Lie-group sets[4,17] have the advantages of separating operators of $\hat{K}$ type and $\hat{K}^*$ type and of having the spin–orbit coupling operator explicitly as one of its members.

$\hat{H}_{PJL} = \hat{H}_{complete}$ is of course not practical since it contains more empirical parameters (14) than energy observables (9). Nevertheless, it is conceptually useful, as we shall now see.

7. Parametrical Multiplet Term Model to Which Spin–Orbit Coupling Has Been Added

The model brought to practical use in this work has the purpose of allowing the determination of the best possible parameter values for the one-electron spin–orbit coupling parameter, ζ_{nd}, of d^q systems. Therefore, it was decided to try to see if the PMT model,

---

(80) For repeated terms each seniority has its own λ-value (cf. eq 7), and the observed λ-values for the d^3 eigenterms ${}^{2}_{\mathrm{a}}\mathrm{D}$ and ${}^{2}_{\mathrm{b}}\mathrm{D}$ of $\hat{K}$ will be linear combinations of those corresponding to pure seniorities. The coefficients of these combinations are eigenvector components. It is actually through the observation of spin–orbit splittings of ${}^{2}_{\mathrm{a}}\mathrm{D}$ and ${}^{2}_{\mathrm{b}}\mathrm{D}$ that the nondiagonal element of $\hat{K}$ becomes determinable. This is also the factor that allows the codetermination of nondiagonal elements of $\hat{K}$ simultaneously with ζ_{nd} in the regression analysis (cf. section 9). There are two papers[17,18] in which the effective three-electron operators and four-electron operators have been used in spectral analysis. However, common to these papers is that, in their final results, they have either refrained from using the complete set[17] of structure operators or they have used the operators in batches[18] rather than simultaneously. In either case this means that their additional fine-structure operators (that is, those on top of the spin–orbit coupling operator) may be decisive in determining eigenvector components of the above-mentioned kind. This is, at least in principle, unfortunate because these components are fundamentally defined by structure operators. For d^4, d^5, and d^6 systems, the spin–orbit coupling operator, playing a role in the PMTζ model, serves to determine thus five nondiagonal PMT parameters.

(81) These classifications agree with the results directly obtainable from the selection rules of S and L applied to all $n\mathrm{d}^2$ multiplet-term levels $|\mathrm{SLJ}\}$ when the rank-2 operators come in additionally and belong to $|{}^1\mathrm{P}_2\}\{{}^3\mathrm{F}_2|$, $|{}^3\mathrm{P}_2\}\{{}^3\mathrm{P}_2|$, and $|{}^3\mathrm{F}_2\}\{{}^3\mathrm{F}_2|$. Here the latter two operator sets have in our scheme the property that they associate with two energy parameters, one associated with an operator of vector–vector type and one with an operator of tensor–tensor type, where those of tensor–tensor type are orthogonal to the spin–orbit coupling operator.

which, as discussed toward the end of section 5, is more[80] than complete in parametrizing the multiplet term energies, could be used for this purpose. The simplest way of investigating this, conceptually as well as practically, would be to combine the PMT model, which is a pure and complete structure model, with the conventional SCS spin–orbit coupling operator $\hat{Q}_\zeta\zeta$. We name the model thus obtained the PMTζ model. Its Hamiltonian operator $\hat{H}_{PMT\zeta}$ is given in eq 23, where $\hat{K}_{SCS\perp}$ acting on the most general d^q embodies $\hat{Q}_{D\perp}$, $\hat{Q}_{B\perp}$, and the 4 three-electron operators and 12 four-electron operators of eq 19. We emphasize also the simple form of $\hat{K}^*_{SCS} = \hat{Q}_\zeta\zeta$ (eq 12).

$$\hat{H}_{PMT\zeta} = \hat{H}_{PMT} + \hat{K}^*_{SCS} = \hat{H}_{av} + \hat{K}_{PMT} + \hat{K}^*_{SCS} = \hat{H}_{av} + \hat{K}_{SCS} + \hat{K}_{SCS\perp} + \hat{K}^*_{SCS} = \hat{H}_{av} + \hat{K}_{complete} + \hat{K}^*_{SCS} \quad (23)$$

We may write the complete Hamiltonian acting on d^q in the following form

$$\hat{H}_{complete} = \hat{H}_{PJL} = \hat{H}_{PMT\zeta} + \hat{R}_{PMT\zeta} \quad (24)$$

where the residual operator $\hat{R}_{PMT\zeta}$ for instance for d^2 is the sum of the eight fine-structure operators remaining after the spin–orbit coupling operator, $z_v\zeta = \hat{Q}_\zeta\zeta$, has been removed from the Hansen–Judd set of nine operators contained in $\hat{K}^*_{complete}[\mathrm{d}^2]$ (cf. end of section 6). For general d^q, the symbol $\hat{R}_{PMT\zeta}$ similarly denotes the residual operator defined by eq 25. For the SCS model we then have eq 26, where the right-hand side operators are orthogonal being pure fine-structure and structure operators, respectively.

$$\hat{R}_{PMT\zeta} \equiv \hat{K}^*_{complete} - \hat{Q}_\zeta\zeta = \hat{K}^*_{PJL} - \hat{Q}_\zeta\zeta \quad (25)$$

$$\hat{R}_{SCS\zeta} = \hat{R}_{PMT\zeta} + \hat{K}_{SCS\perp} \quad (26)$$

The model hierarchies, already given in the expressions (2) and (3), can now be fully appreciated by reference to eqs 21, 23, 13, 12, and 11.

8. Experimental J Level Data Sets for nd^q: Preliminary Analysis

An experimental energy level data set for an nd^q system consists of energies of J levels whose J labels have been identified and for which some zero point of energy, usually that of the ground level of the atomic species in question, has been chosen. In the whole of the conceptual part of this paper, only *complete* data sets for nd^q systems will be discussed. This means that if the degeneracies of all the observed J levels, $2J + 1$, are introduced, the number of states $N_s = \binom{10}{q}$, is obtained (cf. eq 4).

It is useful from the beginning to set up the data in an $N_s \times N_s$ diagonal matrix $\mathbf{E}_{\mathbf{exp}}$, where each J level is repeated $2J + 1$ times. The trace of this matrix is N_sE_{av}. The norm square[1] $<\mathbf{E}_{\mathbf{exp}}|\mathbf{E}_{\mathbf{exp}}>$ (one might call it the area) of the matrix is the sum of the squares of its elements, and if E_{av} is subtracted from every element in advance, the norm square of the resulting traceless matrix $<\bar{\mathbf{E}}_{\mathbf{exp}}|\bar{\mathbf{E}}_{\mathbf{exp}}>$ may be called the area of the *total structure* or the sum square splitting[6] of the d^q configuration. All these quantities are exactly and *a priori* calculable quantities, directly from the data. The relationship between this presentation of data and the presentation based upon the complete, symmetry-based model $\hat{H}_{PJL}$ of section 6 is given by eq 27. However, the right-hand side of eq 27 is not practical since there is no way the exact parameter values contained in $\hat{H}_{PJL}$ can be found. This is where the usable models come in, be it SCSζ, PMTζ, or others. We may generalize eq 24 by writing

$$\langle \mathbf{E}_{\mathbf{exp}}|\mathbf{E}_{\mathbf{exp}}\rangle = \langle \hat{H}_{PJL}|\hat{H}_{PJL}\rangle \quad (27)$$

$$\hat{H}_{complete} = \hat{H}_{model} + \hat{R}_{model} \quad (28)$$

or by subtraction of $\hat{H}_{av}$

$$\hat{H}_{PJL} - \hat{H}_{av} = (\hat{H}_{model} - \hat{H}_{av}) + \hat{R}_{model} \quad (29)$$

which shows that $\hat{R}_{model}$ is always barycentered. If $\hat{H}_{PJL}$ is expressed in terms of a complete set of mutually orthogonal operators and $\hat{H}_{model}$ in terms of the same set truncated according to choice, we have using eqs 27 and 28

$$\langle \hat{H}_{PJL}|\hat{H}_{PJL}\rangle = \langle \mathbf{E}_{\mathbf{exp}}|\mathbf{E}_{\mathbf{exp}}\rangle = \langle \hat{H}_{model}|\hat{H}_{model}\rangle + \langle \hat{R}_{model}|\hat{R}_{model}\rangle \quad (30)$$

and the last equality of eq 30 is as practical as this effective-operator theory can be. As we shall discuss in the next section, the quantity $<\hat{R}_{model}|\hat{R}_{model}>$ is the so-called *variance* in a conventional adaptation of model to experiment. We may thus view $<\mathbf{E}_{\mathbf{exp}}|\mathbf{E}_{\mathbf{exp}}>$ as the roof that we aim at approaching optimally from below by varying the parameters embodied in the expression $<\hat{H}_{model}|\hat{H}_{model}>$ while seeking to minimize the variance.

In this paper we have used for comparisons with experimental data only three of the many possible models on d^q ($2 \leq q \leq 8$). $\hat{H}_{model}$ is either equal to $\hat{H}_{SCS\zeta}$ of eq 13 or $\hat{H}_{PMT\zeta}[\mathrm{d}^q]$ of eq 23, or when in a few cases the data is incomplete, $\hat{H}_{PMT\zeta}[\mathrm{d}^2]$ of eq 15 is used to act on d^q for $3 \leq q \leq 7$.[82]

9. Adaptation of Effective Hamiltonians to Experimental Data by Parameter Fitting: Approximate Invariance of ζ_{nd} on Extension of $\hat{H}_{SCS\zeta}$ to $\hat{H}_{PMT\zeta}$

This section is concerned with a few special features of an otherwise standard nonlinear least squares procedure[83,84] whose purpose is to fit the parameters embodied in our effective d^q Hamiltonians so that their eigenvalues match the corresponding J level energy data as closely as possible. If we decide to measure this closeness in terms of areas and define it as the following minimum difference, $<\hat{R}_{model}|\hat{R}_{model}> = <\mathbf{E}_{\mathbf{exp}}|\mathbf{E}_{\mathbf{exp}}> - <\hat{H}_{model}|\hat{H}_{model}>$ (cf. eq 30), then we have under one special condition a complete analogy with the conventional least-squares expression for the variance[87] (cf. here eq 4)

$$\chi^2_w = \sum_i (2J_i + 1)(E^i_{exp} - E^i_{model})^2 = \sum_k (E^k_{exp} - E^k_{model})^2 = \langle \hat{R}_{model}|\hat{R}_{model}\rangle \quad (31)$$

where *i* and *k* refer to levels and states, respectively. This condition

---

(82) With reference to footnote 80, it should be noted that while the nondiagonal PMT model parameters are determined mainly by the diagonal elements of the spin–orbit coupling in the vSL eigenbasis, the determination of diagonal PMT parameters associated with *unobserved terms* must be based upon nondiagonal effects of the spin–orbit coupling in this eigenbasis. This means that the parameters of unobserved terms become very little well-defined.

(83) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes. The Art of Scientific Computing*. Cambridge University Press: Cambridge, U.K., 1986; Chapter 14.

(84) The overall quality of the fit is here measured by means of the root mean square parameter $\sigma'_w \equiv [\chi'_w/\sum_i(2J_i + 1)]^{1/2}$ (cf. eq 16.1 of ref 85). This quantity measures the simple root mean square difference between experimental and calculated state energies or, equivalently, the *weighted* average difference between J level energies. Unlike the usually used error or standard deviation σ_w, σ'_w compares directly with the difference between one experimental eigenenergy and its calculated value, since σ'_w does not involve the number of degrees of freedom ν of the problem. The relation between σ_w and σ'_w is $\sigma_w = \sigma'_w[N_o/(N_o - N_p)]^{1/2}$ (cf. ref 86) where N_o is the number of observables and N_p is the number of fitting parameters (*i.e.*, $\nu = N_o - N_p$). Following common practice, the parameter covariance matrix has been scaled by χ^2_w/ν corresponding to the model being acceptable on a 50% statistical confidence level.

(85) Judd, B. R. *Rep. Prog. Phys.* **1985**, *48*, 907–954.

(86) Uylings, P. H. M.; Raassen, A. J. J.; Wyart, J. F. *J. Phys. B: At. Mol. Phys.* **1984**, *17*, 4103–4126.

(87) Uylings *et al.*[86] use a slightly different formulation based upon so-called normalized weight factors. Our χ_w^2 (cf. eq 31) is multiplied by N_o/N_s and is then called R^2. However, since the reciprocal of their unscaled covariance matrix is also multiplied by the factor N_o/N_s, the two approaches end up giving identical results when the respective unscaled covariance matrices are multiplied by χ^2_w/ν and R^2/ν to give identical conventional covariance matrices.

Table I. Analyses of the $3d^8$ Energy Level Data[40] of Ni^{2+} (g), with All Energy Quantities in Units of μm^{-1} ($1\ \mu m^{-1} = 10^4\ cm^{-1}$)[a]

Slater–Condon–Shortley model calcd energies		exptl energies		parametrical multiplet term model calcd energies	
SL terms	J levels			J levels	SL terms
5.4029	5.4104	$\{^1S\}_0$	5.2532	5.2532	5.2456(53)
2.2239	2.2259	$\{^1G\}_4$	2.3109	2.3109	2.3089(18)
	1.7525	$\{^3P\}_0$	1.7231	1.7204	
1.6926	1.7263	$\{^3P\}_1$	1.6978	1.6946	1.6612(21)
	1.7038	$\{^3P\}_2$	1.6662	1.6691	
1.4836	1.4475	$\{^1D\}_2$	1.4032	1.4026	1.4350(30)
	0.2325	$\{^3F\}_2$	0.2270	0.2269	
0.1063	0.1400	$\{^3F\}_3$	0.1361	0.1357	0.1023(12)
	0.0030	$\{^3F\}_4$	0.0000	0.0003	
$\sigma_w = 0.0664$				$\sigma_w = 0.0024$	
$\sigma'_w = 0.0495$				$\sigma'_w = 0.0014$	
$\zeta_{3d} = 0.0675(228)$				$\zeta_{3d} = 0.0668(8)$	

[a] In the middle columns the experimental energy levels have been assigned the symbols $\{^{2S+1}L\}_J$, the braces being used to signify that though J is a good quantum number, the Russell–Saunders term symbol ^{2S+1}L is fuzzyfied. For example $\{^1S\}_0$ is mainly $^1S_0$, but it is amalgamated with a small amount of $^3P_0$. From this middle column we obtain $\langle \mathbf{E}_{exp}|\mathbf{E}_{exp}\rangle = 111.385\ \mu m^{-2}$ and $\langle \bar{\mathbf{E}}_{exp}|\bar{\mathbf{E}}_{exp}\rangle = 55.158\ \mu m^{-2}$ (cf. section 8). In the left-hand columns are the energy values of terms and levels, respectively, calculated by use of the SCSζ model. Here we have in units of μm^{-2} $\langle \hat{K}_{SCS\zeta}|\hat{K}_{SCS\zeta}\rangle = 54.502$, $\langle \hat{K}^*{}_{SCS\zeta}|\hat{K}^*{}_{SCS\zeta}\rangle = 0.546$, and $\langle \hat{R}_{SCS\zeta}|\hat{R}_{SCS\zeta}\rangle = \chi^2{}_w = 0.110$ adding up to $\langle \bar{\mathbf{E}}_{exp}|\bar{\mathbf{E}}_{exp}\rangle$. In the right-hand columns, the levels and terms of the PMTζ model are to be found. Here we have in units of μm^{-2} $\langle \hat{K}_{PMT\zeta}|\hat{K}_{PMT\zeta}\rangle = 54.624$, $\langle \hat{K}^*{}_{PMT\zeta}|\hat{K}^*{}_{PMT\zeta}\rangle = 0.535$, and $\langle \hat{R}_{PMT\zeta}|\hat{R}_{PMT\zeta}\rangle = 0.0001$ again adding up to $\langle \bar{\mathbf{E}}_{exp}|\bar{\mathbf{E}}_{exp}\rangle$. It is seen that going from $\hat{H}_{SCS\zeta}$ to $\hat{H}_{PMT\zeta}$ mainly results in a transfer of area from $\hat{R}$ to $\hat{K}$ keeping $\hat{K}^*$ roughly constant. So the parameter value for ζ_{3d} is hardly changed while its error is decreased by a factor of 28, following the reduction in σ_w when going from the SCSζ to the PMTζ model.

is that the weighting[88] of the J level data points be $(2J+1)$. This weighting has at least three additional advantages. (1) It serves as a preparatory means for the consistent introduction of ligand fields or an external magnetic field into the model. (2) It allows an operator analysis of the residual operator according to eq 25 and its analog for other models. (3) The parameter, E_{av}, will be uncorrelated with the other parameters when the observed space is complete. Under this condition E_{av} can either be calculated directly from the data before the regression analysis is made or E_{av} can be found in the analysis itself.

Let us now consider our numerical results for the spin–orbit coupling parameter, ζ_{nd}. Table I contains the detailed results of the application of the SCSζ model to the data for Ni^{2+}. Table II contains a collection of best-fit SCSζ-model spin–orbit coupling parameter values for 3d, 4d, and 5d transition metal ions. The 3d part of the table is an updating and augmentation of Table II of ref 1.[88] For those metal ions for which new and more complete energy level data have appeared in the literature after the extensive collections by Sugar and Corliss,[33–40] we have used the new data[42–46] in the calculations.

From Table II it can be seen that the SCSζ model errors on ζ_{nd} are typically around 200 cm^{-1} (0.020 μm^{-1}) for the chemically interesting metal ions of the first transition period. This means that the errors are of the same order of magnitude as the ζ_{nd} values themselves. The results of Table I suggest that a shortcoming of the SCS model is the model's inability to describe with sufficient accuracy the energies, $h(^{2S+1}L)$, of the multiplet terms.

Extending the SCSζ model so as to make it become the PMTζ model reduces the errors on the best-fit ζ_{nd} values by a factor of 10–50. In view of such a drastic reduction, one might have expected a major change also in the ζ_{nd} value itself. However, this is not found, as it can be seen by comparing the two sets of ζ_{nd} values of Table II. Such an approximate constancy of parameter values has previously[3] been attributed to the orthogonality of the operators associated with the different parameters in the fits. This is, however, only an incomplete description.

An analysis of the origin of the approximate equality of the ζ_{nd} values obtained when adapting the SCSζ and the PMTζ models reveals two conditions for the invariance. The first one is the approximate lack of correlation between the spin–orbit coupling parameter and the parameters necessary to extend the SCS model to make it become the PMT model. The second condition, which only is important if the first one is met, is that the model eigenbasis is not significantly perturbed by the additional parametric terms. This latter condition is firmly connected with the degree of linearity on going from SCSζ to PMTζ though it is also important that the area, $<\hat{R}_{SCS\zeta}|\hat{R}_{SCS\zeta}>$, is already small before extension of the Hamiltonian (cf. Table I).

We now discuss these problems in a little more detail turning ourselves gradually toward the spin–orbit coupling's special properties. From fitting theory it follows that, *in a given basis*, the parameters associated with two different operators are mutually completely uncorrelated provided the *diagonal part* of the overlap between the matrix representatives of the two operators is vanishing. This condition for obtaining uncorrelated parameters is not necessarily fulfilled by the orthogonality of the two operators since the operator overlap is the sum of a diagonal and a nondiagonal part. However, in the limit of small nondiagonal contributions, the correlation is, of course, also small. This is probably the reason the operator overlap has become established as the quantity that determines the correlation between parameters.[3,17,18,76,85,86]

Consider now an SL basis. As a consequence of eq 5, the spin–orbit coupling is barycentered within each multiplet term. This ensures a vanishing diagonal overlap between the spin–orbit coupling and any of the SCS or PMT model operators describing the term separations. In an SL basis the spin–orbit coupling parameter and the term-energy parameters are therefore uncorrelated, and were we—for the sake of the argument—to fit a value for ζ_{nd} in this fixed basis, then this value would be independent of whether the SCS or the PMT parametrization was used. It is, however, important to note that fitting in a fixed basis is a hypothetical situation and that the standard procedure here and elsewhere is to vary the basis to make it at any stage of the iteration the eigenbasis of the Hamiltonian containing the so far optimized parameter values.

For actual atomic d^q systems, the eigenbases are not pure SL bases and accordingly the spin–orbit coupling parameter and the structure parameters are correlated. The loss of diagonal orthogonality compared with the SL situation may be looked upon as an effect of the nondiagonal spin–orbit coupling matrix elements, which cause the barycentration of the J levels within each fuzzyfied multiplet term $\{^{2S+1}L\}$ to break down. If the spin–orbit coupling is small, as for the $3d^q$ and $4d^q$ metal ions, then the eigenbases of these systems are, however, not too far from being pure SL bases. Therefore, the spin–orbit coupling parameter and the structure parameters will only be weakly correlated. The second condition necessary to ensure the invariance of the spin–orbit coupling parameter on extending the SCSζ model to the PMTζ model is fulfilled since both the SCS and PMT models have the SL basis as their eigenbasis and the spin–orbit coupling matrix elements are small in comparison to the term energy differences.

For certain metal ions too many J levels are lacking in the observed d^q spectra for the PMTζ model to be applicable. In these cases the model invariance of ζ_{nd} discussed above has the important practical implication that one may use the SCSζ-model ζ_{nd} values from Table II with the well-founded hope that they are

---

(88) This weighting is now common practice in atomic spectroscopy, and it was also our proclaimed intention in the previous paper.[1] We later found that a programming error had led us to use a weighting of $(2J+1)^2$ rather than $(2J+1)$. This, unfortunately, led to *slightly* incorrect parameter values in ref 1.

Table II. Empirical Values (in Units of μm^{-1}) for the One-Electron Spin–Orbit Coupling Parameter, ζ_{nd}, Referring to Gaseous Ions of nd^q Configurations[a]

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$3d^1$	0.0079^{33}	0.0153^{34}	0.0250^{35}	0.0376^{36}	0.0540^{37}	0.0734^{38}	0.0980^{39}	0.1271^{40}	0.1624^{41}
$3d^2$	$0.0052(1)^{33}$	$0.0118(2)^{34}$	$0.0206(3)^{35}$	$0.0319(4)^{36}$	$0.0466(5)^{42}$	$0.0649(6)^{43}$	$0.0873(7)^{39}$		
	0.0049(97)	0.0120(150)	0.0214(172)	0.0336(199)	0.0492(223)	0.0683(240)	0.0907(266)	b^{40}	b^{41}
$3d^3$	$0.0044(4)^{33}$	$0.0089(2)^{34,c}$	$0.0169(3)^{35}$	$0.0274(4)^{36}$	$0.0408(6)^{37}$	$0.0578(9)^{38}$			
	0.0020(307)	0.0282(186)	0.0150(190)	0.0254(226)	0.0398(259)	0.0590(285)	d^{39}	d^{40}	e^{41}
$3d^4$		f^{34}	$0.0132(11)^{35,c}$	$0.0229(5)^{36,c}$	$0.0351(8)^{44,c}$	$0.0505(8)^{38}$	$0.0700(16)^{39}$	f^{40}	
		0.0078(4)	0.0086(281)	0.0228(197)	0.0344(233)	0.0487(263)	0.0684(279)	0.0863(334)	e^{41}
$3d^5$			f^{35}	$0.0178(19)^{36,c}$	$0.0315(16)^{37,c}$	$0.0464(14)^{38}$	$0.0656(19)^{39}$	$0.0888(24)^{40}$	$0.1163(30)^{41}$
			i	0.0297(228)	0.0415(215)	0.0583(205)	0.0662(235)	0.0948(237)	0.1191(251)
$3d^6$					$0.0257(14)^{37,c}$	$0.0427(5)^{45,c}$	$0.0619(10)^{39,c}$	$0.0858(12)^{40,c}$	$0.1139(16)^{41,c}$
				b^{36}	0.0441(226)	0.0488(208)	0.0669(233)	0.0881(256)	0.1130(273)
$3d^7$						$0.0356(4)^{38}$	$0.0533(5)^{46}$	$0.0749(7)^{40}$	$0.1009(9)^{41}$
					b^{37}	0.0372(165)	0.0545(169)	0.0752(186)	0.0999(202)
$3d^8$							$0.0466(5)^{39,c}$	$0.0668(9)^{40}$	$0.0911(12)^{41}$
						b^{38}	0.0149(273)	0.0675(228)	0.0934(237)
$3d^9$							0.0389^{39}	0.0603^{40}	0.0829^{41}

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
$4d^1$	0.0290^{47}	0.0500^{48}	0.0748^{49}	0.1034^{50}	e^{51}	e^{51}	e^{51}	e^{51}	e^{51}
$4d^2$	$0.0208(4)^{51,c}$	$0.0409(2)^{52}$	$0.0646(2)^{53}$	$0.0921(2)^{50}$					
	0.0086(210)	0.0436(168)	0.0669(83)	0.0937(67)	e^{51}	e^{51}	e^{51}	e^{51}	e^{51}
$4d^3$				$0.0810(3)^{50}$					
	b^{51}	d^{51}	b^{51}	0.0834(88)	e^{51}	e^{51}	e^{51}	e^{51}	e^{51}
$4d^4$				$0.0714(7)^{50,c}$					
		b^{51}	d^{51}	0.0743(146)	e^{51}	e^{51}	e^{51}	e^{51}	e^{51}
$4d^5$				$0.0480(46)^{50,c}$				$0.2003(5)^{54}$	
			b^{51}	0.0175(411)	e^{51}	e^{51}	e^{51}	0.1923(71)	e^{51}
$4d^6$				f^{50}				$0.1843(6)^{55,c}$	$0.2316(6)^{56,c}$
				0.0182(21)	b^{51}	b^{51}	e^{51}	0.1844(71)	0.2244(79)
$4d^7$						$0.0932(18)^{51}$	$0.1211(88)^{51}$	$0.1690(3)^{57}$	
					g^{51}	0.0911(113)	0.1204(260)	0.1655(68)	e^{51}
$4d^8$								$0.1556(9)^{58}$	$0.1997(8)^{59}$
						d^{51}	d^{51}	0.1504(75)	0.1937(80)
$4d^9$							0.0939^{51}	0.1416^{51}	0.1844^{60}

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au
$5d^1$	0.0641^{51}	0.1877^{61}	0.2643^{62}	0.3483^{63}	0.4398^{64}	e^{51}	e^{51}	e^{51}	e^{51}
$5d^2$	$0.0557(28)^{51,c}$	$0.1370(144)^{61,c}$	$0.2254(21)^{65}$	$0.3093(13)^{66}$					
	0.0860(416)	0.1673(471)	0.2306(164)	0.3108(91)	e^{51}	e^{51}	e^{51}	e^{51}	e^{51}
$5d^3$				$0.2686(31)^{67}$					
	g^{51}	d^{51}	e^{51}	0.2654(159)	e^{51}	e^{51}	e^{51}	e^{51}	e^{51}
$5d^4$									
		g^{51}	b^{51}	e^{51}	e^{51}	e^{51}	e^{51}	e^{51}	e^{51}
$5d^5$									
			b^{51}	d^{51}	e^{51}	e^{51}	e^{51}	e^{51}	e^{51}
$5d^6$									
				g^{51}	g^{51}	e^{51}	e^{51}	e^{51}	e^{51}
$5d^7$									
					g^{51}	g^{51}	e^{51}	e^{51}	e^{51}
$5d^8$									
						b^{68}	h^{69}	e^{51}	e^{51}
$5d^9$							i^{51}	0.3368^{51}	e^{51}

[a] The upper values have been obtained by using the parametrical multiplet term model, PMTζ, and the lower values, by using the Slater–Condon–Shortley model, SCSζ. All calculations were made by means of the ligand-field program LIGFIELD (J. Bendix, Proceedings of the 29th ICCC, Lausanne, Switzerland, 1992). The errors on the ζ_{nd} values are given in parentheses. The d^1 and d^9 configurations consist of a single ^{2}D term only, and for the metal ions of these configurations the value of ζ_{nd} was modeled without a statistical error, directly from the energy difference between $^2D_{5/2}$ and $^2D_{3/2}$ (eq 8). For the lowest oxidation states of 3d^q ions, the ζ_{nd} values may be well-determined within the models used, but less appropriate. The reason is that the concept of the characterizing d^q configuration may become less meaningful when levels of for instance d^{q-1}s lie inside the range of levels of d^q. [b] The small number of observed d^q terms do not allow a determination of ζ_{nd} using the SCSζ model. [c] In order to apply the PMTζ model, the energies of one or a few missing terms have been calculated from the experimental data available by means of the PMTζ[d^2] model (section 5). For d^2 and d^8 systems, with ^{1}S missing, a reduced version of this model was used. [d] The SCSζ and/or the PMTζ model description of the d^q energy levels of this atomic species gave an unusually large σ_w. [e] No experimental data apparently exist for this atomic species. [f] The number of missing terms is so large that application of the PMTζ model was considered inappropriate. [g] No experimental data apparently exist for the d^q levels of this atomic species. [h] The d^q configuration is strongly intermingled with other configurations. [i] The value obtained for ζ_{nd} was highly unrealistic.

much better than their errors would suggest. This is what has been done in the past, but no justification has been attempted before, other than the purely empirical one that the ζ_{nd} values obtained by using the SCSζ model varied smoothly with Z, z, and q in spite of their large errors.[1]

10. Results and Discussion

This section is mainly concerned with the variation of the empirical spin–orbit coupling parameters within the periodic table. First, however, we want to summarize the accomplishments achieved by substituting the PMTζ model for the SCSζ model.

In the SCSζ model the J level energies are, independently of the number of electrons q, parametrized by E_{av}, D, B, and ζ_{nd} (cf. eq 13). This is a much harder task, the larger q is, since the number of observable J levels is 9, 19, 34, and 37 for d^2, d^3, d^4, and d^5, respectively, with the usual symmetry around d^5 for $q > 5$. For the PMT model, the number of parameters is for the above configurations 5, 9, 21, and 21, respectively, as it can be

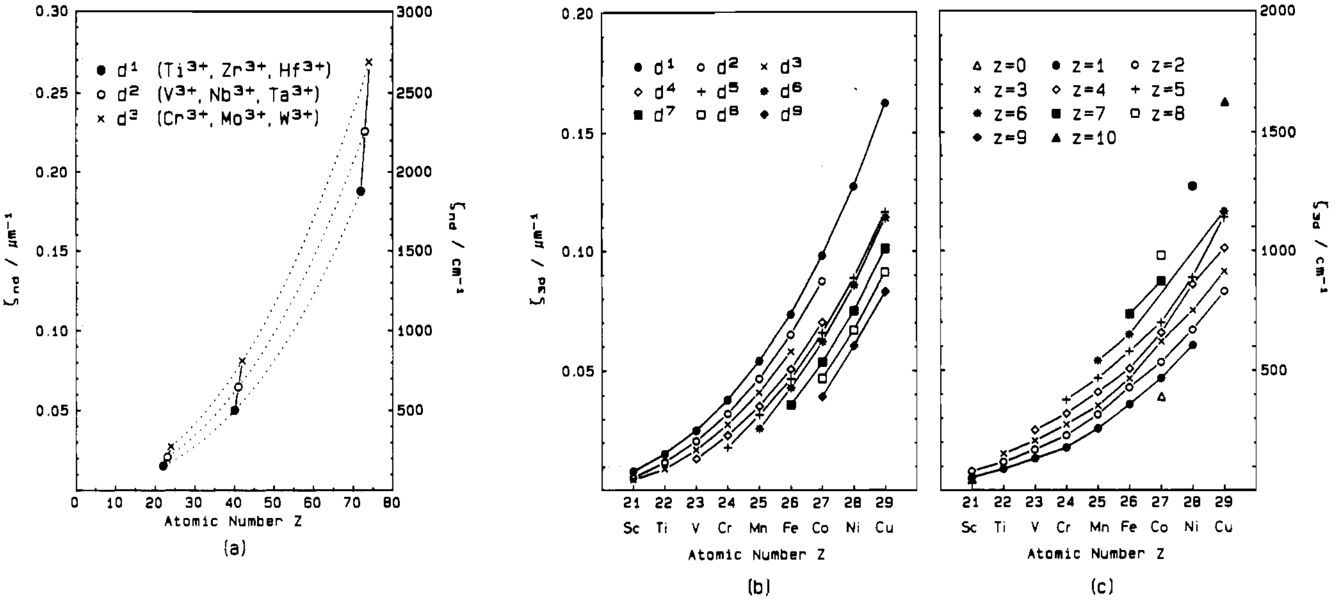

Figure 1. (a) ζ_{nd} values for the tripositive metal ions having d^1, d^2, and d^3 configurations. The dotted curves connecting the data points are visual aids. We emphasize how closely the directly determined ζ_{nd} values for the d^1 systems Ti^{3+}, Zr^{3+}, and Hf^{3+} compare with the ζ_{nd} values derived by means of the PMTζ model for the d^2 systems V^{3+}, Nb^{3+}, and Ta^{3+} and the d^3 systems Cr^{3+}, Mo^{3+}, and W^{3+}. Though the principal quantum number n has hardly any significance as a number, it is still of dominating significance for the numerical value of ζ_{nd} (cf. eq 34). For each n, the data points for $q = 1$ lies only just significantly to the left of the extension of the fully drawn line joining the data points for $q = 2$ and $q = 3$ (see section 10). (b) ζ_{3d} values for the metal ions of the first transition period. Data points belonging to the same $3d^q$ configuration, *i.e.*, having the same q value, have been connected by straight lines. Notice that the difference quotients $(\Delta\zeta_{3d}/\Delta Z)_q$ increase quite smoothly with Z for all q. (c) Plot of the same data as shown in Figure 1b but with the data points connected by straight lines according to the ionic charge z rather than the number of electrons q. The difference quotients $(\Delta\zeta_{3d}/\Delta Z)_z$ vary less smoothly with Z than those of Figure 1b.

Table III. Values for $\chi^2_w = \langle \mathbf{R}|\mathbf{R}\rangle$ and $\zeta^2_{nd}\langle \hat{Q}_\zeta|\hat{Q}_\zeta\rangle$ for d^3 systems[a]

	Cr^{3+}	Mo^{3+}	W^{3+}
$\langle \mathbf{R}_{SCS\zeta}|\mathbf{R}_{SCS\zeta}\rangle$	0.5203	0.1160	0.4422
$\zeta^2_{nd}(\mathrm{SCS})\langle \hat{Q}_\zeta|\hat{Q}_\zeta\rangle$	0.2706	2.9198	29.5910
$\langle \mathbf{R}_{PMT\zeta}|\mathbf{R}_{PMT\zeta}\rangle$	0.000119	0.000044	0.01074
$\zeta^2_{nd}(\mathrm{PMT})\langle \hat{Q}_\zeta|\hat{Q}_\zeta\rangle$	0.3145	2.7555	30.2630

[a] Cf. section 8. The values are in units of μm^{-2}.

counted from eq 19. The PMTζ model has $\hat{Q}_\zeta\zeta$ as its only additional operator (cf. eq 23). This means that $\hat{Q}_\zeta\zeta$ still has to account for 4, 10, 13, and 16 fine-structure energy differences, respectively, for the four d^q configurations mentioned.

To exemplify this discussion, we give the explicit results for the nd^3 systems with $z = 3$ in Table III. The variances using the SCSζ and PMTζ models are here written as areas of the respective residual operators for which eq 32 applies (cf. eq 26), where the

$$\langle \hat{R}_{SCS\zeta}|\hat{R}_{SCS\zeta}\rangle = \langle \hat{R}_{PMT\zeta}|\hat{R}_{PMT\zeta}\rangle + \langle \hat{K}_{SCS\perp}|\hat{K}_{SCS\perp}\rangle \quad (32)$$

right-hand side consists of a pure fine-structure part and a pure structure part, respectively. It is evident from Table III that going from SCSζ to PMTζ has as its essential consequence that most of $\hat{R}_{SCS\zeta}$ is absorbed in $\hat{K}_{SCS\perp}$. Furthermore, it may be concluded that the fine-structure operators additional to $\hat{K}'_{SCS} = \hat{Q}_\zeta\zeta$, whose areas add up to $\langle \hat{R}_{PMT\zeta}|\hat{R}_{PMT\zeta}\rangle$, contribute only very little to reaching the roof of $\langle \mathbf{E}_{exp}|\mathbf{E}_{exp}\rangle$ as compared with the contribution from the spin–orbit coupling operator itself (cf. eq 30). This is extremely satisfactory from a chemical point of view because it means that the experimental data for all practical purposes[89] can be accounted for without use of fine-structure operators whose origin[17] is made somewhat obscure by the loosened contact between model and physics (cf. section 2).

It is a general feature (*e.g.* Table III) that the PMTζ model works better for second-row transition metal ions than for those of the other rows. This may be caused by the energy difference between nd and $(n + 1)s$ being largest for $n = 4$.

We now discuss the body of ζ_{nd} values, which make up this paper's broadly applicable results (Table II).

The ζ_{nd} values vary so smoothly with the integers Z, z, and q that even difference quotients of ζ_{nd} with respect to these integers reveal regularities. In a few cases, small irregularities might in the future turn out to be caused by incorrect premises, that is, wrong assignments of one or two spectral lines.

It should at the outset be noted that the ζ_{nd} values for d^1 and d^9 given in Table II are proportional to a simple energy difference between two J levels according to eq 8. These parametric results are thus independent of the PMTζ model, yet they fall perfectly into place in Table II (cf. also Figure 1).

Figure 1 visualizes the variations of ζ_{nd} that are most interesting from an inorganic chemical point of view. In an appreciation of the notation for the difference quotients, the relationship of eq 33 should be noted for the $3d^q$ systems.

$$Z - 18 = z + q \quad (33)$$

Figure 1a visualizes the values of ζ_{nd} for the tripositive ions of d^1, d^2, and d^3 configurations from the three transition metal series. The ζ_{nd}-variation with the principal quantum number n dominates the issue. Equation 34 thus holds as a rule of thumb. Figure 1a

$$\zeta_{3d}:\zeta_{4d}:\zeta_{5d} \approx 1:3:10 \quad (34)$$

also illustrates the values of the unit-denominator difference quotients $(\Delta\zeta_{nd}/\Delta Z)_{z=3}$ within the early parts of each of the three transition series. These difference quotients, obtained from the d^2 and d^3 PMT model data, are for $n = 3$, 4, and 5 equal to 68, 164, and 432 cm^{-1}, respectively. The ζ_{nd} values for d^1 obtained by a linear extrapolation of these model data are 138, 482, and 1822 cm^{-1}, which are to be compared with the directly observed and, therefore, model-independent values for d^1 of 153, 500, and 1877 cm^{-1}. The deviations are small, and moreover, it is gratifying

---

[89] However, if the purpose of modeling atomic energy levels is to allow prediction of positions of unobserved spectral lines, one may want to bring the variance further down. This may be done either by substituting fine-structure operators for one or two small structure operators[17] or by adding extra fine-structure operators. We would prefer the latter choice as the simpler, but the decision should be based on comparisons of spectra with varying n, Z, and z.

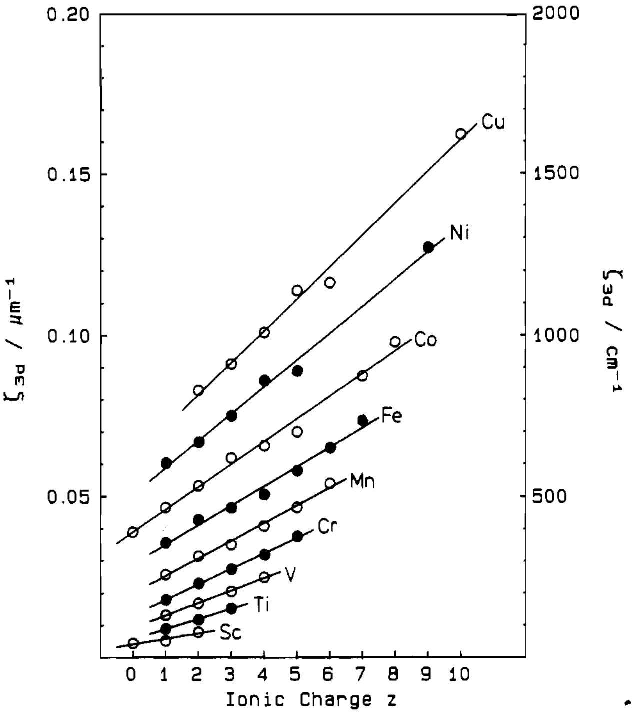

Figure 2. Dependence of the spin–orbit coupling parameter ζ_{3d} on the ionic charge z. For a particular metal ζ_{3d} increases to a good approximation linearly with z. One observes that going from one end of the transition period (Sc) to the other (Cu), the slope characterizing this linear dependence increases smoothly. The observation based on this figure has served as an impetus[90] to the six-parameter model of eq 40. The reason why—for a particular metal—the dependence of ζ_{3d} on the ionic charge is not perfectly smooth is that the different integer values of z correspond to different d^q configurations. Each d^q configuration appears to have its own small individual characteristics. Thus one observes, for example, that the ζ_{3d} values for all d^6-configuration systems lie *above* the straight lines of the figure. The chemical problem of estimating the ζ_{3d} value for a fractional value of z should therefore not be solved by using an interpolation based upon the present approximately straight lines but rather by parabolic interpolation on the ζ_{3d} *vs* z curve for the d^q configuration in question (cf. Figure 1b together with eq 33).

that their systematics agrees with the rest of Table II (cf. also Figure 1b,c). We finally note that the (d^3-d^2)-difference quotients $(\Delta\zeta_{nd}/\Delta Z)_{z=3}$ for n = 3, 4, and 5, normalized by division by $[\zeta_{nd}(d^2) + \zeta_{nd}(d^3)]/2$, are 0.28, 0.23, and 0.17, a fact from which we learn that the pronounced increase in the absolute values of ζ_{nd} with n (eq 34) is moderated as far as the difference in ζ_{nd} values for different configurations with the same n is concerned. For example, while the ratio $\zeta_{3d}(Cr^{3+})/\zeta_{5d}(W^{3+}) \approx {}^1/_{10}$ (eq 34), the difference ratio $[\zeta_{3d}(Cr^{3+}) - \zeta_{3d}(V^{3+})]/[\zeta_{5d}(W^{3+}) - \zeta_{5d}(Ta^{3+})] = (274 - 206)/(2686 - 2254) \approx 1/6$.

We now want to use Figure 1b,c to illustrate how ζ_{3d} depends on our independent chemical variables, *i.e.*, the element (Z) and the oxidation number (z). Let us with this purpose in mind focus attention upon a triangle of neighboring data points. This triangle shall further be specified by having one side of constant q, one of constant z, and finally one of constant Z. The energy cycle relationship (35) is most easily seen by looking at such a triangle

$$\left(\frac{\Delta\zeta_{3d}}{\Delta Z}\right)_q = \left(\frac{\Delta\zeta_{3d}}{\Delta Z}\right)_z + \left(\frac{\Delta\zeta_{3d}}{\Delta z}\right)_Z \tag{35}$$

$$\left(\frac{\Delta\zeta_{3d}}{\Delta q}\right)_Z = -\left(\frac{\Delta\zeta_{3d}}{\Delta z}\right)_Z \tag{36}$$

using Figure 1b, and the relationship (36) is a consequence of eq 33. The difference quotients of eq 35 are always positive and the two sides of eq 36 accordingly negative. Let us illustrate the ζ_{3d} dependencies described in eqs 35 and 36 by choosing the example of the triangle $\{\zeta_{3d}(Cr^{3+});\zeta_{3d}(Mn^{3+});\zeta_{3d}(Mn^{4+})\}$ or, in a $\zeta_{3d}(Z,z)$ notation, $\{\zeta_{3d}(24,3);\zeta_{3d}(25,3);\zeta_{3d}(25,4)\}$. The $\Delta q = 0$ step from $\zeta_{3d}(24,3)$ to $\zeta_{3d}(25,4)$ can be made in a way that follows either the left- or the right-hand side of eq 35. The left-hand (Δq = 0) route is direct and corresponds to $(\Delta Z,\Delta z) = (1,1)$. The right-hand-side route means a division of it into two steps. First, one goes from $\zeta_{3d}(24,3)$ to $\zeta_{3d}(25,3)$, thus making the step $(\Delta Z,\Delta z) = (1,0)$, and then from $\zeta_{3d}(25,3)$ to $\zeta_{3d}(25,4)$, *i.e.*, making the step $(\Delta Z,\Delta z) = (0,1)$. In terms of the actual numbers associated with our present example, eq 35 reads as follows: 134 = 77 + 57 cm^{-1}.

It is generally true for the 3d period that the following inequalities hold

$$\left(\frac{\Delta\zeta_{3d}}{\Delta Z}\right)_q > \left(\frac{\Delta\zeta_{3d}}{\Delta Z}\right)_z > \left(\frac{\Delta\zeta_{3d}}{\Delta z}\right)_Z \tag{37}$$

and as a rough rule of thumb for the average 3d situation, one may write

$$\left(\frac{\Delta\zeta_{3d}}{\Delta Z}\right)_q : \left(\frac{\Delta\zeta_{3d}}{\Delta Z}\right)_z : \left(\frac{\Delta\zeta_{3d}}{\Delta z}\right)_Z = 3{:}2{:}1 \tag{38}$$

although the ratio values $(\Delta\zeta_{3d}/\Delta Z)_q/(\Delta\zeta_{3d}/\Delta z)_Z$ vary some and have extremum values of 2.4 and 4.4. For the 5d period the ratio corresponding to that of eq 38 is close to 2:1:1 and for the 4d period in between. These results lead to the following pronounced rule

$$\zeta_{3d}(Z,z) < \zeta_{3d}(Z+1,z-1) \tag{39}$$

but there are many examples in the 3d period where the more transcendent rule $\zeta_{3d}(Z,z) \approx \zeta_{3d}(Z+1,z-2)$ is valid. It applies for instance to Cr^{4+}–Mn^{2+}, Mn^{3+}–Fe^{+}, Mn^{5+}–Fe^{3+}, Fe^{3+}–Co^{+}, Fe^{6+}–Co^{4+}, and Co^{4+}–Ni^{2+}. There are even some extreme examples where the rule $\zeta_{3d}(Z,z) < \zeta_{3d}(Z+1,z-2)$ is valid: Mn^{4+}–Fe^{2+}, Fe^{4+}–Co^{2+}, Fe^{5+}–Co^{3+}, Co^{5+}–Ni^{3+}, Co^{7+}–Ni^{5+}, and Ni^{5+}–Cu^{3+}.

In summary, ζ_{nd} values are, at least for n = 3 and 4, both in an absolute and in a relative sense more dependent on the atomic number of the species in question than on its charge although ζ_{nd} increases with both of these chemical parameters.

We finally note the empirical model of eqs 40 and 41, which

$$\zeta_{3d}(Z,z)/\text{cm}^{-1} = (P_1Z^2 + P_2Z + P_3)z + (P_4Z^2 + P_5Z + P_6) \tag{40}$$

$$P_1 = 0.94856;\ P_2 = -38.320;\ P_3 = 414.05;$$
$$P_4 = 6.2017;\ P_5 = -236.63;\ P_6 = 2260.7 \tag{41}$$

$$\chi^2/\nu = 2.83 \tag{42}$$

conveniently summarizes the 3d^q PMTζ-model results of Table II in terms of six parameters. The modeling that is specified[90] in eqs 40-42 is based upon the observation that ζ_{3d}, for a given element, roughly increases linearly with z (Figure 2).

11. Conclusion

The Hamiltonian, $\hat{H}_{PJL}$ on d^q, of the parametrical J level model is a mathematically complete sum of effective, parametrical operators. It consists of two sets of operators: the structure operators that separate the states of the configuration into multiplet terms and mix seniority numbers and the fine-structure

---

[90] The values of the six parameters P_n given in eqs 41 were obtained by a nonlinear least-squares fitting[83] of the expression (40) to the 48 PMTζ model ζ_{3d} values of Table II. Each ζ_{3d} value entered the calculation with a weight of $1/\sigma^2$, where σ is its error (cf. Table II). The 3d^1 and 3d^9 results of Table II were given a finite weight corresponding to σ = 0.0010 μm^{-1}, which is the value that gives a minimum σ' (cf. note 84). This root mean square difference between the PMTζ model ζ_{3d} values of Table II and the ζ_{3d} values calculated by means of eqs 40 and 41 is σ' = 0.0017 μm^{-1}.

operators that split the multiplet terms into J levels and mix these. $\hat{H}_{PJL}$ is not practical, but when truncated by the leaving out of all fine-structure operators but the spin–orbit coupling operator $\hat{Q}_{\zeta}\zeta$, this paper's practical Hamiltonian, $\hat{H}_{PMT\zeta}$, is obtained. Thus $\hat{H}_{PMT\zeta}$, which has been shown to be a parametrical extension of the conventional parametrical Slater–Condon–Shortley model, is mathematically complete with regard to structural splitting of d^q and takes spin–orbit coupling to account for all further splitting observed.

The operator, $\hat{H}_{PMT\zeta}$, is the *best possible* model Hamiltonian for semiempirical determination of the one-electron spin–orbit coupling parameter, ζ_{nd}. It has been applied here for the first time on d^3, d^4, d^5, d^6, and d^7 gaseous metal ions.[80] A comprehensive compilation of numerically[91] extremely well-defined ζ_{nd} values for all nd^q systems of chemical interest for which sufficient experimental data are available has been provided (Table II). We emphasize that $\hat{H}_{PMT}[d^q]$ for $3 \le q \le 7$ is much more complex than $\hat{H}_{PMT}[d^2]$. Therefore, in view of the model's problems with first principles (cf. section 2), we find it remarkable that the ζ_{nd} values obtained for $3 \le q \le 7$ compare so smoothly with those obtained for d^2 (and d^8)[92] and especially with the model-independent values for d^1 (and d^9) (cf. eq 8). We finally remark that $\hat{H}_{PMT\zeta}$ accounts for the atomic d^q energy level data by using only one fine-structure parameter, namely ζ_{nd}. Moreover we stress that the model handles the data so well that little room is left for fitting additional fine-structure parameters (cf. Table III).[93]

In conclusion, the theoretically well-defined as well as operationally well-suited parametrical multiplet term model provides the hitherto best atomic model platform from where to view transition metal chemistry and analyze its data in ligand-field and magnetism contexts. This statement applies to energy parametrization as well as eigenfunction specification within the characterizing d^q configuration. In forthcoming papers, the model's *structure* parameters will be discussed and it will be shown how the PMT model and/or the PMTζ model can be used to add ligand fields and/or external magnetic fields.

Acknowledgment. We are indebted to the Danish Natural Science Research Council, which supported this work under Grant 11-7623. M.B. is furthermore grateful for travel grants from the Otto Mønsteds Fond and Knud Højgaards Fond.

---

(91) The fact that the fitted *values* for ζ_{nd} are numerically well-defined does not reveal anything about the well-definedness of the *concept* of the one-electron spin–orbit coupling parameter ζ_{nd} in this many-electron d^q context. As mentioned in section 3, the PMT model is not based upon a pure d^q configuration but rather upon a classifying d^q configuration. Since the spin–orbit coupling operator is a one-electron operator, the degree of theoretical well-definedness of its associated parameter ζ_{nd} might well depend on the goodness of the independent particle model (Hartree–Fock model) for the system under consideration since this is a measure of the degree of purity of the d^q configuration. This problem was, however, not this paper's problem (cf. section 2). Rather the paper was concerned with the determination of well-defined *values* for ζ_{nd}, which is probably the closest one can get to what is needed as a reference in ligand-field and electron spin resonance contexts.

(92) Our results for d^2 and d^8 agree to the last decimal point with previously published results.[86] The only exception is the $h(^1S)$ parameter for Ni^{2+} (cf. Table I). Here ref 86 appears to have used a different value for the experimental energy level $^1S_0$ than we have.

(93) We do find, however, that there are some systematic trends left in the residual operator $\hat{R}_{PMT\zeta}$.