UCRL-11523

University of California

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

CONFIGURATION INTERACTION IN THE $4f^3$ CONFIGURATION OF PrIII

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-11523

For Journal of Optical Society

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

CONFIGURATION INTERACTION IN THE $4f^3$ CONFIGURATION OF PrIII

K. Rajnak

July 1964

CONFIGURATION INTERACTION IN THE $4f^3$ CONFIGURATION OF PrIII*

K. Rajnak

Lawrence Radiation Laboratory
University of California
Berkeley, California

ABSTRACT

The energies of the 38 observed levels of the $4f^3$ configuration of PrIII have been calculated with an rms deviation of ±66 cm^{-1} by use of 12 adjustable parameters, including 4 parameters which account for non-linear configuration interaction effects. The physical significance of the non-linear parameters is discussed in terms of the relative roles of various mechanisms of configuration interaction.

CONFIGURATION INTERACTION IN THE $4f^3$ CONFIGURATION OF PrIII*

K. Rajnak

Lawrence Radiation Laboratory
University of California
Berkeley, California

INTRODUCTION

The analysis of the complex spectra of the rare earth elements has usually been carried out by determining the values of the Slater integrals F_2, F_4, and F_6,[1] or the equivalent E^1, E^2, and E^3 of Racah,[2] and the spin-orbit coupling constant ζ which best reproduce the experimental spectrum. Inherent in the method is the assumption that the energy levels may be described in terms of a pure f^N configuration. Attempts have been made to improve on this approximation by including the additional parameters α, β, and γ arising from the linear theory of configuration interaction.[3-10] This has lead to considerable improvement, but, in many cases, the differences between calculated and experimental spectra are still several hundred cm^{-1}. It has recently been shown[11] (in a paper hereafter referred to as I) that the "non-linear" effects, arising from interaction with configurations differing from ℓ^N in the quantum numbers of only one electron, may be accounted for by adding several new parameters to those discussed above. Such effects have been considered in d-electron systems,[10,12] but until the recent work of Sugar[13] on the spectrum of doubly ionized Pr ($4f^3$), sufficient data has not been available to allow determination of the many parameters of the non-linear theory for systems of f-electrons.

This detailed investigation was undertaken with three goals in mind: first, to determine the values of a selected set of non-linear configuration interaction parameters in the particular case of PrIII; second to

gain a qualitative understanding of the relative importance of various mechanisms of configuration interaction in PrIII, in particular of the $4f^3 \rightarrow 4f^2nf$, $4f^3 \rightarrow 4f^2np$ and $n'p^6 4f^3 \rightarrow n'p^5 4f^4$ interactions; third, to provide a starting point for determination of these non-linear effects in other rare earths where an a priori estimate of the parameters may aid in the analysis of the experimental data. When a similar investigation is carried out for another ion at the heavy end of the rare earth series, it is hoped that estimates of the parameters for the other rare earths may be made by interpolation between them.

Choice of the parameters of configuration interaction

Since there are several different ways in which the non-linear parameters may be chosen, it is important that the particular choice be carefully defined. From Eq. (47a) of I the correction to the electrostatic matrix element between the states ψ and ψ' of ℓ^N may be written as

$$C(\psi,\psi') = \Sigma_{kk'k''_{\text{even}}} \mathcal{P}(kk',\ell')\,(2k''+1) \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix}$$
$$\times (\psi \| \Sigma_{hij} (\{\underset{\sim}{u}_h^{(k)} \underset{\sim}{u}_i^{(k'')}\}^{(k')} \underset{\sim}{u}_j^{(k')})^{(0)} \| \psi'), \qquad (1)$$

where

$$\mathcal{P}(kk',\ell') = P'(kk',\ell') - P(kk',\ell') \quad . \qquad (2)$$

$P(kk',\ell')$, given by Eq. (5) of I, is a function of the radial integrals $R^k(\ell\ell,\ell\ell')$, $R^{k'}(\ell\ell,\ell\ell')$ and the energy separation between the configurations ℓ^N and $\ell^{N-1}\ell'$. $P'(kk',\ell')$ is a similar function representing interaction between the configuration ℓ^N and $\ell'^{4\ell'+1}\ell^{N+1}$.

Many of the terms in the triple-tensor matrix elements of Eq. (1) can be shown to be proportional to the coefficients of the Slater integrals, F^k, or of the "linear" parameters α, β, and γ. If these terms are included in the computation of the triple-tensor matrix elements, effects of one-electron excitations, which are normally absorbed in the fitting process by the Slater integrals and α, β, and γ, will be redistributed among all of the parameters. The values of the parameters $\mathcal{P}(kk',\ell')$ will then not necessarily be a true indication of the importance of including one-electron terms. If, however, we remove from the triple-tensor matrix elements all terms which have the same angular dependence as the effective two-electron interactions which give rise to the linear theory, the resulting parameters will give a much better indication of the importance of including the one-electron interactions.

Thus, we rewrite Eq. (1) as

$$C(\psi,\psi') = \Sigma_{kk'} X(kk',\ell')\, Y(kk',\ell') \ , \tag{3}$$

where the coefficients $X(kk',\ell')$ are given by

$$X(kk',\ell') = \Sigma_{k''_{\text{even}} > 0} (2k'' + 1) \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix}$$

$$\times (\psi \| \Sigma_{h \neq i \neq j} (\{ \underset{\sim}{u}_h^{(k)} \underset{\sim}{u}_i^{(k'')} \}^{(k')} \underset{\sim}{u}_j^{(k')})^{(0)} \| \psi') \ . \tag{4}$$

$Y(kk',\ell')$ is a new parameter whose form is still given by Eq. (5) of I; i.e., it is still the difference of core and non-core terms, but whose

numerical value will be different from that of $\mathcal{P}(kk',\ell')$. All terms in Eq. (1) where h = i, i = j, or h = j can be shown to have the same angular dependence as the Slater integrals or α, β, and γ. Since, when $h \neq i \neq j$, the triple tensor is antisymmetric in k", the terms with k" odd cancel term by term. k and k' are always even.

The matrix elements in Eq. (4) are now symmetric in k, k' and k" (all even) and we could write a new parameter

$$Z(kk'k'') = \Sigma_{\substack{\text{all permutations}\\ \text{of } k,\ k',\ \text{and } k''}} \Sigma_{\ell'} Y(kk',\ell')(2k''+1) \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix} . \qquad (5)$$

For f^N there are 10 such terms, and a total of 17 parameters could then include, to second order, all configuration interaction in such a system.[11] But for f^3, the number of parameters then equals the number of electrostatic terms in the configuration and such a fit could not be meaningful. Even for other configurations, these parameters have the disadvantage of being a sum over all types of interacting configurations, and of many terms which may or may not have the same sign. Thus it is much more difficult to deduce from the values of the parameters any physical picture of the dominant interactions or even to make an educated guess as to which parameters should be large and which small. The parameters $Y(kk',\ell')$ of Eq. (3), however, are associated with particular types of interacting configurations and, on the basis of a smooth decrease in the integrals $R^k(\ell\ell,\ell\ell')$ with increasing k, one can predict, for example, that Y(66,3) should be considerably smaller than Y(22,3). If lack of data forces one to restrict the number of parameters used, it should be possible to choose the most important ones to include. If the Z(kk'k") parameters are used, however, this is impossible.

On the basis of these considerations, the parameters $Y(kk',\ell')$ of Eq. (3) were chosen for this calculation. Only ℓ' values of 1 and 3 were used since these are expected to represent the lowest lying configurations differing from f^N in the quantum numbers of only one electron.

From Eq. (5) of I it is readily seen that $P(kk',\ell')$ is always positive. Similarly $P'(kk',\ell')$ is given by Eq. (5) and is always positive. The only difference between these two functions is that $P(kk',\ell')$ represents an excitation from the ℓ^N shell to the unfilled ℓ' shell while $P'(kk',\ell')$ represents the corresponding core excitation, i.e., interaction between ℓ^N and $\ell'^{4\ell'+1}\ell^{N+1}$. Where both mechanisms of configuration interaction are possible, the sign of the parameter $Y(kk',\ell')$ indicates which mechanism is the most important. If the core excitation is the dominant mechanism, $Y(kk',\ell')$ is positive. If the excitation from the ℓ^N shell is the more important one, $Y(kk',\ell')$ is negative. When $\ell' = 1$ both core and non-core interactions are possible and it cannot be decided *a priori* which effect should dominate, i.e., we do not know what sign to expect for $Y(kk',1)$. In the lanthanides, however, there are no core f-electrons, the first term in Eq. (2) is zero, and $Y(kk',3)$ is expected to be negative.

If we consider only the contribution from two-electron excitations, it is readily seen from Eq. (4), (5), (6) and (19) of I that α is expected to be positive, β, negative and γ, positive. Orbit-orbit interactions within the ℓ^N configuration make contributions to α, β, and γ which are of opposite phase to the terms arising from the linear theory of configuration interaction.[15] These parameters also contain contributions from the

matrix elements of the triple tensor when k" is odd and h = j. The sign of these contributions is determined by the product of the 6-j symbols

$$\begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix} \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell \end{Bmatrix},$$

where k" is odd. Consideration of these 6-j symbols for various values of k, k' and k" when $\ell = 3$ and $\ell' = 1$ or 3 leads to the following conclusions:

1. The contribution to α is positive;
2. The contribution to β is positive when $\ell' = 1$ and negative when $\ell' = 3$;
3. The contribution to γ is negative when $\ell' = 1$ and positive when $\ell' = 3$.

Thus, even though these parameters represent the sum of many different interactions, it may be possible, by consideration of their signs, to draw some conclusions as to the nature of the dominant interaction.

The above considerations are based on the assumption that the radial integrals $R^k(\ell\ell,\ell\ell')$ and $R^{k'}(\ell\ell,\ell\ell')$ have the same sign. On the basis of calculations with approximate excited eigenfunctions for PrIV[16] this is always the case. However, one cannot rule out the possibility of some functions for which this is not true.

Calculations

The coefficients $X(kk', \ell')$ were computed on an IBM 7094 and are given in Table I. The equations for this calculation are given in the

Appendix. These coefficients range in magnitude from zero to ±.06, most of them being of the order of 10^{-3}. Thus, in most cases, the parameters $Y(kk',\ell')$ must be quite large before the correction $C(\psi,\psi')$ becomes appreciable. Because of the small coefficients, rather large variations in the parameters are possible without significant changes in the energy levels. If the parameters determined from a least squares fit are small, their signs may not have any physical significance.

The coefficients of the Slater integrals and ζ were kindly supplied on magnetic tape by C. W. Nielson.[17] The coefficients of α, β, and γ are easily computed from the L, W and U quantum numbers of the states.[11]

These were combined with the coefficients in Table I to give fifteen coefficient matrices which were put on one magnetic tape in the same format as that of Nielson. This tape was then used as input data for each calculation. Any parameters not used in a particular calculation were given an initial value of zero and not allowed to vary.

G-zero, the sum of the squares of the deviations between experimental and calculated energy levels, was minimized directly using a variable metric minimization routine.[18] This is an iterative procedure in which the complete energy matrices are rediagonalized after each change in the parameters. If the eigenvalues are linear functions of n parameters, n iterations are necessary to minimize G-zero.

For ten to twelve parameters, the 38 levels of PrIII can be fit in about 10 minutes on the IBM 7094. The time depends somewhat on how close the initial parameters are to the final ones. Since most of the time is

spent in diagonalization, it will increase rapidly for more complex systems where the ranks of the matrices are larger than those of f^3.

Results and discussion

Calculations on the $4f^3$ configuration of PrIII have been carried out by Trees,[19] using only the linear theory of configuration interaction. Using his final parameters, it is possible to reproduce his eigenvalues but not the rms deviations which he quotes. From the numbers in columns 3, 4, and 5 of his Table I, one can compute the rms deviation

$$\sigma = \sqrt{\frac{\Sigma_i \Delta_i^2}{N-K}} ,$$

where Δ_i is the difference between the calculated and observed energies of the $i^{\underline{th}}$ level, N is the number of levels (38) and K is the number of parameters. The results are ±528 cm^{-1} for five parameters, ±452 cm^{-1} when α is included and ±369 cm^{-1} when two polarization parameters are used. Thus, the improvement in the fit with the inclusion of two configuration interaction parameters is not nearly so great as indicated by the ±484, ±292 and ±168 cm^{-1} quoted by Trees.

Using the parameters given by Trees as initial values in the present program it is possible to improve each of these deviations by about 30 cm^{-1}. These results are given in Table II (calc. 1-3). It should be noted that in several cases the changes in the parameters are outside the rms errors quoted by Trees.

In the present calculations E^o has been determined so that $\Sigma_i \Delta_i = 0$. Since it affects only the center of gravity of the configuration and not

its structure, it is not a free parameter in quite the same sense as the others. It has been counted as one in the calculation of σ, however.

The validity of the addition of the parameter γ is open to some question. This correction is equivalent[11] to the Q correction previously used by Trees[20] and Racah.[21] In this form it is obvious that the effect of γ is to shift groups of levels of different seniority with respect to each other. But all the terms of f^3 have the same seniority, with the exception of the $(100)(10)^2F$ which has not been observed experimentally. Although LS coupling is, in general, a good approximation for this system, several levels are appreciably mixed. The 20% (100)(10) character of the $(210)(21)^2F$ probably accounts for the fact that the calculated position of the lower $^2F_{5/2}$ in calc. 3 is 1460 cm^{-1} too low when σ is only 338 cm^{-1}. Trees[19] used the deviation of the $^2F_{5/2}$ to estimate a value for the Q correction parameter,[22] but found its sign to be opposite that predicted by the linear theory. He, therefore, questioned the reality of the experimental $^2F_{5/2}$ level. If, however, we consider that there can be contributions to γ from one- as well as two-electron substitutions, such a change in sign is possible.

The $^2F_{5/2}$ level is the least well established of the experimental levels, although all the transitions which are expected to be strong were observed. If further experimental work should prove the $^2F_{5/2}$ level to be wrong, the values of γ, and probably E^1, would change, but the effect on other energy levels would be very small. Thus, since the present theory cannot exclude the possibility of a negative value for γ, it seems justified to include this parameter.

When γ is included (calc. 4), σ is reduced to 149 cm^{-1} and the $^2F_{5/2}$ level fits to within a few cm^{-1}. Since $(100)(10)^2F$ makes only very small contributions to other levels, the value of γ is being determined primarily by the position of the $^2F_{5/2}$ level. Therefore, the good fit of this level cannot really be interpreted as verifying its position. But, it should be noted that even if the $^2F_{5/2}$ is correct, there may be considerable changes in γ when the upper ^2F levels are included in the fit.

Assuming that the $^2F_{5/2}$ level is correct, there are two possible explanations for the negative sign of γ. Wybourne's estimate[15] of an orbit-orbit contribution to γ of -89.9 cm^{-1} for PrIV makes it highly unlikely that the change of sign is primarily due to this type of interaction. The other negative contributions to γ arise from one-electron excitations of the type $4f^3 \rightarrow 4f^2np$ or $n'p^6 4f^3 \rightarrow np^5 4f^4$. In order for γ to have a large negative value these contributions (plus the orbit-orbit interactions) must dominate over all two-electron excitations and one-electron contributions to γ from $4f^3 \rightarrow 4f^2 n'f$ type interactions.

The addition of Y(22,1) and Y(44,1) to take into account interaction with $4f^2np$ and $n'p^5 4f^4$ reduced the standard deviation to about ±115 cm^{-1}. However, the two parameters had opposite signs and nearly equal magnitudes which are difficult to explain on the basis of a smooth decrease of the integrals $R^k(ff,fp)$ with increasing k. In all subsequent calculations, regardless of the combination of parameters, Y(44,1) immediately changed from its large negative value to about +100. Thus the negative value of Y(44,1) cannot be deemed physically significant and this calculation was not included in Table II. However, it does point

up the fact that a single calculation may not be sufficient to establish values of those parameters which have only very small effects on most of the eigenvalues. Y(22,1) alone does not appreciably reduce the rms deviation.

The parameters Y(22,3) and Y(44,3), however, which account for the major part of the interaction with $4f^2n'f$ reduce the deviation to ± 93 cm^{-1} (calc. 5). Thus it seems that interactions of the type $4f^3 \rightarrow 4f^2n'f$ are somewhat more important than the corresponding p excitations. Since the parameters Y(kk',1) represent the difference of the two possible types of p interactions it is not surprising that the net effect is smaller than the f interactions. The sign of γ indicates that where both of the p interactions enter with the same sign, their total effect is greater than that of the f interactions. Thus the relative importance of the f and p interactions may be quite different in the case of the actinides where there is the possibility of a core excitation from the 4f shell.

Inclusion of four non-linear parameters simultaneously leads to a σ of ± 66 cm^{-1} (calc 7). The sign of the parameter Y(22,1) is still positive, indicating that the core p excitation dominates over interactions of the type $4f^3 \rightarrow 4f^2np$. But, since Y(22,1) is only 3780, the difference between the two interactions must be quite small and it does not follow that the core interaction will necessarily dominate in other rare earth ions. Trees[12] found a similar core interaction necessary to fit the spectrum of the $3d^6$ configuration in FeIII.

Addition of Y(42,3) reduces the rms deviation slightly but the resulting value of Y(42,3) is very large and positive whereas the theory

predicts that it should be negative and between Y(22,3) and Y(44,3) in absolute magnitude. This behavior seems to be associated with the fact that the $(100)(10)^2F$ levels are not yet known. Whenever the parameter Y(42,3) is included these levels lie at least 500 cm^{-1} above their position when this parameter is excluded. Thus, it appears that without knowing the position of these levels it is impossible to determine even the sign of Y(42,3). Since the improvement gained by including it cannot be deemed physically significant, this parameter has generally been excluded.

As soon as the parameter Y(22,3) in included, the upper $^2D_{5/2}$ level at 27597.13 cm^{-1} begins to exhibit a deviation well outside the expected limits of $\pm 2\sigma$. Until that time, however, this level gave no cause for suspicion. Examination of the angular matrix elements of Y(22,3) shows that the $(210)(21)^2D$, is one of several levels having coefficients of the order of ±.01. Thus a Y(22,3) value of 10^4 means changes in the energy of these states of the order of 100 cm^{-1} but has relatively little effect on other levels. The subsequent calculations have been carried out both with and without the $(210)(21)^2D_{5/2}$ level. No matter how many parameters are used, it never fits much better than 200 cm^{-1} when it is included in the calculation and is always in the same position 355±10 cm^{-1} above the experimental position when it is excluded. The $(210)(21)^2D_{3/2}$ level, on the other hand, always fits very well. Excluding one of 38 levels from a least squares fit should not make an appreciable difference in its calculated position. Indeed, excluding the $b^2D_{5/2}$ when only the p parameters are used has very little effect.

The calculated positions of the upper ^2F levels are about 300 cm^{-1} higher when the $b^2D_{5/2}$ level is included in the calculation than when it is excluded. This apparant correlation between these levels may result in considerable changes in the calculated position of the $b^2D_{5/2}$ level when the b^2F levels are known. Further consideration of the large deviation of the $b^2D_{5/2}$ level must await the outcome of additional experimental work, however.

The remaining parameters, Y(44,1), Y(64,3) and Y(66,3), are never greater than 200 cm^{-1} and consequently have no appreciable effect on the energy levels. Thus, of the sixteen possible parameters, only twelve are necessary for the present calculation. If further reduction in the number of parameters were necessary, Y(62,3) could also be eliminated without appreciable change in σ. Y(22,1), however, while only slightly larger than Y(62,3), has some very large coefficients (see Table I). Thus it has an appreciable effect on many energy levels.

The final deviation of ± 40 cm^{-1} is as good as can be expected, since interactions with configurations containing an electron of angular momentum greater than three, spin-spin and spin-other-orbit effects have been neglected. Spin-spin effects have been estimated by Judd[23] to be of the order of 10 cm^{-1} in Pr^{3+}. The other effects are more difficult to estimate, but are probably of the same order of magnitude.

The experimental and calculated eigenvalues, eigenvectors and g values derived from calculation 8 are given in Table III. Except for the $b^2D_{5/2}$ and $b^2H_{9/2}$, all levels fit within $\pm 2\sigma$. The $b^2H_{9/2}$ level seems to fit quite well when the $b^2D_{5/2}$ level is included in the fit but deviates by about 120 cm^{-1} when it is excluded. Most of the changes in

eigenvectors from one calculation to another are small and, in general, LS coupling is a good approximation. The ^4G and ^2G levels are badly mixed as are the ^2P and the lower ^2D of $J = 3/2$. In these cases LS labels for the states are meaningless. The major component sometimes changes from one calculation to another.

The F_2 value associated with calculation 8 is 289 cm^{-1} which is less than the 298 cm^{-1} given by Judd and Lindgren[24] for the neutral atom. The F_k ratios are even larger than 5f hydrogenic ratios.

Conclusions

It has been shown that by including both the linear and non-linear effects of configuration interaction, it is possible to obtain a very good fit to the spectrum of the $4f^3$ configuration of PrIII—with the exception of the upper $^2D_{5/2}$ level. The values of these parameters should provide at least a first estimate to be used as guide in the analysis of other rare earth spectra. It is somewhat disconcerting, however, to find that even in this most favorable case where all but three levels have been observed, the data is insufficient to completely determine all of the parameters. This may be a special case, but the possibility of a similar situation should be kept in mind when analyzing other spectra on the basis of incomplete data.

It is possible to draw some conclusions regarding the relative magnitudes of various mechanisms of configuration interaction. It seems that the two competing types of p interactions come close to cancelling in PrIII while interactions of the type $4f^3 \rightarrow 4f^2n'f$ are quite large. The parameters Y(44,1), Y(64,3) and Y(66,3) are negligible.

While these conclusions will not necessarily hold for all rare earth ions, they do provide a starting point for other analyses, particularly if the data is not complete enough to allow one to fit all of the possible parameters. Before conclusions drawn from the study of PrIII can really be generalized to other rare earths, however, a similar analysis of an ion at the other end of the series should be carried out. Unfortunately, the necessary data is not available at the present time.

Acknowledgments

The program for calculation of the angular matrix elements was written by Jim Eusibio and Les Wilson of the Mathematics and Computing Group. The author is particularly grateful to Tom Clements of that group for development of the fitting routine and to Dr. C. W. Nielson for the magnetic tape of f^N matrices. The continued advice and encouragement of Dr. B. G. Wybourne and Mr. John Conway have been extremely helpful.

Appendix

Calculation of Triple Tensor Matrix Elements for the Configuration f^3

The triple tensor matrix elements of Eq. (4) can be computed in several different ways. The most straight forward one is simply to subtract from the matrix elements

$$(\psi\|\Sigma_{h,i,j}(\{\underset{\sim}{u}_h^{(k)}\underset{\sim}{u}_i^{(k'')}\}^{(k')}\underset{\sim}{u}_j^{(k')})^{(0)}\|\psi')$$

those terms in which h = i, i = j or h = j. Eq. (4) then becomes

$$X(kk',\ell') = \Sigma_{k''_{\text{even}}>0}(2k''+1)\begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix}\Bigg\{(\psi\|\Sigma_{hij}(\{\underset{\sim}{u}_h^{(k)}\underset{\sim}{u}_i^{(k'')}\}^{(k')}\underset{\sim}{u}_j^{(k')})^{(0)}\|\psi')$$

$$-\begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell \end{Bmatrix}\Bigg[(\psi\|(\underset{\sim}{u}^{(k)})^2\|\psi') + (\psi\|(\underset{\sim}{u}^{(k)})^2\|\psi') + (\psi\|(\underset{\sim}{u}^{(k'')})^2\|\psi')$$

$$-\frac{2N}{2\ell+1}\,\delta(\psi,\psi')\Bigg]\Bigg\}\,, \tag{6}$$

where

$$(\psi\|(\{\underset{\sim}{u}_h^{(k)}\underset{\sim}{u}_i^{(k'')}\}^{(k')}\underset{\sim}{u}_j^{(k')})^{(0)}\|\psi') = \sum_{\bar\psi\,\bar\psi'}\begin{Bmatrix} k & k' & k'' \\ \bar L & \bar L' & L \end{Bmatrix}(\psi\|\underset{\sim}{u}^{(k)}\|\bar\psi)$$

$$\times(\bar\psi\|\underset{\sim}{u}^{(k'')}\|\bar\psi')(\bar\psi'\|\underset{\sim}{u}^{(k')}\|\psi')\,, \tag{7}$$

and

$$(\psi\|(\underset{\sim}{u}^{(k)})^2\|\psi') = \frac{1}{2L+1}\sum_{\bar\psi}(-1)^{L-\bar L}(\psi\|\underset{\sim}{u}^{(k)}\|\bar\psi)(\bar\psi\|\underset{\sim}{u}^{(k)}\|\psi')\,. \tag{8}$$

Appendix (continued)

Since it is a general expression, applicable to any ℓ^N configuration, Eq. (6) was used to compute the coefficients in Table I. The $\underset{\sim}{u}^k$ matrices were computed from the coefficients of fractional parentage for f^3 tabulated by Judd.[25]

The computer program was checked using two equations which are more amenable to hand calculations. Eq. (4) may be rewritten as

$$X(kk',\ell') = 6\,\Sigma_{k''\,\text{even}>0}(2k''+1)\begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix}\Sigma_{\bar{\psi}\,\tilde{\psi}}(-1)^{L+\ell+\tilde{L}}\sqrt{(2\bar{L}+1)(2\tilde{L}+1)}$$

$$\times\,(\psi\{|\,\bar{\psi})(\tilde{\psi}\,|\}\psi')\begin{Bmatrix} \bar{L} & \tilde{L} & k' \\ \ell & \ell & L \end{Bmatrix}\begin{Bmatrix} \ell & \ell & k \\ \ell & \ell & k'' \\ \bar{L} & \tilde{L} & k' \end{Bmatrix}. \tag{9}$$

The 9-j symbol can be eliminated by making use of the relation[23]

$$\Sigma_{k''>0}(2k''+1)\begin{Bmatrix} \ell & \ell & k'' \\ \ell & \ell & k \\ \tilde{L} & \bar{L} & k' \end{Bmatrix}\begin{Bmatrix} \ell & \ell & k'' \\ k & k' & \ell' \end{Bmatrix} = \begin{Bmatrix} \bar{L} & \ell & \ell' \\ k & \ell & \ell \end{Bmatrix}\begin{Bmatrix} \ell & k' & \ell' \\ \bar{L} & \ell & \tilde{L} \end{Bmatrix}$$

$$-\frac{(-1)^{\tilde{L}+\ell+\ell'}}{(2k+1)(2\ell+1)}\begin{Bmatrix} \bar{L} & k & \tilde{L} \\ \ell & \ell & \ell \end{Bmatrix}\delta(k,k'), \tag{10}$$

and noting that the sum on $\bar{\psi}$ and $\tilde{\psi}$ will remove all terms in Eq. (10) with odd k''. When k'' is odd and $\bar{L}+\tilde{L}$ is even, interchanging $\bar{\psi}$ and $\tilde{\psi}$ changes the sign of the 9-j symbol and such terms drop out. When $\bar{L}$ and $\tilde{L}$ are of opposite parity and k'' is odd, the 9-j symbol does not change sign, but the phase factor in Eq. (9) does. Thus these terms drop out also.

Using these results, Eq. (9) becomes

$$X(kk',\ell') = 6 \sum_{\bar{\psi}\,\tilde{\psi}} (-1)^{\tilde{L} + \ell + L} \sqrt{(2\bar{L} + 1)(2\tilde{L} + 1)}\ (\psi\{|\ \bar{\psi})(\tilde{\psi}\ |\}\psi') \begin{Bmatrix} \bar{L} & \tilde{L} & k' \\ \ell & \ell & L \end{Bmatrix}$$

$$\times \left[\begin{Bmatrix} \bar{L} & \ell & \ell' \\ k & \ell & \ell \end{Bmatrix} \begin{Bmatrix} \bar{L} & k' & \tilde{L} \\ \ell & \ell & \ell' \end{Bmatrix} - \frac{(-1)^{\tilde{L} + \ell + \ell'}}{(2k+1)(2\ell+1)} \begin{Bmatrix} \bar{L} & k & \tilde{L} \\ \ell & \ell & \ell \end{Bmatrix} \right] . \qquad (11)$$

The generalization of Eq. (9) to more than three electrons would involve calculation of three-particle coefficients of fractional parentage, $(\ell^N\ \psi\{|\ \ell^{N-3}\bar{\psi})$ and would not afford any great simplification over Eq. (6). Equations (9) and (11) do provide convenient methods of checking the present results, however.

Hand calculations using these equations indicate that the results are good to the six decimal places quoted in Table I. Thus, even with parameters values of 10^5, round off errors affect the eigenvalues by at most a few tenths of a cm^{-1}. More accurate results could be obtained using the powers of primes notation, but this does not seem warranted at the present time.

FOOTNOTES AND REFERENCES

*This work was carried out under the auspices of the U. S. Atomic Energy Commission.

1. E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, New York, 1935).
2. G. Racah, Phys. Rev. 76, 1352 (1949).
3. R. F. Bacher and S. Goudsmit, Phys. Rev. 46, 948 (1934).
4. D. R. Layzer, dissertation, Harvard University, Cambridge, Massachusetts, (1950), unpublished.
5. R. E. Trees, Phys. Rev. 83, 756 (1951).
6. R. E. Trees, Phys. Rev. 84, 1089 (1951).
7. R. E. Trees, Phys. Rev. 85, 382 (1952).
8. G. Racah, Phys. Rev. 85, 381 (1952).
9. G. Racah, Lunds Univ. Arssk. 2 50, 31 (1954).
10. R. E. Trees and C. K. Jørgensen, Phys. Rev. 123, 1278 (1961).
11. K. Rajnak and B. G. Wybourne, Phys. Rev. 132, 280 (1963).
12. R. E. Trees, Phys. Rev. 129, 1220 (1963).
13. Jack Sugar, J. Opt. Soc. Am. 53, 831 (1963).
14. C. W. Nielson and George F. Koster, Spectroscopic Coefficients for the p^n, d^n and f^n Configurations, (The M.I.T. Press, Mass. Institute of Technology, Cambridge, Mass., 1963).
15. B. G. Wybourne, J. Chem. Phys. 40, 1457 (1964).
16. K. Rajnak, J. Chem. Phys. 37, 2440 (1962).
17. G. F. Koster and C. W. Nielson, a magnetic tape entitled "Energy Matrices for all Configurations of Equivalent f Electrons," Mass. Inst. of Tech., Cambridge, Mass.

18. Davidon, William C., "Variable Metric Method for Minimization," Argonne National Laboratory Report, ANL-5990 (Rev.), 1959. This general procedure has been adapted for spectroscopic problems by Tom Clements of our Math and Computing group.

19. Richard E. Trees, J. Opt. Soc. Amer. 54, 651 (1964).

20. R. E. Trees, Phys. Rev. 84, 1089 (1951).

21. G. Racah, Phys. Rev. 89, 381 (1952).

22. The present notation for the linear parameters is that of I. The β used by Trees[19] is related to the present γ, although they are not identical. Tree's γ is 1/12 of our β.

23. B. R. Judd, Operator Techniques in Atomic Spectroscopy (McGraw-Hill Book Co., New York, 1963).

24. B. R. Judd and I. Lindgren, Phys. Rev. 122, 1802 (1961).

25. B. R. Judd, Proc. Roy. Soc. A 250, 562 (1959). These coefficients also appear in the tabulation of Nielson and Koster.[14]

Table I. Angular dependence of non - linear configuration interaction parameters ($\times 10^2$)

ψ[a]	ψ'	X(22,1)	X(44,1)	X(22,3)	X(44,3)	X(42,3)	X(62,3)	X(64,3)	X(66,3)
4S	4S	6.530611	3.968253	.748299	.566894	.340136	.340136	.340136	.497122
4D	4D	.680272	.699168	-1.870748	-.120249	-.736961	.510205	.654505	1.221398
4F	4F	-1.632653	-1.020408	.280613	.505051	.170068	.637756	.448362	.307728
4G	4G	.362812	.310360	-1.295351	.172723	-.448361	1.096424	.706977	.318576
4I	4I	- .136054	-.300625	2.414966	1.004167	1.025562	.231912	.140084	.036220
2P	2P	4.399092	.204711	.062359	-.632744	.727513	-.311791	.145159	-.353416
2D1	2D1	1.566569	-2.204135	-.058794	.600514	.188695	.313412	-.766778	.142120
	2D2	.681085	.267855	-.281924	-.890459	-.036372	.777767	-.201084	.168004
2D2	2D2	.705539	.676100	-1.546646	.992566	-.240745	.660615	-.274478	-.545720
2F1	2F1	.000000	.056689	-.935374	-1.293549	-.510204	-1.445578	-1.066790	-.864017
	2F2	.319076	.390787	-1.874570	-.465868	-.761431	.235681	.247218	.382490
2F2	2F2	-1.360544	-.314368	1.147958	-.287663	.092764	-1.055194	.413223	-.140687
2G1	2G1	-3.213475	2.162947	.977486	-.141600	-.202462	-.514253	.292282	-.276905
	2G2	.721391	.141985	-.472087	.255232	-.107694	-.417115	.243074	-.010849
2G2	2G2	.437965	-.173667	-.309119	-.192238	.009718	.482202	-.494857	.148074
2H1	2H1	-2.585033	-.897581	-.175737	.052316	-.270563	.012884	-.111739	-.009064
	2H2	2.031498	-1.319154	-.991564	.706214	-.065958	-.131070	.043818	-.116523
2H2	2H2	.285714	-.348725	1.107710	-.064029	.435993	-.544732	-.090062	-.120510
2I	2I	3.129251	.279152	-.697278	-.300626	.028345	-.019623	-.075124	.052374
2K	2K	-.362812	-.043519	.274944	-.564811	-.001718	-.006441	-.038838	-.009195
2L	2L	.000000	.144300	-1.062925	.141490	-.386518	-.010406	.000757	.003341

[a]The notation is that of Nielson and Koster,[14] 4S = ^4S, etc. 2D1 = $(210)(20)^2D$, 2D2 = $(210)(21)^2D$, 2F1 = $(100)(10)^2F$, 2F2 = $(210)(21)^2F$, 2G1 = $(210)(20)^2G$, 2G2 = $(210)(21)^2G$, 2H1 = $(210)(11)^2H$, 2H2 = $(210)(21)^2H$.

Table II. Parameter values for the $4f^3$ configuration of Pr III (in cm^{-1})

Calc. No.	1	2	3	4	5	6[a]	7	8[a]
E^0	10966.	10608.	11262.	14976.	14711.	14577.	14914.	14757.
E^1	4291.39	4261.5	4369.3	4906.4	4794.2	4771.7	4823.8	4804.5
E^2	21.44	21.14	20.60	19.62	19.97	20.23	19.71	19.93
E^3	398.1	406.7	414.5	419.2	409.3	407.6	410.2	408.4
ζ	644.9	642.7	657.3	666.9	662.5	664.8	662.4	664.0
α		16.72	26.26	31.69	31.47	29.71	32.18	30.54
β			- 890.1	- 963.1	- 959.6	-861.4	-888.0	-798.6
γ				-3072.	-2765.	-2696.	-3006.	-2924.
Y (22,1)							3780	3770
Y (22,3)					-13990	-14540.	-13810	-15220
Y (44,3)					-10680	-9660.	-6320	-3500
Y (62,3)							-3740	-2390
σ	± 500	± 406	± 338	± 149	± 93	± 78	± 66	± 40

[a]The $b\,^2D_{5/2}$ level was excluded from this calculation.

Table III. Calculated energy levels, eigenvectors and g factors for the $4f^3$ configuration.

J	Observed energy (cm^{-1})	Calculated minus observed energy	Eigenvector	g factor
1/2	18693.65	-67.27	$.2199\|^4D\rangle + .9755\|^2P\rangle$	.634
	23465.43	53.67	$-.9755\|^4D\rangle + .2199\|^2P\rangle$	.034
3/2	9370.66	-53.06	$.0408\|^4S\rangle + .0101\|^4D\rangle - .9738\|^4F\rangle + .0511\|^2P\rangle - .2106\|^2D1\rangle + .0552\|^2D2\rangle$	.423
	10950.24	46.78	$.9743\|^4S\rangle + .0133\|^4D\rangle + .0610\|^4F\rangle + .2128\|^2P\rangle - .0403\|^2D1\rangle + .0031\|^2D2\rangle$	1.964
	17095.63	-10.98	$.1837\|^4S\rangle - .1155\|^4D\rangle - .1850\|^4F\rangle - .6475\|^2P\rangle + .6948\|^2D1\rangle - .1292\|^2D2\rangle$	1.056
	20856.86	-9.48	$-.1228\|^4S\rangle + .0768\|^4D\rangle - .1170\|^4F\rangle + .7168\|^2P\rangle + .6514\|^2D1\rangle - .1648\|^2D2\rangle$	1.089
	23091.70	-1.00	$.0152\|^4S\rangle + .9042\|^4D\rangle + .0012\|^4F\rangle - .1100\|^2P\rangle + .1175\|^2D1\rangle + .3953\|^2D2\rangle$	1.134
	26921.49	-21.40	$-.0087\|^4S\rangle - .4036\|^4D\rangle + .0111\|^4F\rangle + .0835\|^2P\rangle + .1820\|^2D1\rangle + .8926\|^2D2\rangle$	.869
5/2	10138.18	39.59	$.0029\|^4D\rangle - .9895\|^4F\rangle + .0132\|^4C\rangle - .1389\|^2D1\rangle + .0177\|^2D2\rangle + .0193\|^2F1\rangle + .0264\|^2F2\rangle$	1.032
	14187.35	8.28	$.0056\|^4D\rangle - .0161\|^4F\rangle - .9961\|^4G\rangle + .0015\|^2D1\rangle + .0114\|^2D2\rangle - .0545\|^2F1\rangle - .0663\|^2F2\rangle$	.573
	19046.09	2.07	$.0162\|^4D\rangle + .1386\|^4F\rangle - .0051\|^4G\rangle - .9895\|^2D1\rangle - .0354\|^2D2\rangle + .0127\|^2F1\rangle + .0054\|^2F2\rangle$	1.197
	23245.99	34.12	$.9007\|^4D\rangle + .0076\|^4F\rangle + .0176\|^4G\rangle - .0006\|^2D1\rangle + .4244\|^2D2\rangle - .0559\|^2F1\rangle - .0712\|^2F2\rangle$	1.337
	27597.66	359.60	$-.4336\|^4D\rangle + .0133\|^4F\rangle + .0251\|^4G\rangle - .0390\|^2D1\rangle + .8750\|^2D2\rangle - .0981\|^2F1\rangle - .1826\|^2F2\rangle$	1.217
	34193.20	1.54	$-.0106\|^4D\rangle + .0337\|^4F\rangle - .0801\|^4G\rangle + .0074\|^2D1\rangle + .2293\|^2D2\rangle + .4699\|^2F1\rangle + .8478\|^2F2\rangle$	.873
	62397.77 (calc.)		$-.0147\|^4D\rangle - .0027\|^4F\rangle + .0153\|^4G\rangle - .0092\|^2D1\rangle - .0029\|^2D2\rangle - .8734\|^2F1\rangle + .4864\|^2F2\rangle$	.857
7/2	10859.06	-19.73	$.0029\|^4D\rangle + .9672\|^4F\rangle + .0305\|^4G\rangle - .0215\|^2F1\rangle - .0338\|^2F2\rangle - .1944\|^2G1\rangle + .1553\|^2G2\rangle$	1.216
	13887.60	-6.10	$.0007\|^4D\rangle + .2311\|^4F\rangle - .4916\|^4G\rangle - .0057\|^2F1\rangle - .0062\|^2F2\rangle + .6382\|^2G1\rangle - .5456\|^2G2\rangle$	.930
	15443.48	-11.47	$-.0050\|^4D\rangle + .0991\|^4F\rangle + .8685\|^4G\rangle + .0349\|^2F1\rangle + .0468\|^2F2\rangle + .3795\|^2G1\rangle - .2974\|^2G2\rangle$	.965
	24886.51	-19.00	$.9978\|^4D\rangle - .0038\|^4F\rangle + .0080\|^4G\rangle - .0544\|^2F1\rangle - .0373\|^2F2\rangle + .0057\|^2G1\rangle + .0001\|^2G2\rangle$	1.428
	34977.73 (calc.)		$.0574\|^4D\rangle - .0343\|^4F\rangle + .0514\|^4G\rangle - .4194\|^2F1\rangle - .9026\|^2F2\rangle + .0468\|^2G1\rangle + .0084\|^2G2\rangle$	1.143
	39909.06	-33.34	$.0034\|^4D\rangle - .0070\|^4F\rangle + .0189\|^4G\rangle + .0374\|^2F1\rangle - .0566\|^2F2\rangle - .6384\|^2G1\rangle - .7664\|^2G2\rangle$	.890
	62087.75 (calc.)		$.0335\|^4D\rangle + .0048\|^4F\rangle - .0123\|^4G\rangle + .9044\|^2F1\rangle - .4211\|^2F2\rangle + .0332\|^2G1\rangle + .0474\|^2G2\rangle$	1.143
9/2	0.00	-5.56	$-.0026\|^4F\rangle - .0066\|^4G\rangle - .9862\|^4I\rangle + .0150\|^2G1\rangle - .0133\|^2G2\rangle - .0534\|^2H1\rangle + .1550\|^2H2\rangle$	.732
	10032.92	37.33	$.3253\|^4F\rangle + .1280\|^4G\rangle - .1475\|^4I\rangle - .3193\|^2G1\rangle + .2678\|^2G2\rangle + .2938\|^2H1\rangle - .7720\|^2H2\rangle$	.989
	11761.69	-11.08	$.8849\|^4F\rangle - .0225\|^4G\rangle + .0647\|^4I\rangle - .1471\|^2G1\rangle + .1039\|^2G2\rangle - .1396\|^2H1\rangle + .4005\|^2H2\rangle$	1.248
	15705.13	4.68	$-.2382\|^4F\rangle + .7369\|^4G\rangle + .0334\|^4I\rangle - .4158\|^2G1\rangle + .3724\|^2G2\rangle - .1138\|^2H1\rangle + .2733\|^2H2\rangle$	1.139
	16763.98	-8.03	$.2329\|^4F\rangle + .6606\|^4G\rangle - .0167\|^4I\rangle + .5418\|^2G1\rangle - .4324\|^2G2\rangle - .0130\|^2H1\rangle - .1682\|^2H2\rangle$	1.144
	26979.66	120.87	$.0028\|^4F\rangle + .0566\|^4G\rangle + .0034\|^4I\rangle - .0165\|^2G1\rangle - .0930\|^2G2\rangle + .9340\|^2H1\rangle + .3399\|^2H2\rangle$	.911
	39225.60	-9.17	$.0139\|^4F\rangle - .0203\|^4G\rangle + .0004\|^4I\rangle + .6399\|^2G1\rangle + .7636\|^2G2\rangle + .0769\|^2H1\rangle + .0318\|^2H2\rangle$	1.110
11/2	1398.34	-5.54	$.0063\|^4G\rangle + .9953\|^4I\rangle + .0338\|^2H1\rangle - .0899\|^2H2\rangle - .0133\|^2I\rangle$	.966
	12494.63	26.38	$-.2057\|^4G\rangle + .0946\|^4I\rangle - .3623\|^2H1\rangle + .9031\|^2H2\rangle - .0441\|^2I\rangle$	1.097
	17409.58	12.40	$-.9723\|^4G\rangle - .0134\|^4I\rangle + .1807\|^2H1\rangle - .1478\|^2H2\rangle - .0053\|^2I\rangle$	1.263
	24357.98	-5.22	$.0561\|^4G\rangle - .0145\|^4I\rangle + .3702\|^2H1\rangle + .1179\|^2H2\rangle - .9196\|^2I\rangle$	.949
	28101.77	19.06	$.0960\|^4G\rangle + .0101\|^4I\rangle + .8354\|^2H1\rangle + .3750\|^2H2\rangle + .3900\|^2I\rangle$	1.067
13/2	2893.14	1.75	$.9983\|^4I\rangle - .0197\|^2I\rangle + .0547\|^2K\rangle$	1.079
	16089.14	22.85	$.0563\|^4I\rangle + .0893\|^2I\rangle - .9944\|^2K\rangle$	.935
	25391.75	1.05	$.0147\|^4I\rangle + .9958\|^2K\rangle + .0902\|^2K\rangle$	1.076
15/2	4453.76	14.34	$.9950\|^4I\rangle + .1001\|^2K\rangle - .006\|^2L\rangle$	1.199
	17642.06	2.66	$-.0100\|^4I\rangle + .9792\|^2K\rangle - .1768\|^2L\rangle$	1.064
	25244.61	-21.42	$-.0114\|^4I\rangle + .1765\|^2K\rangle + .9842\|^2L\rangle$	.945
17/2	26447.88	-51.38	$1.000\|^2L\rangle$	1.059

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.