the capture cross sections as given by Eq. (8). First, for a sufficiently high incident-proton velocity and for all neutralizers we have the well-known result that the s-state capture distribution varies as n^{-3}, as deduced from the coefficient of the asymptotic form for $F^2(nl)$. Second, captures into the very high angular-momentum states are in general not expected to contribute appreciably to the total cross section since the magnitude of $F^2(nl)$ is dominated by the coefficient

$$2^{4l}(l!)^2[(n-l-1)!]^2[(n+l)!]^{-2}.$$

In this connection, we note that the large resonance reported by Butler and Johnston[23] at $p^2=1$ is not reproduced in these calculations.

Note added in proof: This resonance has been discussed further by S. T. Butler, R. M. May, and I. D. S. Johnston, Phys. Letters **10**, 281 (1964).

ACKNOWLEDGMENTS

The author would like to thank Dr. J. B. Adams for the hospitality extended by the Culham Laboratory during the course of this visit.

[23] S. T. Butler, and I. D. S. Johnston, Phys. Letters **9**, 141 (1964).

PHYSICAL REVIEW VOLUME 137, NUMBER 2A 18 JANUARY 1965

Generalization of the "Linear Theory" of Configuration Interaction*

B. G. WYBOURNE

Chemistry Division, Argonne National Laboratory, Argonne, Illinois

(Received 31 August 1964)

The "linear" theory of configuration interaction has met with considerable success in giving a phenomenological description of the energy levels of equivalent-electron systems. In the present paper the generalization of the "linear" theory to configurations containing nonequivalent electrons is examined from the point of view of second-order perturbation theory. It is shown that most second-order electrostatic interactions can be phenomenologically described by the first-order terms of a set of effective two-body scalar interactions. The significance of these interactions in atomic energy-level calculations is considered.

I. INTRODUCTION

IT is well known[1] that the solutions of the Hartree-Fock equations for complex atoms or ions yield multiplet energy separations that are considerably *larger* than those found experimentally. The discrepancies are usually so great that these calculations are of little value in the prediction and correlation of atomic energy levels. As a result, atomic spectroscopists have tended to correlate their observations with theoretical energy levels calculated by constructing the energy matrices for the relevant electron configurations and then treating the radial integrals as phenomenological parameters.[2] The parameters are usually found to be substantially *smaller* than the Hartree-Fock radial integrals. The agreement between the theoretical and experimental energy levels has frequently been strikingly close considering that in most cases configuration interaction has been explicitly ignored. It is as if the parameters have adjusted themselves so as to accommodate part of the effects of configuration interaction.

The "linear" theory of configuration interaction has been a natural outgrowth of an early paper of Bacher and Goudsmit[3] who demonstrated that most, though not all, of the second-order electrostatic interactions can be added linearly. Originally Bacher and Goudsmit used linear relations to express the unknown energy levels in terms of the *observed* energy levels of the atom and its ions. Later developments by Trees[4–9] and Racah[10–13] have sought to replace the second-order effects by the first-order terms of an effective two-body interaction. A detailed analysis of the physical content of these interactions in l^N-type configurations has been given by Rajnak and Wybourne.[14–17] The use of effective two-body interactions has found extensive application

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I.

[2] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).

[3] R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).

[4] R. E. Trees, Phys. Rev. **83**, 756 (1951).

[5] R. E. Trees, Phys. Rev. **85**, 381 (1952).

[6] R. E. Trees, J. Res. Natl. Bur. Std. **53**, 35 (1954).

[7] R. E. Trees and C. K. Jørgensen, Phys. Rev. **123**, 1278 (1961).

[8] R. E. Trees, Phys. Rev. **129**, 1220 (1963).

[9] R. E. Trees, J. Opt. Soc. Am. **54**, 651 (1964).

[10] G. Racah, Phys. Rev. **85**, 381 (1952).

[11] G. Racah, *L. Farkas Memorial Volume* (Research Council of Israel, Jerusalem, 1952), p. 294.

[12] G. Racah, Lunds Univ. Arsskr. Avd. 2 **50**, 31 (1954).

[13] G. Racah and Y. Shadmi, Phys. Rev. **119**, 156 (1960).

[14] K. Rajnak and B. G. Wybourne, Phys. Rev. **132**, 280 (1963).

[15] K. Rajnak and B. G. Wybourne, Phys. Rev. **134**, A596 (1964).

[16] K. Rajnak and B. G. Wybourne, J. Chem. Phys. **41**, 565 (1964).

[17] K. Rajnak, J. Opt. Soc. Am. (to be published).

not only in atomic spectroscopy but also in nuclear shell models.[11,18,19]

Briefly, the central idea of the "linear" theory is to augment the Hamiltonian of the N-electron system with additional two-body *scalar* interactions. Associated with each interaction is an adjustable parameter. In general, the number of additional interactions is chosen so that the total number of adjustable parameters equals the number of allowed LS terms occurring in all distinct two-electron configurations that may be formed by deleting $N-2$ of the electrons from the configuration under study. That is, we may take into account the distortion of a pair of electrons by interactions with other configurations and then generalize the result to say that the distortions add linearly when we form the N-electron system. Previous work has been devoted almost exclusively to configurations of equivalent electrons. In this paper we shall show that the "linear" theory can be systematically extended to configurations containing nonequivalent electrons. The relationship of the parameters that are derivable from the "linear" theory to those calculated from the solutions of the Hartree-Fock equations is noted.

II. CONFIGURATION INTERACTION IN TWO-ELECTRON SYSTEMS

Let us first consider the role of configuration interaction in two-electron systems and then extend our results to N-electron systems. For greatest generality we shall assume the configuration $nln'l'$ is perturbed by some other configuration $n''l''n'''l'''$. The following abbreviated quantities will be found useful for our purposes:

$$D^k=(l\|\mathbf{C}^{(k)}\|l'')(l'\|\mathbf{C}^{(k)}\|l''')\times R^k(nln'l';n''l''n'''l'''), \quad (1a)$$

$$E^k=(l\|\mathbf{C}^{(k)}\|l''')(l'\|C^{(k)}\|l'')\times R^k(nln'l';n'''l'''n''l''), \quad (1b)$$

$$\mathfrak{F}^\tau=(l\|\mathbf{C}^{(\tau)}\|l)(l'\|\mathbf{C}^{(\tau)}\|l')F^\tau(nl;n'l'), \quad (1c)$$

$$\mathfrak{G}^\tau=(l\|\mathbf{C}^{(\tau)}\|l')(l'\|\mathbf{C}^{(\tau)}\|l)G^\tau(nl;n'l'), \quad (1d)$$

$$\mathfrak{F}'^t=\frac{-1}{\Delta E}\sum_{k,k'}(-1)^t[t]\left[\begin{Bmatrix} t & l' & l' \\ l''' & k & k'\end{Bmatrix}\begin{Bmatrix} t & l & l \\ l'' & k & k'\end{Bmatrix}+\begin{Bmatrix} t & l' & l' \\ l'' & k & k'\end{Bmatrix}\begin{Bmatrix} t & l & l \\ l''' & k & k'\end{Bmatrix}\right]D^kD^{k'}, \quad (1e)$$

$$\mathfrak{G}'^t=\frac{-2}{\Delta E}\sum_{k,k'}(-1)^t[t]\begin{Bmatrix} t & l' & l' \\ l'' & k & k'\end{Bmatrix}\times\begin{Bmatrix} t & l' & l \\ l''' & k & k'\end{Bmatrix}D^kE^{k'}, \quad (1f)$$

and

$$\Delta E=E(n''l''n'''l''';SL)-E(nln'l';SL). \quad (1g)$$

[18] I. Talmi, Rev. Mod. Phys. 34, 704 (1962).
[19] A. de-Shalit and I. Talmi, *Nuclear Shell Theory* (Academic Press Inc., New York, 1963).

In general we shall follow the notations used by Rajnak and Wybourne[14] (henceforth referred to as I). The $\mathbf{C}^{(k)}$'s are tensor operators related to the usual spherical harmonics,[20] the R^k, F^τ, and G^τ are Slater radial integrals, while ΔE is the first-order energy difference between the mutually perturbing states.

The electrostatic matrix elements between the states of $nln'l'$ and $n''l''n'''l'''$ may be written as follows[21]:

$$\sum_k M^k(SL)=\left(nslnsl';SL\left|\sum_k\frac{r_<^k}{r_>^{k+1}}(\mathbf{C}^{(k)}\cdot\mathbf{C}^{(k)})\right|\times n''sl''n'''sl''';SL\right)$$

$$=\sum_k(-1)^{l'+l''}\left[(-1)^L\begin{Bmatrix} l''' & l'' & L \\ l & l' & k\end{Bmatrix}D^k-(-1)^S\begin{Bmatrix} l'' & l''' & L \\ l & l' & k\end{Bmatrix}E^k\right]. \quad (2)$$

The second-order perturbation between two states will be

$$P=\frac{-1}{\Delta E}\sum_{k,k'}M^k(SL)M^{k'}(SL)$$

$$=\sum_t(-1)^{l+l'}\left[(-1)^L\begin{Bmatrix} l & l & t \\ l' & l' & L\end{Bmatrix}\mathfrak{F}'^t-(-1)^S\begin{Bmatrix} l & l' & t \\ l & l' & L\end{Bmatrix}\mathfrak{G}'^t\right]. \quad (3)$$

[In deriving Eq. (3) use has been made of the Biedenharn-Elliott sum rule.[20]] Let us now assume the perturbing configurations are sufficiently separated to allow us to replace the quantities $\mathfrak{F}'^t$ and $\mathfrak{G}'^t$ by the quantities $\langle\mathfrak{F}'^t\rangle_{\rm av}$ and $\langle\mathfrak{G}'^t\rangle_{\rm av}$, which are understood to represent the weighted average that would be obtained by summing Eq. (3) over all the perturbing configurations. Under these circumstances the summation index t may assume *both* even and odd integral values subject to the restrictions that for $\langle\mathfrak{F}'^t\rangle_{\rm av}$ we have $0\leq t\leq 2l_<$, where $l_<$ is the lesser of l and l', and for $\langle\mathfrak{G}'^t\rangle_{\rm av}$ we have $|l-l'|\leq t\leq l+l'$. In fact, there are as many values of $\langle\mathfrak{F}'^t\rangle_{\rm av}$ and $\langle\mathfrak{G}'^t\rangle_{\rm av}$ as there are LS states in the unperturbed configuration $nln'l'$.

[20] B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1963).
[21] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959).

The electrostatic matrix elements within the $nln'l'$ configuration are given by

$$\left(nsln'sl';SL\left|\sum_\tau \frac{r_<^\tau}{r_>^{\tau+1}}(\mathbf{C}^{(\tau)}\cdot\mathbf{C}^{(\tau)})\right|nsln'sl';SL\right)$$
$$=\sum_\tau(-1)^{l+l'}\left[(-1)^L\begin{Bmatrix} l & l & \tau \\ l' & l' & L\end{Bmatrix}\mathfrak{F}^\tau - (-1)^S\begin{Bmatrix} l & l' & \tau \\ l & l' & L\end{Bmatrix}\mathfrak{G}^\tau\right]. \quad (4)$$

Comparison of Eqs. (3) and (4) shows that the formal structure of their dependence upon S and L is the same except that the range of values of τ are restricted to only *even* integral values for $\mathfrak{F}^\tau$ and to integral values of parity $(-1)^{l+l'}$ for $\mathfrak{G}^\tau$ while for t there are no parity restrictions. The upper and lower bounds on t and τ are the same.

Part of the distortion produced in the $nln'l'$ configuration by the perturbing configurations may be included by simply treating the $2l_<+2$ radial integrals contained in Eq. (4) as adjustable parameters. The complete distortion, to second order, could be included by introducing $2l_<$ additional parameters to represent those terms in the averaged form of Eq. (3) having values of t different from those of τ in Eq. (4). However, we would then have as many parameters as there are LS terms in the $nln'l'$ configuration and no significance could be attached to any agreement between the calculated and observed energy levels. To obtain a physically significant result the theory has to be extended to configurations that have more LS terms than there are parameters.

III. CONFIGURATION INTERACTION IN N-ELECTRON SYSTEMS

To extend the theory to N-electron systems we first note that Eq. (4) may be expanded in terms of the tensor operators $\mathbf{u}^{(\tau)}$ and $\mathbf{v}^{(1\tau)}$ to yield[20–23]

$$\left(nsln'sl';SL\left|\sum_\tau \frac{r_<^\tau}{r_>^{\tau+1}}(\mathbf{C}^{(\tau)}\cdot\mathbf{C}^{(\tau)})\right|nsln'sl'\right)$$
$$=\sum_\tau\left[(\mathbf{u}^{(\tau)}\cdot\mathbf{u}^{(\tau)})\mathfrak{F}^\tau+\tfrac{1}{2}\sum_\kappa(-1)^{\tau+\kappa}[\kappa]\times\begin{Bmatrix} l & l & \tau \\ l' & l' & \kappa\end{Bmatrix}[(\mathbf{u}^{(\kappa)}\cdot\mathbf{u}^{(\kappa)})+4(\mathbf{v}^{(1\kappa)}\cdot\mathbf{v}^{(1\kappa)})]\mathfrak{G}^\tau\right], \quad (5)$$

where we have suppressed the quantum numbers associated with the matrix elements of the scalar products. An analogous expression may be developed for the averaged form of Eq. (3) except that t, unlike τ, is of unrestricted parity.

Consider the case of electrostatic interaction in a configuration $nl^Nn'l'$. The electrostatic energy matrix will contain the matrix elements of the interactions within the nl^N core as well as those between the core and $n'l'$. The effects of one- or two-electron substitutions involving the nl^N core but leaving the quantum numbers of the added $n'l'$ electron unchanged may be included by the introduction of the effective two- and three-body interactions discussed in I. The electrostatic matrix elements that express the interaction of the $n'l'$ electron with the nl^N core may be found from Eq. (5) by replacing the tensor operators that operate on the nl electron by operators that operate on the states of the nl^N core, viz.,

$$\left(nl^N\alpha_1S_1L_1n'sl';SL\left|\sum_\tau\sum_{i<j}\frac{r_<^\tau}{r_>^{\tau+1}}(\mathbf{C}_i^{(\tau)}\cdot\mathbf{C}_j^{(\tau)})\right|\times nl^N\alpha_3S_3L_3n'sl';SL\right)$$
$$=\sum_\tau\left[(\mathbf{U}^{(\tau)}\cdot\mathbf{u}^{(\tau)})\mathfrak{F}^\tau+\tfrac{1}{2}\sum_\kappa(-1)^{\tau+\kappa}[\kappa]\times\begin{Bmatrix} l & l & \tau \\ l' & l' & \kappa\end{Bmatrix}((\mathbf{U}^{(\kappa)}\cdot\mathbf{u}^{(\kappa)})+4(\mathbf{V}^{(1\kappa)}\cdot\mathbf{v}^{(1\kappa)}))\mathfrak{G}^\tau\right]. \quad (6)$$

In this equation the upper-case tensors operate on the states of the nl^N core while the lower case operates on $n'l'$.

The energy levels of the $nl^Nn'l'$ configuration will be distorted by interactions with other configurations. If we make a closure over the states of the perturbing configurations of the type $nl^Nn''l''$ we obtain an expression identical to Eq. (6) apart from the replacement of $\mathfrak{F}^\tau$ and $\mathfrak{G}^\tau$ by $\langle\mathfrak{F}'^\tau\rangle_{\rm av}$ and $\langle\mathfrak{G}'^\tau\rangle_{\rm av}$ where, as in Eq. (3), the summation index τ ranges over both parities. A similar result is found for most other types of configurations that interact in second order.[24]

Again we see that part of the linear distortion is taken up by treating the $2l_<+2$ radial integrals that arise in the expression of the electrostatic interaction between the nl^N core and the $n'l'$ electron as adjustable parameters. In fact for the nl^Nn's configurations the entire linear distortion, to second order, will be accommodated.[25] The total second-order linear distortion may be included by supplementing the $2l_<+2$ radial integrals by $2l_<$ additional parameters, exactly as discussed in the previous section.

[22] G. Racah, Phys. Rev. **62**, 438 (1942).
[23] A. Arima, H. Horie, and Y. Tanabe, Progr. Theoret. Phys. (Kyoto) **11**, 143 (1954).
[24] The sole exception is the perturbation due to the nl^{N+1} configuration. This configuration gives rise to nonlinear distortions in the $nl^Nn'l'$ configuration that cannot be accommodated in the simple linear theory. These nonlinear effects will arise only if l and l' are of the same parity.
[25] Nonlinear effects will be felt in the d^Ns configurations though not, of course, in the p^Ns or f^Ns configurations.

Let us consider the case of a configuration $l^N p (l>0)$. Four parameters F^0, F^2, G^1, and G^3 arise from the interaction of p with the l^N core. We need two additional parameters to fully account for the second-order linear distortions. The choice of these parameters is not unique. One choice might be to introduce $\langle \mathcal{F}'^1 \rangle_{\rm av}$, and $\langle \mathcal{G}'^2 \rangle_{\rm av}$ as parameters. The coefficient $(\mathbf{U}^{(1)} \cdot \mathbf{u}^{(1)})$ of $\langle \mathcal{F}'^1 \rangle_{\rm av}$ may be evaluated to yield [20]

$$(l^N \alpha_1 S_1 L_1 s l'; SL | (\mathbf{U}^{(1)} \cdot \mathbf{u}^{(1)}) | l^N \alpha_3 S_3 L_3 s l'; SL) \langle \mathcal{F}'^1 \rangle_{\rm av}$$
$$= \langle \mathcal{F}'^1 \rangle_{\rm av} \frac{[L(L+1) - L_1(L_1+1) - l'(l'+1)]}{[l(l+1)(2l+1)l'(l'+1)(2l'+1)]^{1/2}}$$
$$\times \delta(\alpha_1, \alpha_3) \delta(S_1, S_3) \delta(L_1, L_3)$$
$$= aL(L+1) + \alpha L_1(L_1+1) + c. \quad (7)$$

The terms involving $\alpha L_1(L_1+1)$ and c may be discarded as they are already included as parameters for the l^N core (see I). Thus the appropriate parameter would be just $aL(L+1)$. The angular coefficient of $\langle \mathcal{G}'^2 \rangle_{\rm av}$ is represented as a sum over several tensor operators as in Eq. (6). While we could use $\langle \mathcal{G}'^2 \rangle_{\rm av}$ as the second parameter it would clearly be better to choose a parameter that possesses simpler angular coefficients.[26] This may be done easily by recognizing that the number of distinct tensor operators contained in Eq. (6) is equal to the number of states that arise in the configuration $nln'l'$. Thus we are free to make our choice from any of these provided they do not already occur in association with the $\mathcal{F}^\tau$ parameters, e.g., in $l^N p$ we may not choose $(\mathbf{U}^{(0)} \cdot \mathbf{u}^{(0)})$ or $(\mathbf{U}^{(2)} \cdot \mathbf{u}^{(2)})$.

The simplest choice for $l^N p$ configurations is to introduce parameters proportional to the matrix elements of $(\mathbf{U}^{(1)} \cdot \mathbf{u}^{(1)})$ and $(\mathbf{V}^{(10)} \cdot \mathbf{v}^{(10)})$. We note that[20]

$$(l^N \alpha_1 S_1 L_1 s l'; SL | (\mathbf{V}^{(10)} \cdot \mathbf{v}^{(10)}) | l^N \alpha_3 S_3 L_3 s l'; SL)$$
$$= (\mathbf{S}_1 \cdot \mathbf{s}) / ([l,l'])^{1/2}$$
$$= \frac{[S(S+1) - S_1(S_1+1) - s(s+1)]}{2([l,l'])^{1/2}}. \quad (8)$$

We may discard $S_1(S_1+1)$ and $s(s+1)$ from our scheme of parameters since they are already associated with the parameters of the l^N core. Thus for $l^N p$ configurations we may include the effects of second-order linear distortions by the introduction of two additional parameters $aL(L+1)$ and $bS(S+1)$ as has already been noted by Sack[27] though from a different but equivalent argument.

The extension to other $l^N l'$ configurations is not difficult. For $l^N d (l>1)$ configurations we need four additional parameters. Here we may choose $L(L+1)$ and $S(S+1)$, as in $l^N p$, leaving two additional parameters to be found. One choice would be to have parameters proportional to the matrix elements of $(\mathbf{U}^{(3)} \cdot \mathbf{u}^{(3)})$ and $(\mathbf{V}^{(11)} \cdot \mathbf{v}^{(11)})$. The reduced matrix elements of these tensor operators have been tabulated for p^N, d^N, and f^N configurations by Nielson and Koster.[28] It should be noted that these matrix elements will not be diagonal in the states of the l^N core.

The phenomenological treatment of second-order linear distortions in more complex configurations proceeds in a similar manner. We first expand in terms of tensor operators the formulas for the electrostatic matrix elements ignoring configuration interaction, and then for each distinct pair of electrons pick out the simplest possible set of $2l_<$ operators to be used as the coefficients of our $2l_<$ additional parameters.

In practice we must be careful not to select so many parameters as to destroy the physical significance of a fit to the observed energy levels. For example, in the $l^N l' l''$ configuration we would be justified in choosing additional parameters to correct for linear distortions involving l^N and l' and for l^N and l'' but not for the $l' l''$ pair. In the latter case we would end up with as many parameters as there are LS terms in $l' l''$. Where $N \geq 2$ there will normally be more LS terms than there are parameters, and significance could be attached to the fitting of the observed energy levels.

IV. "LINEAR" PARAMETERS AND HARTREE-FOCK RADIAL INTEGRALS

Several problems arise when a comparison is made between the phenomenological "linear" parameters and the corresponding radial integrals computed from solutions of the Hartree-Fock equations in their various modifications. Comparisons are most commonly made for the Slater radial integrals F^k and G^k. The relationship between the parameters and the integrals is by no means clear. First we note that since the choice of the additional parameters in the "linear" theory is not unique, different choices of these parameters will yield different values for the F^k and G^k "integrals." Even if no additional parameters were to be introduced the parameters corresponding to the F^k and G^k integrals would contain contributions from the many interacting configurations and hence could not be expected to correspond to the integrals calculated for a pure wave function. In deriving the linear parameters it is assumed that they are independent of the state of the configuration under study and hence the phenomenological parameters represent the average effect over an entire configuration. The corresponding Hartree-Fock solutions are usually obtained for a particular state of the configuration, normally the ground state.

[26] The use of $\langle G'^2 \rangle_{\rm av}$ would, however, have the advantage that its radial dependence is more readily visualized in terms of the perturbing configuration.

[27] N. Sack, Phys. Rev. **102**, 1302 (1956).

[28] C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations* (Technology Press, Cambridge, Massachusetts, 1963).

V. CONCLUDING REMARKS

The additional parameters that enter the "linear" theory can be considered to be physically significant only if they lead to a definite improvement in the description of the observed energy levels. Their general validity could be best established by deriving them from a series of ions of fixed ionization. In this case we could expect the parameters to exhibit a systematic linear variation across the series. Having established the variation of the parameters in one stage of ionization for the series it should then be possible to extrapolate the parameters for the other stages of ionization once the parameters are known at the commencement and end of the new ionization series. This has indeed been the great virtue of the "linear" theory; it has been highly successful in predicting the positions of unknown levels.

Sack[27] has examined the effect of the $aL(L+1)$ and $bS(S+1)$ corrections in Ti II($3d^2 4p$) and Ni II($3d^8 4p$) and found a substantial reduction in the deviations between the observed and calculated energy levels. Racah and Spector[29] have studied the role of these corrections in Cr II($3d^4 4p$) and Fe II($3d^6 4p$) and concluded that the corrections have no statistical significance. However, their calculations, like those of Sack, ignored the effects of spin-orbit interaction. Several multiplets of these configurations show gross deviations from the Landé interval rule. The calculations need to be repeated with the inclusion of the spin-orbit interaction before a final conclusion for the second spectra of the iron group can be reached.

The linear" parameters should give a very good phenomenological description of the effects of electrostatic interactions with configurations well removed from the configuration of immediate interest. The effects of overlapping interacting configurations will still need to be included explicitly by constructing the energy matrices in a basis that includes the states of the relevant configurations. Likewise, the nonlinear effects produced by certain interacting configurations[24,25] will not be entirely included. It is unlikely that any of the "linear" parameters can be completely associated with a particular interacting configuration; rather they will represent the weighted contributions of many configurations.

The "linear" theory allows us to make statements about the relationships between the parameters of one configuration and those of a related configuration, not necessarily of the same parity. Consider the $4f^3$ and $4f^2 5d$ configurations of Pr III that have been studied experimentally by Sugar[30] and theoretically by Trees.[9] The parameters associated with electrostatic interactions among the $4f$ electrons, on both configurations, will be affected principally by perturbations from configurations differing by a two-electron substitution in the $4f^N$ core. All the possible two-electron substitutions that can be made in $4f^3$ can also be made in $4f^2 5d$, and hence we would predict that the "linear" parameters for the $4f$–$4f$ interactions would be approximately equal. This equality will tend to be weakened by one- and two-electron substitutions involving the $5d$ electron of the $4f^2 5d$ configuration as may be seen from an inspection of Eq. (7). When the additional "linear" parameters are introduced to account for distortion of the $4f$–$5d$ interaction we can expect the $4f$–$4f$ parameters to be modified as well. This is in accord with the observation of Trees[9] that the $4f$–$4f$ parameters in $4f^2 5d$ and $4f^3$ are indeed different though this may not be the sole cause of the discrepancy. One-electron substitutions involving the $4f^3$ configuration will give rise to nonlinear effective three-body interactions that are not included in the usual two-body "linear" theory.[14] In the $4f^2 5d$ configuration these same one-electron substitutions can only give rise to linear effects. These linear effects will be felt by the $4f$–$4f$ parameters of the $4f^2 5d$ configuration.

In the foregoing we have demonstrated that the "linear" theory, which has had much success in explaining the properties of equivalent electron systems, may be readily generalized to the case where nonequivalent electrons are involved. The generalization has been shown to be a direct consequence of second-order perturbations. It should be of considerable interest to atomic spectroscopists to see if the generalized "linear" theory will meet with the same success that the "linear" theory has had in l^N configurations. The theory should be particularly useful in the analysis of the higher stages of ionization where, at least for the lower configurations, the perturbing configurations will be at higher energies and thus more in accord with the approximations of the theory. While we have confined our discussion exclusively to atomic shells the same types of effective interactions will also arise in the nuclear shell model.

[29] G. Racah and N. Spector, Bull. Res. Council Israel **9F**, 75 (1960).

[30] J. Sugar, J. Opt. Soc. Am. **53**, 831 (1963).