

Ground-State Energy Eigenvalues and Eigenfunctions for an Electron in an Electric-Dipole Field*

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Ground-state energy eigenvalues and eigenfunctions are obtained by a variational method for an electron in the field of a finite, stationary, permanent electric dipole. The dipole moments studied cover the range from the minimum value required for binding ($D_{\min} = 0.6393 ea_0$) to $D = 400 ea_0$, where the system is equivalent to the hydrogen atom perturbed slightly by a distant stationary negative charge. The eigenvalues obtained agree with those reported by Wallis, Herman, and Milnes, who determined them by another method in the range $D = 0.84 ea_0$ to $30 ea_0$. The normalized eigenfunctions display the manner in which the electronic charge density changes from that of the hydrogen atom at very large D to a flat distribution approaching that which is characteristic of a zero-energy continuum state as the minimum moment is approached from above. Optimized variational wave functions for different values of D are presented for use in other calculations. Contour maps and profiles of electronic charge density are shown for a number of values of D . Mean values of the powers -1 , 1 , and 2 of the distances of the electron from the dipole charges are also calculated.

I. INTRODUCTION

The motion of an electron in an electric-dipole field has been considered recently as a model for low-energy electron scattering by polar molecules¹⁻¹¹ and ion pairs in semiconductors,¹² and for color-center problems.^{13, 14} Experimental results on the drift of electron-swarms through polar gases^{15, 16} led to the suggestion that electrons might be temporarily captured into loosely bound states through rotational excitation of polar molecules.¹⁶ Wallis, Herman, and Milnes¹⁴ have calculated binding energies for an electron in the field of a finite, stationary, permanent electric dipole for values of dipole moment D between $0.84 ea_0$ and $30 ea_0$ (e = electronic charge and a_0 = radius of first Bohr orbit in hydrogen). Until more recent work it was not known whether a model⁵ invoking the existence of a bound state in a dipole field would apply to molecules with arbitrarily small dipole moments.

Analysis of the electron-dipole system by the WKB method¹⁷ indicated that a minimum dipole moment is required to bind an electron, and a preliminary variational calculation^{4, 18} showed that a bound state exists for D as small as $0.6495 ea_0$. After these results were found, several investigators^{7, 19-21} showed that the minimum dipole moment required for binding an electron is $D_{\min} = 0.6393 ea_0$ ($= 1.625 \times 10^{-18}$ esu cm).²² Some experimental evidence from electron-swarm data has been presented²³ in support of this conclusion. The properties of excited states of the electron in the dipole field have also been studied.^{24, 25}

We calculate below by means of a variational technique the lowest energy eigenvalue for dipole moments ranging from $D_{\min} = 0.6393 ea_0$ to D

$= 400 ea_0$.²⁶ Our method differs from that of Ref. 14 and will be described in detail. We also calculate ground-state energy eigenfunctions for a number of values of D . These functions are applicable in calculations of cross sections for electron capture and for scattering involving intermediate bound states.^{5, 6}

The ground-state motion of a bound charged particle in the field of a stationary electric dipole has intrinsic interest as a quantum-mechanical system. Classically, there is always a bound state for an arbitrarily small dipole moment.^{27, 28} The calculations below show the manner in which the electronic charge density behaves as the minimum dipole moment is approached from above.

In the following sections we discuss the forms of variational functions used in our calculations, the elements of the Hamiltonian and normalization matrices, the methods of obtaining the energy eigenvalues and eigenfunctions, and the numerical results. Contour maps and profiles of the electronic charge distributions about the dipole are also presented.

II. VARIATIONAL WAVE FUNCTIONS

In Fig. 1 we represent the finite, stationary, permanent electric dipole by charges $\pm q$ located at fixed points $z = \pm R/2$. The dipole moment is $D = qR$. The position of an electron of charge $-e$ and mass m is determined by its distances r_1 and r_2 from the charges $\pm q$ and by the azimuthal angle about the z axis. The Schrödinger equation is separable in elliptic-hyperbolic coordinates defined by

$$\xi = (r_1 + r_2)/R \text{ and } \eta = (r_1 - r_2)/R. \quad (1)$$

The ranges of the variables are $1 \leq \xi \leq \infty$ and $-1 \leq \eta \leq 1$, negative values of η corresponding to posi-

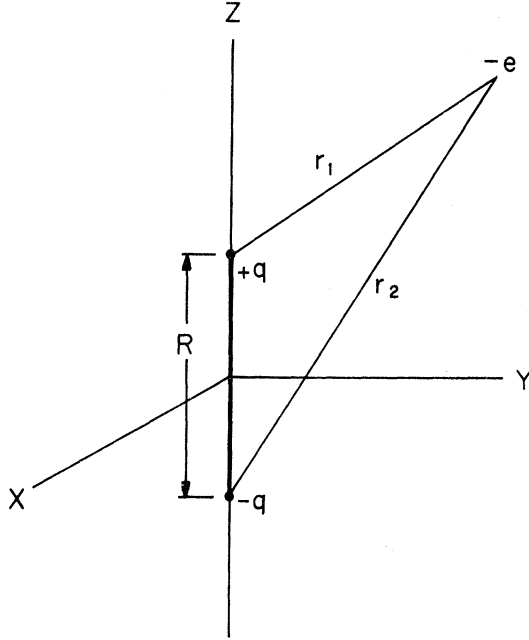


FIG. 1. Coordinate system for an electron in the field of a dipole.

tive values of z . Surfaces of constant ξ and η are, respectively, ellipsoids and hyperboloids of revolution about the z axis.

We used two forms for the trial function in calculating ground-state energy eigenvalues. First, we used the trial function previously employed by us²⁰ to calculate the minimum dipole moment, $D_{\min} = 0.6393$, required for binding an electron:

$$\psi(\xi, \eta) = e^{-\frac{1}{2}\alpha\xi^t} \sum_{p,q=0}^{\infty} C_{pq} \xi^p \eta^q. \quad (2)$$

Here the adjustable parameters are α , t , and the C_{pq} . This expansion is appropriate for low values of D , where letting α and, more importantly, t be small extends the wave function out to large distances from the dipole. The exponential term in Eq. (2) thus characterizes states with small binding energies. We used Eq. (2), which we shall call the low- D expansion, in the range $D_{\min} \leq D \leq 2$.

A second, high- D , expansion²⁹

$$\begin{aligned} \psi(\xi, \eta) &= e^{-\alpha r_1/R} \sum_{p,q=0}^{\infty} C_{pq} \xi^p \eta^q \\ &= e^{-\frac{1}{2}\alpha(\xi+\eta)} \sum_{p,q=0}^{\infty} C_{pq} \xi^p \eta^q \end{aligned} \quad (3)$$

was used in the range $2 \leq D \leq 40$. Here coefficients C_{pq} and α are the adjustable parameters. In the limit as $R \rightarrow \infty$ and with $q=e$ the electron and the positive charge of the dipole form the hydrogen atom. As a numerical check on the results obtained with Eq. (3), we expect, therefore, at large D that

$$\psi(\xi, \eta) \rightarrow \pi^{-\frac{1}{2}} e^{-r_1/a_0}. \quad (4)$$

Thus, as shown below, we find in the numerical calculations that $\alpha \rightarrow R$, $C_{00} \rightarrow 1/\sqrt{\pi} = 0.564190$, $C_{pq} \rightarrow 0$ for $p, q \neq 0$, and that the energy eigenvalue $\lambda \rightarrow -e^2/2a_0 = -1$ Ry. Poor results were obtained with Eq. (3) for $D \lesssim 2$. Both the high- and low- D expansions were used in the range $2 \leq D \leq 5$, where they gave the same results.

III. MATRIX ELEMENTS

We shall outline the calculation of the matrix elements for the low- D trial function. Details for this and other trial functions can be found elsewhere.³⁰

The kinetic-energy operator for the electron is³¹

$$T = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{2\hbar^2}{mR^2(\xi^2 - \eta^2)} \left\{ \frac{\partial}{\partial \xi} \left[(\xi^2 - 1) \frac{\partial}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial}{\partial \eta} \right] \right\}. \quad (5)$$

Its potential energy in the field of the electric dipole, as depicted in Fig. 1, is

$$V = qe(1/r_2 - 1/r_1) = 4De\eta/R^2(\xi^2 - \eta^2). \quad (6)$$

We write the trial function (2) in the form

$$\psi(\xi, \eta) = \sum_{p,q=0}^{\infty} C_{pq} \phi_{pq} \quad (7)$$

$$\text{where } \phi_{pq} = e^{-\frac{1}{2}\alpha\xi^t} \xi^p \eta^q. \quad (8)$$

The elements of the kinetic-energy matrix, representing the differential operator in Eq. (5), are given by

$$T_{pq,ij} = -(\hbar^2/2m) \int \phi_{pq} \nabla^2 \phi_{ij} d\tau \quad (9)$$

where $d\tau = \pi R^3(\xi^2 - \eta^2) d\xi d\eta/4$ is the volume element in elliptic-hyperbolic coordinates, including a factor of 2π from integration over the azimuthal angle. We find that

$$\begin{aligned} T_{pq,ij} &= (\pi R \hbar^2/4m)^{\frac{1}{2}} [1 + (-1)^{q+j}] \\ &\times (q+j+1)^{-1} \{ 2e^{-\alpha} + [-(p-i)^2 + 1 + t(p+i+1)] I_{p+i} \\ &+ [(p-i)^2 - 1 - t(p+i-1)] I_{p+i-2} \\ &+ 8jq I_{p+i}/(q+j-1) \}. \end{aligned} \quad (10)$$

$$\text{Here } I_r = \int_1^\infty e^{-\alpha\xi^t} \xi^r d\xi, \quad (11)$$

and use has been made of the identity $\alpha I_{p+i+t} = e^{-\alpha} + (p+i+1) I_{p+i}$. The elements of the potential-energy and normalization matrices are

$$V_{pq,ij} = \frac{2\pi De R I_{p+i}}{q+j+2} \frac{1 + (-1)^{q+j+1}}{2} \quad (12)$$

$$\text{and } N_{pq,ij} = \frac{\pi R^3}{2} \frac{1 + (-1)^{q+j}}{2} \left(\frac{I_{p+i+2}}{q+j+1} - \frac{I_{p+i}}{q+j+3} \right). \quad (13)$$

To calculate the ground-state energy eigenvalue for a given value of D , we use the determinantal equation

$$\det(T + V - \lambda N) = 0 \quad (14)$$

and find the smallest value of λ that results when α and $\beta (= 1/t)$ are varied. By the variational theorem, this value gives an upper bound to the true ground-state energy eigenvalue for the value of D chosen. Repeating this procedure with determinants of increasing rank gives a sequence of values of λ that converges to the true ground-state energy eigenvalue from above. The coefficients C_{pq} in Eq. (7) are then calculated for this value of λ .

We see from Eqs. (10)–(13) that, for a given value of D ,

$$\mu \equiv \frac{1}{4}\lambda R^2 \quad (15)$$

rather than the energy λ , is the quantity actually determined.

IV. NUMERICAL RESULTS

A summary of numerical results is contained in the accompanying tables and figures. Details of the calculations and numerical cross-checks are given in Ref. 30. It is believed that the values of λ as a function of D are accurate to within ± 2 in the last digit shown.

In Tables I and II we summarize the energy eigenvalues and variational parameters for the complete range of dipole moments. The results in Table I were obtained with the low- D expansion (2) and those in Table II with the high- D expansion (3). With the variational parameters optimized, both forms of the trial function give about the same rate of conver-

TABLE I. Energy eigenvalues λ and optimized variational parameters α and β obtained with low- D expansion (2) and dipole charge $q = e$.

D (ea_0)	$-\mu$	$-\lambda$ (Ry) This calculation	$-\lambda$ (Ry) Wallis <i>et al.</i> ^a	Rank	α (For rank 15)	β (For rank 15)
0.639 315	0	0	...	4 ^b	∞	∞
0.667 0	1.000×10^{-20}	8.973×10^{-20}	...	36	1.83	6.23
0.674 65	$1.000 0 \times 10^{-16}$	$8.777 9 \times 10^{-16}$...	36	1.54	5.08
0.692 72	$1.000 0 \times 10^{-12}$	$8.334 6 \times 10^{-12}$...	36	1.32	4.00
0.723 65	$1.000 0 \times 10^{-9}$	$7.635 0 \times 10^{-9}$...	36	1.18	3.19
0.740 99	$1.000 0 \times 10^{-8}$	$7.284 9 \times 10^{-8}$...	36	1.15	2.93
0.764 49	$1.000 0 \times 10^{-7}$	$6.843 7 \times 10^{-7}$...	36	1.12	2.68
0.797 368	$1.000 00 \times 10^{-6}$	$6.291 17 \times 10^{-6}$...	21	1.10	2.41
0.840 374	$8.194 03 \times 10^{-6}$	$4.640 96 \times 10^{-5}$	4.643×10^{-5}	21	1.11	2.20
0.902 195	$6.386 63 \times 10^{-5}$	$3.138 53 \times 10^{-4}$	3.142×10^{-4}	21	1.30	2.32
1.000 02	$5.123 40 \times 10^{-4}$	$2.049 28 \times 10^{-3}$	2.049×10^{-3}	21	1.22	1.87
1.188 00	$5.000 00 \times 10^{-3}$	$1.417 09 \times 10^{-2}$	1.419×10^{-2}	15	1.35	1.52
1.647 57	$6.400 00 \times 10^{-2}$	$9.430 88 \times 10^{-2}$	9.431×10^{-2}	15	1.70	1.50

^a Obtained by linear or quadratic interpolation from Table I of Wallis *et al.* (Ref. 14).

^b With factored determinant (see Ref. 20). (The last two digits found for D_{\min} in Ref. 20 are not correct.)

TABLE II. Energy eigenvalues λ and optimized variational parameter α obtained with high- D expansion (3) and dipole charge $q = e$.

D (ea_0)	$-\mu$	$-\lambda$ (Ry) This calculation	$-\lambda$ (Ry) Wallis <i>et al.</i> ¹⁴	Rank	α (For rank shown)
2	0.176 264	0.176 264	0.176 266	21	1.616
3	0.855 681	0.380 303	0.380 302	21	2.981
4	2.066 35	0.516 588	0.516 587	15	4.03
5	3.794 35	0.607 096	0.607 097	10	4.99
6	6.031 35	0.670 150	0.670 150	10	6.12
7	8.773 19	0.716 179	0.716 179	10	7.12
8	12.017 8	0.751 113	0.751 112	6	7.809
9	15.764 1	0.778 474	0.778 472	6	8.799
10	20.011 4	0.800 456	0.800 455	6	9.800
15	48.755 0	0.866 756	0.866 756	6	14.872
20	90.002 8	0.900 028	0.900 028	C	19.90
25	143.752	0.920 013	0.920 011	3	24.58
30	210.001	0.933 338	0.933 339	3	29.60
40	380.001	0.950 003	...	3	39.71
50	600.000	0.960 000	...	1	50.00
100	2450.00	0.980 000	...	1	100.0
250	1.55×10^4	0.992	...	1	250.0
400	3.98×10^4	0.995	...	1	400.0

gence with increasing rank in the region $D \sim 1.65$ to $D \sim 2$. At $D=2$, a 21-term high- D function gives the energy eigenvalue slightly better – six parts in the sixth digit – than the low- D function of the same rank. At $D=1$, on the other hand, the convergence of the high- D expansion is very poor. As seen below in Fig. 6, the electronic charge density in this region of D loses its hydrogenic character of rapid decrease away from the positive charge and assumes

a much flatter distribution, characteristic of the dipole with its critical value, $D_{\min}=0.6393$.

The electronic probability density, $|\psi(\xi, \eta)|^2$, was calculated with the coefficients in Tables III and IV. Figure 2 is a contour map, showing the positions at which $\psi^2(=|\psi|^2)$ is equal to inverse powers of 10 when $D=10$. The vertical z axis shows the distance along the axis of the dipole, having charges located at $z=\pm 5$, and the horizontal ρ axis gives the perpen-

TABLE III. Coefficients in low- D expansion (2) of trial functions. The column headings give the dipole moment D . (Dipole charge: $q=e$).

C_{pq}	0.6670	0.67465	0.60272	0.73265	0.74099	0.76449
C_{00}	1.02319×10^{-9}	8.41227×10^{-8}	6.80160×10^{-6}	1.87080×10^{-4}	5.53976×10^{-4}	1.60324×10^{-3}
C_{01}	-6.41480×10^{-10}	-5.32521×10^{-8}	-4.40743×10^{-6}	-1.26000×10^{-4}	-3.80941×10^{-4}	-1.13295×10^{-3}
C_{10}	6.41043×10^{-15}	5.14399×10^{-12}	3.96626×10^{-9}	5.83018×10^{-7}	2.97015×10^{-6}	1.42153×10^{-5}
C_{02}	1.39202×10^{-10}	1.17108×10^{-8}	9.84756×10^{-7}	2.93584×10^{-5}	9.07882×10^{-5}	2.78143×10^{-4}
C_{11}	-4.03870×10^{-15}	-3.27440×10^{-12}	-2.57437×10^{-9}	-3.93224×10^{-7}	-2.04538×10^{-6}	-1.00605×10^{-5}
C_{20}	2.86450×10^{-22}	4.58585×10^{-18}	6.90473×10^{-14}	9.90231×10^{-11}	1.09576×10^{-9}	1.13143×10^{-8}
C_{03}	-1.49140×10^{-11}	-1.25652×10^{-9}	-1.12939×10^{-7}	-3.51370×10^{-6}	-1.11084×10^{-5}	-3.50045×10^{-5}
C_{12}	8.21247×10^{-16}	6.59525×10^{-13}	5.79354×10^{-10}	9.15606×10^{-8}	4.85404×10^{-7}	2.44842×10^{-6}
C_{21}	-1.72150×10^{-22}	-2.75100×10^{-18}	-4.42750×10^{-14}	-6.61370×10^{-11}	-7.47100×10^{-10}	-7.92336×10^{-9}
C_{30}	1.23826×10^{-30}	8.66862×10^{-25}	4.98105×10^{-19}	1.09141×10^{-14}	2.78298×10^{-13}	6.00560×10^{-12}
C_{04}	1.10432×10^{-12}	9.75388×10^{-11}	7.40330×10^{-9}	2.38389×10^{-7}	7.69712×10^{-7}	2.50054×10^{-6}
C_{13}	-1.15140×10^{-16}	-9.62860×10^{-14}	-5.89540×10^{-11}	-9.69137×10^{-9}	-5.28339×10^{-8}	-2.78403×10^{-7}
C_{22}	5.46145×10^{-23}	9.85215×10^{-19}	9.24623×10^{-15}	1.52683×10^{-11}	1.81113×10^{-10}	2.04172×10^{-9}
C_{31}	-9.72350×10^{-31}	-6.81640×10^{-25}	-3.27080×10^{-19}	-7.38740×10^{-15}	-1.92540×10^{-13}	-4.28990×10^{-12}
C_{40}	5.97061×10^{-40}	1.79861×10^{-32}	2.49654×10^{-25}	2.24859×10^{-20}	-9.00470×10^{-20}	-1.08600×10^{-16}
C_{05}	-4.11990×10^{-10}	-1.43203×10^{-8}	-4.78159×10^{-8}	-1.61214×10^{-7}
C_{14}	5.57057×10^{-12}	9.85113×10^{-10}	5.53695×10^{-9}	3.00710×10^{-8}
C_{23}	-1.93960×10^{-15}	-3.28930×10^{-12}	-3.83480×10^{-11}	-4.11860×10^{-10}
C_{32}	8.69300×10^{-20}	1.81651×10^{-15}	4.58870×10^{-14}	9.79650×10^{-13}
C_{41}	-1.72230×10^{-25}	-2.19280×10^{-20}	-3.13400×10^{-19}	6.79650×10^{-17}
C_{50}	2.20323×10^{-32}	1.72919×10^{-25}	2.24373×10^{-23}	7.79253×10^{-22}
C_{pq}	0.797368	0.840374	0.902195	1.00002	1.18800	1.64757
C_{00}	4.50037×10^{-3}	1.13354×10^{-2}	2.96957×10^{-2}	6.16712×10^{-2}	1.30733×10^{-1}	2.82724×10^{-1}
C_{01}	-3.29818×10^{-3}	-8.69168×10^{-3}	-2.41770×10^{-2}	-5.46855×10^{-2}	-1.33410×10^{-1}	-3.71080×10^{-1}
C_{10}	6.51627×10^{-5}	2.40318×10^{-4}	3.88507×10^{-4}	1.69273×10^{-3}	7.91603×10^{-3}	-1.69758×10^{-2}
C_{02}	8.42223×10^{-4}	2.33100×10^{-3}	6.91062×10^{-3}	1.71522×10^{-2}	4.86076×10^{-2}	1.83918×10^{-1}
C_{11}	-4.78899×10^{-5}	-1.84657×10^{-4}	-3.18681×10^{-4}	-1.52001×10^{-3}	-8.02142×10^{-3}	2.23072×10^{-2}
C_{20}	1.20984×10^{-7}	8.68274×10^{-7}	-7.12493×10^{-7}	1.47508×10^{-5}	3.19286×10^{-4}	4.09622×10^{-4}
C_{03}	-1.10173×10^{-4}	-3.19239×10^{-4}	-1.00952×10^{-3}	-2.74734×10^{-3}	-8.97716×10^{-3}	-4.89149×10^{-2}
C_{12}	1.21063×10^{-5}	4.88468×10^{-5}	9.15759×10^{-5}	4.89058×10^{-4}	3.13595×10^{-3}	-1.09963×10^{-2}
C_{21}	-8.70254×10^{-8}	-6.56091×10^{-7}	6.39748×10^{-7}	-1.14812×10^{-5}	-3.23453×10^{-4}	-5.02101×10^{-4}
C_{30}	1.18700×10^{-10}	1.15210×10^{-9}	-2.23480×10^{-10}	-1.70236×10^{-7}	-1.60954×10^{-6}	-6.33671×10^{-6}
C_{04}	8.19184×10^{-6}	2.51633×10^{-5}	9.07401×10^{-5}	2.68923×10^{-4}	1.30488×10^{-3}	7.21738×10^{-3}
C_{13}	-1.45082×10^{-6}	-6.39060×10^{-6}	-1.32096×10^{-5}	-8.40555×10^{-5}	-8.19085×10^{-4}	2.38293×10^{-3}
C_{22}	2.34181×10^{-8}	1.89499×10^{-7}	-1.91982×10^{-7}	2.74214×10^{-6}	1.05307×10^{-4}	1.88808×10^{-4}
C_{31}	-9.16330×10^{-11}	-9.46840×10^{-10}	-1.74840×10^{-10}	1.09760×10^{-7}	8.99382×10^{-7}	4.05598×10^{-6}
C_{40}	-2.57810×10^{-15}	-2.52800×10^{-13}	8.96648×10^{-13}	6.38234×10^{-10}	1.02979×10^{-11}	5.70809×10^{-8}
C_{05}	-5.54058×10^{-7}	-1.77963×10^{-6}	-5.90211×10^{-6}	-2.04145×10^{-5}
C_{14}	1.64649×10^{-7}	7.37649×10^{-7}	9.98298×10^{-7}	8.66910×10^{-6}
C_{23}	-4.55460×10^{-9}	-3.28563×10^{-8}	2.36285×10^{-8}	-1.69905×10^{-7}
C_{32}	2.08919×10^{-11}	1.86825×10^{-10}	8.47278×10^{-11}	-1.82549×10^{-8}
C_{41}	5.33322×10^{-15}	3.19703×10^{-13}	-1.21380×10^{-13}	-2.27320×10^{-10}
C_{50}	-1.39570×10^{-18}	-1.15680×10^{-16}	-3.36920×10^{-16}	-8.43580×10^{-13}

C_{pq}	2	3	4	5	6	7	8	9
C_{00}	$2.758\ 03 \times 10^{-1}$	$3.641\ 33 \times 10^{-1}$	$4.074\ 46 \times 10^{-1}$	$4.182\ 86 \times 10^{-1}$	$4.388\ 20 \times 10^{-1}$	$4.237\ 33 \times 10^{-1}$	$4.576\ 51 \times 10^{-1}$	$4.660\ 84 \times 10^{-1}$
C_{01}	$-1.959\ 84 \times 10^{-1}$	$-2.201\ 64 \times 10^{-1}$	$-2.181\ 03 \times 10^{-1}$	$-2.171\ 31 \times 10^{-1}$	$-1.947\ 33 \times 10^{-1}$	$-1.992\ 24 \times 10^{-1}$	$-2.464\ 09 \times 10^{-1}$	$-2.464\ 07 \times 10^{-1}$
C_{10}	$-3.672\ 27 \times 10^{-2}$	$-4.451\ 65 \times 10^{-2}$	$-5.456\ 77 \times 10^{-2}$	$-4.299\ 11 \times 10^{-2}$	$-3.582\ 01 \times 10^{-2}$	$1.422\ 39 \times 10^{-2}$	$-1.070\ 58 \times 10^{-1}$	$-1.153\ 55 \times 10^{-1}$
C_{02}	$-3.251\ 99 \times 10^{-4}$	$-5.122\ 95 \times 10^{-2}$	$-9.093\ 31 \times 10^{-2}$	$-8.715\ 02 \times 10^{-2}$	$-1.163\ 43 \times 10^{-1}$	$-1.281\ 82 \times 10^{-1}$	$-8.154\ 08 \times 10^{-2}$	$-8.069\ 37 \times 10^{-2}$
C_{11}	$2.637\ 90 \times 10^{-2}$	$2.123\ 06 \times 10^{-2}$	$9.020\ 18 \times 10^{-3}$	$-7.962\ 81 \times 10^{-3}$	$-2.550\ 58 \times 10^{-2}$	$-2.481\ 58 \times 10^{-2}$	$-2.083\ 12 \times 10^{-3}$	$-1.456\ 94 \times 10^{-5}$
C_{20}	$2.237\ 22 \times 10^{-2}$	$4.775\ 03 \times 10^{-2}$	$6.841\ 38 \times 10^{-2}$	$4.004\ 56 \times 10^{-2}$	$4.641\ 99 \times 10^{-2}$	$7.122\ 10 \times 10^{-3}$	$4.525\ 86 \times 10^{-2}$	$4.682\ 10 \times 10^{-2}$
C_{03}	$6.493\ 04 \times 10^{-3}$	$6.311\ 49 \times 10^{-3}$	$2.596\ 19 \times 10^{-3}$	$-8.345\ 90 \times 10^{-3}$	$-2.086\ 26 \times 10^{-2}$	$-2.443\ 05 \times 10^{-2}$
C_{12}	$-2.310\ 00 \times 10^{-4}$	$-1.452\ 75 \times 10^{-4}$	$5.598\ 63 \times 10^{-3}$	$-1.578\ 26 \times 10^{-2}$	$-2.284\ 51 \times 10^{-2}$	$-2.040\ 70 \times 10^{-2}$
C_{21}	$-1.610\ 94 \times 10^{-2}$	$-2.478\ 53 \times 10^{-2}$	$-1.844\ 21 \times 10^{-2}$	$-1.144\ 84 \times 10^{-2}$	$-7.824\ 97 \times 10^{-3}$	$-6.081\ 57 \times 10^{-3}$
C_{30}	$-2.391\ 27 \times 10^{-3}$	$-6.883\ 39 \times 10^{-3}$	$-1.164\ 94 \times 10^{-2}$	$2.175\ 70 \times 10^{-4}$	$1.708\ 85 \times 10^{-3}$	$1.111\ 06 \times 10^{-2}$
C_{04}	$5.914\ 82 \times 10^{-4}$	$3.687\ 39 \times 10^{-3}$	$5.520\ 78 \times 10^{-3}$
C_{13}	$-5.435\ 99 \times 10^{-4}$	$2.542\ 21 \times 10^{-4}$	$-1.092\ 04 \times 10^{-3}$
C_{22}	$6.166\ 87 \times 10^{-5}$	$-2.383\ 98 \times 10^{-3}$	$-9.168\ 26 \times 10^{-3}$
C_{31}	$1.774\ 18 \times 10^{-3}$	$2.785\ 80 \times 10^{-3}$	$-9.629\ 71 \times 10^{-4}$
C_{40}	$2.098\ 37 \times 10^{-4}$	$1.010\ 06 \times 10^{-3}$	$1.820\ 68 \times 10^{-3}$
C_{05}	$2.976\ 10 \times 10^{-6}$	$8.526\ 82 \times 10^{-4}$
C_{14}	$1.019\ 14 \times 10^{-4}$	$8.415\ 17 \times 10^{-4}$
C_{23}	$3.203\ 08 \times 10^{-4}$	$4.134\ 30 \times 10^{-4}$
C_{32}	$-7.015\ 76 \times 10^{-6}$	$-3.561\ 66 \times 10^{-4}$
C_{41}	$-1.613\ 50 \times 10^{-4}$	$-4.346\ 66 \times 10^{-4}$
C_{50}	$1.097\ 76 \times 10^{-6}$	$-8.437\ 94 \times 10^{-6}$
C_{pq}	10	15	20	25	30	40	50	100
C_{00}	$4.734\ 92 \times 10^{-1}$	$4.990\ 24 \times 10^{-1}$	$5.134\ 74 \times 10^{-1}$	$5.199\ 87 \times 10^{-1}$	$5.271\ 98 \times 10^{-1}$	$5.362\ 45 \times 10^{-1}$	$5.461\ 73 \times 10^{-1}$	$5.641\ 90 \times 10^{-1}$
C_{01}	$-2.440\ 44 \times 10^{-1}$	$-2.177\ 34 \times 10^{-1}$	$-2.026\ 97 \times 10^{-1}$	$-1.383\ 50 \times 10^{-1}$	$-1.296\ 15 \times 10^{-1}$	$-9.521\ 41 \times 10^{-2}$
C_{10}	$-1.209\ 51 \times 10^{-1}$	$-1.253\ 76 \times 10^{-1}$	$-1.296\ 01 \times 10^{-1}$	$-9.424\ 62 \times 10^{-2}$	$-9.268\ 59 \times 10^{-2}$	$-6.728\ 52 \times 10^{-2}$
C_{02}	$-8.048\ 21 \times 10^{-2}$	$-8.208\ 11 \times 10^{-2}$	$-8.056\ 41 \times 10^{-2}$
C_{11}	$9.853\ 11 \times 10^{-4}$	$1.095\ 05 \times 10^{-4}$	$1.366\ 28 \times 10^{-4}$
C_{20}	$4.844\ 51 \times 10^{-2}$	$5.484\ 67 \times 10^{-2}$	$5.826\ 48 \times 10^{-2}$
C_{03}
C_{12}
C_{21}
C_{30}
C_{04}
C_{13}
C_{22}
C_{31}
C_{40}
C_{05}
C_{14}
C_{23}
C_{32}
C_{41}
C_{50}

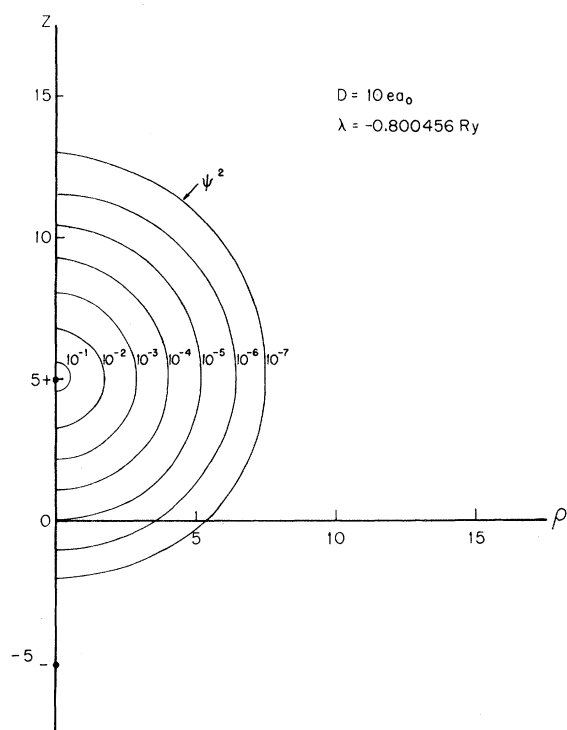


FIG. 2. Probability-density contours for $D = 10 ea_0$. The dipole has charges $\pm e$. Distances are in units of a_0 .

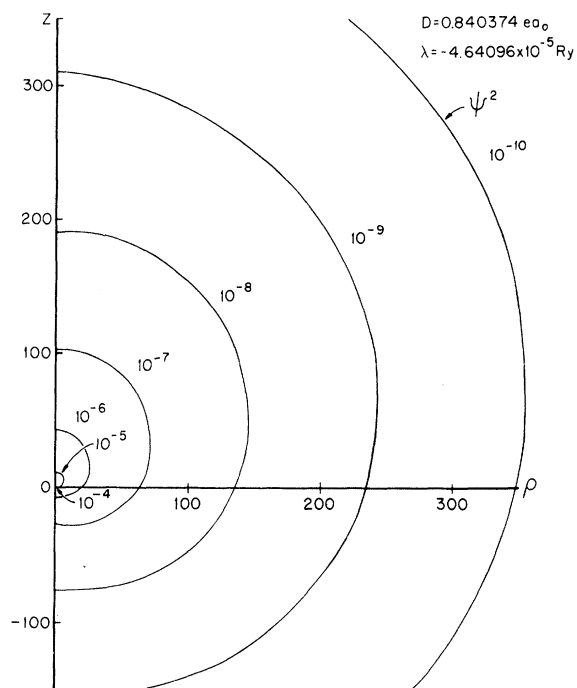


FIG. 4. Probability-density contours for $D = 0.840374 ea_0$. The dipole has charges $\pm e$. Distances are in units of a_0 .

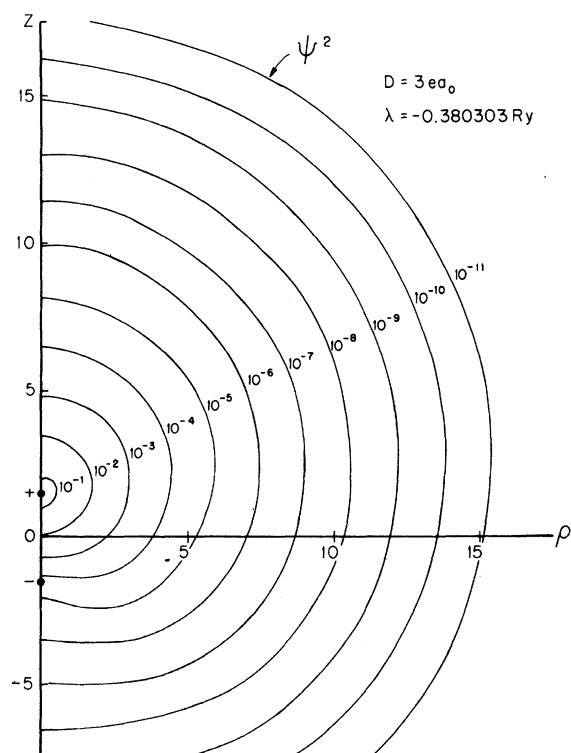


FIG. 3. Probability-density contours for $D = 3 ea_0$. The dipole has charges $\pm e$. Distances are in units of a_0 .

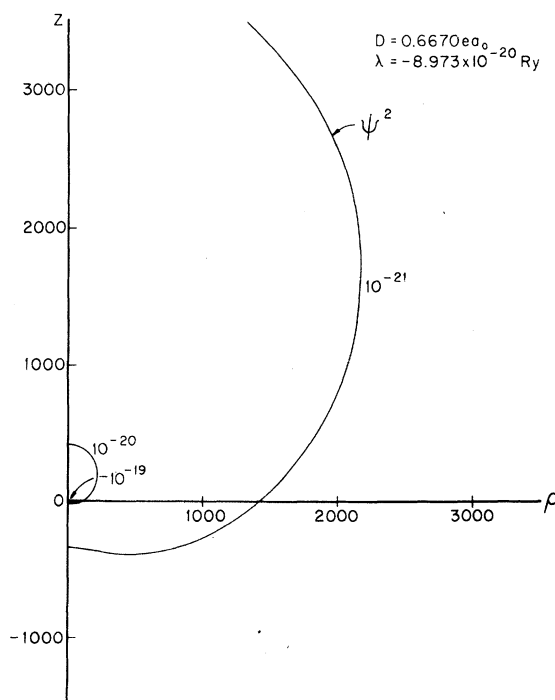


FIG. 5. Probability-density contours for $D = 0.6670 ea_0$. The dipole has charges $\pm e$. Distances are in units of a_0 .

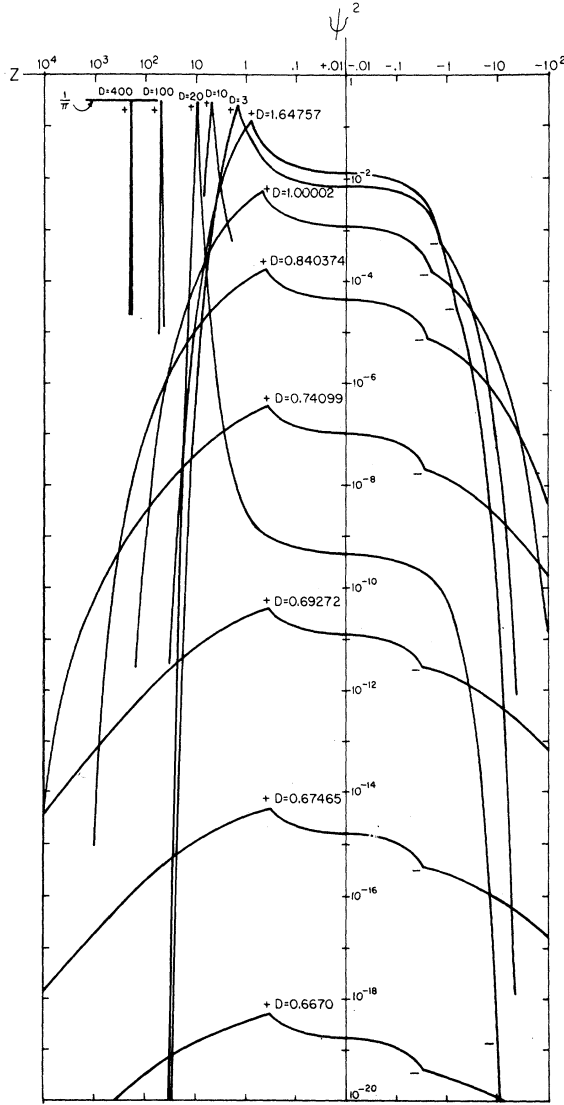


FIG. 6. Profiles of probability density along the dipole axis for a number of values of dipole moment.

limits³³ as D becomes large. Figure 7 shows how the mean distance of the electron from the positive dipole charge ($q=e$) varies with dipole moment. When $D \sim 2$, the quantity $\langle r_1 \rangle$ is within a factor of 2 of its value $\frac{3}{2}$ for the isolated hydrogen atom. As we have already seen, between $D=2$ and $D=1$ the charge distribution changes dramatically and becomes extremely strongly dependent on D , as evidenced by the steep slope of the curve in Fig. 7.

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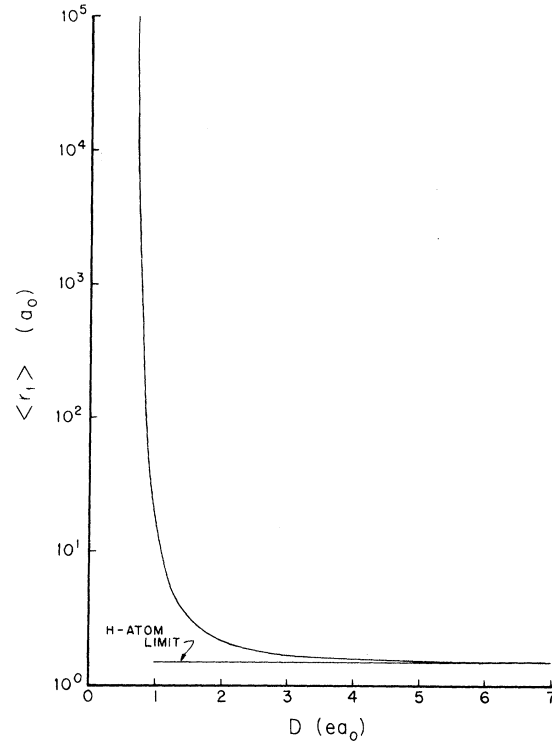


FIG. 7. Mean distance $\langle r_1 \rangle$ of the electron from the positive dipole charge ($q=e$) as a function of dipole moment D . (Atomic units).

TABLE V. Mean values of powers of r_1 and r_2 (see Fig. 1) in atomic units.

$D (ea_0)$	$\langle 1/r_1 \rangle$	$\langle 1/r_2 \rangle$	$\langle r_1 \rangle$	$\langle r_2 \rangle$	$\langle r_1^2 \rangle$	$\langle r_2^2 \rangle$
0.667 0	$1.988 44 \times 10^{-9}$	$1.988 44 \times 10^{-9}$	$1.680 90 \times 10^9$	$1.680 90 \times 10^9$	$6.025 33 \times 10^{18}$	$6.025 33 \times 10^{18}$
0.675 65	$1.631 75 \times 10^{-7}$	$1.631 75 \times 10^{-7}$	$1.854 35 \times 10^7$	$1.854 35 \times 10^7$	$6.841 69 \times 10^{14}$	$6.841 69 \times 10^{14}$
0.692 72	$1.276 93 \times 10^{-5}$	$1.276 84 \times 10^{-5}$	$2.231 86 \times 10^5$	$2.231 86 \times 10^5$	$9.420 90 \times 10^{10}$	$9.420 91 \times 10^{10}$
0.723 65	$3.601 40 \times 10^{-4}$	$3.597 19 \times 10^{-4}$	$7.367 61 \times 10^3$	$7.367 89 \times 10^3$	$9.540 85 \times 10^7$	$9.541 27 \times 10^7$
0.740 99	$1.074 28 \times 10^{-3}$	$1.071 19 \times 10^{-3}$	$2.405 22 \times 10^3$	$2.405 52 \times 10^3$	$9.963 40 \times 10^6$	$9.964 83 \times 10^6$
0.764 49	$3.153 58 \times 10^{-3}$	$3.131 70 \times 10^{-3}$	$7.947 04 \times 10^2$	$7.950 17 \times 10^2$	$1.069 92 \times 10^6$	$1.070 41 \times 10^6$
0.797 368	$9.056 08 \times 10^{-3}$	$8.908 68 \times 10^{-3}$	$2.668 08 \times 10^2$	$2.671 43 \times 10^2$	$1.191 61 \times 10^5$	$1.193 40 \times 10^5$
0.840 374	$2.310 83 \times 10^{-2}$	$2.231 24 \times 10^{-2}$	$1.003 55 \times 10^2$	$1.007 20 \times 10^2$	$1.665 92 \times 10^4$	$1.673 27 \times 10^4$
0.902 195	$5.568 99 \times 10^{-2}$	$5.184 51 \times 10^{-2}$	$3.978 01 \times 10^1$	$4.018 95 \times 10^1$	$2.602 99 \times 10^3$	$2.635 73 \times 10^3$
1.000 02	$1.292 28 \times 10^{-1}$	$1.120 49 \times 10^{-1}$	$1.617 23 \times 10^1$	$1.665 27 \times 10^1$	$4.177 62 \times 10^2$	$4.335 51 \times 10^2$

TABLE V (continued)

D (ea_0)	$\langle 1/r_1 \rangle$	$\langle 1/r_2 \rangle$	$\langle r_1 \rangle$	$\langle r_2 \rangle$	$\langle r_1^2 \rangle$	$\langle r_2^2 \rangle$
1.188 00	$2.965\,08 \times 10^{-1}$	$2.219\,46 \times 10^{-1}$	6.546 33	7.165 79	$6.657\,05 \times 10^1$	$7.510\,94 \times 10^1$
1.647 57	$6.184\,81 \times 10^{-1}$	$3.405\,37 \times 10^{-1}$	2.821 10	3.786 65	$1.183\,49 \times 10^1$	$1.830\,59 \times 10^1$
2	$7.591\,62 \times 10^{-1}$	$3.485\,99 \times 10^{-1}$	2.191 31	3.428 82	6.963 32	$1.403\,46 \times 10^1$
3	$9.235\,67 \times 10^{-1}$	$2.918\,30 \times 10^{-1}$	1.689 37	3.740 03	3.960 64	$1.525\,78 \times 10^1$
4	$9.703\,78 \times 10^{-1}$	$2.347\,66 \times 10^{-1}$	1.572 29	4.492 26	3.360 59	$2.125\,98 \times 10^1$
5	$9.866\,74 \times 10^{-1}$	$1.932\,94 \times 10^{-1}$	1.532 66	5.362 38	3.162 92	$2.977\,72 \times 10^1$
6	$9.932\,76 \times 10^{-1}$	$1.633\,13 \times 10^{-1}$	1.516 58	6.283 01	3.083 02	$4.047\,87 \times 10^1$
7	$9.962\,85 \times 10^{-1}$	$1.410\,12 \times 10^{-1}$	1.509 22	7.230 14	3.046 53	$5.327\,06 \times 10^1$
8	$9.978\,00 \times 10^{-1}$	$1.239\,07 \times 10^{-1}$	1.505 44	8.192 78	3.028 17	$6.811\,53 \times 10^1$
9	$9.986\,19 \times 10^{-1}$	$1.104\,25 \times 10^{-1}$	1.503 42	9.165 15	3.017 82	$8.499\,32 \times 10^1$
10	$9.990\,92 \times 10^{-1}$	$9.954\,88 \times 10^{-2}$	1.502 25	$1.014\,41 \times 10^1$	3.011 80	$1.038\,95 \times 10^2$
15	$9.998\,21 \times 10^{-1}$	$6.657\,73 \times 10^{-2}$	1.500 44	$1.508\,65 \times 10^1$	3.002 40	$2.285\,99 \times 10^2$
20	$9.999\,43 \times 10^{-1}$	$4.997\,18 \times 10^{-2}$	1.500 14	$2.006\,12 \times 10^1$	3.000 78	$4.034\,50 \times 10^2$
25	$9.999\,79 \times 10^{-1}$	$3.998\,96 \times 10^{-2}$	1.499 89	$2.504\,65 \times 10^1$	2.999 25	$6.283\,25 \times 10^2$
30	$9.999\,90 \times 10^{-1}$	$3.332\,83 \times 10^{-2}$	1.499 92	$3.003\,78 \times 10^1$	2.999 49	$9.032\,70 \times 10^2$
40	$9.999\,97 \times 10^{-1}$	$2.499\,84 \times 10^{-2}$	1.499 98	$4.002\,75 \times 10^1$	2.999 88	$1.603\,20 \times 10^3$
50	1.000 00	$2.000\,00 \times 10^{-2}$	1.500 00	$5.002\,00 \times 10^1$	3.000 00	$2.503\,00 \times 10^3$
100	1.000 00	$1.000\,00 \times 10^{-2}$	1.500 00	$1.000\,10 \times 10^2$	3.000 00	$1.000\,30 \times 10^4$

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Magnetic Parameters for the Configuration f^3 [†]

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The energy-level schemes of several atomic configurations f^3 are analyzed in terms of effective operators. These include all possible Hermitian two-electron scalar operators and six three-body spin-independent scalar operators. This collection of operators allows for spin-spin and spin-other-orbit interactions as well as for the most important effects of configuration interaction. Several alterations and extensions are suggested for the terms of Pr III $4f^3$. The positions of the free-ion levels of Nd IV $4f^3$ and Er IV $4f^{11}$ are inferred from the crystal spectra of Nd³⁺ in LaCl₃, and analyses with restricted sets of operators are carried out.

I. INTRODUCTION

It is often useful to introduce effective operators in the analysis of the energy-level systems of electronic configurations for free atoms and ions. This method avoids the construction of accurate eigenfunctions. Instead, the eigenfunctions of a particular configuration under study are assumed pure, and the responsibility for getting a good fit with experiment rests with the choice of an effective Hamiltonian. It is convenient to express this as a sum of coupled tensors, for then a wide variety of effects can be taken into account by comparatively few operators. The coefficients of these operators can be treated as parameters, through which the experimental data can be represented in a more concise and significant form. This approach works best for configurations that are comparatively isolated from their neighbors.

Considerable work has been carried out by Shadmí¹ on the configurations $(d+s)^N$. Our own interest in the spectra of the doubly and triply ionized rare earths has led us to investigate the configurations f^N . These are more appealing from a theoretical standpoint, because there are many more levels to be fitted. The only difficulty is in finding experimental data that have been analyzed extensively enough. Preliminary analyses for several configurations of the type f^N have been reported recently.² Although only partial-term schemes are known in some cases, it was found to be highly desirable to introduce an operator that would represent magnetic interactions between the f electrons. The success of this approach has encouraged us to attempt an analysis of several $4f^3$ species in which the number of experimentally determined levels makes it feasible to go beyond the conventional analysis and include operators

that represent not only the direct magnetic interactions but also certain kinds of configuration interaction. We shall pay particular attention to the Pr III free-ion levels of Sugar.³

II. EFFECTIVE OPERATORS

A straightforward first-order analysis of the levels of a configuration f^N involves the Slater parameters F^k (where $k=0, 2, 4$, and 6) and the spin-orbit coupling constant ζ . To allow for two-electron excitations (as well as certain electrostatic shielding effects and the magnetic orbit-orbit interaction), the three parameters α , β , and γ are required. Rajnak and Wybourne^{4,5} introduced certain scalar three-electron operators to take into account single-electron excitations; it was shown later⁶ that a complete parametrization is possible with just six parameters T^k . The inclusion of magnetic spin-spin and spin-other-orbit interactions introduces three parameters M^k (where $k=0, 2$, and 4). Rather than treat these interactions as they stand, it is highly advantageous to decompose them into parts that have irreducible representations of certain continuous Lie groups as their labels. Four operators z_i ($1 \leq i \leq 4$) are required for the spin-spin interaction,⁷ and ten ($5 \leq i \leq 14$) for the spin-other-orbit interaction.² Of the latter, z_{13} has matrix elements proportional to the ordinary spin-orbit interaction, and a linear relationship exists that allows us to replace z_{12} and z_{14} by a combined operator z_c , where, for the states of f^2 , the equivalence

$$z_c \equiv (13/3)z_{12} - 40z_{13} + (4/3)z_{14}$$

is valid. In addition to satisfying many selection rules, the operators z_i are effective operators