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Résumé. — Les corrections aux intégrales de Slater calculées par la méthode Hartree-Fock, dues aux interactions de configuration électrostatiques, ont été calculées pour la configuration 4 f^2 du Pr IV, en utilisant la théorie des perturbations et des méthodes graphiques. Le paramètre α de Trees, ainsi que les paramètres β et γ ont été calculés également. Au second ordre, les interactions avec 27 configurations liées et 8 excitations monoélectroniques vers le continuum donnent $\alpha = -4{,}24$, $\beta = 103{,}85$, $\gamma = -200{,}30$ Ceci est à comparer avec les valeurs empiriques : $F^2 = 72\,549$, $F^4 = 53\,874$, $F^6 = 35\,973$, $\alpha = 24$, $\beta = -586$ et $\gamma = 728$.

Abstract. — Corrections to the Hartree-Fock Slater integrals due to electrostatic configuration interaction are calculated for the 4 f^2 configuration of Pr IV using perturbation theory and graphical methods. The Trees parameter α and the additional parameters β and γ are also calculated. To second order the interaction with 27 bound configurations and 8 single particle excitations to the continuum give $F^2 = 88\,963{,}14$, $F^4 = 61\,000{,}08$, $F^6 = 33\,353{,}80$. This may be compared with empirical values $F^2 = 72\,549$, $F^4 = 53\,874$, $F^6 = 35\,973$, $\alpha = 24$, $\beta = -586$, $\gamma = 728$.

I. **Introduction.** — There are a number of atomic systems, for which the ground configuration is well separated from the next higher lying configuration of the same parity. Examples of well separated ground configurations are provided by the f^N configurations of the triply ionized rare earth and actinide series and to a lesser extent by the doubly ionized members of the iron group.

The perturbing effects of configurations which are sufficiently far removed from the configuration of interest may be included by adding effective operators to the ordinary first order Hamiltonian. Two-body effective operators of this kind were introduced by Trees [1] and by Rajnak and Wybourne [2]. Three-body scalar operators were introduced by Rajnak [3] and by Judd [4] ; and, more recently two-body magnetic operators [5] have been used. However, apart from two papers by Trees [6], and Trees and Jørgensen [7] on the effect of configuration interaction in the spectra of the iron group, few attempts have been made to calculate the values of these parameters.

The purpose of this paper is to present results, which we have obtained in a calculation of the two-body scalar operators for Pr^{3+}. The configuration 4 f^2 of Praeseodymium was chosen partly because the matrix elements of three-body operators vanish for a two electron configuration of this kind, and because all of the experimental levels of 4 f^2 have been identified.

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The ordinary Coulomb interaction within a configuration $(nl)^N$ can be expanded in terms of products of single electron tensor operators

$$H_{\text{Coul}} = \sum_{k \text{ even}} \sum_{i>j} F^k(l, l) \left(l \parallel C^{(k)} \parallel l\right)^2 \mathbf{u}_i^{(k)} . \mathbf{u}_j^{(k)} .$$

One effect of configuration interaction is to reduce the values of the Slater integrals below their Hartree-Fock values. Configuration interaction also gives rise to scalar products $\mathbf{u}_i^{(k)} . \mathbf{u}_j^{(k)}$ for which k is odd. It is customary to take linear combinations of these operators, which correspond to the Casimir operators of the continuous groups R_3, G_2, and R_7. The additional parameters which are associated with these effective operators are called α, β, and γ respectively.

II. **Choice of potential.** — In order to carry out a perturbative calculation it is necessary to define a potential, and to generate a complete set of single particle states in that potential.

The Hartree-Fock equation for an electron with principal quantum numbers nl can be cast into the form of an equation for a particle moving in a central potential [8]

$$u_{nl}(r) = -\frac{1}{r}\left(Z - Y(r) - X(r)\, P_{nl}^{-1}(r)\right),$$

where $Y(r)$ and $X(r)$ are the direct and exchange terms (in atomic units). The appearance of the wave function P_{nl} in the potential makes it clear that the potential will be different for each orbital in the atom. It possible is to approximate the exchange term [9, 10, 11] and the direct term and to obtain a single potential for the

entire atom. We have chosen instead to take as our potential for Pr^{3+}, the potential which the 4 f electron sees. This is analogous to the potential which Kelly used in his oxygen calculation [12]. It has a number of advantages. The HF 4 f wave function is reproduced exactly in this potential, and the very near cancellation which occurs between the potential graphs and certain of the Coulomb graphs is particularly easy to calculate.

The matrix elements of this potential are given by the equations [13]

$$(n'\,l' \mid u_{nl} \mid nl) = (N-1)\left\{ R^0(n'\,l'\,nl,\,nl\,nl) - \frac{1}{2(2l+1)^2}\sum_{k>0}(l \parallel C^{(k)} \parallel l)^2\, R^k(n'\,l'\,nl,\,nl\,nl)\right\} +$$

$$+ \sum_{n''l''\neq nl} N''\left\{ R^0(n'\,l'\,n''\,l'',\,nln''\,l'') - \frac{1}{2(2l+1)(2l''+1)}\sum_k (l \parallel C^{(k)} \parallel l'')^2\, R^k(n'\,l'\,n''\,l'',\,n''\,l''\,nl)\right\} \quad (1)$$

$$(n'\,l' \mid u_{nl} \mid n'\,l') = (N-1)\left\{ F^0(nl,\,n'\,l') - \frac{1}{2(2l+1)^2}\sum_{k>0}(l \parallel C^{(k)} \parallel l)^2\, F^k(nl,\,n'\,l')\right\} +$$

$$+ \sum_{n''l''\neq nl} N''\left\{ F^0(n'\,l',\,n''\,l'') - \frac{1}{2(2l+1)(2l''+1)}\sum_k (l \parallel C^{(k)} \parallel l'')^2 \times \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{r_<^k}{r_>^{k+1}} P_{nl}(1)\, P_{n''l''}(1)\,[P_{n'l'}(2)]^2 \frac{P_{n''l''}(2)}{P_{nl}(2)}\right\}. \quad (2)$$

The functions $P_{n'l'}$ are generated in the single particle potential ; however, since the potential itself is generated in a Hartree-Fock run for $(nl)^N$, the functions $P_{n''l''}$ are Hartree-Fock functions. The contribution to the matrix element $(n'\,l' \mid u_{nl} \mid nl)$ from a particular closed shell $n''\,l'' \neq nl$ is just [14]

$$\sum_{m''} \frac{N''}{4l''+2}\left[< n'\,l'\,n''\,l''\,m'' \mid 1/r_{12} \mid n''\,l''\,m''\,nl > - < n'\,l'\,n''\,l''\,m'' \mid 1/r_{12} \mid n''\,l''\,m''\,nl >\right]. \quad (3)$$

In dealing with a perturbation $H_{\text{Coul}} - u(r)$, this formula is useful to see what cancellations will occur between the potential graphs and the Coulomb graphs ; however, since the functions $P_{n''l''}$ in the matrix éléments of the potential are HF functions cancellations of this kind are never exact.

III. Perturbation theory and effective operators. — The perturbing effects of a higher lying configuration upon the ground configuration may be taken into account by adding to the first order Hamiltonian the effective operator

$$H_{\text{eff}} = -\frac{1}{\Delta E} V^{\downarrow} V^{\uparrow} + \frac{1}{\Delta E^2} V^{\downarrow} V^{+} V^{\uparrow} - \frac{1}{\Delta E^2} V^{\downarrow} V^{\downarrow} V^{-} + \cdots,$$

where ΔE is the energy separation of the two configurations. $V^{\uparrow}$ is that part of the perturbation which joins the ground configuration to the excited configuration, V^{+} operates within the excited configuration $V^{\downarrow}$ joins the excited configurations to the ground configuration and V^{-} operates within the ground configuration.

The noncentral part of the Coulomb interaction

$$V = H_{\text{Coul}} - u(r)$$

is the largest of the terms in the perturbative Hamiltonian, and is mainly responsible for distorting the configurations. In second quantized form

$$V = \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta} a_\alpha^\dagger\, a_\beta^\dagger < \alpha_1\,\beta_2 \mid 1/r_{12} \mid \gamma_1\,\delta_2 > a_\delta\, a_\gamma - \sum_{\alpha,\beta} a_\alpha^\dagger < \alpha \mid u \mid \beta > a_\beta .$$

The angular part of the Coulomb interaction may be written in terms of the angular momentum graphs of Jucys [15],

$$< \alpha_1\,\beta_2 \mid 1/r_{12} \mid \gamma_1\,\delta_2 > = (-)^{l_\alpha - m_l^\alpha}(-)^{l_\beta - m_l^\beta} \times \delta(m_s^\alpha, m_s^\gamma)\,\delta(m_s^\beta, m_s^\delta)\sum_k [(-)^k (l_\alpha \parallel C^{(k)} \parallel l_\gamma) \times (l_\beta \parallel C^{(k)} \parallel l_\delta)\, R^{(k)}(l_\alpha\, l_\beta,\, l_\gamma\, l_\delta)]\, G ,$$

where G is the angular momentum graph given in figure (1*a*). The creation and annihilation operator part of the Coulomb interaction is represented by the Feynman graph given in figure (1*b*).

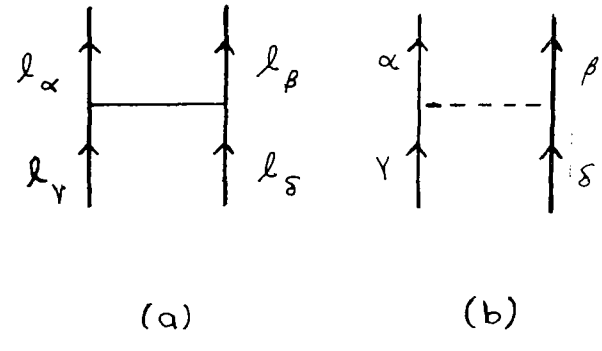

FIG. 1. — Graphs of the Coulomb interaction. (a) angular momentum graph of Jucys. (b) Faynman graph.

The calculation of a particular effect begins typically with two or three graphs of this kind. When two lines are joined together, the phase factor $(-)^{l-m_l}$ ensures that the resulting graph is a standard Jucys graph.

IV. **Second order calculations.** — The five graphs which occur to second order are shown in figure 2.

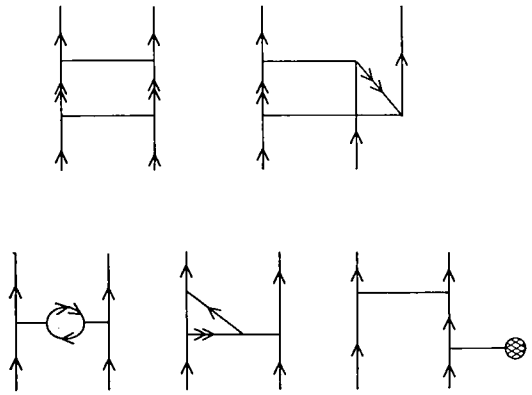

FIG. 2. — Second order graphs.

The first graph corresponds to the excitation of one or two electrons from the f-shell or of two electrons from the core into the f-shell. The second, third, and fourth graphs correspond to the excitation of a single electron from the core. The three graphs in the second row each have a removeable portion and a Coulomb line. These graphs modify the values of the Slater integrals, but they do not contribute to α, β, or γ.

The leading contributions from the first two graphs are given in Table I. The most important process is the one in which two electrons are excited from the 4 d shell into the 4 f. Several of the other core excitations are large. Although configurations for which one or two particles are excited from the f-shell lie close to 4 f^2 in energy, they have a relatively small effect. The very large change in the Slater integrals given in Table I for the excitation 4 f → 5 f is nearly cancelled by the potential graph.

The total contribution to α, β, γ and the F^k, from 27 bound configurations is given in Table I. The total F^k values include contributions from all 5 graphs. Comparison with the empirical values at the bottom of Table III indicates that

TABLE I

Second order contributions to α, β, γ, F^2, F^4 and F^6

Excited Configuration	α	β	γ	F^2	F^4	F^6
$4s^0\,4f^4$	—	—	87.59	− 93.84	− 247.74	− 279.12
$4s\,4d^9\,4f^4$	2.74	− 65.70	− 54.73	− 111.42	464.45	− 436.06
$4d^8\,4f^4$	52.39	− 760.76	1 508.37	− 3 550.46	− 5 563.17	− 5 110.61
$5s^0\,4f^4$	—	—	93.11	− 99.76	− 263.36	− 296.72
$4p^4\,4f^4$	3.79	− 145.89	426.67	− 658.53	− 777.75	− 1 404.31
$5p^4\,4f^4$	4.45	− 160.96	540.05	− 821.14	− 1 024.31	− 1 921.41
$4p^5\,4f^3$	13.18	23.61	− 685.60	− 841.66	1 317.41	1 206.43
$5p^5\,4f^3$	5.11	68.21	− 310.61	− 389.50	620.41	402.41
$5p^4\,4f^2\,6p$	0.53	− 18.41	68.60	103.12	133.58	255.68
$5d^2$	6.14	− 93.57	211.03	− 385.28	− 786.68	− 773.09
4f 5f	− 0.39	− 32.05	190.12	− 5 018.44	− 3 644.68	− 2 840.91
Total 2nd Order from 27 Bound Configurations	87.67	− 1 189.53	2 070.42	− 6 963.23	− 2 741.85	− 8 952.30

TABLE II

Excitations of one particle to the Continuum

	α	β	γ	F^2	F^4	F^6
4f → *k*p	.37	− .88	− 18.13	21.83	− 33.54	− 35.88
*k*f	− 1.02	− 76.52	488.12	− 1 508.38	− 1 645.65	− 1 625.29
*k*h	− 3.96	94.01	− 306.82	− 89.34	− 247.25	− 446.77
4p → *k*f	1.71	− 9.97	− 78.81	− 253.71	563.57	− 172.29
*k*h	− 7.96	150.30	− 255.07	− 537.50	973.08	1 013.23
4d → *k*g	− 76.98	1 087.98	− 1 883.10	− 5 694.77	− 2 449.71	− 4 540.16
5p → *k*f	2.31	− 22.39	− 98.83	− 1 311.46	790.20	− 243.01
*k*h	− 2.00	38.80	− 68.24	− 133.77	283.65	333.24
Total	− 87.53	1 261.33	− 2 220.88	− 8 164.56	− 1 765.65	− 4 886.33

TABLE III

Summary of Results

	α	β	γ	F^2	F^4	F^6
Hartree Fock				104 089.93	65 507.58	47 192.43
2nd Ord. Bound States	87.67	− 1 189.53	2 070.42	− 6 962.23	− 2 741.85	− 8 952.30
Modified 2nd Ord. Cont'm.	− 87.53	1 261.33	− 2 220.88	− 8 164.56	− 1 765.65	− 4 886.33
Orbit-Orbit	− 4.38	32.05	− 49.84			
Total Calc.	4.24	103.85	200.30	88 963.14	61 000.08	33 353.80
Exp.	24	− 586	728	72 549	53 874	35 973

so the values obtained from a second order treatment of the bound states are far from the empirical values.

V. **Excitations to the continuum.** — The next general class of processes which we have considered are the single particle excitations from the l shell into the continuum. The second order graphs which describe this process are, of course, the same as for the bound states. The leading third order graphs are shown in figure 3. In the first graph, for instance, one electron is excited into a higher lying orbital by means of the Coulomb interaction. The excited l' electron and the l electron interact with the scalar part of the direct

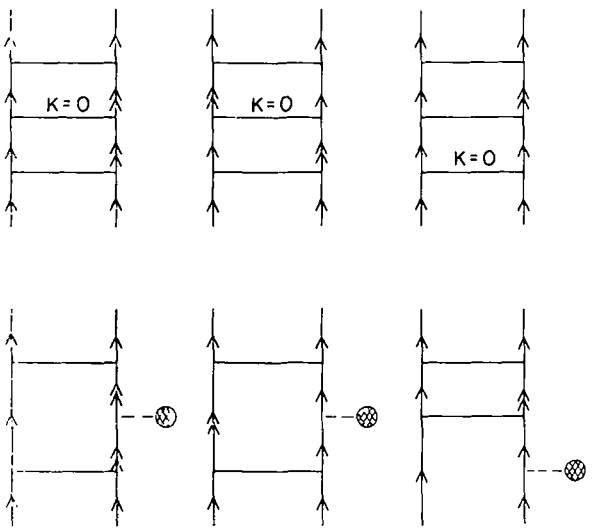

FIG. 3. — Leading third order graphs.

interaction, and the outer electron returns to the l shell. A $k = 0$ bar and an external line can be removed from a graph of this kind. What remains in each case is an ordinary second order graph.

So the leading third order terms are proportional to the second order term. The proportionality constant is $-C/\Delta E$, where

$$C = < nl \mid u \mid nl > - < n'l' \mid u \mid n'l' > + \\ + F^0(nl, n'l') - G^0(nl, nl') - F^0(nl, nl) . \quad (3)$$

Using Equations (1) and (2) for the matrix elements of the potential,

$$C = -\frac{1}{2(2l+1)^2} \sum_{k>0} (l \| C^{(k)} \| l)^2 F^k(nl, nl) - \\ - \left[G^0(nl, nl') - \frac{1}{2(2l+1)^2} \right. \\ \left. \times \sum_{k>0} (l \| C^{(k)} \| l')^2 F^k(nl, nl') \right] . \quad (4)$$

These graphs in which the ordinary second order graph is modified by $k = 0$ bars and by external potential lines may be summed to give the second order term with the denominator ΔE replaced by $\Delta E + C$.

The contributions from eight single particle excitations to the continuum are given in Table II. The entries corresponding to excitations from the f shell have been modified to include higher order effects. The most striking feature of these contributions is the importance of continuum states for which $l > 3$. The largest contribution is due to the excitation 4 d $\rightarrow$ kg. The excitations 4 f $\rightarrow$ kh and 4 p $\rightarrow$ kh. are also important.

The p, f, and h continuum functions which overlap the 4 f function the most are shown in figure 4. The f continuum function which contributes the most has a wave number $k = .6$. In the free region this corresponds to a wave length $\lambda = 10.5$. Near the nucleus the continuum f function is pulled in a great deal ; however, as it moves out its wavelength increases to its value in the free region. For wave numbers less than .6 the position of the first maximum remains stationary, but decreases gradually in magnitude as the wave number approaches zero. The first maximum of the continuum f function occurs inside the maximum of the 4 f for all values of the energy.

The centrifugal potential of the p function is much less than for the f. So the first maximum of the p function occurs far inside the maximum of the 4 f and the integral R^k(4 f 4 f, 4 fkp) is very small. The h function, however, has a much larger centrifugal

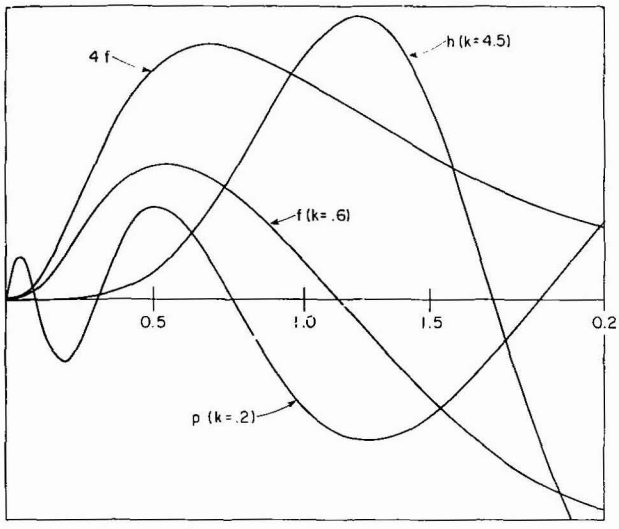

FIG. 4. — p, f and h continuum functions with maximum overlap with 4 f function.

potential than the f function. For $k = .6$ its first maximum occurs far outside the maximum of the 4 f. As the wave number of the h function increases its first maximum comes in until it overlaps the 4 f function very favorably. Another general feature of the p, f, and h continuum function concerns the relation between their energy and their amplitude inside the atom. The p and f functions correspond to electrons which have a very small energy eigenvalue and hence very little kinetic energy in the free region. So they spend much of their time outside the atom, and their amplitude inside the atom is small. The h function which overlaps the 4 f function the most is more energetic, and its amplitude inside the atom is comparable to the amplitude of the 4 f function.

The importance of excitations to continuum states with large angular momenta is easy to understand in physical terms.

VI. **Concluding remarks.** — There are several very important processes which remain to be calculated ; however, the results which we have obtained thus far are summarized in Table III. The Hartree-Fock Hamiltonian does not contain any scalar products of odd rank, and the HF values of the Slater integrals are much too large. The values of α, β, γ, and the Slater integrals we have obtained are still far from the empirical values. The correction to F^2 is too small by about a factor of 2.

The discrepancies between calculated and empirical values are probably due mainly to the remaining single particle excitations to the continuum, two particle excitations to the continuum, and third order contributions from those configurations for which one or two particles are excited into the f shell. This work is in progress.

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