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Many-Body Calculations for the Heavy Atoms*

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Corrections to the Hartree-Fock (HF) theory which arise as a result of electrostatic configuration interaction are calculated for a heavy ion Pr^{3+}. The effect of configuration interaction upon the $4f^2$ configuration is represented by effective two-body operators of the form $\sum_k a_k C_1^{(k)} C_2^{(k)}$. These operators are evaluated using perturbation theory and graphical methods. The effect of the operators of even rank is to depress the values of the Slater F^k integrals below their HF values. The two-body operators of odd rank do not appear within the ordinary HF theory. The Trees parameter α is the coefficient of an operator of this kind. It is found that the corrections to the Slater integrals converge slowly. The contributions to the operators of odd rank converge properly, however, and we obtain the values $\alpha = 28$, $\beta = -616$, and $\gamma = 1611$. This may be compared with the empirical values $\alpha = 24$, $\beta = -586$, and $\gamma = 728$. The value of γ is determined empirically by the position of a single level, ^1S. It is suggested that the free-ion ^1S level has not been properly identified.

I. INTRODUCTION

The most accurate first-principles calculations of the properties of rare-earth ions have been carried out within the framework of the Hartree-Fock (HF) or self-consistent-field method. Extensive HF calculations have been reported by Freeman and Watson,[1] Froese Fischer,[2] Mann,[3] Clementi and Raimondi,[4] and others. More recently a number of relativistic Hartree-Fock (RHF) calculations have been reported.[5–10]

The optical and magnetic properties of the heavy elements are due mainly to the outer electrons, which are usually quite nonrelativistic. The fact that the RHF calculations of interaction constants of the outer electrons are often significantly more accurate than the nonrelativistic HF calculations may be attributed to differences in the relativistic and nonrelativistic Hamiltonians. For instance, the spin-orbit interaction is contained implicitly in the Dirac Hamiltonian which is used in relativistic self-consistent-field calculations, while it is added as a first-order perturbation to the nonrelativistic HF calculations. This is probably the reason that relativistic calculations of the spin-orbit constant of $5f$ electrons[10] are often considerably more accurate than nonrelativistic calculations. On the other hand, the effects of electrostatic configuration interaction are not included in HF or RHF calculations, and may be expected to give rise to the same kind of discrepancies in both cases. Figure 1 shows the energy levels of Pr^{3+}, which has two $4f$ electrons moving outside a xenon core. There is an obvious correlation between the HF and the experimental levels. However, the energy scale is different in the two cases, and there are a number of crossovers. If instead of using HF values of the integrals we regard them as parameters, we may fit the experimental levels. Table I shows the HF and the empirical values of the Slater integrals. The fact that the HF integrals are much larger than the empirical values corresponds to the fact that the HF energy-level scheme is expanded with respect to what is actually found experimentally. The fit is improved considerably by adding to the Hamiltonian effective operators of odd rank.[11] The qualitative features of these discrepancies may be understood in terms of configuration interaction. The HF calculation assumes that the ground configuration is a pure $4f^2$ configuration, but the $4f$ electrons spend part of their time in higher-lying configurations where they move in large orbits and interact less

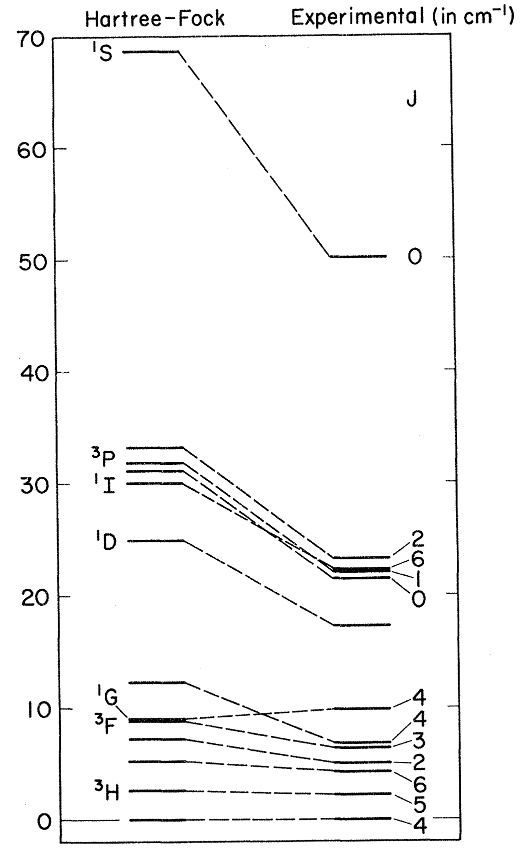

FIG. 1. Comparison of the energy levels of the $4f^2$ configuration of Pr^{3+} calculated with a HF $4f$ radial function and the experimental energy levels.

strongly. So the real integrals, so to speak, are smaller than the HF integrals.

For a heavy atom such as a rare earth, it is clearly not possible to calculate the effect of configuration interaction upon quantities such as the ground-state or correlation energy, which are properties of the atom as a whole. In order to calculate a correlation energy one would, in principle, have to consider correlations between all possible pairs of electrons. It is only possible to calculate the effect of configuration interaction upon the relative structure of the lower levels. Effective operators which represent the effect of configuration interaction upon the structure of the ground configuration have been introduced by a number of authors,[11–14] and they have been added to empirical fits of energy levels. However, few attempts have been made to calculate the values of these parameters.[15,16]

The purpose of this paper is to give the results of a calculation of the two-body scalar operators for Pr^{3+}. Some of the preliminary results of this calculation have already been presented.[17]

In a future paper the effect of Coulomb excitations will be represented by one- and two-particle perturbed functions in a way which is analogous to Sternheimer's[18] treatment of the quadrupole problem.

II. PERTURBATION THEORY AND EFFECTIVE OPERATORS

Using the Rayleigh-Schrödinger form of perturbation theory, the effect of a higher-lying configuration may be taken into account by adding to the first-order Hamiltonian the effective operator

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

where ΔE is the energy separation of the two configurations, $V^{\uparrow}$ is that part of the perturbation which joins the ground-state configuration to the excited-state configuration, $V^{\downarrow}$ joins the excited-state configuration to the ground-state configuration, and V^{+} operates within the excited-state configuration and V^{-} within the ground-state 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 mixing the configurations. In our calculation we used as the central potential the HF potential seen by the $4f$ electron.[17,19] In this potential we generated all of the single-particle functions (including the continuum functions), and so this is the potential, of course, which we should use in the perturbation. The angular part of the Coulomb interaction may be written in terms of the angular momentum graphs of Jucys[20]:

$$\begin{aligned}\langle \alpha_1\beta_2 | 1/r_{12} | \gamma_1\delta_2\rangle &= (-1)^{l_\alpha - m_l^\alpha}\ (-1)^{l_\beta - m_l^\beta} \\ &\quad\times \delta(m_s^\alpha, m_s^\gamma)\ \delta(m_s^\beta, m_s^\delta) \textstyle\sum_k [(-1)^k (l_\alpha \| C^{(k)} \| l_\gamma) \\ &\quad\times (l_\beta \| C^{(k)} \| l_\delta)\ R^k(l_\alpha l_\beta l_\gamma l_\delta)] G,\end{aligned} \tag{2}$$

where G is the angular momentum graph given in Fig. 2(a). The creation- and annihilation-operator part of the Coulomb interaction is represented by the Feynman graph given in Fig. 2(b). This graph shows what the initial and final states are, and how they are joined together in the interaction.

The calculation of a particular effect begins typi-

TABLE I. Comparison of Hartree-Fock and experimental parameters (in cm⁻¹).

	α	β	γ	F^2	F^4	F^6
Hartree-Fock	···	···	···	104 089	65 507	47 192
Experimental	24	−586	728	72 549	53 874	35 973

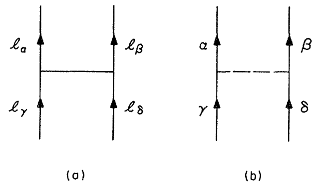

FIG. 2. Graphs of the Coulomb interaction: (a) angular momentum graph of Jucys; (b) Feynman graph.

cally with two or three graphs of this kind, and lines are joined together to form the final graph.[17]

III. SECOND-ORDER CALCULATIONS

The five graphs which occur to second order are shown in Fig. 3. 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. They may be attributed physically to the polarization of the core by the open-shell electrons.[21] This polarization then interacts back on the open-shell electrons to give an effective two-particle interaction. The contribution to the Slater integrals and to α, β, and γ from the bound-state configurations which interact most strongly with $4f^2$ are given in Table II. The most important single process is the one in which two electrons are excited from the $4d$ core into the $4f$ shell. Several other core excitations are large. The total contribution to α, β, γ, and the F^k integrals from 32 bound-state configurations is given at the bottom of Table II.

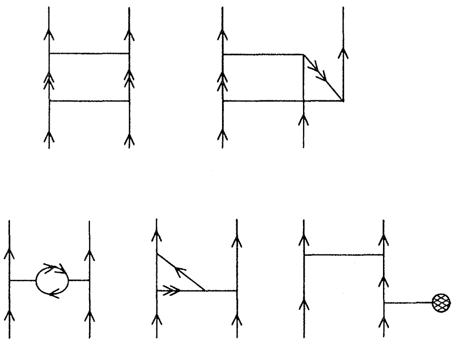

FIG. 3. Second-order graphs.

The next general class of processes which we have considered are those for which a single particle is excited from the ground-state configuration into the continuum (see Table III). The HF $4f$ potential which we used to generate our single-particle states was obtained by averaging the interaction of the two $4f$ electrons over all possible m_l states.[22] So Brillouin's theorem, which rules out single-particle excitations arising from the nonlocal Hartree-Fock residual interaction, does not apply. The most striking feature of these contributions is the importance of the continuum states for which $l > 3$.

TABLE II. Second-order contributions to α, β, γ, and F^k from the bound-state configurations (in cm^{-1}).

	α	β	γ	$F^2(f,f)$	$F^4(f,f)$	$F^6(f,f)$
$4s^0 4f^4$			87.586	−93.842	−247.742	−279.123
$4s4d^9 4f^4$	2.737	−65.679	−54.733	−111.420	464.447	−436.064
$4d^8 4f^4$	52.389	−760.760	1508.373	−3550.458	−5563.173	−5110.607
$5s^0 4f^4$			93.109	−99.760	−263.365	−296.725
$4p^4 4f^4$	3.793	−145.894	426.667	−658.532	−777.752	−1404.308
$5p^4 4f^4$	4.448	−160.964	540.047	−821.143	−1024.314	−1921.414
$3d^8 4f^4$	0.613	−8.406	16.227	−40.741	−59.696	−53.749
$3d^9 4d^9 4f^4$	1.421	−16.112	28.652	−89.553	−104.536	−86.251
$3p^4 4f^4$	0.098	−3.842	10.771	−16.704	−19.373	−34.455
$3p^5 4p^5 4f^4$	0.124	−5.173	12.511	−19.736	−21.363	−35.430
$4d^9 4f^2 5d$	0.168	3.612	−3.633	6.503	−13.717	−23.036
$4p^5 4f^3$	13.179	23.611	−685.602	−457.720	4195.703	1206.433
$5p^5 4f^3$	5.106	68.210	−310.612	−440.561	1647.940	402.413
$5p^5 4f^2 6p$	0.534	−18.411	68.569	57.343	133.582	255.678
$3p^5 4f^3$	0.338	2.756	−19.232	−21.449	108.850	28.538
$4f6p$	0.240	1.138	−13.014	16.106	−25.392	−21.138
$6p^2$	0.033	−1.098	4.445	−6.628	−8.829	−17.099
$5d^2$	5.135	−93.570	211.031	−385.283	−786.681	−773.089
$4f5f$	−0.388	−32.046	190.118	−272.963	−426.481	−460.346
$5f^2$	−0.007	−0.452	3.062	−50.753	−40.524	−33.106
$6d^2$	0.076	−1.523	3.732	−6.066	−13.979	−14.190
Total	90.38	−1223.26	2122.13	−7161.04	−2831.90	−9169.97

TABLE III. Contribution from excitations of one particle to the continuum (in cm^{-1}).

	α	β	γ	F^2	F^4	F^6
$4s\to ks$			1.433	1.536	4.055	4.568
d	0.049	−1.179	−0.982	−149.903	−8.335	7.826
g	0.950	−22.798	−52.245	−167.930	−796.009	45.408
i	−1.422	34.125	−44.688	119.700	34.474	−362.582
$4p\to kp$	0.070	−2.560	8.661	6.000	16.569	30.405
f	1.713	−9.965	−78.807	−253.708	563.568	172.291
h	−7.959	150.296	−255.068	537.500	973.076	1013.234
k	−0.778	18.674	−24.455	65.504	18.865	192.962
$4d\to ks$	0.034	−0.817	−0.681	−20.812	−5.778	5.425
d	0.157	−2.471	10.411	−71.667	−11.746	39.223
g	−76.978	1087.984	−1883.102	−5694.771	−2449.713	−4540.156
i	−1.597	21.731	−62.288	69.594	−878.404	−509.837
l	−0.431	10.346	−13.549	36.291	10.452	−282.472
$4f\to kp$	0.376	−0.951	−18.264	21.965	−33.705	−36.331
f	−0.983	−76.961	474.544	−1508.382	−1645.651	−1625.290
h	−3.960	93.221	−303.968	−85.594	−245.322	−430.937
k	−0.503	5.768	−25.212	−12.548	−102.412	−10.039
m	−0.224	5.382	−7.048	−18.878	−5.437	−0.079
$5s\to ks$			27.947	29.943	79.050	89.063
d	0.836	−20.061	−16.718	−2087.062	−141.860	133.191
g	0.406	−9.750	−22.343	−71.816	−550.230	19.419
i	−0.528	12.662	−16.582	44.415	12.791	−176.388
$5p\to kp$	0.801	−27.274	104.663	137.755	205.387	394.817
f	2.305	−22.389	−98.830	−1311.457	790.200	243.007
h	−1.998	38.795	−68.241	133.767	283.645	333.238
k	−0.229	5.507	−7.211	19.316	5.563	64.648
$3s\to ks$			1.070	1.147	3.028	3.411
d	0.033	−0.787	−0.656	−83.995	−5.562	5.222
g	0.061	−1.464	−3.356	−10.786	−57.726	2.916
i	−0.110	2.641	−3.459	9.265	2.668	−26.483
$3p\to kp$	0.034	−1.163	4.407	4.172	8.622	16.546
f	0.296	−0.468	−14.624	−137.299	102.340	28.289
h	−0.581	10.680	−17.676	39.323	61.888	66.154
k	−0.049	1.175	−1.539	4.121	1.187	11.604
$3d\to ks$	0.009	−0.206	−0.172	−10.500	−1.455	1.366
d	0.290	−5.545	12.801	−77.210	1.689	47.056
g	−3.778	48.836	−78.366	−339.219	−99.622	−179.588
i	−0.078	0.999	−2.828	3.447	−42.807	−23.156
Total	−93.77	1340.01	−2477.02	−10868.10	−3902.66	−5232.05

The largest single contribution comes from $4d\to kg$. The excitations $4p\to kh$ and $4f\to kh$ are also important. As we have already shown,[17] the importance of states with large angular momenta is easy to understand in physical terms if one considers the form of these continuum functions.

Table IV shows the contributions from two-particle excitations to the continuum. Again the g states are the most important. The excitation of two $4f$ electrons to continuum g states gives a contribution which is about one-half of the single-particle excitation $4d\to kg$. The factor of $\frac{1}{2}$ may be understood physically in terms of the exclusion principle. Because two g electrons are equivalent, only about half of the available states may actually be occupied.

The largest contribution from the excitations $4f\to kf$ come near the ionization limit,[17] so it is clear that we must sum the contributions coming from the bound nf series. For large r the radial function of an electron with quantum numbers nl can be written[23]

$$P_{nl}(r)=K(\nu_n,l)\,W_{\nu_n,l+1/2}\,(2Zr/\nu_n), \tag{3}$$

where W is a Whittaker function and ν_n is the effective principal quantum number. ν_n can be written

$$\nu_n=n-u,$$

TABLE IV. Contributions from excitations of two particles to the continuum (in cm^{-1}).

	α	β	γ	F^2	F^4	F^6
$4f^2 \rightarrow kpk'p$	0.599	−18.357	88.458	−129.545	−182.390	−357.623
f	1.597	−23.633	−61.501	64.873	−85.298	−179.790
h	−1.131	23.839	−47.992	−71.558	−116.596	−9.755
$4f^2 \rightarrow kdk\ d$	3.030	−68.477	201.096	−280.164	−754.813	−811.135
g	−4.261	91.797	−210.170	−348.311	−147.879	−199.223
i	−0.453	7.837	−25.186	−16.928	−90.195	−8.486
l	−0.228	5.462	−7.153	−19.159	−5.518	−0.080
$4f^2 \rightarrow kfk'f$	−0.707	−31.852	311.315	−3284.623	−3008.511	−2665.899
h	−0.475	20.292	−99.899	−65.477	−33.688	−174.265
k	−0.279	4.216	−18.640	−5.172	−76.637	−7.416
$4f^2 \rightarrow kgk'g$	37.604	−559.860	1163.329	−3094.880	−3165.335	−3142.346
i	0.154	18.598	−113.641	−28.778	−13.914	−222.368
l	−0.280	3.572	−20.152	−1.569	−88.924	−8.732
$4f^2 \rightarrow khk'h$	9.619	−212.696	540.980	−1128.022	−1406.812	−1511.302
k	0.284	2.999	−44.439	−15.182	12.341	−102.300
$4f^2 \rightarrow kik'i$	1.426	−37.651	115.015	−212.187	−306.146	−345.809
l	0.193	−0.240	−21.020	−9.175	11.787	−54.049
Total	46.69	−774.15	1750.40	−8645.86	−9458.53	−9800.58

where u is the quantum defect. For large n, $P_{nl}(r)$ assumes the form[24]

$$P_{nl}(r) = (\nu_n)^{-3/2} \left(\frac{2Z^3}{\pi^2}\right)^{1/4} (r)^{1/4} \times \cos[(8Zr)^{1/2} - \nu_n \pi + \pi/4]. \quad (4)$$

From Eq. (4) we obtain the sum rule[19]

$$C \int_{N_f+1}^{\infty} \nu_n^{-3}\, dn = C/2(N_f - u + 1)^2,$$

where N_f is the last n value calculated by discrete summation. We solved for the nf functions for $n = 6, 7, \ldots, 12$. u approaches the limiting value 1.112. The total contribution to α, β, and γ from the excitations $4f \rightarrow nf$ is $\alpha = -0.394$, $\beta = -31.466$, and $\gamma = +190.034$.

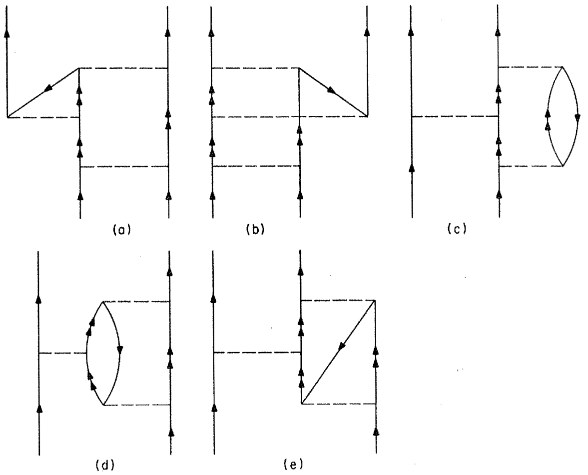

FIG. 4. Direct Feynman graphs which describe the third-order interaction of the configurations l^N and $l'^{4l'}\, l^{N+2}$.

IV. HIGHER-ORDER GRAPHS

In order to be confident that the perturbation series converges properly it is necessary to consider higher-order terms. In Fig. 4 are shown the direct Feynman graphs which describe the third-order interaction of the configurations l^N and $l'^{4l'}\, l^{N+2}$. Each graph describes a process in which two electrons are excited from the l' shell into the l shell, an l and l' electron interact within the configuration $l'^{4l'}\, l^{N+2}$ by means of the direct part of the Coulomb interaction, and two electrons return to the l' shell. Other graphs occur for which the electrons interact within the excited configuration by means of the exchange part of the Coulomb interaction and for which they interact entirely within the l or l' shell. The third-order contributions from the most important

TABLE V. Third-order contributions to α, β, γ, and F^k integrals (in cm^{-1}).

	α	β	γ	F^2	F^4	F^6
$4d^8 4f^4$	−6.27	7.33	−64.30	3251.72	3121.23	1025.72
$4p^4 4f^4$	0.03	−0.02	4.56	153.63	−0.67	−30.11
$5p^4 4f^4$	0.18	0.14	41.81	1451.05	−0.51	−116.61
$4p^5 4f^3$	−0.44	7.34	26.42			
$5p^5 4f^3$	−1.77	−7.61	119.05			
Total	−8.27	7.18	127.54	4856.40	3120.05	879.00

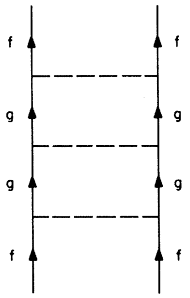

FIG. 5. Ladder diagram.

configuration of the type $l'^{4l'}\,l^{N+2}$ are given in Table V. The large contributions to the Slater integrals come from graphs such as Fig. 4(c), which consist of a removable 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 contributions to α, β, and γ indicate a satisfactory convergence of the perturbation theory. For instance, the third-order contribution to α from the configuration $4d^8 4f^4$ is about one-eighth of the second-order result. All other contributions are considerably smaller. However, the large third-order contributions to the F^k integrals raise serious doubts about their convergence properties. The third-order contribution to the integral F^2 from the configuration $4d^8 4f^4$ is nearly as large as the second-order contribution. In Table V the third-order contributions to α, β, and γ from two configurations for which a single electron is excited into the $4f$ shell are also shown.

The most important ladder diagram[19] is expected to be one in which two $4f$ electrons are excited into continuum g functions which in turn scatter from another pair of g states. This diagram is shown in Fig. 5. It is difficult to evaluate since it involves a fourfold integration over momentum space together with a single space integration. For this purpose, we used a rough grid in momentum space having 13 points and a Herman-Skillman[25] grid in position space with 60 points. The effect of this diagram was found to be very small. For instance, the contribution to α was -0.006. The contribution to α, β, and γ from the hole-particle diagrams is also expected to be small.

V. DISCUSSION

All of the contributions to α, β, and γ which we have obtained are summarized in Table VI. The second-order contribution from the bound states includes the effect of the excitations $4f \rightarrow nf$ discussed previously, and the contributions from single-particle excitations to the continuum include a family of higher-order diagrams which have been summed to all orders of the perturbation theory.[17] The HF $4f$ function was used to calculate the effect of the magnetic orbit-orbit interaction within $4f^2$.

The values of α and β which we have obtained agree quite well with values of these parameters obtained by fitting the experimental energy levels.[26,27] Our value of γ is far from the empirical free-ion value[27]; however, it is important to realize that the value of γ is determined empirically by the position of a single level, ^1S, which lies far above all of the other levels of $4f^2$ and is near the energy levels of other configurations. The ^1S level is observed in the absorption spectra of Pr^{3+} in the LaF_3 crystal,[28] and the value of γ which is obtained in the fit of the crystal data is 1411, which agrees very well with our result. The $4f$ wave function in Pr^{3+} is shielded from the crystal environment by the outer-lying $5s$ and $5p$ electrons, and so one usually finds that the free-ion parameters change by a very small amount in going from the free ion to the crystal environment.[28,29] If the free-ion value of γ were a factor of 2 smaller than the value of γ for $\mathrm{Pr}^{3+}:\mathrm{LaF}_3$, it would represent a definite anomaly. The free-ion levels of Pr^{2+},[30] which has a $4f^3$ configuration, have also been fitted empirically,[31] and one obtains the values $\alpha = 30.4$, $\beta = -801$, and $\gamma = 1940$. All of these results taken together very strongly suggest that the free-ion ^1S level has not been properly identified.

VI. CONCLUSION

We have calculated configuration-interaction parameters which do not appear in the ordinary HF theory, and which have been determined in the past only by empirically fitting the energy levels. Other first-principles calculations of this kind should be most helpful for ions such as U^{3+} which have not been properly understood.

The most difficult part of the calculation was to

TABLE VI. Summary of results (in cm^{-1}).

	α	β	γ
2nd-order bound states	87.67	-1221.00	2260.45
Modified 2nd-order single-electron excitation to continuum	-93.77	1340.01	-2477.02
2nd-order two electrons to continuum	46.69	-774.15	1750.40
3rd order	-8.27	7.18	127.54
Magnetic orbit-orbit interaction within $4f^2$	-4.38	32.05	-49.84
Total calculated	27.94	-615.91	1611.53
Experimental	$24^{a,b}$	$-586^{a,b}$	728^{b}

[a] Reference 26. [b] Reference 27.

carry out the integrations over the continuum states. In a future paper, the single-particle excitations to the continuum will be represented by a perturbed function which satisfies an inhomogeneous differential equation, and the two-particle excitations will be represented by a pair function. This should facilitate future calculations of this kind, and it may yield insight into the nature of these Coulomb excitations.

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