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### Term dependence in the Hartree-Fock approximation for heavy atoms

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Cases of substantial term dependence are found in the Hartree-Fock approximation for heavy atoms that are not attributable to large dipole exchange interaction. They may be associated with "giant resonances" in electron impact excitation and ionization.

In the nonrelativistic Hartree-Fock approximation, the wave function of an  $N$ -electron atom is represented by a product of  $N$  one-electron orbitals  $\phi_{nlm\sigma}$  that is antisymmetrized so as to conform to the Pauli principle and to be an eigenfunction of both total orbital and spin angular momenta  $L$  and  $S$ . The Hartree-Fock equations provide a variational prescription for determining the  $\phi_{nlm\sigma}$ , which are expressed as products of a radial wave function  $P_{nl}(r)$  with standard angular and spin functions. It should occasion no surprise that, for a given configuration (the set of all states with common  $nl$  occupation numbers), the  $P_{nl}(r)$  are found to vary somewhat among its several terms (the states of the configuration with common values of  $L$  and  $S$ ). However, in many cases these variations are sufficiently minor that the same  $P_{nl}(r)$  can be used for all terms of a configuration. This additional "average-of-configuration" approximation is such a great practical convenience that, just as in the past, when individual computations were laborious, the demands of modern life have almost elevated it to a necessity.

There is a well-known class of atomic states in which the term dependence of radial orbitals is so pronounced that the average-of-configuration approximation results in substantial qualitative errors: The  $J=1$  states of the configurations  $sp$ ,  $p^5d$ , and  $d^9f$ . These states play a prominent role in photoabsorption processes in the soft x-ray region, since they provide the main channels for electric dipole excitation of a single electron out of a closed shell. In particular, the "giant resonances" which occur in photoabsorption by closed  $3p$  and  $4d$  shells are associated with  $^1P^\circ$  terms of  $p^5d$  and  $d^9f$  configurations, respectively. The Hartree-Fock orbitals for the  $^1P^\circ$  terms of these configurations differ significantly from those of the  $^3P^\circ$  and  $^3D^\circ$  terms (the other two terms with  $J=1$  components); this has been attributed to the larger contribution of the dipole exchange interaction to the energy of the  $^1P^\circ$  term. Considerable attention has been paid to this

fact and its consequences,<sup>1-6</sup> the most significant of which is that the basic mechanism of giant-resonance formation, which has been described<sup>7-9</sup> in terms of a collective oscillation of an electron shell, can also be understood within the framework of an independent particle model.<sup>1,6,10</sup>

The purpose of this paper is to point out that substantial radial orbital variation occurs throughout *all* terms of these configurations, that it is not attributable solely to the dipole exchange interaction, and that in some cases it is so extensive that no single orbital adequately represents the majority of terms of the configuration. The  $^1P^\circ$  term is thus not an isolated, but rather the extreme example of a phenomenon that affects whole configurations. Such cases are known in discrete emission spectra,<sup>11</sup> but their core-excited counterparts have received little attention. Presumably this is because states with other than  $J=1$ , odd parity, can be excited from a  $^1S$  closed shell only by nondipole interactions, and so they are irrelevant to photoabsorption. However, such states can be excited by electron impact, and they have appeared as strong and distinctive features in electron-energy-loss (EELS) spectra of rare-earth solids.<sup>12</sup> Nondipole interactions also contribute to the cross section for atomic ionization by electron impact, especially at energies near threshold. Younger has recently discussed<sup>13</sup> the role of giant resonances in electron impact ionization of  $\text{Cs}^+$ , with emphasis on the importance of term dependence in the  $^1P^\circ$  channel. The present results suggest that other channels may require similar treatment.

The specific case which will be discussed here is the configuration  $4s^2 4p^6 4d^9 4f^1 5s^2 5p^6$  of Xe-like  $\text{Cs}^+$ . The  $LS$  terms of this configuration are  $^1,3P, D, F, G, H^\circ$ . The nonrelativistic energies  $E_{LS}$  of these terms are given by weighted sums of direct  $F^k$  and exchange  $G^k$  Slater integrals:

$$E_{LS} = \sum_k f_{kLS} F^k(4d, 4f) + g_{kLS} G^k(4d, 4f), \quad (1)$$

TABLE I. Weights  $f_{kLS}$  and  $g_{kLS}$  of the  $d$ - $f$  direct and exchange contributions to the energies  $E_{LS}$  of all terms of the  $4d^9 4f$  configuration, and of the average-of-configuration energy (last row). The monopole coefficient  $f_{0LS}=9$  is common to all terms.

	70 $g_1$	105 $f_2$	105 $g_3$	693 $f_4$	2541 $g_5$
$^3P^\circ$	-30	-24	-20	-66	-550
$^1P^\circ$	110	-24	-20	-66	-550
$^{3,1}D^\circ$	-30	-6	-20	99	-550
$^3F^\circ$	-30	11	-20	-66	-550
$^1F^\circ$	-30	11	20	-66	-550
$^{3,1}G^\circ$	-30	15	-20	22	-550
$^3H^\circ$	-30	-10	-20	-3	-550
$^1H^\circ$	-30	-10	-20	-3	150
Average	-27	0	-18	0	-495

TABLE II. Values (in a.u.) of the direct  $F^k(4d,4f)$  and exchange  $G^k(4d,4f)$  Slater radial integrals, and principal quantum numbers  $n^*$ , for the  $LS$  terms of the  $4d^9 4f$  configuration of  $\text{Cs}^+$ , as computed in the Hartree-Fock approximation.

	$G^1$	$F^2$	$G^3$	$F^4$	$G^5$	$n^*$
$^3P^\circ$	0.460	0.389	0.283	0.245	0.199	2.804
$^1P^\circ$	0.0004	0.003	0.0002	0.0005	0.0002	3.957
$^{3,1}D^\circ$	0.336	0.293	0.206	0.180	0.144	3.764
$^3F^\circ$	0.328	0.286	0.201	0.175	0.140	3.827
$^1F^\circ$	0.008	0.011	0.005	0.005	0.003	3.934
$^{3,1}G^\circ$	0.018	0.020	0.011	0.010	0.008	3.914
$^3H^\circ$	0.411	0.352	0.252	0.219	0.177	3.301
$^1H^\circ$	0.320	0.280	0.195	0.171	0.137	3.789
Average	0.046	0.045	0.028	0.025	0.019	3.871

where

$$F^k(4d,4f) = \int \int dr_1 dr_2 P_{4d}(r_1) P_{4f}(r_2) \times (r_1^k / r_2^{k+1}) P_{4d}(r_1) P_{4f}(r_2), \quad (2a)$$

$$G^k(4d,4f) = \int \int dr_1 dr_2 P_{4d}(r_1) P_{4f}(r_2) \times (r_1^k / r_2^{k+1}) P_{4d}(r_2) P_{4f}(r_1), \quad (2b)$$

and the coefficients  $f_{kLS}$  and  $g_{kLS}$  are given in Table I. The Hartree-Fock method requires that  $E_{LS}$  be stationary with respect to variations of the  $P_{nl}$ . When this principle is applied to generate differential equations for the  $P_{nl}$ , the weighted  $F^k$  and  $G^k$  integrals give rise to identically weighted local and nonlocal potentials in a Schrödinger equation.<sup>14</sup>

In the average-of-configuration approximation, the radial orbitals are generated by the solution of a set of Hartree-Fock equations in which the electronic interactions are averaged over all terms of the configuration: in

this case, using the  $f_k$  and  $g_k$  given in the bottom row of Table I. The resulting  $4d$  and  $4f$  orbitals would then be used to compute the  $E_{LS}$  from Eqs. (1) and (2). This procedure is a shortcut to the separate self-consistent solution of the Hartree-Fock equations for each term, but is justified *post hoc* if it gives equivalent results. In the present case it does not.

Figure 1 shows the  $4f$  orbitals for each term of the  $4d^9 4f^1$  configuration, as well as for the fictitious "average" term. The computations were carried out with a modified version of the MCHF77 code.<sup>15</sup> The self-consistent equations for all orbitals were solved independently for each term. No great qualitative term dependence of other orbitals was found, the only notable variation being in the  $5s$  and  $5p$  orbitals, which show a slight expansion or contraction opposite to that of the  $4f$ . The computed values of the Slater integrals are given in Table II. The effective principal quantum numbers  $n^* = 2(E/\text{Ry})^{-1/2} \equiv n - \mu$  are defined with respect to the fully relaxed Hartree-Fock  $\text{Cs}^{2+}$  ion core. The spin-orbit split-

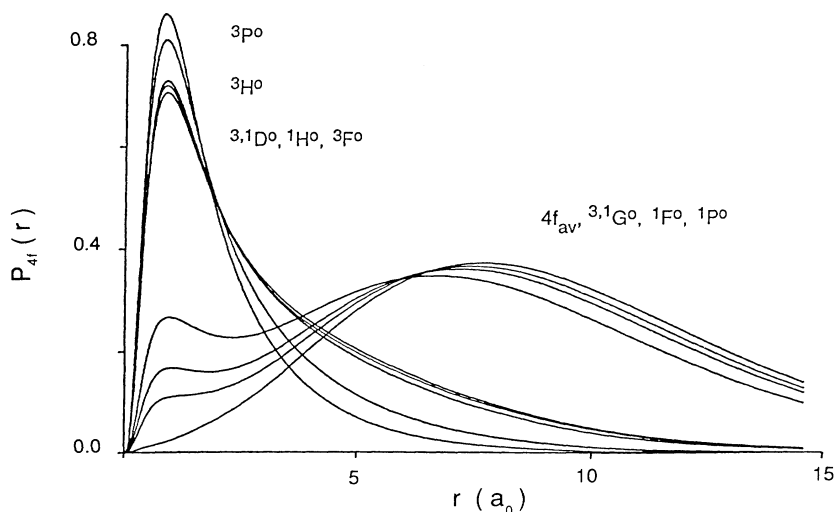


FIG. 1. The Hartree-Fock  $4f$  orbitals for all  $LS$  terms of the  $4d^9 4f$  configuration of  $\text{Cs}^+$ , and for the "average-of-configuration" orbital  $4f_{av}$ . Labels, as read from top to bottom and left to right, are in order of increasing energy and displacement of orbital maximum.

ting of the  $4d^9$  term of the  $\text{Cs}^{2+}$  ion is computed to be 2.2 eV. It has not been taken into account here, but certainly would have to be included in a quantitative treatment of the term spectrum. The effects of spin-orbit interaction in the isoelectronic configuration of Ba have been discussed in Ref. 6.

The origin of the large variation of radial orbitals between terms must be sought in the coefficients  $f_{kLS}$  and  $g_{kLS}$ , which provide the only differences between the separate self-consistent field calculations. There is no straightforward way of predicting the outcome of such calculations, so the following remarks are based only on the comparison of results. Note that for odd  $L$ , the energies of  $^1L^\circ$  and  $^3L^\circ$  terms differ only in the weights of the  $L$ -pole exchange interaction  $G^L(4d,4f)$ . This difference is most pronounced for  $L=1$ , the two terms which define the extremities of the spectrum. The  $4f$  orbital of the highest term,  $^1P^\circ$ , corresponds very nearly to the  $4f$  orbital of  $\text{He}^+$ , as reflected by the small quantum defect,  $\mu=0.043$ . The form of this orbital is thus governed by the interplay of the long-range Coulomb field and the centrifugal potential. The dipole exchange interaction depends very strongly on the overlap of  $4d$  and  $4f$  electrons, so in the solution of the self-consistent field equations it repels the  $^1P^\circ$   $4f$  orbital from the vicinity of the  $4d$  shell. The  $^3P^\circ$  term lies lowest in energy, and its  $4f$  orbital overlaps the  $4d$  orbital. Its quantum defect is greater than unity,  $\mu=1.20$ , which is the signature of "orbital collapse" near the beginning of the lanthanide sequence. The form of this orbital is governed by the effective potential in the interior of the Cs ion. It cannot be reconstructed from knowledge of the long-range potentials alone.

The  $^1P^\circ$  term is unique in its large positive coefficient of the dipole exchange interaction, but on the other hand its  $4f$  orbital is not the only one which remains primarily in the hydrogenic region. The  $^1F^\circ$  orbital also displays hydrogenic behavior which can be related to an exchange interaction. The  $^3F^\circ$  orbital is collapsed, and as noted above, the only difference between  $^1F^\circ$  and  $^3F^\circ$  energies is in the coefficient of the octupole exchange integral  $G^3$ . Thus the octupole exchange interaction is sufficiently repulsive to keep the  $^1F^\circ$   $4f$  orbital away from the core. The  $^3G^\circ$  and  $^1G^\circ$  terms are degenerate in  $LS$  coupling, and their common  $4f$  orbital is seen to be extended. Table I shows that only for the  $G$  states is the energy associated with the  $F^2$  and  $F^4$  interactions necessarily positive, so in this case the direct electrostatic interaction repels the  $4f$  orbital from the core.

Through these results cannot be described strictly in terms of the properties of an effective local potential for the  $f$  electron, such an effective potential can be generated from the computed orbitals by inverting the Schrödinger equation:  $V_{\text{eff}} = E + (2\psi)^{-1}\nabla^2\psi$ , in atomic units. Such potentials reproduce fairly well the Hartree-Fock  $nf$  orbitals for higher members of the Rydberg series, so they may be considered to provide a reasonable representation of the dynamics over a limited energy range.<sup>6</sup> The effective potential for the  $^1P^\circ$   $f$  wave exhibits a barrier of height  $\sim 19$  eV above threshold. This is in correspondence with the energy of the  $ef$   $^1P^\circ$  shape resonance calculated by Younger.<sup>13</sup> Barriers are also found in the  $^1F^\circ$  and  $^3G^\circ$  potentials, with heights of  $\sim 0.4$  eV. These channels may

thus exhibit shape resonances near threshold. Such a resonance in the  $^1F^\circ$  channel could be excited in electron impact via the long-range electric octupole interaction. The  $4d^{10} \rightarrow 4d^9 4f^1 F^\circ$  excitation has been identified<sup>12</sup> in electron-impact excitation of metallic La and of  $\text{CeO}_2$ , appearing with significant intensity even at primary energies thirty times greater than the excitation energy. Excitation of  $G$  states does not occur in the plane-wave Born approximation, and so it presumably would be important only at relatively low excess energies.

Other core-excited configurations of  $\text{Cs}^+$ , which have not yet elicited experimental interest to my knowledge, display similar cases of term dependence. In particular, the  $4p^5 4f$  and  $4s 4f$  configurations show both hydrogenic and collapsed terms. Though details of the calculations will not be given here, it is found that the  $4p^5 4f^1 D$  and  $4s 4f^1 F^\circ$  terms are hydrogenic ( $\mu=0.073$  and  $0.105$ , respectively). This can be associated with positive coefficients of the lowest-order exchange interactions  $G^2(4p,4f)$  and  $G^3(4s,4f)$ . Note that the  $^1D$  and  $^1F^\circ$  states can be produced by electric quadrupole and octupole excitation of the  $p^6$  and  $s^2$  shells, respectively. Such excitations have been observed in EELS of lanthanide metals,<sup>16</sup> for which all terms of these configurations are collapsed. The present results suggest that for Cs, the bulk of the excitation strength in these channels should be associated with shape resonances near the  $4p$  and  $4s$  thresholds.

The instantaneous interaction of an electron with an open-shell ion is inherently anisotropic, in that it consists of direct and exchange multipole interactions. The anisotropy is concealed by the central field approximation, in which each electron is constrained to have an angular momentum of definite magnitude  $l_i$ . However, some of its effects are retained through the dependence of the electron-ion interaction energy upon the total angular momentum  $L$ . As will now be shown, the occurrence of orbital term dependence can be related in some cases to a breakdown of the picture of an electron moving in the central potential of an ion. However, this need not involve a failure of the independent electron model or nonconservation of the individual angular momenta  $l_i$ .

Consider a simple semiclassical description of the orbit of a single electron outside an ion with an open shell. If the true electron-ion interaction is replaced by its spherical average, then the electron moves in a central potential. Its orbit is contained in a plane, and the electronic orbital and spin angular-momentum vectors  $\mathbf{l}_e, \mathbf{s}_e$  and corresponding ionic angular momenta  $\mathbf{l}_i, \mathbf{s}_i$  are constants of the motion. Now let the true electron-ion interaction be turned on slowly. Only the net angular momenta  $\mathbf{L} = \mathbf{l}_e + \mathbf{l}_i$  and  $\mathbf{S} = \mathbf{s}_e + \mathbf{s}_i$  are conserved, so if the interaction is weak the electronic and ionic angular momenta will precess about their vector sum. Thus the electronic orbit remains essentially planar, but the plane precesses slowly about the axis of total orbital angular momentum.

The period of precession can be evaluated by the same method that relates the period of precession of an atom in a magnetic field to the Zeeman splitting of the energy levels. We consider the time-dependent wave function  $\psi(t)$  which corresponds to a definite orientation of the orbital plane with respect to the ion at  $t=0$ , i.e., to given values

of the orbital and spin angular-momentum projections  $m_e, m_i, \sigma_e, \sigma_i$ :

$$\psi(t) = \sum_{LS} \langle l_e m_e l_i m_i | l_e l_i L M_L \rangle \langle s_e \sigma_e s_i \sigma_i | s_e s_i S M_S \rangle \exp(-2\pi i E_{LS} t / \hbar) | n l_e a l_i L M_L \rangle | s_e s_i S M_S \rangle, \quad (3)$$

where  $n$  is the principal quantum number of the electron and  $a$  designates the ionic configuration. The wave function  $\psi(t)$  will be strictly periodic, corresponding to a regular precession of the plane of the electron orbit, only if all differences of term energies  $\Delta E_{LS}$  are rational multiples of a common energy. This is the case in the linear Zeeman effect, where the difference in energy between adjacent levels is a constant. It need not be true for the term spectrum of an atomic configuration, so  $\psi(t)$  will not necessarily exhibit a strictly periodic evolution in time. However, if  $\Delta E_{LS}$  is the difference in energy between the highest and lowest terms of the configuration, these terms will first return to their initial relative phase at a time  $\tau_p = \hbar / \Delta E_{LS}$ . Thus  $\tau_p$  can be regarded as a minimal period of precession of the plane of the orbit.

Now consider the period of the electronic orbit  $\tau_n$ . The Bohr model gives

$$\tau_n = n^3 \hbar / z^2 \text{ (a.u.)}, \quad (4)$$

for the orbital period of an electron bound to a hydrogenic ion with nuclear charge  $z$ . This result applies to a Rydberg atom if  $n$  is replaced by the effective principal quantum number  $n^* = z / \sqrt{2E}$ . The condition for validity of the central potential approximation is that the period of precession be much greater than the orbital period,  $\tau_p \gg \tau_n$ , otherwise it is not meaningful to distinguish the two motions. From  $E = z^2 / 2n^{*2}$ , we get  $\Delta E_{LS} = (\Delta n^*) z^2 n^{*-3}$ , where  $\Delta n^*$  is the variation of the effective principal quantum number over the  $LS$  terms of the configuration. Then

$$\tau_p = \hbar / \Delta E_{LS} = (\Delta n^*)^{-1} n^{*3} \hbar / z^2, \quad (5)$$

so the condition  $\tau_p \gg \tau_n$  is equivalent to  $\Delta n^* \ll 1$ . This is the usual criterion for the applicability of the average-of-configuration approximation. Its breakdown is sometimes due to failure of the independent electron model: For example, in the  $2p^2$  configuration of Be, the  $^1D$  and  $^1S$  terms are displaced by interaction with  $2snd$  and  $2sns$  states, respectively, but the  $^3P$  term is relatively undisturbed. However, it is clear that this criterion can be strongly violated within the framework of the Hartree-Fock approximation, as is the case in the present example, and also in neighboring isoelectronic configurations in the periodic table.<sup>5,6</sup>

Thus, the breakdown of the average-of-configuration approximation, as manifested by orbital term dependence, does not necessarily involve collective behavior of atomic electrons. The picture of a single electron orbiting an ion can remain valid, though the effective potential is anisotropic. The  $4f$  orbital of any one term (e.g.,  $^1P^o$ ) can indeed be represented as a superposition of all discrete and continuum  $f$  orbitals of any other (e.g., the configuration average). This could be construed as a type of "configuration interaction," but it is akin to building an elliptical orbit from epicycles.

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