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Term values and ionization potentials have been calculated for several ions in the promethium ($N = 61$) isoelectronic sequence. As the nuclear charge is increased, the ground configuration changes from $4f^{13}5s^2$ to $4f^{14}5s$ giving the upper portion of the sequence an alkali-like character. According to our most recent Hartree–Fock calculations with first-order relativistic corrections, the ground term is 5s ^2S for $Z > 77$ (Ir XVII) and the first excited term is 5p $^2P^0$ for $Z > 84$ (P_0 XXIV). Comparisons are made with calculations of Cowan in W XIV. The prospects for observation of these spectra in fast ion beams are discussed.

Heavy ions isoelectronic to Li, Na and Cu are known to produce long sequences of alkali-like spectra – that is, simple spectra due to a single electron outside a compact core consisting of closed K, L and M shells. These spectra vary in a smooth and predictable way as the core charge ζ changes along an isoelectronic sequence, and they have proven useful in studies of high-temperature plasmas. It is therefore natural to consider the possibility that the very heavy ions of the promethium isoelectronic sequence (61 electrons) might behave similarly for large enough values of ζ, forming configurations of the type $4f^{14}nl$ in which a single electron moves outside a core consisting of filled K, L, M and N shells.

In a recent paper [1] we reported the following results of a series of single-configuration Hartree–Fock calculations on the Pm sequence:

(1) If E_0 is the nonrelativistic average energy of a configuration, then $E_0(4f^{14}5s) < E_0(4f^{13}5s^2)$ for $\zeta \geq 14(W^{+13})$ and $E_0(4f^{14}5s) < E_0(4f^{14}5p) < E_0(4f^{13}5s^2)$ for $\zeta > 17$ (Ir^{+16}).

(2) Including relativistic corrections, the wavelengths of the 5s $^2S_{1/2}$–5p $^2P^0_{1/2,3/2}$ transitions in W XIV, Ir XVII, Au XIX, Pb XXII and U XXXII were predicted to an expected accuracy of about 4%. (For example the Au XIX lines were predicted to be at 297 Å and 199 Å with corresponding meanlives of 56 and 16 ps.)

In the present paper we report new Hartree–Fock results for these ions, in which the Pauli relativistic corrections to the lowest configuration energies have been calculated. The collapse of the 4f orbital as one moves from the lower to the upper portion of this sequence is a complex problem in which both relativity and electron correlation are important; a definitive treatment, using for example a multiconfiguration Dirac–Fock approach, would be a major project and to our knowledge has not yet been done. In the meantime we can justify our approach as reasonable if not precise as follows: First, if we stay on the high-ζ side of the transition, where the HF solution has a well-defined core with a single outer electron, then correlation effects can be expected to be minor and the single-configuration solution to have some validity. Second, if the Pauli corrections to the energy are only 5–7% of the HF

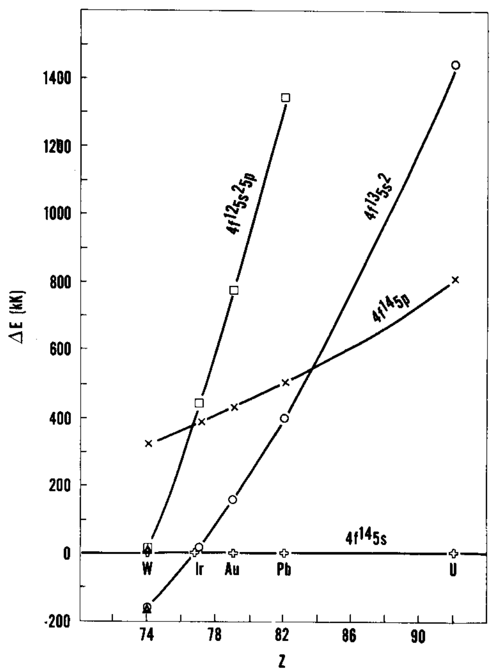

Fig. 1. Upper promethium sequence. The average energies of the indicated configurations ($4f^{14}5p$, $4f^{13}5s^2$, $4f^{12}5s^25p$), relative to that of $4f^{14}5s$, are plotted against nuclear charge. Included are both the Hartree–Fock energy (HF) and its lowest-order relativistic correction (Pauli). Also plotted for W^{+13} are the relativistic Hartee–Fock (HFR) results of Cowan [5] indicated by triangles. Other symbols indicate results of the present work. Energies are given in units of 10^3 cm^{-1} (kK).

Table 1
Pm-sequence average configuration energies with relativistic corrections. The negative of the total energy is listed, in a.u.

	Ion	W^{+13}	Ir^{+16}	Au^{+18}	Pb^{+21}	U^{+31}
	Z	74	77	79	82	92
5s	HF	15234.06	16719.74	17750.72	19357.89	25240.21
	Pauli	741.73	876.34	975.86	1140.92	1847.11
	Total	15975.79	17596.08	18726.58	20498.81	27087.32
5p	HF	15232.99	16718.50	17749.37	19356.37	25238.13
	Pauli	741.33	875.81	975.23	1140.11	1845.47
	Total	15974.32	17594.31	18724.60	20496.48	27083.60
$5s^2$	HF	15233.90	16718.45	17748.55	19354.21	25229.87
	Pauli	742.61	877.54	977.30	1142.78	1850.87
	Total	15976.51	17595.99	18725.85	20496.99	27080.74
$5s^25p$	HF	15232.57	16715.79	17744.88	19348.81	25217.16
	Pauli	743.14	878.26	978.16	1143.88	1853.06
	Total	15975.71	17594.05	18723.04	20492.69	27070.22

energy, as we find here, then they can be expected to give a reasonable approximation to the effects of relativity. This latter point is supported by consideration of the Cu sequence 4s and 4p energies [1]; there we find also, for nuclear charge Z in the same range as we have here, that the Pauli corrections are 5–6% of the HF energies and that they represent the major portion (about 85%) of the total relativistic correction [2].

The Pauli corrections quoted here were calculated from nonrelativistic single-configuration wavefunctions which were produced by the computer program MCHF77 [3]. The expectation values of the Darwin term and the relativistic mass increase term [4] were calculated for all the orbitals in the HF solutions for the $4f^{14}5s$, $4f^{14}5p$, $4f^{13}5s^2$ and $4f^{12}5s^25p$ configurations; each configuration was solved self-consistently with no frozen core. In the case of the mass increase term, the expectation value of the square of the kinetic energy was calculated by an explicit numerical integration for each radial wavefunction. The results are given in table 1 and also in fig. 1. Since the 5s and 5p orbitals approach the nucleus more closely than does the 4f, the relativistic corrections naturally lower the 5s and 5p energies relative to the 4f and thus cause the change in ground configuration from $4f^{13}5s^2$ to $4f^{14}5s$ to occur at a higher value of ζ than is indicated by the HF energies alone, namely at $\zeta = 17$ (Ir^{+16}) rather than $\zeta = 14$ (W^{+13}). Higher-order relativistic effects can be expected to raise this crossing point a little further. Also shown are the earlier results of a relativistic HF calculation [5] for W^{+13}. We have also calculated the HF and Pauli energies for the ($4f^{14}$) ^1S level of Au^{+19}: we estimate the first ionization energy of Au^{+18} to be about 470 eV. We can compare this with Mo^{+13} of the Cu sequence, which has a first ionization potential of 302.6 eV [6] and has recently been observed [7] to be strongly foil excited at a specific beam energy of 0.1 MeV/amu. It should be noted, however, that the predicted Au^{+18} lines have not been evident in recent beam foil studies at similar specific beam energies [8].

In conclusion, our results indicate that from $Z = 79$ to 92 the Pm-sequence spectra should be amenable to both theoretical and experimental study, and provide an interesting opportunity for us to test and improve our understanding of many-electron ions.

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