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Further studies of the promethium isoelectronic sequence

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We have performed a fully relativistic calculation, using the Dirac-Fock approximation, of energy levels and excitation energies for several ions in the promethium isoelectronic sequence. Our results verify the overall predictions on level ordering of the Hartree-Fock calculations, which included some relativistic effects perturbatively. Some differences were found concerning the atomic number at which the ground state of the ion has alkali-metal–like configuration.

In two recent studies, Curtis and Ellis[1,2] considered some highly ionized members of the promethium isoelectronic sequence as candidates for producing strong resonance lines in the uv spectra of hot plasmas. The ground state of Pm has the configuration $4f^5 5s^2 5p^6 6s^2$. As one proceeds along the isoelectronic sequence, however, i.e., increasing nuclear and ionic charge, the character of the $4f$ orbitals changes, so that eventually the ground-state ionic configuration becomes $4f^{14}5s$. In that case we have an alkali-metal–like ion. In hot plasmas many excited states of these ions would be excited which would decay with highest probability along the yrast sequence

$$l \rightarrow l-1 \rightarrow l-2 \rightarrow \cdots \rightarrow f \rightarrow d \rightarrow p \rightarrow s \ ,$$

which results in strong $p \rightarrow s$ transition lines.

The question which was addressed by Curtis and Ellis[1,2] is "at what ionic state is $4f^{14}5s$ the ground state?" In their work they performed single-configuration nonrelativistic Hartree-Fock calculations, using a standard computer code.[3] In addition, they included perturbatively the first-order relativistic corrections from Pauli's equation. Namely, the expectation values of the Darwin and relativistic mass correction terms[4] were calculated separately and added to the total energy of each configuration. Furthermore, higher-order relativistic corrections were included in a semiempirical approach. Even though nonrelativistic Hartree-Fock calculations predict the turning point where $4f^{14}5s$ rather than $4f^{13}5s^2$ is the ground state to happen at W^{13+} (ionicity $\zeta = 14$), their relativistic approach predicts the change to happen at Ir^{16+} ($\zeta = 17$).

These predictions were tested for the case of gold in a preliminary experimental investigation by Johnson *et al.*[5] without clear evidence of any strong lines around the expected area of the spectrum. This study prompted our present investigation. We used from the outset a fully relativistic approach using the multiconfiguration Dirac-Fock (MCDF) computer codes of Desclaux[6] and of Grant *et al.*[7] Our objective was to either verify the previous calculations or make better predictions of the location of the expected strong yrast-series originated lines. The particular atoms of the sequence chosen for study are not significant, since as we will see, the predicted curves have a smooth Z dependence.

Our results on total energies for the various configurations and ions studied, using Desclaux's code,[6] are shown in Table I. This table also includes the values of Ellis and Curtis[2] in the Hartree-Fock plus Pauli terms (HFP) approximation. There is an overall qualitative agreement between the two results. Some of the data are depicted in Fig. 1 as excitation energies from the configuration $4f^{14}5s$. We notice that the fully relativistic treatment yields a $4f^{13}5s^2$ configuration for W^{13+} less tightly bound than the predictions

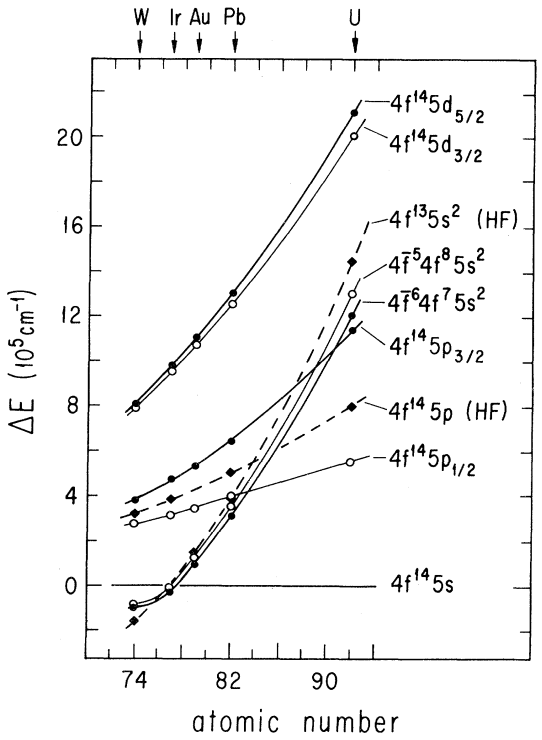

FIG. 1. Total energies of the lower-energy configurations in the promethium isoelectronic sequence, relative to the $4f^{14}5s$ configuration. Solid lines connect the DF results and dashed lines connect the average HF results.

TABLE I. Total energies of ions in the *Pm* sequence. (The negative of the energy is given in atomic units.) DF: single configuration Dirac-Fock calculation using Desclaux's program plus the analytic 1*s*, 2*s*, and $2p_{1/2}$ Lamb shifts. HFP: calculation of Ellis and Curtis including the Pauli Hamiltonian corrections (Darwin and relativistic mass).

Ion	$5s$	$5p_{1/2}$	$5p_{3/2}$	$5d_{3/2}$	$5d_{5/2}$	$4f_{5/2}$	$4f_{7/2}$
W^{13+}							
DF	16074.134 50	16072.905 70	16072.398 25	16070.531 13	16070.447 15	16074.936 41	16075.016 00
HFP	15975.784 96	15974.579 75	15974.187 08	15972.311 23	15972.234 21	15976.456 35	15976.545 35
In^{16+}							
DF	17726.754 03	17725.323 01	17724.612 08	17722.403 55	17722.279 92	17726.785 62	17726.898 21
HFP	17596.076 81	17594.667 87	17594.122 70	17591.906 71	17591.792 69	17595.920 45	17596.044 21
Au^{18+}							
DF	18883.805 62	18882.236 25	18881.361 62	18878.925 47	18878.770 00	18883.229 65	18883.368 46
HFP	18726.577 62	18725.037 85	18724.372 51	18721.922 73	18721.778 91	18725.764 67	18725.916 04
Pb^{21+}							
DF	20704.335 47	20702.553 58	20701.385 53	20698.607 76	20698.395 38	20702.722 78	20702.907 99
HFP	20498.808 85	20497.066 84	20496.190 81	20493.393 75	20493.196 70	20496.872 10	20497.072 37
U^{31+}							
DF	27557.411 21	27554.874 63	27552.188 96	27548.265 15	27547.765 75	27551.483 05	27551.898 21
HFP	27087.322 22	27084.863 96	27082.972 75	27079.121 42	27078.657 75	27078.590 20	27079.032 99

of HFP.[2] (A relativistic Hartree-Fock calculation by Cowan[8] yielded results for W^{13+} that are essentially identical to those of HFP.) This trend is reversed, however, at higher atomic numbers; this is direct evidence of purely relativistic effects resulting from higher-order corrections or, more accurately self-consistent-field results due to relativity. In the case of $4f^{14}5p$ and $4f^{14}5d$ configurations, the HF excitation energies are systematically lower than the DF ones. In spite of these differences, the first excited state is $4f^{14}5p$ ($j=\frac{1}{2}$) for $Z > 84$ independent of the calculational approach. An interesting indication of the rearrangement of the various inner subshells along the isoelectronic sequence $4f^{14}5l$, $l = s,p,d$, is obtained from Fig. 2, where we plot the expectation values $\langle r \rangle_{nlj}$ for the various orbitals of the M and N shells. These expectation values decrease as the atomic number increases, since they characterize the size of the respective subshell. The most striking result is the behavior of the $4f$ orbitals: They are seen to contract faster than the others as a function of the atomic number Z, and in the case of uranium their expectation values $\langle r \rangle$ are smaller than those of $4d_{3/2,5/2}$ and $4p_{3/2}$. In both HF and DF, nevertheless, the various shells (different principal quantum numbers n) are distinct from one another.

We should probably mention here that the results obtained using the computer code of Grant *et al.*[7] were practically identical to the ones presented here for the cases with closed $4f$ subshell. We experienced, however, serious instabilities towards convergence, most notably for the two $4f^{13}5s^2$ states which never converged to reasonable values, based on our HF guidelines for overall expected behavior, in any of the five ions considered. To quote the example of gold, the program of Grant *et al.* yielded, without including retardation and magnetic effects, $-18\,940.371\,11$ and $-18\,961.189\,85$ a.u. for $4f^{13}5s^2$, $j=\frac{3}{2}$ and $\frac{5}{2}$, respectively, compared to $-18\,883.229\,65$ and $-18\,883.368\,46$ a.u. from Desclaux's program[6]; these differences of the order of 80 a.u. are unacceptable. We consider the former program to be in error, based on these huge "fine-structure" splittings of about 20.8 a.u. compared with 0.14 and 0.15 a.u. predicted by Desclaux's code and HFP, respectively.

From the calculated total energies we obtained the transition wavelengths between the alkali-metal–like configurations $4f^{14}5p$ and $4f^{14}5s$. They are listed in Table II where they are compared to the HF and HFP results. We observe that the DF wavelengths are smaller than the HFP ones by about 6 to 8 Å for $\frac{1}{2}$-$\frac{1}{2}$ and 9 to 15 Å for $\frac{1}{2}$-$\frac{3}{2}$ transitions

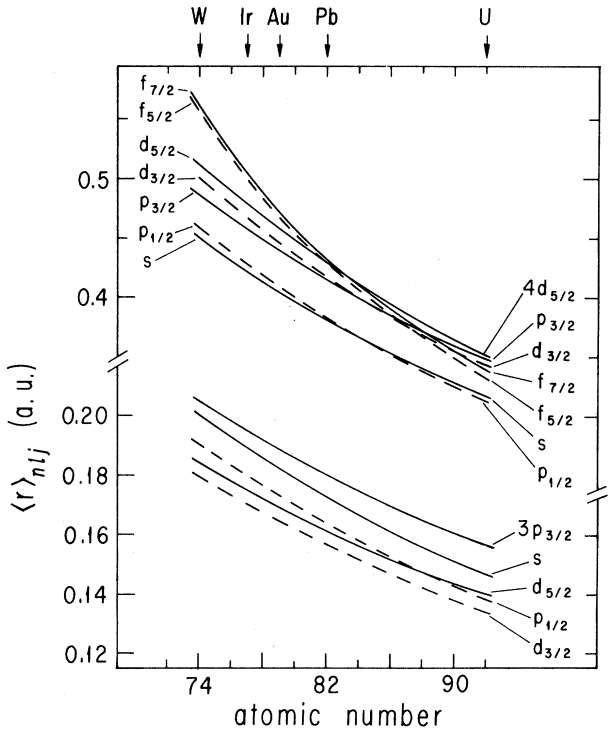

FIG. 2. DF expectation values $\langle r \rangle_{nlj}$ for the various M-shell and N-shell orbitals vs atomic number. The calculations were done for the $4f^{14}5l$ configurations.

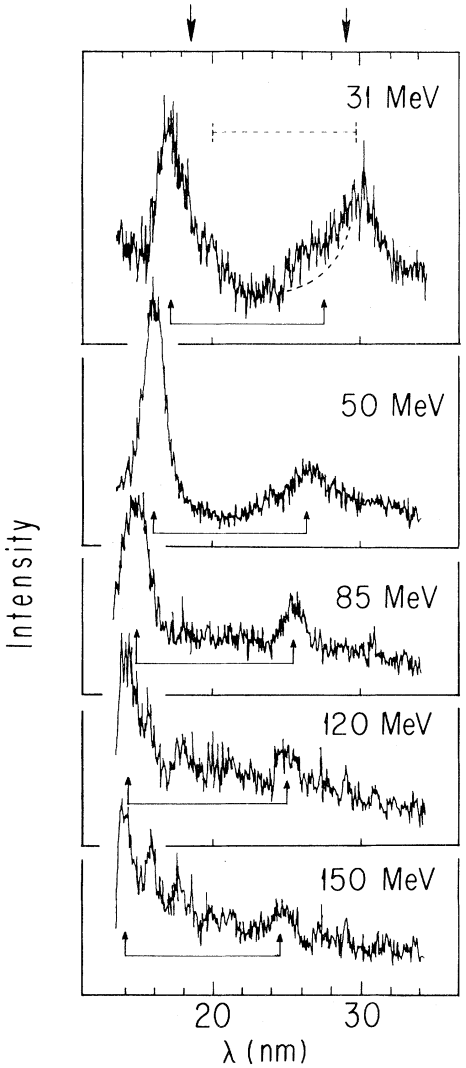

FIG. 3. Experimental spectra obtained by colliding 31- to 150-MeV gold ions on carbon foils (adapted from Ref. 5). The two large arrows at the top of the figure indicate the $5s\ ^2S-5p\ ^2P$ line wavelengths predicted by the DF approximation. The dotted line indicates the HFP predictions (from Ref. 1). The solid lines ending in the two arrows give the predicted DF line separation *shifted* to overlap with the experimental lines. The energy *splittings* are seen to agree very well.

and are generally closer to the HF values (which do not include any relativistic corrections). The larger differences between HFP and DF for $\frac{1}{2}$-$\frac{3}{2}$ transitions are due to the fact that the self-consistent DF approach yields larger relativistic effects for $p_{1/2}$ rather than $p_{3/2}$, since the former penetrates closer to the atomic nucleus, and this is correctly reproduced by the fully relativistic DF treatment.

TABLE II. $5s\ ^2S-5p\ ^2P$ lines in the *Pm* sequence.

Z	Spectrum	Line	λ (Å) HF	HFP[a]	DF
74	W XIV	$\frac{1}{2}$-$\frac{1}{2}$	376.49	379	370.79
		$\frac{1}{2}$-$\frac{3}{2}$	284.26	277	262.42
77	Ir XVII	$\frac{1}{2}$-$\frac{1}{2}$	323.58	325	319.21
		$\frac{1}{2}$-$\frac{3}{2}$	233.27	226	212.38
79	Au XIX	$\frac{1}{2}$-$\frac{1}{2}$	295.92	297	290.33
		$\frac{1}{2}$-$\frac{3}{2}$	206.63	199	186.43
82	Pb XXII	$\frac{1}{2}$-$\frac{1}{2}$	261.55	263	255.70
		$\frac{1}{2}$-$\frac{3}{2}$	174.04	166	154.98
92	U XXXII	$\frac{1}{2}$-$\frac{1}{2}$	185.34	186	179.63
		$\frac{1}{2}$-$\frac{3}{2}$	104.75	96	87.25

[a] These values include higher-order relativistic corrections semiempirically (from Ref. 1).

There exists only the experimental investigation of Johnson *et al.*[5] on the Au XIX lines to compare with our predictions. The data of Ref. 5 are adapted and shown in Fig. 3. We can clearly identify two lines for impact energies 31, 50, and 85 MeV. The line *separation* is in very good agreement with our DF results. We are troubled, however, by the apparent synchronous shifting of the two lines towards lower wavelengths as the impact energy increases. We might attribute this shifting of the doublet to inaccuracies of the experimental energy calibration. These inaccuracies will have to be rather large and we do not find ourselves competent to argue for or against the assumption. The poor statistics at higher energies are expected, since the probability of producing the relevant states diminishes drastically with increasing impact energy.[5] It is evident that more experimental investigations of these systems, preferably in the higher–atomic-number region and with significantly improved statistics at lower energies, are highly desirable in order to resolve the discrepancies.

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