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EFFECTS OF RELATIVITY AND OF THE LANTHANIDE CONTRACTION ON THE ATOMS FROM HAFNIUM TO BISMUTH

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(ABSTRACT)

In order to help elucidate the effect of the 4f shell of electrons, Hartree-Fock (HF) calculations were made for the pseudo-atoms corresponding to Hf, Re, Au, Hg, Tℓ, Pb, and Bi without 4f electrons and with atomic numbers reduced by 14. The orbital energies for these pseudo-atoms are compared with those from HF and relativistic (DHF) calculations for the same atoms. It is found that the relativistic effect and that of the 4f shell are of comparable magnitude and both are larger for 6s than for 5d or 6p electrons.

The elements following the lanthanide or rare earth series show a number of anomalous features in relation to trends from lighter elements in the same groups of the periodic table. Possible causes for these anomalies include (1) the introduction of an f-shell of 14 electrons and (2) relativistic effects.

The f-shell effect is commonly called the "lanthanide contraction"; it arises from the incompleteness of shielding by 4f electrons of the additional nuclear charge and yields a contraction of the radii of outer electrons as well as other effects. While one can attribute spin-orbit coupling effects in even the lightest atoms to relativity, it is only when electron velocities approach the speed of light in an appreciable portion of the atom that electron orbital energies are significantly changed. Recently both non-relativistic Hartree-Fock[1,2] (HF) and relativistic[3] (DHF) atomic calculations have been made for these elements, and from these results the relativistic effects can be evaluated. In order to compare these with the effects of introducing the 4f shell, we made non-relativistic (HF) calculations for pseudo-atoms without a 4f shell and with atomic numbers less by 14. The pseudo-atom calculations were performed using the numerical HF program of C. Froese Fischer[4] slightly modified by one of us (P.S.B.).

The comparative magnitude of these two effects is of interest on its own account, but it is also important in considerations of the expected properties of even heavier

elements. For elements 104-118, which correspond to the series Hf - Rn, the f-shell effect should remain about the same but the relativistic effects should increase greatly.

Calculations were made for the LS configuration average for pseudo-atoms of Hf, Re, Au, Hg, Tℓ, Pb, and Bi. Table 1 gives the orbital energies for 5d, 6s, and 6d levels and gives comparable HF and DHF values for the corresponding LS configuration average for the real atoms. All the results shown are for wave functions which have been obtained by direct numerical integration[1,3,4] of the appropriate, Fock or Dirac-Fock, integro-differential equations. The computational methods used yield quite accurate results. Thus, the differences among the results are not related to any limitations of computational accuracy. Rather, they are consequences of the different physical models used.

Of the trends in orbital energies shown in Table 1 and Figures 1 and 2, the simplest and most important is that for s electrons. These orbitals penetrate deeply into the atom and even more strongly in relativistic theory than for non-relativistic. The effect of the f-shell (0.82 ev in Au) is somewhat less than half as large as that of relativity (1.92 ev in Au).

The orbital energies for the 5d electrons show smaller percentage differences but in the reverse direction for many atoms. Evidently these d electrons are so non-penetrating with respect to the 4f shell that the lanthanide contraction of the 5s and 5p electrons is dominant. Thus, when the 4f shell is introduced, the 5d electrons are , in some cases,

even more fully shielded from the nucleus.

The f-shell effects on the 6p electrons, shown in Figure 2, are smaller but otherwise similar to those for 6s electrons. But the picture is complicated by the $p_{1/2}$ - $p_{3/2}$ splitting which is becoming substantial, and the relativistic effect for the weighted average (1/3 $p_{1/2}$ + 2/3 $p_{3/2}$) is very small.

Table 2 and Figure 3 show the expectation values for the radius for the valence electrons in these same atoms. The lanthanide contraction (4f-shell) effects are now more nearly comparable to the relativistic effects in magnitude. The various differences can be understood on the same basis as that given for the energies. Here we note that $\langle r \rangle_{5d}$ for the pseudo-atoms is always larger than the HF value for the real atom. By this measure, the 4f screening of the 5d shell is incomplete for all atoms considered. Table 3 gives, for the pseudo-atoms only, the values of the expectation values of r^2, r^4, and $1/r^3$, as well as of r. These data may be of interest in further interpretation of particular phenomena.

Since the relativistic effects are expected to increase several fold for the atoms from 104 to 115 as compared to Hf to Bi, it is clear that extrapolation of trends downward in the periodic table will be a dangerous procedure. Relativistic (DHF) calculations are available for these heavier atoms and predictions of the chemical behavior should be based primarily upon the DHF calculations for those atoms.

Acknowledgement

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Table 1

Orbital Binding Energies (Atomic Units)

	5d		6S	6P	
	$(5d_{3/2})$	$(5d_{5/2})$	$(6S_{1/2})$	$(6P_{1/2})$	$(6P_{3/2})$
pseudo Hf	.3192		.1805		
Hf(HF)[a]	.2992		.2104		
Hf(DHF)[b]	.2473	.2355	.2397		
pseudo Re	.4660		.2031		
Re(HF)	.4538		.2347		
Re(DHF)	.3972	.3661	.2783		
pseudo Au	.5372		.1905		
Au(HF)	.5210		.2208		
Au(DHF)	.4935	.4287	.2917		
pseudo Hg	.7191		.2288		
Hg(HF)	.7142		.2610		
Hg(DHF)	.6501	.5746	.3280		
pseudo Tℓ	.9472		.3162	.1836	
Tℓ(HF)	.9683		.3611	.1924	
Tℓ(DHF)	.8945	.8062	.4492	.2114	.1765
pseudo Pb	1.1772		.4025	.2268	
Pb(HF)	1.2245		.4589	.2398	
Pb(DHF)	1.1388	1.0360	.5665	.2751	.2199
pseudo Bi	1.4131		.4906	.2693	
Bi(HF)	1.4874		.5582	.2862	
Bi(DHF)	1.1389	1.2710	.6862	.3385	.2612

[a] Ref. 1

[b] Ref. 3

Table 2

Comparison of Radial Expectation Values <R>

	5d		6s	6p	
	$d_{3/2}$	$d_{5/2}$	$p_{1/2}$		$p_{3/2}$
pseudo Hf	2.5048		4.6934		
Hf(HF)	2.2277		4.0684		
Hf(DHF)	2.3376	2.4198	3.6939		
pseudo Re	2.0326		4.2162		
Re(HF)	1.7999		3.6942		
Re(DHF)	1.8301	1.9047	3.2770		
pseudo Au	1.7228		4.2230		
Au(HF)	1.5433		3.7006		
Au(DHF)	1.5359	1.6185	3.0609		
pseudo Hg	1.6040		3.7500		
Hg(HF)	1.4327		3.3284		
Hg(DHF)	1.4312	1.4987	2.8434		
pseudo Tℓ	1.5042		3.3294	4.2434	
Tℓ(HF)	1.3412		2.9669	3.9262	
Tℓ(DHF)	1.3387	1.3940	2.5792	3.5166	4.0123
pseudo Pb	1.4214		3.0475	3.7532	
Pb(HF)	1.2671		2.7242	3.4569	
Pb(DHF)	1.2641	1.3119	2.3916	3.0739	3.5162
pseudo Bi	1.3506		2.8336	3.4116	
Bi(HF)	1.2046		2.5939	3.1366	
Bi(DHF)	1.2012	1.2439	2.2429	2.7802	3.1862

Table 3

Radial Expectation Values for Pseudo-Atoms

		$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^4 \rangle$	$\langle 1/r^3 \rangle$
pseudo Hf	5d	2.5048	7.3458	96.6674	3.0145
	6s	4.6934	25.0072	989.1202	0.0
pseudo Re	5d	2.0326	4.8066	40.2388	5.3119
	6s	4.2162	20.2725	662.4436	0.0
pseudo Au	5d	1.7228	3.4691	21.4367	8.4351
	6s	4.2230	20.5556	709.0442	0.0
pseudo Hg	5d	1.6040	2.9796	15.1079	10.0037
	6s	3.7500	16.1430	431.9519	0.0
pseudo Tℓ	5d	1.5042	2.6024	11.1225	11.7073
	6s	3.3294	12.6143	254.6935	0.0
	6p	4.2434	20.6855	711.8831	5.4981
pseudo Pb	5d	1.4214	2.3134	8.5795	13.5069
	6s	3.0475	10.5138	172.8892	0.0
	6p	3.7532	16.1076	424.2517	7.9580
pseudo Bi	5d	1.3506	2.0819	6.8258	15.4086
	6s	2.8336	9.0566	126.1273	0.0
	6p	3.4116	13.2660	283.8559	10.5510

FIGURE CAPTIONS

Figure 1. Orbital energies for valence-shell s-electrons. Dotted lines connect relativistic (DHF) values: solid lines connect non-relativistic (HF) values; pseudo-atoms are indicated as ps. Au and ps. Hg.

Figure 2. Orbital energies for valence-shell p-electrons. Separate $6p_{1/2}$ and $6p_{3/2}$ values are shown as well as the weighted average ($1/3\ p_{1/2} + 2/3\ p_{3/2}$) connected with the dotted line.

Figure 3. Expectation values for the radius $\langle r \rangle$ for the valence-shell s-electron.

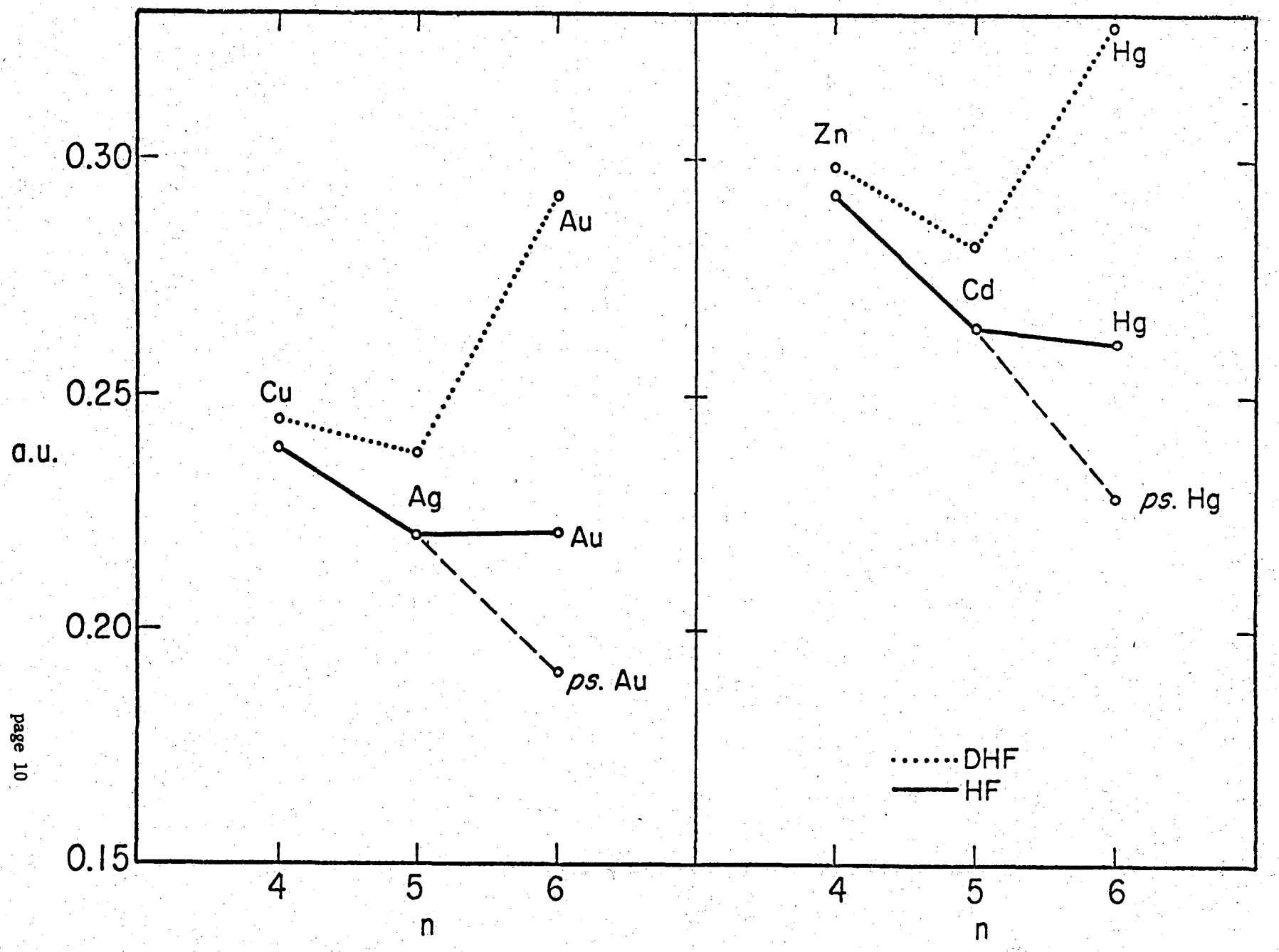

Fig. 1

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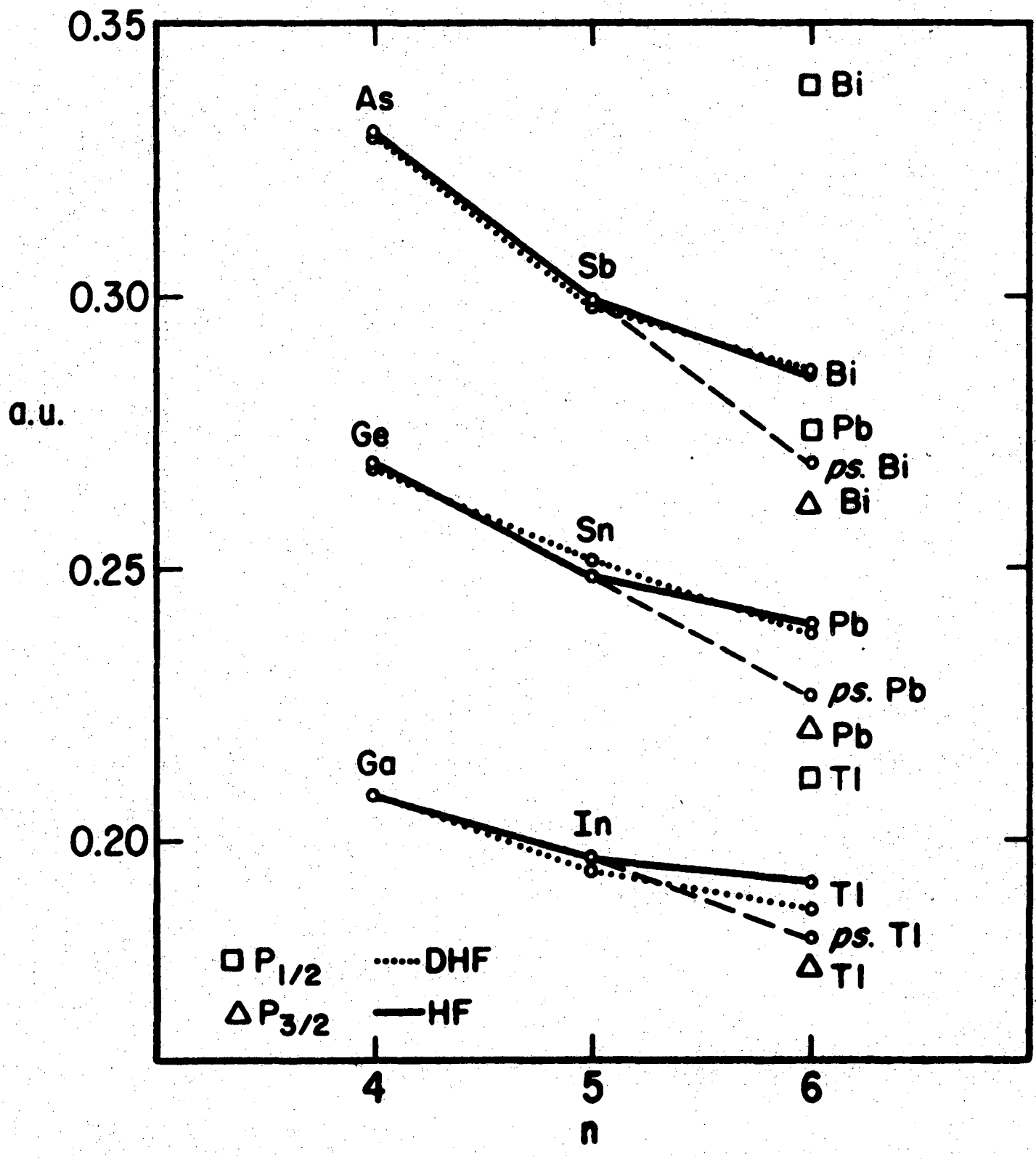

Fig. 2

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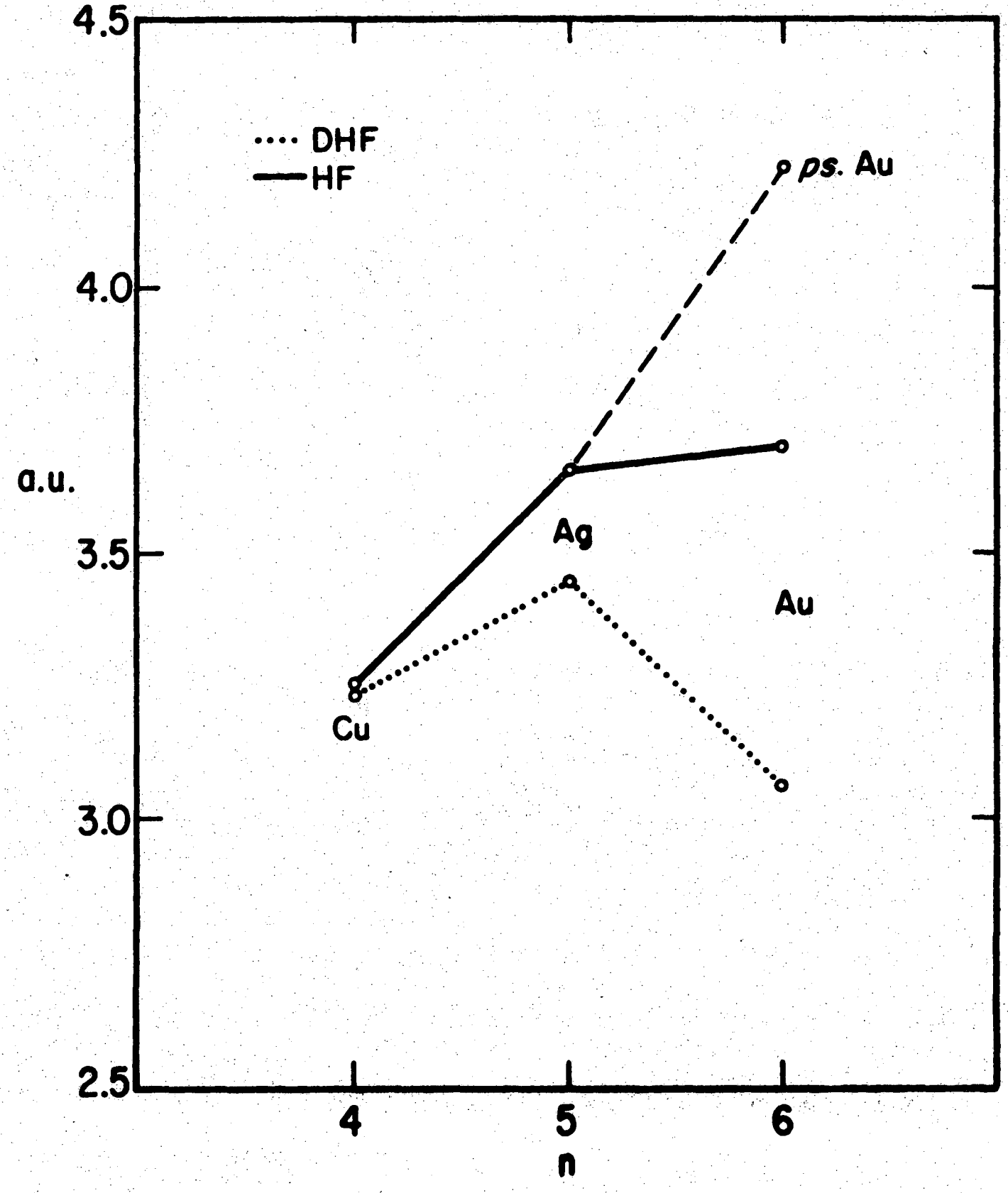

Fig. 3

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