Relativistic Effects on Atomic Properties

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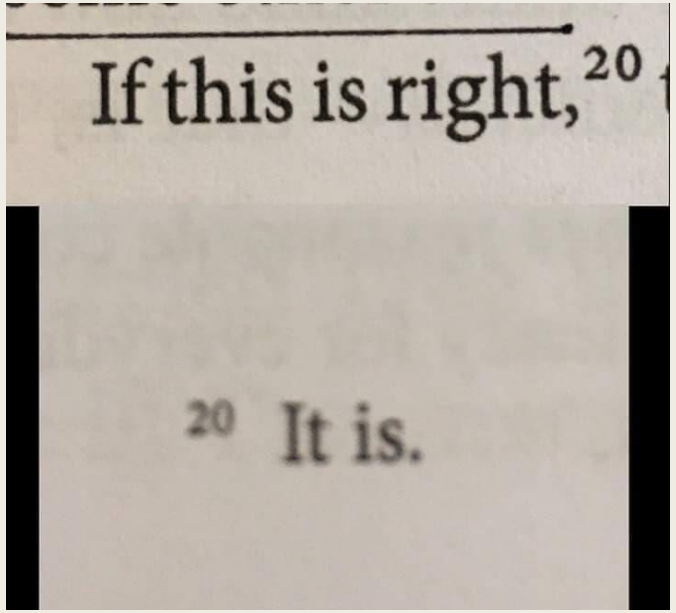
- Special Relativity
- Relativistic calculation of atoms
- Changes of properties in heavier elements

Sources

Kenneth S. Pitzer: Relativistic effects on chemical properties (1978)

Peter Schwerdtfeger: Relativistic effects in properties of gold (2002)



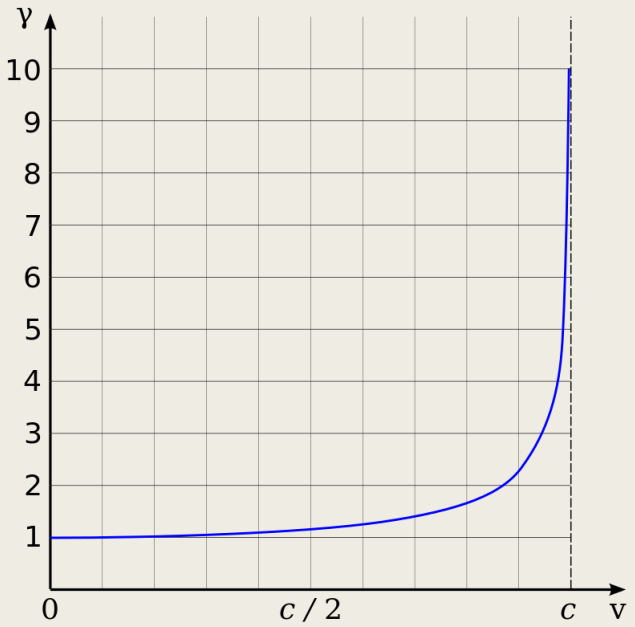
Special Theory of Relativity

Albert Einstein (1905)

Physical laws have the same form in each inertial references.

In heavy atoms: Bohr radius's mass dependence

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c\alpha}$$



$$m_{\mathrm{rel}} = \frac{m_e}{\sqrt{1-(v_e/c)^2}} \qquad a_{\mathrm{rel}} = \frac{\hbar\sqrt{1-(v_e/c)^2}}{m_e c\alpha}$$

Relativity in Atomic calculations

Many problems can be adequately approximated using the non-relativistic Schrödinger equation + rel. perturbations (such as spin-orbit interact.)

Heavier elements: high momentum electrons

Fully relativistic approach required.

Energy-momentum relation:

$$\hat{E}^2\psi = c^2\hat{\mathbf{p}}\cdot\hat{\mathbf{p}}\psi + (mc^2)^2\psi\,,$$

Dirac Equation

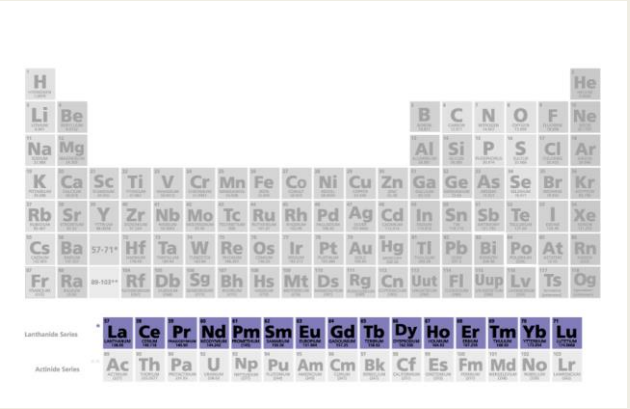
Anomalies: Lanthanide contraction, inert pair effect, unique properties of heavy elements (as gold or mercury), etc.

Table 1. Energy Terms for Fourth Group Elements in Electron Volts.

Element X	Ionization Potential	X_2 Bond D_e	Spin-Orbit $^3P_2$-$^3P_0$
C	11.26	6.1	0.005
Si	8.15	3.2	.03
Ge	7.88	2.8	.17
Sn	7.34	2.0	.42
Pb	7.42	1.0	1.32

Lanthanide Contraction

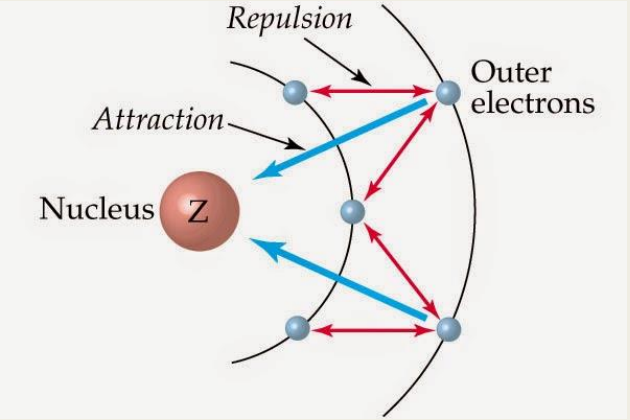
The decrease of the ionic radii of the elements in the lanhanide series.



Caused due to poor shielding of nuclear charge by the 4f electrons

- Shielding: s > p > d > f
- Lanthanides: increased effective core charge

Relativistic effect: The density of the s (and to a lesser degree p) electrons near the nucleus is high, thus these experience significant relativistic effects



Special relativity increases the contraction effect by

about 10%.

Post-lanthanides

To measure the effect of the 4f electrons, calculations can be made on relativistic, non-relativistic, and pseudo-atoms.

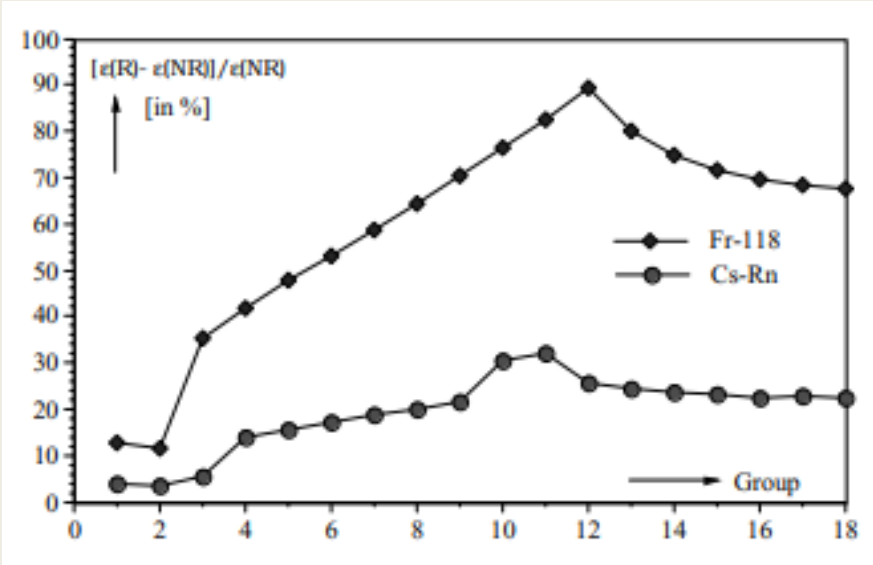
Increasing atomic number, the relativistic effects remain the same in magnitude, while the 4f effects decrease.

Note that the radius of d (and f) subshells increase in the relativistic case.

Table 3. Radii <r> in Å, Weighted Averages for Relativistic 5d and 6p.

	Pseudo-atom nonrelativ.			Real Atom nonrelativ.			Real Atom relativistic		
	5d	6s	6p	5d	6s	6p	5d	6s	6p
Hf	1.325	2.484		1.179	2.153		1.263	1.955	
Re	1.076	2.231		.952	1.955		.992	1.734	
Au	.912	2.235		.817	1.958		.839	1.620	
Hg	.849	1.984		.758	1.761		.779	1.515	
Tl		1.762	2.245		1.570	2.078		1.365	2.036
Pb		1.613	1.986		1.442	1.829		1.266	1.783
Bi		1.499	1.805		1.373	1.660		1.187	1.614

Pseudo atom: 4f orbitals deleted, atomic charge reduced by 14



Gold (group 11)

The relativistic effects in gold are very significant. (~0.58c for 1s electrons, ~22% contraction)

Due to contraction and expansion effects, the plasma frequency shifts into the visible range.

Relativistic increase in gold's electronegativity causes anomalies in its bonding properties:

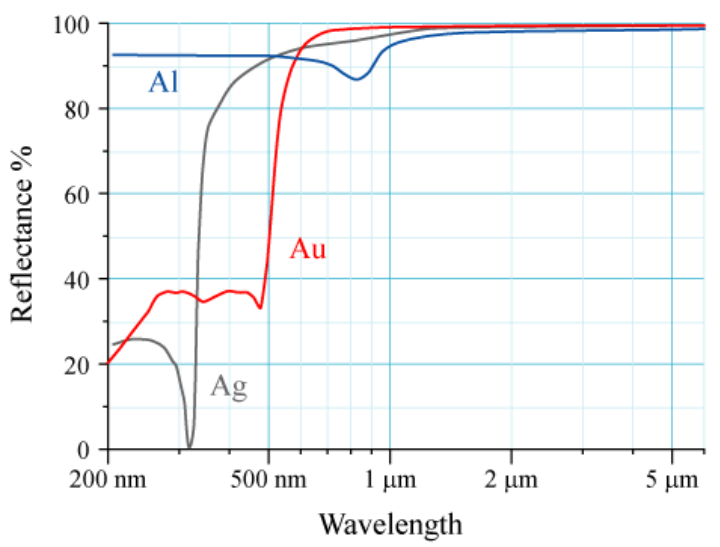
-$CsAu$ forms non-metallic semicond.

-High IP: difficult to oxidize

-5d participation: strong covalent bonds

-Aurophilicity (~28% of binding energy)

-Bond distance contraction



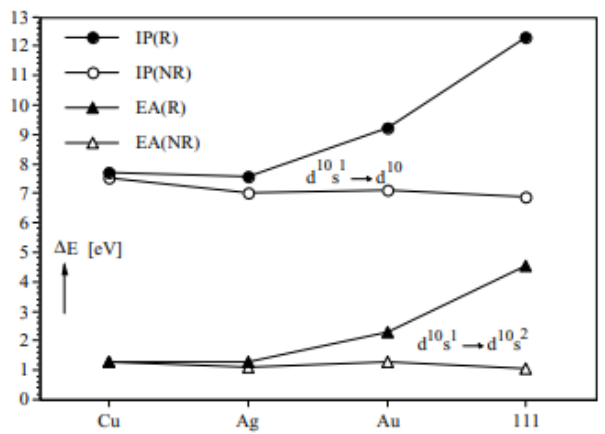


FIGURE 4 Nonrelativistic (NR) and relativistic (R) ionization potentials and electron affinities of the group 11 atoms. Data from Refs. [20] and [21].

Other relativistic phenomena

-Mercury is liquid at room temperature (~120 °C change in melting point)

-Metallophilic interactions in general

-Inert pair effect

-Lead forms FCC lattice instead of diamond