
# Relativistische Effekte

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Anorganische Experimentalchemie

# Wiederholung

Bohr

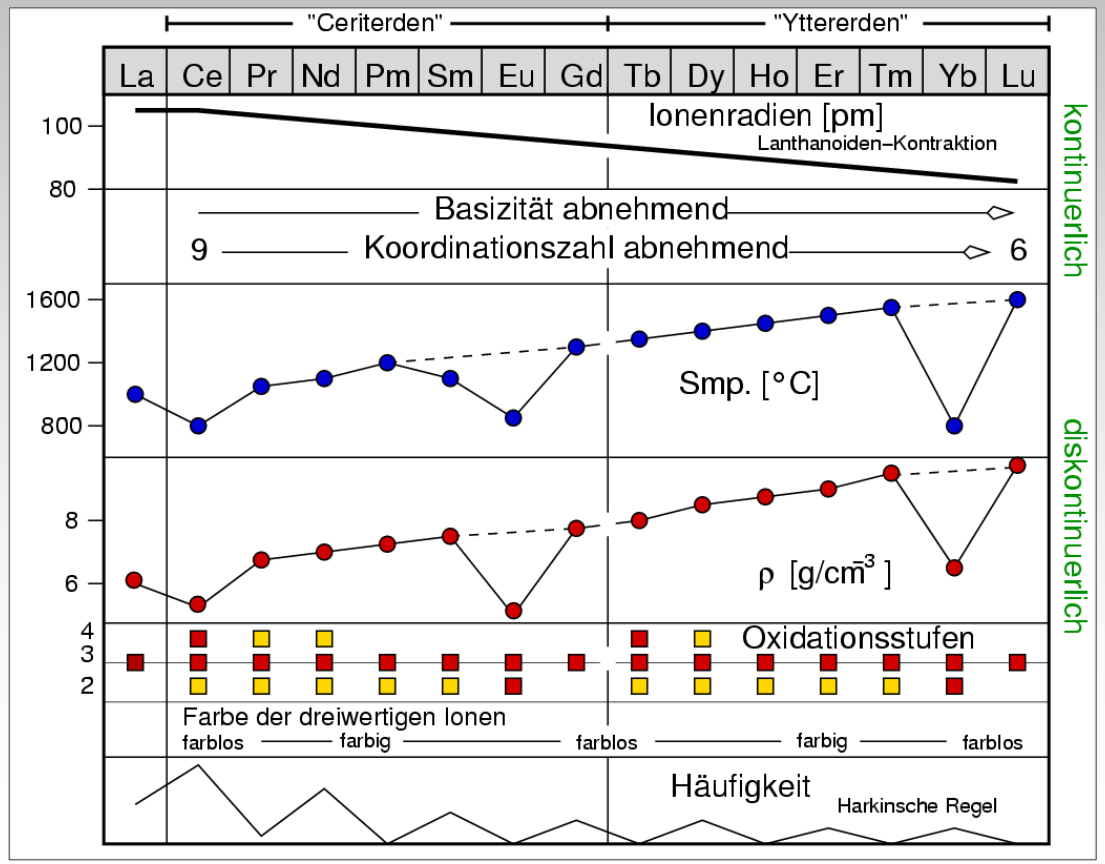
$$E = -\frac{Z\,e^2}{8\pi\varepsilon_0 r}$$

$$E = -\frac{Z\,e^2}{8\pi\varepsilon_0 r} = -\frac{Z^2 e^4 m}{8h^2\varepsilon_0^2}\frac{1}{n^2}$$

$$r = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2 Z}$$

# Lanthanoidenkontraktion (F-Block Kontaktion)

Ionenradius der Lanthanoide nimmt von Lanthan (57) zum Lutetium (71) ab. Außerdem ähneln sich die Atomgrößen der 2. und 3. Periode der Übergangsmetalle.




***Begr.:*** f-Orbitale sind sehr groß und diffus und schirmen Kernladung schlechter ab.

# d-Block-Kontraktion

## Post-transition-metal-Effekt

- Nichtmetalle der ersten langen Periode (Ga, Ge, As, Se, Br) bilden thermodynamisch instabile Verbindungen in ihren höchsten Oxidationsstufen (z.B. $BrO_4^-$ vs. $ClO_4^-$ und $IO_4^-$)

- Atomvolumen nimmt z.B. vom Aluminium zum Gallium ab.

Größere energetische Absenkung der 4s Orbitale im Vergleich zu den 4p Orbitalen!

| | $PCl_3$ | $AsCl_3$ |
|---|---|---|
| *l* / eV | 10.5 | 11.7 |
| > (Cl-E-Cl) / ° | 100 | 98 |

# Wiederholung

Bohr

$$E = -\frac{Z\,e^2}{8\pi\varepsilon_0 r}$$

$$E = -\frac{Z\,e^2}{8\pi\varepsilon_0 r} = -\frac{Z^2\,e^4\,m}{8h^2\varepsilon_0^2}\,\frac{1}{n^2}$$

$$r = \frac{n^2h^2\varepsilon_0}{\pi m e^2 Z}$$

$$n\hbar = mvr \qquad v = \frac{n\hbar}{mr}$$

$$r = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2 Z} \qquad r \propto n^2 \qquad r \propto \frac{1}{m}$$

$$v = \frac{Ze^2}{2nh\varepsilon_0} \qquad v \propto \frac{1}{n} \qquad v \propto Z$$

$$m = \frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \qquad c = 3 * 10^8 \,\mathrm{ms}^{-1} = 137 \,\mathrm{a.u.}$$

$$v \approx Z \,\mathrm{a.u.}$$

$$E = -\frac{e^2 Z}{8\pi\varepsilon_0 r} = -\frac{e^4 m Z^2}{8h^2 {\varepsilon_0}^2} \frac{1}{n^2}$$

# Relativistische Effekte

Quecksilber (Hg) $Z = 80$ $\frac{v}{c} = 0.58$

## I. Relativistische Kontaktion

1s Orbital: $r = a_0 = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2 Z}$

$$a_0(n-r) = \frac{\varepsilon_0 h^2}{\pi Z e^2 m_{n-r}} \qquad a_0(r) = \frac{\varepsilon_0 h^2}{\pi Z e^2 m_r}$$

$$\frac{a_0(n-r)}{a_0(r)} = \frac{m_r}{m_{nr}} = \frac{1.23 m_0}{m_0} = 1.23$$

$$a_r(\mathrm{Hg}) = \frac{a_{nr}(\mathrm{Hg})}{1.23} = 0.8\, a_{nr}(\mathrm{Hg})$$

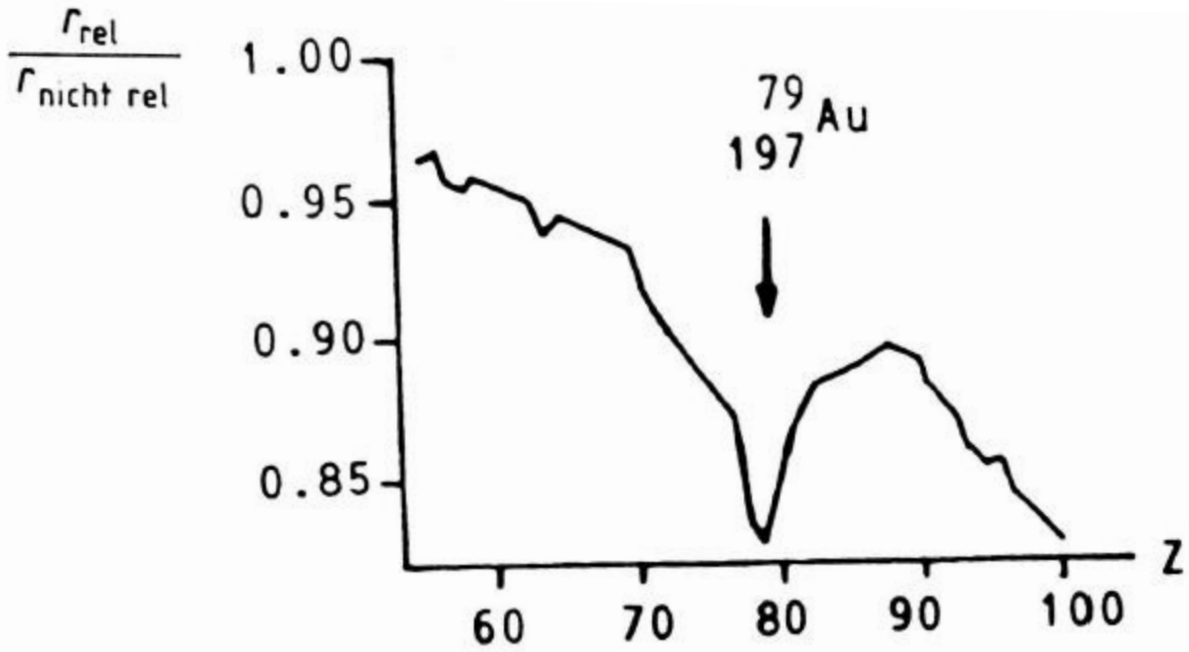
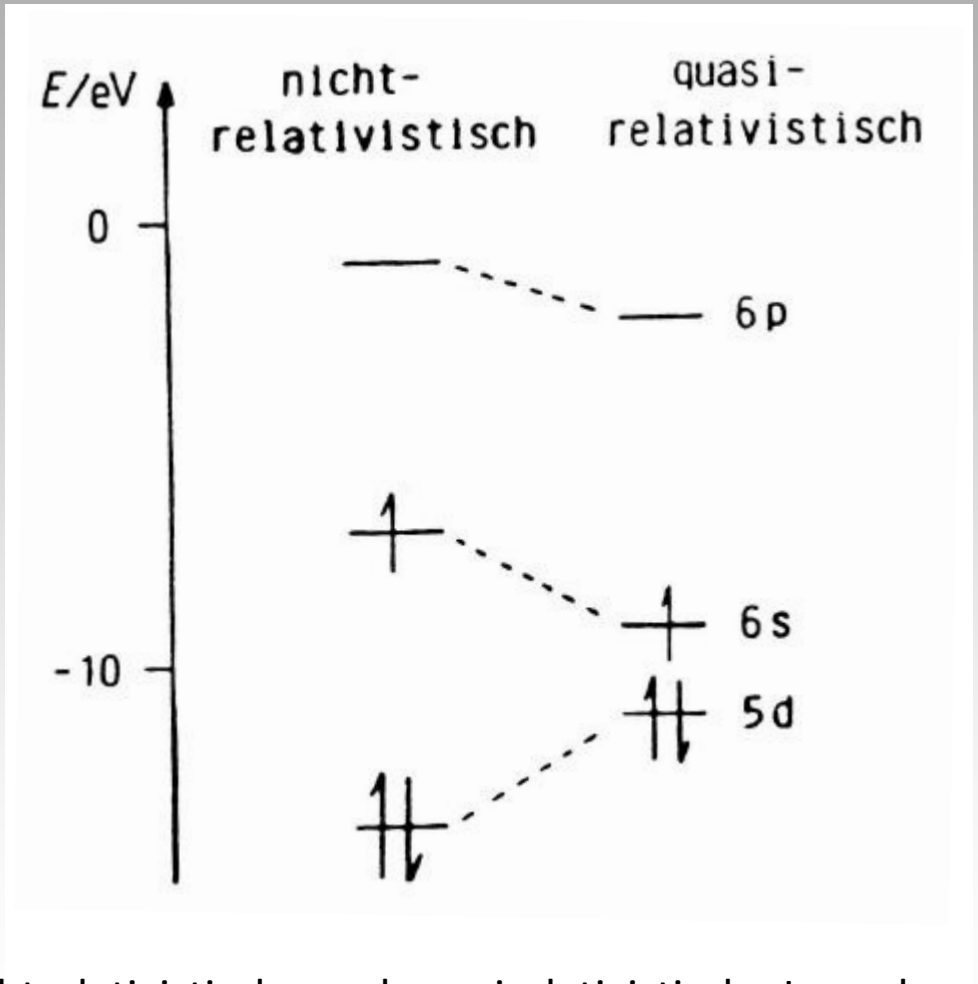



**Abbildung 1-46.** Relativistische Kontraktion der 6s-Orbitale (Werte von Dirac-Fock- und Hartree-Fock-Berechnungen).

der Elemente Cs ($Z = 55$) bis Fm ($Z = 100$)




Nichtrelativistische und quasirelativistische Lage der Grenzorbitale des Gold-Atoms

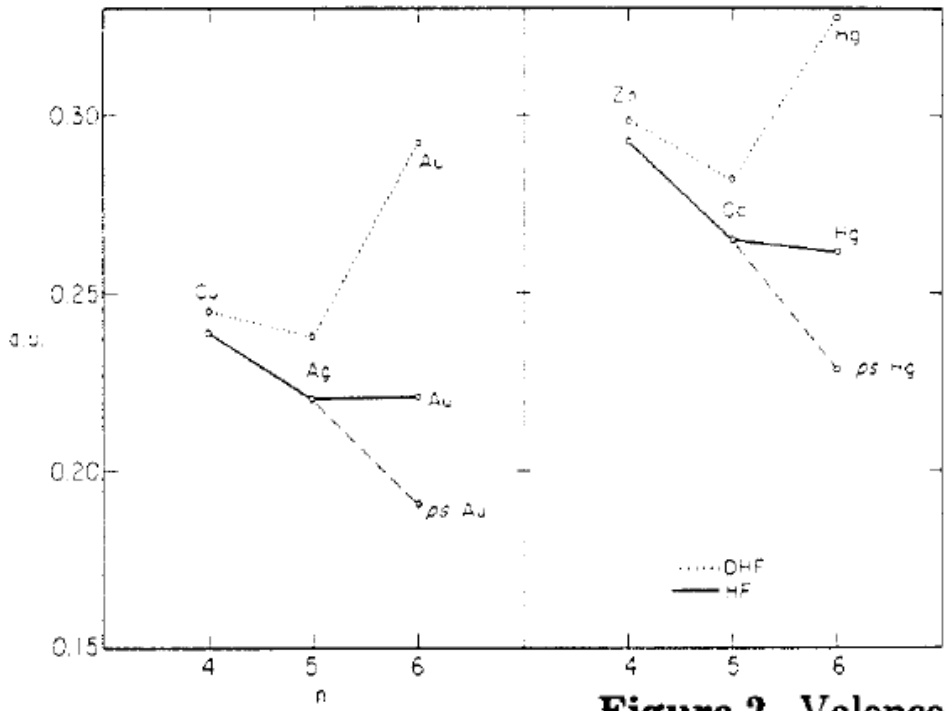





**Figure 2.** Valence s-orbital energies for the group 11 metals Cu, Ag, and Au and for the group 12 metals Zn, Cd, and Hg. The uppermost dotted curves are the relativistic curves, and the full curves in the middle are the nonrelativistic Hartree–Fock results of Desclaux.[37] The lowest, dashed curves are for the nonrelativistic "pseudoatoms" without 4f electrons.[54] The difference between "real" and "pseudo" is a measure of the "lanthanoid contraction". As seen, it is comparable with the relativistic effects. (Reproduced with permission from ref 54). The experimental $IP_1$ (7.726, 7.576, and 9.225 eV for Cu, Ag, and Au or 9.394, 8.993, and 10.437 eV for Zn, Cd, and Hg, respectively) parallel the highest dotted curve.

# Relativistische Effekte

Bohr:

$$v = \frac{n\hbar}{rm}$$

$$r = \frac{h^2 \varepsilon_0 n^2}{\pi m Z e^2}$$

$$c \to \infty$$
$$m = m_0$$

Relativistisch:

$$\Delta m = m - m_0$$

Kinematisch:

$$m = \frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

$$c = 3 * 10^8 \,\mathrm{ms}^{-1} = 137 \,\mathrm{a.u.}$$

$$v = \mathrm{Z} * \mathrm{a.u.}$$

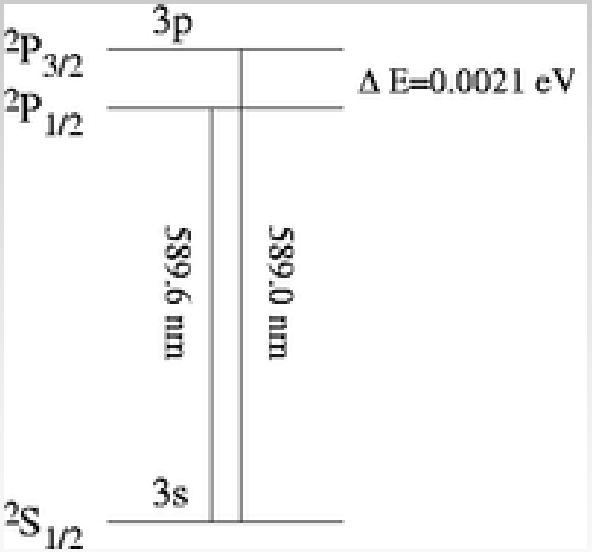
Hg: $\mathrm{Z} = 80$ $\quad v = 80 \,\mathrm{a.u.}$ $\quad m = \frac{m_0}{\sqrt{1-\left(\frac{80}{137}\right)^2}} = 1.23 m_0$

## II. Spin-Orbit Splitting

$$j = l + s$$

p Elektron: $l = 1, \quad s = \frac{1}{2}$

$$\Rightarrow \quad j = \frac{1}{2}, \frac{3}{2}$$




## II. rel self-consistent expansion

| | |
|---|---|
| **s, p** | **Kontraktion** |
| **d,f** | **Expansion** |

**Table 11.7** Relativistic bond-length contractions

| Element | Molecule | $d_{nr}$ (in Å) | $d_r$ (in Å) | $d_{exp.}$ (in Å) | C (in Å)[a] |
|---|---|---|---|---|---|
| H | $H_2$ | 0.73354 | 0.73352 | 0.74152 | 0.000017 |
| Ge | $GeH_4$ | 1.596 | 1.586 | 1.527 | 0.01 |
| Sn | $SnH_4$ | 1.736 | 1.717 | 1.701 | 0.02 |
| Pb | $PbH_4$ | 1.890 | 1.782 | 1.754 | 0.11 |

[a] *C*, the relativistic contraction, is the difference between the non-relativistic and relativistic bond lengths.

**Table 11.8** Energy terms for group 14 elements (eV)

| Element E | Ionization energy | $E_2$ bond dissociation energy | Spin–orbit coupling[a] $^3p_2$–$^3p_0$ |
|---|---|---|---|
| C | 11.26 | 6.1 | 0.005 |
| Si | 8.15 | 3.2 | 0.03 |
| Ge | 7.88 | 2.8 | 0.17 |
| Sn | 7.34 | 2.0 | 0.42 |
| Pb | 7.42 | 1.0 | 1.32 |

[a] 3P stands for S=1 and L=1.

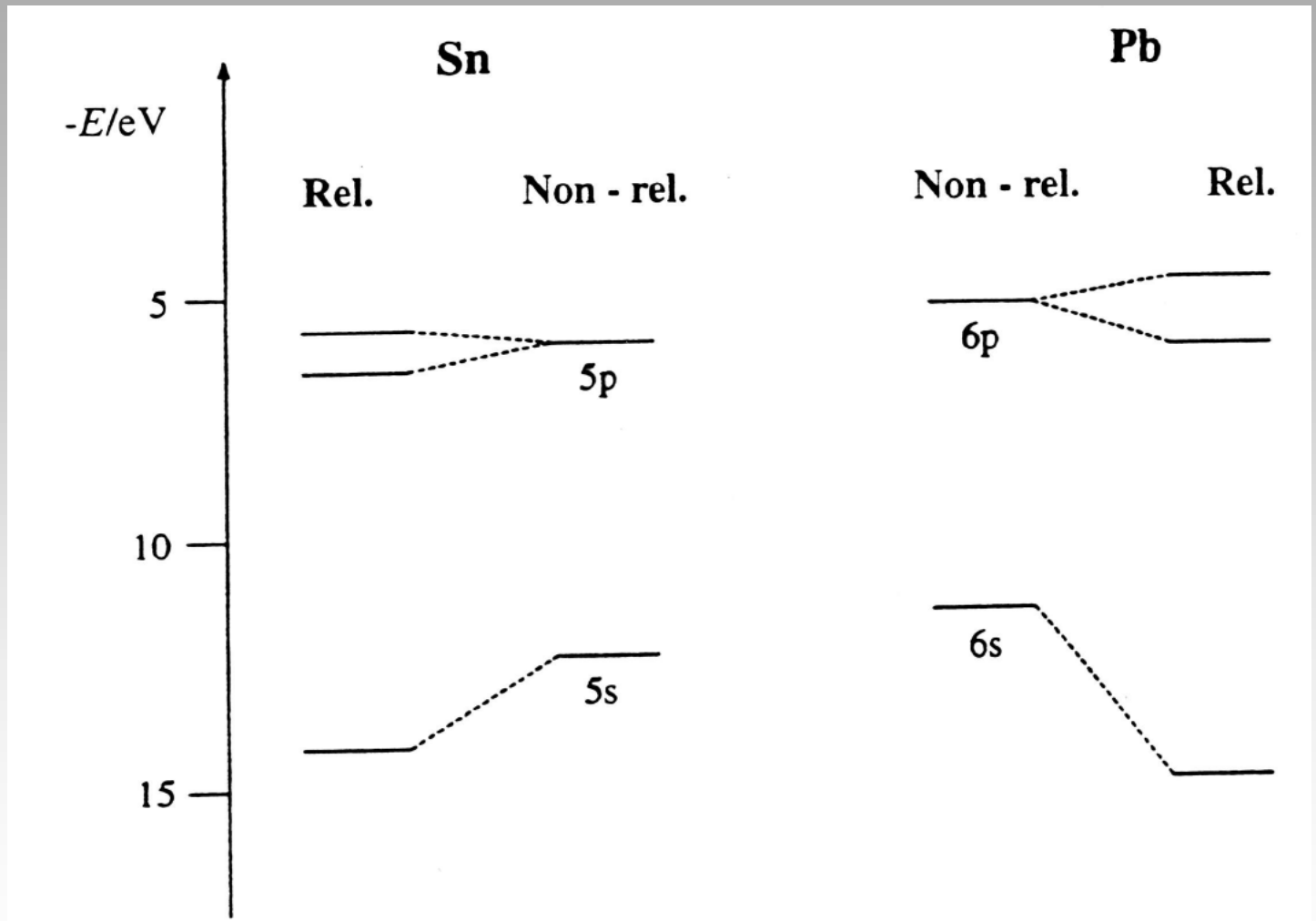
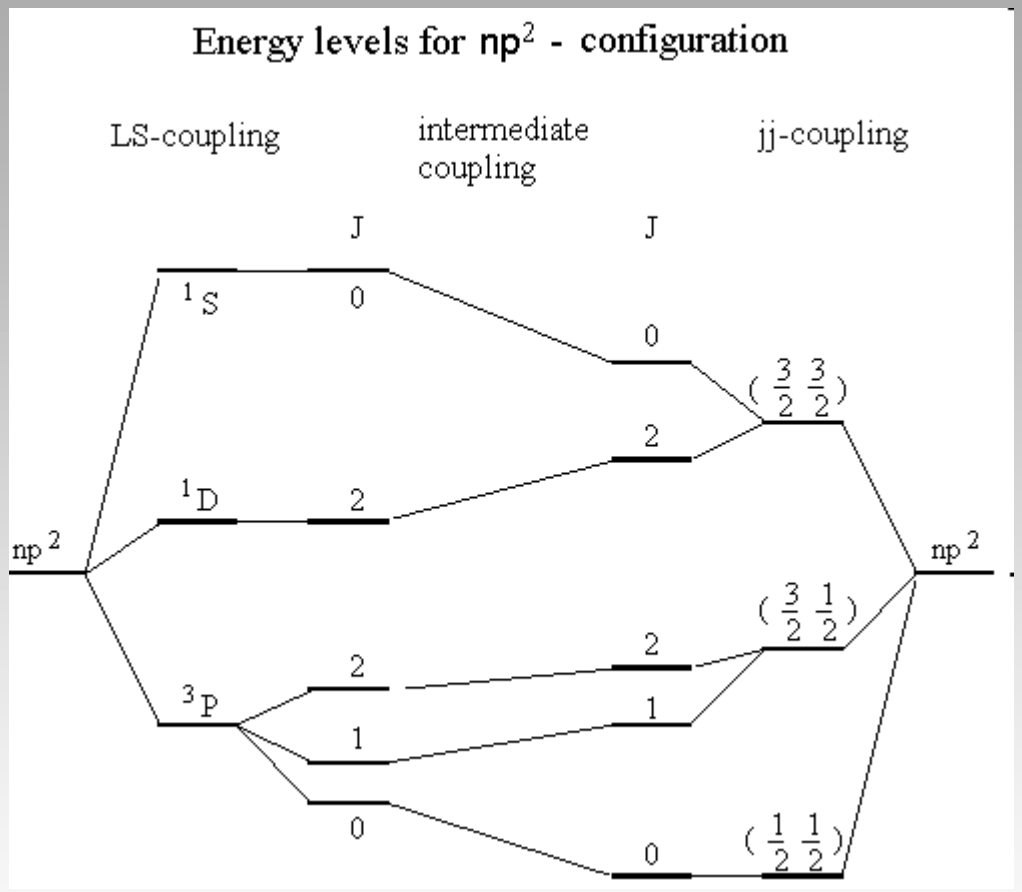



**Figure 11.9** Relativistic and non-relativistic Hartree–Fock orbital energies for tin and lead

# j-j-Kopplung




L-S-Kopplung

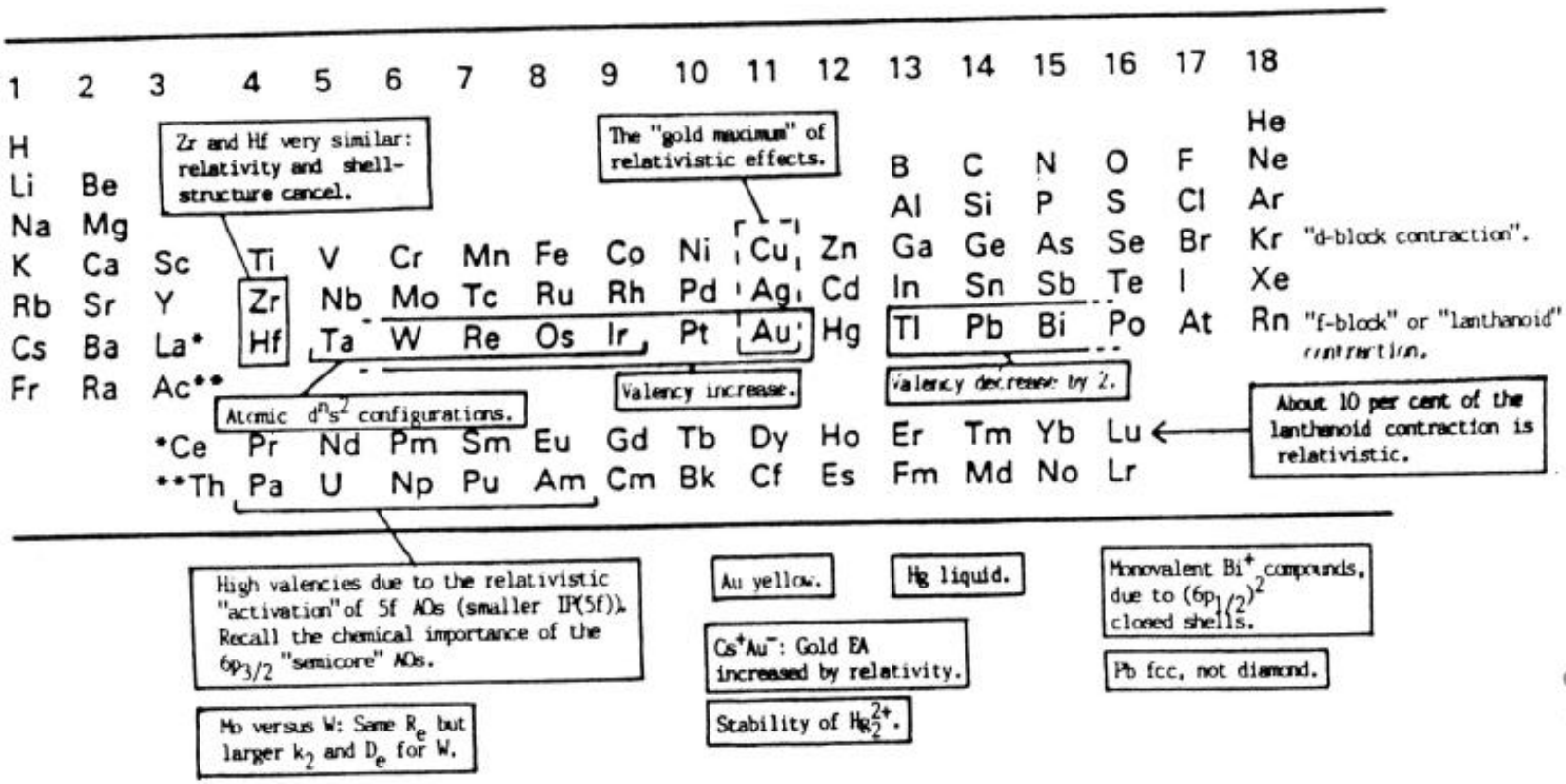
$$J = L + S$$

$$L = \sum_i l_i$$

$$S = \sum_i s_i$$

j-j-Kopplung

$$J = \sum_i j_i = \sum_i (l_i + s_i)$$




Relativity and the Periodic Table: a summary.

# Copernicium

**Copernicium** ist ein radioaktives, künstlich erzeugtes, nicht natürlich vorkommendes chemisches Element mit dem Elementsymbol Cn und der Ordnungszahl 112, das zu den Transactinoiden gehört und im Periodensystem der Elemente in der 12. IUPAC-Gruppe, der Zinkgruppe, steht.

**Inhaltsverzeichnis** [Verbergen]



## Gewinnung und Darstellung [ Bearbeiten | Quelltext bearbeiten ]


Nikolaus Kopernikus, Namenspatron des Copernicium

Copernicium wurde erstmals am 9. Februar 1996 bei der Gesellschaft für Schwerionenforschung (GSI) in Darmstadt von Sigurd Hofmann und Victor Ninov durch Fusion eines Zink-($^{70}$Zn)- und eines Blei-($^{208}$Pb)-Atomkerns erzeugt:[2]

$$^{70}_{30}\mathrm{Zn} + {}^{208}_{82}\mathrm{Pb} \rightarrow {}^{278}_{112}\mathrm{Cn}^{*} \rightarrow {}^{277}_{112}\mathrm{Cn} + {}^{1}_{0}\mathrm{n}$$

## Eigenschaften [ Bearbeiten | Quelltext bearbeiten ]

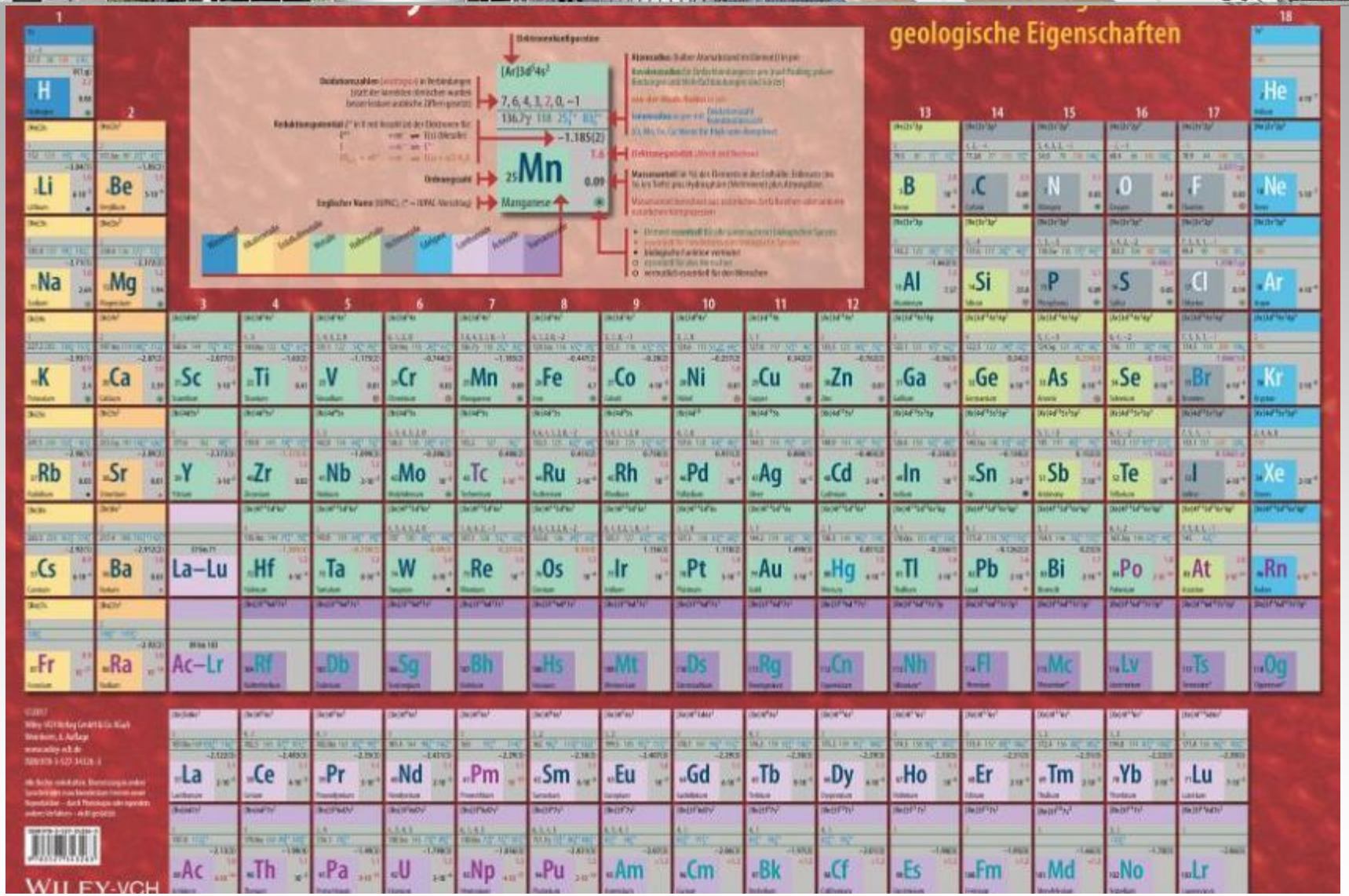
Nach Pressemitteilungen des Paul Scherrer Instituts und der Universität Bern am 31. Mai 2006 ergaben Experimente, dass Copernicium sich chemisch ähnlich wie Quecksilber (Hg) verhalte.[3][4] Diese Aussage stützt sich auf die Beobachtung von lediglich zwei Atomen $^{283}$Cn. Diese entstanden durch den Beschuss von Plutonium mit Calcium und hatten eine Halbwertszeit von etwa vier Sekunden.[5]

## Namensgebung [ Bearbeiten | Quelltext bearbeiten ]

Vor der endgültigen Namensgebung hatte das Element den systematischen Namen **Ununbium** (chemisches Symbol *Uub*), eine Bildung aus lateinisch *unum* für ‚eins' und lateinisch *bis* für ‚zweimal', entsprechend der Ordnungszahl 112. Es wurde auch als **Eka-Quecksilber** bezeichnet, zusammengesetzt aus Sanskrit एक *eka* für ‚eins' und *Quecksilber*, mit Bezug auf seine Einordnung im Periodensystem ‚eine Stelle unterhalb des Quecksilbers'.

Die Entdeckung wurde im Mai 2009 von der IUPAC anerkannt[6] und am 10. Juni 2009 offiziell bestätigt.[7] Am 14. Juli 2009 wurde von der GSI der Name *Copernicium* (zunächst mit dem chemischen Symbol Cp) zu Ehren von Nikolaus Kopernikus (1473–1543) vorgeschlagen.[8] Dieser Vorschlag wurde durch die IUPAC geprüft und am 19. Februar 2010, dem 537. Geburtstag des Astronomen, offiziell bekanntgegeben, nun mit dem chemischen Symbol Cn.[9][10]

Das zunächst vorgeschlagene Symbol Cp wurde bis 1949 im deutschen Sprachraum für das Element *Cassiopeium* verwendet, das heute Lutetium (Lu) genannt wird.[11][12] Darüber hinaus wird das Symbol Cp in der metallorganischen Chemie verwendet, um den Cyclopentadienyl-Liganden zu bezeichnen. Aus diesem Grund erlaubte die IUPAC nicht den Gebrauch des Symbols Cp für Copernicium und schlug stattdessen das Symbol Cn als Alternative vor.[9]


geologische Eigenschaften
[Ar]3d⁵4s²
7, 6, 4, 3, 2, 0, −1
−1.185(2)
25 Mn
0.09
Manganese
WILEY-VCH

**Superheavy Elements**

International Edition: DOI: 10.1002/anie.201906966
German Edition: DOI: 10.1002/ange.201906966

# Copernicium: A Relativistic Noble Liquid

*Jan-Michael Mewes,* Odile R. Smits, Georg Kresse, and Peter Schwerdtfeger*

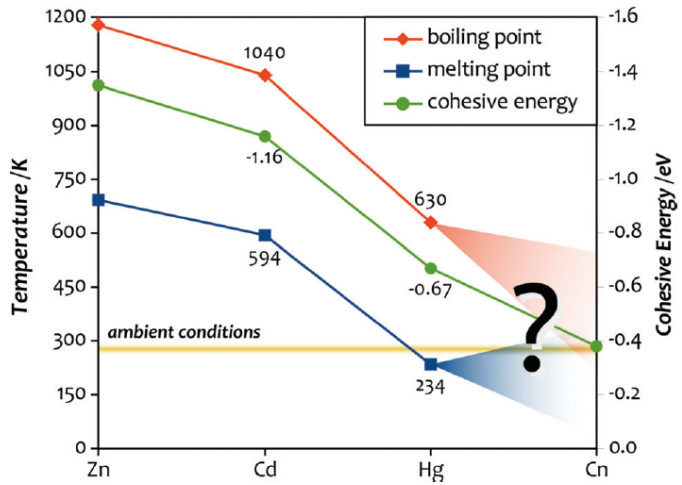



***Figure 1.*** Melting and boiling points (in K) as well as cohesive energies (lattice energy of the most stable phase in eV/atom) of the Group 12 elements zinc (Zn), cadmium (Cd), mercury (Hg), and copernicium (Cn).[17,18] The yellow area indicates ambient conditions, for which we assume a temperature range of 288.15–298.15 K (15–25 °C) based on the standard ambient temperature and pressure (SAPT of IUPAC: 25 °C), normal temperature and pressure (NTP of NIST, 15 °C), and international standard atmosphere (ISA, 20 °C).

***Table 1:*** Experimental and calculated cohesive energies ($E_{coh}$, in eV) and nearest-neighbor distances ($R_{nn}$, in Å) for the most stable *hcp* phase of Cn at the reference method-of-increments CCSD(T) level compared to spin–orbit, scalar-relativistic, and non-relativistic DFT/PBEsol. More functionals are shown in the Supporting Information.

| Level | $E_{coh}$ | Δref | $R_{nn}$ |
|---|---|---|---|
| Experimental[a] | −0.37 ± 0.11 | | |
| *spin–orbit relativistic* | | | |
| MOI-CCSD(T) | −0.376 ± 0.030 | | 3.465 |
| PBEsol ($c/a$ = 1.635) | −0.349 | +0.027 | 3.478 |
| λPBEsol | −0.373 | +0.003 | 3.478 |
| *scalar-relativistic* | | | |
| MOI-CCSD(T)[b] | −0.319 | | 3.465 |
| PBEsol ($c/a$ = 1.620) | −0.298 | +0.021 | 3.503 |
| λPBEsol | −0.317 | +0.002 | 3.503 |
| *non-relativistic*[c] | | | |
| PBEsol ($c/a$ = 1.737) | −1.333 | | 3.503 |

[a] Estimated from the adsorption enthalpy on gold[4] using the updated relation from Ref. [19]. See also Ref. [25]. [b] SR-CCSD(T) calculations employ the same structure as SO. [c] Because of the distorted $c/a$ ratio, $R_{nn}$ is between in-plane atoms, whereas it is across two planes at the relativistic level.

## Conclusion

In summary, we have explored the physicochemical properties of bulk copernicium by means of free-energy and band-structure calculations. This revealed that at ambient conditions, Cn is a volatile liquid with a melting point of 283 ± 11 K and a boiling point of 340 ± 10 K and only slightly more dense than Hg ($\rho_l^{300K} = 14.0\ g\,cm^{-3}$). We can thus fully confirm Pitzer's original hypothesis that Cn is either gaseous or a volatile liquid bound by dispersion.[16] Although the calculated boiling point is just below and well within the error bars of the evaporation temperature of $357^{+111}_{-108}$ K suggested by Eichler,[4] we can most certainly exclude the inferred metallic character based on the calculated band gap of 6.4 eV. On the contrary, we found a dominance of dispersion interactions in bulk Cn very similar to Rn, which together with the band gap and the structural parameters of solid Cn strongly suggests a weakly interacting, noble-gas-like character. The similarity to the noble gases is reflected also in the reactivity of Cn towards fluorine, which has been predicted to be similar to that of Xe (data available for Rn is insufficient to draw any such conclusions). Like Xe, Cn forms thermodynamically stable di- and tetrafluorides with calculated energies of formation ($\Delta U_0$ with respect to $F_2$ and atomic Cn) of −2.5 eV for $CnF_2$ and −3.6 eV for $CnF_4$ at the SO–CCSD(T)/DZ level.[10] Taking into account the basis-set superposition error resulting from the small DZ basis, and moreover the absence of zero-point and thermo-chemical corrections in these calculations, the values for Cn are at least comparable to the respective standard enthalpies of formation ($\Delta H_f^\circ$) of $XeF_2$ (−1.0 eV) and $XeF_4$ (−2.5 eV).[35] Hence, while the noble-gas-like character of Cn certainly has to be confirmed in further investigations focusing on the chemical bonding of Cn with electropositive and electronegative elements, and specifically the comparison to Xe and Rn, our results strongly suggest that bulk Cn behaves more like a noble gas than Og as the actual Group 18 member, and may thus be seen as the clandestine noble gas of the seventh period. Finally, the non-group-conforming behavior of Cn was traced back to the presence of strong scalar-relativistic effects. Neglecting relativity leads to an almost fourfold increase of the cohesive energy, and in turn to an increase of the melting and boiling points by 300 K and 700 K. Hence, the liquid aggregate state as well as the weakly interacting nature of Cn are both due to relativistic effects or, in other words, Cn is a relativistic noble liquid.

**Literatur**: K. S. Pitzer, *Acc. Chem. Res.* **1979**, *12(8)*, 271 – 276.

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