



Relativistische Effekte

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29. Oktober 2025

Anorganische Experimentalchemie

Wiederholung

Bohr

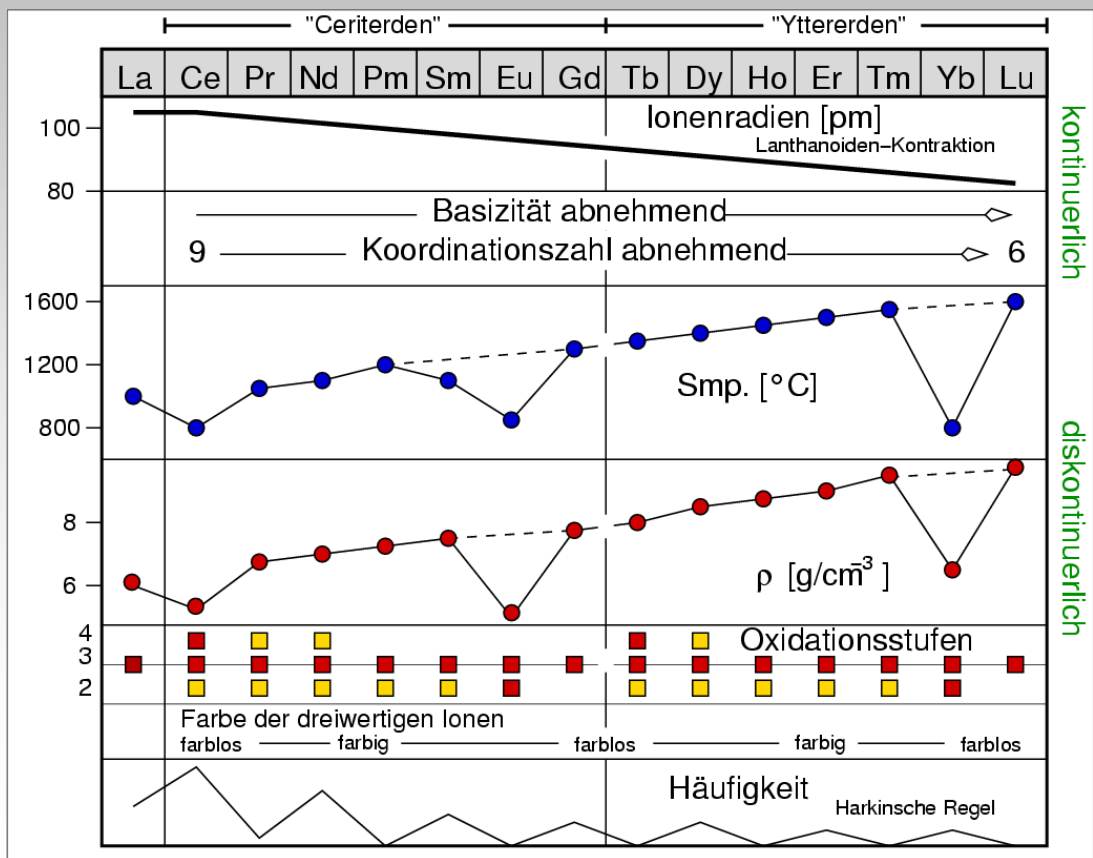
$$E = - \frac{z e^2}{8\pi\epsilon_0 r}$$

$$E = - \frac{z e^2}{8\pi\epsilon_0 r} = - \frac{z^2 e^4 m}{8h^2 \epsilon_0^2} \frac{1}{n^2}$$

$$r = \frac{n^2 h^2 \epsilon_0}{\pi m e^2 z}$$

Lanthanoidenkontraktion (f-Block Kontraktion)

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
I / eV	10.5	11.7
$\angle (\text{Cl-E-Cl}) / ^\circ$	100	98

Wiederholung

Bohr

$$E = - \frac{z e^2}{8\pi\epsilon_0 r}$$

$$E = - \frac{z e^2}{8\pi\epsilon_0 r} = - \frac{z^2 e^4 m}{8h^2 \epsilon_0^2} \frac{1}{n^2}$$

$$r = \frac{n^2 h^2 \epsilon_0}{\pi m e^2 z}$$

$$n\hbar = mvr$$

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

$$r = \frac{n^2 h^2 \epsilon_0}{\pi m e^2 Z}$$

$$r \propto n^2$$

$$r \propto \frac{1}{m}$$

$$v = \frac{Ze^2}{2nh\epsilon_0}$$

$$v \propto \frac{1}{n}$$

$$v \propto Z$$

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

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

$$v \approx Z \text{ a. u.}$$

$$E = -\frac{e^2 Z}{8\pi\epsilon_0 r} = -\frac{e^4 m Z^2}{8h^2 \epsilon_0^2} \frac{1}{n^2}$$

Relativistische Effekte

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

I. Relativistische Kontraktion

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

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

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

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

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

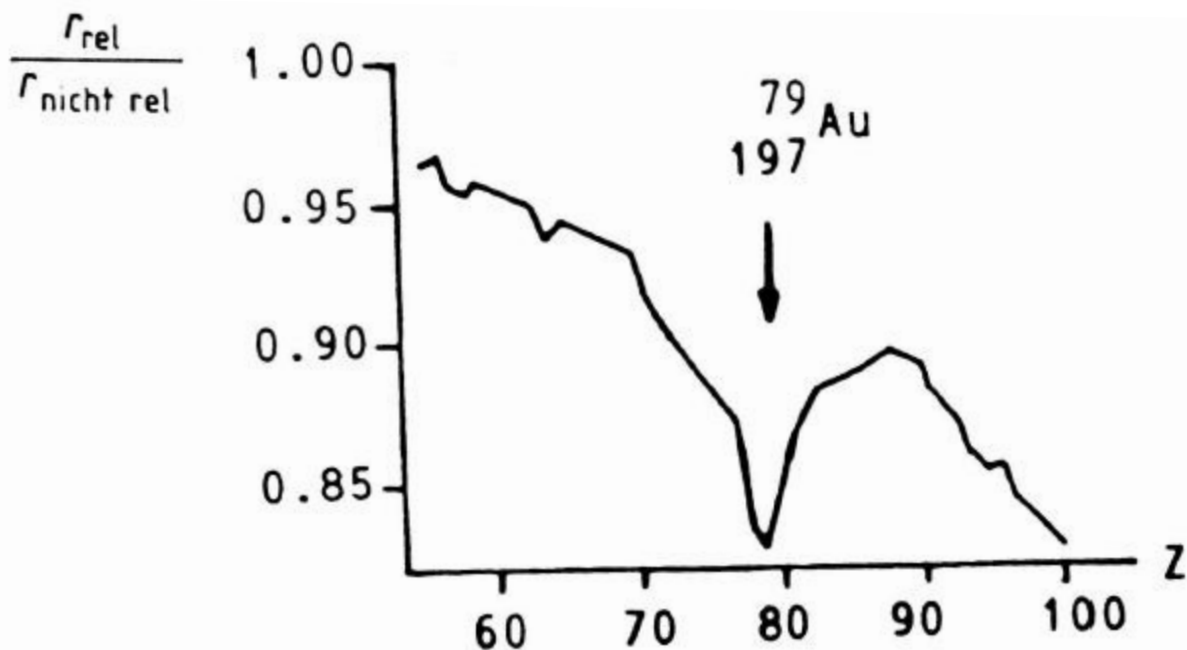
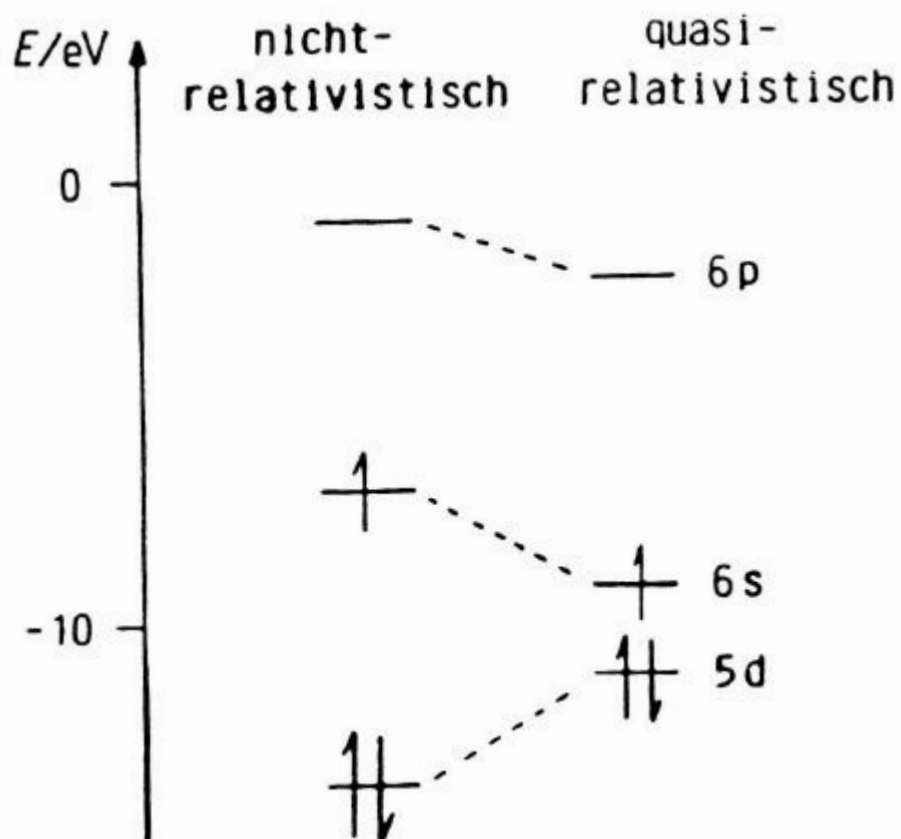


Abbildung 1-46. Relativistische Kontraktion der 6s-Orbitale (Werte von Dirac-Fock- und Hartree-Fock-Berechnungen).
der Elemente Cs ($Z = 55$) bis Fm ($Z = 100$)



Nichtrelativistische und quasirelativistische Lage der Grenzorbitale des Gold-Atoms

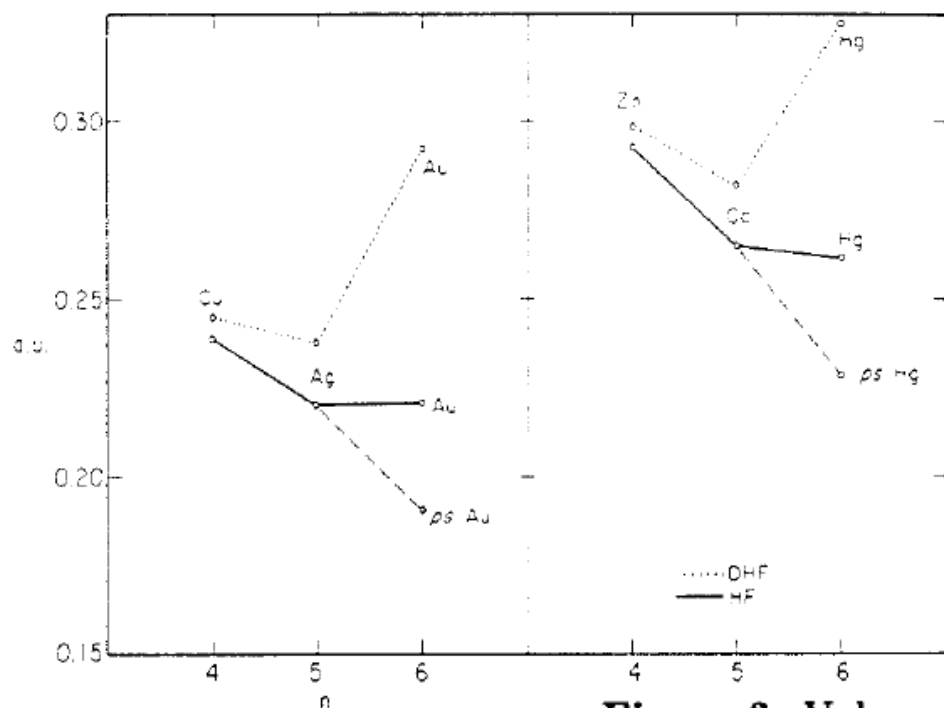


Figure 2. Valence s-orbital energies for the group 11 metals Cu, Ag, and Au and for the group 12 metals Zn, Cd, and Hg. The uppermost dotted curves are the relativistic curves, and the full curves in the middle are the nonrelativistic Hartree–Fock results of Desclaux.³⁷ The lowest, dashed curves are 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:

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

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

$$\begin{aligned} c &\rightarrow \infty \\ m &= m_0 \end{aligned}$$

Relativistisch:

$$\Delta m = m - m_0$$

Kinematisch:

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

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

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

Hg: $Z = 80$

$$v = 80 \text{ a.u.}$$

$$m = \frac{m_0}{\sqrt{1 - \left(\frac{80}{137}\right)^2}} = 1.23 m_0$$

II. Spin-Orbit Splitting

$$j = l + s$$

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

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

II. rel self-consistent expansion

s, p
d, f

Kontraktion
Expansion

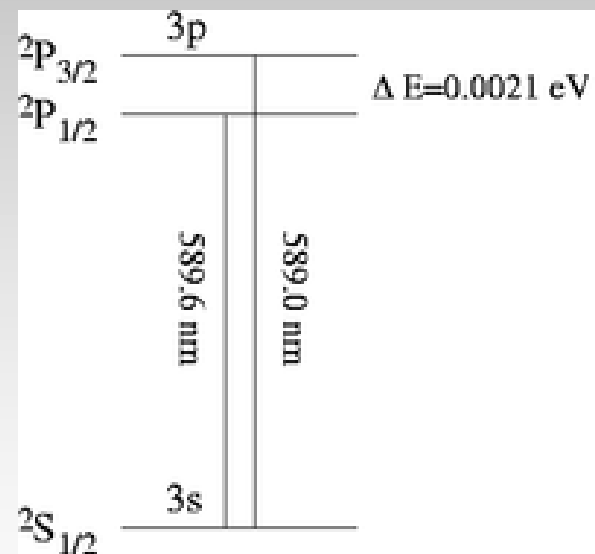


Table 11.7 Relativistic bond-length contractions

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 $L=1$.

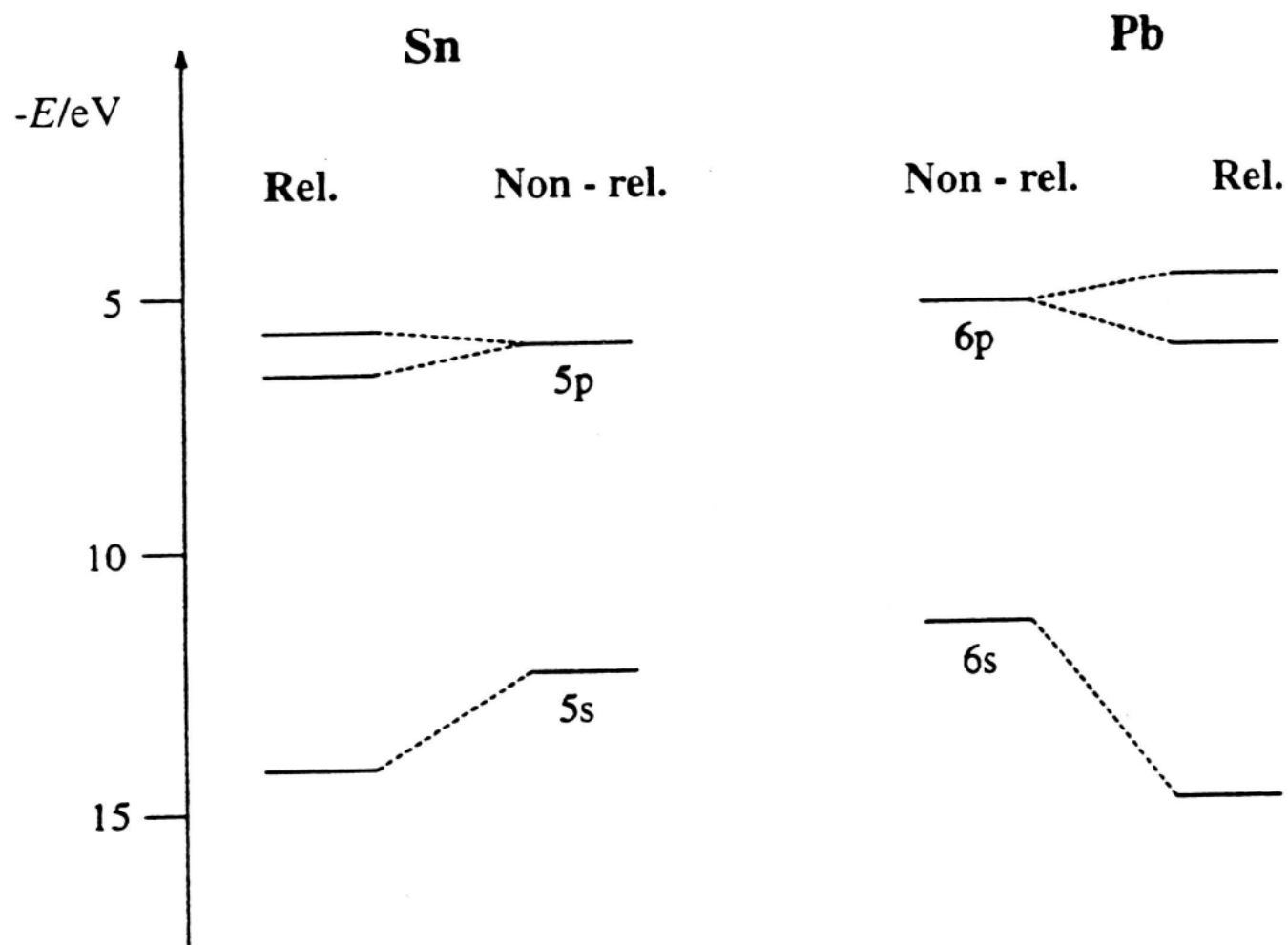


Figure 11.9 Relativistic and non-relativistic Hartree-Fock orbital energies for tin and lead

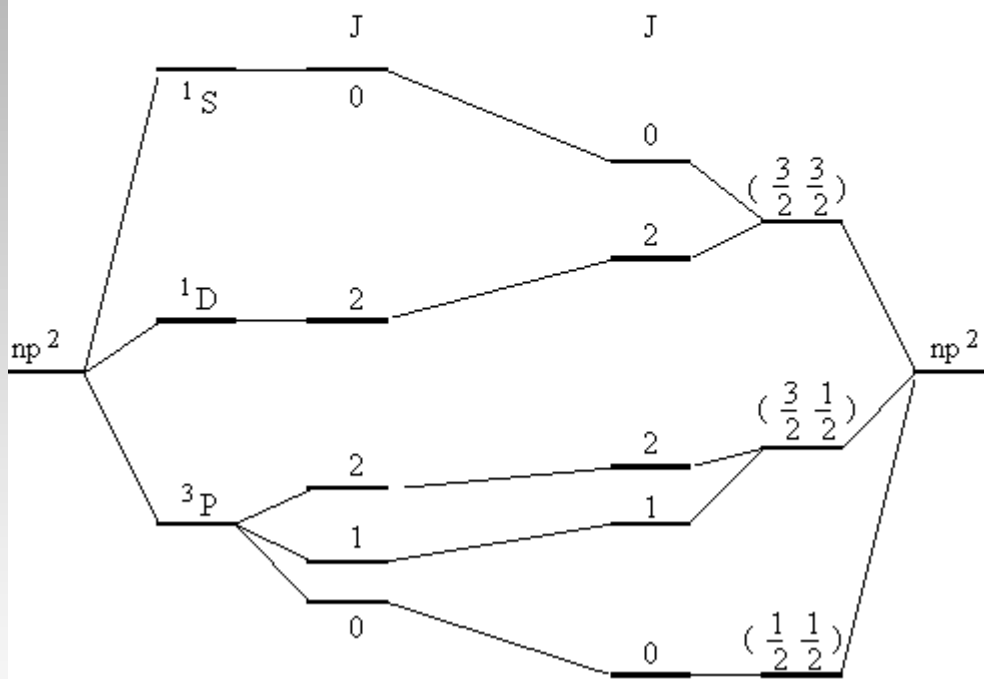


Energy levels for np^2 - configuration

LS-coupling

intermediate
coupling

jj-coupling



L-S-Kopplung

j-j-Kopplung

$$J = L + S$$

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

$$L = \sum_i l_i$$

$$S = \sum_i s_i$$

Recommended Format for the Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**															
		*Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		**Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Zr and Hf very similar: relativity and shell-structure cancel.
 The "gold maximum" of relativistic effects.
 "d-block contraction".
 "f-block" or "lanthanoid" contraction.
 About 10 per cent of the lanthanoid contraction is relativistic.
 Atomic $d^n s^2$ configurations.
 Valency increase.
 Valency decrease by 2.
 High valencies due to the relativistic "activation" of 5f AOs (smaller $IP(5f)$). Recall the chemical importance of the $6p_{3/2}$ "semicore" AOs.
 Mo versus W: Same R_e but larger k_2 and D_e for W.
 Au yellow.
 Hg liquid.
 Monovalent Bi^+ compounds, due to $(6p_{1/2})^2$ closed shells.
 Pb fcc, not diamond.
 Cs^+Au^- : Gold EA increased by relativity.
 Stability of Hg_2^{2+} .

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.

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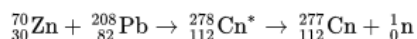
- 1 Gewinnung und Darstellung
- 2 Eigenschaften
- 3 Namensgebung
- 4 Einzelnachweise
- 5 Weblinks

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]



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]

1 H 1.00794 2 Li 6.941 Be 9.01218 3 Na 22.98976928 Mg 24.30409												geologische Eigenschaften 13 B 10.811 14 C 12.0107 15 N 14.00643 16 O 15.999 17 F 18.9984032 18 He 4.002602					
4 He 4.002602 5 Li 6.941 6 Be 9.01218 7 B 10.811 8 C 12.0107 9 N 14.00643 10 O 15.999 11 F 18.9984032 12 Ne 19.99244												19 Na 22.98976928 20 Mg 24.30409 21 Al 26.9815386 22 Si 28.08558 23 P 30.973762 24 S 32.06 25 Cl 35.453 26 Ar 39.948					
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37 Rb 85.4678 38 Sr 87.62 39 Y 88.90584 40 Zr 91.224 41 Nb 92.90638 42 Mo 95.94 43 Tc 98 44 Ru 101.07 45 Rh 102.9055 46 Pd 106.42 47 Ag 107.8682 48 Cd 112.4118 49 In 114.818 50 Sn 118.710 51 Sb 121.757 52 Te 127.6 53 I 126.90549 54 Xe 131.29												73 Fr 223 74 Ra 226 75 Ac-Lr 76 Rf 261 77 Db 262 78 Sg 266 79 Bh 264 80 Hs 277 81 Mt 268 82 Ds 271 83 Pg 269 84 Cn 277 85 Nh 288 86 Fl 288 87 Mc 289 88 Lv 293 89 Og 294					
55 Cs 132.90545196 56 Ba 137.327 57 La-Lu 58 Hf 178.49 59 Ta 180.94788 60 W 183.84 61 Re 186.207 62 Os 190.23 63 Ir 192.222 64 Pt 195.084 65 Au 196.966569 66 Hg 200.59 67 Tl 204.38 68 Pb 207.2 69 Bi 208.9804 70 Po 209 71 At 210 72 Rn 222												91 Pr 140.90766 92 Ce 140.12 93 La 138.90547 94 Pm 145 95 Sm 150.36 96 Eu 151.964 97 Gd 157.25 98 Tb 158.92535 99 Dy 162.50014 100 Ho 164.93033 101 Er 167.259 102 Tm 168.93274 103 Yb 173.05468 104 Lu 174.967					
91 Pr 140.90766 92 Ce 140.12 93 La 138.90547 94 Pm 145 95 Sm 150.36 96 Eu 151.964 97 Gd 157.25 98 Tb 158.92535 99 Dy 162.50014 100 Ho 164.93033 101 Er 167.259 102 Tm 168.93274 103 Yb 173.05468 104 Lu 174.967												105 Ac 227 106 Th 232.0377 107 Pa 231.036889 108 U 238.02891 109 Np 237.048173 110 Pu 244 111 Am 243 112 Cm 247 113 Bk 247 114 Cf 251 115 Es 252 116 Fm 257 117 Md 258 118 No 259 119 Lr 262					

Superheavy Elements

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Copernicium: A Relativistic Noble Liquid

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

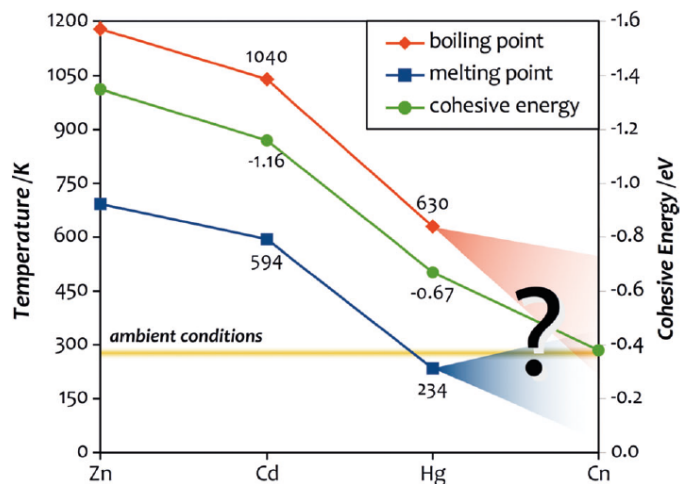


Figure 1. Melting and boiling points (in K) as well as cohesive energies (lattice energy of the most stable phase in eV/atom) of the Group 12 elements zinc (Zn), cadmium (Cd), mercury (Hg), and copernicium (Cn).^[17,18] The yellow area indicates ambient conditions, for which we assume a temperature range 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}	Δ_{ref}	R_{nn}
Experimental ^[a]	-0.37 ± 0.11		
<i>spin-orbit relativistic</i>			
MOI-CCSD(T)	-0.376 ± 0.030		3.465
PBEsol ($c/a = 1.635$)	-0.349	+0.027	3.478
λ PBEsol	-0.373	+0.003	3.478
<i>scalar-relativistic</i>			
MOI-CCSD(T) ^[b]	-0.319		3.465
PBEsol ($c/a = 1.620$)	-0.298	+0.021	3.503
λ PBEsol	-0.317	+0.002	3.503
<i>non-relativistic</i> ^[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 $283 \pm$

11 K and a boiling point of $340 \pm 10 \text{ K}$ and only slightly more dense than Hg ($\rho_1^{300\text{K}} = 14.0 \text{ g cm}^{-3}$). 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 $357_{-108}^{+111} \text{ K}$ 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 (ΔU_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 (ΔH_f°) 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.
- C. W. Haigh, *J. Chem Educ.* **1995**, 72(3), 206 – 210.
- P. Pyykkö, *Chem. Rev.* **1988**, 88, 563 – 594.
- T. M. Klapötke, I. C. Tornieporth-Oetting,
Nichtmetallchemie, VCH, Weinheim, **1994**, 71 – 77.