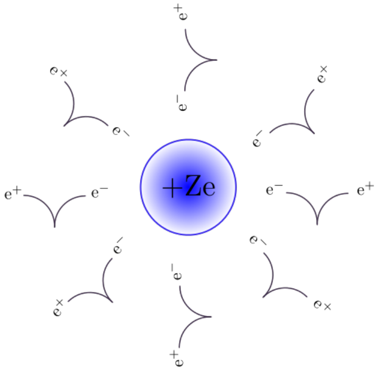

The role of relativity and vacuum in chemistry

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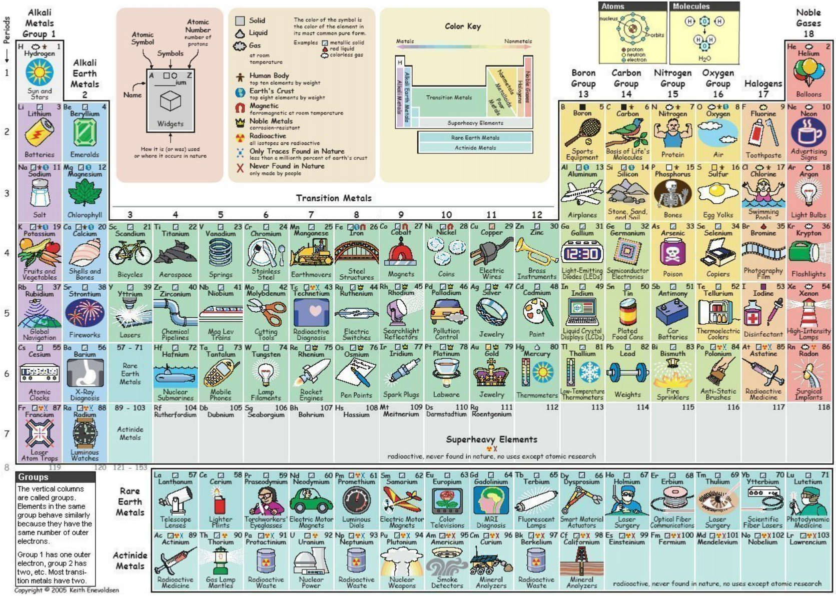
Our playground: the periodic table



The periodic table ... of 1871

Tabelle II.

Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

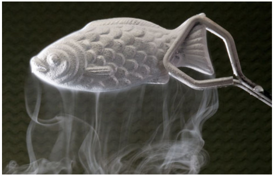
eka-aluminium:
gallium (1875)

eka-silicon:
germanium (1886)

eka-boron:
scandium (1879)

Without relativity

.. gold would have the same color as silver

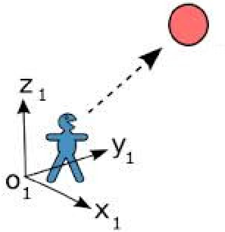


...mercury would not be liquid
at room temperature

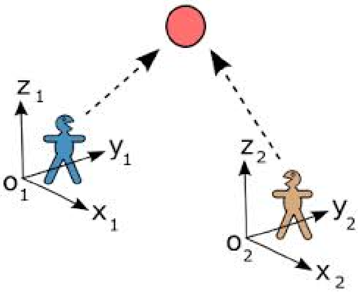
.. your car would not start

Einstein's special theory of relativity

Reference frames



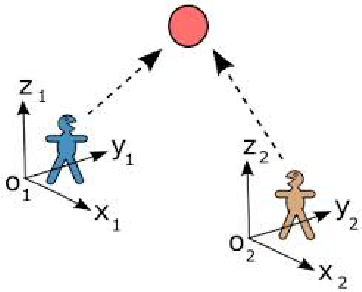
Reference frames



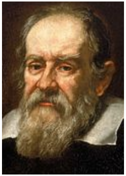
The theory of *special* relativity is restricted to **inertial frames :** reference frames related by constant velocity

It is based on two postulates:

The principle of relativity



The laws of motion are the same in all inertial frames

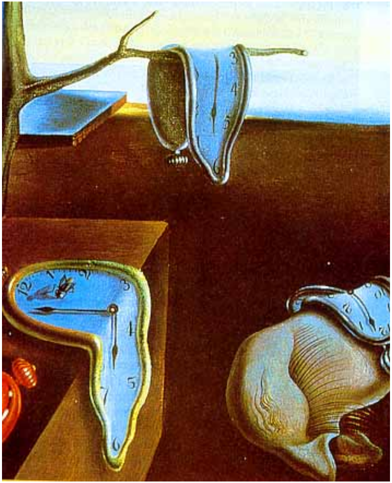


Galileo Galilei (1632)

Einsteins contribution (1905)

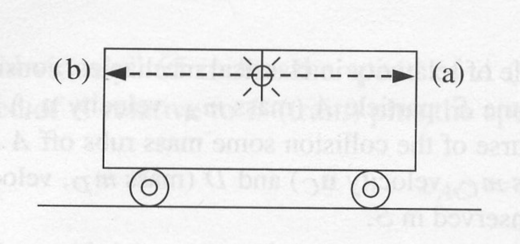
The speed c of light is the same in all inertial frames

$$\text{speed} = \frac{\text{distance}}{\text{time}}$$



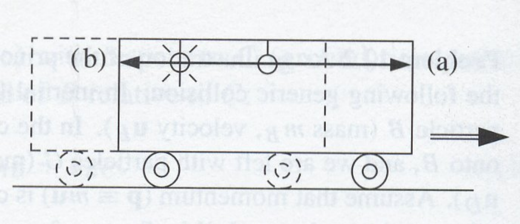
Implies plasticity of space and time

Simultaneity: a relative concept



Observer in the train:

$$t_b = t_a$$

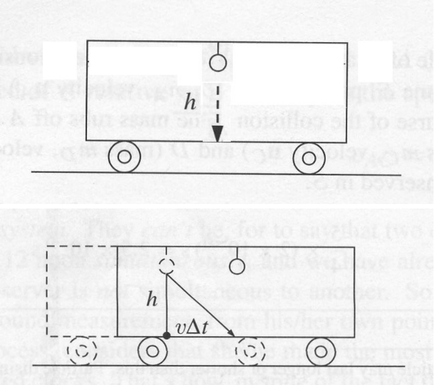


Observer on the ground:

$$t_b < t_a$$

Two events that are simultaneous in one inertial frame are generally not so in another inertial frame.

Time dilation



Observer in the train:

$$c\Delta\bar{t} = h$$

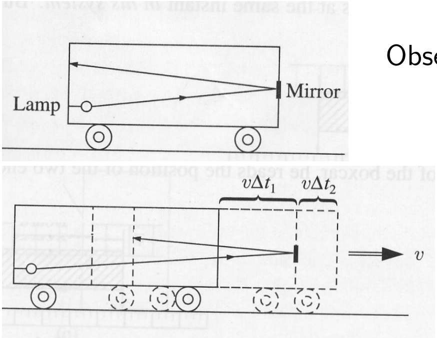
Observer on the ground:

$$c\Delta t = \sqrt{h^2 + (v\Delta t)^2}$$

$$\Delta t = \gamma\Delta\bar{t} > \Delta\bar{t}; \qquad \text{Lorentz factor:} \quad \gamma = \frac{1}{\sqrt{1 - v^2/c^2}}$$

Clocks in movement go slower.

Length contraction



Observer in the train:

$$c\Delta\bar{t} = 2\Delta\bar{x}$$

Observer on the ground:

$$\begin{aligned} c\Delta t_1 &= \Delta x + v\Delta t_1 \\ c\Delta t_2 &= \Delta x - v\Delta t_2 \end{aligned}$$

$$\Delta t = \Delta t_1 + \Delta t_2 = \frac{\Delta x}{c - v} + \frac{\Delta x}{c + v}$$

$$\Delta t = 2\frac{\Delta x}{c}\gamma^2 = \gamma\Delta\bar{t} = \gamma\frac{2\Delta\bar{x}}{c}$$

$$\Delta\bar{x} = \gamma\Delta x$$

An object in movement is contracted in the direction of movement

Relativistic effects in chemistry

- The Lorentz factor

$$\gamma = \frac{1}{\sqrt{1 - v^2/c^2}}; \quad \begin{cases} v & \text{- speed of particle} \\ c & \text{- speed of light} \end{cases}$$

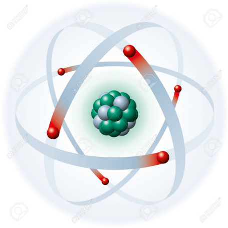
  is a diagnostic of relativistic effects.

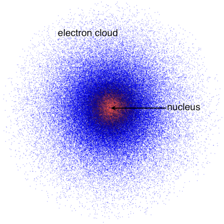
- The speed of light is very large !

$$c = 299,792,458\,\mathrm{m/s} \; = \; 1079252848.8\,\mathrm{km/h}$$

- So what goes fast in an atom or a molecule ?

Relativity and the atom

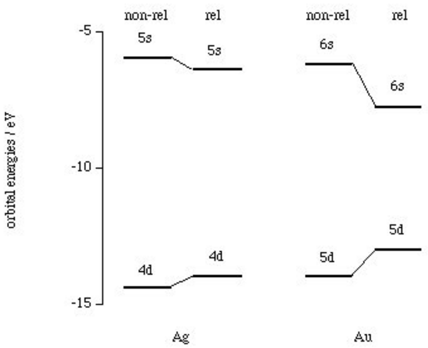




- Atoms are small
  - One meter can accomodate 7407407407 gold atoms
  - Rather than metric (SI) units we use **atomic units**
- In atomic units
  - the speed of an electron in a one-electron atom is equal to the nuclear charge Z.
  - the speed of light $c = 137.0359998\,\text{a.u.}$
- The ratio v/c is small for hydrogen ($Z = 1$)
  - but not for gold ($Z = 79$), mercury ($Z = 80$) or lead ($Z = 82$).

The colour of gold

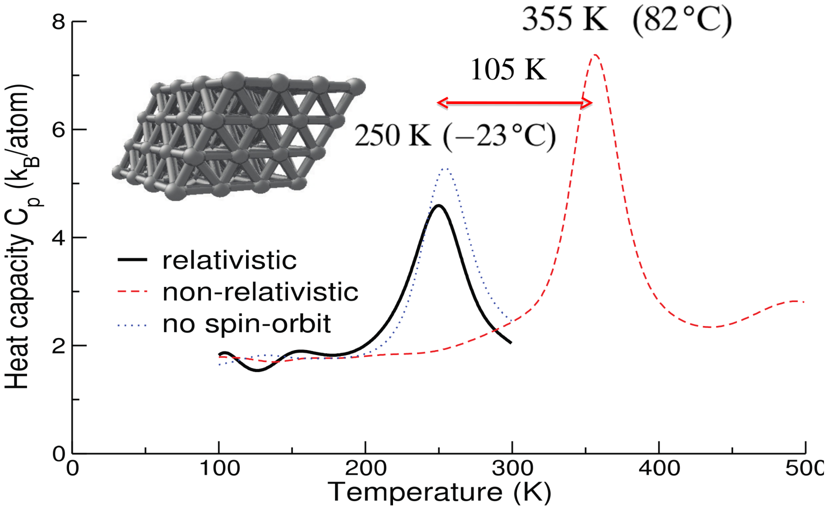
- **Relativity changes the energy and orbital motion of electrons in heavy atoms**



Melting point of mercury

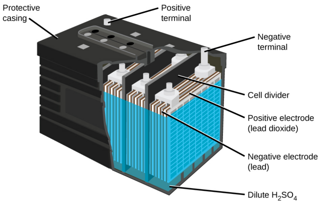
Florent Calvo, Elke Pahl, Michael Wormit and Peter Schwerdtfeger,
Ang. Chemie. Int. Ed. 52 (2013) 7583

Mercury melts at 234.32 K (-38.83 °C)



Cars start due to relativity

R. Ahuja, A. Blomqvist, P. Pyykkö and P. Zaleski-Ejgjerd, Phys. Rev. Lett. 106 (2011) 018301

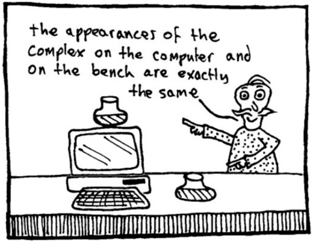


non-relativistic calculation:	+0.39 V
relativistic calculation:	+2.13 V
experiment:	+2.11 V

Relativistic effects can not be studied directly by experiment.

Playground for theory !

Asking Nature ... and the computer

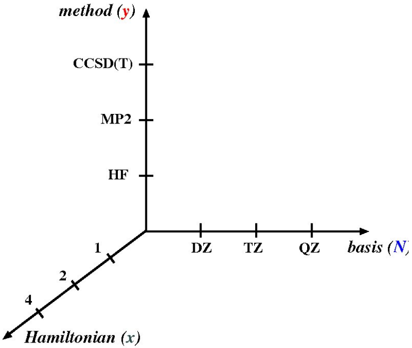


Computational Chemistry

To learn about the world

- the **experimentalist** asks Nature using his experimental apparatus
- the **theoretician** asks the wave function Ψ using mathematical operators $\hat{\Omega}$
- The most important operator is the **Hamiltonian** (energy)

Theoretical model chemistries



The electronic Hamiltonian, relativistic or not, has the same generic form

$$\hat{H} = V_{NN} + \sum_i \hat{h}(i) + \frac{1}{2}\sum_{i\neq j}\hat{g}(i,j); \quad V_{NN} = \frac{1}{2}\sum_{K\neq L}\frac{Z_K Z_L}{R_{KL}}$$

Computational cost: xN^y

The electronic Hamiltonian

$$\hat{H} = V_{NN} + \sum_{i} \hat{h}(i) + \tfrac{1}{2}\sum_{i\neq j} \hat{g}(i,j); \quad V_{NN} = \tfrac{1}{2}\sum_{K\neq L} \tfrac{Z_K Z_L}{R_{KL}}$$

- One- and two-electron operators:

$$\hat{h} = \hat{h}_0 + \hat{v}_{eN}; \quad \hat{g}\,(1,2) = \frac{1}{r_{12}} + (\text{relativistic corrections})$$

- Non-relativistic free-particle Hamiltonian

$$\hat{h}_0 = \frac{p^2}{2m}$$

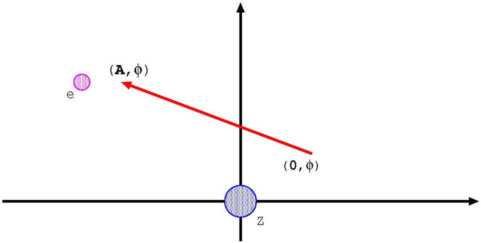
- Relativistic free-particle Hamiltonian

$$\hat{h}_0 = \beta mc^2 + c\,(\boldsymbol{\alpha}\cdot\mathbf{p}) = \left[\begin{array}{cc} +mc^2 & c\,(\boldsymbol{\sigma}\cdot\mathbf{p}) \\ c\,(\boldsymbol{\sigma}\cdot\mathbf{p}) & -mc^2 \end{array}\right]$$

Spin-orbit interaction

Trond Saue, ChemPhysChem 12 (2011) 3077

- One of the most misunderstood interactions in physics and chemistry
- Typically represented by an operator on the form $h^{SO} = \zeta\,\hat{\boldsymbol{\ell}}\cdot\hat{\mathbf{s}}$
  - Spin-orbit *coupling* is a consequence, not the cause.
- The underlying interaction is **magnetic induction**



- the electron spin interacts with the magnetic field generated by charges in relative motion, e.g. a nucleus
- the orbital angular momentum operator $\hat{\boldsymbol{\ell}}$ represents the relative motion

Does chemistry need any more physics ?

P. Pyykkö, Chem. Rev. 112, 371-384 (2012)

- In the past thirty years it has become clear that relativistic effects are important for the theoretical description of molecules containing heavy atoms
- Do we need anything more from physics ?
- **Parity violation** induces a *tiny* energy difference between enantiomers of chiral molecules

  R. Bast, A. Koers, A. Severo Pereira Gomes, M. Iliaš, L. Visscher, P. Schwerdtfeger and T. Saue, Phys. Chem. Chem. Phys. **13** (2011) 854

  - Could explain the origin of biochirality.
- What about **quantum electrondynamics (QED)** ?
  - We usually think about the quantized electromagnetic field
    - ★ needed to explain spontaneous emission
  - We here consider vacuum effects (no-photon QED)

Negative energy states in classical mechanics

- Non-relativistic free particle:

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}; \quad \Rightarrow \quad E \in [0, \infty\rangle$$

- Relativistic free particle:

$$E^2 = m^2c^4 + c^2p^2; \quad \Rightarrow \quad E \in \left\langle -\infty, -mc^2\right] \cup \left[+mc^2, \infty\right\rangle$$

- We can ignore the negative energy states since the energy can only change in a *continuous* manner
- We can connect the non-relativistic and relativistic energy expression by a Taylor-expansion of the former

$$E = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} = \underbrace{mc^2}_{\text{rest mass}} + \underbrace{\frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots}_{\text{kinetic energy}}$$

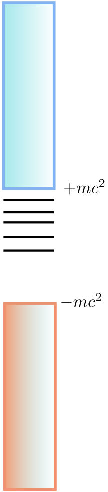
- One can not take the non-relativistic limit of both energy branches at the same time !

Negative-energy states in quantum mechanics

- Dirac equation for an electron in a molecular field

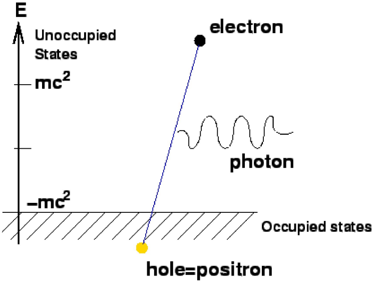
$$\left[\begin{array}{cc} V+mc^2 & c(\boldsymbol{\sigma}\cdot\mathbf{p}) \\ c(\boldsymbol{\sigma}\cdot\mathbf{p}) & V-mc^2 \end{array}\right]\left[\begin{array}{c}\psi^L\\ \psi^S\end{array}\right]=\left[\begin{array}{c}\psi^L\\ \psi^S\end{array}\right]E$$

- Negative energy solutions can *not* be ignored, since quantum leaps are allowed
- **Problem:**
  - Matter is not stable !
  - The hydrogen atom would have a lifetime of about a nanosecond...



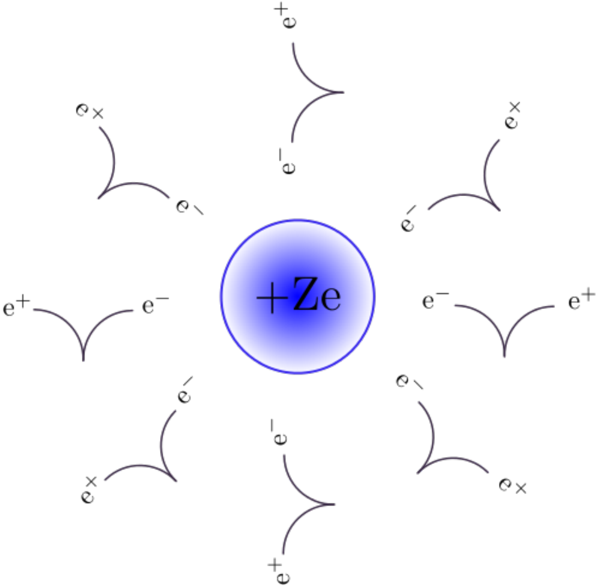
Anti-particles

- **The solution proposed by Dirac**
  - All negative-energy solutions are occupied.
  - The Pauli exclusion principle then hinder electrons descending down the negative-energy branch.
  - The excitation of an electron from the negative-energy band leaves a hole of positive charge, corresponding to the creation of a electron-positron pair.



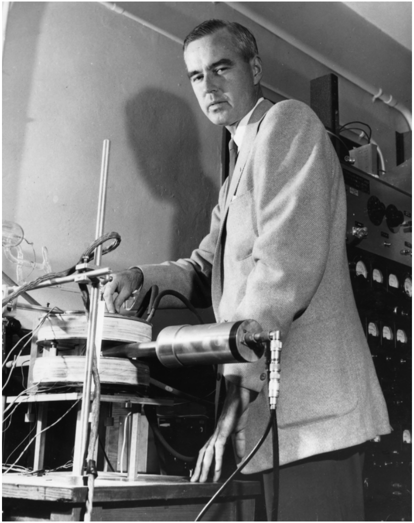
The theory of Dirac is confirmed in 1932 when the US physicist Carl Anderson discovers the positron.

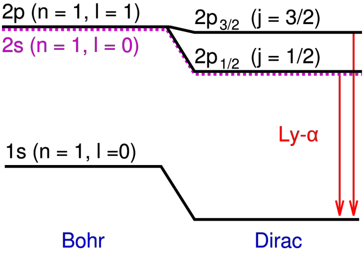
The vacuum has become a polarizable medium



Lamb shift

Lamb, Willis E.; Retherford, Robert C., Physical Review. 72 (1947) 241





- In 1947 Lamb and Retherford measured a tiny splitting of about 4 meV between the $^2S_{1/2}$ and $^2P_{1/2}$ states of the hydrogen atom
- For hydrogen-like uranium (Z=92) this splitting has grown to 469 eV

Electron Affinity and Ionization Potential of Gold

- The effect of relativity:
  O. Fossgaard, O. Gropen, E. Eliav and T. Saue, J. Chem. Phys. **119** (2003) 9355

	EA/eV	IP/eV
NR	1.287	7.064
+R	2.301	9.195
Δ_{rel}	78.8%	30.2%

- The effect of QED:
  L. F. Pašteka, E. Eliav, A. Borschevsky, U. Kaldor, and P. Schwerdtfeger, Phys. Rev. Lett. **118** (2017) 023002

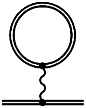
	EA/eV	IP/eV
R	2.3188	9.2546
+QED	2.3072	9.2288
Δ_{QED}	-0.50%	-0.28%
$\Delta_{QED/R}$	-1.14%	-1.21%
Exp.	2.3086	9.2256

- QED effects **reduce** relativistic effects by about 1%.

Electron Affinity and Ionization Potential of Gold

- Separate QED effects:

Electron self-energy



Vacuum polarization

- Contributions to EA/IP of gold:

		EA/eV	IP/eV	Effective QED-potential
SE	MLSO	−0.0112	−0.0261	Shabaev *et al.*, Phys. Rev. A **88** (2013) 012513
	ENLO	−0.0114	−0.0264	Flambaum and Ginges, Phys. Rev. A **72** (2005) 052115
	LGO	−0.0117	−0.0272	P. Pyykkö and L.-B. Zhao, J. Phys. B **36** (2003) 1469
VP		+0.0021	+0.0049	E.A. Uehling, Phys. Rev. **48** (1935) 55
Total	MLSO	−0.0091	−0.0212	

- Self-energy tends to dominate vacuum polarization

What about molecules ?

Pekka Pyykkö, Davidson lecture, UNT, Oct 25 2013
[http://www.chem.helsinki.fi/˜pyykko/Videos/UNT.mp4]

Accurate structures for molecular MCN, M=Cu,Ag,Au

- Microwave molecular structures exist for Cu [1], Ag, Au [2].
- Carry out large-basis relativistic pseudopotential CCSD(T) calculations, correlating the 5s5p semicore and adding BSSE and spin-orbit corrections. cc-pVQZ basis. 19-VE Figgen pseudopotential.
- Final **M-C bond-lengths** agree with experiment within 0.7 pm.

1. D.B. Grotjahn, M.A. Brewster, L.M. Ziurys, JACS 124 (2001) 5895.
2. T. Okabayashi, E. Y. Okabayashi, F. Koto, T. Ishida, M. Tanimoto, JACS 131 (2009) 11712.
3. P. Zaleski-Ejgierd, M. Patzschke, P. Pyykkö, J. Chem. Phys.128 (2008) 224303.
4. J. G. Hill, A.O. Mitrushchenkov,K.A. Peterson, J. Chem. Phys. 138 (2013) 134314.

	CuCN	AgCN	AuCN
Exp	182.962(4)(r_m)	203.1197(23)(r_m)	191.22519(84)(r_s)
Calc.[3]	182.36 (r_e)	202.42 (r_e)	191.05 (r_e)
Calc.[4]	182.65 (r_e)	202.99 (r_e)	190.71 (r_e)

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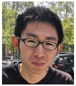
The molQED project
funded by ANR

- The main objective of the project is to investigate the effect of quantum electrodynamics on molecular properties.
- Laboratoire de Chimie et Physique Quantiques, Toulouse


Trond Saue


Ayaki Sunaga


Alexander Efremov


Maen Salman

- Université Paris-Dauphine


Mathieu Lewin


Maria Esteban


Eric Séré


Guillaume Legendre

- **First milestone:** Effective QED potentials, designed for atoms, implemented in the dirac code for relativistic molecular calculations (Ayaki Sunaga)

Orbital sizes $\langle r^2 \rangle^{1/2}$ of the neutral gold atom

B3LYP/dyall.3zp/QED:VP(Uehling)+SE(ENLO)

- The effect of relativity (in pm):

	$5s_{1/2}$	$5p_{1/2}$	$5p_{3/2}$	$5d_{3/2}$	$5d_{5/2}$	$6s_{1/2}$
NR	81.617	89.327	89.327	128.787	128.787	196.070
+R	73.863	80.303	88.203	128.418	135.406	167.538
Δ_{rel}	-9.50%	-10.10%	-1.26%	-0.29%	5.14%	-14.55%

- The effect of QED (in pm):

	$5s_{1/2}$	$5p_{1/2}$	$5p_{3/2}$	$5d_{3/2}$	$5d_{5/2}$	$6s_{1/2}$
R	73.863	80.303	88.203	128.418	135.406	167.538
+QED	73.929	80.306	88.214	128.379	135.382	167.791
Δ_{QED}	0.09%	0.00%	0.01%	-0.03%	-0.02%	0.15%
$\Delta_{QED/R}$	-0.85%	-0.03%	-0.98%	10.57%	-0.36%	-0.89%

- Does the $\Delta_{QED} = +0.25$ pm for the valence $6s_{1/2}$ orbital translate into a corresponding bond extension ?

Effects of relativity and QED on bond lengths

B3LYP/dyall.3zp/QED:VP(Uehling)+SE(ENLO)

- The effect of relativity (in pm):

	AuH	Au_2
NR	174.844	280.295
+R	154.152	253.708
Δ_{rel}	-11.83%	-9.49%

- The effect of QED (in pm):

	AuH	Au_2
R	154.152	253.708
+QED	154.294	253.921
Δ_{QED}	0.09%	0.08%
$\Delta_{QED/R}$	-0.69%	-0.80%

Conclusions and perspectives

- Relativity plays an important role in heavy-element chemistry
- Effective QED potentials have been implemented in the dirac code for relativistic molecular calculations
- QED effects tend to reduce relativistic effects by about 1%.
  - this rule of thumb applies to **valence***e* properties
- **Core properties** (e.g. NMR and Mössbauer parameters) are possibly beyond the domain of validity of effective QED potentials
- The main goal of the molQED project is to develop a **variational** approach to QED

TODO

- HF, discuss direct and exchange contributions