Relativistic quantum chemistry

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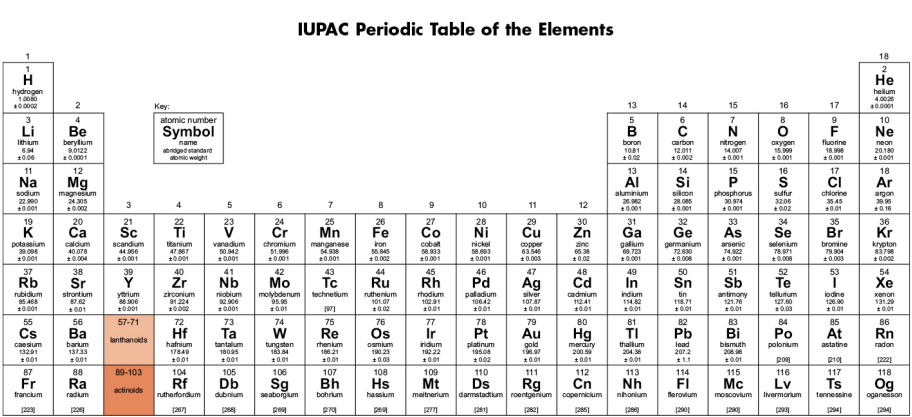
The Dirac village

Our playground: the periodic table



The periodic table ... of 1871

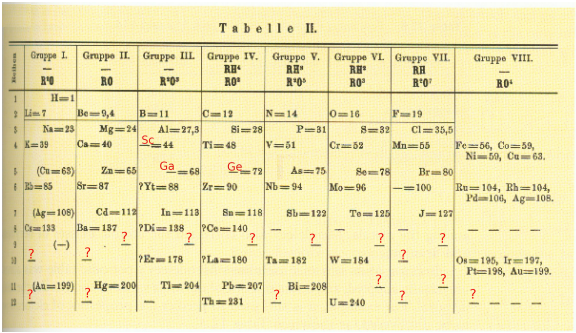
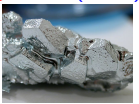


Tabelle II.

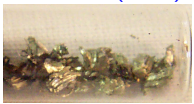
Reihen	Gruppe I. — R^1O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	?Sc=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	?Ga=68	?Ge=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)



- For heavier elements, Mendeleev's predictions would be less successful

Broken trends

- **Relativistic effects**
  - dictated by the Lorentz factor

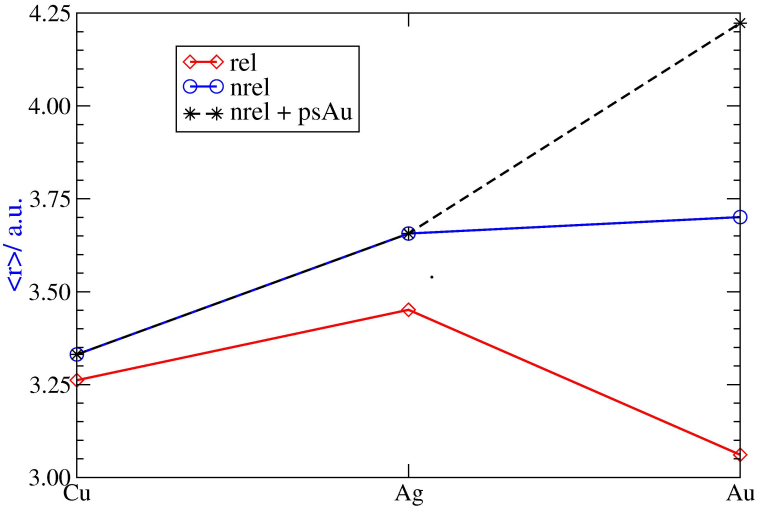
$$\gamma = \frac{1}{\sqrt{1 - v^2/c^2}} \qquad \begin{cases} v & \text{- speed of particle} \\ c & \text{- speed of light} \end{cases}$$

  - One-electron atoms: $v_{1s} = Z$ a.u.; $\quad c = 137.0359998$ a.u.
    - ★ scalar relativistic effects
  - spin-orbit interaction
    - ★ magnetic induction !
- **Lanthanide contraction**
  - La^{3+} - Lu^{3+} (117.2 - 100.1 pm)
  - Ca^{2+} - Zn^{2+} (114 - 88 pm)
  - Cu (138 pm) < Au (144 pm) < Ag (153 pm)
  - V. M. Goldschmidt, T. Barth, G. Lunde:
    Norske Vidensk. Selsk. Skrifter I Mat. Naturv. Kl. **7**, 1 (1925)

Goldschmidt and Einstein in Norway 1920

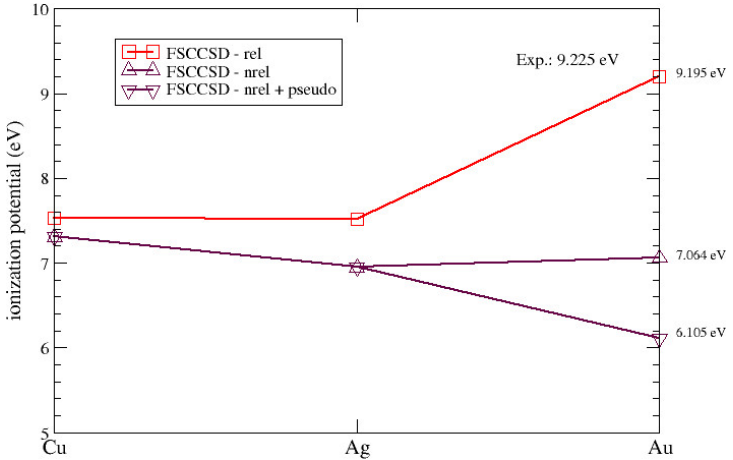
A playground for theory

P.S. Bagus *et al.*, Chem. Phys. Lett. **33** (1975) 408



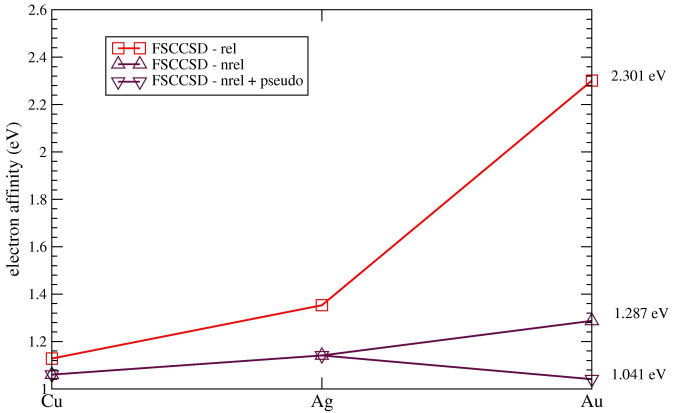
Ionization energy of gold

O. Fossgaard, O. Gropen, E. Eliav and T. Saue, J. Chem. Phys. 119 (2003) 9355



Electron affinity of gold

O. Fossgaard, O. Gropen, E. Eliav and T. Saue, J. Chem. Phys. 119 (2003) 9355



- Gold and caesium are extremes on the electron affinity scale — 2.309 eV vs. 0.472 eV
- CsAu is a semi-conductor with a CsCl crystal structure in the solid state; it forms an ionic melt. **The oxidation state of gold is -I.**

Without relativity

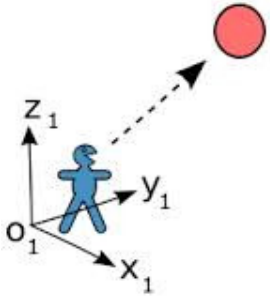
.. gold would have the same color as silver

...mercury would not be liquid
at room temperature

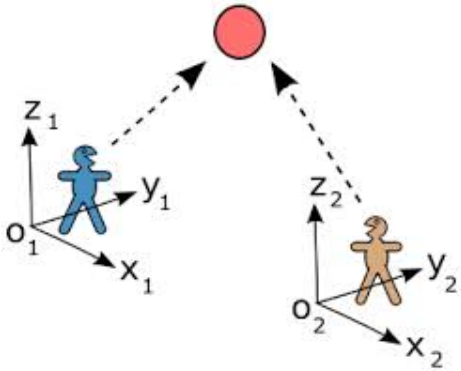
.. your car would not start


CRASH
COURSE

Reference frames



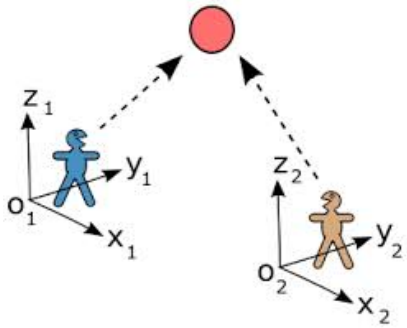
Reference frames



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



1. The laws of motion are the same in all inertial frames

Galileo Galilei (1632)

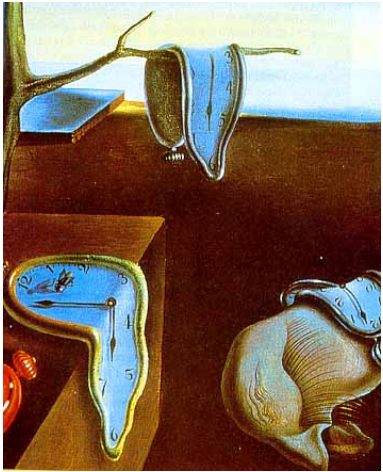
... but some frames may be better than others

- Speed of boat with respect to the river bank: 3 km/h
- Speed of water with respect to the river bank: 7 km/h
- **Hint:** you do not need this information....

Einsteins contribution (1905)

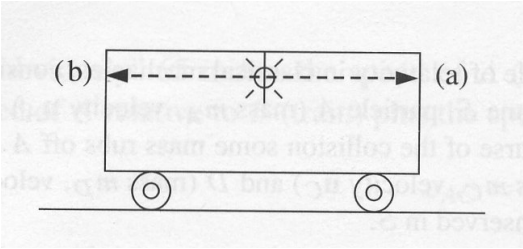
2. The speed c of light is the same in all inertial frames

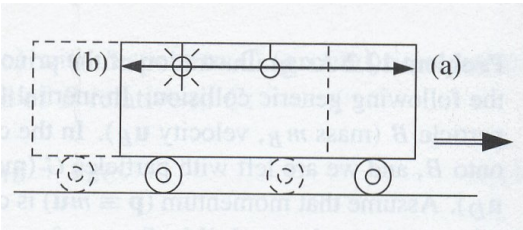
$$\text{speed} = \frac{\text{distance}}{\text{time}}$$



Implies plasticity of space and time

Simultaneity: a relative concept





Observer in the train:

$$t_b = t_a$$

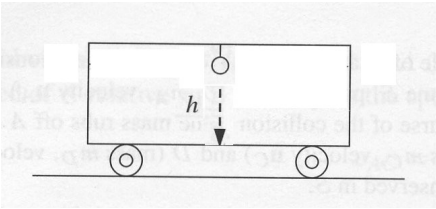
Observer on the ground:

$$t_b < t_a$$

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

Picture credit: Griffiths: Introduction to Electrodynamics (1999)

Time dilation



Observer in the train:

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

Observer on the ground:

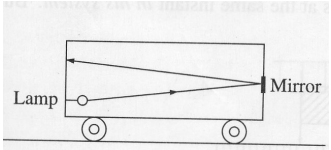
$$c\Delta t = \sqrt{h^2 + (v\Delta t)^2}$$

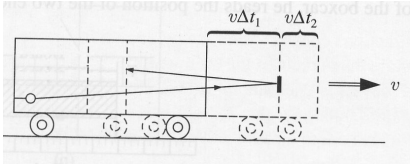
$$\Delta t = \gamma\Delta\bar{t} > \Delta\bar{t}; \qquad \text{Lorentz factor:} \quad \gamma = \frac{1}{\sqrt{1 - v^2/c^2}}$$

Clocks in movement go slower.

Picture credit: Griffiths: Introduction to Electrodynamics (1999)

Length contraction





Observer in the train:

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

Observer on the ground:

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

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

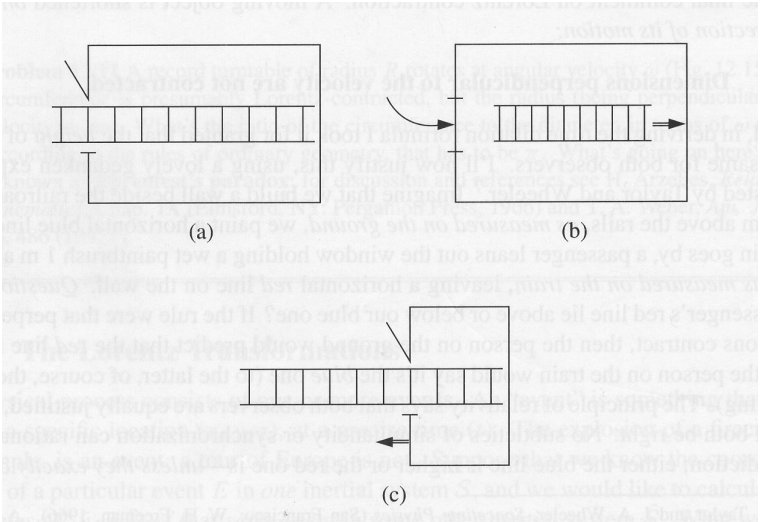
$$\Delta t = 2\frac{\Delta x}{c}\gamma^2 = \gamma\Delta\overline{t} = \gamma\frac{2\Delta\overline{x}}{c}$$

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

An object in movement is contracted in the direction of movement

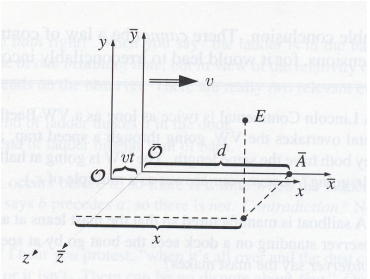
Picture credit: Griffiths: Introduction to Electrodynamics (1999)

Paradox of the barn and the ladder



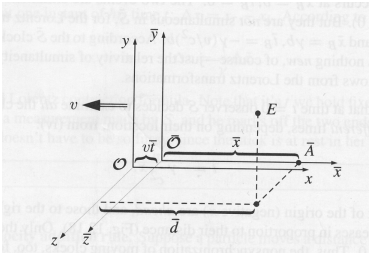
Picture credit: Griffiths: Introduction to Electrodynamics (1999)

Lorentz transformation



$$
\begin{aligned}
x &= d + vt \\
d &= \begin{cases} \bar{x}; & \text{(Galilei)} \\ \gamma^{-1}\bar{x}; & \text{(Lorentz)} \end{cases} \\
\bar{x} &= \gamma\left(x - vt\right)
\end{aligned}
$$

$$
\begin{aligned}
x &= \gamma\left(\bar{x} + v\bar{t}\right) \\
\bar{t} &= \gamma\left(t - \frac{v}{c^2}x\right)
\end{aligned}
$$



Electrodynamics

Maxwell's equations

(SI-based atomic units: $\hbar = m_e = e = 4\pi\varepsilon_0 = 1$)

- The homogeneous pair:

$$\begin{aligned} \boldsymbol{\nabla} \cdot \mathbf{B} &= 0 \\ \boldsymbol{\nabla} \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} &= \mathbf{0} \end{aligned}$$

- The inhomogeneous pair includes sources:
  the charge density ρ and current density $\mathbf{j}$ (c is the speed of light)

$$\begin{aligned} \boldsymbol{\nabla} \cdot \mathbf{E} &= 4\pi\rho \\ \boldsymbol{\nabla} \times \mathbf{B} - \frac{1}{c^2}\frac{\partial \mathbf{E}}{\partial t} &= \frac{4\pi}{c^2}\mathbf{j} \end{aligned}$$

- Are the electric field $\mathbf{E}$ and the magnetic field $\mathbf{B}$ uniquely determined by their divergence ($\nabla \cdot \ldots$) and curl ($\nabla \times \ldots$) ?

Maxwell's equations: boundary conditions

- **The answer is NO !!!!**
  The two vectors

$$\begin{aligned} \mathbf{F}_1 &= (0,0,0) \\ \mathbf{F}_2 &= (yz, zx, xy) \end{aligned}$$

  both have zero divergence and zero curl
- Boundary conditions must be introduced:
  - **E and B go to zero at infinity** (Helmholtz theorem)

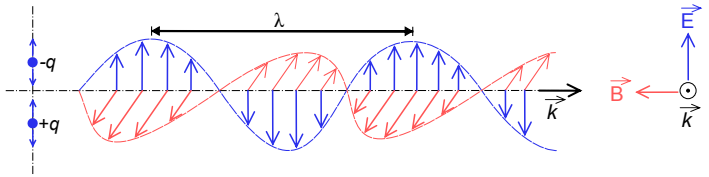
Jefimenko's solutions

- General solutions of Maxwell's equations are

$$\mathbf{E}(\mathbf{r}_1, t) = \int \left\{ \frac{\rho(\mathbf{r}_2, t_r)\,\mathbf{r}_{12}}{r_{12}^3} + \frac{\dot{\rho}(\mathbf{r}_2, t_r)\,\mathbf{r}_{12}}{r_{12}^2} - \frac{\dot{j}(\mathbf{r}_2, t_r)}{c^2 r_{12}} \right\} d^3\mathbf{r}_2$$

$$\mathbf{B}(\mathbf{r}_1, t) = \frac{1}{c^2} \int \left\{ \frac{\mathbf{j}(\mathbf{r}_2, t_r) \times \mathbf{r}_{12}}{r_{12}^3} + \frac{\dot{j}(\mathbf{r}_2, t_r) \times r_{12}}{c r^2{}_{12}} \right\} d^3\mathbf{r}_2$$

  where $\dot{x} = \frac{dx}{dt}$.
- Note that we can always add the solutions of the homogeneous (source-free) equations, that is, electromagnetic waves.



- A nasty fellow:
  - Retarded time

$$t_r = t - \frac{r_{12}}{c}$$

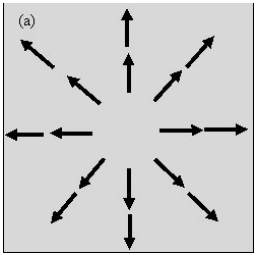

Looking into space ...
@Jeff的星空之旅

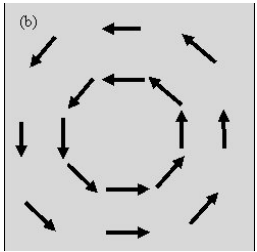

Looking into space ...
... and time
@Jeff的星空之旅

Helmholtz decomposition

Any vector function **F** (differentiable) who goes to zero faster than $\frac{1}{r}$ when $r \to \infty$ can be expressed as the sum of the gradient of a scalar and the curl of a vector

$$\mathbf{F}(\mathbf{r}) = -\boldsymbol{\nabla} s(\mathbf{r}) + \boldsymbol{\nabla} \times \mathbf{v}(\mathbf{r})$$





Longitudinal component ("parallel"):

$$\mathbf{F}_{\parallel} = -\boldsymbol{\nabla} s(\mathbf{r}); \quad \boldsymbol{\nabla} \times \mathbf{F}_{\parallel} = \mathbf{0}$$

Solenoidal component ("perpendicular"):

$$\mathbf{F}_{\perp} = \boldsymbol{\nabla} \times \mathbf{v}(\mathbf{r}); \quad \boldsymbol{\nabla} \cdot \mathbf{F}_{\perp} = 0$$

Maxwell's equations: homogeneous pair

- $\boldsymbol{\nabla} \cdot \mathbf{B} = 0$ means that magnetic fields are always solenoidal

$$\mathbf{B} = \mathbf{B}_\perp = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r}) \quad \text{and} \quad \mathbf{B}_\parallel = \mathbf{0}$$

- $\boldsymbol{\nabla} \times \mathbf{E} + \dfrac{\partial \mathbf{B}}{\partial t} = 0$ then becomes $\boldsymbol{\nabla} \times \left(\mathbf{E} + \dfrac{\partial \mathbf{A}}{\partial t} \right) = 0$ and one may write

$$\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\boldsymbol{\nabla}\phi(\mathbf{r}) \quad \Rightarrow \quad \mathbf{E} = -\boldsymbol{\nabla}\phi(\mathbf{r}) - \frac{\partial \mathbf{A}}{\partial t}$$

- The electric field generally has both a longitudinal and solenoidal component

$$\mathbf{E}_\parallel = -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}_\parallel}{\partial t}; \quad \mathbf{E}_\perp = -\frac{\partial \mathbf{A}_\perp}{\partial t}$$

- With the introduction of the **scalar potential** ϕ and the **vector potential** $\mathbf{A}$, the homogeneous pair of Maxwell's equations is automatically satisfied.

Maxwell's equations: inhomogeneous pair

- $\boldsymbol{\nabla} \cdot \mathbf{E} = 4\pi\rho$ becomes

$$\nabla^2 \phi + \frac{\partial}{\partial t} \left(\boldsymbol{\nabla} \cdot \mathbf{A} \right) = -4\pi\rho$$

$$\text{or} \quad \left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] \phi + \frac{\partial}{\partial t} \left[\left(\boldsymbol{\nabla} \cdot \mathbf{A} \right) + \frac{1}{c^2} \frac{\partial \phi}{\partial t} \right] = -4\pi\rho$$

- $\boldsymbol{\nabla} \times \mathbf{B} - \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi}{c^2} \mathbf{j}$ becomes

$$\left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] \mathbf{A} - \boldsymbol{\nabla} \left[\left(\boldsymbol{\nabla} \cdot \mathbf{A} \right) + \frac{1}{c^2} \frac{\partial \phi}{\partial t} \right] = -\frac{4\pi}{c^2} \mathbf{j}$$

Lorentz transformation and 4-vectors

- The Lorentz transformation

$$\bar{\mathbf{r}}_{\parallel} = \gamma\left(\mathbf{r}_{\parallel} - \mathbf{v}t\right); \quad \bar{\mathbf{r}}_{\perp} = \mathbf{r}_{\perp}; \quad \bar{t} = \gamma\left(t - \frac{(\mathbf{r}\cdot\mathbf{v})}{c^2}\right)$$

  is the relativistic transformation between inertial frames.

- It involves space and time which can be combined into **4-position**: $r_\mu = (\mathbf{r}, ict)$ whose norm $\left(r_\mu r_\mu = r^2 - c^2t^2\right)$ is conserved under Lorentz transformations

- Other **4-vectors** are
  - **4-velocity:** $v_\mu = \gamma(\mathbf{v}, ic)$; $v_\mu v_\mu = -c^2$
  - **4-momentum:** $p_\mu = \gamma\left(m\mathbf{v}, imc\right)$; $p_\mu p_\mu = -m^2c^2$
  - **4-gradient:** $\partial_\mu = (\boldsymbol{\nabla}, -(i/c)\frac{\partial}{\partial t})$; $\partial_\mu\partial_\mu = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} = \Box^2$; (d'Alembertian)
  - **4-potential:** $A_\mu = (\mathbf{A}, (i/c)\phi)$
  - **4-current::** $j_\mu = (\mathbf{j}, ic\rho)$

- They all transform in the same way !

Maxwell's equations: 4-vector notation

- We start from:

$$\left[\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right]\phi + \frac{\partial}{\partial t}\left[(\boldsymbol{\nabla}\cdot\mathbf{A}) + \frac{1}{c^2}\frac{\partial \phi}{\partial t}\right] = -4\pi\rho$$

$$\left[\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right]\mathbf{A} - \boldsymbol{\nabla}\left[(\boldsymbol{\nabla}\cdot\mathbf{A}) + \frac{1}{c^2}\frac{\partial \phi}{\partial t}\right] = -\frac{4\pi}{c^2}\mathbf{j}$$

- This can be written more compactly as

$$\begin{aligned} \Box^2\phi &+ \frac{\partial}{\partial t}(\partial_\mu A_\mu) = -4\pi\rho \\ \Box^2\mathbf{A} &- \boldsymbol{\nabla}(\partial_\mu A_\mu) = -\frac{4\pi}{c^2}\mathbf{j} \end{aligned} \quad ; \quad \Box^2 = \partial_\mu\partial_\mu = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}$$

- .. and finally squashed into

$$\Box^2 A_\beta - \partial_\beta(\partial_\alpha A_\alpha) = -\frac{4\pi}{c^2} j_\beta$$

Gauge transformations

- $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$ implies that the longitudinal component $\mathbf{A}_{\parallel}$ of the vector potential can be modified without changing $\mathbf{B}$, that is

$$\mathbf{A} \quad \rightarrow \quad \mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla}\chi$$

- However

$$\mathbf{E} = -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t}$$

  implies that a modification of $\mathbf{A}$ requires a corresponding modification of the scalar potential

$$\phi \quad \rightarrow \quad \phi' = \phi - \frac{\partial \chi}{\partial t}$$

- Lorentz covariant form :

$$A_\mu \quad \rightarrow \quad A'_\mu = A_\mu + \partial_\mu \chi$$

- The electric and magnetic fields are gauge invariant.

Lorentz gauge: $\partial_\mu A_\mu = \boldsymbol{\nabla} \cdot \mathbf{A} + \frac{1}{c^2}\frac{\partial \phi}{\partial t} = 0$

- Maxwell's equations simplifies to

$$\Box^2 A_\beta = -\frac{4\pi}{c^2} j_\beta$$

- General solution:

$$A(\mathbf{r}_1, t) = \int \frac{\mathbf{j}(\mathbf{r}_2, t_r)}{r_{12}} d^3\mathbf{r}_2; \quad \phi(\mathbf{r}_1, t) = \int \frac{\rho(\mathbf{r}_2, t_r)}{r_{12}} d^3\mathbf{r}_2$$

where appears retarded time

$$t_r = t - \frac{r_{12}}{c}$$

Coulomb gauge: $\nabla \cdot \mathbf{A} = 0$

- Maxwell's equations simplifies to:

$$\begin{aligned} \nabla^2 \phi &= -4\pi\rho \\ \left(\nabla^2 \mathbf{A} - \frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2}\right) - \boldsymbol{\nabla}\frac{1}{c^2}\frac{\partial \phi}{\partial t} &= -\frac{4\pi}{c^2}\mathbf{j} \end{aligned}$$

- The scalar potential is the solution of the Poisson equation

$$\phi(\mathbf{r}_1, t) = \int \frac{\rho(\mathbf{r}_2, t)}{r_{12}} d^3\mathbf{r}_2$$

  and describes the instantaneous Coulomb interaction.
- Problem (?):
  - The theory of relativity does not allow instantaneous interactions.
- Retardation is hidden in the solution for the purely transversal vector potential

$$\mathbf{A}(\mathbf{r}_1, t) = \mathbf{A}_\perp(\mathbf{r}_1, t) = \frac{4\pi}{c^2} \int \frac{\mathbf{j}_\perp(\mathbf{r}_2, t_r)}{r_{12}} d^3\mathbf{r}_2$$

Particles and fields

- Complete Hamiltonian

$$H = H_{\text{particles}} + H_{\text{interaction}} + H_{\text{fields}}$$

- Fields specified:

Non-relativistic limit

$$(i\gamma_\mu \partial_\mu - mc)\,\psi = 0 \qquad \rightarrow \qquad \left(\frac{p^2}{2m} - i\frac{\partial}{\partial t}\right)\psi = 0$$

Dirac equation — Schrödinger equation

- Particles (sources) specified:

Non-relativistic limit

$$\Box^2 A_\mu - \partial_\mu(\partial_\nu A_\nu) = -\frac{4\pi}{c^2} j_\mu \qquad \rightarrow \qquad \text{???}$$

Maxwell's equations

The non-relativistic limit of electrodynamics

T. Saue, Adv. Quantum Chem., 48 (2005) 383

$$
\begin{aligned}
\boldsymbol{\nabla}\cdot\mathbf{B} &= 0 \\
\boldsymbol{\nabla}\times\mathbf{E}+\frac{\partial\mathbf{B}}{\partial t} &= 0 \\
\boldsymbol{\nabla}\cdot\mathbf{E} &= 4\pi\rho \\
\boldsymbol{\nabla}\times\mathbf{B}-\frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t} &= \frac{4\pi}{c^2}\mathbf{j}
\end{aligned}
\qquad c\to\infty \quad \Rightarrow \qquad
\begin{aligned}
\boldsymbol{\nabla}\cdot\mathbf{B} &= 0 \\
\boldsymbol{\nabla}\times\mathbf{E} &= 0 \\
\boldsymbol{\nabla}\cdot\mathbf{E} &= 4\pi\rho \\
\boldsymbol{\nabla}\times\mathbf{B} &= 0
\end{aligned}
$$

- In the strict non-relativistic limit there are no magnetic fields and no effects of retardation !
- The Coulomb gauge bears its name because it singles out the instantaneous Coulomb interaction, which constitutes the proper non-relativistic limit of electrodynamics and which is the most important interaction in chemistry.
- All retardation effects as well as magnetic interactions are to be considered corrections of a perturbation series of the total interaction (in $1/c^2$).

Scalar relativistic effects in chemistry

Relativistic effects in chemistry

- The Lorentz factor

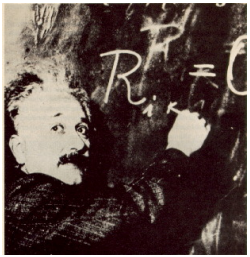
$$\gamma = \frac{1}{\sqrt{1 - v^2/c^2}}; \quad \begin{cases} v & \text{- speed of particle} \\ c & \text{- speed of light} \end{cases}$$

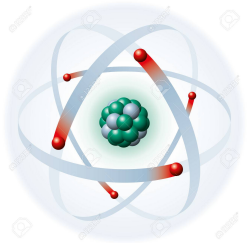
  is a diagnostic of relativistic effects.
- The speed of light is very large !

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

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

Scalar-relativistic effects: hydrogen-like atoms





- In atomic units the average speed of the $1s$ electron is equal to the nuclear charge

$$v_{1s} = Z\,a.u. \quad \text{and} \quad c = 137.0359998\,a.u.$$

- The relativistic mass increase of the $1s$ electron is thus determined by the nuclear charge

$$m = \gamma m_e = \frac{m_e}{\sqrt{1 - Z^2/c^2}}$$

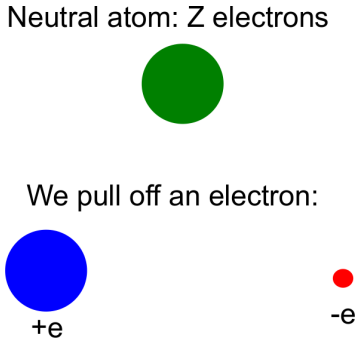
- The Bohr radius is inversely proportional to electron mass

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m}$$

- Relativity will *contract* orbitals of one-electron atoms, e.g.
  - Au^{78+}: $Z/c = 58\%$
  - *18% relativistic contraction of the 1s orbital*

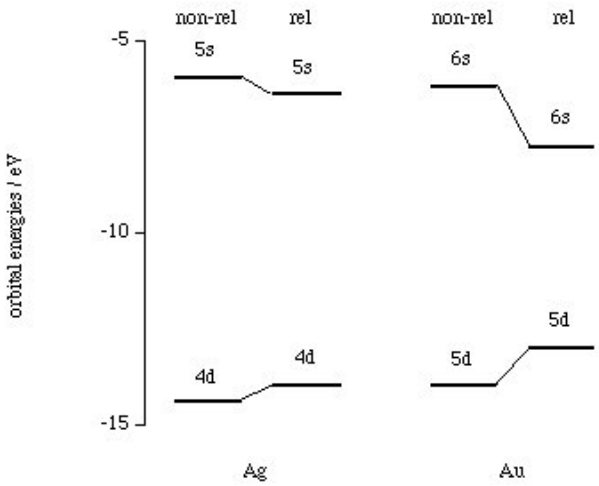
Scalar-relativistic effects: many-electron atoms

- The effect of the other electrons is effectively to screen the nuclear charge:



- The relativistic contraction of orbitals will *increase* screening of nuclear charge and thus *indirectly* favor orbital expansion.
- In practice we find:
  - s, p orbitals : contraction
  - d, f orbitals : expansion

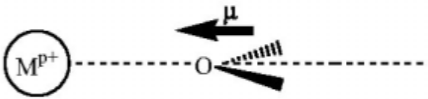
The colour of gold



The colours of silver and gold can be traced back to the energy difference between the $(n-1)d$ and ns orbitals in the atom. For silver this transition is in the ultraviolet, giving the metallic luster. For gold it is in the visible, but only when relativistic effects are included.

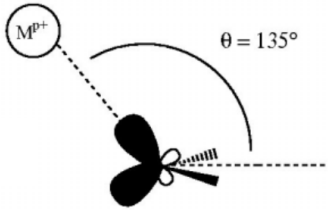
Metal-water interaction

C. Gourlaouen, J.-P. Piquemal, T. Saue and O. Parisel, J. Comp. Chem. 27 (2006) 142



$[Ag(H_2O)]^+$:
electrostatic interaction

bonding dominated by charge-dipole interaction

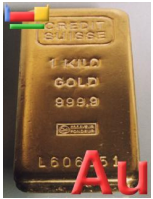


$[Au(H_2O)]^+$:
orbital interaction

relativistic stabilisation of the Au 6*s* orbital induces charge transfer and covalent bonding

Two contrasting neighbours: gold and mercury

L. J. Norrby, J. Chem. Ed. 68 (1991) 110

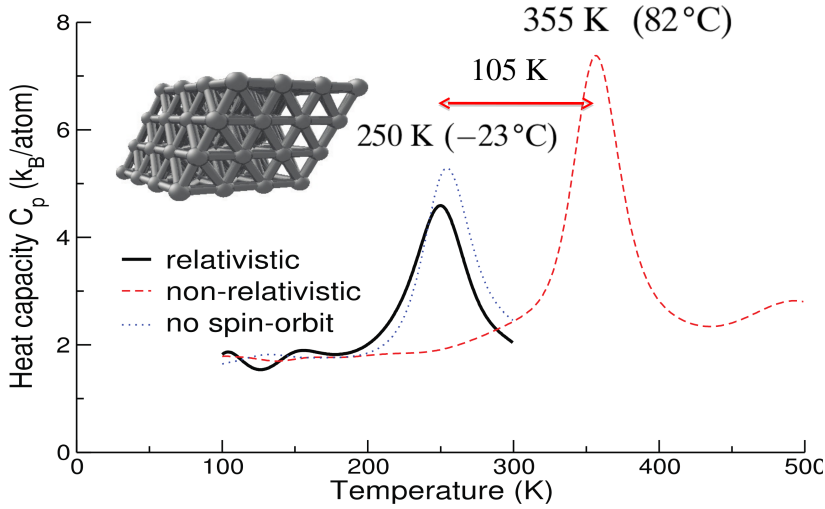


1064°C	Mp.	-39°C
12.5 kJ/mol	ΔH_{fus}	2.29 kJ/mol
9.29 J/Kmol	ΔS_{fus}	9.81 J/Kmol
19.32 g/cm^3	ρ	13.53 g/cm^3
426 kS/m	Conductivity	10.4 kS/m
dimer	Gas phase	monomer
[Xe]4f^{14}5d^{10}6s^1		[Xe]4f^{14}5d^{10}6s^2
pseudo halogen		pseudo noble gas

The low-temperature melting of mercury is a relativistic effect

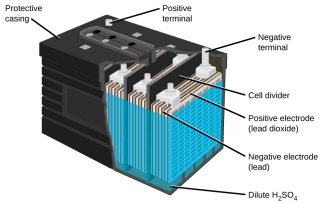
Florent Calvo, Elke Pahl, Michael Wormit and Peter Schwerdtfeger, Ang. Chemie. Int. Ed. 52 (2013) 7583

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



- Cathode reaction: $\mathrm{Pb\,(s) + HSO_4^-\,(aq) \longrightarrow PbSO_4\,(s) + H^+\,(aq) + 2\,e^-}$
- Anode reaction: $\mathrm{PbO_2\,(s) + HSO_4^-\,(aq) + 3\,H^+\,(aq) + 2\,e^- \longrightarrow PbSO_4\,(s) + 2\,H_2O\,(l)}$
- Total reaction: $\mathrm{Pb\,(s) + PbO_2\,(s) + 2\,H_2SO_4\,(aq) \longrightarrow 2\,PbSO_4\,(s) + 2\,H_2O\,(l)}$
- Cell potential: $E^0_{\mathrm{cell}} = -\frac{\Delta G^0}{nF} \approx -\frac{\Delta H\,(0K)}{nF}$

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

Spin-orbit interaction

Spin-orbit interaction

a much misunderstood interaction !

- Often seen formula:

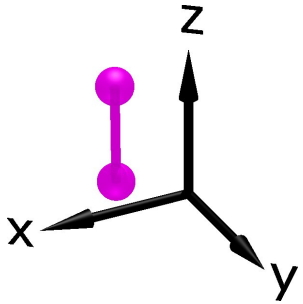
$$\hat{h}^{\mathrm{so}} = \frac{1}{2m^2c^2}\hat{\mathbf{s}} \cdot [(\boldsymbol{\nabla} V) \times \hat{\mathbf{p}}] \qquad \underset{\rightarrow}{V = -\frac{Z}{r}} \qquad \frac{Z}{2m^2c^2r^3}\hat{\mathbf{s}} \cdot \hat{\ell}$$

- **The spin-orbit interaction is not the interaction between spin and angular momentum of an electron.**
- **An electron moving alone in space is subject to no spin-orbit interaction !**
- The basic mechanism of the spin-orbit interaction is **magnetic induction**:
  - An electron which moves in a molecular field will feel a magnetic field in its rest frame, in addition to an electric field.
  - The spin-orbit term describes the interaction of the spin of the electron with this magnetic field due to the relative motion of other charges.
- This operator couples the degrees of freedom associated with spin and space and therefore makes it impossible to treat spin and spatial symmetry separately.

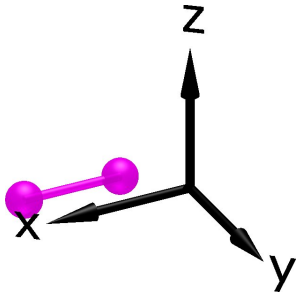
Spin-orbit interaction couples spin and space.

Example: I_2^+ (open-shell)

C. van Wüllen, J. Comput. Chem. 23 (2002) 779



Energy:$\equiv 0\ E_h$



Energy:$= +0.001469972\ E_h$

- These are DFT calculations using *collinear* magnetization: $s = m_z = \rho^\alpha - \rho^\beta$
- **Spin magnetization** : $\mathbf{m} = \sum_i \psi_i^\dagger \boldsymbol{\sigma} \psi_i$
- A solution is to use *non-collinear* magnetization: $s = |\mathbf{m}|$

Spin-orbit interaction in atoms

- Without spin-orbit interaction the orbital angular momentum and spin of orbitals are decoupled and can be specified separately

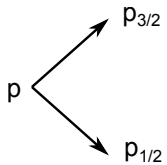
$$(l, m_l) \cup (s, m_s)$$

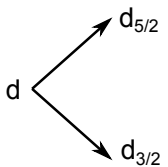
- With spin-orbit interaction only the total angular momentum is conserved

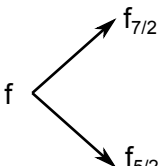
$$\mathbf{j} = \mathbf{l} + \mathbf{s}; \quad j = |l - s|, \ldots, l + s$$

- Orbitals are accordingly characterized by quantum numbers j and m_j

$$\hat{j}^2 |j, m_j\rangle = \hbar^2 j(j+1) |j, m_j\rangle ; \quad \hat{j}_z |j, m_j\rangle = \hbar m_j |j, m_j\rangle$$







Example: the oxygen atom

- Without spin-orbit coupling atomic electronic states are specified as ^{2S+1}L, with the notation S, P, D, ... for $L = 0, 1, 2, \ldots$.
- The ground state configuration of oxygen is $1s^2 2s^2 2p^4$ which in a non-relativistic framework (LS-coupling) gives rise to three states:

Term	L	S	Possible J values
^3P	1	1	2,1,0
^1D	2	0	2
^1S	0	0	0

- The actual energy levels are

Term	J	Level (cm^{-1})
^3P	2	0.000
	1	158.265
	0	226.977
^1D	2	15867.862
^1S	0	33792.583

http://physics.nist.gov/PhysRefData/Handbook/Tables/oxygentable1.htm

Spin-orbit splitting in group 8

Term	J	Oxygen	Sulfur	Selenium	Tellurium	Polonium
^3P	2	0.000	0.000	0.000	0.00	0.00
	1	158.265	396.055	1989.497	4706.500	7514.69
	0	226.977	573.640	2534.360	4750.712	16831.61
^1D	2	15867.862	9238.609	9576.149	10557.877	21679.11
^1S	0	33792.583	22179.954	22446.202	23198.392	

- For light atoms the fine structure approximately satisfies **Landé's interval rule**

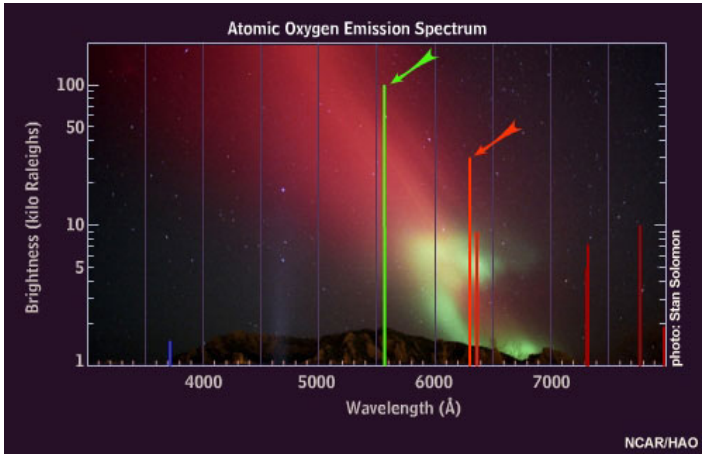
$$\Delta E\left(J, J'\right) = E_{SO}\left(LSJ\right) - E_{SO}\left(LSJ'\right) = \frac{1}{2}\zeta(^{2S+1}L)\left[J\left(J+1\right) - J'\left(J'+1\right)\right]$$

- ...which for neighbour levels reads

$$\Delta E\left(J, J-1\right) = \zeta(^{2S+1}L) \cdot J$$

- For heavier atoms the interval rule breaks down because of coupling between different LS terms as well as change in the spatial extent of radial parts between spin-orbit components.

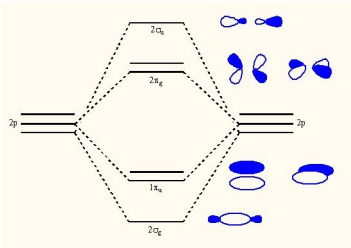
Atomic oxygen emissions in northern lights



	Transition	Wavelength(Å)	Type	Lifetime(s)
Green line	$^1S_0 \rightarrow {}^1D_2$	5577	E2	0.75
Red line	$^1D_2 \rightarrow {}^3P_2$	6300	M1	110

Molecular oxygen: the spinfree picture

- In the absence of spin-orbit interaction, molecular states are denoted $^{2S+1}\Lambda$, with $\Lambda = |M_L|$.



- Ground-state electron configuration: [core]$2\sigma_g^2 1\pi_u^4 2\pi_g^2$ $\Rightarrow$ $\begin{pmatrix} 4 \\ 2 \end{pmatrix} = 6$ micro-states
  - Electronic states: $^3\Sigma$, $^1\Sigma$, $^1\Delta$
- All states are gerade: $g \times g = g$.
- Σ-states are further characterized by reflection in planes containing the molecular axis:
  - $\pi_+ \leftrightarrow \pi_-$
  - We make the following table:

$$^1\Sigma_g: \quad \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \quad \times \quad \frac{1}{\sqrt{2}}(\pi_+\pi_- + \pi_-\pi_+) \quad \rightarrow \quad ^1\Sigma_g^+$$

$$^3\Sigma_g: \quad \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \quad \times \quad \frac{1}{\sqrt{2}}(\pi_+\pi_- - \pi_-\pi_+) \quad \rightarrow \quad ^3\Sigma_g^-$$

Molecular oxygen: adding spin-orbit interaction

- In the absence of spin-orbit interaction, molecular states are denoted $^{2S+1}\Lambda$, with $\Lambda = |M_L|$

Term	$T_e(\mathrm{cm}^{-1})$
$X^3\Sigma_g^-$	0.0
$a^1\Delta_g$	7918.1
$b^1\Sigma_g^+$	13195.1

http://webbook.nist.gov/chemistry/

- In the presence of spin-orbit interaction, molecular states are characterized by $\Omega = |M_L + M_S|$.
- Reflection symmetry: We now have to consider spin and spatial symmetry combined
  - Singlets are totally symmetric; triplets transform as rotations.
  - We obtain:

$$^3\Sigma_g^-: \qquad \tfrac{1}{2}\left(\pi_+\pi_- - \pi_-\pi_+\right)\left(\alpha\beta + \beta\alpha\right) \quad \rightarrow \quad 0_g^+$$

$$^1\Sigma_g^+: \qquad \tfrac{1}{2}\left(\pi_+\pi_- + \pi_-\pi_+\right)\left(\alpha\beta - \beta\alpha\right) \quad \rightarrow \quad 0_g^+$$

- The ground state of the oxygen molecule is a triplet.
  - It is split by spin-orbit interaction into 0_g^+ and 1_g (zero-field splitting).
  - A magnetic interaction such as spin-orbit interaction is required for interaction with singlet states.
  - This is crucial for life !

Chalcogen dimers: zero-field splitting

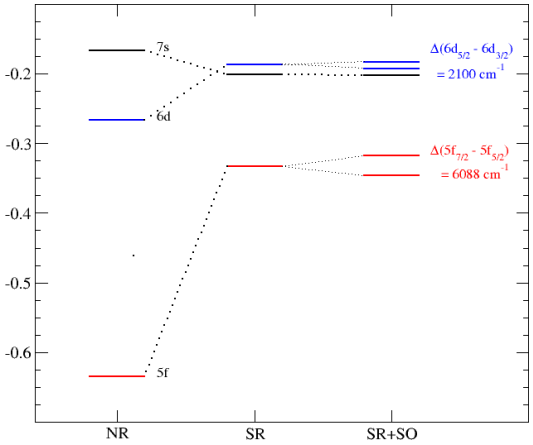
- Oxygen dimer:

Term	$T_e(\mathrm{cm}^{-1})$
$X^3\Sigma_g^-$	0.0
$a^1\Delta_g$	7918.1
$b^1\Sigma_g^+$	13195.1

http://webbook.nist.gov/chemistry/

- Zero-field splitting:
  - O_2 : $0.156\,\mathrm{cm}^{-1}$
  - S_2 : $23.5\,\mathrm{cm}^{-1}$
  - Se_2 : $510.0\,\mathrm{cm}^{-1}$
  - Te_2 : $1974.9\,\mathrm{cm}^{-1}$
  - Po_2 : $\sim 7000\,\mathrm{cm}^{-1}$

Relativistic effects: valence orbital energies (E_h) of the uranium atom



- **Scalar relativistic effects (SR):** relativistic mass increase of the electron
- **Spin-orbit effects (SO):** the interaction of the electron spin with the magnetic field induced by charges (e.g. nuclei and other electrons) in relative motion

Summary so far

- Relativistic effects are important for heavy elements (Z>40). We distinguish between:
  - **scalar relativistic effects** are associated with the relativistic mass increase of the electron

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}; \quad c = 137.0359998\,a.u.; \quad \text{One-electron atom:} \quad v_{1s} = Z\,a.u.$$

    and modifies size and energetics of orbitals
  - **spin-orbit interaction** is due to magnetic induction and modifies energy levels and allowed transitions
- Since relativistic effects are most pronounced in the core region, a straightforward and widely used way to introduce relativity in quantum chemical calculations is to replace the core orbitals by an effective potential, leading to the **pseudopotential** approach.
- In the following we shall, however, first look at Hamiltonians derived directly from the Dirac equation.

Wolfgang Pauli and 137

Wolfgang Pauli (1900-1958)

Throughout his life, Pauli was preoccupied with the question of why the fine structure constant, a dimensionless fundamental constant, has a value nearly equal to 1/137.

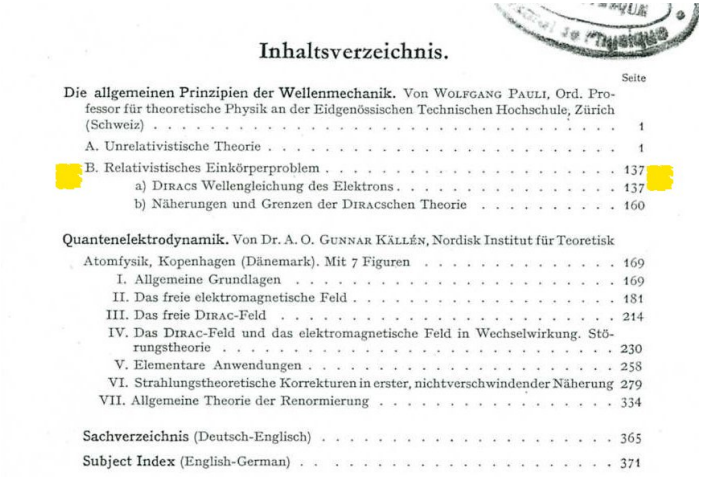
Wolfgang Pauli and 137

Wolfgang Pauli (1900-1958)

In 1958, Pauli fell ill with pancreatic cancer. When his last assistant, Charles Enz, visited him at the Rotkreuz hospital in Zurich, Pauli asked him: "Did you see the room number?" It was number 137. Pauli died in that room on December 15, 1958.

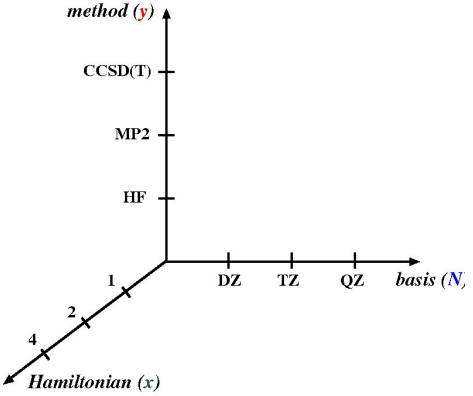
The Old and the New Testament

- Handbuch der Physik (1926): The Old Testament
- Handbuch der Physik (1933): The New Testament



Inhaltsverzeichnis.

Theoretical model chemistries

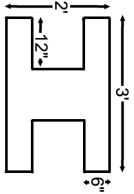


The electronic Hamiltonian, relativistic or not, has the same generic form

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

Computational cost: $x N^y$

Constructing the relativistic Hamiltonian



The non-relativistic electronic Hamiltonian

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

- One- and two-electron operators:

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

- Quantization:

$$E \quad \rightarrow \quad i\frac{\partial}{\partial t}; \quad \mathbf{p} \quad \rightarrow \quad \hat{\mathbf{p}} = -i\boldsymbol{\nabla}$$

- Wave equation for non-relativistic free particle:

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}; \quad \rightarrow i\frac{\partial}{\partial t}\psi = \frac{\hat{p}^2}{2m}\psi = \hat{h}_0\psi$$

Relativistic free particle: classical mechanics

- Relativistic free-particle

$$E = \pm\sqrt{m^2c^4 + c^2p^2} \in \langle -\infty, -mc^2 | \cup | +mc^2, +\infty \rangle$$

- Classical particles can only change energy continuously, so we can exclude the negative-energy branch
- Connecting to the non-relativistic expression

$$E = +mc^2\sqrt{1 + \left(\frac{p}{mc}\right)^2} = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots$$

- The first term explodes in the non-relativistic limit ($c \to \infty$), but can be avoided by aligning the relativistic energy scale with the non-relativistic one

$$E \quad \to \quad E - mc^2$$

(only works for positive-energy branch)

Dirac equation for a relativistic free particle

- Dirac equation

$$\left(\hat{h}_0 - i\frac{\partial}{\partial t}\right)\psi \quad = \quad 0$$

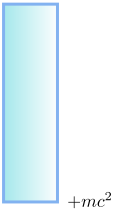
with relativistic free-particle Hamiltonian

$$\hat{h}_0 = \beta mc^2 + c\,(\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}) = \begin{bmatrix} +mc^2 & c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \\ c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) & -mc^2 \end{bmatrix}$$

- The solutions are 4-component vector functions

$$\psi = \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \begin{bmatrix} \psi^{L\alpha} \\ \psi^{L\beta} \\ \psi^{S\alpha} \\ \psi^{S\beta} \end{bmatrix}$$

- Why four components ?



Adding electromagnetic fields: The principle of minimal electromagnetic coupling

(M. Gell-Mann, Nuovo Cimento Suppl. 4 (1956) 848)

- The Hamiltonian of a particle interacting with external fields is obtained from the free-particle Hamiltonian through the substitutions:

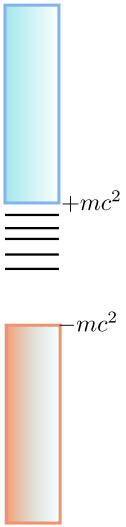
$$p_\mu \to p_\mu - qA_\mu \quad \Rightarrow \quad \text{Electron: } q = -e \quad \Rightarrow \quad \begin{array}{rcl} \hat{\mathbf{p}} & \to & \hat{\mathbf{p}} + e\mathbf{A} \\ E & \to & E + e\phi \end{array}$$

- The coupling of particle and field is minimal because it involves only the charge of the particle.
- The complete Dirac Hamiltonian reads

$$\hat{h}_D = \beta' mc^2 + c\,(\boldsymbol{\alpha}\cdot\hat{\boldsymbol{\pi}}) - e\phi = \begin{bmatrix} -e\phi & c\,(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\pi}}) \\ c\,(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\pi}}) & -2mc^2 - e\phi \end{bmatrix}$$

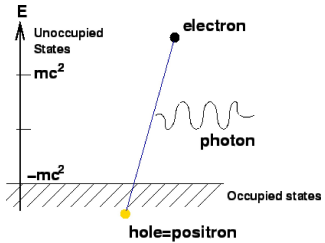
  where appears the **mechanical momentum** $\hat{\boldsymbol{\pi}} = \hat{\mathbf{p}} + e\mathbf{A}$
- Energy shift: $\beta \to \beta' - mc^2 \quad \Rightarrow \quad E \to E' = E - mc^2$

Negative-energy solutions



- Classical mechanics does not allow energy discontinuities, and so one may reject the negative-energy solutions.
- In quantum mechanics, these solutions are problematic because there is always a finite transition probability.
  - It can be shown that the hydrogen atom would not be stable and would disintegrate in 10^{-9} s.
  - The electron descending down the negative-energy band would cause an ultraviolet catastrophe.

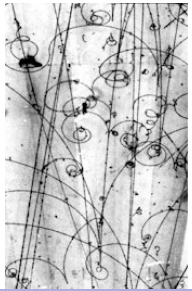
Electron-positron pair creation



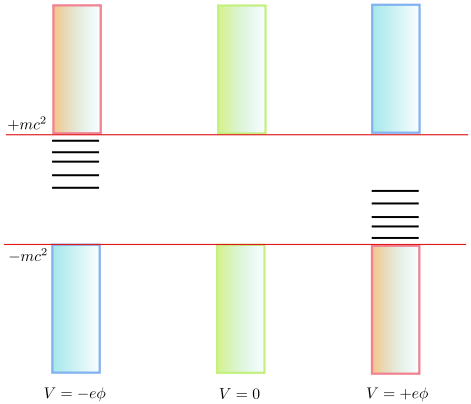
The solution proposed by Dirac

- 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 discover the positron.



Charge conjugation symmetry



- Introduction of fields require specification of charge.
- For $q = -e$, all solutions, of both positive and negative energy, are *electronic*.
- For $q = +e$, all solutions are *positronic*.
- Solutions of opposite charge are related by charge conjugation symmetry.

Constants of motion

- Heisenberg's equation:

$$\frac{d\langle\Psi|\hat{A}|\Psi\rangle}{dt} = -i\langle\Psi|[\hat{A},\hat{H}]|\Psi\rangle + \langle\Psi|\frac{\partial\hat{A}}{\partial t}|\Psi\rangle$$

- Constant of motion:

$$\frac{d\langle\Psi|\hat{A}|\Psi\rangle}{dt} = 0$$

- Free particle : conservation of (linear) momentum

$$\left[\hat{\mathbf{p}},\hat{h}_0^{NR}\right] = 0 = \left[\hat{\mathbf{p}},\hat{h}_0^{R}\right]$$

Spin and angular momentum

- Non-relativistic free particle:

$$\left[\hat{\boldsymbol{\ell}}, \hat{h}_0^{NR}\right] = \frac{i}{m}\left(\hat{\mathbf{p}} \times \hat{\mathbf{p}}\right) = 0$$

$$\left[\hat{\mathbf{s}}, \hat{h}_0^{NR}\right] = 0$$

- Relativistic free particle:

$$\left[\hat{\boldsymbol{\ell}}, \hat{h}_0^{R}\right] = i\left(c\boldsymbol{\alpha} \times \hat{\mathbf{p}}\right) \neq 0$$

$$\left[\boldsymbol{\Sigma}, \hat{h}_0^{R}\right] = -2i\left(c\boldsymbol{\alpha} \times \hat{\mathbf{p}}\right) \neq 0$$

- The relativistic free-particle Hamiltonian commutes with total angular momentum $j = \ell + \frac{1}{2}\boldsymbol{\Sigma}$ and carries spin.
- The economy of Nature's laws.

Non-relativistic Hamiltonian in external fields

- Minimal substitution gives

$$h_0^{NR} = \frac{\hat{p}^2}{2m} \quad \rightarrow \quad h^{NR} = \frac{\hat{\pi}^2}{2m} - e\phi = \frac{\hat{p}^2}{2m} + \frac{e}{2m}\left[\hat{\mathbf{p}}\cdot\mathbf{A} + \mathbf{A}\cdot\hat{\mathbf{p}}\right] + \frac{e^2A^2}{2m} - e\phi$$

  - no spin interactions

- The Dirac identity

$$(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{B}) = \mathbf{A}\cdot\mathbf{B} + i\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{B})$$

- A special case

$$(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) = \hat{p}^2$$

  suggests that spin is "hidden" in the non-relativistic operator.

- Minimal substitution then gives

$$\begin{aligned} h_0^{NR} = \frac{(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})^2}{2m} \quad \rightarrow \quad h^{NR} &= \frac{(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\pi}})^2}{2m} - e\phi \\ &= \frac{\hat{p}^2}{2m} + \frac{e}{2m}\left[\hat{\mathbf{p}}\cdot\mathbf{A} + \mathbf{A}\cdot\hat{\mathbf{p}}\right] + \frac{e^2A^2}{2m} + \frac{e}{2m}(\boldsymbol{\sigma}\cdot\mathbf{B}) - e\phi \end{aligned}$$

- **Is spin a relativistic effect ?**

Charge and current density

- The coupling of particles and fields is relativistic

$$\langle \hat{h}_{int} \rangle = \int \left[\rho(\mathbf{r},t)\phi(\mathbf{r},t) - \mathbf{j}(\mathbf{r},t) \cdot \mathbf{A}(\mathbf{r},t) \right] d^3\mathbf{r} = -\int j_\mu A_\mu d^3\mathbf{r}$$

- .. and allows us to extract charge and current density

$$\rho^R = \frac{\delta \langle \hat{h}_{int} \rangle}{\delta \phi} = \psi^\dagger(\mathbf{r}) \underbrace{\{-e\mathbf{I}_4\}}_{\text{density operator}} \psi(\mathbf{r}); \quad \mathbf{j}^R = -\frac{\delta \langle \hat{h}_{int} \rangle}{\delta \mathbf{A}} = \psi^\dagger(\mathbf{r}) \underbrace{\{-ec\boldsymbol{\alpha}\}}_{\text{current operator}} \psi(\mathbf{r})$$

- The corresponding non-relativistic expressions are

$$\begin{aligned} \rho^{NR} &= -e\psi^\dagger(\mathbf{r})\psi(\mathbf{r}) \\ \mathbf{j}^{NR} &= -\frac{e}{2m}\left\{\psi^\dagger(\mathbf{r})\hat{\mathbf{p}}\psi(\mathbf{r}) - \psi^T(\mathbf{r})\hat{\mathbf{p}}\psi^*(\mathbf{r})\right\} - \frac{e^2}{2m}\psi^\dagger(\mathbf{r})\mathbf{A}\psi(\mathbf{r}) \\ &- \frac{e}{2m}\boldsymbol{\nabla} \times \psi^\dagger(\mathbf{r})\boldsymbol{\sigma}\psi(\mathbf{r}) \end{aligned}$$

  - The expression for current density is clearly more complicated.

Velocity operators

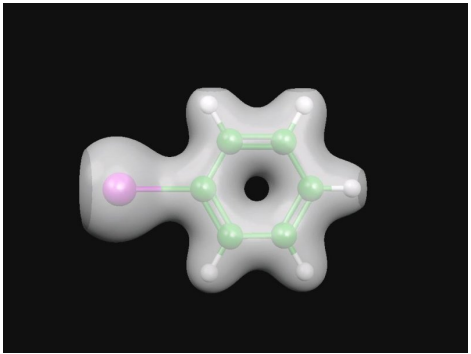
- Consider the non-relativistic and relativistic velocity operators obtained by the Heisenberg equation of motion

$$\begin{aligned} \frac{d\mathbf{r}}{dt} &= -i\left[\mathbf{r}, \hat{h}^{\mathrm{NR}}\right] = -i\left[\mathbf{r}, \frac{\hat{p}^2}{2m}\right] = \frac{\hat{\mathbf{p}}}{m} \\ \frac{d\mathbf{r}}{dt} &= -i\left[\mathbf{r}, \hat{h}^{\mathrm{R}}\right] = c\boldsymbol{\alpha} \end{aligned}$$

- The curious form of the relativistic velocity operator is due to *Zitterbewegung*, to be explained later.

(Number) density of iodobenzene

$$\rho^R = \rho^L + \rho^S$$



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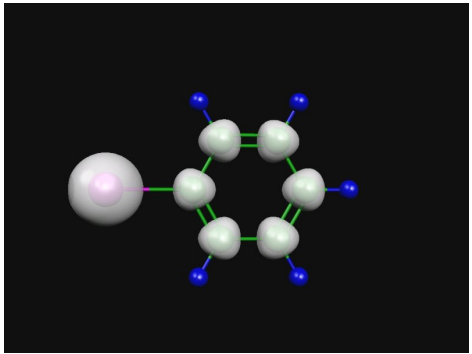
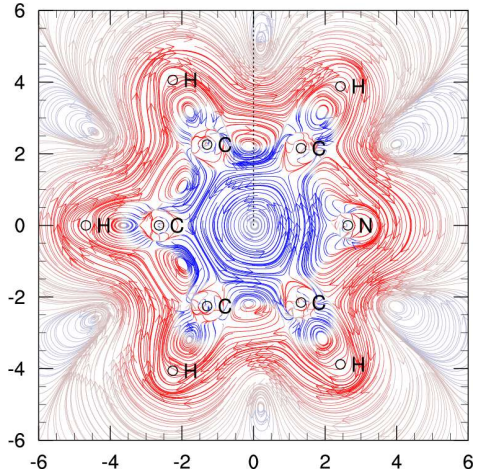
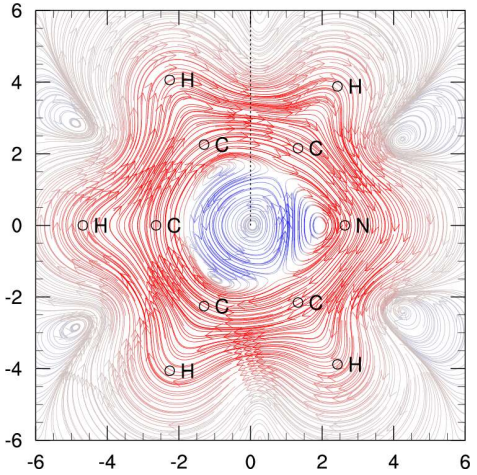


(isosurface 0.0001)

(Number) density of iodobenzene



(molecular plane)



(molecular plane $\pm 1 a_0$)

Two-electron interaction

- General form:

$$g(1,2) = q_1\phi_2 - q_1\mathbf{v}_1 \cdot \mathbf{A}_2$$

- Coulomb gauge:

$$\phi(\mathbf{r}_1, t) = \int \frac{\rho(\mathbf{r}_2, t)}{r_{12}} d^3\mathbf{r}_2; \quad \mathbf{A}(\mathbf{r}_1, t) = \mathbf{A}_\perp(\mathbf{r}_1, t) = \frac{4\pi}{c^2} \int \frac{\mathbf{j}_\perp(\mathbf{r}_2, t_r)}{r_{12}} d^3\mathbf{r}_2$$

- Quantification and truncation

$$\hat{g}(1,2) = \frac{1}{r_{12}} - \underbrace{\left[\underbrace{\frac{c\boldsymbol{\alpha}_i \cdot c\boldsymbol{\alpha}_j}{c^2 r_{12}}}_{\text{Gaunt}} + \frac{(c\boldsymbol{\alpha}_1 \cdot \boldsymbol{\nabla}_1)(c\boldsymbol{\alpha}_2 \cdot \boldsymbol{\nabla}_2) r_{12}}{2c^2} \right]}_{\text{Breit}} + O(c^{-2})$$

4-component relativistic Hamiltonian

- Generic form of electronic Hamiltonian:

$$\hat{H} = V_{NN} + \sum_i \hat{h}(i) + \frac{1}{2}\sum_{i\neq j} \hat{g}(i,j); \quad \hat{h}(i) = \hat{h}_0 + V_{eN}$$

- **One-electron operator**: Dirac operator in the molecular field

$$\hat{h}_D(i) = \beta_i' mc^2 + c\,(\boldsymbol{\alpha}_i \cdot \hat{\mathbf{p}}_i) + \hat{V}_{eN};$$

  - where we have introduced $\beta' = \beta - 1$ to align with the non-relativistic energy scale

- **Two-electron operator**: (Coulomb gauge)

$$\begin{aligned} \hat{g}(i,j) &= \frac{1}{r_{ij}} \\ &- \frac{c\boldsymbol{\alpha}_i \cdot c\boldsymbol{\alpha}_j}{c^2 r_{ij}} - \frac{(c\boldsymbol{\alpha}_i \cdot \boldsymbol{\nabla}_i)\,(c\boldsymbol{\alpha}_j \cdot \boldsymbol{\nabla}_j)\, r_{ij}}{2c^2} \\ &+ \ldots \end{aligned}$$

2-component relativistic Hamiltonians

2-component relativistic Hamiltonians

- Starting from the Dirac equation in a molecular field

$$\begin{bmatrix} V & c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \\ c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) & V-2mc^2 \end{bmatrix} \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} E$$

  we would like to generate a 2-component Hamiltonian h_{++} which reproduces the positive-energy spectrum of the parent Hamiltonian.

- This can be accomplished by a **unitary block diagonalization**

  L. L. Foldy, S. A. Wouthuysen, Phys. Rev. **78** (1950) 29

$$\hat{U}^\dagger \begin{bmatrix} \hat{h}_{LL} & \hat{h}_{LS} \\ \hat{h}_{SL} & \hat{h}_{SS} \end{bmatrix} \hat{U} = \begin{bmatrix} \hat{h}_{++} & 0 \\ 0 & \hat{h}_{--} \end{bmatrix}$$

  - or, equivalently, by **elimination of the small components** followed by renormalization of the transformed large components.

- The transformation can be expressed as

  J.-L. Heully, I. Lindgren, E. Lindroth, A.-M. Mårtensson-Pendrill, Phys. Rev. A **33** (1986) 4426;
  W. Kutzelnigg in *Relativistic Electronic Structure Theory*. Part 1. Fundamentals, (Ed.: P. Schwerdtfeger), Elsevier, Amsterdam, 2002, p. 66

$$\hat{U} = \hat{W}_1\hat{W}_2; \quad \hat{W}_1 = \begin{bmatrix} 1 & -\hat{R}^\dagger \\ \hat{R} & 1 \end{bmatrix}; \quad \hat{W}_2 = \begin{bmatrix} \hat{\Omega}_+ & 0 \\ 0 & \hat{\Omega}_- \end{bmatrix}; \quad \begin{aligned} \hat{\Omega}_+ &= \left(1+\hat{R}^\dagger\hat{R}\right)^{-1/2} \\ \hat{\Omega}_- &= \left(1+\hat{R}\hat{R}^\dagger\right)^{-1/2} \end{aligned}$$

Decoupling transformation

- We have seen that the decoupling transformation is given by

$$\hat{U} = \hat{W}_1 \hat{W}_2 = \begin{bmatrix} \hat{\Omega}_+ & -\hat{R}^\dagger \hat{\Omega}_- \\ \hat{R}\hat{\Omega}_+ & \hat{\Omega}_- \end{bmatrix}$$

- The identification of the operator R becomes clear when considering the effect of the Foldy-Wouthuysen transformation on the orbitals

$$\hat{U}^\dagger \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \begin{bmatrix} \hat{\Omega}_+ \left(\psi^L + \hat{R}^\dagger \psi^S\right) \\ \hat{\Omega}_- \left(\psi^S - \hat{R}\psi^L\right) \end{bmatrix}$$

- For the positive energy solutions we want the lower component to be zero, thus implying

$$\psi_+^S = \hat{R}\psi_+^L$$

- The 2-component positive-energy solutions take the form

$$\psi_+ = \frac{1}{\sqrt{1+\hat{R}^\dagger \hat{R}}} \left(\psi^L + \hat{R}^\dagger \psi^S\right) = \frac{1}{\sqrt{1+\hat{R}^\dagger \hat{R}}} \left(\psi^L + \hat{R}^\dagger \hat{R} \psi^L\right) = \sqrt{1+\hat{R}^\dagger \hat{R}}\,\psi^L$$

Approximate 2-component relativistic Hamiltonians in one step

- The exact decoupling requires in principle to solve the Dirac equation

$$\hat{R} = \left(2mc^2 - V + E\right)^{-1} c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})$$

- **One-step procedures:**
  - Using the approximate decoupling

$$\hat{R} = \frac{1}{2mc}\left[1 + \frac{E-V}{2mc^2}\right]^{-1}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \sim \frac{1}{2mc}\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})$$

    and retaining terms only to $O(c^{-2})$ gives the **Pauli Hamiltonian**.
  - Using the approximate decoupling (regular approximation)

$$\hat{R} = \frac{c}{2mc^2 - V}\left[1 + \frac{E}{2mc^2 - V}\right]^{-1}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \sim \frac{c}{2mc^2 - V}\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})$$

    without/with renormalization gives the **ZORA/IORA Hamiltonians**.

Pauli Hamiltonian

- The Pauli Hamiltonian is based on an approximative decoupling of the large and small components

$$\hat{R} = \left(2mc^2 - V + E\right)^{-1} c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) = \frac{1}{2mc}\left[1 + \frac{E-V}{2mc^2}\right]^{-1}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \sim \frac{1}{2mc}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})$$

- Applying the unitary transformation and retaining terms only to $O(c^{-2})$gives the Pauli Hamiltonian

$$\hat{h}^{\text{Pauli}} = V + \hat{T} \underbrace{-\frac{\hat{p}^4}{8m^3c^2}}_{\text{mass-velocity}} \underbrace{+\frac{1}{8m^2c^2}\left(\nabla^2 V\right)}_{\text{Darwin}} \underbrace{+\frac{1}{4m^2c^2}\boldsymbol{\sigma}\cdot[(\boldsymbol{\nabla}V)\times\hat{\mathbf{p}}]}_{\text{spin-orbit}}$$

- Let us investigate the physics it contains !

Mass-velocity term

- Relativistic mass correction

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

- Problem: The mass-velocity term has no lower bound.
  - The Pauli-Hamiltonian can not be used in variational calculations.

Darwin term

$$\hat{h}^{\mathrm{Darwin}} = \frac{1}{8m^2c^2}\left(\nabla^2 V\right) = \frac{-e}{8m^2c^2}\left(\nabla^2\phi\right)$$

- The origin of the Darwin term is *Zitterbewegung*, an oscillatory motion of the electron.
- Assume that the electron has a rapid oscillatory motion $\boldsymbol{\delta}$ about the *average* position $\mathbf{r}$.
  - The instantaneous Coulomb interaction is modified

$$-e\phi(\mathbf{r}) \quad \rightarrow \quad -e\phi(\mathbf{r}+\boldsymbol{\delta})$$

  - We perform a Taylor expansion

$$\phi(\mathbf{r}+\boldsymbol{\delta}) \quad = \quad \phi(\mathbf{r}) + (\boldsymbol{\delta}\cdot\boldsymbol{\nabla})\,\phi(\mathbf{r}) + \frac{1}{2}(\boldsymbol{\delta}\cdot\boldsymbol{\nabla})^2\,\phi(\mathbf{r}) + \ldots$$

Darwin term cont'd

- We consider the time average of the interaction

$$\begin{aligned} -e\left\langle \phi(\mathbf{r}+\boldsymbol{\delta})\right\rangle_T &= -e\phi(\mathbf{r}) - e\left\langle (\boldsymbol{\delta}\cdot\boldsymbol{\nabla})\right\rangle_T \phi(\mathbf{r}) - \frac{1}{2}e\left\langle (\boldsymbol{\delta}\cdot\boldsymbol{\nabla})^2\right\rangle_T \phi(\mathbf{r}) + \ldots \\ &= -e\phi(\mathbf{r}) - e\frac{\left\langle \delta^2\right\rangle_T}{6}\nabla^2\phi(\mathbf{r}) + \end{aligned}$$

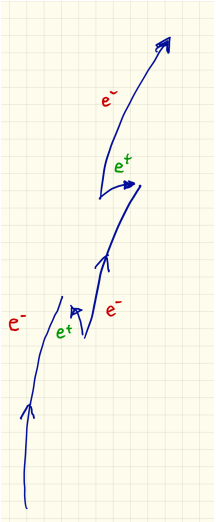
- We make the identification

$$\left\langle \delta^2\right\rangle_T = \frac{3}{4m^2c^2}; \quad \Rightarrow \delta_x = \delta_y = \delta_z = \frac{1}{2mc}$$

  - which gives the Darwin term

$$\hat{h}^{\mathrm{Darwin}} = \frac{-e}{8m^2c^2}\left(\nabla^2\phi\right)$$

What is Zitterbewegung ?



- One interpretation is that in the vicinity of an electron its field is sufficiently strong to allow the creation of a electron-positron pair.
- The positron annihilates the original electron and the "new" electron takes over.
- Consider the energy-time uncertainity relation

$$\Delta E \Delta t \geq 1$$

- The creation of an electron-positron pair requires at least $2mc^2$ from which we obtain

$$\Delta t \approx \frac{1}{2mc^2}$$

- In this time a particle can move a maximum distance of

$$\Delta x \approx \frac{1}{2mc} \quad !$$

Spin-orbit interaction

- Spin-orbit interaction term of the Pauli Hamiltonian

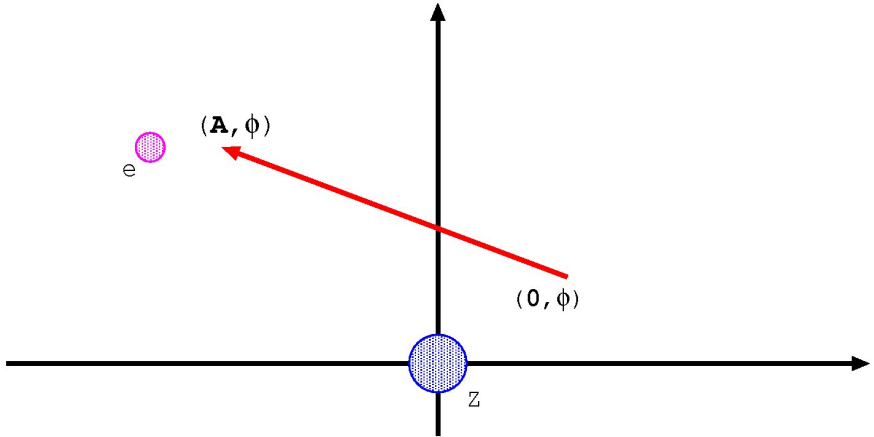
$$\hat{h}^{\mathrm{so}} = \frac{1}{2m^2c^2}\hat{\mathbf{s}} \cdot [(\boldsymbol{\nabla} V) \times \hat{\mathbf{p}}] \qquad \underset{\rightarrow}{V = -\frac{Z}{r}} \qquad \frac{Z}{2m^2c^2r^3}\hat{\mathbf{s}} \cdot \hat{\boldsymbol{\ell}}$$

- **Digression:** Dirac-Coulomb Hamiltonian

$$\hat{H} = V_{NN} + \sum_i \left\{ \beta_i mc^2 + c\,(\boldsymbol{\alpha}_i \cdot \hat{\mathbf{p}}_i) + V_{eN}(i) \right\} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

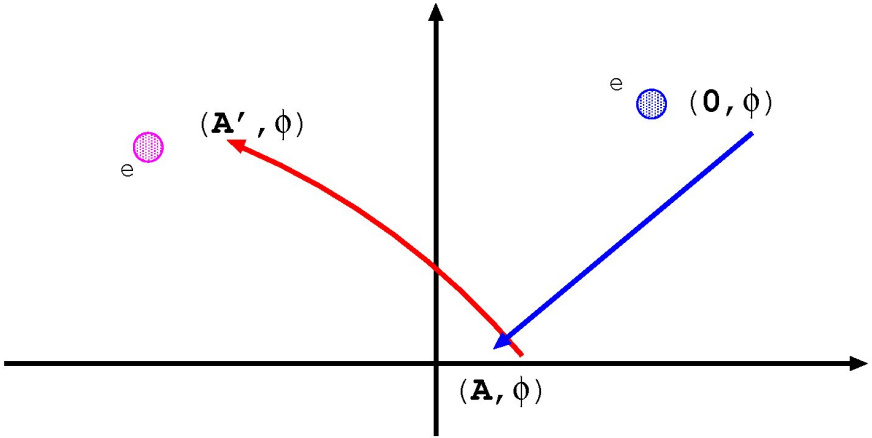
- Where is the spin-orbit interaction operator $\left(\sim \hat{\mathbf{s}} \cdot \hat{\boldsymbol{\ell}} \right)$???
  - There is no explicit operator since
    the electronic Hamiltonian is formulated in the nuclear frame.

Spin-orbit interaction is magnetic induction



By insisting on Coulomb gauge $\phi = \frac{Z}{r}$ in all reference frames.

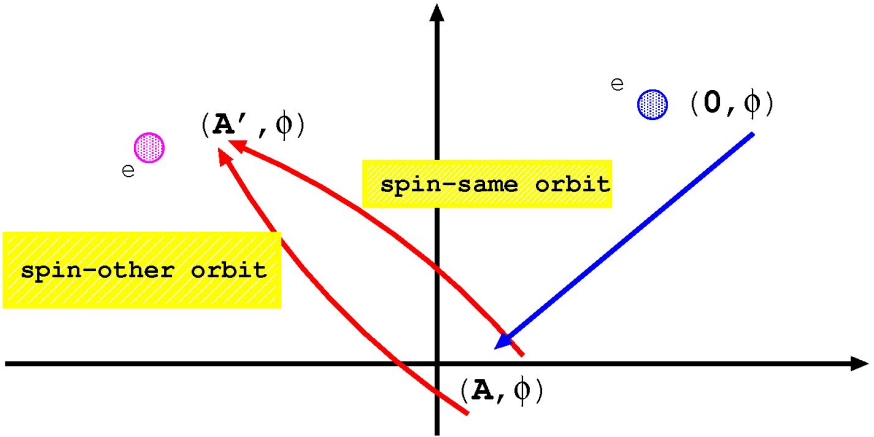
Spin-orbit interaction with other electrons



By insisting on Coulomb gauge $\phi = \frac{1}{r_{12}}$ in all reference frames.

Spin-same-orbit (SSO) interaction arises from the Coulomb term.

Spin-orbit interaction with other electrons



By insisting on Coulomb gauge $\phi = \frac{1}{r_{12}}$ in all reference frames.

Spin-other-orbit (SOO) interaction arises from the Gaunt term.

The spin-orbit interaction with nuclei is of type spin-own orbit

The ZORA Hamiltonian

- The ZORA Hamiltonian is based on an approximative decoupling of the large and small components

$$\hat{R} = \frac{c}{2mc^2 - V}\left[1 + \frac{E}{2mc^2 - V}\right]^{-1}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) \sim \frac{c}{2mc^2 - V}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})$$

- Zeroth-Order Regular Approximation (ZORA)
  [renormalization terms ignored]:

$$\hat{h}^{\mathrm{ZORA}} = V + \frac{1}{2m}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\frac{2mc^2}{2mc^2 - V}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})$$

  - The second term can be thought of as an *effective* kinetic energy operator that goes to the non-relativistic one when $V \to 0$.
- **Electric gauge-dependence**: $(V \to V + \Delta \quad \not\Rightarrow \quad E \to E + \Delta)$
  - Usually fixed by approximating the potential in the denominator by a superposition of atomic potentials.

- We are solving
$$\hat{h}^{\mathrm{ZORA}}\varphi_p = \varepsilon_p^{\mathrm{ZORA}}\varphi_p,$$
- ..but should be solving
(NESC: normalized elimination of small components)
$$\hat{h}^{\mathrm{ZORA}}\phi_p = \left[1 + \hat{R}^\dagger\hat{R}\right]\varepsilon_p^{\mathrm{IORA}}\phi_p.$$
- We introduce the approximate equation
$$\hat{h}^{\mathrm{ZORA}}\varphi_p = \left[1 + \langle\varphi_p|\hat{R}^\dagger\hat{R}|\varphi_p\rangle\right]\tilde{\varepsilon}_p^{\mathrm{IORA}}\varphi_p$$
- This leads to the **scaled ZORA** approach (only correcting eigenvalues)
$$\varepsilon_p^{\mathrm{IORA}} \approx \varepsilon_p^{\mathrm{scZORA}} = \frac{\varepsilon_p^{\mathrm{ZORA}}}{1 + \langle\varphi_p|\hat{R}^\dagger\hat{R}|\varphi_p\rangle}$$
  - For one-electron systems the Dirac eigenvalues are reproduced.

Approximate 2-component relativistic Hamiltonians in two steps

- **Two-step procedures:**
  - 1a) Using the exact free-particle decoupling

$$\hat{R} = \frac{c\,(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})}{\hat{E}_p + mc^2} \sim O\left(c^{-1}\right); \quad \hat{E}_p = \sqrt{m^2c^4 + c^2\hat{p}^2}$$

    provides regularized and variationally stable Hamiltonians,
    - ★ but not exact decoupling

$$\hat{h} \rightarrow \begin{bmatrix} \hat{E}_p - mc^2 & 0 \\ 0 & -\hat{E}_p - 3mc^2 \end{bmatrix} + \begin{bmatrix} \hat{A}\left[V + \hat{R}V\hat{R}\right]\hat{A} & \hat{A}\left[\hat{R}, V\right]\hat{A} \\ -\hat{A}\left[\hat{R}, V\right]\hat{A} & \hat{A}\left[V + \hat{R}V\hat{R}\right]\hat{A} \end{bmatrix}$$

$$\hat{A} = \frac{1}{\sqrt{1 + \hat{R}^\dagger\hat{R}}} = \sqrt{\frac{\hat{E}_p + mc^2}{2\hat{E}_p}} \sim O\left(c^0\right)$$

  - 2a) Subsequent decoupling transformations in orders of the potential defines **Douglas-Kroll-Hess (DKH) Hamiltonians** to given order.
    - ★ DKH1 means no further transformation, DKH2 is the standard form.
  - 2b) Iterating the coupling equation of the free-particle transformed Hamiltonian to obtain the coupling correct through some odd order $2k-1$ in c^{-1} and then perform a *single* unitary transformation defines the **Barysz, Sadlej and Snijders (BSS) Hamiltonian** to order $2k$.

Exact 2-component (X2C) Hamiltonians

M. Iliaš, H. J. Aa. Jensen, V. Kellö, B. O. Roos and M. Urban, Chem. Phys. Lett. 408 (2005) 210; W. Kutzelnigg and W. Liu, J. Chem. Phys. 123 (2005) 241102; M. Iliaš and T. Saue, J. Chem. Phys. 126 (2007) 064102

- Two important realizations:
  - solving the one-electron problem is cheap compared to the many-electron problem
  - use matrix algebra
- ... led to this **simple algorithm for exact decoupling:**
  - 1. Solve the Dirac equation on matrix form
  - 2. Extract the coupling R from the solutions
  - 3. Construct the transformation matrix U, next h^{X2C}
- **Advantages:**
  - reproduces exactly the positive-energy spectrum of the Dirac Hamiltonian
  - all matrix manipulations; no new operators to program
  - explicit representation of transformation matrix
    - ⋆ any property operator can be transformed on the fly
    - ⋆ no **picture change errors**

Picture change errors

- The 2-component Hamiltonian is obtained as

$$H^{2c} = \left[U^\dagger H^{4c} U \right]_{++}$$

- Property operators Ω^{4c} must be subjected to the same decoupling transformation as the Hamiltonian, that is

$$\Omega^{2c} = \left[U^\dagger \Omega^{4c} U \right]_{++}$$

- Use of the approximate expression

$$\Omega^{2c} \approx \left[\Omega^{4c} \right]_{LL}$$

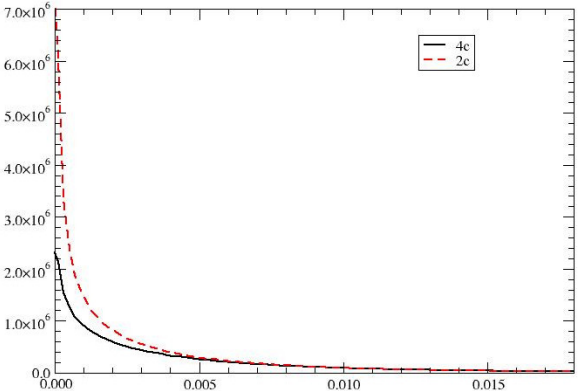
leads to **picture change errors**

  - may be larger than the relativistic effects !

An example: the electron density

$$\rho^{4c}(\mathbf{P}) = -e\sum_i \langle\psi_i^{4c}|\delta(\mathbf{r}-\mathbf{P})|\psi_i^{4c}\rangle = -e\sum_i \psi_i^{4c\dagger}(\mathbf{P})\,\psi_i^{4c}(\mathbf{P})$$

$$\rho^{2c}(\mathbf{P}) = -e\sum_i \langle\psi_i^{2c}|\left[U^\dagger\delta(\mathbf{r}-\mathbf{P})\,U\right]_{++}|\psi_i^{2c}\rangle \neq -e\sum_i \psi_i^{2c\dagger}(\mathbf{P})\,\psi_i^{2c}(\mathbf{P})$$



$\sum_i \psi_i^{4c\dagger}\psi_i^{4c}$ *vs.* $\sum_i \psi_i^{2c\dagger}\psi_i^{2c}$ *for the mercury atom*

An example: the electron density

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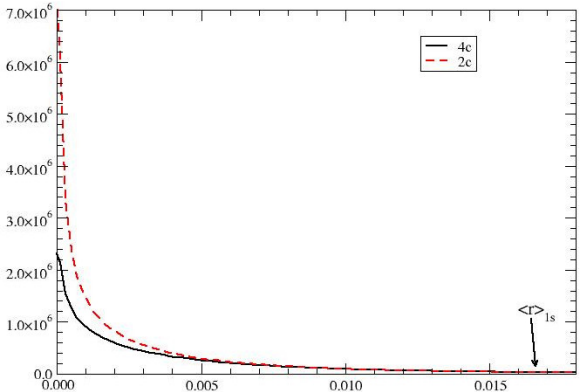
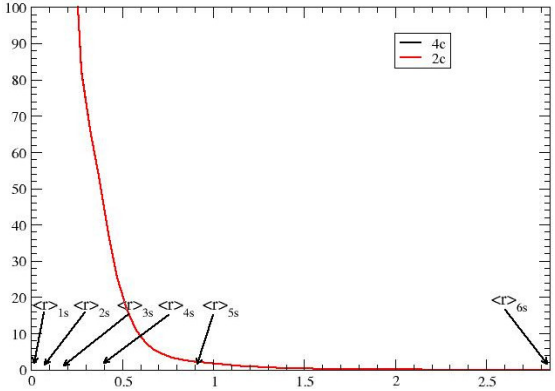


$\sum_i \psi_i^{4c\dagger}\psi_i^{4c}$ *vs.* $\sum_i \psi_i^{2c\dagger}\psi_i^{2c}$ *for the mercury atom*

An example: the electron density

- On a "chemical" scale the difference is no longer visible:



- However, many molecular properties probe the electron density near nuclei, providing local information with great sensitivity to the chemical environment,
  - for instance electric field gradients at nuclei, NMR parameters, molecular gradients and Mössbauer isomer shifts.

Numerical example: the uranium atom

	DCG	DC	X2C(AMFI)	DKH2	DKH1	ZORA	scZORA
$1s_{1/2}$	-4262.599	-4281.813	-4272.178	-4253.946	-4568.402	-4890.081	-4267.639
$2s_{1/2}$	-804.292	-806.637	-804.996	-802.931	-840.315	-829.339	-804.400
$2p_{1/2}$	-773.067	-777.035	-775.649	-774.270	-791.143	-799.722	-775.573
$2p_{3/2}$	-633.274	-635.783	-635.010	-635.027	-634.978	-651.542	-634.900
$3s_{1/2}$	-206.265	-206.730	-206.350	-205.894	-214.216	-208.368	-206.214
$3p_{1/2}$	-192.463	-193.251	-192.949	-192.624	-196.579	-194.945	-192.940
$3p_{3/2}$	-159.897	-160.378	-160.206	-160.220	-160.067	-161.622	-160.178
$3d_{3/2}$	-138.721	-139.070	-138.997	-139.024	-138.568	-140.214	-138.982
$3d_{5/2}$	-132.183	-132.426	-132.367	-132.393	-131.938	-133.477	-132.350
$4s_{1/2}$	-54.250	-54.355	-54.259	-54.140	-56.332	-54.425	-54.223
$4p_{1/2}$	-48.048	-48.232	-48.161	-48.077	-49.085	-48.334	-48.159
$4p_{3/2}$	-39.454	-39.554	-39.515	-39.522	-39.437	-39.633	-39.508
$4d_{3/2}$	-29.688	-29.744	-29.734	-29.743	-29.590	-29.817	-29.730
$4d_{5/2}$	-28.100	-28.130	-28.123	-28.132	-27.980	-28.197	-28.119
$4f_{5/2}$	-15.207	-15.202	-15.211	-15.220	-15.089	-15.247	-15.210
$4f_{7/2}$	-14.802	-14.786	-14.795	-14.803	-14.676	-14.828	-14.792

Numerical example: the uranium atom

	DCG	DC	X2C(AMFI)	DKH2	DKH1	ZORA	scZORA
$5s_{1/2}$	-12.582	-12.603	-12.582	-12.553	-13.081	-12.587	-12.573
$5p_{1/2}$	-10.098	-10.136	-10.122	-10.103	-10.320	-10.133	-10.122
$5p_{3/2}$	-8.077	-8.095	-8.088	-8.091	-8.049	-8.094	-8.087
$5d_{3/2}$	-4.347	-4.352	-4.353	-4.356	-4.305	-4.356	-4.353
$5d_{5/2}$	-4.040	-4.041	-4.042	-4.045	-3.995	-4.044	-4.041
$5f_{5/2}$	-0.350	-0.346	-0.349	-0.350	-0.321	-0.349	-0.349
$5f_{7/2}$	-0.323	-0.318	-0.321	-0.322	-0.294	-0.321	-0.321
$6s_{1/2}$	-2.135	-2.139	-2.135	-2.130	-2.234	-2.134	-2.133
$6p_{1/2}$	-1.338	-1.344	-1.342	-1.339	-1.371	-1.343	-1.342
$6p_{3/2}$	-0.983	-0.985	-0.984	-0.985	-0.968	-0.984	-0.984
$6d_{3/2}$	-0.193	-0.193	-0.193	-0.194	-0.181	-0.193	-0.193
$6d_{5/2}$	-0.183	-0.183	-0.184	-0.184	-0.173	-0.184	-0.184
$7s_{1/2}$	-0.202	-0.202	-0.202	-0.202	-0.211	-0.202	-0.202

The uranium atom: spin-orbit splittings

SO	DCG	DC	X2C(AMFI)	DKH2	DKH1	ZORA	scZORA
2p	139.793	141.252	140.638	139.244	156.165	148.179	140.672
3p	32.565	32.874	32.743	32.404	36.512	33.324	32.762
3d	6.538	6.644	6.630	6.631	6.631	6.737	6.632
4p	8.594	8.678	8.645	8.555	9.648	8.701	8.651
4d	1.588	1.614	1.611	1.611	1.611	1.620	1.612
4f	2.021	2.041	2.034	2.012	2.271	2.038	2.035
5p	0.307	0.312	0.311	0.311	0.310	0.312	0.312
5d	0.307	0.312	0.311	0.311	0.310	0.312	0.312
5f	0.027	0.028	0.028	0.028	0.027	0.028	0.028
6p	0.797	0.795	0.793	0.790	0.862	0.791	0.791
6d	0.009	0.010	0.010	0.010	0.008	0.010	0.010

Basis set considerations

Villa Casale, Sicily

The non-relativistic case

- Hydrogen atom (bound solutions):

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)\, Y_{\ell m}(\theta,\phi)\,; \quad R_{nl}(r) = \mathcal{N}_{n\ell}\rho^{\ell} e^{-\rho/2} L_{n-\ell-1}^{2\ell+1}(\rho)\,; \quad \rho = \frac{2r}{na_0}$$

- Slater-type orbitals (STOs)

$$\chi_{nlm}^{STO}(\mathbf{r}) = \mathcal{N} r^{\ell} \exp\left[-\zeta r\right] Y_{\ell m}(\theta,\phi)$$

- Gaussian-type orbitals (GTOs)
  - Spherical-harmonics GTOs:

$$\chi_{n\ell m}^{GTO}(\mathbf{r}) = \mathcal{N} r^{\ell} \exp\left[-\alpha r^2\right] Y_{\ell m}(\theta,\phi)$$

  - Cartesian GTOs:

$$\chi_{ijk}^{GTO}(\mathbf{r}) = \mathcal{N} x^i y^j z^k \exp\left[-\alpha r^2\right]; \quad i+j+k = \ell$$

- What about relativistic atomic solutions ?

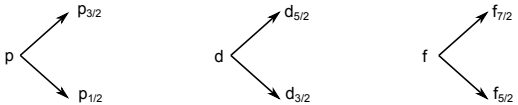
The 2-component relativistic case

- Hydrogen atom (bound solutions):

$$\psi_{njm_j}(\mathbf{r}) = R_{nj}(r)\,\chi_{j,m_j}(\theta,\phi)\,; \quad \begin{cases} \hat{j}^2\chi_{j,m_j} &= j(j+1)\,\chi_{j,m_j} \\ \hat{j}_z\chi_{j,m_j} &= m_j\chi_{j,m_j} \end{cases}$$

  where χ_{j,m_j} are 2-component angular functions.

- Spin-orbit splitting: $\mathbf{j} = \boldsymbol{\ell} + \mathbf{s}; \quad j = \ell \pm \frac{1}{2}$



- Parent orbital has well-defined orbital angular momentum ℓ
  - Suggests that

$$\hat{\ell}^2\chi_{j,m_j} = \ell(\ell+1)\,\chi_{j,m_j}$$

  - such that

$$\chi_{j,m_j} = c_\alpha Y_{\ell m_\alpha}\alpha + c_\beta Y_{\ell m_\beta}\beta$$

  - where

$$m_j = m_\ell + m_s \quad \Rightarrow \quad m_\alpha = m_j - \frac{1}{2}; \quad m_\beta = m_j + \frac{1}{2}$$

A new quantum number: κ

- The 2-component angular functions χ_{j,m_j} are eigenfunctions of both $\hat{j}^2$ and $\hat{\ell}^2$
- However

$$\mathbf{j} = \boldsymbol{\ell} + \mathbf{s} = \boldsymbol{\ell} + \frac{1}{2}\boldsymbol{\sigma} \quad \Rightarrow \quad \hat{j}^2 = \hat{\ell}^2 + \frac{1}{2}\left(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\ell}}\right) + \frac{3}{4}$$

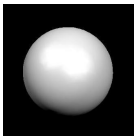
- We introduce a new angular operator

$$\hat{\kappa} = -\left[\left(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\ell}}\right) + 1\right]$$

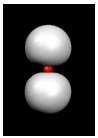
- with convenient eigenvalues

	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$
κ	-1	+1	-2	+2	-3	+3	-4

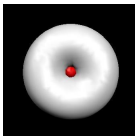
- Associated densities



$2(s,p)_{1/2,1/2}$



$2(p,d)_{3/2,1/2}$



$2(p,d)_{3/2,3/2}$

The 4-component relativistic case

- Hydrogen atom (bound solutions):

$$\psi = \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \begin{bmatrix} R^L \chi_{\kappa,m_j}(\theta,\phi) \\ iR^S \chi_{-\kappa,m_j}(\theta,\phi) \end{bmatrix}$$

- Radial functions

$$\begin{bmatrix} R^L \\ R^S \end{bmatrix} = \mathcal{N} r^{\gamma-1} e^{-\lambda r} \begin{bmatrix} \mathcal{N}^L [F_1(r) + F_2(r)] \\ \mathcal{N}^S [F_1(r) - F_2(r)] \end{bmatrix}$$

  - where $\lambda = \frac{1}{\hbar c}\sqrt{m^2c^4 - E^2}$; $\gamma = \sqrt{\kappa^2 - (Z\alpha)^2}\,|\kappa|$

- Radial functions with $|\kappa| = 1$ have a weak singularity at the origin
  - serves as a "black hole" in basis set optimizations

Basis sets for relativistic calculations

- Solution: use finite nuclei
  - Radial functions become gaussian at the origin
  - Gaussian nuclear charge distribution:

$$\rho^G(\mathbf{r}_n) = \rho_0^G \exp\left[-\eta r_n^2\right]; \quad \rho_0^G = \frac{Z}{(\pi/\eta)^{3/2}}$$

  - The exponent is chosen to satisfy the semi-empirical rule

    W. R. Johnson and G. Soff. At. Data Nucl. Data Tables, **33** (1985) 405

$$\left\langle r_n^2 \right\rangle^{1/2} = \left[0.836A^{1/3} + 0.570\right] \text{fm}$$

- 2-component basis functions

$$\chi^X(\mathbf{r}) = \mathcal{N} r^\ell \exp\left[-\alpha r^2\right] \chi_{\kappa,n_j}(\theta,\phi); \quad X = L, S$$

- Scalar basis functions: spherical or Cartisian GTOs
  - Allows the use of non-relativistic integral codes

Kinetic balance

- Pioneer 4c molecular calculation in the 80s showed variational collapse
- Ignored the exact coupling of the large and small components

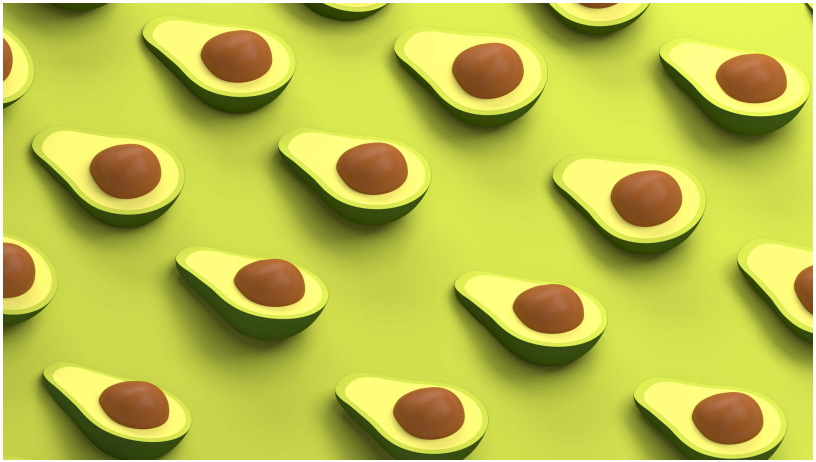
$$c\Psi^S = \frac{1}{2m}\left[1 + \frac{E-V}{2mc^2}\right]^{-1} (\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\,\psi^L$$

  - Modified by the introduction of magnetic fields: $\hat{\mathbf{p}} \to \hat{\mathbf{p}} + e\mathbf{A}$
- Modern-day basis sets are generated according to the non-relativistic limit

$$\lim_{c\to\infty} c\Psi^S = \frac{1}{2m}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})\,\psi^L$$

- Assumes $E \ll 2mc^2$
  - vaild for positive-energy solutions only
- Assumes $V \ll 2mc^2$
  - non-singular potential; finite nuclei

Relativistic effective core potentials



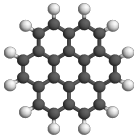
- Hg: polarizability (Å^{-3})

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2$	6.61
$5s^2 5p^6 5d^{10} 6s^2$	6.61
$5d^{10} 6s^2$	6.60
$6s^2$	6.31

- Au: ionization potential/electron affinity (eV)

	IP	EA
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^1$	7.688	0.581
$5s^2 5p^6 5d^{10} 6s^1$	7.689	0.580
$5d^{10} 6s^1$	7.693	0.579
$6s^1$	7.923	0.505

- Heavy elements = many electrons !



coronene

176 electrons

Pt_2

Philips–Kleinman equation

Valid for a single valence orbital φ_v outside a closed-shell core $\{\varphi_c\}$

- Hartree–Fock equation

$$\hat{F}|\varphi_v\rangle = |\varphi_v\rangle\varepsilon_v; \quad \langle\varphi_v|\varphi_c\rangle = 0, \quad \forall\varphi_c$$

- We introduce a pseudo-valence orbital

$$|\chi_v\rangle = |\varphi_v\rangle + \sum_c |\varphi_c\rangle a_{cv}; \quad a_{cv} = \langle\varphi_c|\chi_v\rangle$$

- and set up a new Hartree–Fock equation

$$\begin{aligned}\hat{F}|\chi_v\rangle &= |\varphi_v\rangle\varepsilon_v + \sum_c |\varphi_c\rangle a_{cv}\varepsilon_c \\ &+ \sum_c |\varphi_c\rangle a_{cv}\varepsilon_v - \sum_c |\varphi_c\rangle\langle\varphi_c|\chi_v\rangle\varepsilon_v\end{aligned}$$

- This can be rearranged to

$$\left(\hat{F} + \sum_c (\varepsilon_v - \varepsilon_c)\,|\varphi_c\rangle\langle\varphi_c|\right)|\chi_v\rangle = |\chi_v\rangle\varepsilon_v$$

- Further manipulation gives

$$\left(\hat{F}_v + V_{PP}\right)|\chi_v\rangle = |\chi_v\rangle\varepsilon_v; \quad V_{PP} = \hat{F}_c + \sum_c (\varepsilon_v - \varepsilon_c)\,|\varphi_c\rangle\langle\varphi_c|$$

Effective core potentials

- **Model core potentials**: Valence orbitals with full nodal structure

$$V_{MCP} = \sum_A \left\{ \sum_k A_k r_{iA}^{n_k} e^{-\alpha_k r_i^2} + \sum_b B_c |\varphi_{A;c}\rangle\langle\varphi_{A;c}| \right\}$$

  - Can be combined with relativistic Hamiltonians
  - Moderate basis set reduction
- **Pseudopotentials**: Nodeless pseudo-valence orbitals
  - Relativistic Hamiltonians can not be used since they in particular probe the core region
    - ★ Relativistic effects enter through parametrization
  - Significant basis set reduction

Semi-local pseudopotentials

- Valence-only electronic Hamiltonian

$$H_v = \sum_i^{n_v} \left[-\frac{1}{2}\nabla_i^2 + \sum_A \left(V_{PP;A}\left(\mathbf{r}_{iA}\right) - \frac{Q_A}{r_{iA}} \right) \right] + \frac{1}{2}\sum_{i\neq j}^{n_v} \frac{1}{r_{ij}} + \frac{1}{2}\sum_{A\neq B} \frac{Q_A Q_B}{R_{AB}}$$

  - Core charges: $Q_A = Z_A - n_C^A$

- Semi-local pseudopotential

$$V_{PP;A}\left(\mathbf{r}_{iA}\right) = \tilde{V}_{\text{local}}\left(r_{iA}\right) + \sum_{\ell=0}^{\ell_{max}} \tilde{V}_\ell\left(r_{iA}\right) \sum_{m_\ell=-\ell}^{\ell} |\ell m_\ell\rangle\langle \ell m_\ell|$$

$$\tilde{V}\left(r\right) = \sum_k A_k r^{n_k} \exp\left[-\alpha_k r^2\right]$$

- How do we determine parameters $\{A_k, \alpha_k, n_k\}$?

Pseudopotential parametrization

- **Energy-consistent pseudopotentials**:
  (Preuss, Stoll, Dolg, Schwerdtfeger.....)
  - Semi-empirical vs. *ab initio*
- **Shape-consistent pseudopotentials**:
  (Hay, Wadt, Christiansen, Ermler, Cundari, Stevens....)
  - Pseudovalence orbital

$$R_p(r) = \begin{cases} R_v(r); & r \geq r_c \\ f(r); & r < r_c \end{cases}$$

  - V_{PP} is then found by inversion of radial equation for the pseudovalence orbital

$$\left(\hat{F}_v(r) + V_{PP}\right) R_p(r) = R_p(r)\,\varepsilon_v \quad \Rightarrow \quad V_{PP}(r) = \frac{\left(\varepsilon_v - \hat{F}_v(r)\right) R_p(r)}{R_p(r)}$$

Introducing relativistic effects

- With both scalar relativistic (SR) and spin-orbit (SO) interaction included one would expect the form

$$V_{PP;A}\left(\mathbf{r}_{iA}\right) = \sum_{\ell=0}^{\ell_{max}} \sum_{j=|\ell-1/2|}^{\ell+1/2} \tilde{V}_{\ell j}\left(r_{iA}\right) \sum_{m_j=-j}^{j} |\ell j m_j\rangle\langle \ell j m_j|$$

- In practice the contributions are separated

$$V_{PP;A}^{SR} = \sum_{\ell=0}^{\ell_{max}} \frac{1}{(2\ell+1)} \left[(\ell+1)\,\tilde{V}_{\ell,\ell+1/2} + \ell \tilde{V}_{\ell,\ell-1/2}\right] \sum_{m_\ell=-\ell}^{\ell} |\ell m_\ell\rangle\langle \ell m_\ell|$$

$$V_{PP;A}^{SO} = \boldsymbol{\sigma} \cdot \sum_{\ell=0}^{\ell_{max}} \frac{1}{(2\ell+1)} \left[\tilde{V}_{\ell,\ell+1/2} - \tilde{V}_{\ell,\ell-1/2}\right] \sum_{m_\ell, m'_\ell=-\ell}^{\ell} |\ell m_\ell\rangle\langle \ell m_\ell|\boldsymbol{\ell}|\ell' m'_\ell\rangle\langle \ell' m'_\ell|$$

Some important points

- Size of core
- Choice of valence basis
- RECPs have names, just like basis sets !
- Effective core potentials have limited applicability (in principle no core properties), but are an excellent choice for many applications.

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