Relativistic quantum chemistry

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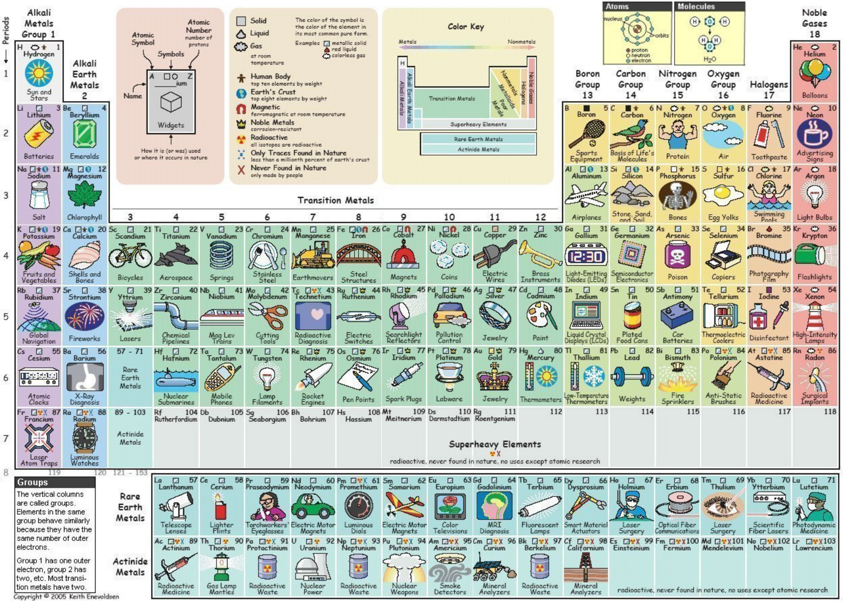
The Dirac village

Our playground: the periodic table



The periodic table ... of 1871

Tabelle II.

Reihen	Gruppe I. — R^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	—	— — — —

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eka-aluminium:
gallium (1875)

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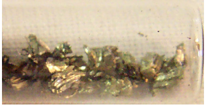
gallium (1875)

eka-silicon:
germanium (1886)

eka-boron:
scandium (1879)



Broken trends

Goldschmidt and Einstein in Norway 1920

Relativistic effects

- scalar effects
- spin-orbit interaction

Lorentz factor:

$$\gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$$

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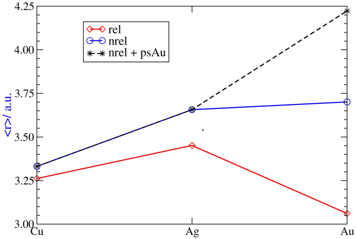
Lanthanide contraction

V.M. Goldschmidt, T. Barth, G. Lunde: Norske Vidensk. Selsk. Skrifter I Mat. Naturv. Kl. 7, 1 (1925)
D. R. Lloyd, J. Chem. Ed. **63** (1986) 503

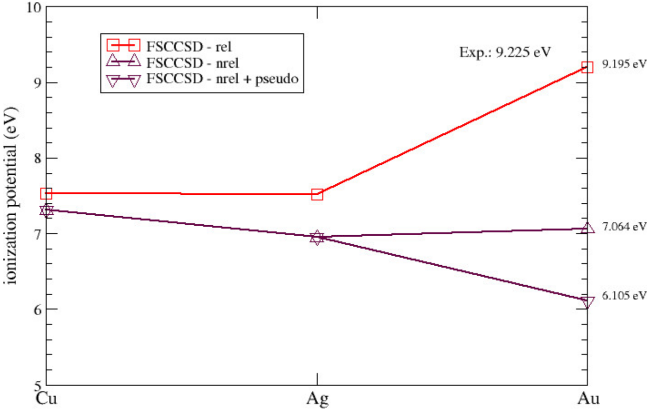
- La^{3+} - Lu^{3+} (117.2 - 100.1 pm)
- Ca^{2+} - Zn^{2+} (114 - 88 pm)
- Cu (138 pm) < Au (144 pm) < Ag (153 pm)



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

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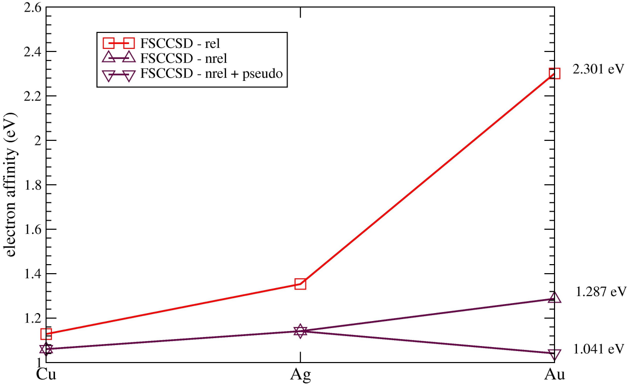

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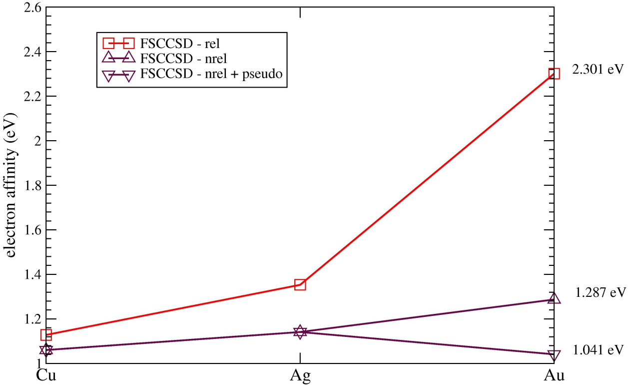

- Gold and caesium are extremes on the electron affinity scale — 2.309 eV vs. 0.472 eV

Electron affinity of gold

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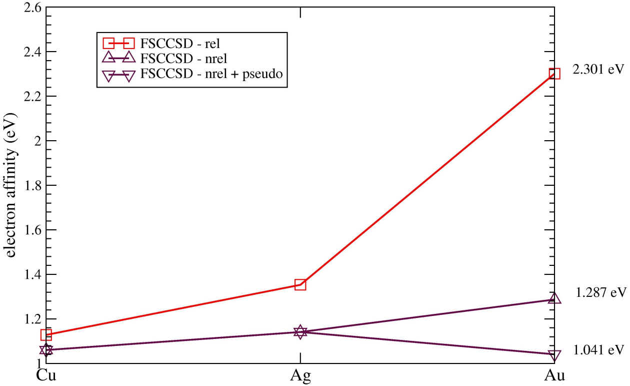


- Gold and caesium are extremes on the electron affinity scale — 2.309 eV vs. 0.472 eV
- CsAu is a semi-conductor with a CsCl crystal structure in the solid state; it forms an ionic melt. **The oxidation state of gold is -I.**

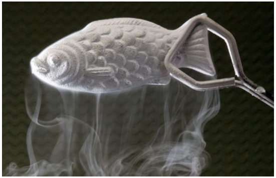
Spectroscopic constants of CsAu and homologues

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

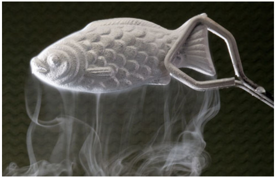
	Method		r_e (pm)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e^{cov}(eV)	μ (D)
CsAu	CCSD(T)	rel	326.3	89.4	0.21	2.52	11.73
		nrel	357.1	67.9	0.08	1.34	11.05
		nrel-ps	376.3	59.9	0.13	1.17	9.47
	Exp.[1]a		(320)	(125)		2.58±0.03	
	Exp.[1]b		-	-	-	2.53±0.03	-
CsAg	CCSD(T)	rel	331.6	88.0	0.17	1.51	10.69
		nrel	345.9	78.5	0.02	1.26	10.89
CsCu	CCSD(T)	rel	319.8	101.6	0.09	1.36	10.34
		nrel	327.7	97.1	0.18	1.31	10.88

1) B. Busse and K. G. Weil, Ber. Bunsenges. Phys. Chem. **85**(1981) 309

Without relativity



Without relativity



.. gold would have the same color as silver

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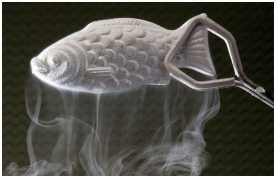

...mercury would not be liquid
at room temperature

Without relativity

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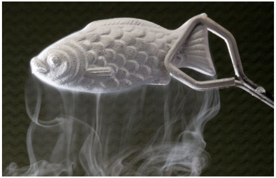


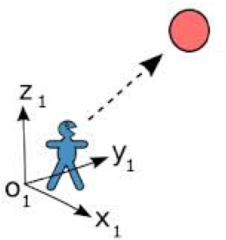
...mercury would not be liquid
at room temperature

.. your car would not start

Einstein's special theory of relativity

Einstein's special theory of relativity

Reference frames



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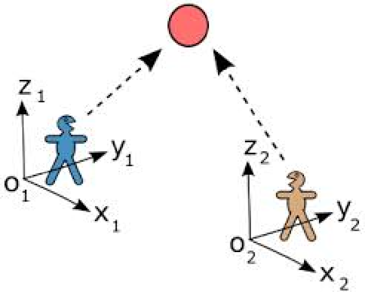

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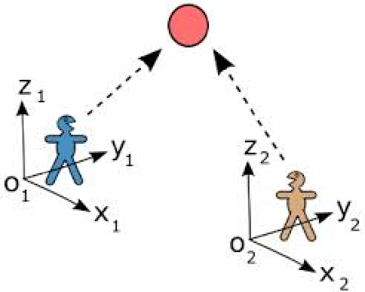
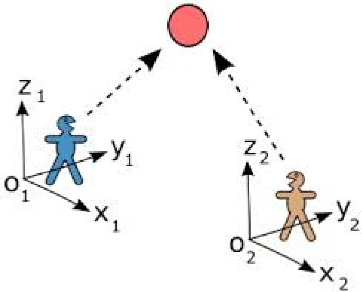


The theory of *special* relativity is restricted to **inertial frames :**
reference frames related by constant velocity

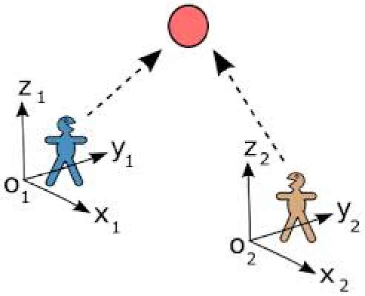
Reference frames



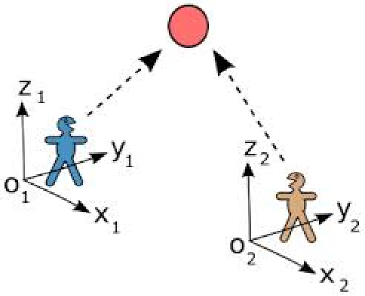
The theory of *special* relativity is restricted to **inertial frames :** reference frames related by constant velocity

It is based on two postulates:

The principle of relativity

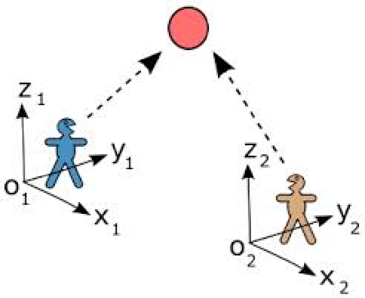


The principle of relativity



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

The principle of relativity



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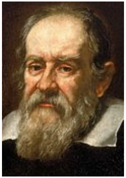

Galileo Galilei (1632)

... but some frames may be better than others

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- Speed of boat with respect to the river bank: 3 km/h

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- Speed of boat with respect to the river bank: 3 km/h
- Speed of water with respect to the river bank: 7 km/h

... 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

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

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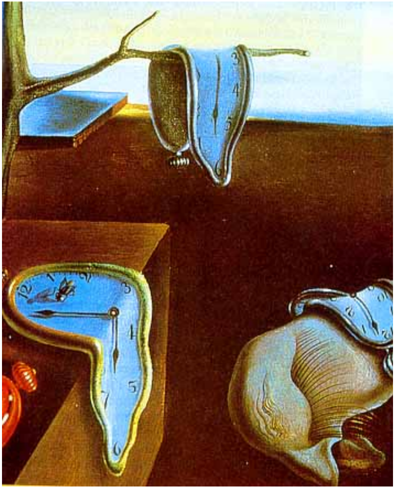
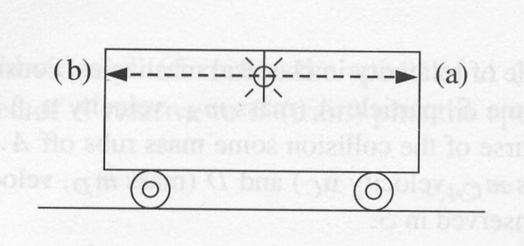


Implies plasticity of space and time

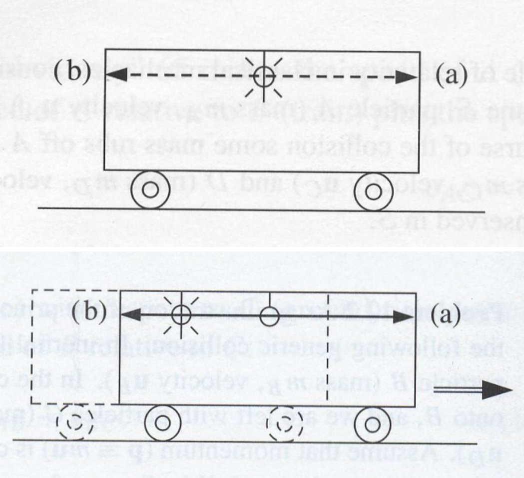
Simultaneity: a relative concept



Observer in the train:

$$t_b = t_a$$

Simultaneity: a relative concept



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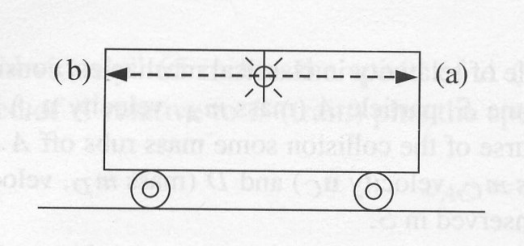

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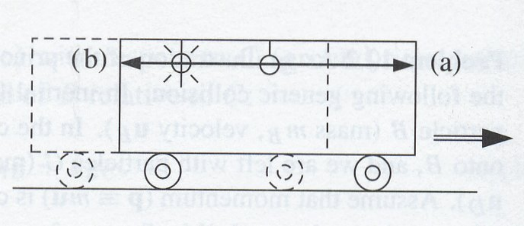

Observer on the ground:

$$t_b < t_a$$

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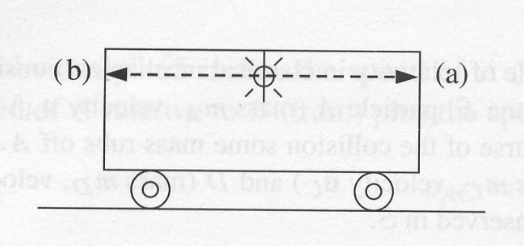

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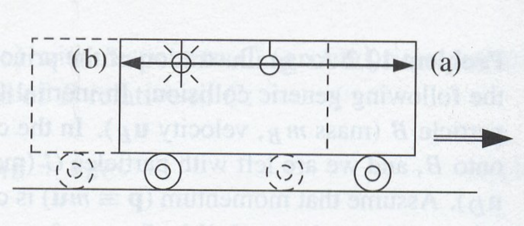

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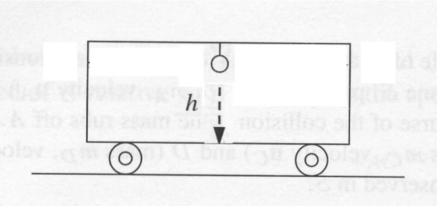
Two events that are simultaneous in one inertial frame are generally not so in another inertial frame.

Picture credit: Griffiths: Introduction to Electrodynamics (1999)

Time dilation



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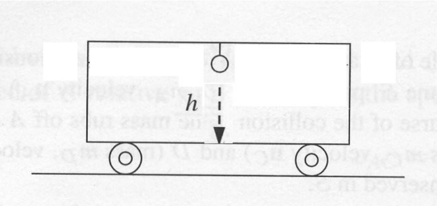
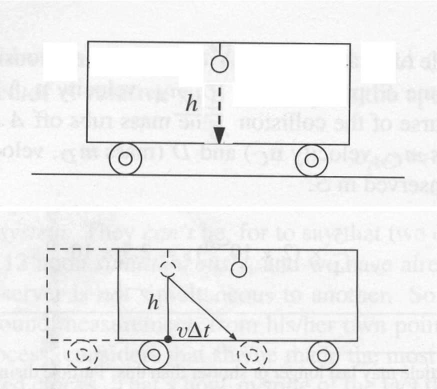


Observer in the train:

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



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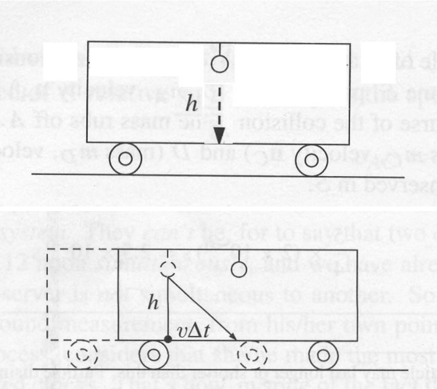

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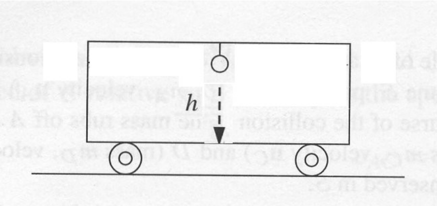
$$c\Delta t = \sqrt{h^2 + (v\Delta t)^2}$$



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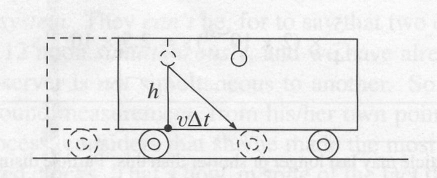

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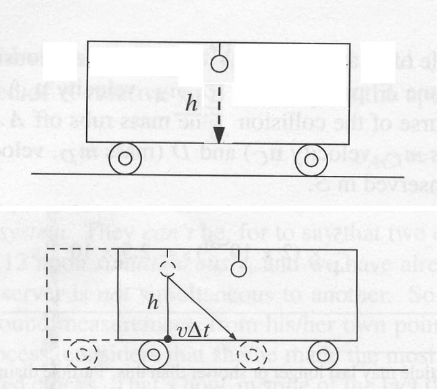
Time dilation



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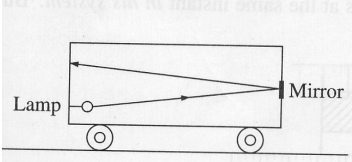
Clocks in movement go slower.

Picture credit: Griffiths: Introduction to Electrodynamics (1999)

Length contraction



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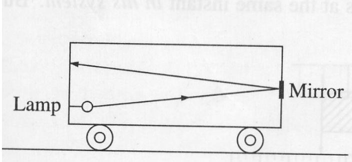

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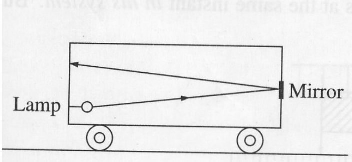

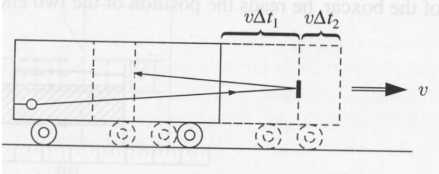

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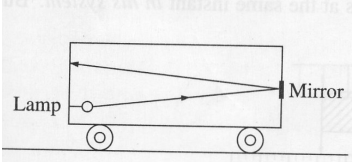
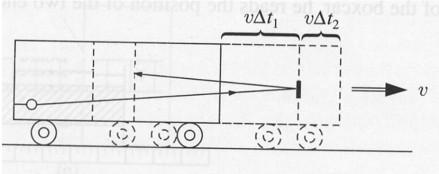
Length contraction



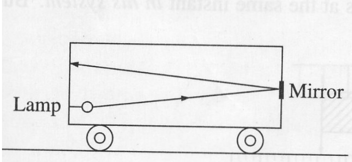


Observer in the train:

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

Observer on the ground:

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



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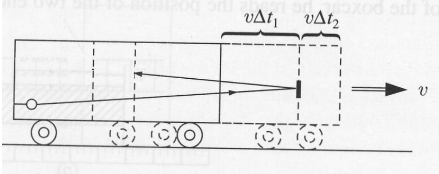

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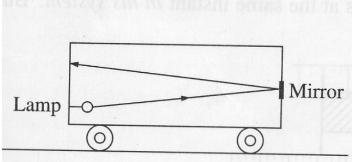

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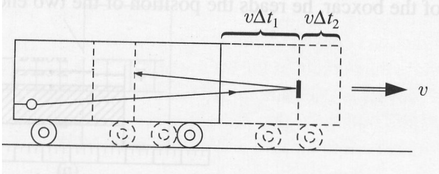

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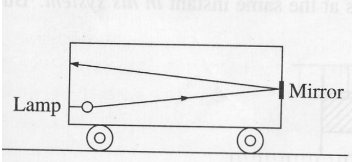

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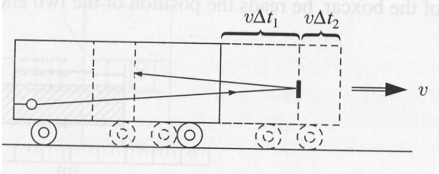

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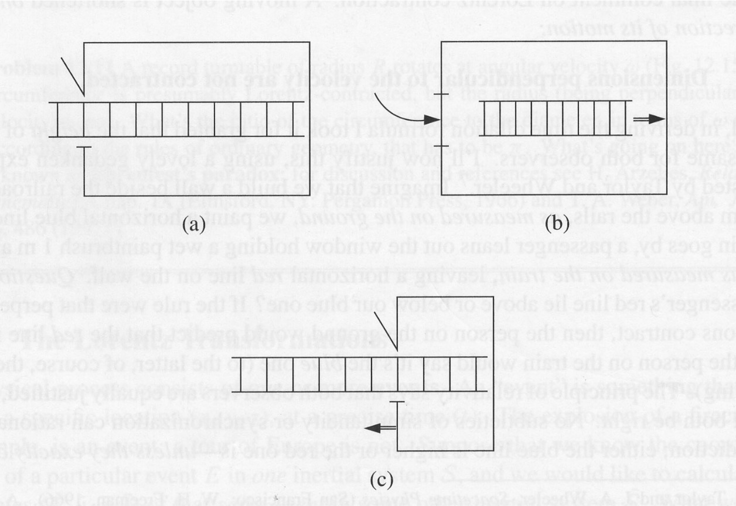
$$\Delta\bar{x} = \gamma\Delta x$$

An object in movement is contracted in the direction of movement

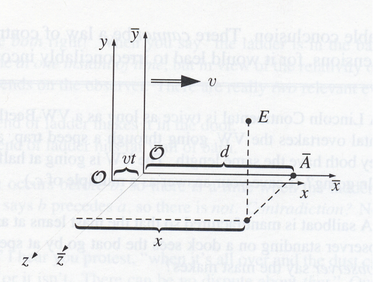
Picture credit: Griffiths: Introduction to Electrodynamics (1999)

Paradox of the barn and the ladder



Picture credit: Griffiths: Introduction to Electrodynamics (1999)

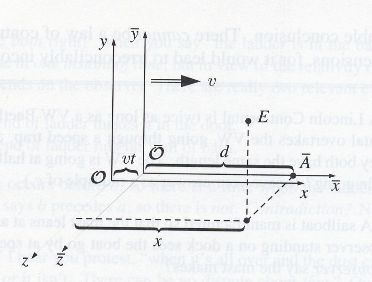
Lorentz transformation



$$x = d + vt$$

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

$$\bar{x} = \gamma\,(x - vt)$$



$$
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\overline{x} &= \gamma\left(x - vt\right)
\end{aligned}
$$

$$
\begin{aligned}
x &= \gamma\left(\overline{x} + v\overline{t}\right) \\
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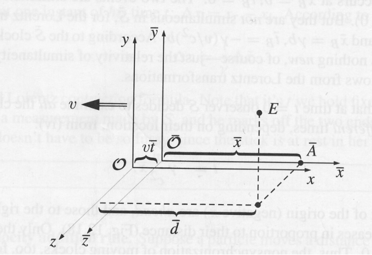
$$



Let us look at a relativistic theory ...

Electrodynamics

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

- The homogeneous pair:

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

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

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

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- Are the electric field **E** and the magnetic field **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

- **The answer is NO !!!!**
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  both have zero divergence and zero curl
- Boundary conditions must be introduced:
  - **E and B go to zero at infinity**

The Helmholtz theorem

- The vector relation

$$\nabla^2 \mathbf{F} = \boldsymbol{\nabla}\left(\boldsymbol{\nabla}\cdot\mathbf{F}\right) - \boldsymbol{\nabla}\times\left(\boldsymbol{\nabla}\times\mathbf{F}\right)$$

can also be seen as an equation

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  can also be seen as an equation

- and has solution

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

  where

$$s\left(\mathbf{r}_1\right) = \frac{1}{4\pi}\int\frac{\boldsymbol{\nabla}_2\cdot\mathbf{F}(\mathbf{r}_2)}{r_{12}}d^3\mathbf{r}_2; \quad \mathbf{v}(\mathbf{r}_1) = \frac{1}{4\pi}\int\frac{\boldsymbol{\nabla}_2\times\mathbf{F}(\mathbf{r}_2)}{r_{12}}d^3\mathbf{r}_2$$

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- The divergence and curl of **F** must go to zero faster than $\frac{1}{r^2}$; otherwise the above integrals blow up in the limit.

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- The divergence and curl of **F** must go to zero faster than $\frac{1}{r^2}$; otherwise the above integrals blow up in the limit.
- This results show that we can reconstruct a vector function from knowledge of its divergence and curl combined with proper boundary conditions.

Jefimenko's solutions

- General solutions of Maxwell's equations are

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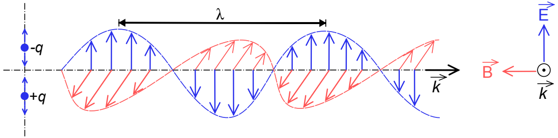
$$\mathbf{B}(\mathbf{r}_1, t) = \frac{1}{c^2}\int \left\{ \frac{\mathbf{j}\left(\mathbf{r}_2, t_r\right)\times\mathbf{r}_{12}}{r_{12}^3} + \frac{\dot{j}\left(\mathbf{r}_2, t_r\right)\times r_{12}}{c{r^2}_{12}} \right\} d^3\mathbf{r}_2$$

- Note that we can always add the solutions of the homogeneous (source-free) equations, that is, electromagnetic waves.



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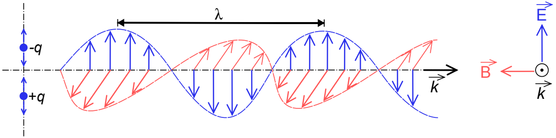

- A nasty fellow:

Jefimenko's solutions

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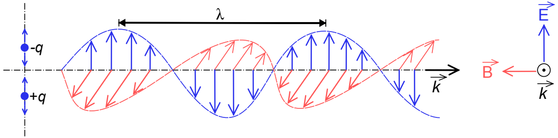
\mathbf{B}(\mathbf{r}_1,t) &= \frac{1}{c^2}\int\left\{\frac{\mathbf{j}\left(\mathbf{r}_2,t_r\right)\times\mathbf{r}_{12}}{r_{12}^3}+\frac{\dot j\left(\mathbf{r}_2,t_r\right)\times r_{12}}{c{r^2}_{12}}\right\}d^3\mathbf{r}_2
\end{aligned}$$

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

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

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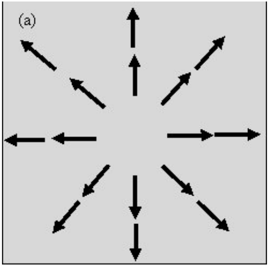

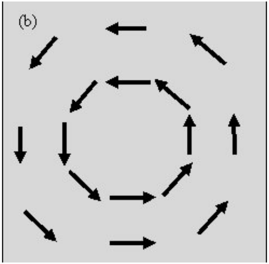

Longitudinal component ("parallel"):

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

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

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

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

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

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

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

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

Maxwell's equations: homogeneous pair

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- $\boldsymbol{\nabla}\times\mathbf{E}+\dfrac{\partial\mathbf{B}}{\partial t}=0$ 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: homogeneous pair

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

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

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

Maxwell's equations: homogeneous pair

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

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  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

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  - **4-velocity:** $v_{\mu} = \gamma(\mathbf{v}, ic); \quad v_{\mu}v_{\mu} = -c^2$
  - **4-momentum:** $p_{\mu} = \gamma\left(m\mathbf{v}, imc\right); \quad p_{\mu}p_{\mu} = -m^2c^2$

Lorentz transformation and 4-vectors

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

  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
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  - **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:

$$\begin{aligned}
\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}
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- This can be written more compactly as

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

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\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

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

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- 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

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- 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: $\boldsymbol{\nabla} \cdot \mathbf{A} = 0$

- Maxwell's equations simplifies to:

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

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- 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.

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- 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

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

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- Fields specified:

Non-relativistic limit

$$\underset{\text{Dirac equation}}{\left(i\gamma_\mu\partial_\mu - mc\right)\psi = 0} \quad \rightarrow \quad \underset{\text{Schrödinger equation}}{\left(\frac{p^2}{2m} - i\frac{\partial}{\partial t}\right)\psi = 0}$$

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- Particles (sources) specified:

Non-relativistic limit

$$\underset{\text{Maxwell's equations}}{\Box^2 A_\mu - \partial_\mu(\partial_\nu A_\nu) = -\frac{4\pi}{c^2}j_\mu} \qquad \rightarrow$$

???

The non-relativistic limit of electrodynamics

$$
\begin{aligned}
\boldsymbol{\nabla}\cdot\mathbf{B} &= 0 & & & \boldsymbol{\nabla}\cdot\mathbf{B} &= 0\\
\boldsymbol{\nabla}\times\mathbf{E}+\frac{\partial\mathbf{B}}{\partial t} &= 0 & c\rightarrow\infty & & \boldsymbol{\nabla}\times\mathbf{E} &= 0\\
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- 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 $1/c^2$).

The old Masters knew

P. A. M. Dirac, Proc. Roy. Soc. A **123** (1929) 714

Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

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W. Heisenberg: *The Physical principles of the quantum theory* (1930)

§ 8. THE WAVE CONCEPT FOR MATTER AND RADIATION: CLASSICAL THEORY

The classical wave theory is that of the de Broglie waves for matter and of electromagnetic waves for radiation. This section will treat primarily those waves which are associated with the electron (the proton waves can be treated in an entirely similar manner), though light waves will also be considered briefly. No attempt will be made to include relativistic effects, and it is then logical to treat only electrostatic forces and to neglect magnetic and retardational phenomena.

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.

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

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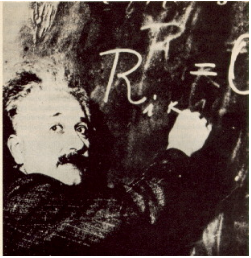
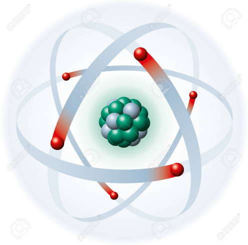
- So what goes fast in an atom or a molecule ?

Scalar-relativstic effects: hydrogen-like atoms

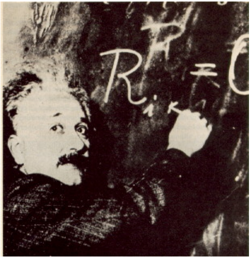


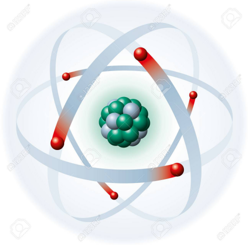


- In atomic units the average speed of the 1s electron is equal to the nuclear charge

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

Scalar-relativstic effects: hydrogen-like atoms





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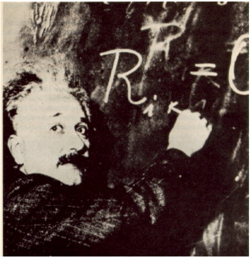
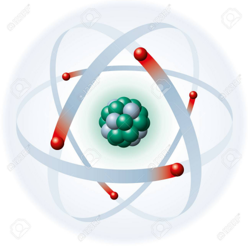
Scalar-relativstic effects: hydrogen-like atoms





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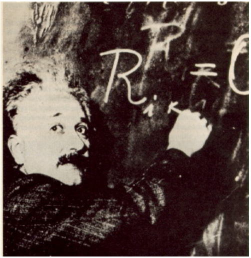
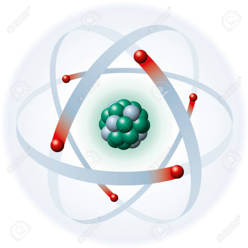
- The Bohr radius is inversely proportional to electron mass

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

Scalar-relativstic effects: hydrogen-like atoms





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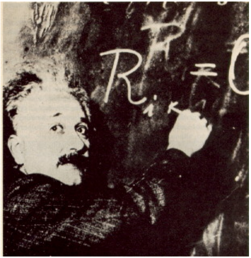

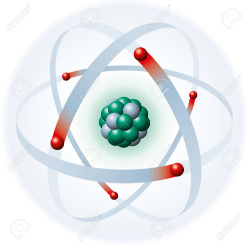

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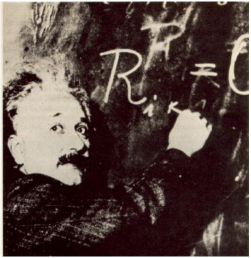
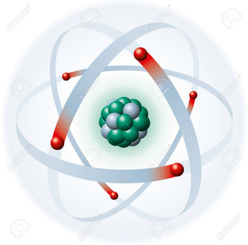
Scalar-relativstic effects: hydrogen-like atoms





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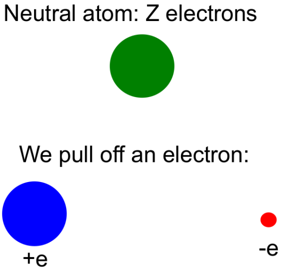
  - *18% relativistic contraction of the 1s orbital*

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



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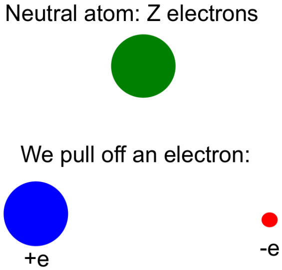

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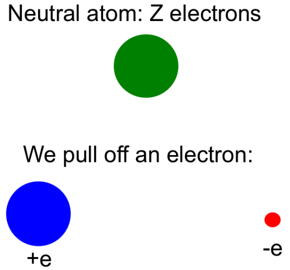

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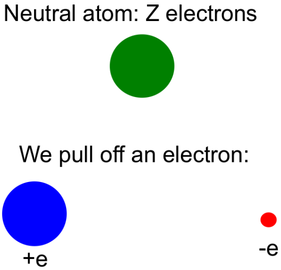

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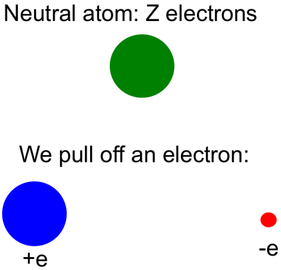

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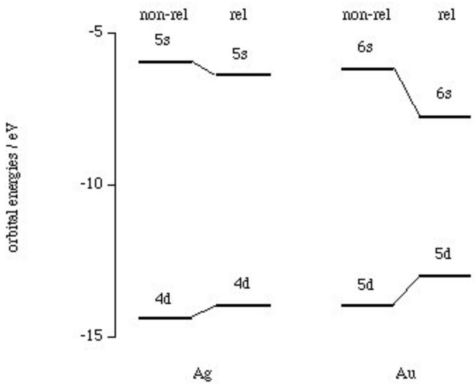
  - d, f orbitals : expansion

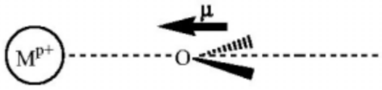
The colour of gold



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



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electrostatic interaction

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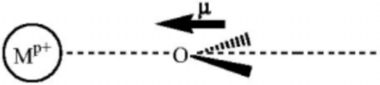

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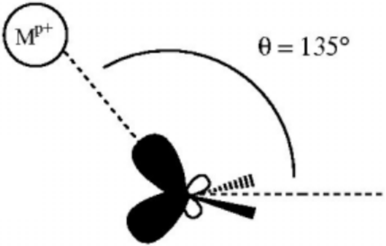
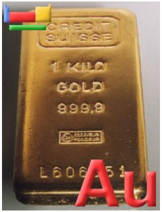


$[Au(H_2O)]^+$:
orbital interaction

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)

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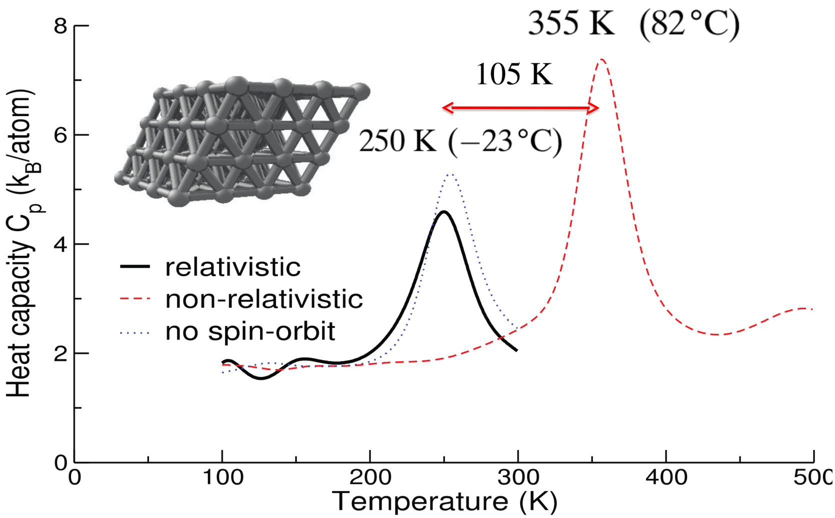
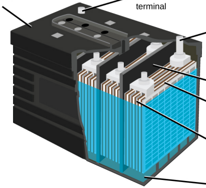


Cars start due to relativity

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



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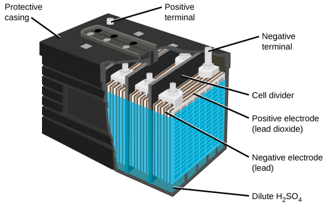

- Cathode reaction: $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$
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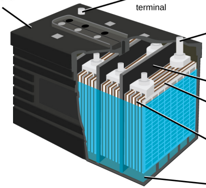

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non-relativistic calculation:	+0.39 V
relativistic calculation:	+2.13 V
experiment:	+2.11 V

Spin-orbit interaction

Spin-orbit interaction

a much misunderstood interaction !

- Often seen formula:

$$h^{\mathrm{so}} = \frac{1}{2m^2c^2}\mathbf{s}\cdot\left[(\boldsymbol{\nabla}V)\times\mathbf{p}\right] \quad \overset{V=-\frac{Z}{r}}{\rightarrow} \quad \frac{Z}{2m^2c^2r^3}\mathbf{s}\cdot\mathbf{l}$$

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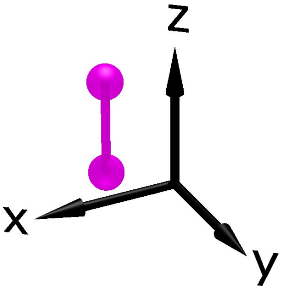
- This operator couples the degrees of freedom associated with spin and space and therefore makes it impossible to treat spin and spatial symmetry separately.

Spin-orbit interaction couples spin and space.
Example: I_2^+ (open-shell)

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



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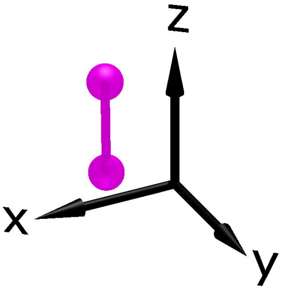

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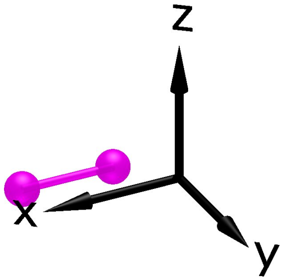

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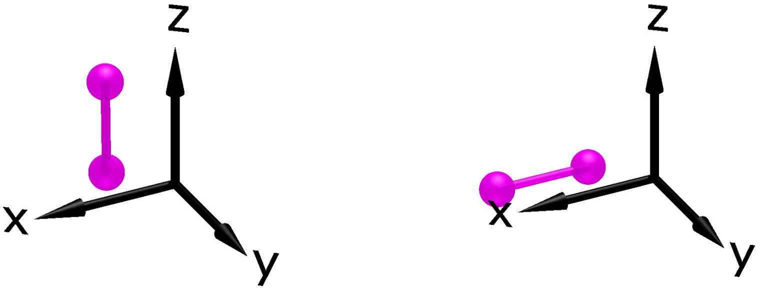

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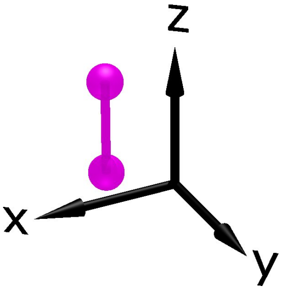

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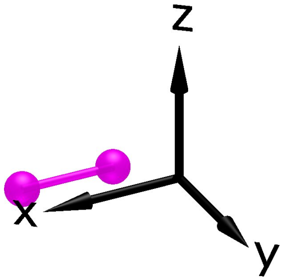

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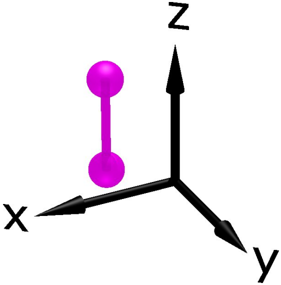

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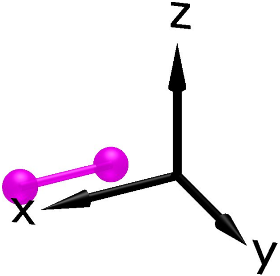

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- A solution is to use *non-collinear* magnetization: $s = |\mathbf{m}|$

Spin-orbit interaction in atoms

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

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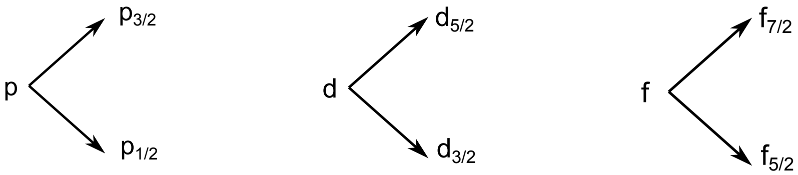
- Orbitals are accordingly characterized by quantum numbers j and m_j

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



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Term	L	S	Possible J values
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- The actual energy levels are

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	0	226.977
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http://physics.nist.gov/PhysRefData/Handbook/Tables/oxygentable1.htm

Spin-orbit splitting in group 8

Term	J	Oxygen	Sulfur	Selenium	Tellurium	Polonium
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	0	226.977	573.640	2534.360	4750.712	16831.61
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- ...which for neighbour levels reads

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

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	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**

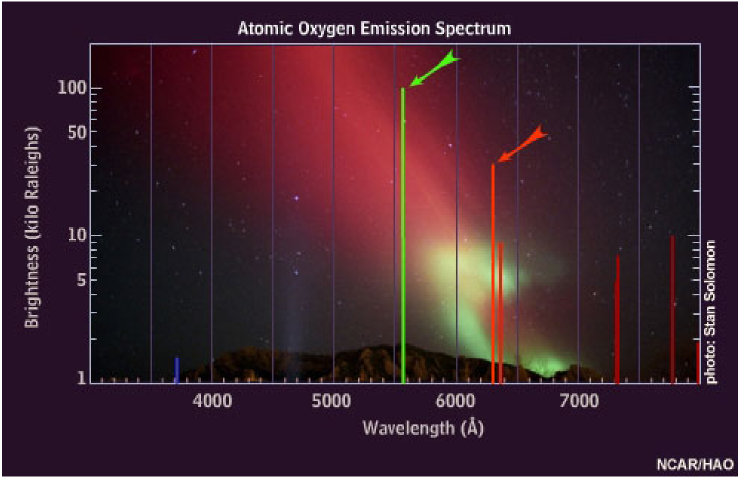
$$\Delta E\left(J,J'\right) = E_{SO}\left(LSJ\right) - E_{SO}\left(LSJ'\right) = \frac{1}{2}\zeta(^{2S+1}L)\left[J\left(J+1\right) - J'\left(J'+1\right)\right]$$

- ...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.

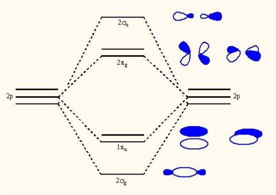
Atomic oxygen emissions in northern lights



	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 $\Lambda = |M_L|$.



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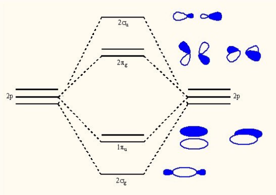

- Ground-state electron configuration: $[\text{core}]2\sigma_g^2 1\pi_u^4 2\pi_g^2 \quad \Rightarrow \quad \begin{pmatrix} 4 \\ 2 \end{pmatrix} = 6$ micro-states

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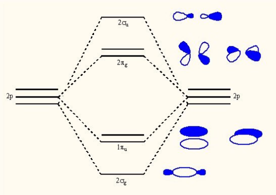

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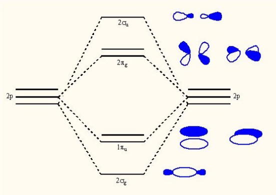

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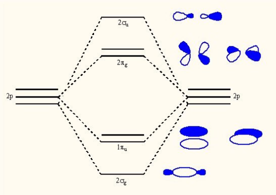

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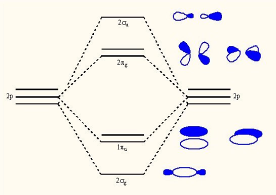

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  - We make the following table:

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

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

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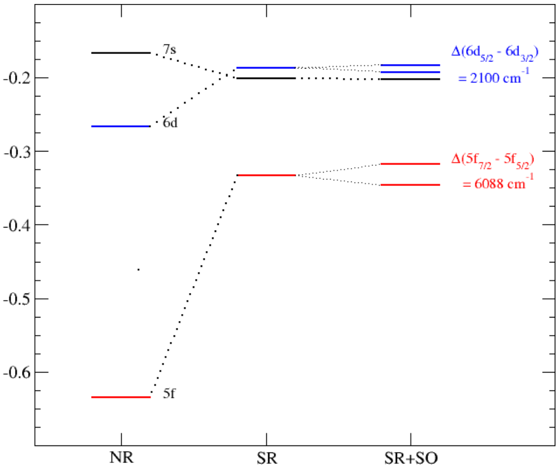
Relativistic effects: valence orbital energies (E_h) of the uranium atom



- **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

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- 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
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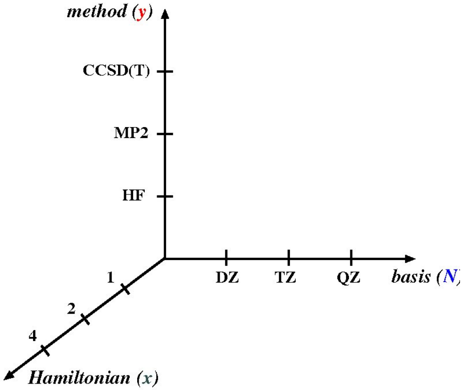
Inhaltsverzeichnis.

Theoretical model chemistries



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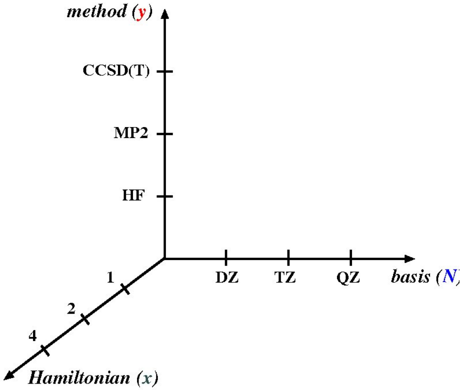

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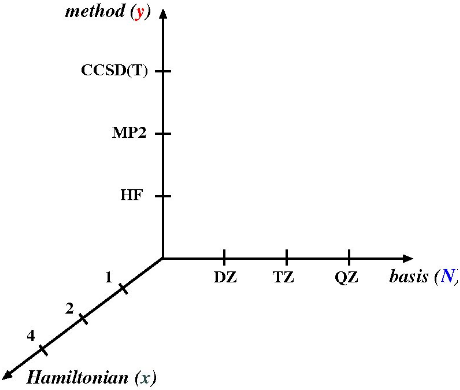

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Computational cost: xN^y

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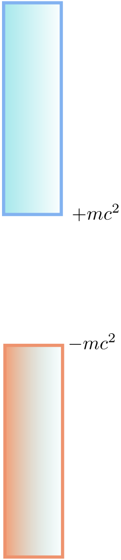
- Wave equation for non-relativistic free particle:

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

Relativistic free particle: classical mechanics

- Relativistic free-particle

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



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- Connecting to the non-relativistic expression

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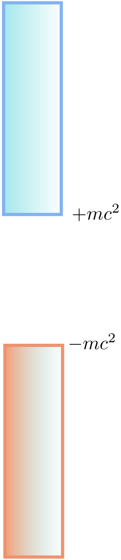

Relativistic free particle: classical mechanics

- Relativistic free-particle

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

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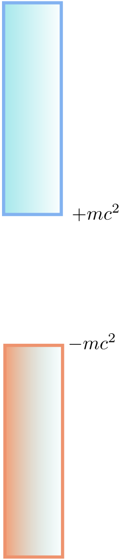
- The first term explodes in the non-relativistic limit ($c \rightarrow \infty$), but can be avoided by aligning the relativistic energy scale with the non-relativistic one

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

(only works for positive-energy branch)



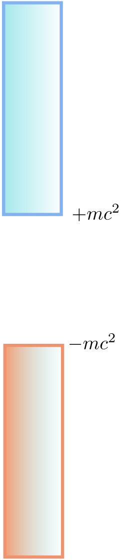
Dirac equation for a relativistic free particle

- Dirac equation

$$\left(h_0 - i\frac{\partial}{\partial t}\right)\psi \quad = \quad 0$$

with relativistic free-particle Hamiltonian

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



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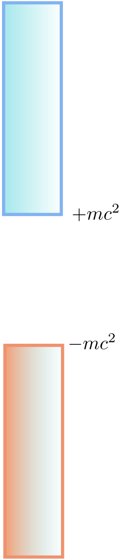
- The solutions are 4-component vector functions

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



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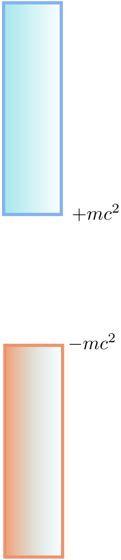
- Why four components ?



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:

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

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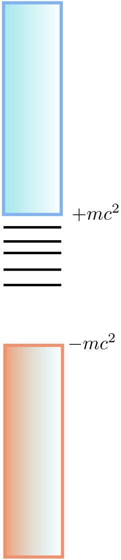
  where appears the **mechanical momentum** $\boldsymbol{\pi} = \mathbf{p} + e\mathbf{A}$
- Energy shift: $\beta \rightarrow \beta' - mc^2 \quad \Rightarrow \quad E \rightarrow E' = E - mc^2$

Negative-energy solutions



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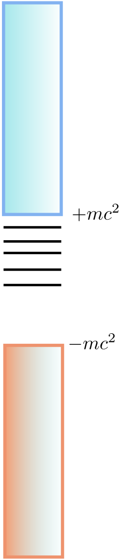

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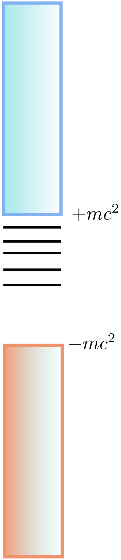

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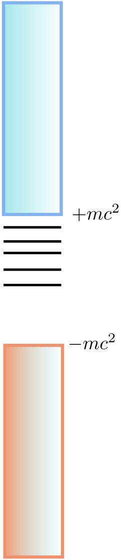

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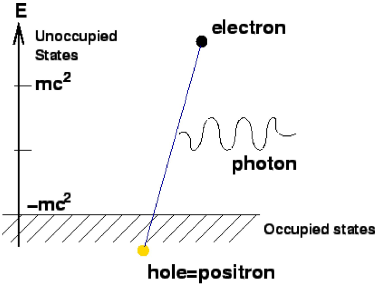
  - It can be shown that the hydrogen atom would not be stable and would disintegrate in 10^{-9} s.
  - The electron descending down the negative-energy band would cause an ultraviolet catastrophe.

Electron-positron pair creation



The solution proposed by Dirac

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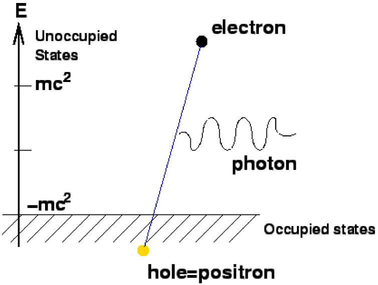

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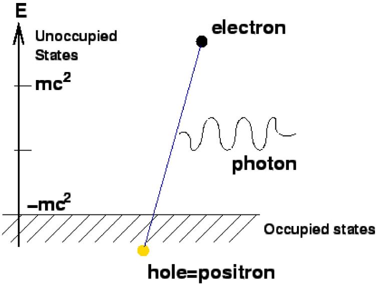

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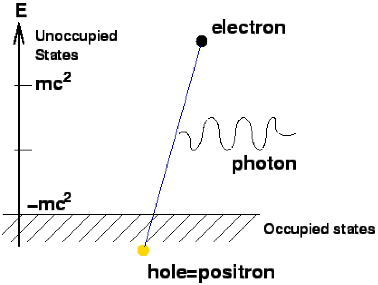

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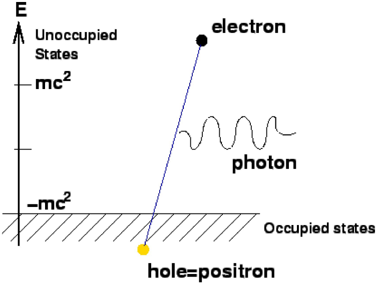

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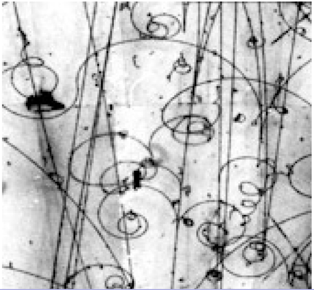
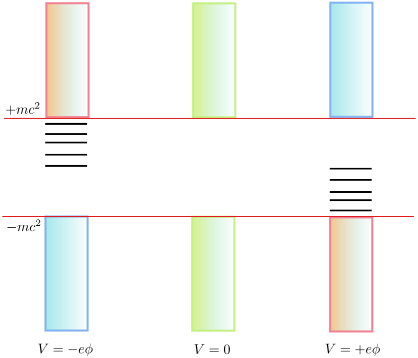
The theory of Dirac is confirmed in 1932 when the US physicist Carl Anderson discover the positron.



Charge conjugation symmetry



- Introduction of fields require speceification of charge.

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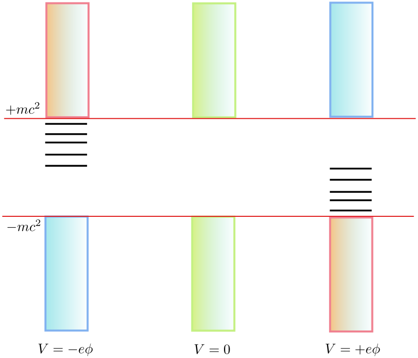

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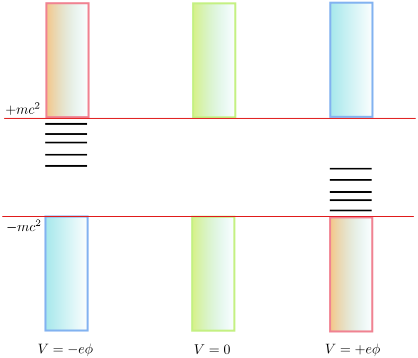

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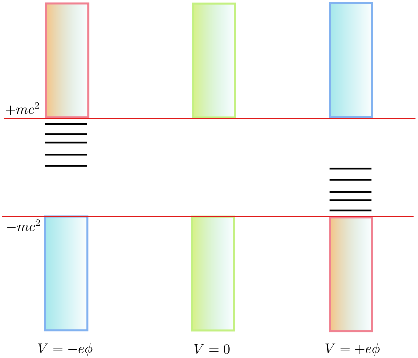

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- Solutions of opposite charge are related by charge conjugation symmetry.

Constants of motion

- Heisenberg's equation:

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

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- Free particle : conservation of (linear) momentum

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

Spin and angular momentum

- Non-relativistic free particle:

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

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- The economy of Nature's laws.

Non-relativistic Hamiltonian in external fields

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

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- **Is spin a relativistic effect ?**

Charge and current density

- The coupling of particles and fields is relativistic

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

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

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- The corresponding non-relativistic expressions are

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

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$$\rho^R = \frac{\delta\langle \hat{h}_{int}\rangle}{\delta\phi} = \psi^\dagger(\mathbf{r}) \underbrace{\{-e I_4\}}_{\text{density operator}} \psi(\mathbf{r}); \quad \mathbf{j}^R = -\frac{\delta\langle \hat{h}_{int}\rangle}{\delta\mathbf{A}} = \psi^\dagger(\mathbf{r}) \underbrace{\{-ec\boldsymbol{\alpha}\}}_{\text{current operator}} \psi(\mathbf{r})$$

- 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

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

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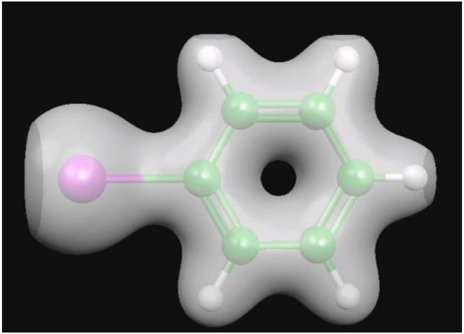
- The curious form of the relativistic velocity operator is due to *Zitterbewegung*, to be explained later.

(Number) density of iodobenzene

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



(isosurface 0.01)

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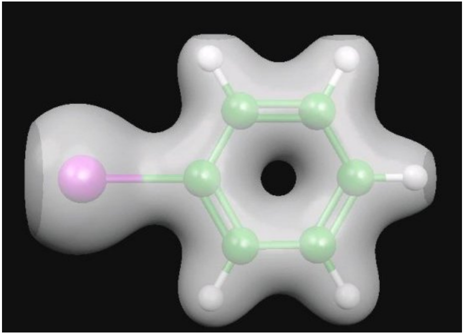

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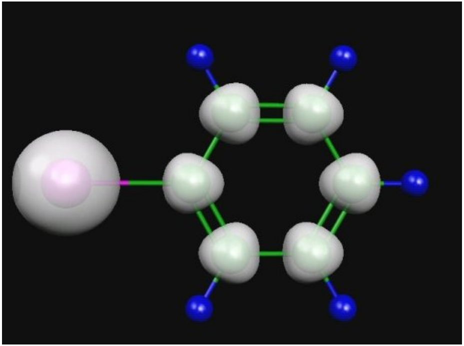

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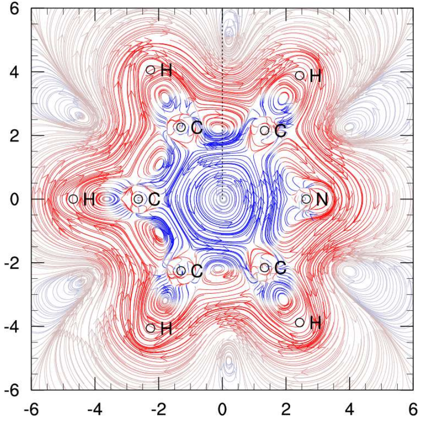

(molecular plane)

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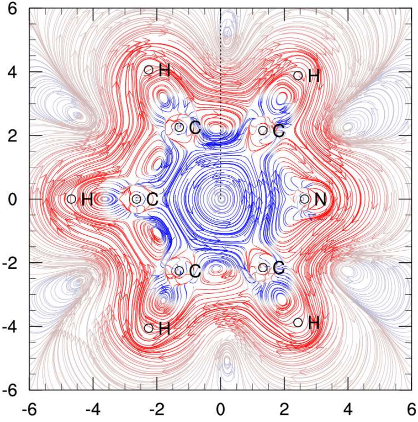

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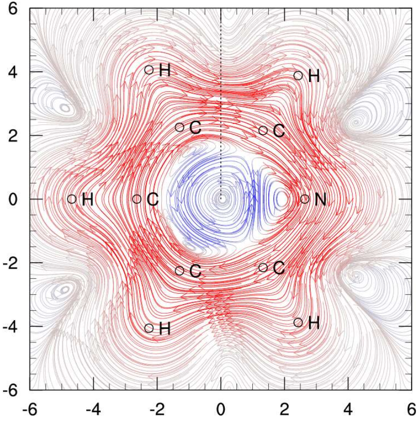

(molecular plane $\pm 1 a_0$)

Two-electron interaction

- General form:

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

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- 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:

$$H = V_{NN} + \sum_{i} h(i) + \frac{1}{2}\sum_{i\neq j} g(i,j)\,; \quad h(i) = h_0 + V_{eN}$$

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

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

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

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

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- 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

$$U=W_1W_2;\quad W_1=\left[\begin{array}{cc} 1 & -R^{\dagger} \\ R & 1 \end{array}\right];\quad W_2=\left[\begin{array}{cc} \Omega_+ & 0 \\ 0 & \Omega_- \end{array}\right];\quad \begin{array}{ccc} \Omega_+ & = & \left(1+R^{\dagger}R\right)^{-1/2} \\ \Omega_- & = & \left(1+RR^{\dagger}\right)^{-1/2} \end{array}$$

Decoupling transformation

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

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

Approximate 2-component relativistic Hamiltonians in one step

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

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  - Using the approximate decoupling (regular approximation)

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

    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

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- Let us investigate the physics it contains !

Mass-velocity term

- Relativistic mass correction

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

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  - The Pauli-Hamiltonian can not be used in variational calculations.

Darwin term

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

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  - 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<\phi(\mathbf{r}+\boldsymbol{\delta})\right>_T &= -e\phi(\mathbf{r}) - e\left<(\boldsymbol{\delta}\cdot\boldsymbol{\nabla})\right>_T\phi(\mathbf{r}) - \frac{1}{2}e\left<(\boldsymbol{\delta}\cdot\boldsymbol{\nabla})^2\right>_T\phi(\mathbf{r}) + \ldots \\
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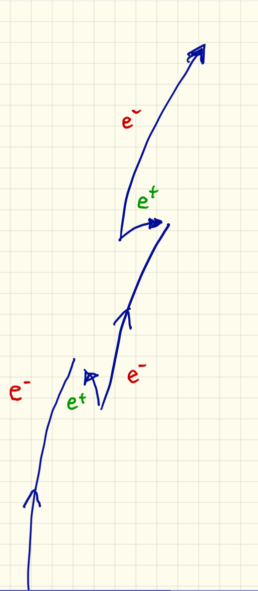
What is Zitterbewegung ?



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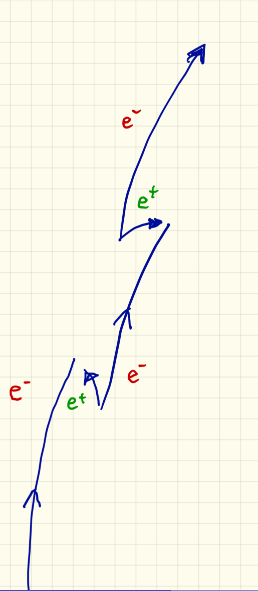

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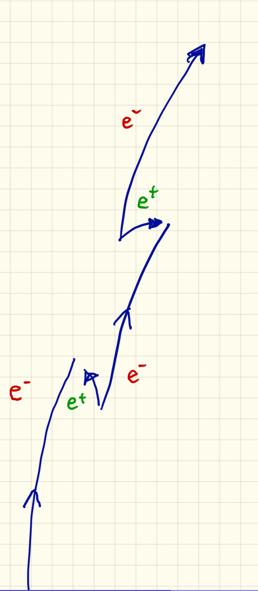

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- Consider the energy-time uncertainity relation

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

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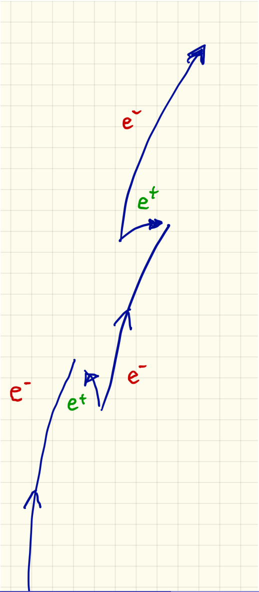

- One interpretation is that in the vicinity of an electron its field is sufficiently strong to allow the creation of a electron-positron pair.
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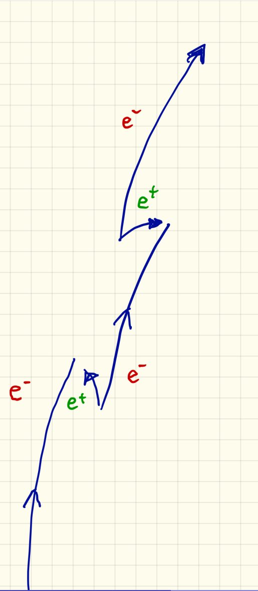

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- In this time a particle can move a maximum distance of

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Spin-orbit interaction

- Spin-orbit interaction term of the Pauli Hamiltonian

$$h^{\mathrm{so}} = \frac{1}{2m^2c^2}\mathbf{s}\cdot\left[(\nabla V)\times\mathbf{p}\right] \quad \xrightarrow{V=-\frac{Z}{r}} \quad \frac{Z}{2m^2c^2r^3}\mathbf{s}\cdot\mathbf{l}$$

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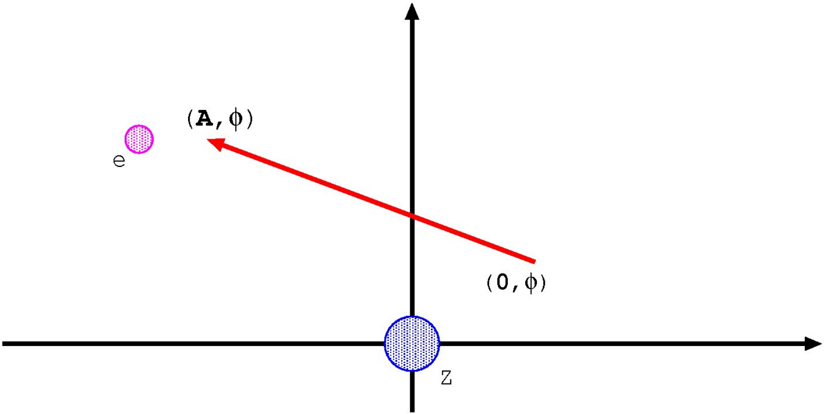
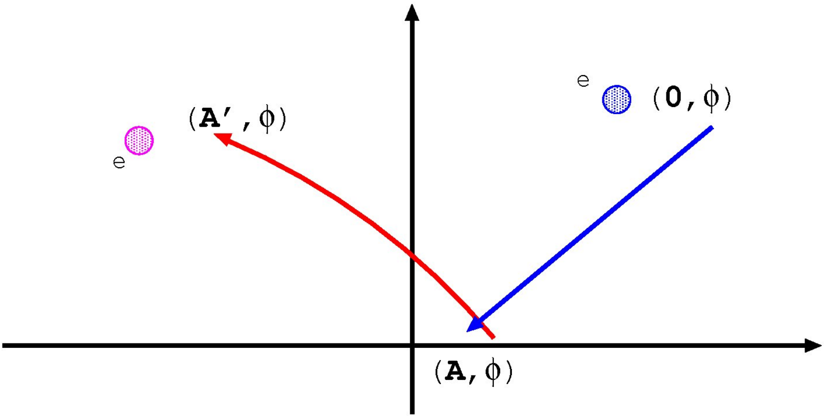
  - There is no explicit operator since
    the electronic Hamiltonian is formulated in the nuclear frame.

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



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

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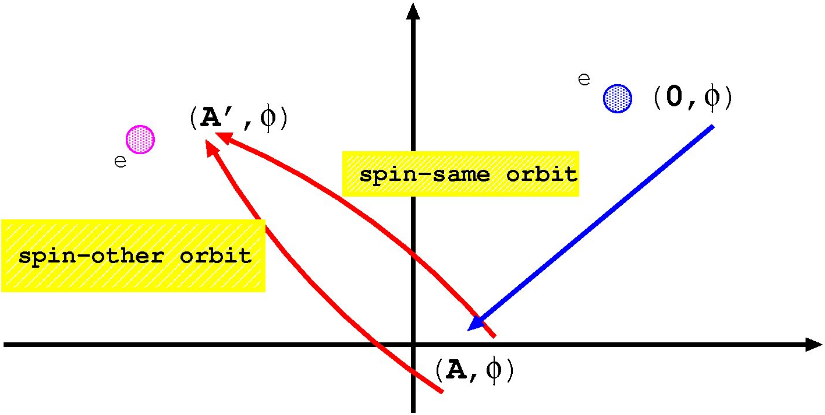

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Spin-other-orbit (SOO) interaction arises from the Gaunt term.

The spin-orbit interaction with nuclei is of type spin-own orbit in the Born-Oppenheimer approximation.

The ZORA Hamiltonian

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

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

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  - Usually fixed by approximating the potential in the denominator by a superposition of atomic potentials.

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  - For one-electron systems the Dirac eigenvalues are reproduced.

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- The 2-component Hamiltonian is obtained as

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

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An example: the electron density

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

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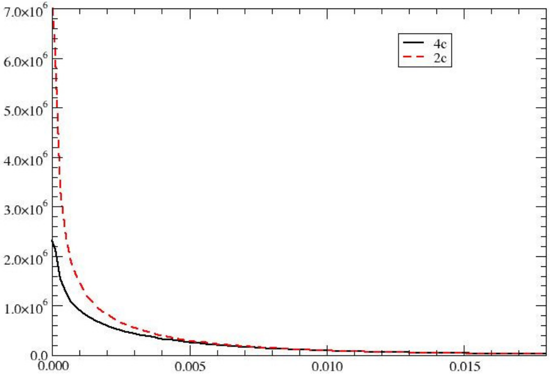

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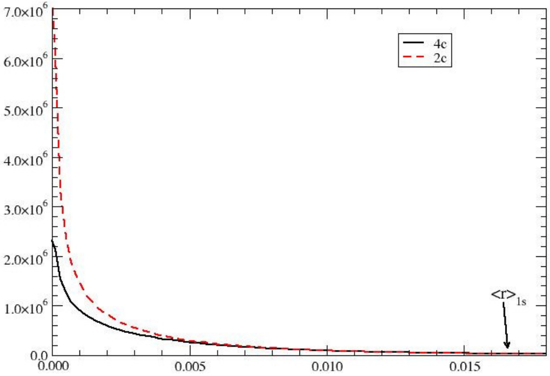

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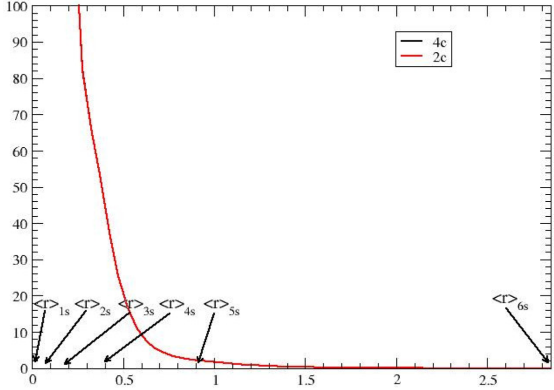

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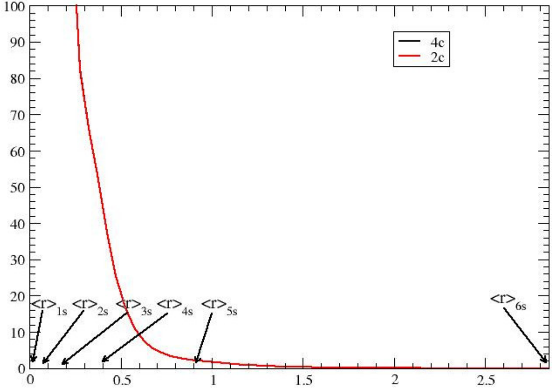

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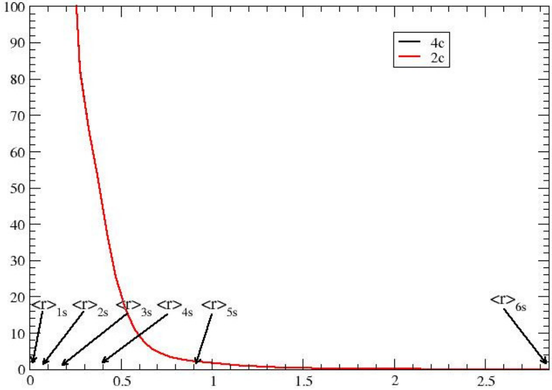

- However, many molecular properties probe the electron density near nuclei, providing local information with great sensitivity to the chemical environment,
  - for instance electric field gradients at nuclei, NMR parameters, molecular gradients and Mössbauer isomer shifts.

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):

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

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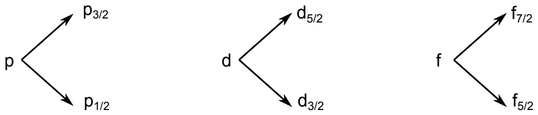

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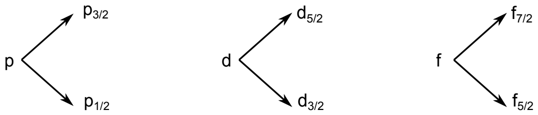

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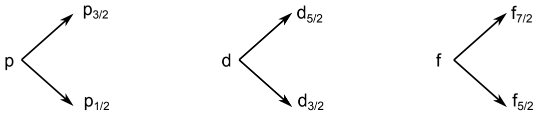

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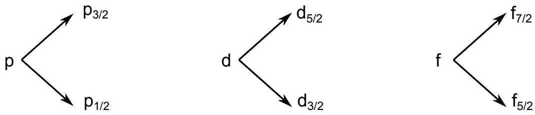

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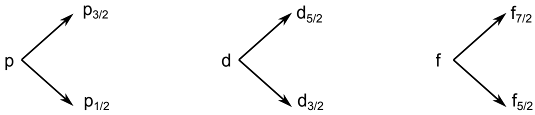

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$$m_j = m_\ell + m_s \quad \Rightarrow \quad m_\alpha = m_j - \frac{1}{2}; \quad m_\beta = m_j + \frac{1}{2}$$

A new quantum number: κ

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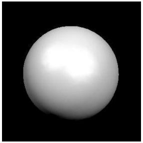
- Associated densities



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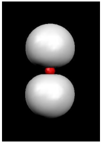

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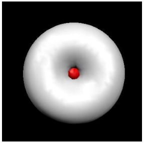

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The 4-component relativistic case

- Hydrogen atom (bound solutions):

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

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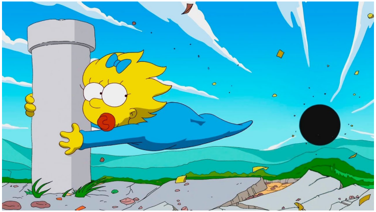
  - serves as a "black hole" in basis set optimizations



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Relativistic effective core potentials

The frozen-core approximation

4-component relativistic Hartree–Fock calculations

- Hg: polarizability ($\mathring{A}^{-3}$)

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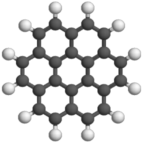

coronene

176 electrons

Pt_2

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- Further manipulation gives

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Effective core potentials

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

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- 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

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

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

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

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

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

  - 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

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

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- In practice the contributions are separated

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

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- 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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