# Some relativistic elements

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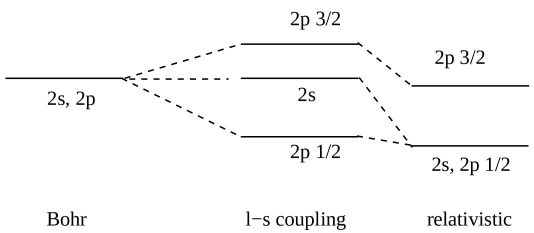
# Motivation

- Why should we bother about relativity ? Organic chemistry deals with light atoms
- But already hydrogen: fine structure




- Heavy-element chemistry: nuclear waste, Pb-induced diseases, Pt catalysts
- Relativistic effets may be important already around $Z = 30$ (Zn)

# Lorentz transformations

Two reference systems with relative speed $v$ with respect to each other should maintain the same laws of physics, in particular the same speed of light $c$:

$$\begin{aligned} \vec{r}' &= \frac{\vec{r} - \vec{v}\,t}{\sqrt{1 - v^2/c^2}} \\ t' &= \frac{t - r\,v^2/c^2}{\sqrt{1 - v^2/c^2}} \end{aligned}$$

$$x^2 + y^2 + z^2 = c^2 t^2 \qquad \text{yields} \qquad (x')^2 + (y')^2 + (z')^2 = c^2 (t')^2$$

- Limit of $v \to 0$ we find again $\vec{r}' = \vec{r} - \vec{v}\,t$ and $t' = t$ (transformation of Galilei)
- Consequence: muons arrive on earth despite their time of life of 2.2 $\mu$s (i.e. 660 m at speed $c$ without $t \to t'$)
- Factor $\sqrt{1 - v^2/c^2}$ may be incorporated in the mass: $m = \dfrac{m_0}{\sqrt{1 - v^2/c^2}}$





# Lorentz transformations

Relativistic energy expression

$$\begin{aligned} E^2 &= m^2\,c^4 \\ &= m^2 \left(1 - \frac{v^2}{c^2}\right) c^4 + m^2\,v^2\,c^2 = m_0^2\,c^4 + p^2\,c^2 \end{aligned}$$

de Broglie

- Particle without mass

$$E \;=\; p\,c \;=\; h\,\nu \;=\; h\frac{c}{\lambda} \;\longrightarrow\; p \;=\; \frac{h}{\lambda}$$

- Particle with mass

$$\begin{aligned} E &= \sqrt{m_0^2\,c^4 + p^2\,c^2} = m_0\,c^2 \sqrt{1 + \frac{p^2}{m_0^2 c^2}} \\ &\approx m_0\,c^2 \left(1 + \frac{1}{2}\frac{p^2}{m_0^2\,c^2}\right) = E_M + \frac{p^2}{2m_0^2} \end{aligned}$$

# Bohr model

- Speed of an electron at level $n$

$$v_n = \frac{e^2}{4\pi\epsilon_0\hbar}\frac{Z}{n} = \alpha\, c\,\frac{Z}{n}$$

with the finestructure constant $\alpha = \frac{e^2\, c}{4\pi\epsilon_0\hbar} = \frac{1}{137.037}$

- Orbital radius

$$r_n = \frac{\hbar^2}{m}\frac{4\pi\epsilon_0}{e^2}\frac{n^2}{Z} = \left(\sqrt{1-\frac{v^2}{c^2}}\right)\frac{\hbar}{m_0}\frac{4\pi\epsilon_0}{e^2}\frac{n^2}{Z}$$

- Speed independent of the mass of the electron $\longrightarrow v$ as a parameter

$$\sqrt{1-\frac{v^2}{c^2}} = \sqrt{1-\frac{\alpha^2 Z^2}{n^2}}$$

- Contraction of radii with $Z$ and $n$.





# Bohr model

| element | Z | $1-r'(1s)/r(1s)$ | $1-r'(4s)/r(4s)$ |
|---|---|---|---|
| H | 1 | 0.003 % | |
| Zn | 30 | 2.5 % | 0.15 % |
| Cd | 48 | 6.5 % | 0.38 % |
| Hg | 80 | 19 % | 1.07 % |

- May be transferred to Slater's model. Internal contraction leaves more space for the external electrons $\longrightarrow$ effective $n$ (4.7 for $n=5$ etc.).
- Lanthanide contraction: higher $Z$ and relativistic effects.
- $s$ orbitals will be more touched than $p$ or $d$, $f$
- $s$ and $p$ contracted, better screening, $d$ expanded.

# Relativistic quantum mechanics

- Schrödinger equation

$$\frac{p^2}{2m} = E \quad \longrightarrow \quad \frac{p^2}{2m}\psi = i\hbar\frac{\partial}{\partial t}\psi$$

- Derivatives in space and time in different degree $\longrightarrow$ not Lorentz invariant
- Use $p^2c^2 + m^2c^4 = E^2$ instead:

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\phi = \frac{m^2c^2}{\hbar^2}\phi$$

(Klein-Gordon equation 1927, describes free particles with and without mass)

- But not an equation of first order in time and space!





# Relativistic quantum mechanics

Take the square root of the $\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}$

$$\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} = (A\partial_x + B\partial_y + C\partial_z + \frac{i}{c}D\partial_t)(A\partial_x + B\partial_y + C\partial_z + \frac{i}{c}D\partial_t)$$

only possible with $AB + BA = 0, \ \ldots$ and $A^2 = B^2 = \ldots = 1$

$$(A\partial_x + B\partial_y + C\partial_z + \frac{i}{c}D\partial_t)\psi = \kappa\psi$$

or

$$(\nabla^2 - \frac{1}{c^2}\partial_t^2)\psi = \kappa^2\psi$$

Identify $\kappa = \frac{mc}{\hbar}$ : $(A\partial_x + B\partial_y + C\partial_z + \frac{i}{c}D\partial_t - \frac{mc}{\hbar})\psi = 0$
$(A, B, C) = i\beta\alpha_k$ and $D = \beta \longrightarrow$ Dirac equation

$$\left(\beta m_0 c^2 + \sum_{k=1}^{3}\alpha_k p_k\, c\right)\psi(\vec{x}, t) = i\hbar\frac{\partial\psi(\vec{x}, t)}{\partial t}$$

# Relativistic quantum mechanics

Pauli matrices

$$\sigma_k = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

lead to the $4 \times 4$ matrices

$$\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}$$

Dirac equation: (4-component matrix notation with two-component spinors $\phi_+$, $\phi_-$):

$$\begin{pmatrix} mc^2 & c\sigma \cdot p \\ c\sigma \cdot p & -mc^2 \end{pmatrix} \begin{pmatrix} \phi_+ \ \phi_- \end{pmatrix} = i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \phi_+ \\ \phi_- \end{pmatrix}$$

Still only for one free particle, but relativistic





# Relativistic quantum mechanics

- Dirac Hamiltonian with external fields

$$\hat{H}_D(i) = \left[ q_i V(\vec{r}_i) + c \sum_{k=x,y,z} \alpha_k(i)(p_k - \frac{q}{c} A_k) + \beta m_0 c^2 \right]$$

  $V$: electrostatic potential
  $\vec{A}$: vector potential for magnetic fields $\vec{B} = \vec{\nabla} \times \vec{A}$

- Breit equation: add to the Dirac Hamiltonian an electron-electron coupling term

$$\left\{ \sum_i \hat{H}_D(i) + \sum_{i>j} \frac{1}{r_{ij}} - \sum_{i>j} \hat{B}_{ij} \right\} \Psi = E\Psi$$

  with

$$\hat{B}_{ij} = -\frac{1}{2r_{ij}} \left[ \vec{a}(i) \cdot \vec{a}(j) + \frac{(\vec{a}(i) \cdot \vec{r}_{ij})\,(\vec{a}(j) \cdot \vec{r}_{ij})}{r_{ij}^2} \right]$$

# Relativistic quantum mechanics

Take only terms to order $(Z\alpha)^2$ ( i.e. $Z < 136$ )

$$
\begin{aligned}
H_{MV} &= -\frac{\alpha^2}{8}\sum_i \Delta_i^2 && \text{Mass-velocity term} \\
H_{D1} &= -\frac{\alpha^2 Z}{8}\sum_i \Delta_i \left(\frac{1}{r_i}\right) && \text{Darwin term} \\
H_{SO} &= \frac{\alpha^2 Z}{2}\sum_i \frac{1}{r_i^3}\vec{\ell}_i \cdot \vec{s}_i && \text{Spin-orbit (of one electron)} \\
H_{D2} &= -\frac{\alpha^2}{4}\sum_{i<j} \delta_i \left(\frac{1}{r_{ij}}\right) && \text{2-electron Darwin term} \\
H_{SOO} &= -\frac{\alpha^2}{2}\sum_{i<j} \frac{\vec{r}_{ij} \times \vec{p}_i}{r_{ij}^3}\left(\vec{s}_i + 2\vec{s}_j\right) && \text{Spin-other-orbit}
\end{aligned}
$$

Have to developed and applied to spinors $\longrightarrow$ very heavy



# In practice

The 4-component formalism may be reduced to a 1-component formalism for $\alpha$ (spin up) and $\beta$ (spin down) spinors

- 1-electron terms:
  - Mass-velocity, Darwin term: spin independent
  - Spin-orbit: depends explicitely on the spin

  additional 1-electron integrals
- 2-electron terms: additional (or modified) 2-electron integrals

What can be incorporated in a pseudopotential ?

- A pseudopotential should not change the symmetry of an electronic state
- No way to have spin-orbit pseudopotentials
- But mass-velocity and Darwin terms can be included
- Treat spin-orbit coupling through CAS-SCF/MR-CI mixing all states which contribute to the final multiplets (atoms, diatomics)
- Closed-shell systems: no spin-orbit