# An introduction to Relativistic Quantum Chemistry

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# Outline

## • Why do we care about relativity in chemistry ?

- What are relativistic effects ?
- Relativistic effects in atoms
- Relativistic effects in molecules
- Dirac Hamiltonian

## • How can we include relativity in calculations ?

- Perturbation theory of relativistic effects
- 2-component methods
- 4-component methods
- Effective Core Potentials

## Some recommendations / best practices

- Comparison light / heavy element calculations
- Importance of spin-orbit coupling

# Assumptions in Quantum Chemistry

## Born-Oppenheimer approximation

- Electronic and nuclear motion can be decoupled
- Electronic energies for motion around clamped nuclei provide potential energy surfaces for nuclear motion
- Coupling between surfaces is studied by perturbation theory
- Nuclear charge distribution
  - Point nucleus approximation
  - Nuclear deformations are treated in perturbation theory
- Relativity
  - The speed of electrons is always far below the speed of light
  - Goal is to find time-independent wave functions (stationary states)
  - Magnetic fields can be neglected or treated in perturbation theory

## Dirac's view on relativity



#### Dirac (1929)

- The general theory of quantum mechanics is now almost complete, the imperfection that still remain being in connection with the exact fitting in of the theory with relativistic 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 wich 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 fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.

# Later insights



- Pekka Pyykkö and Jean-Paul Desclaux (1979)
  - The chemical difference between the fifth row and the sixth row seems to contain large, if not dominant, relativistic contributions which, however, enter in an individualistic manner for the various columns and their various oxidation states, explaining, for example, both the inertness of Hg and the stability of Hg<sub>2</sub><sup>2+</sup>. These relativistic effects are particularly strong around gold. A detailed understanding of the interplay between relativistic and shell-structure effects will form the impact of relativity on chemistry.



#### Jan Almlöf & Odd Gropen (1996)

 While the incorporation of these effects sometimes increases the computation labor, the increase is generally reasonable, and certainly much less than in, e.g. the transition from semiempirical to ab initio methods for routine quantum chemistry applications. We predict, therefore, that relativistic corrections in one form or another will be included in the majority of all quantum chemistry calculations before the end of this decade.

# The hydrogenic atom: Energies

• The exact non-relativistic energy

$$E^{NR} = -\frac{Z^2}{2n^2}$$

• The exact relativistic energy

$$E = mc^{2} / \sqrt{1 + \left\{ \frac{Z/c}{n - j - \frac{1}{2} + \sqrt{(j + 1/2)^{2} - \frac{Z^{2}}{c^{2}}} \right\}^{2}}$$

• Spin-orbit couping :  $j = l \pm s$ 

Energy depends on orbital and spin variables

# The hydrogenic atom: Orbitals

- I and s are not separate quantum numbers for the relativistic atom:  $p_x$ ,  $p_y$  and  $p_z$  can not be chosen as eigenfunctions
- Correct eigenfunctions with spin-orbit coupling: p<sub>i,mi</sub>

• 
$$p_{\frac{1}{2}\frac{1}{2}} = \frac{1}{\sqrt{3}} \left( p_x \beta + i p_y \beta - p_z \alpha \right)$$



1/3 sigma + 2/3 pi

• 
$$p_{\frac{3}{2}\frac{1}{2}} = \frac{1}{\sqrt{6}} \left( p_x \beta + i p_y \beta + 2 p_z \alpha \right)$$



2/3 sigma + 1/3 pi

• 
$$p_{\frac{3}{2}\frac{3}{2}} = \frac{1}{\sqrt{2}} \left( p_x \alpha + i p_y \alpha \right)$$



## Hartree-Fock orbital energies

**Relativistic effects for valence orbitals** 



## Orbital stabilization of valence s-orbitals



## **Orbital contraction**

### • The valence s-orbital shrinks



## Orbital destabilization and spin-orbit splitting



## **Orbital expansion**

### • The outermost p- and d-orbitals expand



# Ln-An contraction



- Ln-An contraction is partly caused by relativistic effects
- Trend expected from the atomic calculations are validated with calculations on LnF, AnF, LnH<sub>3</sub> and AnH<sub>3</sub> molecules.

# Atomization energies

- Example: Halogen molecules
- Molecular energy is hardly affected by SOcoupling (SO quenching)
- First order perturbation theory Nonrelativistic





Relativistic

# Atomization energies

- Atomic asymptotes are lowered by SO-coupling
- First order perturbation theory



#### Relativistic effect on atomization energies (kcal/mol)



Spin-Orbit effect on atomization energies is wellreproduced by correcting only the separate atoms limit

#### Relativistic effect on vibrational frequencies (cm<sup>-1</sup>)



Bond weakening by admixture of the antibonding sigma orbital in the pi bonding orbitals due to spin-orbit coupling.

#### Relativistic effect on equilibrium distances (Å)



Important and slightly method dependent for 6p elements

## Relativistic effect on atomization energies (kcal/mol)



Make orbital diagram and identify possible SOC effects. Always include scalar effects.

# Ir(ppy)3 spinor magnetization densities



Use spin-orbit coupling of iridium to increase OLED efficiency

# Special relativity

Postulate 1: All inertial frames are equivalent

# Postulate 2: The laws of physics have the same form in all inertial frames

Lorentz coordinate transformations mix time and space

Postulates hold for electromagnetism (Maxwell relations) Postulates do not hold for Newtonian mechanics

Develop quantum theory from classical relativistic equations and make sure electron spin is described

## Non-relativistic quantization

The nonrelativistic Hamilton function

$$H = T + V = \frac{p^2}{2m} + q\phi(\mathbf{r})$$

#### Quantization

$$H \rightarrow i\hbar \frac{\partial}{\partial t} ; \mathbf{p} \rightarrow -i\hbar \nabla$$
$$\hat{H} \psi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t)$$
$$\hat{H} = -\frac{\hbar}{2m} \hat{\nabla}^2 + q \hat{\phi}(\mathbf{r})$$

## Non-relativistic quantum mechanics

The nonrelativistic Hamiltonian

$$\mathsf{H}=\mathsf{T}+V=\frac{p^2}{2\mathsf{m}}+q\phi$$

Usually only electric field via scalar potential  $\phi$ 

Magnetic fields via vector potential A:

 $\boldsymbol{p} \rightarrow \pi = \boldsymbol{p} - q\boldsymbol{A}$  (minimal coupling substitution)

$$\mathsf{H} = \frac{p^2}{2m} + q\phi - \frac{q}{m}\mathbf{A}\cdot\mathbf{p} + \frac{q^2}{m}A^2$$

Zeeman interaction, but no spin-orbit coupling.

## Non-relativistic quantization 2

## The nonrelativistic Hamilton function

$$H = T + V = \frac{\pi^2}{2m} + q\phi(\mathbf{r})$$

$$\pi = \mathbf{p} - q\mathbf{A}$$

Mechanical  $(\pi)$  and canonical momentum (p) Principle of minimal electromagnetic coupling

Quantization

$$\begin{split} H &\to i\hbar \frac{\partial}{\partial t}; \mathbf{p} \to -i\hbar \nabla \\ \hat{H} \,\psi(\mathbf{r},t) &= i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r},t) \\ \hat{H} &= -\frac{\hbar}{2m} \hat{\nabla}^2 + \frac{iq\hbar}{2m} \Big( \hat{\nabla} \cdot \hat{\mathbf{A}} + \hat{\mathbf{A}} \cdot \hat{\nabla} \Big) + \frac{q^2}{2m} \hat{\mathbf{A}}^2 + q \hat{\phi}(\mathbf{r}) \\ &\downarrow \\ \text{Coulomb gauge:} (\hat{\nabla} \cdot \hat{\mathbf{A}}) = 0 \end{split}$$

## Spin and non-relativistic quantization 1

We can, however, also write the the Hamilton function as



Quantization

$$\sigma_{i}\sigma_{j} = \delta_{ij} + i\varepsilon_{ijk}\sigma_{k}$$
$$\varepsilon_{xyz} = \varepsilon_{zxy} = \varepsilon_{yzx} = 1$$
$$\varepsilon_{xzy} = \varepsilon_{zyx} = \varepsilon_{yxz} = -1$$

Kronecker delta and Levi-Civita tensor, Summation over repeated indices

$$\begin{split} \hat{H} &= q\hat{\phi} + \frac{1}{2m} \Big\{ \boldsymbol{\sigma} \cdot \left( -i\hbar\hat{\nabla} + q\hat{\mathbf{A}} \right) \Big\}^2 \\ &= q\hat{\phi} - \frac{\hbar^2}{2m} \left( \boldsymbol{\sigma} \cdot \hat{\nabla} \right)^2 + \frac{q^2}{2m} \left( \boldsymbol{\sigma} \cdot \hat{\mathbf{A}} \right)^2 + \frac{iq\hbar}{2m} \Big[ \left( \boldsymbol{\sigma} \cdot \hat{\nabla} \right), \left( \boldsymbol{\sigma} \cdot \hat{\mathbf{A}} \right) \Big]_+ \end{split}$$

## Spin and non-relativistic quantization 2

$$(\mathbf{\sigma} \cdot \mathbf{u})(\mathbf{\sigma} \cdot \mathbf{v}) = (\mathbf{u} \cdot \mathbf{v}) + i\mathbf{\sigma} \cdot (\mathbf{u} \times \mathbf{v})$$

$$\begin{split} \hat{H} &= -\frac{\hbar}{2m}\hat{\nabla}^2 + q\hat{\phi} + \frac{q^2}{2m}\hat{A}^2 \\ &+ \frac{iq\hbar}{2m} \Big(\hat{\nabla}\cdot\hat{A} + \hat{A}\cdot\hat{\nabla}\Big) - \frac{q\hbar}{2m}\sigma\cdot\Big(\hat{\nabla}\times\hat{A} + \hat{A}\times\hat{\nabla}\Big) \end{split}$$

$$\hat{\nabla} \times \mathbf{A}(\mathbf{r}) f(\mathbf{r}) = \hat{\nabla} \times \left( f(\mathbf{r}) \mathbf{A}(\mathbf{r}) \right) \quad \longleftarrow \text{ A is a multiplicative operator}$$
$$= \left( \hat{\nabla} f(\mathbf{r}) \right) \times \mathbf{A}(\mathbf{r}) + f(\mathbf{r}) \hat{\nabla} \times \mathbf{A}(\mathbf{r}) \leftarrow \text{ chain rule}$$
$$= -\hat{\mathbf{A}} \times \left( \hat{\nabla} f(\mathbf{r}) \right) + \mathbf{B} f(\mathbf{r}) \leftarrow \text{ Use definition of B}$$

$$\hat{H} = \hat{T} + q\hat{\phi} + iq\hat{\mathbf{A}}\cdot\hat{\nabla} + \frac{q^2}{2}\hat{\mathbf{A}}^2 - \frac{q}{2}\boldsymbol{\sigma}\cdot\mathbf{B} \quad \text{(in atomic units)}$$

# Spin in NR quantum mechanics

The Pauli Hamiltonian in two-component form

$$\begin{pmatrix} -\frac{1}{2}\nabla^2 + q\phi + iq\mathbf{A}\cdot\nabla + \frac{q^2}{2m}A^2 - \frac{q}{2}B_z & -\frac{q}{2}(B_x - iB_y) \\ -\frac{q}{2}(B_x + iB_y) & -\frac{1}{2}\nabla^2 + q\phi + iq\mathbf{A}\cdot\nabla + \frac{q^2}{2m}A^2 + \frac{q}{2}B_z \end{pmatrix}$$

Second derivatives w.r.t. position, first derivative w.r.t. time Linear in scalar, quadratic in vector potential  $\rightarrow$  Is not Lorentz-invariant

Ad hoc introduction of spin. No explanation for the anomalous g-factor (ratio of 2 between magnetic moment and intrinsic angular momentum)
No interaction between angular momenta due to the orbital and spin: spin-orbit coupling is relativistic effect

## **Relativistic quantization 1**

Take the classical relativistic energy expression

Quantization recipe gives

$$i\hbar\frac{\partial\psi}{\partial t} = q\phi\psi + \sqrt{m^2c^4 + c^2\pi^2} \ \psi$$

After series expansion of the square root this could provide relativistic corrections to the Schrödinger Equation

**Disadvantage** : Difficult to define the square root operator in terms of a series expansion (**A** and **p** do not commute). Not explored much.

## **Relativistic quantization 2**

### Eliminate the square root before quantization

$$\left(E-q\phi\right)^2 = m^2c^4 + c^2\pi^2$$

Quantization

$$\left(i\hbar\frac{\partial}{\partial t}-q\hat{\phi}\right)^{2}\psi = \left(m^{2}c^{4}+c^{2}\hat{\pi}^{2}\right)\psi$$

**Klein-Gordon Equation** 

Solution Soluti Solution Solution Solution Solution Solution

The KG-equation can be used for spinless particles

## Relativistic quantization 3

Define a new type of "square root"

$$E - q\phi = \beta mc^{2} + c \alpha \cdot \pi$$
$$\left[\alpha_{i}, \alpha_{j}\right]_{+} = 2\delta_{ij} \wedge \left[\alpha_{i}, \beta\right]_{+} = 0 \wedge \beta^{2} = 1$$

Quantization

$$i\hbar\frac{\partial\psi}{\partial t} = \left(\beta mc^2 + c\alpha\cdot\hat{\pi} + q\hat{\phi}\right)\psi$$

The Dirac equation

Suitable for description of one electron

- Relativistic kinematics
- Charged spin 1/2 particle

## The Dirac equation

$$(\beta mc^2 + c \, \boldsymbol{\alpha} \cdot \boldsymbol{\pi} + q \, \phi) \psi(r, t) = i\hbar \frac{\partial \psi(r, t)}{\partial t}$$

First derivatives with respect to time and position
Linear in scalar and vector potentials

#### © Lorentz invariant

 $\alpha$  and  $\beta$  are 4-component matrices

$$\alpha_{x} = \begin{pmatrix} 0 & \sigma_{x} \\ \sigma_{x} & 0 \end{pmatrix} \alpha_{y} = \begin{pmatrix} 0 & \sigma_{y} \\ \sigma_{y} & 0 \end{pmatrix} \alpha_{z} = \begin{pmatrix} 0 & \sigma_{z} \\ \sigma_{z} & 0 \end{pmatrix} \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

## The Dirac Hamiltonian

$$\begin{split} \hat{H} &= \beta mc^{2} + c \, \alpha \cdot \hat{\pi} + q \phi \\ &= \begin{pmatrix} mc^{2} + q \phi & 0 & c \pi_{z} & c(\pi_{x} - i\pi_{y}) \\ 0 & mc^{2} + q \phi & c(\pi_{x} + i\pi_{y}) & -c \pi_{z} \\ c \pi_{z} & c(\pi_{x} - i\pi_{y}) & -mc^{2} + q \phi & 0 \\ c(\pi_{x} + i\pi_{y}) & -c \pi_{z} & 0 & -mc^{2} + q \phi \end{pmatrix} \end{split}$$

Four component wave function

1) Spin doubles the number of components

2) Relativity doubles the number of components again

# Charge and current density

• Charge density

 $\rho(\mathbf{r},t) = q\psi^{\dagger}(\mathbf{r},t)\psi(\mathbf{r},t)$ 

• Current density

$$\mathbf{j}(\mathbf{r},t) = q\psi^{\dagger}(\mathbf{r},t) c \alpha \psi(\mathbf{r},t)$$
  $\leftarrow$  c $\alpha$  is the relativistic velocity operator

• Continuity relation

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r},t) = 0$$

## Free particle Dirac equation

- Take simplest case :  $\phi = 0$  and  $\mathbf{A} = 0$
- Use plane wave trial function

## Free particle Dirac equation

• Two doubly degenerate solutions

$$(E^{2} - m^{2}c^{4} - c^{2}\hbar^{2}k^{2}) = 0$$
$$E_{+} = +\sqrt{m^{2}c^{4} + c^{2}\hbar^{2}k^{2}}$$
$$E_{-} = -\sqrt{m^{2}c^{4} + c^{2}\hbar^{2}k^{2}}$$

• Compare to classical energy expression

$$E = \sqrt{m^2 c^4 + c^2 p^2}$$

• Quantization (for particles in a box) and prediction of negative energy solutions

## Free particle Dirac equation

• Wave function for  $E = E_+$ 

$$a_2 = 0$$
;  $a_3 = a_1 \frac{c\hbar k_z}{E_+ + mc^2}$ ;  $a_4 = a_1 \frac{c\hbar k_+}{E_+ + mc^2}$ 

 $\hbar |k| = p << mc$  For particles moving with "nonrelativistic" velocities

$$a_{3} = a_{1} \frac{cp_{z}}{mc^{2} + \sqrt{m^{2}c^{4} + c^{2}p^{2}}} \approx a_{1} \frac{p_{z}}{2mc}$$

$$a_4 \approx a_1 \frac{p_+}{2mc}$$

- Upper components are the "Large components"
- Lower components are the "Small components"
## Free particle Dirac equation

• Wave function for  $E = E_{-}$ 

$$a_4 = 0$$

$$a_1 = a_3 \frac{c\hbar k_z}{E_- - mc^2} \approx a_3 \frac{p_z}{-2mc}$$

$$a_2 = a_3 \frac{c\hbar k_+}{E_- - mc^2} \approx a_3 \frac{p_+}{-2mc}$$

- Role of large and small components is reversed
- Application of variational principle is more difficult
  - Variational Collapse
  - Minmax optimization instead of straight minimization

## Dirac sea of electrons





- Negative energy solutions are all occupied
- Pauli principle applies
- Holes in this sea of electrons are seen as particles with positive charge: positrons (1933)
- Infinite background charge
- QED (Quantum Electrodynamics) to properly account for contribution of negative energy states
- No-pair approximation

## The hydrogenic atom

- Starting point for the LCAO approach
- Can be solved by separating the radial and angular variables (see Dyall & Faegri or Reiher & Wolf)

$$\begin{pmatrix} mc^2 - \frac{Z}{r} & c \,\sigma \cdot \mathbf{p} \\ c \,\sigma \cdot \mathbf{p} & -mc^2 - \frac{Z}{r} \end{pmatrix} \begin{pmatrix} \psi^L(\mathbf{r}) \\ \psi^S(\mathbf{r}) \end{pmatrix} = E \begin{pmatrix} \psi^L(\mathbf{r}) \\ \psi^S(\mathbf{r}) \end{pmatrix}$$

 The exact solutions help in devising basis set approaches and in understanding the chemical bonding in the relativistic regime

# The hydrogenic atom: orbitals

• Write orbitals as product of radial and angular (2-spinor functions)

 $\begin{pmatrix} \psi^{L}(\mathbf{r}) \\ \psi^{S}(\mathbf{r}) \end{pmatrix} = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r)\xi_{\kappa,m}(\vartheta,\varphi) \\ iQ_{n\kappa}(r)\xi_{-\kappa,m}(\vartheta,\varphi) \end{pmatrix}$ 

• Solutions to the radial equation

 $P_{n\kappa}(r) = N_{n\kappa}^{P} e^{-\lambda r} r^{\gamma} (F_{1}(r) + F_{2}(r))$  $Q_{n\kappa}(r) = N_{n\kappa}^{Q} e^{-\lambda r} r^{\gamma} (F_{1}(r) - F_{2}(r))$  $R_{nl}(r) = N_{nl}^{R} e^{-(\sqrt{-2E})r} r^{l+1} F(r)$ 

Large component

Small component

Nonrelativistic





l	0	1	1	2	2	3	3
j	1/2	1/2	3/2	3/2	5/2	5/2	7/2
К	-1	1	-2	2	-3	3	-4
	<i>s</i> <sub>1/2</sub>	<i>p</i> <sub>1/2</sub>	<i>p</i> <sub>3/2</sub>	<i>d</i> <sub>3/2</sub>	<i>d</i> <sub>5/2</sub>	$f_{5/2}$	$f_{7/2}$

## More than one electron

General form of a time-independent Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_{i} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{g}_{ij}$$

• Wave function

 $\Psi(1,...,N) \quad \longleftarrow \text{ N x 4 components}$  $\Psi(...,i,...,j,...) = -\Psi(...,j,...,i,...) \quad \text{anti-symmetry}$ 

- Difference between relativistic and non-relativistic calculations is in the calculation of integrals over *h* and *g*
- Second-quantized form of equations is identical to nonrelativistic theory when using the no-pair approximation

## **Electron-electron interactions**

• In molecular calculations:

$$g_{12}^{Coulomb-Breit} = \frac{1_{1}1_{2}}{r_{12}} = \frac{1}{r_{12}}$$
Coulomb: diagonal operator  

$$-\frac{1}{c^{2}r_{12}}c\alpha_{1} \cdot c\alpha_{2}$$
Gaunt: off-diagonal operator  

$$-\frac{1}{2c^{2}}(c\alpha_{1} \cdot \nabla_{1})(c\alpha_{2} \cdot \nabla_{2})r_{12}$$
Retardation

- Coulomb, Gaunt and retardation terms
  - Zeroth order is the instantaneous electrostatic interactions
  - First correction describes the magnetic interactions
  - Second correction describes retardation of the interaction

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- Relativistic effects in atoms
- Relativistic effects in molecules
- Dirac Hamiltonian

#### • How can we include relativity in calculations ?

- Perturbation theory of relativistic effects
- 2-component methods
- 4-component methods
- Effective Core Potentials

#### • Some recommendations / best practices

- Comparison light / heavy element calculations
- Importance of spin-orbit coupling

## Expansion of the energy expression

• The exact Hydrogenic energy expression

$$E = mc^{2} / \left\{ \frac{1 + \left\{ \frac{Z/c}{n - j - \frac{1}{2} + \sqrt{(j + 1/2)^{2} - \frac{Z^{2}}{c^{2}}} \right\}^{2} \right\}$$

• Can be expanded to  

$$\begin{bmatrix} (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots \\ (1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^{2} - \dots$$

# **Dirac-Coulomb** equation

Hamiltonian:

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_{i} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{g}_{ij}$$

• 
$$h_i = \beta_i' c^2 + \vec{\alpha}_i \cdot \vec{p}_i + V_i$$

Couples spins and large and small components

• 
$$g_{ij} = \frac{1_i 1_j}{r_{ij}}$$

Coulomb operator: does not couple different components

- Approximation methods focus on  $h_i$ 
  - Decouple large and small components
  - Two-component equation: Schrödinger equation plus correction terms (scalar=diagonal and spin-orbit=off-diagonal)

## The extra dimension





Development of **relativistic** molecular electronic structure theory

### **Approximate Hamiltonians**

- Find 2-component operators that describe these scalar relativistic and spin-orbit coupling energy corrections in molecular systems
- Start by decoupling the large and small component equations

$$V\psi^{L} + c \,\sigma \cdot \mathbf{p}\psi^{S} = E\psi^{L}$$
$$c \,\sigma \cdot \mathbf{p}\psi^{L} + \left(V - 2mc^{2}\right)\psi^{S} = E\psi^{S}$$

• Rewrite the lower equation as

### Approximate Hamiltonians

• Substitute in the upper equation

$$\left\{\frac{1}{2m}(\boldsymbol{\sigma}\cdot\mathbf{p})K(\boldsymbol{E},\mathbf{r})(\boldsymbol{\sigma}\cdot\mathbf{p})+V\right\}\psi^{L}(\mathbf{r})=E\psi^{L}(\mathbf{r})$$

- <u>Unnormalized</u> Elimination of the Small Component (UESC)
  - The full spinor is normalized to 1, so the large component only must have a norm < 1</li>
  - Large component spinors are not orthogonal to each other (only the full spinors are orthogonal)
- The UESC equation is exact: is used as starting point for approximations

## Pauli Hamiltonian

• Crudest approximation :  $K(E,\mathbf{r}) \approx 1$ 

$$K(E,\mathbf{r}) = \left(1 + \frac{E - V}{2mc^2}\right)^{-1}$$

$$\begin{cases} \frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) (\boldsymbol{\sigma} \cdot \mathbf{p}) + V \\ \frac{p^2}{2m} + V \end{cases} \psi^L(\mathbf{r}) = E \psi^L(\mathbf{r}) \end{cases}$$

$$\begin{cases} \frac{p^2}{2m} + V \\ \frac{p^2}{2m} + V \\ \frac{p^2}{2m} + V \end{cases} \psi^L(\mathbf{r}) = E \psi^L(\mathbf{r}) \qquad \text{Schrödinger equation} \end{cases}$$

• Take K=1 but include also a magnetic field

$$\left\{\frac{1}{2m}(\sigma \cdot \pi)(\sigma \cdot \pi) + V\right\}\psi^{L}(\mathbf{r}) = E\psi^{L}(\mathbf{r}) \quad \text{Pauli equation}$$

• Find an operator to normalize the wave function :

$$\psi = N\psi^{L}$$
$$N = \sqrt{1 + \frac{1}{4m^{2}c^{2}}(\sigma \cdot \mathbf{p})K^{2}(\sigma \cdot \mathbf{p})}$$



• Multiply the UESC equation by N<sup>-1</sup>

$$N^{-1}\left\{\frac{1}{2m}(\boldsymbol{\sigma}\cdot\mathbf{p})K(E,\mathbf{r})(\boldsymbol{\sigma}\cdot\mathbf{p})+V\right\}N^{-1}N\psi^{L}(\mathbf{r})=N^{-1}E\psi^{L}(\mathbf{r})$$
$$N^{-1}\left\{\frac{1}{2m}(\boldsymbol{\sigma}\cdot\mathbf{p})K(E,\mathbf{r})(\boldsymbol{\sigma}\cdot\mathbf{p})+V\right\}N^{-1}\psi(\mathbf{r})=EN^{-2}\psi(\mathbf{r})$$

• Use series expansions and keep terms up to order c<sup>-2</sup>

$$\hat{N}^{-1} = \left[ 1 + \frac{1}{4m^2c^2} (\sigma \cdot \mathbf{p}) K^2 (\sigma \cdot \mathbf{p}) \right]^{-1/2}$$
  
=  $1 - \frac{1}{8m^2c^2} (\sigma \cdot \mathbf{p}) K^2 (\sigma \cdot \mathbf{p}) + \dots$   
=  $1 - \frac{p^2}{8m^2c^2} + O(c^{-4})$   
 $\hat{N}^{-2} = \left[ 1 + \frac{1}{4m^2c^2} (\sigma \cdot \mathbf{p}) K^2 (\sigma \cdot \mathbf{p}) \right]^{-1}$   
=  $1 - \frac{p^2}{4m^2c^2} + O(c^{-4})$ 

$$K^{2} = \left(1 + \frac{E - V}{2mc^{2}}\right)^{-2} = 1 + O(c^{-2})$$

• Expansion of K

$$K(E,\mathbf{r}) = \left[1 + \frac{(E-V)}{2mc^2}\right]^{-1} = 1 - \frac{(E-V)}{2mc^2} + O(c^{-4})$$

• Substitute everything and keep only terms to order c<sup>-2</sup>

$$\hat{N}^{-1} \left[ \hat{V} + \frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) K(\boldsymbol{\sigma} \cdot \mathbf{p}) \right] \hat{N}^{-1} \boldsymbol{\psi} = EN^{-2} \boldsymbol{\psi}$$
$$\left( \hat{V} + \hat{T} + \frac{-Ep^2 + (\boldsymbol{\sigma} \cdot \mathbf{p}) V(\boldsymbol{\sigma} \cdot \mathbf{p}) - Tp^2 - \frac{1}{2} \left[ p^2, V \right]_+}{4m^2 c^2} \right) \boldsymbol{\psi} = \left[ E - \frac{Ep^2}{4m^2 c^2} \right] \boldsymbol{\psi}$$

• The energy dependent term on the lhs is cancelled by the rhs

$$\hat{H}^{BP} = \hat{T} + \hat{V} + \frac{(\boldsymbol{\sigma} \cdot \mathbf{p})V(\boldsymbol{\sigma} \cdot \mathbf{p}) - T\mathbf{p}^2 - \frac{1}{2}[\mathbf{p}^2, V]_+}{4m^2c^2}$$

• Further simplify the equation using

$$(\boldsymbol{\sigma} \cdot \mathbf{p})V(\boldsymbol{\sigma} \cdot \mathbf{p}) = (\mathbf{p}V) \cdot \mathbf{p} + V\mathbf{p}^2 + i\boldsymbol{\sigma} \cdot (\mathbf{p}V) \times \mathbf{p}$$

$$-\frac{1}{2} \left[ \mathbf{p}^2, V \right]_+ = -\frac{1}{2} \left( \mathbf{p}^2 V \right) - \left( \mathbf{p} V \right) \cdot \mathbf{p} - V \mathbf{p}^2$$

• Result : The Breit-Pauli equation

$$\hat{H}^{BP} = \hat{T} + \hat{V} - \frac{\mathbf{p}^2 V}{8m^2 c^2} - \frac{\mathbf{p}^4}{8m^3 c^2} + \frac{i\sigma \cdot (\mathbf{p}V) \times \mathbf{p}}{4m^2 c^2}$$

Darwin Mass-Velocity Spin-Orbit

## Breit-Pauli Hamiltonian applied to hydrogenic atom

$$\begin{split} \hat{H}^{BP} &= \hat{T} + \hat{V} - \frac{\mathbf{p}^2 V}{8m^2 c^2} - \frac{\mathbf{p}^4}{8m^3 c^2} + \frac{i\sigma \cdot (\mathbf{p}V) \times \mathbf{p}}{4m^2 c^2} \\ \text{Darwin Mass-Velocity Spin-Orbit} \\ &< \hat{H}^{Darwin} >= \frac{Z^4}{2n^3 c^2} \quad (l=0) & \longleftarrow \text{Positive: reduces nuclear attraction} \\ &< \hat{H}^{Darwin} >= 0 \quad (l>0) & \longleftarrow \text{Operator is delta-function for V} = -Z/r \\ &< \hat{H}^{MV} >= \frac{Z^4}{2n^4 c^2} \left\{ \frac{3}{4} - \frac{n}{l + \frac{1}{2}} \right\} & \longleftarrow \text{Always negative: decreases kinetic energy} \\ &< \hat{H}^{SO} >= \frac{Z^4}{2n^3 c^2} \frac{l}{l(2l+1)(l+1)} \quad (j = l+1/2) \\ &< \hat{H}^{SO} >= \frac{Z^4}{2n^3 c^2} \frac{-l-1}{l(2l+1)(l+1)} \quad (j = l-1/2) \end{split}$$

## Good relativistic Hamiltonians

The wish list for a relativistic Hamiltonian:

- 1. It should describe the scalar relativistic effects
- 2. It should describe the spin-orbit coupling effect
- 3. There should be a lowest eigenvalue (variational stability)
- 4. Interpretation: comparison with Schrödinger picture
- 5. Implementation: easy integrals, efficient coding
- 6. Errors should be small and systematically improvable

## **Regular Approximation**

• What is wrong with the BP approach? The expansion parameter !

$$K(E,\mathbf{r}) = \left[1 + \frac{(E-V)}{2mc^2}\right]^{-1} = 1 - \frac{(E-V)}{2mc^2} + O(c^{-4})$$

- E should be small relative to 2mc<sup>2</sup>
  - Orbital energies vary over a range of -0.1 to 5,000 au
  - Twice the rest mass energy is 37,558 au
  - This difference should be large enough
- V should be small relative to 2mc<sup>2</sup>
  - The potential is dominated by the nuclear attraction close to the nuclei

$$V \approx -\frac{Z}{r}$$

- Take r = 10<sup>-4</sup> au and Z=6 (carbon) : V = 60,000 au
- Is this inside the nucleus ? No : the nuclear radius is 4.7 10<sup>-5</sup> au for C.

## 0<sup>th</sup> order regular approximation: ZORA

• Can we use a better expansion parameter ? Yes !

$$K(E,\mathbf{r}) = \left[1 + \frac{(E-V)}{2mc^2}\right]^{-1} = \left(1 - \frac{V}{2mc^2}\right)^{-1} \left(1 + \frac{E}{2mc^2 - V}\right)^{-1}$$

- E should be small relative to 2mc<sup>2</sup> V
  - V is negative which *improves* the expansion close to the nuclei
- Zeroth order in this expansion

$$\left\{\frac{1}{2m}(\boldsymbol{\sigma}\cdot\mathbf{p})\left(1-\frac{V}{2mc^{2}}\right)^{-1}(\boldsymbol{\sigma}\cdot\mathbf{p})+V\right\}\psi^{ZORA}(\mathbf{r})=E\psi^{ZORA}(\mathbf{r})$$

- ② Zeroth order equation does describe SO-coupling and scalar relativistic corrections
- ⊗ Gauge dependence of the energy

$$V \to V + C \quad E \to E + C - \frac{EC}{2mc^2}$$

- Affects ionization energies, structures
- Can be avoided by keeping potential in the denominator fixed

#### Approximations to $K(E, \mathbf{r})$ for the 1s orbital of $Fm^{99+}$



#### Approximations to $K(E, \mathbf{r})$ for the 7s orbital of $Fm^{99+}$



#### Uranium atom



#### Uranium atom



## Four-component methods

- Idea
  - Expand Dirac equation in basis set
  - Use kinetic balance condition to prevent "variational collapse"
- Advantages-Disadvantages

© No approximations made

③ Matrix elements over the operators are easily evaluated

Many more two-electron integrals

- <sup>(3)</sup> The Fock matrix is twice as large
- © No picture change

## Basis set expansion

 Use different expansion sets for the large and small component parts of the wave function

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^{N^L} \begin{pmatrix} \chi_{\mu}^L(\mathbf{r}) \\ 0 \end{pmatrix} c_{\mu i}^L + \sum_{\nu=1}^{N^S} \begin{pmatrix} 0 \\ \chi_{\nu}^S(\mathbf{r}) \end{pmatrix} c_{\nu i}^S$$

• Kinetic balance condition

$$\chi^{S}(\mathbf{r}) = \frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2mc} \chi^{L}(\mathbf{r}) \quad \text{or} \quad \{\chi^{S}(\mathbf{r})\} = \left\{\frac{\partial \chi^{L}(\mathbf{r})}{\partial x}, \frac{\partial \chi^{L}(\mathbf{r})}{\partial y}, \frac{\partial \chi^{L}(\mathbf{r})}{\partial z}\right\}$$

• Recovers the non-relativistic limit

$$\int \chi_{\kappa}^{L^{*}}(\mathbf{r}) T \chi_{\lambda}^{L}(\mathbf{r}) d\mathbf{r} = \frac{1}{2} \sum_{\mu=1}^{N^{s}} \int \chi_{\kappa}^{L^{*}}(\mathbf{r}) (\sigma \cdot \mathbf{p}) \chi_{\mu}^{S}(\mathbf{r}) d\mathbf{r} \times \int \chi_{\mu}^{S^{*}}(\mathbf{r}) (\sigma \cdot \mathbf{p}) \chi_{\lambda}^{L}(\mathbf{r}) d\mathbf{r}$$
$$\mathbf{T}^{LL} = \frac{1}{2} (\sigma \cdot \mathbf{p})^{LS} (\sigma \cdot \mathbf{p})^{SL} \quad \longleftarrow \quad \text{Resolution of identity}$$

## Choice of expansion functions

- Large component
  - Atoms: Slaters or Gaussians
  - Molecules: Gaussians
- Small component
  - Same type as large component
  - Should fulfill kinetic balance relation

$$\left\{\chi_{P}^{S}\right\} = \left\{\left(\boldsymbol{\sigma}\cdot\mathbf{p}\right)\chi_{P}^{L}\right\} \qquad \left\{\chi_{P}^{S}\right\} = \left\{\frac{\partial\chi_{P}^{L}}{\partial x}, \frac{\partial\chi_{P}^{L}}{\partial y}, \frac{\partial\chi_{P}^{L}}{\partial z}\right\}$$

**Restricted KB** 

**Unrestricted KB** 

## Kinetic Balance realizations

$$(\vec{\sigma} \cdot \vec{p})(\vec{\sigma} \cdot \vec{p}) = p^2 \Rightarrow \{(\vec{\sigma} \cdot \vec{p})\chi^L\} \subset \{\chi^S\}$$

**Scalar functions** 

Large component **s p d f** Small component **s p d f g** 

Typically 4-5 times...

2-spinor functions

Exactly 4 times ...

...as many basisfunctions as in NR calculation

Conventional integral code

Specialized integral code

## Self Consistent Field: Hartree-Fock

1. Construct Fock operator 
$$F = \beta' c^2 + c\alpha \cdot \mathbf{p} + V + \sum_{j}^{occupied} J_j - K_j$$

2. Find eigensolutions

$$F\psi(\mathbf{r}_1) = \varepsilon\psi(\mathbf{r}_1)$$

3. Check convergence

$$\left\{\psi^{new}\right\} = \left\{\psi^{old}\right\} ?$$

4. Compute energy

$$E^{HF} = E^{Kinetic} + E^{Potential} + E^{Elec.Rep.}$$

$$E^{HF} = \sum_{i}^{occupied} \langle i | \beta' c^{2} + c\alpha \cdot \mathbf{p} | i \rangle + \sum_{i}^{occupied} \langle i | V | i \rangle + \frac{1}{2} \sum_{i,j}^{occupied} \langle i | J_{j} - K_{j} | i \rangle$$

# Fock operator

$$F = \begin{pmatrix} V + \sum_{j} J_{j} - K_{j} & c(\mathbf{\sigma}.\mathbf{p}) - \sum_{j} K_{j} \\ c(\mathbf{\sigma}.\mathbf{p}) - \sum_{j} K_{j} & V - 2c^{2} + \sum_{j} J_{j} - K_{j} \end{pmatrix}$$

$$J_{j}(\mathbf{r}_{1}) = \int \frac{\psi_{j}^{L^{\dagger}}(\mathbf{r}_{2})\psi_{j}^{L}(\mathbf{r}_{2}) + \psi_{j}^{S^{\dagger}}(\mathbf{r}_{2})\psi_{j}^{S}(\mathbf{r}_{2})}{r_{12}}d\mathbf{r}_{2} = \int \frac{\rho_{j}(\mathbf{r}_{2})}{r_{12}}d\mathbf{r}_{2}$$

$$K_{j} \boldsymbol{\psi}_{i}^{L}(\mathbf{r}_{1}) = K_{j}^{LL} \boldsymbol{\psi}_{i}^{L}(\mathbf{r}_{1}) + K_{j}^{SL} \boldsymbol{\psi}_{i}^{L}(\mathbf{r}_{1})$$
$$= \int \frac{\boldsymbol{\psi}_{j}^{L^{\dagger}}(\mathbf{r}_{2}) \boldsymbol{\psi}_{i}^{L}(\mathbf{r}_{2})}{r_{12}} d\mathbf{r}_{2} \boldsymbol{\psi}_{j}^{L}(\mathbf{r}_{1}) + \int \frac{\boldsymbol{\psi}_{j}^{L^{\dagger}}(\mathbf{r}_{2}) \boldsymbol{\psi}_{i}^{L}(\mathbf{r}_{2})}{r_{12}} d\mathbf{r}_{2} \boldsymbol{\psi}_{j}^{S}(\mathbf{r}_{1})$$

$$K_{j}\boldsymbol{\psi}_{i}^{S}(\mathbf{r}_{1}) = K_{j}^{LS}\boldsymbol{\psi}_{i}^{S}(\mathbf{r}_{1}) + K_{j}^{SS}\boldsymbol{\psi}_{i}^{S}(\mathbf{r}_{1})$$
$$= \int \frac{\boldsymbol{\psi}_{j}^{S^{\dagger}}(\mathbf{r}_{2})\boldsymbol{\psi}_{i}^{S}(\mathbf{r}_{2})}{r_{12}}d\mathbf{r}_{2}\boldsymbol{\psi}_{j}^{L}(\mathbf{r}_{1}) + \int \frac{\boldsymbol{\psi}_{j}^{S^{\dagger}}(\mathbf{r}_{2})\boldsymbol{\psi}_{i}^{S}(\mathbf{r}_{2})}{r_{12}}d\mathbf{r}_{2}\boldsymbol{\psi}_{j}^{S}(\mathbf{r}_{1})$$

## The small component density

- The large component wave function resembles the non-relativistic wave function
- Exact relation between large and small component wave functions

$$\psi^{S} = \frac{-i}{2c} \left( 1 + \frac{E - V}{2c^{2}} \right)^{-1} \sigma \cdot \left( \nabla \psi^{L} \right)$$
  
K(E,r)

- Small component wave function is related to the first derivative of large component wave function
- The small component density is **localized** closed to the nuclei: can be easily expressed in fit functions

# **Electron Density of Uranyl**

#### Large component

#### Small component





# Modified and spinfree Dirac equation

• Define an auxilliary function such that

$$\psi^{S} = \frac{1}{2mc} (\sigma \cdot \mathbf{p}) \phi^{L} \quad \longleftarrow \text{ Relation holds by definition}$$

• Transform the Dirac equation accordingly

$$\begin{pmatrix} V & T \\ T & \frac{(\sigma \cdot \mathbf{p})V(\sigma \cdot \mathbf{p})}{4mc^2} - T \end{pmatrix} \begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix} = E \begin{pmatrix} 1 & 0 \\ 0 & \frac{T}{2mc^2} \end{pmatrix} \begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix}$$

• Separate scalar and spin-dependent part and neglect the spin-dependent terms if desired

## Direct perturbation theory

• Consider the modified Dirac equation

$$\begin{pmatrix} V & T \\ T & \frac{(\sigma \cdot \mathbf{p})V(\sigma \cdot \mathbf{p})}{4mc^2} - T \end{pmatrix} \begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix} = E \begin{pmatrix} 1 & 0 \\ 0 & \frac{T}{2mc^2} \end{pmatrix} \begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix}$$

• Non-relativistic limit is related to the Lévy-Leblond equation

$$\begin{pmatrix} V & T \\ T & -T \end{pmatrix} \begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix} = E^{NR} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix} \qquad \begin{pmatrix} V & (\sigma \cdot \mathbf{p}) \\ (\sigma \cdot \mathbf{p}) & -2m \end{pmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = E^{LL} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix}$$

• Define perturbation theory with as first order perturbations

$$H^{(1)} = \begin{pmatrix} 0 & 0 \\ 0 & -Vc^{-2} \end{pmatrix} \qquad S^{(1)} = \begin{pmatrix} 0 & 0 \\ 0 & c^{-2} \end{pmatrix}$$

### Foldy-Wouthuysen transformations

• Define <u>energy-independent</u> unitary transformation to decouple the large and small component equations

$$\begin{aligned} & UH^{D}U^{-1}U\psi_{i}^{D} = EU\psi_{i}^{D} \\ & H^{FW} = U\hat{H}^{D}U^{-1} = \begin{pmatrix} H^{+} & 0 \\ 0 & H^{-} \end{pmatrix} \\ & \psi_{i}^{FW4(+)} = U\psi_{i}^{D(+)} = \begin{pmatrix} \psi_{i}^{FW} \\ 0 \end{pmatrix} \quad \boxed{\text{Picture change}} \\ & \hat{U} = \begin{pmatrix} \left(1 + X^{\dagger}X\right)^{-\frac{1}{2}} & \left(1 + X^{\dagger}X\right)^{-\frac{1}{2}}X^{\dagger} \\ -\left(1 + XX^{\dagger}\right)^{-\frac{1}{2}}X & \left(1 + XX^{\dagger}\right)^{-\frac{1}{2}} \end{pmatrix} \qquad \boxed{X = \frac{1}{2mc}K(\sigma.p)} \end{aligned}$$

 Exact operator expressions are only known for the free particle problem
### Iterative decoupling schemes

• Write Foldy-Wouthuysen decoupling transformation (U) as product of normalization (V) and decoupling (W)

$$\begin{split} \hat{U} &= \begin{pmatrix} \left(1 + \hat{X}^{\dagger} \hat{X}\right)^{-\frac{1}{2}} & \left(1 + \hat{X}^{\dagger} \hat{X}\right)^{-\frac{1}{2}} \hat{X}^{\dagger} \\ -\left(1 + \hat{X} \hat{X}^{\dagger}\right)^{-\frac{1}{2}} \hat{X} & \left(1 + \hat{X} \hat{X}^{\dagger}\right)^{-\frac{1}{2}} \end{pmatrix} \\ &= \begin{pmatrix} \left(1 + \hat{X}^{\dagger} \hat{X}\right)^{-\frac{1}{2}} & 0 \\ 0 & \left(1 + \hat{X} \hat{X}^{\dagger}\right)^{-\frac{1}{2}} \end{pmatrix} \begin{pmatrix} 1 & \hat{X}^{\dagger} \\ -\hat{X} & 1 \end{pmatrix} \\ &= \hat{V} \hat{W} \end{split}$$

• The decoupling requirement provides equations for X

$$(\hat{W}\hat{H}^D\hat{W}^\dagger)^{SL} = 0$$

$$\hat{h}^{SL} + \hat{h}^{SS}\hat{X} - \hat{X}\hat{h}^{LL} - \hat{X}\hat{h}^{LS}\hat{X} = 0 \quad \blacktriangleleft \quad \text{Quadratic equation for X}$$

# Iterative decoupling schemes

All Foldy-Wouthuysen transformed solutions should only have two non-zero components

$$\begin{pmatrix} 1 & \hat{X}^{\dagger} \\ -\hat{X} & 1 \end{pmatrix} \begin{pmatrix} \psi_{+}^{L} & \psi_{-}^{L} \\ \psi_{+}^{S} & \psi_{-}^{S} \end{pmatrix} = \begin{pmatrix} \phi_{+} & 0 \\ 0 & \phi_{-} \end{pmatrix}$$
  
$$\psi_{+}^{S} - \hat{X}\psi_{+}^{L} = 0$$
  
$$\psi_{-}^{L} + \hat{X}^{\dagger}\psi_{-}^{S} = 0$$
  
Linear equations for X

- Equation for X can be solved if all analytical solutions of the Dirac equation can be written in a simple form. This was possible in the free-particle case .
- For atoms and molecules the potential operator is too complicated to work with the exact solutions, but it is possible to derive iterative decoupling schemes (Barysz, Reiher, Hirao) that provide nearly exact (but very complicated) operator expressions based on solutions of the hydrogenic atom.
- Popular realization: Douglas-Kroll-Hess (second order expansion for 1-electron part Hamiltonian, zeroth order for 2-electron part)

#### eXact 2-Component (X2C) theory

Idea: Decouple a matrix representation of the Dirac equation

- 1. Define a 4-component basis and compute matrix elements over the *one-electron operators*
- 2. Find exact solution to the Dirac equation in this matrix representation
- 3. Use the eigenvectors to construct an exact decoupling operator in matrix form
- 4. Transform all other one-electron operators to this decoupled representation
- 5. Add two-electron Coulomb operator in unmodified form (accept picture change error for this operator)

### Exact two-component theory

• A matrix representation of the Dirac matrix is formed and diagonalized: eigenvectors gives access to the exact decoupling *matrix* X in this basis

$$\begin{pmatrix} \mathbf{h}^{LL} & \mathbf{h}^{LS} \\ \mathbf{h}^{SL} & \mathbf{h}^{SS} \end{pmatrix} \begin{pmatrix} \mathbf{y}_{+}^{L} & \mathbf{y}_{-}^{L} \\ \mathbf{y}_{+}^{S} & \mathbf{y}_{-}^{S} \end{pmatrix} = \begin{pmatrix} \mathbf{e}_{+} & \mathbf{0} \\ \mathbf{0} & \mathbf{e}_{-} \end{pmatrix} \begin{pmatrix} \mathbf{y}_{+}^{L} & \mathbf{y}_{-}^{L} \\ \mathbf{y}_{+}^{S} & \mathbf{y}_{-}^{S} \end{pmatrix}$$

• Write the equations for X in matrix form

$$\mathbf{y}_{+}^{S} - \mathbf{X}\mathbf{y}_{+}^{L} = 0$$
$$\mathbf{y}_{-}^{L} + \mathbf{X}^{\dagger}\mathbf{y}_{-}^{S} = 0$$

 Manipulate to get an equation of the form AX = B that can be solved by Cholesky decomposition (A is Hermitian and positive definite)

$$\left[\mathbf{y}_{-}^{S}\mathbf{y}_{-}^{S^{\dagger}}\right]X = \left[\mathbf{y}_{-}^{S}\mathbf{y}_{-}^{L^{\dagger}}\right]$$

• See Ilias & Saue (JCP **126** (2006) 064102) for details

### Matrix-based X2C approaches

- Fully equivalent to the matrix Dirac equation in the no-pair approximation
- 2-component picture is easily compared to the nonrelativistic Schrödinger picture
- Errors made by neglecting corrections to the 2electron operators are small
- The necessary diagonalization and other matrix manipulations are done before the SCF procedure
- Decoupling from molecular Hartree-Fock solutions: molecular mean-field (X2C-MMF) approach
- 4-component property matrices can be readily transformed to the 2-c picture

#### Discussed on Day 2

$$\left\{\frac{1}{2m}(\boldsymbol{\sigma}\cdot\mathbf{p})K(E,\mathbf{r})(\boldsymbol{\sigma}\cdot\mathbf{p})+V\right\}\psi^{L}(\mathbf{r})=E\psi^{L}(\mathbf{r})$$
 Two-component methods



# Chemistry of heavy elements

#### • A different world....



	Au <sub>2</sub>	$C_{20}N_{20}H_{12}$
electrons	178	160
total energy	-36,870 Hartree	-987 Hartree
basis functions	48s38p24d18f2g 426 functions	240s108p24d 684 functions
chemical bonds	1	40
Bond energy	0.1 Hartree 2.3 eV	10 Hartree 272 eV

# Spectroscopy of f-elements

• Low-lying electronic states

	Eu <sup>3+</sup>	C <sub>6</sub> H <sub>6</sub>
electrons	6 f-electrons	6 π-electrons
orbitals	7	6
energies < 0.125 Hartree	3 (with SOC: 8)	1
states < 0.125 Hartree	159 (with SOC:58)	1

- Lanthanides: 4f is shielded from environment
- Actinides: 5f can participate in chemical bonding

# Valence-Only approaches

- All-electron calculations are not always feasible or necessary
- Hierarchy of approximations for "core" electrons
  - 1. Correlate core electrons at a lower level of theory (e.g. MP2)
  - 2. Do not correlate core electrons at all (HF-only)
  - 3. Use atomic orbitals for core electrons (Frozen Core)
  - 4. Model frozen core by a Model Potential (AIMP)
  - 5. Model frozen core by a Effective Core Potential (ECP)
  - 6. Model frozen core by a Local Pseudopotential (LPP)
- Error correction and additional features
  - 1. Estimate higher order correlation effects in another basis set
  - 2.
  - 3. Use a core polarization potential
  - 4.
  - 5. Include valence relativistic effects in RECP
  - 6. Suitable for orbital-free DFT calculations

## Frozen Core approximation

• Consider the Fock operator

$$F = h^{kinetic} - \sum_{A}^{Nuclei} \frac{Z_A}{r_A} + \sum_{j}^{occupied} \left(J_j - K_j\right)$$

• Identify localized (atomic) core orbitals and partition

$$Z_A^* = Z_A - Z_{Core}$$

$$F = h^{kinetic} - \sum_{A}^{Nuclei} \frac{Z_A}{r_A} + \sum_{A}^{Nuclei} \sum_{c}^{core} J_c^A - K_c^A + \sum_{v}^{valence} J_v - K_v$$

$$F = h^{kinetic} - \sum_{A}^{Nuclei} \frac{Z_A^*}{r_A} + \sum_{v}^{valence} J_v - K_v + \sum_{A}^{Nuclei} \left( -\frac{Z_A^{core}}{r_A} + \sum_{c}^{core} J_c^A \right) - \sum_{A}^{Nuclei} \sum_{c}^{core} K_c^A$$

$$V_{Coulomb} = V_{Exchange}$$

- Coulomb potential goes to zero at large distance, contains correction due to imperfect screening of nuclei at short distance
- Exchange potential depends on the overlap with the frozen atomic orbitals: short range
- Approximation made: atomic core orbitals are not allowed to change upon molecule formation, other orbitals stay orthogonal to these AOs

# Core polarization and overlap

• Polarizability of the core can modeled by a classical core polarization correction (see also book II, formula 41.9)

$$E_{CP}^{A} = -\frac{1}{2} \sum_{A} \mathbf{E}_{A}^{T} \boldsymbol{\alpha}_{A} \mathbf{E}_{A} \quad \qquad \text{Field from the electrons and the other nuclei}}$$

$$\mathbf{E}_{CP}^{A} = -\frac{1}{2} \sum_{A} \mathbf{E}_{A}^{T} \boldsymbol{\alpha}_{A} \mathbf{E}_{A} \quad \qquad \text{Field from the electrons and the other nuclei}}$$

$$\mathbf{E}_{CP}^{A} = -\frac{1}{2} \sum_{A} \mathbf{E}_{A}^{T} \boldsymbol{\alpha}_{A} \mathbf{E}_{A} \quad \qquad \text{Field from the electrons and the other nuclei}}$$

- Need a cut-off factor in the field since the multipole expansion is only valid outside the core
- Can be extended to model core-correlation and core-valence correlation as well
- The overlap between cores is assumed to be zero : the Pauli repulsion and Coulomb attraction between neighboring cores should be small
- For "large core" calculations an additional correction may be added

## Ab Initio Model Potentials

Replace the exact, non-local, frozen core potential by a model potential plus a projection operator

$$V_{Frozen\ core}^{A} = \sum_{c}^{core} \left(J_{c}^{A} - Z_{A}^{core}\right) - \sum_{c}^{core} K_{c}^{A} \approx V_{Coul}^{A} + V_{Exch}^{A} + P_{Core}^{A}$$

$$V_{Coul}^{A} = \frac{1}{r_{A}} \sum_{i} c_{i}^{A} e^{-\alpha_{i}^{A} r_{A}^{2}} \qquad \qquad \text{Density fit of spherical density, can be done to arbitrary precision}$$

 $V_{Exch}^{A} = -\sum_{c} \sum_{r,s,t,u} |r\rangle S_{rs}^{-1} \langle s|K_{c}^{A}|t\rangle S_{tu}^{-1} \langle u|$ 

Resolution of identity with non-orthogonal functions



Level shift that shifts the core solutions to high energies

#### Ab Initio Model Potentials

- No freely adjustable parameters
- Core solutions present but shifted to the virtual space
- © Relativistic effects can be included in the reference Fock operator
  - Cowan-Griffin Hamiltonian (scalar)
  - Wood-Boring Hamiltonian (spin-orbit)
  - Douglas-Kroll-Hess Hamiltonian
  - X2C Hamiltonian
- © Can also be used to generate "no-valence" MPs
  - Improves description of ions in crystals
  - May require iterative generation scheme
  - Good results for e.g. calculations of lanthanide spectra by Seijo and coworkers

Get Keeps nodal structure of the valence orbitals

## Nodal structure



#### Valence density



#### Valence orbitals



## Pseudo orbitals



# Pseudopotentials in DFT

#### Easier to consider pseudo-orbitals in Density Functional Theory

$$\left(\hat{T} - \frac{Z_A}{r_A} + J_A[\rho_A] + \hat{V}_A^{xc}[\rho_A]\right)\psi_i^A(\mathbf{r}) = \varepsilon_i^A\psi_i^A(\mathbf{r}) \qquad \text{Reference atomic calculation}$$

Orbitals are solution of a local effective potential

$$\hat{V}_{A}^{eff}(\mathbf{r}) = \varepsilon_{i}^{A} - \frac{\nabla^{2}\psi_{i}^{A}(\mathbf{r})}{2\psi_{i}^{A}(\mathbf{r})}$$

 $\left(\hat{T} + \hat{V}_{A}^{eff}\right)\psi_{i}^{A}(\mathbf{r}) = \varepsilon_{i}^{A}\psi_{i}^{A}(\mathbf{r})$ 

Potential can be constructed if the orbitals are known

$$(\hat{T} + \hat{V}_{A}^{PP})\phi_{i}^{A}(\mathbf{r}) = \varepsilon_{i}^{A}\phi_{i}^{A}(\mathbf{r})$$

Equation that is to be fulfilled by the pseudo-orbital

$$\hat{V}_{A}^{PP}(\mathbf{r}) = \varepsilon_{i}^{A} - \frac{\nabla^{2}\phi_{i}^{A}(\mathbf{r})}{2\phi_{i}^{A}(\mathbf{r})}$$

Construction of the pseudopotential

PP depends on a specific  $\varepsilon$  and  $\phi$ Representation in terms of grid in  ${\bf r}$ 

#### Define a local and a nonlocal potential

$$\left(\hat{T} + \hat{V}_{A}^{L}(\mathbf{r}) + \hat{V}_{A}^{NL}\right) \left|\phi_{i}^{A}\right\rangle = \varepsilon_{i}^{A} \left|\phi_{i}^{A}\right\rangle$$

$$\left|\boldsymbol{\chi}_{i}^{A}\right\rangle = \left(\boldsymbol{\varepsilon}_{i}^{A} - \hat{T} - \hat{V}_{A}^{L}(\mathbf{r})\right)\left|\boldsymbol{\phi}_{i}^{A}\right\rangle$$

$$\hat{V}_{A}^{NL} = rac{\left|\chi_{i}^{A}
ight
angle\!\left\langle\chi_{i}^{A}
ight|}{\left\langle\chi_{i}^{A}\left|\phi_{i}^{A}
ight
angle}$$

V<sup>L</sup> takes care of the long range (screened) nuclear attraction, is identical to V<sup>eff</sup> for r > R

Wavefunction that is only non-zero for r < R (because  $\phi$  matches  $\psi$  at r > R)

 $V^{NL}$  serves to model short range repulsive interactions, is zero for r > R

To use more than one pseudo orbital one can introduce a generalized norm-conserving condition Q that should be fulfilled

 $Q_{ij} = \left\langle \psi_i^A \left| \psi_j^A \right\rangle_R - \left\langle \phi_i^A \left| \phi_j^A \right\rangle_R = 0 \quad \begin{array}{l} \text{Makes sure orthonormality of the original orbitals is} \\ \text{also obeyed by the pseudo-orbitals} \end{array} \right.$ 

$$\hat{V}_{A}^{NL} = \sum_{i,j} B_{ij}^{-1} |\chi_{i}^{A}\rangle \langle \chi_{j}^{A} | \qquad \qquad B_{ij} = \langle \phi_{i}^{A} | \chi_{j}^{A} \rangle$$

#### PPs in plane-wave expansions

 Required in condensed matter DFT calculations that employ a planewave basis. Need to smoothen (soften) wave function and potentials as much as possible.

#### Soft self-consistent pseudopotentials in a generalized eigenvalue formalism

David Vanderbilt Department of Physics, Harvard University, Cambridge, Massachusetts 02138 (Received 23 January 1990)



FIG. 1. Oxygen 2p radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

- Abandon normalization condition and work with generalized eigenvalue problem.
- The more complicated formalism pays off since the number of plane-wave basis functions can be drastically reduced
- Common to also "pseudoize" the lowest solutions of a given symmetry (e.g. 2p)

### **Effective Core Potentials**

Effective Core Potentials allow reduction of the basis set used to describe the valence orbitals by creating smoother orbitals

$$F_{v} \rightarrow F_{v} + \sum_{c} (\varepsilon_{v} - \varepsilon_{c}) |c\rangle \langle c|$$

 $\{\psi_{v}\} \rightarrow \{\tilde{\psi}_{v}\}$ 

Phillips and Kleinman : shift core orbitals to make them degenerate with the valence orbitals

Make nodeless pseudo-orbital by mixing core and valence spinors

$$V_{Frozen\ core}^{A}(\mathbf{r}_{A}) \approx M_{L}^{A}(r_{A}) + \sum_{l=0}^{L-1} \sum_{m_{l}=-l}^{l} |lm_{l}\rangle f_{l}^{A}(r_{A})\langle lm_{l}|$$
 Scalar

$$V_{Frozen\ core}^{A}(\mathbf{r}_{A}) \approx M_{L}^{A}(r_{A}) + \sum_{l=0}^{L-1} \sum_{j=|l-1/2|}^{l+1/2} \sum_{m_{l}=-l}^{l} \left| ljm_{j} \right\rangle f_{lj}^{A}(r_{A}) \left\langle ljm_{j} \right|$$
Spin-Orbit

These *nonlocal pseudopotentials* are determined via a fitting procedure that optimizes the potential for each *l*-value. Takes care of Coulomb and Exchange and core-valence orthogonality.

#### Shape consistent ECPs

- "American school" : Christiansen, Ermler, Pitzer
- "French school" : Barthelat, Durand, Heully, Teichteil
- Make nodeless pseudo-orbitals that resemble the true valence orbitals in the bonding region

$$\psi_{\nu}(\mathbf{r}) \rightarrow \tilde{\psi}_{\nu}(\mathbf{r}) = \begin{cases} \psi_{\nu}(\mathbf{r}) & (r \ge R) \\ f_{\nu}(\mathbf{r}) & (r < R) \end{cases}$$

Original orbital in the outer region

Smooth polynomial expansion in the inner region

- Fit is sometimes done to the large component of Dirac wave function (picture change error)
- Creating a normalized shape consistent orbital necessarily mixes in virtual orbitals
- Intermolecular overlap integrals are well reproduced
- Gives rather accurate bond lengths and structures

#### ECPs and electron correlation

- Integrals are calculated over pseudospinors
- Consider the MP2 valence energy expression

$$E^{MP2} = \sum_{i,j}^{occupied virtual} \frac{\left|\left\langle ij \| ab \right\rangle\right|^{2}}{\varepsilon_{i} + \varepsilon_{i} - \varepsilon_{a} - \varepsilon_{b}}$$
$$\left\langle ij \| ab \right\rangle^{pseudo} - \left\langle ij \| ab \right\rangle^{original} \neq 0$$
$$\varepsilon_{i}^{original} - \varepsilon_{a}^{original} > \varepsilon_{i}^{pseudo} - \varepsilon_{a}^{pseudo}$$

- Orbital energy spectrum is compressed and in particular the intra-atomic 2electron integrals will be different from the reference all-electron calculation
- Absolute correlation energy may be overestimated relative to correlation calculations done with the unmodified orbitals
- Example : for Pt the radial maximum of the 5d is very close to a node of the 6s. Pseudoizing the 6s will remove this node and overestimate the correlation energy. Remedy (small core PP) : takes also the 5s in the valence

#### Energy consistent ECPs

- "German school" : Stoll, Preuss, Dolg
- Initially semi-empirical, later *ab initio* approach that tries to reproduce the low-energy atomic spectrum (using correlated calculations)

$$\min\left(\sum_{I}^{Lowlying} w_{I} \left(E_{I}^{PP} - E_{I}^{Reference}\right)^{2}\right)$$

- Provides good accuracy for many elements and bonding situations
  - Difference in correlation energy due to the nodeless valence orbitals is automatically included in the fit
  - Small cores may still be necessary to obtain stable results
  - Cheap core description allows for good valence basis sets
  - Available in many program packages (a.k.a. "SDD")

# ECPs and molecular properties

- Valence electric and/or magnetic properties (multipoles, polarizabilities, circular dichroisms, etc.)
  - Unmodified operators can be used
- NMR shielding and spin-spin couplings
  - ECPs are valid for the neighboring atoms, not for the ones for which the shielding or couplings are to calculated
- Reconstruction of original wave function
  - Allows calculation of core properties or excitations (mostly applied in solid-state approaches, but some molecular applications have also been reported)
- Spin-Orbit coupling between states
  - Apply SOC-operator that is derived for the ECP that is employed (usually AREP and SOREP)

#### SO-operator in CI (CC) approaches

1. First order quasi-degenerate perturbation theory (inclusion after CI step)

- © Can also be used with unbound operators (Pauli form)
- ☺ Is computationally efficient (one step procedure)
- © Offers convenient (conventional) interpretation scheme
- ☺ Important couplings to excited states may be missed
- 2. Limited variational theory (inclusion in CI step)
  - Unbound operators (Pauli form) are acceptable
  - Does only increase the CI effort, no influence on HF and MO-transformation
  - Interpretation is non-conventional
  - Accuracy is limited when orbital relaxation effects are important

#### 3. Variational theory (inclusion in SCF step)

- Can only be used with bound operators
- ☺ Is computationally demanding (symmetry change already in SCF)
- Interpretation is non-conventional
- © Should be the most accurate theory

# 2-Step treatment of SO-coupling

- Use the proper spin-orbit integrals !
  - 2-electron integrals are usually not explicitly considered: atomic mean field integrals (AMFI)
  - ECPs: come with SO-operators suitable for evaluation over pseudo-orbitals
- Basis for perturbative treatment
  - CI/CASSCF: select limited set of wave functions and form effective Hamiltonian. Diagonalization of this small matrix provides the final wave function
  - CASPT2: shift *diagonal matrix elements* of effective Hamiltonian matrix by adding PT2 correction prior to the diagonalization

# Outline

#### • Why do we care about relativity in chemistry ?

- What are relativistic effects ?
- Relativistic effects in atoms
- Relativistic effects in molecules
- How can we include relativity in calculations ?
  - Perturbation theory of relativistic effects
  - 2-component methods
  - 4-component methods
  - Effective Core Potentials

#### • Some recommendations / best practices

- Comparison light / heavy element calculations
- Importance of spin-orbit coupling

#### Some recommendations

- "Best" method depends on system and property that is calculated !
- Closed shells and simple open shells
  - Use a size-extensive and economical method
  - SOC-inclusive method may be required
- Complicated open shells, bond breaking
  - CASSCF, DMRG followed by PT2, Multi-Reference CI or MR-CC
  - SOC-inclusive methods are usually required
  - Mean-field description of SO (AMFI) is usually sufficient
- Use "best practice" and experience from calculations on light elements to decide on the electronic structure method
- Two examples in which spin-orbit coupling is important

## Fine structure splitting in radicals

- Valence iso-electronic systems O<sub>2</sub><sup>-</sup>, FO, ClO
- Breit interaction and correlation should be included for accurate results



L. Visscher, T.J. Lee, K.G. Dyall, J Chem Phys. 105 (1996) 8769.

# NMR: <sup>1</sup>H shielding trends



[1] L. Visscher, T. Enevoldsen, T. Saue, H.J.Aa. Jensen, J. Oddershede, J Comput Chem. 20 (1999) 1262–1273.

# NMR spin-spin couplings

ZORA-DFT : J. Autschbach, T. Ziegler, J. Chem. Phys. 113 (2001) 9410.



#### Why are SOC effects so important for NMR

 Shielding and sin-spin couplings can be written as a second derivative of the energy relative to the external/internal magnetic fields

$$E_{K}^{(11)} = \frac{d^{2}E}{d\mathbf{M}_{K}d\mathbf{B}} = -\mathbf{I}_{3} + \sigma_{K} \qquad \text{Shielding}$$

$$E_{KL}^{(02)} = \frac{d^2 E}{d\mathbf{M}_K d\mathbf{M}_L} = \frac{\mu_0}{4\pi} \frac{R_{KL}^2 \mathbf{I}_3 - 3\mathbf{R}_{KL} \mathbf{R}_{KL}^T}{R_{KL}^5} + \mathbf{K}_{KL} \quad \text{Indirect nuclear spin-spin coupling}$$

$$E_{K}^{(11)} = \langle 0 | H^{(11)} | 0 \rangle + \sum_{S} \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{(01)} | 0 \rangle}{E_{0} - E_{S}}$$

$$E_{KL}^{(02)} = \langle 0 | H^{(02)} | 0 \rangle + \sum_{S} \frac{\langle 0 | H^{(01)} | S \rangle \langle S | H^{(01)} | 0 \rangle}{E_{0} - E_{S}} + \sum_{T} \frac{\langle 0 | H^{(01)} | T \rangle \langle T | H^{(01)} | 0 \rangle}{E_{0} - E_{T}}$$

• Programs that can handle third derivatives (a.k.a quadratic response) can handle such higher order contributions.

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 Shielding and sin-spin couplings can be written as a second derivative of the energy relative to the internal/external magnetic fields

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$$E_{K}^{(11)} = \langle 0 | H^{(11)} | 0 \rangle + \sum_{S} \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{(01)} | 0 \rangle}{E_{0} - E_{S}} + \sum_{S} \sum_{T} \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{SO} | T \rangle \langle T | H^{(01)} | 0 \rangle}{(E_{0} - E_{S})(E_{0} - E_{T})} + \sum_{S} \sum_{T} \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{(01)} | T \rangle \langle T | H^{SO} | 0 \rangle}{(E_{0} - E_{S})(E_{0} - E_{T})}$$

• Programs that can handle third derivatives (a.k.a quadratic response) can handle such higher order contributions.

# Further reading

*Textbooks on relativistic quantum chemistry / mechanics* 

- M. Reiher and A. Wolf, Relativistic Quantum Chemistry, (Wiley, 2009)
- K. G. Dyall and K. Faegri Jr, Relativistic Quantum Chemistry, (Oxford University Press, 2007)
- R. E. Moss, *Advanced molecular quantum mechanics*. (Chapman & Hall, London, 1973).
- P. Strange, *Relativistic Quantum Mechanics*. (Cambridge University Press, Cambridge, 1998).

#### Reviews on methods

- Primer: T. Saue, ChemPhysChem. 12 (2011) 3077–3094.
- Correlation methods: T. Fleig, Chem Phys. 395 (2012) 2–15.
- Including QED: W. Liu, Natl Sci Rev. 3 (2016) 204–221.
- ECPs: M. Dolg, X. Cao, Chem Rev. 112 (2012) 403–480.

#### *Relativistic effects in chemistry*

- P. Pyykkö, Chem Rev. **112** (2012) 371–384.
- P. Pyykkö, Annu Rev Phys Chem. 63 (2012) 45–64.