

An Introduction to Relativistic Quantum Chemistry

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ESQC-03

Unfortunately unable to come

The replacement

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Material kindly provided by Bernd Hess and slightly modified

Outline

Today:

- Special Relativity and the Minkowski space
- !!! All academic without finite speed of light !!!!
- Why we can't use the Schrödinger equation anymore and what alternatives we have (Klein-Gordon and Dirac)
- How to get the Dirac equation and its properties
- The combination of special relativity and quantum mechanics leads to an infinite particle theory (Quantum-Field Theory)
- Electron spin will show up not only via Pauli-principle anymore

Second lecture:

All-electron Approximations to the Dirac-equation

Third lecture:

Effective Core Potentials (ECP, PP, AIMP ...)

Principle of Relativity

Independence of the laws of nature with respect to the coordinate system of an observer ([system of reference](#))

Preliminary (“Special”) version of the principle of relativity:

The laws of physics are equal in two systems of reference which move with respect to each other with constant velocity (i. e., they are not accelerated)

- It is possible to calculate the coordinates of one system of references expressed in the coordinates of the other system ([Lorentz-Transformation](#))
- The transformation involves space coordinates as well as time coordinates

Inertial systems

Consider a freely floating system of reference
(no measurable gravitational field)

A frame of reference is called an **inertial system** for a limited region of space-time, if within a given accuracy

every test particle, which is in rest with respect to this system, remains in rest.

every test particle, which is in motion with respect to this system, continues to move without changing its velocity

— **Galilei's principle of relativity**

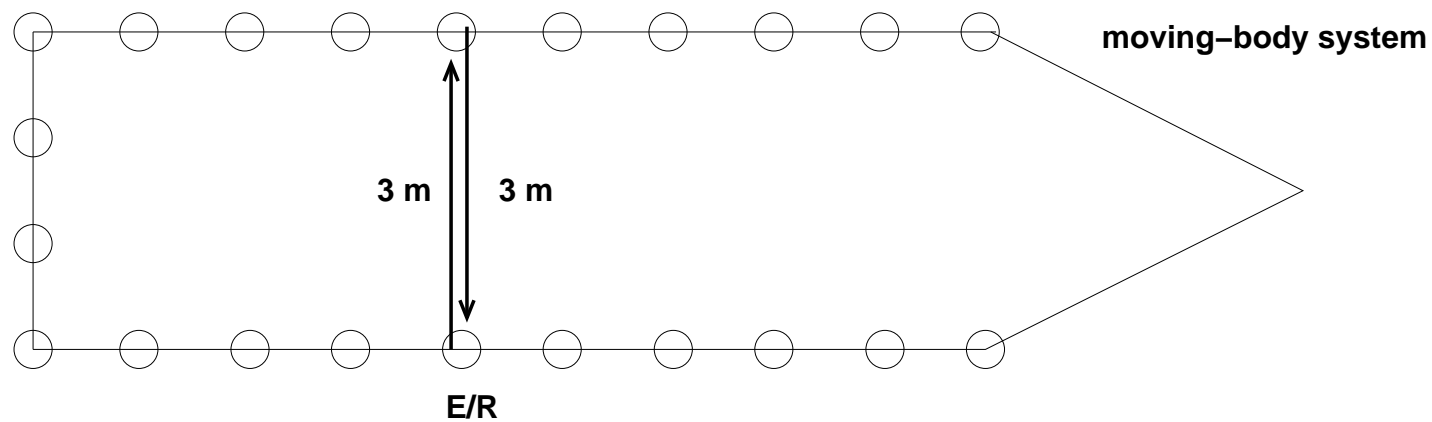
The laws of mechanics are the same in all inertial systems

— **Einstein's principle of relativity**

The laws of physics are the same in all inertial systems

The Speed of Light is Constant in all Inertial Frames

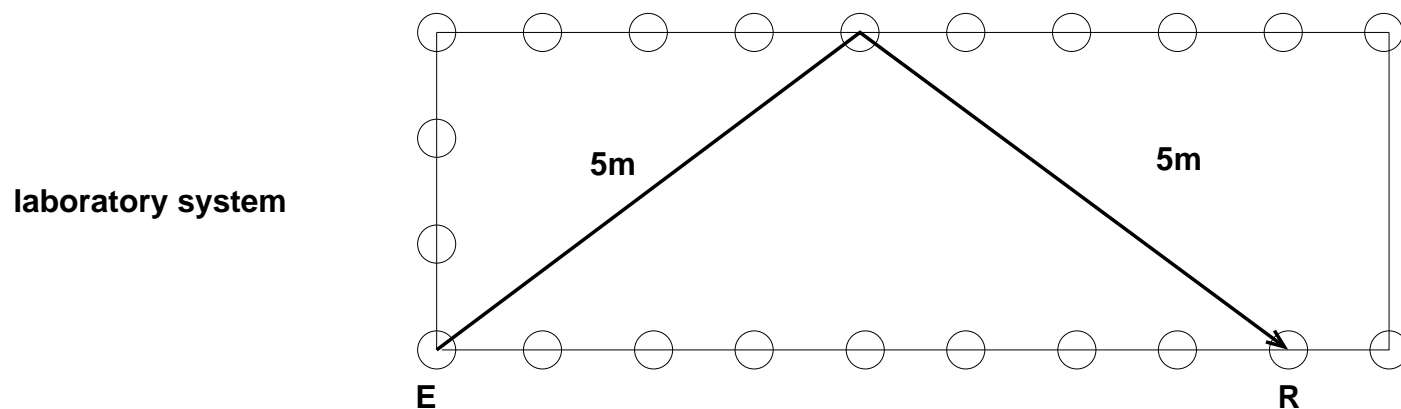
path of light beam travelling from emitter (E) to receiver (R)



$$c\Delta t_{MB} = 6 \text{ m},$$
$$\Delta x_{MB} = 0 \text{ m},$$

“light-time”

$$ct = 6 \text{ m}$$



$$c\Delta t_L = 10 \text{ m},$$
$$\Delta x_L = 8 \text{ m},$$
$$ct = 10 \text{ m}$$

The invariant quantity is $c^2\Delta t^2 - \Delta x^2 = \text{const}$

Four-Vectors

$$(a^\mu)' = \sum_{\nu} L_{\nu}^{\mu} a^{\nu} \equiv L_{\nu}^{\mu} a^{\nu}$$

- Indices run from 0 to 3
- Einstein summation convention
- L_{ν}^{μ} matrix describing the Lorentz transformation
- space-time

$$(a^{\mu}, b^{\mu}) \equiv a_{\mu} b^{\mu} = g_{\mu\nu} a^{\nu} b^{\mu} = a_0 b_0 - a_1 b_1 - a_2 b_2 - a_3 b_3$$

- Metric tensor

$$g_{\mu\nu} = \text{diag} \{1, -1, -1, -1\}$$

- coordinates (in space and in time) of an event in space-time

$$x^{\mu} = (ct, \mathbf{x})$$

- Energy-momentum four-vector

$$p^{\mu} = (E/c, \mathbf{p})$$

Lorentz transformation

- The Lorentz transformation is a length-conserving rotation similar to ordinary euclidean space
- However:
- Indefinite metric $g_{\mu\nu}$
- Therefore, we have to replace sine and cosine by their hyperbolic counterparts
- In short form:
- $\cos^2(x) + \sin^2(x) = 1$ and $\cosh^2(x) - \sinh^2(x) = 1$
- As $a^\mu a_\mu$ is invariant we can distinguish time-like, space-like and light-like four-vectors.
- Note: Not all the X we write as X^μ are four-vectors !

Relativistic Energy Expression for a Free Particle

- Requires treatment of time and space-coordinates at the same level
- Schrödinger equation ruled out as it has a first derivative in time but second derivatives in space
- Norm of energy–momentum four-vector must be invariant when subjected to a Lorentz transformation

$$E^2/c^2 - p^2 = m^2c^2$$

- m is thus a scalar, called the **invariant mass**.
- We obtain immediately the relativistic energy expression

$$E^2 = c^2p^2 + m^2c^4$$

or

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

for a free particle

- Upon quantization, the time-like variable $E/c \equiv i\hbar \frac{\partial}{c\partial t}$ and the space-like momenta $\mathbf{p} \equiv -i\hbar \nabla$ should appear raised to the same power

→ Klein-Gordon equation, valid for particles with spin 0

Problems of the Klein-Gordon-equation:

— Positive and negative solutions for the energy

— Not bound from below (no ground state)

— There is a problem to construct a positive definite density ρ which can be identified with the probability (associated to second derivative in time)

— Solved by Pauli and Weisskopf by a new interpretation as a field theory (1934) where ρ is the charge density

Clifford Algebra

— Linearization of the relativistic energy expression

$$\begin{aligned}(\gamma_\mu p^\mu)(\gamma_\mu p^\mu) &= (\gamma_0 p_0 - \gamma_1 p_1 - \gamma_2 p_2 - \gamma_3 p_3) \cdot (\gamma_0 p_0 - \gamma_1 p_1 - \gamma_2 p_2 - \gamma_3 p_3) \\ &= p_0^2 - p_1^2 - p_2^2 - p_3^2\end{aligned}$$

— Factorization is not possible when the coefficients γ are allowed to take values in the real or complex numbers

— it turns out that the set of objects from which we are allowed to form “numbers” has to be enlarged: [hypercomplex numbers](#)

— We have some freedom to do that; only the anticommutation rules between the γ_μ matter: $[\gamma^\mu, \gamma^\nu]_+ = 2g^{\mu\nu}$

— We get a [Clifford algebra](#) comprising 16 basic entities (formed by the four quantities γ_μ above, six dyadic products $\gamma_\mu \gamma_\nu$, with $\nu < \mu$, four ternary products, one quaternary product of the γ quantities and the real unit) is required to accomplish the factorization.

— $\sqrt{\delta^\mu \delta_\mu} = \gamma^\mu \delta_\mu$. Invented first by William K Clifford (1845-1879), Professor at London University. However, Dirac was not aware of that.

Dirac Algebra

- A matrix representation of the Clifford algebra required to factorize the relativistic energy expression requires at least 4 dimensions to implement the necessary anticommutation rules
- The matrix representation is not unique
- The following “standard form” is the most important one:

$$\beta \equiv \gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \alpha \equiv \gamma^0 \boldsymbol{\gamma} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}.$$

- Supermatrix notation: each entry corresponding to a 2×2 matrix
- The $\boldsymbol{\sigma}$ matrices are the Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Dirac Equation

— The factorized equation

$$(\gamma_0 p_0 - \gamma_1 p_1 - \gamma_2 p_2 - \gamma_3 p_3) \cdot (\gamma_0 p_0 - \gamma_1 p_1 - \gamma_2 p_2 - \gamma_3 p_3) = m^2 c^2$$

leads immediately to the [Dirac Equation\(1928\)](#) (for free particles with spin 1/2)

$$(\gamma_\mu p^\mu - mc)\psi_{\text{Dirac}} = 0$$

- The wave function in Dirac's theory of the relativistic electron thus comprises four discrete extra degrees of freedom besides the space-time variable
- Two spin degrees of freedom (spin up/down) both for the electron and its charge-conjugated partner
- The wave function is a [four-component spinor](#), not a vector !!
- The Dirac equation is manifestly [covariant](#), because only four-scalars are involved

Free-Particle Dirac Equation

$$(\gamma_{\mu}p^{\mu} - mc) \psi_{\text{D}} = 0$$

$$(\gamma_0 p^0 + \gamma_k p^k - mc) \psi_{\text{D}} = 0$$

$$(\gamma_1 p_1 + \gamma_2 p_2 + \gamma_3 p_3 + mc) \psi_{\text{D}} = \gamma_0 E/c \psi_{\text{D}}$$

$$(\gamma_0 \gamma_1 p_1 + \gamma_0 \gamma_2 p_2 + \gamma_0 \gamma_3 p_3 + \gamma_0 mc) \psi_{\text{D}} = \gamma_0 \gamma_0 E/c \psi_{\text{D}}$$

$$(c\boldsymbol{\alpha}p + \beta mc^2)\psi_{\text{D}} = E\psi_{\text{D}}$$

$$\hat{h}_{\text{D}}^{\text{free}}\psi_{\text{D}} = E\psi_{\text{D}}$$

More explicitly ...

$$\begin{aligned}
 & \left[\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} cp_x + \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix} cp_y + \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} cp_z + \right. \\
 & \left. + \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} mc^2 \right] \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} E \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}
 \end{aligned}$$

Properties of the Minkowski representation

- Upon canonical quantization, the Dirac equation is linear in $E/c \equiv i\hbar \frac{\partial}{c\partial t}$ as well as $\mathbf{p} \equiv -i\hbar \nabla$
- The coupling between the four components is accomplished by the γ_μ matrices, which are independent of the dynamical variables
- Potentials may be easily introduced by **minimal coupling**

$$E \rightarrow E - V, \quad \mathbf{p} \rightarrow \mathbf{p} - \frac{e}{c} \mathbf{A}$$

- One-particle Dirac equation for a particle with spin 1/2 in the external potential of a nucleus $V_{\text{ext}} = e\phi(x)$

$$\begin{aligned} \hat{h}_D \psi_D &= E \psi_D \\ \hat{h}_D &= c\boldsymbol{\alpha} \mathbf{p} + \beta mc^2 + e\phi. \end{aligned}$$

Dirac Equation

— “split notation”

$$\begin{aligned}c\boldsymbol{\sigma}\mathbf{p}\psi_S + mc^2\psi_L + V_{\text{ext}}\psi_L &= E\psi_L \\c\boldsymbol{\sigma}\mathbf{p}\psi_L - mc^2\psi_S - V_{\text{ext}}\psi_S &= E\psi_S\end{aligned}$$

— upper and lower components

— For solutions with positive energy and weak potentials, the lower component is suppressed by a factor $1/c^2$ with respect to the upper one, and therefore commonly dubbed **small component** ψ_S , as opposed to the **large component** ψ_L .

— Spectrum (for $Z < 1/\alpha \approx 137$):
positive as well as negative eigenvalues; three regions

$\Sigma_1 = (-mc^2, mc^2)$: bound states of the electron;

$\Sigma_2 = [mc^2, \infty)$: positive continuum, free electron states

$\Sigma_3 = (-\infty, -mc^2]$: negative continuum, Dirac sea, occupied....

— Negative continuum problem solved by hole-theory (Dirac 1930)
and confirmed by Anderson and Blackett who found the positron
(1932).

— The vacuum has infinite negative energy and charge, but that is no
problem

Dirac–Coulomb Hamiltonian

$$H_{\text{DC}} = \sum_i H_{\text{one}}(i) + \sum_{i < j} r_{ij}^{-1}$$

$$H_{\text{one}}(i) = c\boldsymbol{\alpha}\mathbf{p}_i + \beta mc^2 + V_{\text{ext}}$$

- This Hamiltonian is **not** Lorentz covariant; it covers the electron–electron interaction only to order $\alpha = e^2/\hbar c$
- In order to improve the situation, terms of order α^2 (**Gaunt term**, **Breit term** or **transverse interaction**) are often included
- Calculations with this operator are often dubbed **fully relativistic**. This is only a commercial statement.

Dirac–Hartree-Fock method

Bertha Swirles, Proc. Roy. Soc. London A, 152 (1935) 625

Kinematic Relativistic Effects in Chemistry

Pekka Pyykkö, *Adv. Quantum. Chem.* 11 (1978) 353

Centrifugal force along the radius vector should balance Coulomb force

Electric field generated by the electron as measured in the laboratory system

$$E_{\perp} = \frac{e}{4\pi\epsilon_0 r^2} \cdot \gamma = \frac{e}{4\pi\epsilon_0 r^2} \cdot \frac{1}{\sqrt{1 - v^2/c^2}}$$

do not confuse γ with γ^{μ}

$$\frac{Ze^2\gamma}{4\pi\epsilon_0 r^2} = \frac{L^2}{mr^3}$$

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}_{\text{rel}}, \quad p_{\text{rel}} = mv\gamma, \quad \langle L^2 \rangle = l(l+1)\hbar^2$$

→ relativistic Bohr radius

$$r_{\text{Bohr}}^{\text{rel}} = \frac{1}{\gamma} \cdot \frac{4\pi\epsilon_0\hbar^2}{Ze^2m}$$

Electrons in heavy atoms have high velocities close to the nucleus

For Hg: $v/c \approx 0.58$, $\gamma \approx 1.23$

Relativistic Effects in Chemistry

direct relativistic effect

contraction of core-penetrating orbitals

s orbitals, $p_{1/2}$ orbitals, $p_{3/2}$ orbitals in core

energetic stabilization

higher ionization energy, higher electron affinity, smaller polarizability

Relativistic Effects

indirect relativistic effect

orbitals with centrifugal barrier: d, f

$p_{3/2}$ orbitals in valence shell

nuclear charge is shielded to a larger extent because of direct effect on core-penetrating orbitals (in particular of the semi-core)
relativistic **expansion** of core non-penetrating orbitals

energetic destabilization

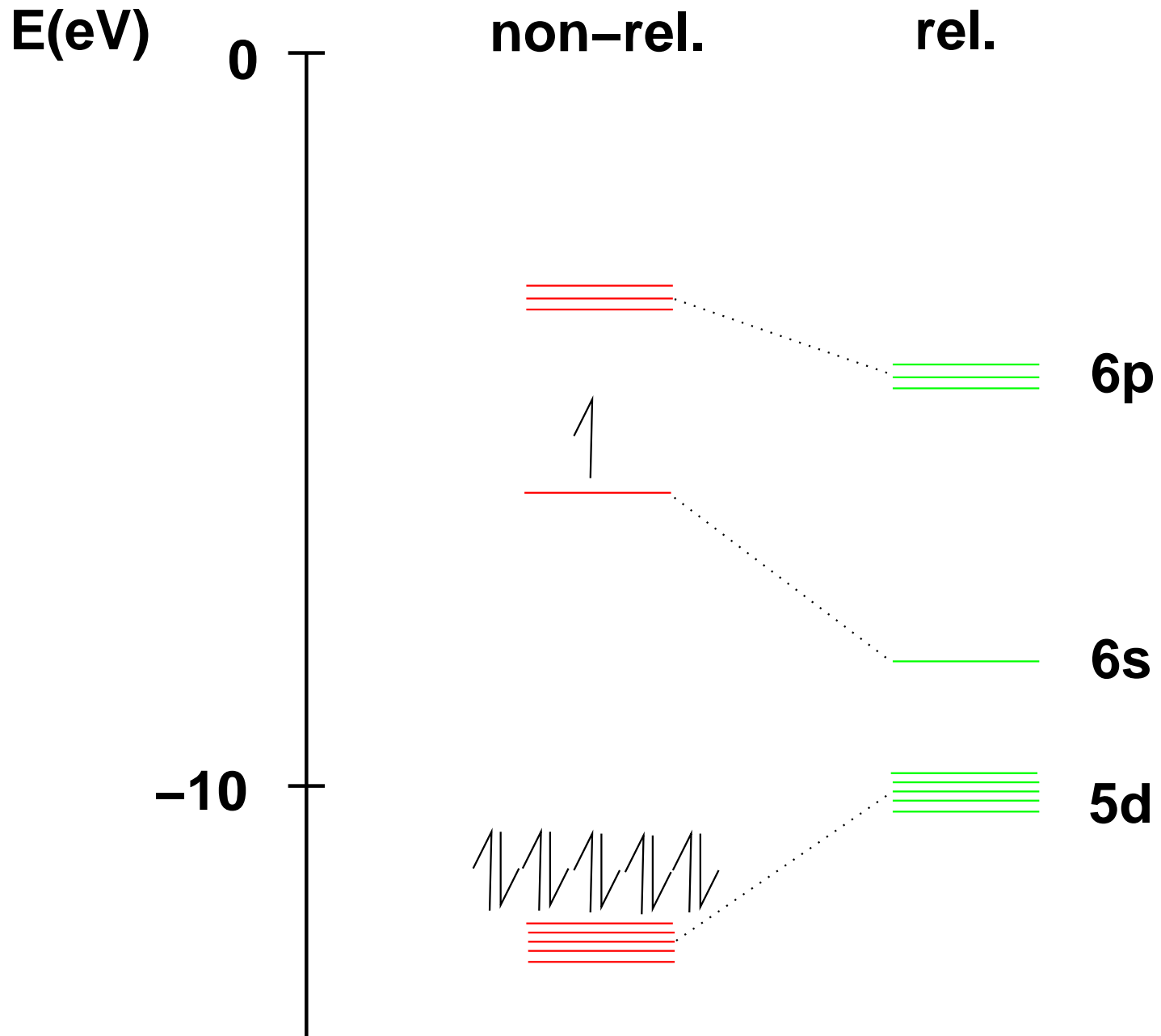
smaller ionization energy, larger polarizability

in turn, stabilization of core-penetrating orbitals in next shell

→ **gold maximum**

see also references in **B. A. Heß, Ber. Bunsenges. Phys. Chem. 101 (1997) 1**

Au atom orbital energies



Gold Atom

All values in eV, averaged over spin components.

Method	$^2S \rightarrow ^2D$	$^2S \rightarrow ^2P$	EA	IP
Nonrel. Self-Consistent Field			0.10	5.92
Nonrel. Multi-reference CI	5.03	3.46	1.02	6.91
Rel. 1-comp. Self-Consistent Field			0.65	7.65
Rel. 1-comp. Multi-reference CI	1.55	5.17	1.97	9.05
Rel. 1-comp. Averaged Pair Functional	1.60	4.99	2.28	9.08
Rel. 1-comp. Coupled Cluster	1.69	5.04	2.26	9.08
Rel. 4-comp. Self-Consistent Field ¹⁾			1.18	7.48
Rel. 4-comp. Coupled Cluster ¹⁾	1.73	5.03	2.28	9.10
Experimental (C. Moore)	1.74	4.95	2.31	9.22

Kaldor, Hess, CPL 230 (1994) 1

¹⁾ Eliav, Kaldor, Ishikawa, PRA 49 (1994) 1724

Relativistic Effects

The non-relativistic Hamiltonian is replaced by a relativistic one

— kinematic effects

— spin-orbit coupling

Atoms: Dynamic variables for charge-conjugated degrees of freedom

Four-component spinors

Dirac Hartree Fock and beyond

I. P. Grant, *Adv. Phys.*, 19 (1970) 747–811

J. P. Desclaux, *Comp. Phys. Commun.*, 9 (1975) 31–45

Parpia, Froese-Fischer, Grant, *Comp. Phys. Commun.* 9 (1996)
249–271

for more information on atomic calculations see

Reiher, Hess,

<http://www.fz-juelich.de/nic-series/Volume1/Volume1.html>

Relativistic Effects in Molecules

Four-component methods implemented by now for most important quantum chemical methods (MP2, MCSCF, CC)

K. G. Dyall, CPL 224 (1994) 186–194

Visscher, Saue, Nieuwpoort, Fægri, Gropen, JCP 99 (1993) 6704–6715

Jensen, Dyall, Saue, Fægri, JCP 104 (1996) 4083–4097

Eliav, Kaldor, CPL 248 (1996) 405

DIRAC program

<http://assens.chem.ou.dk/Dirac>

Alternative methods for molecules(next two lectures):

Molecules: Get rid of the charge-conjugated degrees of freedom

One- and Two-component spinors

Transformed Hamiltonians

RECPs

Two-Component Hamiltonians

- transparent separation of spin effects
interpretation
efficient implementation of spin-averaged theories
see also: Dyall's "modified Dirac equation":
K. Dyall, JCP 100 (1994) 2118
- however: separation of spin not unique:
L. Vischer and E. van Lenthe, CPL 306 (1999) 367
- automatic projection
- smaller number of explicit degrees of freedom
more efficient computer codes possible
systematic definition of approximations,
e. g., mean-field approach:
Hess, Marian, Wahlgren, Gropen, CPL 251 (1996) 365

Two-Component Hamiltonians

Define a formal relationship $\phi_S = X\phi_L$ to decouple lower and upper component:

$$H^{\text{decoupled}} = W^\dagger DW = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix}$$

$$WW^\dagger = 1$$

$$W = \begin{pmatrix} (1 + X^\dagger X)^{-1/2} & (1 + X^\dagger X)^{-1/2}(-X^\dagger) \\ X(1 + XX^\dagger)^{-1/2} & (1 + XX^\dagger)^{-1/2} \end{pmatrix}$$

$$X = \frac{1}{2mc^2}(c\boldsymbol{\sigma}\mathbf{p} + [V, X] - Xc\boldsymbol{\sigma}\mathbf{p}X)$$

If we could solve for X , we would obtain the
exact Foldy–Wouthuysen transformation

Foldy–Wouthuysen Transformation for Free Particle

$$X^{V=0} = \left(mc^2 + \sqrt{m^2c^4 + p^2c^2} \right)^{-1} c\boldsymbol{\sigma} \mathbf{p}$$

$$H^{\text{fpFW}} = \pm \sqrt{m^2c^4 + p^2c^2} = \beta E_p$$

Foldy–Wouthuysen-Transformation

block diagonalization of the Dirac operator

$$D = c\boldsymbol{\alpha}\mathbf{p} + \beta mc^2 + V$$

$$D = \begin{pmatrix} V + mc^2 & 0 \\ 0 & V - mc^2 \end{pmatrix} + \begin{pmatrix} 0 & c\boldsymbol{\sigma}\mathbf{p} \\ c\boldsymbol{\sigma}\mathbf{p} & 0 \end{pmatrix}.$$

even operator $\mathcal{E} = V + \beta mc^2$, odd operator $\mathcal{O} = c\boldsymbol{\alpha}\mathbf{p}$

$$[\mathcal{E}, \beta] = 0, \quad \{\mathcal{O}, \beta\} = 0$$

Foldy–Wouthuysen-Transformation

Look for unitary matrix which removes the odd term.

The Foldy–Wouthuysen transformation uses the ansatz

$$\Phi_1 = \exp(iS_1)\Phi,$$

$$H_1 = H + i[S, H] + \dots$$

$$[\mathcal{E}, \beta] = 0, \quad \{\mathcal{O}, \beta\} = 0$$

The choice $S_1 = -i\beta\mathcal{O}/2m$ removes the odd term, but introduces new odd terms of higher order, which are in turn removed by iteration the transformation: $\Phi_n = \exp(iS_n)\Phi_{n-1}$

The Breit–Pauli operator

In lowest order of the Foldy–Wouthuysen transformation, expanding the result in c^{-2} , the **Pauli Hamiltonian** obtains

$$H_{\text{Pauli}} = \frac{p^2}{2m} + V + \frac{1}{4m^2c^2} \left(\frac{-p^4}{2m} + \frac{1}{2}\Delta V + \boldsymbol{\sigma}(\nabla V) \times \mathbf{p} \right)$$

mass–velocity term, Darwin term, spin–orbit coupling

Singular, not variationally stable; higher orders: even more singular

Morrison, Moss, MP 41 (1980) 491

variational instability of Breit-Pauli operator

The Breit-Pauli operator is unstable with respect to unrestricted variation (\rightarrow **variational collapse**)

$$H_{\text{SO}}^{\text{BP}} = \frac{e^2 \hbar}{4m^2 c^2} \sum_{\alpha} \sum_i Z_{\alpha} \frac{\mathbf{r}_{i\alpha} \times \mathbf{p}_i}{|r_{i\alpha}|^3} \cdot \boldsymbol{\sigma}_i \\ - \frac{e^2 \hbar}{4m^2 c^2} \sum_{i \neq j} \frac{\mathbf{r}_{ij} \times \mathbf{p}_i}{|r_{ij}|^3} \cdot (\boldsymbol{\sigma}_i + 2\boldsymbol{\sigma}_j)$$

- basis set helps in LCAO techniques (\rightarrow **unwanted basis set dependency**)
- prescribed value of wave function at nucleus helps

Elimination of Small Component

$$\begin{aligned}c\boldsymbol{\sigma}\mathbf{p}\psi_S + V\psi_L &= E\psi_L \\c\boldsymbol{\sigma}\mathbf{p}\psi_L - 2mc^2\psi_S + V\psi_S &= E\psi_S,\end{aligned}$$

$$(V - E)\psi^L + \frac{1}{2mc^2}[\boldsymbol{\sigma}\mathbf{p}\omega(\mathbf{r})\boldsymbol{\sigma}\mathbf{p}]\psi_L = 0$$

$$\omega(\mathbf{r}) = \left(1 - \frac{V - E}{2mc^2}\right)^{-1}.$$

Expand

$$\left(1 - \frac{V - E}{2mc^2}\right)^{-1} = \sum_{n=0}^{\infty} \left(\frac{V - E}{2mc^2}\right)^n$$

Keep lowest-order term and expand in $c^{-2} \longrightarrow$ **Breit–Pauli Hamiltonian**

Two-Component Hamiltonians

— Non-hermitean or energy-dependent operators

Blinder, J. Molec. Spectr. 5 (1960) 17

Löwdin, J. Molec. Spectr. 14 (1964) 131

Cowan and Griffin, JOSA 66 (1976) 1010

Wood and Boring, PRB 18 (1978) 2701

Barthelat, Pélissier, Durand, PRA 21 (1981) 1773

Karwowski, Kobus, IJQC 28 (1985) 741

Wood, Grant, Wilson, JPB 18 (1985) 3027

— singular expansions

Pauli-type theories:

Elimination of small component with expansion in c^{-2}

Elimination of the Small Component with expansion in c^{-2}

Relativistic Elimination of the Small Component (RESC)

Nakajima and Hirao, CPL 302 (1999) 383; Barysz, JCP 113 (2000) 4003

Regular Expansions

— non-singular relativistic perturbation theory, “Direct PT”

Sewell, Proc. Camb. Phil. Soc. 45 (1949) 631

Titchmarsh, Proc. Roy Soc. (Lond) A266 (1962) 33

Rutkowski JPB 19 (1986) 149; 3419; 3434

Kutzelnigg ZPD 11 (1989) 15; 15 (1989) 27

— normalized elimination of the small component

Dyall, JCP 106 (1997) 9618

Regular Expansions

— regular approximations (ZORA, FORA, ...)

Chang, Pelissier, Durand, *Phys. Scr.* 34 (1986) 394

Heully et al. *JPB* 19 (1986) 2799

E. van Lenthe, Baerends, Snijders *JCP* 99 (1993) 4597

E. van Lenthe, Baerends, Snijders *JCP* 101 (1994) 9783

— Douglas–Kroll transformation

Douglas, Kroll, *Ann. Phys.* 82 (1974) 89

Hess, *Phys. Rev. A* 33 (1986) 3742

Häberlen, Rösch, *CPL* 199 (1992) 491

Samzow, Hess, Jansen, *JCP* 96 (1992) 1227

Barysz, Sadlej, Snijders, *IJQC* 65 (1997) 225

Nakajima, Hirao, *JCP* 113 (2000) 7786

Brummelhuis, Siedentop, Stockmeyer, *Doc. Math.* 7 (2002) 167

Wolf, Reiher, Hess, *JCP* 117 (2002) 9215

The Douglas-Kroll Transformation

M. Douglas and N. M. Kroll, Ann. Phys. 82 (1974) 89

— transform

$$U_0 H_D U_0^{-1} \equiv H_1 = \beta E_p + \mathcal{E} + \mathcal{O}$$

$$\mathcal{E} \equiv \mathcal{E}^{(1)} = A(V + RVR)A$$

$$\mathcal{O} \equiv \mathcal{O}^{(1)} = \beta A(RV - VR)A$$

$$U_1 = \sqrt{1 + W_1^2} + W_1$$

$$U_1^{-1} = \sqrt{1 + W_1^2} - W_1$$

— determine W_1 by calculating

$$H_2 = U_1 H_1 U_1^{-1},$$

The Douglas-Kroll Transformation

M. Douglas and N. M. Kroll, Ann. Phys. 82 (1974) 89

— expand square root to second order, collect even and odd terms

$$\begin{aligned}\mathcal{E}_1^{(2)} &= \mathcal{E}_1^{(1)} \\ \mathcal{O}_1^{(2)} &= \mathcal{O}_1^{(1)} + [W_1, \beta E_p] \stackrel{!}{=} 0 \\ \mathcal{E}_2^{(2)} &= \frac{1}{2}[W_1, \mathcal{O}_1^{(1)}] \\ \mathcal{O}_2^{(2)} &= \dots\end{aligned}$$

$$W_1 \hat{\varphi}(\mathbf{p}_i) =$$

$$\int d^3 p_j \left[\frac{c\boldsymbol{\alpha}\mathbf{p}_i}{\sqrt{2E_i(E_i + mc^2)}} A_j - \frac{c\boldsymbol{\alpha}\mathbf{p}_j}{\sqrt{2E_j(E_j + mc^2)}} A_i \right] \cdot \frac{\hat{V}(\mathbf{p}_i, \mathbf{p}_j)}{E_i + E_j} \cdot \hat{\varphi}(\mathbf{p}_j)$$

— project on 2 components by replacing Ψ by

$$\begin{aligned}\beta^{(+)}\Psi &= \frac{1 + \beta}{2}\Psi \\ \rightarrow \boldsymbol{\alpha} &\text{ replaced by } \boldsymbol{\sigma}\end{aligned}$$

The Douglas-Kroll Transformation

M. Douglas, N. M. Kroll, Ann. Phys. 82 (1974) 89

B. A. Heß, Phys. Rev. A 33 (1986) 3742

R. Samzow, B. A. Heß, G. Jansen, JCP 96 (1992) 1227

$$H^{\text{DKH2}} = \sum_i E_i + \sum_i V_{\text{eff}}^{\text{sf}}(i) + \frac{1}{2} \sum_{i \neq j} V_{\text{eff}}^{\text{sf}}(i, j)$$

$$E_i = \sqrt{p_i^2 c^2 + m^2 c^4}, \quad A_i = \sqrt{\frac{E_i + mc^2}{2E_i}}, \quad \mathbf{P}_i = \frac{c\mathbf{p}_i}{E_i + mc^2}$$

$$V_{\text{eff}}^{\text{sf}}(i) = A_i [V_{\text{ext}}(i) + \mathbf{P}_i V_{\text{ext}}(i) \mathbf{P}_i] A_i - \\ - W_1(i) E_i W_1(i) - \frac{1}{2} (W_1(i))^2 E_i - \frac{1}{2} E_i (W_1(i))^2$$

$$V_{\text{eff}}^{\text{sf}}(i, j) = A_i A_j \left(\frac{1}{r_{ij}} + \mathbf{P}_i \frac{1}{r_{ij}} \mathbf{P}_i + \mathbf{P}_j \frac{1}{r_{ij}} \mathbf{P}_j + \mathbf{P}_i \mathbf{P}_j \frac{1}{r_{ij}} \mathbf{P}_i \mathbf{P}_j \right) A_i A_j$$

Express kinematic factors in the basis of eigenfunctions of T_e in the uncontracted basis set

The Spin-Dependent Operators

$$H_+^{\text{SO}} = \sum_i \sum_\alpha e^2 Z_\alpha \frac{A_i}{E_i + mc^2} \boldsymbol{\sigma}_i \left(\frac{\mathbf{r}_{i\alpha}}{r_{i\alpha}^3} \times \mathbf{p}_i \right) \frac{A_i}{E_i + mc^2}$$

$$-e^2 \sum_{i \neq j} \frac{A_i A_j}{E_i + mc^2} \left[\boldsymbol{\sigma}_i \left(\frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_i \right) \frac{A_i A_j}{E_i + mc^2} - 2 \boldsymbol{\sigma}_i \left(\frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_j \right) \frac{A_i A_j}{E_j + mc^2} \right]$$

$$E(\mathbf{p}_i) \equiv E_i = \sqrt{p_i^2 c^2 + m^2 c^4}, \quad A_i = \sqrt{\frac{E_i + mc^2}{2E_i}}$$

The Breit-Pauli operator may be recovered expanding E_i and A_i into powers of c^{-2} and keeping only lowest-order terms.

Kinematic factors smoothen the $1/r^3$ singularity

Connection with FW Transform

$$E_p = \sqrt{p^2 c^2 + m^2 c^4} = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots$$

$$A_p = \sqrt{\frac{E_p + mc^2}{2E_p}} = 1 - \frac{p^2}{8m^2 c^2} + \dots$$

$$A_p P_p \equiv \frac{1}{\sqrt{2E_p(E_p + mc^2)}} = \frac{1}{2mc^2} - \frac{3p^2}{16m^3 c^4} + \dots$$

n.b. the Taylor series for the square roots converge for $|cp| < mc$
truncating the series at any finite order will introduce a **wrong**
asymptotic behaviour for $p \rightarrow \infty$.

→ **spectral properties drastically changed** for truncated operators:
they are no longer bounded below!

— because of singularities of E_p , A_p and R_p , a truncation of the series
will result in the **singular** FW-type operators.

— Expansion in powers of $1/c^2$ must be avoided.

The second-order spin-free Douglas–Kroll Hamiltonian

— If the transformation is carried out to second order in the external potential, the binding energies of one-electron atoms are correct to $O(c^{-4})$

Molzberger, Schwarz, TCA 94 (1994) 213

— Spin dependencies are easily factored out; spin–orbit coupling may be treated in a second step

— The operator is **variationally stable**.

— Electrostatic gauge invariance maintained

— Scalar relativistic corrections to two-electron integrals is usually neglected

— Taking into account two-electron contributions is absolutely necessary in case of spin–orbit coupling

Generalized Douglas–Kroll Transformation

Recall the central idea of the Douglas–Kroll transformation:
Eliminate stepwise lowest-order (in V) odd terms by a sequence of unitary transformations U_1, U_2, \dots .

→ Expansion of block diagonal H_{bd} in even terms of ascending order in the external potential V :

$$\begin{aligned} H_{bd} &= \cdots U_4 U_3 U_2 U_1 H_1 U_1^\dagger U_2^\dagger U_3^\dagger U_4^\dagger \cdots = \sum_{k=0}^{\infty} \mathcal{E}_k \\ &= \sum_{k=0}^{\infty} \begin{pmatrix} \mathcal{E}_{k+} & 0 \\ 0 & \mathcal{E}_{k-} \end{pmatrix} = \sum_{k=0}^{\infty} \begin{pmatrix} \mathcal{E}_{k+}^{\text{sf}} + \mathcal{E}_{k+}^{\text{sd}} & 0 \\ 0 & \mathcal{E}_{k-}^{\text{sf}} + \mathcal{E}_{k-}^{\text{sd}} \end{pmatrix} \end{aligned}$$

Parametrization of the unitary transformations

- Use $U_i = f(W_i)$: Analytic function of odd and antihermitean operator W_i , which is of i th order in the external potential V .
Taylor expansion around $W_i = 0$: $U_i = a_{i,0} \mathbf{1} + a_{i,1} W_i + \dots$

- Traditional choice: $U_i = \sqrt{1 + W_i^2} + W_i$

M. Douglas, N. M. Kroll, *Ann. of Phys.* 82 (1974) 89–155

Foldy–Wouthuysen choice: $U_i = \exp(W_i)$

T. Nakajima, K. Hirao, *JCP* 113 (2000) 7786–7789

- Investigate most general parametrization with real $a_{i,k}$:

$$U_i = a_{i,0} \mathbf{1} + a_{i,1} W_i + a_{i,2} W_i^2 + \dots = a_{i,0} \mathbf{1} + \sum_{k=1}^{\infty} a_{i,k} W_i^k$$

A. Wolf, M. Reiher, B. A. Hess:

“The generalized Douglas–Kroll transformation”,

J. Chem. Phys. 117 (2002) 9215–9226

The Generalized Douglas–Kroll Transformation

$$\begin{aligned}\mathcal{E}_0 &= \beta E_p - mc^2, & \mathcal{E}_1 &= A_p (V + R_p V R_p) A_p, & \mathcal{E}_2 &= \frac{1}{2} [W_1, \mathcal{O}_1], \\ \mathcal{E}_3 &= \frac{1}{2} [W_1, [W_1, \mathcal{E}_1]], \\ \mathcal{E}_4 &= \frac{1}{8} [W_1, [W_1, [W_1, \mathcal{O}_1]]] + \frac{1}{2} [W_2, [W_1, \mathcal{E}_1]], \\ \mathcal{E}_5 &= \frac{1}{2} [W_2, [W_2, \mathcal{E}_1]] + \frac{1}{2} [W_2, [W_1, [W_1, \mathcal{O}_1]]] + \frac{1}{2} [W_2, W_1 \mathcal{O}_1 W_1] + \\ &\quad - \frac{1}{8} [W_1^2, [W_1^2, \mathcal{E}_1]] + \frac{a_{1,3}}{a_{1,1}^3} [[W_2, W_1^3], \mathcal{E}_0],\end{aligned}$$

Parametrization of the unitary transformations

Use $W_i^\dagger = -W_i$ and derive unitarity conditions for the coefficients $a_{i,k}$

$$\begin{aligned} a_{i,0} &= \pm 1, \\ a_{i,2} &= \frac{1}{2} a_0 a_1^2, \\ a_{i,4} &= a_0 (a_1 a_3 - \frac{1}{8} a_1^4), \\ &\vdots \\ a_{i,2k} &= f(a_{i,0}, a_{i,1}, a_{i,3}, a_{i,5}, \dots, a_{i,2k-1}), \end{aligned} \tag{1}$$

Even coefficients a_{2k} are uniquely determined by lower odd coefficients, which **may be chosen arbitrarily**.

Determining the optimal parametrization

Do all these **infinitely many unitary parametrizations** yield the same even terms \mathcal{E}_k of the Hamiltonian H_{bd} ?

For the first four orders, the answer is affirmative. For higher orders, determine an optimized U_i^{opt} , which is based on minimization of $|U_i U_i^\dagger - 1|$.

The minimization of $|U_i U_i^\dagger - 1|$ for truncated power series expansions of U_i fixes the odd coefficients $a_{i,2k+1}$ uniquely.

Example:
$$a_{i,3} = \frac{2 - \sqrt{2}}{4} a_{i,1}^3 \approx 0.14645 a_{i,1}^3$$

The Generalized Douglas–Kroll Transformation

W_1 and W_2 have to be **uniquely chosen** in order to eliminate the lowest order odd term in each step. Their integral kernels are given as

$$W_1(i, j) = \beta \frac{\mathcal{O}_1(i, j)}{E_i + E_j},$$

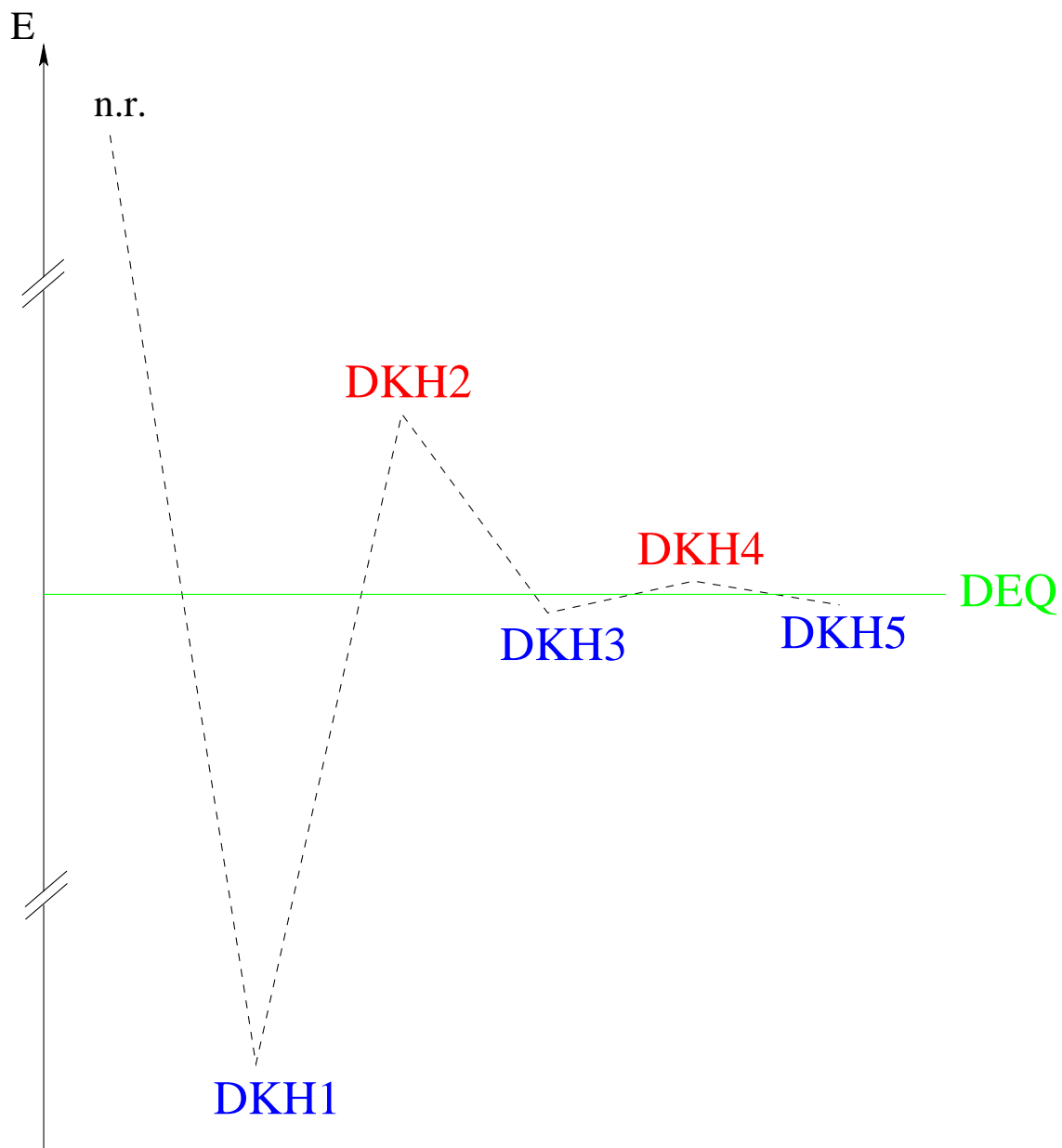
$$W_2(i, j, k) = \beta \frac{W_1(i, j)\mathcal{E}_1(j, k) - \mathcal{E}_1(i, j)W_1(j, k)}{E_i + E_k}.$$

The DK Hamiltonians consist of 4-component, block-diagonal operators.

Questions:

1. How accurate are the DKH $_n$ Hamiltonians with respect to total and relative energies?
2. Which Hamiltonian should be employed for chemical investigations on atoms and molecules?

One-electron atoms



Example: $Z=10$

n.r. +939.20

DKH1 -533.2

DKH2 +33.00

DKH3 -3.17

DKH4 +2.72

DKH5 -2.33

a. u., all w.r.t

DEQ -5939.

Scaling of 1s energies of hydrogenlike atoms

Expansion in power series in $\gamma = Z\alpha$

$$E = E^{\text{nr}}(1 + a_2\gamma^2(1 + a_4\gamma^2(1 + a_6\gamma^2(1 + \dots))))$$

Dirac equation	$-0.5Z^2(1 + 0.250\gamma^2(1 + 0.50\gamma^2(1 + 0.625\gamma^2(1 + \dots))))$
DKH4 *)	$-0.5Z^2(1 + 0.250\gamma^2(1 + 0.50\gamma^2(1 + 0.619\gamma^2(1 + \dots))))$
DKH2 **)	$-0.5Z^2(1 + 0.250\gamma^2(1 + 0.45\gamma^2(1 + \dots)))$
DKH1	$-0.5Z^2(1 + 0.250\gamma^2(1 - 1.6\gamma^1(1 + \dots)))$

*) Wolf, Reiher, Hess, in: *Relativistic Quantum Chemistry*, edited by Peter Schwerdtfeger, Elsevier Science, Amsterdam, (2002), ISBN 0444 51249 7, pp. 622–663

***) Molzberger and Schwarz, *TCA* 94 (1996) 213



counterpoise-corrected CCSD(T), 'large basis', 34 correlated electrons

Hess, Kaldor, JCP 112 (2000) 1809

	R_e pm	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}	D_e eV	$E_{\text{tot}}(R = 4.7)$ a.u.
DKH2	248.8	187.7	0.4152	2.19	-37979.81070104
DKH5	248.6	188.2	0.4159	2.20	-38014.61925915



CCSD(T) / $4f2g1h1i$ basis / 34 electrons / cp corrected / DKH2

	R_e (pm)	ω_e cm^{-1}	D_0 (eV)
CCSD(T)	248.8	186.9	2.19
exp.	247.2	191	2.29
neglect of			
semicore correlation	1.0	-2.7	-0.05
triples	0.6	-0.3	-0.21
counterpoise	-1.8	7.4	
g, h, i fcts	1.4	-4.5	-0.10
h, i fcts	0.4	-0.3	-0.01
i fcts	0.1	-0.2	0.00

B. A. Hess, U. Kaldor, JCP 112 (2000) 1809

DKH Summary

- DKH1 – DKH4 are independent of the chosen parametrizations of U_i .
- Ambiguity of DKH5 and all higher-order approximations may be fixed by choosing U^{opt} .
- Already DKH2 yields accurate relative energies and properties of the valence shell.
- For inner-shell properties (NMR, ...) the higher-order approximations DKH4 and DKH5 are expected to yield improvements with respect to the accuracy of the results.

DKH Summary

- Odd DK approximations (DKH1, DKH3, DKH5) always overestimate the binding energy. They hence establish only variationally stable, but not variational schemes.

W. Kutzelnigg, *Chem. Phys.* 225 (1997) 203–222

- Even DK approximations (DKH2, DKH4) are most likely variational. For DKH2 this has been rigorously proven for coupling constants below

$$\gamma_c := 4\pi \frac{\pi^2 + 4 - \sqrt{-\pi^4 + 24\pi^2 - 16}}{(\pi^2 - 4)^2} = 1.00607734$$

R. Brummelhuis, H. Siedentop, E. Stockmeyer:

“The ground state energy of relativistic one-electron atoms according to Hess and Jansen”, *Doc. Math.* 7 (2002) 167–182

Mean-field approach to spin-orbit coupling

Hess, Marian, Wahlgren, Gropen, CPL 251 (1996) 365

calculate two-electron contribution (shielding) from a fixed configuration

→ effective one-electron integrals

Fock operator technique

$$H_{ij}^{\text{mean field}} = \langle i | H^{\text{SO}}(1) | j \rangle + \frac{1}{2} \sum_{\substack{k \\ \text{fixed } \{n_k\}}} n_k \left\{ \langle ik | H^{\text{SO}}(1, 2) | jk \rangle - \langle ik | H^{\text{SO}}(1, 2) | kj \rangle - \langle ki | H^{\text{SO}}(1, 2) | jk \rangle \right\}$$

Mean-field approach: Atomic approach

Spin–Orbit Coupling is short-ranged

Calculate the Mean-field integrals for each atom separately

Use atomic orbitals and groundstate averaged occupations

Exploit spherical symmetry

Atomic Mean-Field SO-Integral approach (AMFI) (BS 1996)

Splittings identical with full SO-operator within a few wavenumbers

Available in MOLCAS, DALTON, DeMon ...

But: Explicit multi-center terms might be important for lifetimes of excited triplet states.

Valence-only Effective Hamiltonians

- Effective Core-Potentials (ECPs)
- Core-Polarization Potentials (CPPs)
- Ab Initio Model Potentials (AIMPs)
attempt to retain radial node structure of orbitals
- Pseudopotential (PPs)
simplified nodal structure
- integrate out core degrees of freedom
Hamiltonian only for valence degrees of freedom
- scalar quasirelativistic ECPs (one-component)
quasirelativistic ECPs (two-component)

Valence-only Effective Hamiltonians

- Why bother ???
- smaller valence basis sets
- don't want to work later on with core anyway (frozen-core)
- computational savings (fewer 2-el. integrals)
- sometimes can avoid complicated coupling of open-shells by parametrisation (large-core ECPs for lanthanides)
- black-box procedure

Effective Core Potentials

$$\hat{H}_v = \sum_i^{n_v} h_v(i) + \sum_{i < j}^{n_v} r_{ij}^{-1} + V_{cc} + V_{cpp}$$

n_v	number of valence electrons
N	number of frozen closed-shell atomic-like cores
V_{cc}	repulsion between all cores and nuclei of the system
V_{cpp}	CPPs
Z_λ	charges of the nuclei
Q_λ	core charges

$$n_v = n - \sum_{\lambda}^N (Z_\lambda - Q_\lambda) .$$

$$h_v(i) = -\frac{1}{2}\Delta_i + V_{cv}(i)$$

Parametrization of Effective Core Potentials

$$V_{cv}(i) = \sum_{\lambda}^N \left[-\frac{Q_{\lambda}}{r_{\lambda i}} + \Delta V_{cv}^{\lambda}(\mathbf{r}_{\lambda i}) \right]$$

$$V_{cc} = \sum_{\lambda < \mu}^N \left[\frac{Q_{\lambda} Q_{\mu}}{r_{\lambda \mu}} + \Delta V_{cc}^{\lambda \mu}(\mathbf{r}_{\lambda \mu}) \right]$$

parametrize ΔV_{cv}^{λ} and $\Delta V_{cc}^{\lambda \mu}$

AIMPs

- Use the Fock operator \hat{F}_v for a valence orbital φ_a^V and model effective one-particle potential; assume non-overlapping cores and make use of

$$-\sum_{\lambda}^N \frac{Z_{\lambda}}{r_{\lambda i}} + \sum_{c \in \text{core}} [2J_c(i) - K_c(i)] = \sum_{\lambda}^N \left[-\frac{Q_{\lambda}}{r_{\lambda i}} + \Delta V_{cv}^{\lambda}(\mathbf{r}_{\lambda i}) \right]$$

- obtain atomic potentials from **relativistic** atomic calculation

Barandiaran, Seijo, JCP 101 (1994) 4049

Seijo, Barandiaran, Harguindey, JCP 114 (2001) 118

AIMPs

— long-range local Coulombic part for atomic core λ :

$$-\frac{Z_\lambda - Q_\lambda}{r_{\lambda i}} + 2 \sum_{c \in \lambda} J_c^\lambda(i) = \frac{1}{r_{\lambda i}} \sum_k C_k^\lambda e^{-c_k^\lambda r_{\lambda i}^2} = \Delta V_C^\lambda(i)$$

— c_k^λ and C_k^λ adjusted to the all-electron potential in a least-squares sense under the constraint that $\sum_k C_k^\lambda = Z_\lambda - Q_\lambda$

— use spectral representation in the space of expansion functions χ_p^λ centered on core λ for nonlocal exchange part

$$-\sum_{c \in \lambda} K_c^\lambda(i) = \sum_{p,q} A_{pq}^\lambda |\chi_p^\lambda(i)\rangle \langle \chi_q^\lambda(i)| = \Delta V_X^\lambda(i)$$

— in practice, the primitive Gaussians on centre λ are used for $\{\chi_p^\lambda\}$.

AIMPs

- Need level-shift operator to ensure (approximate) orthogonality on core-like solutions of valence Fock operator:

$$P^\lambda(i) = \sum_{c \in \lambda} D_c^\lambda |\varphi_c^\lambda(i)\rangle \langle \varphi_c^\lambda(i)|$$

- φ_c^λ denotes core orbital localized on core λ
matrix representation by a sufficiently large (all-electron) basis set
- choose $D_c^\lambda = -2\epsilon_c^\lambda$
- A parametrized spin-orbit operator may be included as well:

$$\Delta V_{cv,so}^\lambda(i) = \sum_l \left(\sum_k \frac{S_{lk}^\lambda}{r_{\lambda i}^2} e^{-s_{lk}^\lambda r_{\lambda i}^2} \right) \hat{P}_l^\lambda(i) \mathbf{l}_i \mathbf{s}_i \hat{P}_l^\lambda(i)$$

\hat{P}_l^λ is projection operator onto the subspace of angular quantum number l with respect to core λ

AIMPs

Alternative treatment of the spin-orbit operator (e.g. in MOLCAS):
Mapping all-electron atomic SO-integrals (AIMP) to be used with
AIMPs (or general PP)

Example:

$$\langle 5d | H^{SO} | 5d \rangle_{AIMP} = \langle 5d | H^{SO} | 5d \rangle_{AE}$$

in Pt, as the integral should be independent of the choice between AE
or relativistic AIMP

References:

C.M. Marian and U. Wahlgren, CPL 251, 357-364 (1996) (AIMP)

B. Schimmelpfennig, L. Maron, U. Wahlgren, C. Teichteil, H. Fagerli
and O. Gropen, CPL 286, 267-271 (1998) (PP)

Pseudopotentials

— local ansatz for ΔV_{cv}^λ too inaccurate; rather use semilocal form

$$\Delta V_{cv}^\lambda(\mathbf{r}_{\lambda i}) = \sum_{l=0}^{L-1} (V_l^\lambda(r_{\lambda i}) - V_L^\lambda(r_{\lambda i})) \hat{P}_l^\lambda(i) + V_L^\lambda(r_{\lambda i})$$

$$\hat{P}_l^\lambda(i) = \sum_{m_l=-l}^l |\lambda l m_l(i)\rangle \langle \lambda l m_l(i)|$$

— two-component version possible using projection on spinor spherical harmonics

— Model each V_l^λ ($l = 0$ to $l = L$) as

$$V_l^\lambda = \frac{1}{r_{\lambda i}} \sum_k G_{kl}^\lambda r_{\lambda i}^{\gamma_{kl}} e^{-g_{kl}^\lambda r_{\lambda i}^2}$$

alternatively, use nonlocal representation in a (nearly) complete auxiliary basis set

— Born-Mayer ansatz for $\Delta V_{cc}^{\lambda\mu}$:

$$\Delta V_{cc}^\lambda(\mathbf{r}_{\lambda\mu}) = B_{\lambda\mu} \exp(-b_{\lambda\mu} r_{\lambda\mu})$$

Shape-Consistent Pseudopotentials

Durand, Barthelat, TCA 38 (1975) 283; Christiansen, Lee, Pitzer, JCP 71 (1979) 4445; Nash, Bursten, Ermler, JCP 106 (1997) 5133; Hay, Wadt, JCP 82 (1985) 299; Stevens, Basch, Krauss, JCP 81 (1984) 6026

— Generate pseudo valence orbitals $\varphi_{p,lj}$

$$\varphi_{v,lj}(r) \rightarrow \varphi_{p,lj}(r) = \begin{cases} \varphi_{v,lj}(r) & \text{for } r \geq r_c \\ f_{lj}(r) & \text{for } r < r_c \end{cases}$$

— matching radius r_c separating the spatial core and valence regions

— In $[0, r_c]$, discard nodal structure and replace orbital by smooth polynomial expansion $f_{lj}(r)$

— determine PP pointwise solving radial Fock equation

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{lj}^{PP}(r) + W_{p,lj}[\{\varphi_{p',l'j'}\}] \right) \varphi_{p,lj}(r) = \epsilon_{v,lj} \varphi_{p,lj}(r)$$

and fit to LCGTF

— $W_{p,lj}$ is the effective valence Coulomb and exchange potential for $\varphi_{p,lj}$, $\epsilon_{v,lj}$ the (relativistic) orbital energy

Energy-Consistent Pseudopotentials

Metz, Stoll, Dolg, JCP 113 (2000) 2563

Stoll, Dolg, Seth, Schwerdtfeger, CPL 2001

- Fit potentials to reproduce low-lying experimental atomic spectra or atomic MCDF calculations correlation

Core-Polarization Potential

Müller, Flesch, Meyer, JCP 80 (1984) 3297

— account for static polarization of core (orbital relaxation effect) and dynamic (1-core-hole) core–valence correlation

$$V_{cpp} = -\frac{1}{2} \sum_{\lambda} \alpha_{\lambda} \mathbf{f}_{\lambda}^2 + \sum_{\lambda, i} V^{\lambda}(i)$$

\mathbf{f}_{λ} is electric field at core λ generated by all other cores and nuclei as well as all valence electrons, α_{λ} is dipole polarizability of core

— Need cut-off function

$$\mathbf{f}_{\lambda} = - \sum_i \frac{\mathbf{r}_{i\lambda}}{r_{i\lambda}^3} (1 - \exp(-\delta_e^{\lambda} r_{i\lambda}^2))^{n_e} + \sum_{\mu \neq \lambda} Q_{\mu} \frac{\mathbf{r}_{\mu\lambda}}{r_{\mu\lambda}^3} (1 - \exp(-\delta_c^{\lambda} r_{\mu\lambda}^2))^{n_c}$$

— additional short-ranged local potential for cases where ns and np valence orbitals are present together with $(n-1)d$ and $(n-2)f$ valence orbitals

Dolg, TCA 93 (1996) 141

$$V^{\lambda}(i) = C^{\lambda} \exp(-\gamma^{\lambda} r_{i\lambda}^2)$$

Pseudopotentials: Practical Considerations

- valence correlation energies calculated in the PP framework tend to be too large
- large-core ECPs for TM (2–12 VE for groups 3–12) fail by and large

Seth, Schwerdtfeger, CPL 318 (2000) 314

may still be useful for modelling purposes

- use small core (11–20 VE) potentials, comprising $(n - 1)spd$ and ns in the valence
- large-core ECP+CPP are OK for post- d -group elements

(111)H

	R_e (pm)	ω_e (cm ⁻¹)	D_e (eV)
nonrel. HF	201.5		
BP, HF	162.6		
AE, DHF	152.1	2743	1.56
EC-PP(19), SO, HF	151.8	2777	1.67
SC-PP(19), SO, HF	151.6	2786	1.59
AE, DHF+CCSD(T)	152.3	2674	2.83
EC-PP(19), SO, ACPF	152.4	2661	2.81
SC-PP(19), SO, CCSD(T)	150.6	2721	3.16
SC-PP(34), SO, CCSD(T)	151.2	2668	2.87

Seth, Schwerdtfeger, Dolg, Fægri, Hess, Kaldor, CPL 250 (1996) 461

Seth, Schwerdtfeger, CPL 318 (2000) 314

Stoll, Dolg, Seth, Schwerdtfeger, CPL 2001

Han, Hirao, CPL 328 (2000) 453

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edited by Peter Schwerdtfeger, Elsevier Science, Amsterdam,
(2002),
ISBN 0444-51249-7
- *Relativistic Effects in Heavy-Element Chemistry and Physics*,
edited by B. A. Hess, Wiley, Chichester, (2003), ISBN 0470-84138-9
- One more to come by Ken Dyall and Knut Fægri

General comments

- For closed shell systems, one-component methods work well
- Don't use non-relativistically contracted basis sets
- As usual correlation is important, esp. as there are often a lot of close lying states with different correlation effects (d^8s^2 , d^{10})
- There are a lot of PPs, ECPs, AIMPs on the market. If you are not sure, compare to some all-electron method, perhaps even four-component (in line with Peter Taylor)
- In case you go four-component, do it properly !!!!
- An approximate method with a good basis set should be preferable to a more accurate method with a too small basis set.
- Spin-orbit effects can often be treated with lower accuracy than the scalar part including correlation (perturbation theory)
- SO-effects can allow drastic changes in reaction paths and barriers

What about ECP with DFT ?

- DFT is assuming a local external potential
- More seriously: $(\rho_c + \rho_v)^{1/3} \neq \rho_c^{1/3} + \rho_v^{1/3}$
- Nevertheless, a lot of people do it with good results
- Don't ask me for a recommendation

Back to the beginning..

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My participation was on short notice, so forgive me if not everything was as you might have expected

Don't hesitate to contact me, in case you have further questions