Relativistic effects

for lanthanide elements

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Outline

- Relativistic Hamiltonians
- Spin Separation - Unitary transformations of the Dirac Hamiltonian
- DKH and X2C Hamiltonian
- Hands on exercises: Relativistic calculations for Ce^{3+} ion
- Homework exercise: Relativistic calculations for Pr^{3+} ion

Relativistic effect will affect chemical properties of heavy elements

- atomic ionization potential and electron affinities
- electronic excitation energies (this affects dissociation asymptotes)
- change of bond length and strength when relativistic effects are included

Relativistic effect will affect chemical properties of heavy elements

- electronic states of transition metal, lanthanide, actinide complexes undergo spin orbit splittings
- special relativity effect increases the contraction of ionic radii in the lanthanide series by 10%

Configuration	Term	J	Level (cm^{-1})
$5p^6 4f$	^2F	5/2	0
		7/2	2253
$5p^6 5d$	^2D	3/2	49737
		5/2	52226
$5p^6 6s$	^2S	1/2	86602
$5p^6 6p$	^2P	1/2	122585
		3/2	127292
$5p^6 56$	^2D	5/2	177198
		3/2	178913

Martin et. al (1978)

Relativistic effect will affect chemical properties of heavy elements

- electronic states of transition metal, lanthanide, actinide complexes undergo spin orbit splittings
- special relativity effect increases the contraction of ionic radii in the lanthanide series by 10%

Element	**Radius** Ln^{3+} **[pm]**
La	103
Ce	102
Pr	99
Nd	98.3
Pm	97
Sm	95.8
Eu	94.7
Gd	93.8
Tb	92.3
Dy	91.2
Ho	90.1
Er	89
Tm	88
Yb	86.8
Lu	86.1

Within the Born–Oppenheimer approximation electronic relativist and non-relativistic Hamiltonians have form

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

- $\hat{h}(i)$ is one electron operator
- $\hat{g}(i,j)$ is electron-electron operator (Breit/Gaunt)
- V_{NN} nucleus-nucleus interaction '

See for example mini-review T.Saue, ChemPhysChem **12** 3077 (2011)

Dirac equation of an electron in external static field

$$\hat{h}_D = c\boldsymbol{\alpha}\hat{\boldsymbol{p}} + \hat{V} + E_0\hat{\beta}$$

$\hat{V}$ is an external field (molecular) potential;
$E_0 = m_e c^2$ is a rest mass energy of the electron;
$\beta, \boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ quantities are 4x4 matrices

$$\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \alpha_x = \begin{pmatrix} 0 & \boldsymbol{\sigma}_x \\ \boldsymbol{\sigma}_x & 0 \end{pmatrix}, \quad \alpha_y = \begin{pmatrix} 0 & \boldsymbol{\sigma}_y \\ \boldsymbol{\sigma}_y & 0 \end{pmatrix}, \quad \alpha_z = \begin{pmatrix} 0 & \boldsymbol{\sigma}_z \\ \boldsymbol{\sigma}_z & 0 \end{pmatrix}$$

expressed in terms of the Pauli matrices

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

The four-component wave function Ψ is formed of two two-component parts: Large Ψ^L, Small Ψ^S

$$\Psi = \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix}, \quad \Psi^L = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \quad \Psi^S = \begin{pmatrix} \psi_3 \\ \psi_4 \end{pmatrix}.$$

$\hat{h}_D$ couples large and small components

$$\begin{pmatrix} \hat{V} & c(\boldsymbol{\sigma} \cdot \boldsymbol{p}) \\ c(\boldsymbol{\sigma} \cdot \boldsymbol{p}) & \hat{V} - 2m_e c^2 \end{pmatrix} \begin{pmatrix} \Phi^L \\ \Phi^S \end{pmatrix} = E^+ \begin{pmatrix} \Phi^L \\ \Phi^S \end{pmatrix}$$

Please note that energy is shifted by subtracting rest mass of electron ($E^+ = E - m_e c^2$).

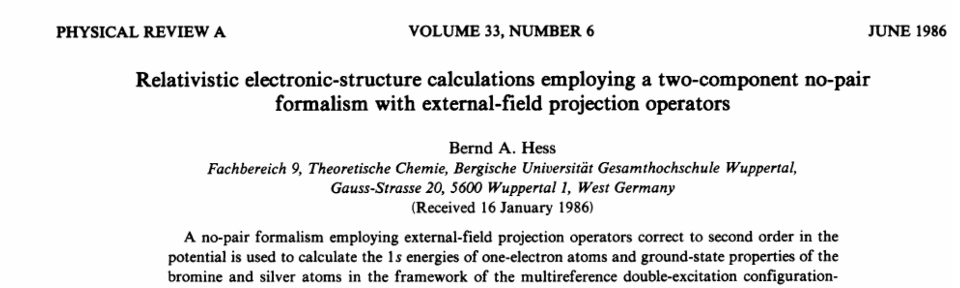
There are many approaches of carrying out unitary transformation $\hat{U}$ which decouples solution of positive and negative energy

$$\hat{U}^\dagger \begin{pmatrix} \hat{h}_{11} & \hat{h}_{12} \\ \hat{h}_{21} & \hat{h}_{22} \end{pmatrix} \hat{U} = \begin{pmatrix} \hat{h}_+ & 0 \\ 0 & \hat{h}_- \end{pmatrix}$$

Review Books:

K. Dyall, K. Faegri "Introduction to Relativistic Quantum Chemistry"

M. Reiher, A. Wolf "Relativistic Quantum Chemistry"



PHYSICAL REVIEW A VOLUME 33, NUMBER 6 JUNE 1986

Relativistic electronic-structure calculations employing a two-component no-pair formalism with external-field projection operators

Bernd A. Hess
Fachbereich 9, Theoretische Chemie, Bergische Universität Gesamthochschule Wuppertal,
Gauss-Strasse 20, 5600 Wuppertal 1, West Germany

(Received 16 January 1986)

A no-pair formalism employing external-field projection operators correct to second order in the potential is used to calculate the 1*s* energies of one-electron atoms and ground-state properties of the bromine and silver atoms in the framework of the multireference double-excitation configuration-

- Bernard Hess as the first designed practical algorithm of constructing projection operators corresponding to a particle in the external field of the nucleus (Douglas-Kroll).
- Douglas-Kroll-Hess Hamiltonian is bounded from below
- transformation to two-component Hamiltonian allows for partitioning the relativistic effects into two parts: the scalar relativistic effects and spin–orbit coupling.

Relativistic calculations in MOLCAS

Relativistic Hamiltonians implemented in MOLCAS

- arbitrary-order Douglas-Kroll-Hess (DKH) Hamiltonian
- Barysz–Sadlej–Snijders (BSS) Hamiltonian
- one-component exact decoupling (X2C) Hamiltonian

Basis sets to be used in relativistic calculations

- The ANO-RCC basis set (Douglas-Kroll Hamiltonian)
- ANO-R basis set - (X2C)

Spin-free formalism in MOLCAS

"A further approximation is made by neglecting all explicitly spin dependent operators for the variational determination of the wave function. The spin-orbit coupling terms of may be calculated by perturbation theory at a later stage."
B. Hess Phys. Rev. A **33** 3742 (1986)

- The CASSCF/RASSCF wave functions are constructed for a specified total spin, which reflect permutation symmetry of the electrons.
- The CASSCF/RASSCF wave functions are not assumed to be eigenstates of $\hat{S}_z$.
- $(2S + 1)$ CASSCF/RASSCF wave functions for total spin S form representation of all possible spin states within the given multiplet.

Relativistic calculations of Ce^{3+} free ion

CASSCF/CASPT2/RASSI-SO method

- Ce^{3+} electronic configuration [Xe]$4f^15d^16s^2$
- for calculation use abelian C_i point group

Configuration	Term	J	Level (cm^{-1})
$5p^64f$	^2F	5/2	0
		7/2	2253
$5p^65d$	^2D	3/2	49737
		5/2	52226
$5p^66s$	^2S	1/2	86602
$5p^66p$	^2P	1/2	122585
		3/2	127292
$5p^656$	^2D	5/2	177198
		3/2	178913

Martin et. al (1978) NIST

Ce^{3+}

Relativistic calculations of Ce^{3+} free ion

```
&GATEWAY
Title
Cerium
SYmmetry
xyz
Basis set
Ce.ano-rcc.Roos.25s22p15d11f4g2h.9s8p5d4f3g2h
Ce  0 0 0
end of basis
AUXShow
AMFI
ANGMOM=0.0 0.0 0.0
&SEWARD
```

- Ce.ano-rcc.Roos will activate DKH
- `AMFI` Atomic mean field integrals

Input file:

`Cerium3.casscf_rassi.input`

Relativistic calculations of Ce^{3+} free ion

```
&SCF &END
Title
Cerium3+ atom
Occupied
15 19
occnumbers
*1 2 3 4 5 6 7 8 9 10
2 2 2 2 2 2 2 2 2 2
2 2 2 2 2
2 2 2 2 2 2 2 2 2 2
2 2
0.1428571428571428 0.1428571428571428
0.1428571428571428 0.1428571428571428
0.1428571428571428 0.1428571428571428
0.1428571428571428
Iterations
40
End of Input
```

C_i	E	i	Orbital
A_g	+1	+1	s, d
A_u	+1	-1	p, f

A_g: $1s^2s^23s^24s^23d^{10}5s^24d^{10}$

1+1+1+1+5+1+5=15

A_u: $2p^63p^64p^65p^64f^1$

3+3+3+3+7=19

Relativistic calculations of Ce^{3+} free ion

```
&RASSCF &END
Title
Cerium 3+    CAS2 (4f5d6s)1   2Au
Symmetry
2
Spin
2
Nactel
1    0    0
Frozen
0    0
Inactive
15   12
Ras2
6    7
CiRoot
7 7
1 2 3 4 5 6 7
1 1 1 1 1 1 1
LumOrb
End of Input
>>COPY $Project.JobIph JOB001
```

Active space: one electron on 13 orbitals
^2A_u irrep
$(2 \cdot 3 + 1) = 7$ degenerate 4f states L=3
command COPY saves CASSCF wave functions for further calculations

Relativistic calculations of Ce^{3+} free ion

```
&RASSCF &END
Title
Cerium 3+ ion,  CAS2:4f5d6s  States 2Ag
Symmetry
1
Spin
2
Nactel
1    0    0
Frozen
0    0
Inactive
15  12
Ras2
6    7
CiRoot
6 6
1 2 3 4 5 6
1 1 1 1 1 1
LumOrb
End of Input
>>COPY $Project.JobIph JOB002
```

Active space: one electron on 13 orbitals
^2A_g irrep
$(2 \cdot 2 + 1) + (2 \cdot 0 + 1) = 6$ degenerate 5d states L=2 plus one 6s
command COPY saves CASSCF wave functions for further calculations

Relativistic calculations of Ce^{3+} free ion

```
&RASSI &END
CIprint
NROF JOBIPHS
2 7 6
1 2 3 4 5 6 7
1 2 3 4 5 6
Spin
End of input
```

RASSI-SO calculations,
The JobIph files copied as JOB001, JOB002 are used. The Nr of JobIphs keyword is followed by: The number of JobIph files (2), The number of states to pick from each of JOB00n files (7,6), the serial numbers of these states for the first file (1,2,3,4,5,6,7), the serial numbers of these states for the second file (1,2,3,4,5,6)

Results

```
  Eigenvalues of complex Hamiltonian:
-----------------------------------
(Shifted by EMIN (a.u.) =      -8852.0496747242)

SO State       Relative EMIN(au)   Rel lowest level(eV)    D:o, cm**(-1)     J-value

1             -0.0062960408        0.0000000000             0.0000          2.5
2             -0.0062960408        0.0000000000             0.0000          2.5
3             -0.0062960408        0.0000000000             0.0000          2.5
4             -0.0062960408        0.0000000000             0.0000          2.5
5             -0.0062960408        0.0000000000             0.0000          2.5
6             -0.0062960408        0.0000000000             0.0000          2.5
7              0.0047220306        0.2998169948           2418.1871         3.5
8              0.0047220306        0.2998169948           2418.1871         3.5
9              0.0047220306        0.2998169948           2418.1871         3.5
10             0.0047220306        0.2998169948           2418.1871         3.5
11             0.0047220306        0.2998169948           2418.1871         3.5
12             0.0047220306        0.2998169948           2418.1871         3.5
13             0.0047220306        0.2998169948           2418.1871         3.5
14             0.0047220306        0.2998169948           2418.1871         3.5
15             0.1964870207        5.5180082094          44505.7377         1.5
16             0.1964870207        5.5180082094          44505.7377         1.5
17             0.1964870207        5.5180082094          44505.7377         1.5
```

Exercise 1: MS-CASPT2 and broken degeneracies of J energies

`input file: Cerium3.caspt2_rassi.input`

```
&CASPT2 &END
Title
Cerium 3+ ion  2Au ungerade  states
MultiState=7
1 2 3 4 5 6 7
End of input
>>COPY $Project.JobMix JOB001
... long input ...
&RASSI &END
CIprint
NROF JOBIPHS
2 7 6
1 2 3 4 5 6 7
1 2 3 4 5 6
Spin
ejob
End of input
```

```
SO State  ...  D:o, cm**(-1)    J-value

1     ...      0.0000         2.5
2     ...      0.0000         2.5
3     ...     17.7057         2.5
4     ...     17.7057         2.5
5     ...     21.8429         2.5
6     ...     21.8429         2.5
7     ...   2415.7169         3.5
8     ...   2415.7169         3.5
9     ...   2420.3363         3.5
10     ...   2420.3363         3.5
11     ...   2441.4861         3.5
12     ...   2441.4861         3.5
13     ...   2449.1004         3.5
14     ...   2449.1004         3.5
15     ...  44918.2725         1.5
16     ...  44918.2725         1.5
17     ...  44921.2176         1.5
18     ...  44921.2176         1.5
19     ...  47249.9050         2.5
```

One can see that that $(2J+1)$ components of J level are not degenerated. This error is introduced by MS-CASPT2 method.

```
                                                    |AVERAGED ENERGIES (2J+1)
::   RASSI State   1    Total energy:  -8852.27226716  |4f  -8852.272183570
::   RASSI State   2    Total energy:  -8852.27225926  |4f  -8852.272183570
::   RASSI State   3    Total energy:  -8852.27225182  |4f  -8852.272183570
::   RASSI State   4    Total energy:  -8852.27224297  |4f  -8852.272183570
::   RASSI State   5    Total energy:  -8852.27220762  |4f  -8852.272183570
::   RASSI State   6    Total energy:  -8852.27205902  |4f  -8852.272183570
::   RASSI State   7    Total energy:  -8852.27199714  |4f  -8852.272183570
::   RASSI State   8    Total energy:  -8852.06751354  |5d  -8852.067494002
::   RASSI State   9    Total energy:  -8852.06749892  |5d  -8852.067494002
::   RASSI State  10    Total energy:  -8852.06748936  |5d  -8852.067494002
::   RASSI State  11    Total energy:  -8852.06748638  |5d  -8852.067494002
::   RASSI State  12    Total energy:  -8852.06748181  |5d  -8852.067494002
::   RASSI State  13    Total energy:  -8851.90695416  |6s  -8851.906954160
```

```
&RASSI &END
CIprint
NROF JOBIPHS
2 7 6
1 2 3 4 5 6 7
1 2 3 4 5 6
Spin
HDIAG
-8852.272183570
-8852.272183570
-8852.272183570
-8852.272183570
-8852.272183570
-8852.272183570
-8852.272183570
-8852.067494002
-8852.067494002
-8852.067494002
-8852.067494002
-8852.067494002
-8851.906954160
End of input
```

`HDIAG` The values give an energy for each wave function, to replace the diagonal elements of the Hamiltonian matrix. Please check input file: `Cerium3.hdiag_rassi.input`