The CASSCF/CASPT2/SO-RASSI approach

For heavy elements, relativistic effects including SO coupling affects structure and even chemical valence.

In recent years, we have worked out a combination of quantum chemical methods that seems able to handle many systems involving such elements, at a satisfactory level of accuracy. Radicals, exotic bond types and excited states are all handled at a uniform level of approximations.

This approach has by now been applied to a number of chemical and spectroscopic problems: see e.g. a recent article in PCCP **6**, 2919 (2004).

The Douglas-Kroll-Hess Hamiltonian

The Douglas-Kroll (DK) transformation is a sequence of unitary transformations that remove the coupling of the large and small components of the Dirac one-electron through some order in the one-electron external potential $\hat{V}$.

An ∞-order DK transformation achieves an exact splitting of the Dirac Hamiltonian into two uncoupled two-component parts, one for the positive-energy and one for the negative-energy orbitals.

The lowest-order Hamiltonian is obtained by the transformation to a representation where energy, momentum and helicity are simultaneously diagonalized for the free fields. The external potential, after transforming, yields the relativistic corrections.

The Douglas-Kroll-Hess transformation

The Dirac Hamiltonian is customarily written

$$\hat{H} = \hat{V} + E_0\hat{\beta} + c\hat{\mathbf{p}}\hat{\boldsymbol{\alpha}}$$

where $\hat{V}$ is the external potential, $E_0 = m_e c^2$ is the rest mass energy of the electron, and the other symbols are the standard ones in relativistic quantum mechanics.

The free-field Hamiltonian is the same without the term $\hat{V}$. It is diagonalized by the unitary transformation matrix

$$\hat{U} = (2E_p(E_0 + E_p))^{-1/2} \left(E_0 + E_p + c\hat{\mathbf{p}}\hat{\boldsymbol{\alpha}}\hat{\beta}\right)$$

in a basis of plane helicity waves.

A one-electron basis set approach.

Hess suggested that a suitable basis set would allow a matrix representation of the operators $\hat{A}$ and $\hat{R}$, which are algebraic functions of $\hat{\mathbf{p}}$:

$$\begin{aligned} \hat{U}_0 &= \hat{A}\left(1+\hat{R}\hat{\beta}\right) \\ \hat{A} &= \sqrt{\frac{2E_p}{E_0+E_p}} \\ \hat{R} &= \frac{c\hat{\mathbf{p}}\hat{\boldsymbol{\alpha}}}{E_0+E_p} \\ \Rightarrow \hat{U}_0^\dagger \hat{H}_0 \hat{U}_0 &= E_p\hat{\beta} \end{aligned}$$

and that this approach could easily be extended to higher orders. The resulting transformed potential terms can be subdivided into spin-free and spin-orbit terms. In our approach, they are used separately.

We use a spin-free, or scalar, DK transformation when computing the conventional one-electron integrals. The two-electron integrals are used untransformed; this is known to be a workable approximation.

The Spin-Free basis states

The CASSCF or RASSCF wave functions are in a sense spinless. They are each computed for a specified total spin, but the spin quantum number merely affects the permutation symmetry of the electrons. There is no M_S quantum number, nor is the wave function assumed to be any eigenstate of $\hat{S}_z$. The wave function can be regarded as a joint representative of all possible spin states within the given multiplet. This has consequences for the calculation of matrix elements. We can use the Wigner-Eckart theorem(as will be explained later).

The CASSCF or RASSCF wave functions are invariant to rotations in spin space. This makes them suitable as a basis for computing spin-orbit matrix elements also for light elements, where a UHF approach would introduce an artificial spin dependence.

State-specific RASSCF orbitals

The RASSCF depends on the use of an optimized set of orbitals in order to keep the wave function compactly described by a manageable set of Slater determinants. The orbitals for different states have in general different orbitals. This happens, i.e.

- if the static polarity(dipole, quadrupole. . .) of the states are different
- if their amounts of ionic character(in valence-bond sense) are different
- if the occupation of a local orbital,such as a transition metal d or f orbital, differs

The RASSI method

Matrix elements of one- or two-electron operators over a basis of RASSCF or CASSCF wave functions are easily computed – even when the individual states have individually optimized orbitals! This follows from a special property of the CI space used to express the RASSCF wave function: that it is 'closed under deexcitation'. The MOLCAS package contains a program, called RASSI, which is used to compute matrix elements such as transition dipole matrix elements, and also (for various purposes) to compute matrix elements of the scalar Hamiltonian. It is the latter use that has given the program its name: 'RAS State Interaction'.

For the purposes of computing spin-orbit matrix elements, we use this program to compute so-called reduced matrix elementsof the spin-orbit hamiltonian, over the spin-free basis. We then apply the Wigner-Eckart theorem to produce the matrix elements over all the spin components.

The Spin-Orbit Hamiltonian

The one-electron term of the no-pair spin-orbit Hamiltonian is

$$\hat{H}_{\mathrm{SO}}^{\mathrm{1el}} = \sum_k \left(\frac{A_k}{E_k + mc^2}\right) i\sigma_k \cdot ((p_k V_{\mathrm{ext}}(r_k) \times p_k) \left(\frac{A_k}{E_k + mc^2}\right)$$

(adopted from a manuscript by B. Schimmelpfennig. Notation is conventional).

The two-electron term has two contributions:

$$\begin{aligned}\hat{H}_{\mathrm{SO}}^{\mathrm{2el}} &= \sum_{k\neq l} A_k A_l \left(\frac{i\sigma_k}{E_k + mc^2} \cdot \left((p_k \frac{1}{r_{kl}}) \times p_k\right) \frac{1}{E_k + mc^2}\right) A_k A_l \\ &+ \sum_{k\neq l} A_k A_l \left(\frac{2i\sigma_k}{E_k + mc^2} \cdot \left((p_l \frac{1}{r_{kl}}) \times p_l\right) \frac{1}{E_l + mc^2}\right) A_k A_l\end{aligned}$$

2nd quantized form of $\hat{H}^{\mathbf{1el}}_{\mathbf{SO}}$

Using spin-restricted orbitals, each term of the Hamiltonian is a scalar product of two vectors. One is a vector-valued integral, the other a vector excitation operator:

$$\hat{H}^{\mathsf{1el}}_{\mathsf{SO}} = \sum_{pq} \left(V^x_{pq} \hat{T}^x_{pq} + V^y_{pq} \hat{T}^y_{pq} + V^z_{pq} \hat{T}^z_{pq} \right)$$

where

$$\begin{aligned}
\hat{T}^x_{pq} &= \frac{1}{2} \left(\hat{p}^\dagger_\alpha \hat{q}_\beta + \hat{p}^\dagger_\beta \hat{q}_\alpha \right) \\
\hat{T}^y_{pq} &= \frac{i}{2} \left(-\hat{p}^\dagger_\alpha \hat{q}_\beta + \hat{p}^\dagger_\beta \hat{q}_\alpha \right) \\
\hat{T}^z_{pq} &= \frac{1}{2} \left(\hat{p}^\dagger_\alpha \hat{q}_\alpha - \hat{p}^\dagger_\beta \hat{q}_\beta \right)
\end{aligned}$$

2nd quantized form of $\hat{H}^{\mathbf{2el}}_{\mathbf{SO}}$

The corresponding two-electron terms are similar:

$$\hat{H}^{\mathrm{2el}}_{\mathrm{SO}} = \sum_{pqrs} \left(W^x_{pqrs} \hat{T}^x_{pqrs} + W^y_{pqrs} \hat{T}^y_{pqrs} + W^z_{pqrs} \hat{T}^z_{pqrs} \right)$$

if we simply define two-electron vector excitation operators,

$$\hat{T}^x_{pqrs} = \hat{T}^x_{pq} \hat{E}_{rs} - \delta_{rq} \hat{T}^x_{ps}$$

where the vector integrals can be simply expressed in the spin-other-orbit and spin-same-orbit integrals, which turn out to be identical apart from a simple index permutation.

But without going into any details, we note that the two-electron expression can be fairly well approximated by a one-electron Hamiltonian, e.g. as done by Marian, Wahlgren et al. This involves essentially the contraction of the two-electron vector integrals over a one-particle reference density matrix.

The WE-reduced transition spin density matrix

All matrix elements of $\hat{H}^{\mathrm{SO}}$ over the pair of components from two multiplets can now be obtained from only three reduced matrix elements – one for V^x, one for V^y and one for V^z.

Similarly, in order to compute **any** such matrix element, it is sufficient to have evaluated in beforehand one **single** set of elements σ_{pq}, which is then contracted with suitable integrals to produce the matrix elements over wave functions. The WE-reduced spin-density matrix elements can be computed from standard spin-density matrix elements in either of three ways:

$$\sigma^{AB}_{pq} = \frac{1}{\sqrt{2S+1}} \left\langle \alpha\, S\, S | T^z_{pq} | \alpha'\, S+1\, S \right\rangle$$

$$\sigma^{AB}_{pq} = \frac{1}{S} \left\langle \alpha\, S\, S | T^z_{pq} | \alpha'\, S\, S \right\rangle$$

$$\sigma^{AB}_{pq} = \frac{1}{\sqrt{2S-1}} \left\langle \alpha\, S\, S-1 | T^z_{pq} | \alpha'\, S-1\, S-1 \right\rangle$$

The reduced matrix elements of V^x, V^y, V^z:

Having obtained σ_{pq}^{AB}, it is contracted with the SO-coupling integrals to form

$$
\begin{aligned}
V^{ABx} &= \sum_{pq} \sigma_{pq}^{AB} V_{pq}^{x} \\
V^{ABy} &= \sum_{pq} \sigma_{pq}^{AB} V_{pq}^{y} \\
V^{ABz} &= \sum_{pq} \sigma_{pq}^{AB} V_{pq}^{z}
\end{aligned}
$$

These three scalar quantities are then sufficient to form all the $(2S+1)(2S'+1)$ SO-hamiltonian matrix elements over the $(2S+1)(2S'+1)$ pairs of spin components defined from the two 'spin-free states', A and B.

The SO-coupling Hamiltonian matrix elements

In a Hamiltonian matrix over individual spin states, the following contributions can then be calculated and added, as follows:

$$\left\langle SM|\hat{H}^{\mathsf{SO}}|S+1\,M\pm1\right\rangle = -\frac{\sqrt{(S\pm M+1)(S\pm M+2)}}{2}(\pm V^{ABx}+iV^{ABy}) \quad (1)$$

$$\left\langle SM|\hat{H}^{\mathsf{SO}}|S+1\,M\right\rangle = \sqrt{(S+1)^2-M^2}\,V^{ABz} \quad (2)$$

$$\left\langle SM|\hat{H}^{\mathsf{SO}}|S\,M\pm1\right\rangle = \pm\frac{\sqrt{(S\mp M)(S\pm M+1)}}{2}(\pm V^{ABx}+iV^{ABy}) \quad (3)$$

$$\left\langle SM|\hat{H}^{\mathsf{SO}}|S\,M\right\rangle = MV^{ABz} \quad (4)$$

$$\left\langle SM|\hat{H}^{\mathsf{SO}}|S-1\,M\pm1\right\rangle = \frac{\sqrt{(S\mp M)(S\mp M-1)}}{2}(\pm V^{ABx}+iV^{ABy}) \quad (5)$$

$$\left\langle SM|\hat{H}^{\mathsf{SO}}|S-1\,M\right\rangle = \sqrt{S^2-M^2}\,V^{ABz} \quad (6)$$

The AMFI integrals

The approach we have chosen is just as viable also if the two-electron matrix elements are computed without any approximation. But assuming that we do use the mean-field approximation, a further simplificationis possible. This amounts to replacing the reference density matrix, which defines the mean-field approximation, with the assumption that the first few atomic basis functions, for each atom, are doubly occupied. The density is thus predefined, and the resulting one-electron spin-orbit Hamiltonian is a fixed operator, just like any other one-electron operator. This defines the so-called Atomic Mean Field Integrals, which have been implemented in the SEWARD program by Berndt Schimmelpfennig and Roland Lindh.

The SEWARD input:

In input to SEWARD, the keywords Douglas-Kroll, AMFI, and Finite Nucleus are used for relativistic calculations. In addition, the ANO-RCC basis set should be used.

(Exception: Effective core basis sets.)

```
 &SEWARD  &END
Title
 Iodine atom
Symmetry
  XYZ
Basis set
I.ano-rcc...7s6p4d2f1g.
 I    0.00  0.00  0.00
End of basis
AMFI
Douglas-Kroll
End of Input
```

Calculations involving spin-orbit interactions should be done with low symmetry, preferably none at all or C_{i}.

The ANO-RCC basis set is designed for such calculations, and are available for all the periodic table.

The AMFI integrals are available for most common basis sets, including many ECPs.

The Douglas-Kroll integrals are computed using, internally in SEWARD, the given basis set, uncontracted. This is useless for e.g. STO-3G basis sets.

The CASPT2 input:

For subsequent use in SO-RASSI, the RASSCF wavefunction 'interphase file' JOBIPH is used. The SO-RASSI will compute the Hamiltonian interaction matrix elements for the RASSCF wave functions, and include the spin-orbit terms. However, for better accuracy, the Hamiltonian may be 'dressed' with the contributions from neglected dynamic correlation. This is done by letting CASPT2 produce intermediate 'JOBMIX' files.

```
 &CASPT2 &END
Title
 Iodine atom
Frozen
  3  6
MultiState
  3
  1  2  3
End of Input
```

As usual, we wish to avoid complications that arise from attempts to correlate the core, so a number of orbitals are frozen. Molcas can automatically select a 'decent' core, but we may choose to do it manually.

The multistate input: Number of RASSCF states to dress by CASPT2 (3), and the serial number of these states (The three lowest: 1,2,3).

The CASPT2 program will automatically produce a new interphase file, called JOBMIX. Several such files may be used by the RASSI program.

The RASSI input:

The following RASSI input is actually from another calculation, showing the input for several JOBIPH or JOBMIX files:

```
!ln -fs T.Job JOB001
!ln -fs S.Job JOB002
 &RASSI &END
Nr of JobIph
 2  3  3
 1 2 3
 1 2 3
Spin
EJob
Omega
End of Input
```

The JOBMIX files are linked using soft links named JOB001, etc.

The Nr of JobIphs keyword is followed by: The number of JOBMIX files (2), The number of states to pick from each of them (3,3), and the the serial numbers of these states for the first file (The lowest three, 1,2,3), then those from the second file, etc.

EJob implies that energies are taken from the JOBMIX files instead of being recomputed.

Omega implies that spin-orbit states are annotated with their Omega quantum numbers, appropriate for linear molecules.