

# Relativistic calculations using Molcas

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*Abstract: Relativistic effects affect energies and properties to various degree throughout the periodic table. Some of these effects have chemical implications and must therefore be included to some extent in QC software. In MOLCAS, this can be done at different levels of sophistication, ranging from the simple use of relativistic ECP's up to calculation of spectroscopic properties including spin-orbit interaction.*

## What is wrong with non-relativistic quantum chemistry?

Relativistic corrections will systematically affect **the chemistry of the heavier elements**:

- Atomic ionization potentials, electron affinities, and excitation energies affect the energies of dissociation asymptotes, and thus also the potential curves for bond breaking and positions and height of barriers.
- For the heavier elements, there is a marked change in bond length and in bond strength when relativistic effects are included.
- Some of these changes are just caused by relativity changing the energy balance between the **potential** and the **kinetic energies** of the electrons: "**Scalar relativity**".

## What is wrong with non-relativistic quantum chemistry?

Relativistic corrections can be important **also for lighter elements**.

- Barriers change, and many allowed crossings turn into avoided crossings due to the lower symmetry of interactions involving spin. The valence levels of atoms change, which appreciably affects the bonding properties of atoms.
- Open shells of radicals, transition metal compounds, lanthanide and actinide compounds, and excited states undergo **spin-orbit splitting**.
- There are often a multitude of low-lying electronic states for some or all conformations, especially along bond-breaking parts of reaction paths. **Intrasystem interactions** make them all relevant to reactivity.

## Mainstream relativistic Quantum Chemistry.

The theoretical basis for relativistic quantum chemistry is the Dirac one-electron, four-component equation, which replaces the Schrödinger equation. Together with quantization of the electromagnetic field, this gives a quantum field theory: Quantum Electrodynamics.

It is now well known that *for chemical applications*, it is enough to use approximate theories *properly derived* from QED, at the level of electrons described using self-consistent four-component orbitals with an added two-electron interaction.

Except for the transuranium artificial elements, it is furthermore possible to simplify with acceptable accuracy to a two-component formalism. There are several approaches. One popular scheme is called Douglas-Kroll-Hess transformation.

## The scalar relativistic calculations.

The Douglas-Kroll transformation gives a **two-component formalism** with **an effective Hamiltonian**, containing spin-dependent and spin-independent terms.

Hess worked out a practical formulation in terms of matrix algebra. Averaging over spin gives a spin-independent 'scalar' Hamiltonian. Technically, this just amount to changing the interactions by changing the one- and maybe two-electron integrals.

This can be done for **effective core potentials** by parametrizing to represent the scalar relativistic effects. It can also be done by **including in the integral generator** the procedure for changing the interactions.

## The SEWARD input:

In input to SEWARD, the keywords **Douglas-Kroll**, **AMFI**, and **Finite Nucleus** are used for relativistic calculations. In addition, a relativistic basis set should be used. The **ANO-RCC** basis set already gives Douglas-Kroll as default.

Relativistic effective core basis sets already includes relativity without any DKH corrections.

```
&GATEWAY
Symmetry
  XY
Basis set
Au.ANO-RCC...6s4p3d1f.
Au  0.000  0.000  0.000
End of basis
Basis set
H.ANO-RCC...2s1p.
H   0.000  0.000  3.025
End of basis
End of input
&SEWARD
AngMom
  0.0  0.0  0.0
End of input
```

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.

Calculations involving spin-orbit interactions should be done with low symmetry, maybe none at all,  $C_1$ , or  $C_2$ , if this is necessary in order to have symmetry equivalent orbitals sharing the same irrep.

## 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 Spin-Orbit Interaction

The spin-orbit interaction can be included by either of two approaches.

Two-component quantum-chemistry programs, such as EPCISO, include the spin dependent part already from the start. (However, 'old' users please note that Valerie Vallets interface to the EPCISO program is no longer distributed with MOLCAS, but can presumably be obtained from her).

The CASSCF/CASPT2/SO-RASSI approach uses standard Molcas programs to obtain a small or sometimes large set of multiconfigurational, correlated states with the scalar relativistic approach. Finally, the matrix elements of the spin-orbit Hamiltonian over this set of states is computed. The final answer is thus obtained using the 'spin-free' states as a basis set of wave functions.

## 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. an article in PCCP 6, 2919 (2004).

## 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.

## The Spin-Orbit basis states

**Example:** Suppose we have several calculations of RASSCF wave functions, which yields seven 'spin-free states':

| State | Symmetry         | Energy          | State | Symmetry         | Energy          |
|-------|------------------|-----------------|-------|------------------|-----------------|
| 1     | Singlet $\Sigma$ | -18994.19788204 | 5     | Triplet $\Sigma$ | -18994.07376530 |
| 2     | Singlet $\Sigma$ | -18994.02066430 | 6     | Triplet $\Delta$ | -18993.99394833 |
| 3     | Singlet $\Delta$ | -18993.98648409 | 7     | Triplet $\Delta$ | -18993.99394833 |
| 4     | Singlet $\Delta$ | -18993.98648409 |       |                  |                 |

Three of the states are **triplet** states,  $S = 1$ . Each of these has actually **three components**, but this distinction was not made earlier. When the spin-orbit interaction is to be added, a Hamiltonian matrix is formed with **thirteen** states.

The spin-orbit matrix elements are computed, for example

$$\begin{aligned} \langle \text{SF } 6, M_S = 0 | \hat{S}^{\text{SO}} | \text{SF } 3, M_S = 0 \rangle &= -4700 \text{ cm}^{-1} \\ \langle \text{SF } 7, M_S = -1 | \hat{S}^{\text{SO}} | \text{SF } 6, M_S = -1 \rangle &= +4707 \text{ cm}^{-1} \end{aligned}$$

and so on, and these elements added to the Hamiltonian, which is then diagonalized.

## 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 elements** of 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 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 simplification** is 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 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.

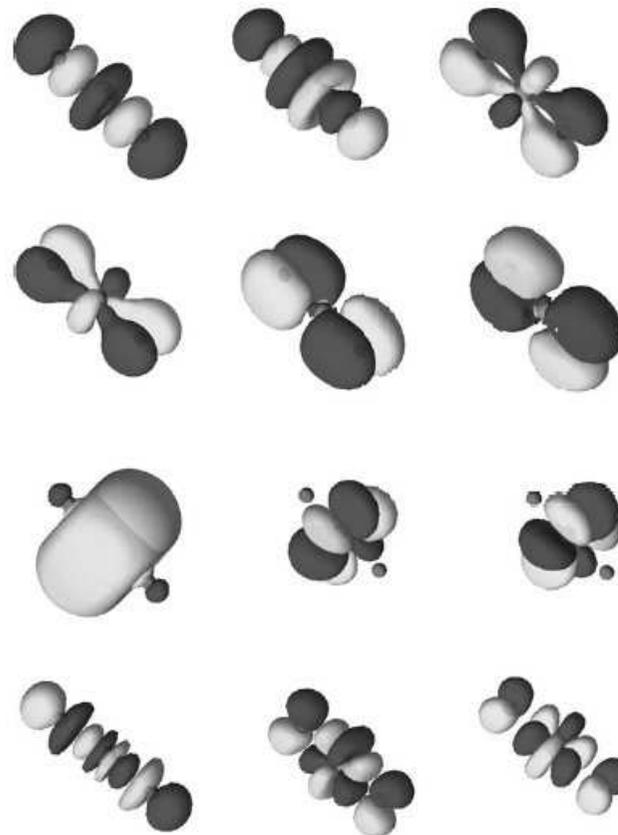
The **Nr of JobIphs** keyword is followed by: The number of JOBMIX files (2), The number of states to pick from each of them (3,3), and the the serial numbers of these states for the first file (The lowest three, 1,2,3), then those from the second file, etc.

**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.

## Sample study: The $\text{UO}_2$ molecule.

The combination RASSCF/CASPT2/SO-RASSI has been used for many studies involving binding and/or spectroscopy of compounds with heavy metals. These orbitals form the two triple bonds in  $\text{UO}_2$ , the three radical orbitals formed from  $\text{U}7s$  and  $\text{U}5f\phi$  of the  ${}^3\Phi_u(\Omega = 2)$ , and three important correlating orbitals.



Other studies include e.g. the discovery of the  $\text{U}_2$  quintuple bond, and many organometallic complexes, some with remarkable bonding.

On the following slides are a short collection of technical details, which are not needed in order to use the programs.

## The Dirac Hamiltonian (in an external static em field)

The conventional relativistic dynamics for an electron in a static four-potential,  $A_\mu = (\phi/c, -\mathbf{A})$ , is determined by the Lagrangian

$$\mathcal{L} = -m_e c^2 \sqrt{1 - u^2/c^2} - e\mathbf{A} \cdot \mathbf{u} + e\phi$$

where  $\mathbf{u}$  is the velocity. (Note: The electron charge is  $-e$ .)

The canonical momentum is thus

$$\mathbf{p} = \frac{\partial \mathcal{L}}{\partial \mathbf{u}} = \frac{m_e \mathbf{u}}{\sqrt{1 - u^2/c^2}} - e\mathbf{A}$$

and the Hamiltonian is obtained when  $\mathbf{p}\mathbf{u} - \mathcal{L}$  is reexpressed as a function of  $\mathbf{p}$ :

$$\mathcal{H} = c\sqrt{m_e^2 c^2 + (\mathbf{p} + e\mathbf{A})^2} - e\phi$$

## The Dirac Hamiltonian, continued

Dirac used a Clifford algebra generated by four quantities  $(\beta, \boldsymbol{\alpha})$ , where  $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$  are three anticommuting square roots of  $-1$ ,  $\boldsymbol{\alpha}\beta = -\beta\boldsymbol{\alpha}$ , and  $\beta^2 = 1$ . With this algebra,

$$\mathcal{H} = c\sqrt{m_e^2c^2 + (\mathbf{p} + e\mathbf{A})^2} - e\phi = c\boldsymbol{\alpha} \cdot (\mathbf{p} + e\mathbf{A}) + \beta m_e c^2 - e\phi$$

The canonical momentum  $\mathbf{p}$  is replaced by  $-i\hbar\nabla$  in a representation where the state vectors are functions of position. Also, if we assume  $\mathbf{A} = 0$  and replace  $-e\phi$  with a potential energy  $V$ , we get the time-independent Dirac equation in the form used in quantum chemistry:

$$-i\hbar c\boldsymbol{\alpha} \cdot \nabla\Psi + (\beta m_e c^2 + V)\psi = E\Psi$$

The noncommutative quantities cannot be represented by structureless scalars, but can be represented by matrices. This requires wave functions to have several components. **At least four-dimensional matrices are needed.**

## The Standard representation.

Dirac used four-by-four matrices to represent the quantities  $(\beta, \alpha)$  in the form

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

in terms of the two-component Pauli matrices,

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The four-component wave function  $\Psi$  is then similarly composed of two two-component parts:

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

The two-component parts  $\Psi^L$  and  $\Psi^S$  are called the large and small components, respectively.

## 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  $\infty$ -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 kinetic energy is already relativistic. **The external potential, after transforming, yields the other relativistic corrections.**

## The Douglas-Kroll-Hess transformation

The Dirac Hamiltonian is

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

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 easily shown to be diagonalized by the unitary transformation matrix

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

in a basis of plane helicity waves.

The energy eigenvalues of these states are just the relativistic kinetic energy,  $\pm E_p$ , where

$$E_p = \sqrt{E_0^2 + p^2 c^2}$$

## 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  $\hat{\mathbf{p}}$ :

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

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-Orbit Hamiltonian

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

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

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

The **two-electron term** has two contributions:

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

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

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**:

$$\hat{H}_{\text{SO}}^{\text{1el}} = \sum_{pq} \left( V_{pq}^x \hat{T}_{pq}^x + V_{pq}^y \hat{T}_{pq}^y + V_{pq}^z \hat{T}_{pq}^z \right)$$

where

$$\hat{T}_{pq}^x = \frac{1}{2} \left( \hat{p}_{\alpha}^{\dagger} \hat{q}_{\beta} + \hat{p}_{\beta}^{\dagger} \hat{q}_{\alpha} \right)$$

$$\hat{T}_{pq}^y = \frac{i}{2} \left( -\hat{p}_{\alpha}^{\dagger} \hat{q}_{\beta} + \hat{p}_{\beta}^{\dagger} \hat{q}_{\alpha} \right)$$

$$\hat{T}_{pq}^z = \frac{1}{2} \left( \hat{p}_{\alpha}^{\dagger} \hat{q}_{\alpha} - \hat{p}_{\beta}^{\dagger} \hat{q}_{\beta} \right)$$

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

The corresponding two-electron terms are similar:

$$\hat{H}_{\text{SO}}^{2\text{el}} = \sum_{pqrs} \left( W_{pqrs}^x \hat{T}_{pqrs}^x + W_{pqrs}^y \hat{T}_{pqrs}^y + W_{pqrs}^z \hat{T}_{pqrs}^z \right)$$

if we simply define **two-electron vector excitation operators**,

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

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  $\hat{H}^{SO}$  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  $\sigma_{pq}$ , 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:

$$\begin{aligned}\sigma_{pq}^{AB} &= \frac{1}{\sqrt{2S+1}} \langle \alpha S S | T_{pq}^z | \alpha' S+1 S \rangle \\ \sigma_{pq}^{AB} &= \frac{1}{S} \langle \alpha S S | T_{pq}^z | \alpha' S S \rangle \\ \sigma_{pq}^{AB} &= \frac{1}{\sqrt{2S-1}} \langle \alpha S S-1 | T_{pq}^z | \alpha' S-1 S-1 \rangle\end{aligned}$$

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

Having obtained  $\sigma_{pq}^{AB}$ , it is **contracted with the  $SO$ -coupling integrals** to form

$$V^{ABx} = \sum_{pq} \sigma_{pq}^{AB} V_{pq}^x$$

$$V^{ABy} = \sum_{pq} \sigma_{pq}^{AB} V_{pq}^y$$

$$V^{ABz} = \sum_{pq} \sigma_{pq}^{AB} V_{pq}^z$$

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:

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

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

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

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

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

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