

# A TRUE $\Omega$ -REPRESENTATION AS AN ADIABATIC TRANSFORMATION OF SPIN-ORBIT INTERACTIONS AND THEIR ASSOCIATED NON-ADIABATIC COUPLINGS

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**SHOULD YOU USE THE  $\Omega$  REPRESENTATION? ... NO, NOT UNLESS YOU WANT A HARD TIME**

## ABSTRACT

• Removal of Spin-Orbit couplings (SO) for diatomic systems is a well established method which is thought to reduce the complexity of the system of study. This is done via diagonalisation of the SO-Hamiltonian matrix, transforming from the coupled  $\Lambda$ -S (diabatic) basis to the  $\Omega$  (adiabatic) representation where SO couplings vanish.

•  $\Omega$ -representation is NOT a desirable single state representation but contains couplings in the form of strong non-adiabatic couplings (NACs/DDRs) are introduced upon transformation of the kinetic energy, often ignored, and should be included.

• We show that removal of SOC is not free and omission of these "spin-orbit induced" NACs leads to gross errors into the rovibronic solution, unsuitable for high resolution spectroscopy, and a numerical equivalence between the  $\Lambda$ -S diabatic representation and  $\Omega$ -adiabatic representation is achieved when all NAC terms are included.

**NOTHING IS ACHIEVED FOR FREE AND SIMPLIFICATION OF ONE PART LEADS TO THE COMPLICATION OF ANOTHER!**

## TRANSFORMING TO THE $\Omega$ -REPRESENTATION

The diatomic non-relativistic Hamiltonian reads

$$\hat{H}_{tot} = \hat{H}_e + \hat{H}_\mu - \frac{\hbar^2}{2\mu r^2} \frac{d^2}{dr^2} + \frac{\hbar^2}{2\mu r^2} (\hat{j} - \hat{L} - \hat{S})^2$$

Which is solved in DUO usually in the  $\Lambda$ -S basis. Transformation to the  $\Omega$ -representation is analogous to a "adiabatising" transformation which transforms the  $\Lambda$ -S to the  $\Omega$  basis when solving the vibronic problem

$$|state, \Lambda, S, \Sigma\rangle \rightarrow |state, \Omega\rangle$$

Such that the Spin-Orbit matrix is diagonalised,

$$\langle state_i, \Omega_i | U \hat{H}_{SO} U^\dagger | state_j, \Omega_j \rangle = 0 \quad \forall i \neq j$$

Which is usually added to the transformed potentials. We must then transform the entire Hamiltonian with  $U$ , yielding modified potentials, couplings, and also non-adiabatic couplings (NACs/DDRs). Transforming the kinetic energy yields said NACs,

$$\begin{aligned} -\frac{\hbar^2}{2\mu r^2} U \frac{d^2}{dr^2} U^\dagger &= -\frac{\hbar^2}{2\mu r^2} \left( -\frac{dU}{dr} \frac{dU^\dagger}{dr} - \left[ \frac{d}{dr} U \frac{dU^\dagger}{dr} - U \frac{dU^\dagger}{dr} \frac{d}{dr} \right] \right) \\ &= -\frac{\hbar^2}{2\mu r^2} \left( K - \left[ \frac{d}{dr} W - W \frac{d}{dr} \right] \right) \end{aligned}$$

**THE  $\Omega$  REPRESENTATION IS A LOT MORE COMPLICATED THAN IT SEEMS!**

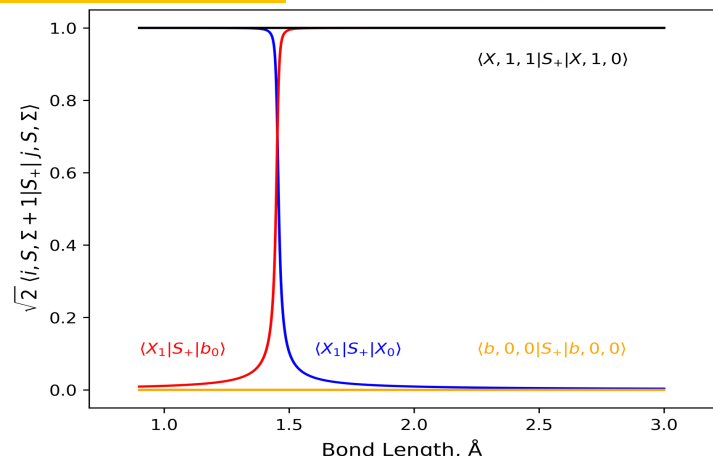
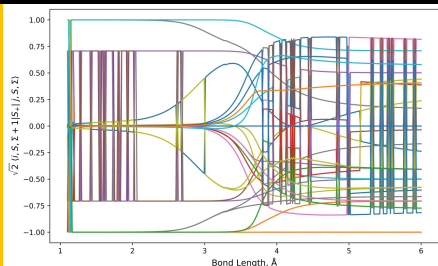


Fig 2: Illustration of elements of the  $\hat{S}_z$  operator in the  $\Omega$  (red, blue) and  $\Lambda$ -S (black and orange) representations. We see a complication of the once simple constants in the  $\Lambda$ -S picture now become curves in the  $\Omega$  picture.

## COMPARISONS

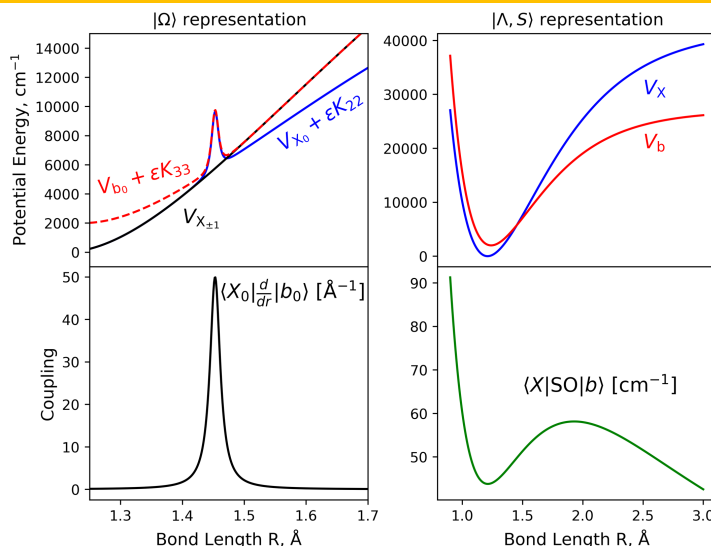


Fig 1: Illustration of the PECs (top) and associated couplings (bottom) in the  $\Omega$ -representation (left) and  $\Lambda$ -S representation (right).

| n  | $[\Omega]$  |             |             |       |    | $[\Lambda, S]$ |             |       |    |  |
|----|-------------|-------------|-------------|-------|----|----------------|-------------|-------|----|--|
|    | E           | E(DDRs=0)   | E(K=0)      | State | v  | E              | E(SO=0)     | State | v  |  |
| 1  | 0           | 0           | 0           | $X_0$ | 0  | 0              | 0           | X     | 0  |  |
| 2  | 968.345455  | 968.354306  | 968.304973  | $X_0$ | 1  | 968.345455     | 968.485302  | X     | 1  |  |
| 3  | 1924.867208 | 1925.231078 | 1924.429095 | $X_0$ | 2  | 1924.867208    | 1925.554298 | X     | 2  |  |
| 4  | 1966.978286 | 1966.59619  | 1966.928886 | $b_0$ | 0  | 1966.978286    | 1964.514372 | b     | 0  |  |
| 5  | 2859.629394 | 2864.714731 | 2857.087255 | $b_0$ | 1  | 2859.629394    | 2862.363719 | b     | 1  |  |
| 6  | 2875.718441 | 2870.521034 | 2872.44166  | $X_0$ | 3  | 2875.718441    | 2871.206988 | X     | 3  |  |
| 7  | 3743.88388  | 3746.544245 | 3724.749937 | $b_0$ | 2  | 3743.88388     | 3743.483993 | b     | 2  |  |
| 8  | 3806.823099 | 3803.67487  | 3770.379262 | $X_0$ | 4  | 3806.823099    | 3805.443372 | X     | 4  |  |
| 9  | 4608.585135 | 4613.974883 | 4461.643064 | $b_0$ | 3  | 4608.585135    | 4607.875192 | b     | 3  |  |
| 10 | 4729.337869 | 4722.247604 | 4550.730178 | $X_0$ | 5  | 4729.337869    | 4728.263448 | X     | 5  |  |
| 11 | 5456.318936 | 5473.798714 | 5106.378331 | $b_0$ | 4  | 5456.318936    | 5455.537318 | b     | 4  |  |
| 12 | 5640.676959 | 5618.439714 | 5300.498571 | $X_0$ | 6  | 5640.676959    | 5639.667218 | X     | 6  |  |
| 13 | 6287.255096 | 6338.303861 | 5976.212596 | $X_0$ | 7  | 6287.255096    | 6286.47037  | b     | 5  |  |
| 14 | 6540.670439 | 6477.847087 | 6238.527487 | $b_0$ | 5  | 6540.670439    | 6539.654681 | X     | 7  |  |
| 15 | 7101.433679 | 7214.262671 | 6971.996148 | $X_0$ | 8  | 7101.433679    | 7100.674348 | b     | 6  |  |
| 16 | 7429.278037 | 7295.604841 | 7280.802461 | $b_0$ | 6  | 7429.278037    | 7428.225842 | X     | 8  |  |
| 17 | 7898.869553 | 8091.348144 | 7867.479901 | $X_0$ | 9  | 7898.869553    | 7898.149252 | b     | 7  |  |
| 18 | 8306.484602 | 8092.493363 | 8276.551687 | $b_0$ | 7  | 8306.484602    | 8305.380717 | X     | 9  |  |
| 19 | 8679.569862 | 8870.870473 | 8521.679569 | $X_0$ | 10 | 8679.569862    | 8678.895083 | b     | 8  |  |
| 20 | 9172.282642 | 8960.013008 | 9041.823978 | $b_0$ | 8  | 9172.282642    | 9171.119361 | X     | 10 |  |

Table 1: The rovibronic ( $J=0$ ) energy term values ( $\text{cm}^{-1}$ ) of the  $X^3\Sigma^-$  and  $b^1\Sigma^+$  states of sulfur monoxide computed in the  $\Lambda$ -S and  $\Omega$  representations. The energies are listed relative to the lowest  $J=0$  state.

## DIPOLE MOMENT CURVES

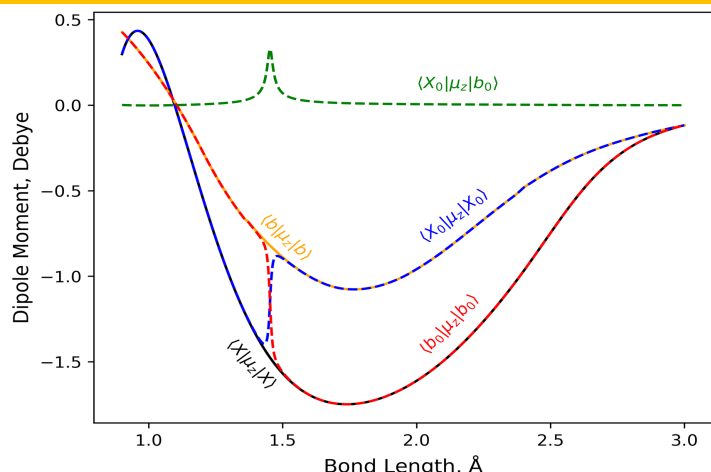


Fig 3: Illustration of the transition dipole moment curve for the forbidden  $X^3\Sigma^- - b^1\Sigma^+$  transition in the  $\Omega$ -representation (green). The mixed diagonal DMCs can be seen superimposed on their  $\Lambda$ -S analogue.