

A TRUE Ω -REPRESENTATION AS AN ADIABATIC TRANSFORMATION OF SPIN-ORBIT INTERACTIONS AND THEIR ASSOCIATED NON-ADIABATIC COUPLINGS

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SHOULD YOU USE THE Ω 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 Λ - S (diabatic) basis to the Ω (adiabatic) representation where SO couplings vanish.
- Ω -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 Λ - S diabatic representation and Ω -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 Ω -REPRESENTATION

The diatomic non-relativistic Hamiltonian reads

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

Which is solved in Duo usually in the Λ - S basis. Transformation to the Ω -representation is analogous to a "adiabatising" transformation which transforms the Λ - S to the Ω basis when solving the vibronic problem

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

Such that the Spin-Orbit (plus potential) matrix is diagonalised,

$$\langle state_i, \Omega_i | U(H_{SO} + V_e) U^\dagger | state_j, \Omega_j \rangle = 0 \quad \forall i \neq j$$

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 Ω REPRESENTATION IS A LOT MORE COMPLICATED THAN IT SEEMS!

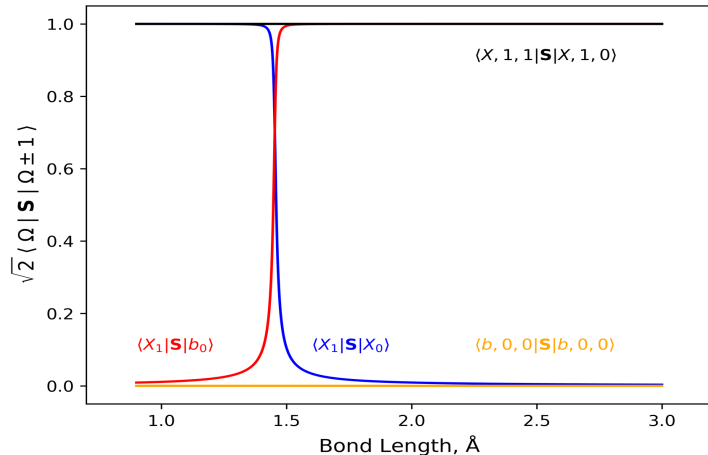
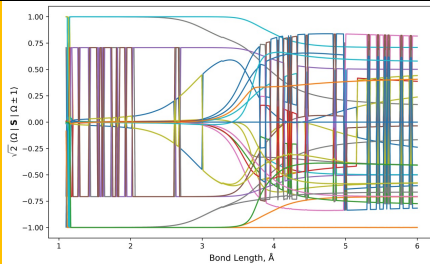


Fig 2: Illustration of elements of the \hat{S} operator in the Ω (red, blue) and Λ - S (black and orange) representations. We see a complication of the once simple constants in the Λ - S picture now become curves in the Ω picture.

COMPARISONS

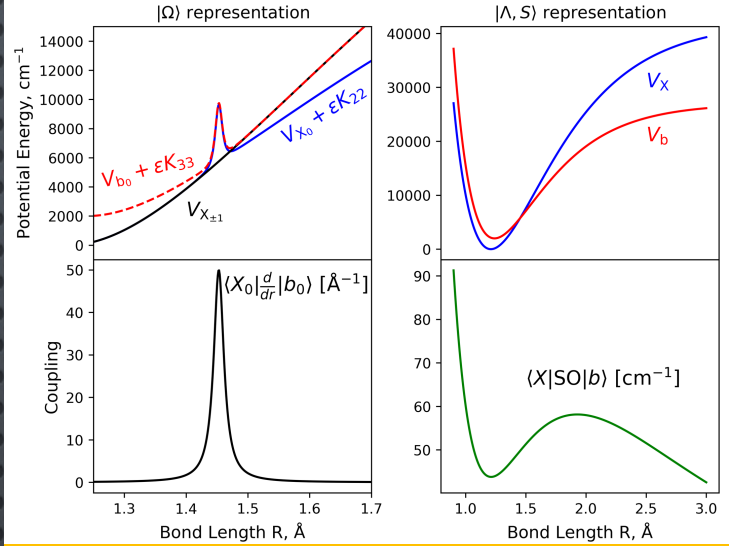


Fig 1: Illustration of the PECs (top) and associated couplings (bottom) in the Ω -representation (left) and Λ - S representation (right).

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	b_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 (cm^{-1}) of the $X^3\Sigma^-$ and $b^1\Sigma^+$ states of sulfur monoxide computed in the Λ - S and Ω representations. The energies are listed relative to the lowest $J=0$ state.

DIPOLE MOMENT CURVES

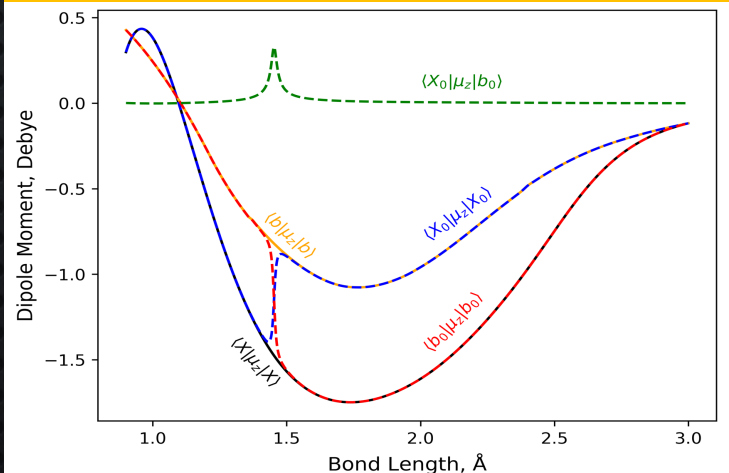


Fig 3: Illustration of the transition dipole moment curve for the forbidden $X^3\Sigma^- - b^1\Sigma^+$ transition in the Ω -representation (green). The mixed diagonal DMCs can be seen superimposed on their Λ - S analogue.