Cross-Contamination of the Fitting Parameters $\Delta\nu_1$, $\Delta\nu_2$, $\Delta\nu_3$ etc. in Multidimensional Tunneling Treatments

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Introductory Material

There are two ways to treat MULTI-dimensional tunneling problems. Why do we need two ways? Because (as usual) each method has its own strengths and weaknesses.

Two methods: TRUE H & TUNNELING H

TRUE: $H = T(\partial/\partial x_1,\ldots\partial/\partial x_n) + V_{ab\text{-}initio}(x_1,\ldots x_n)$ has fitting parameters with clear physical meaning, but usually obs-calcs >> exp. measurement accuracy.

TUNNELLING: $H(A,B,C,\Delta\nu_1,\ldots,\Delta\nu_n)$ gives obs-calcs ≈ exp. measurement accuracy, but usually the fitting parameters have unclear physical meaning.

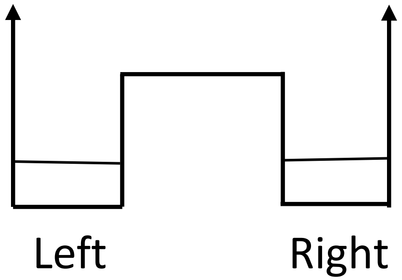
Molecules studied with multi-D tunneling formalism

2-D: CH_3NH_2, CH_3NHD, CH_3CHO (S_1 state), CH_3-tropolone, CH_3-malonaldehyde.

3-D: N_2H_4, $(H_2O)_2$, $(CH_3OH)_2$, $(CH_3)_2$-methylphosphonate.

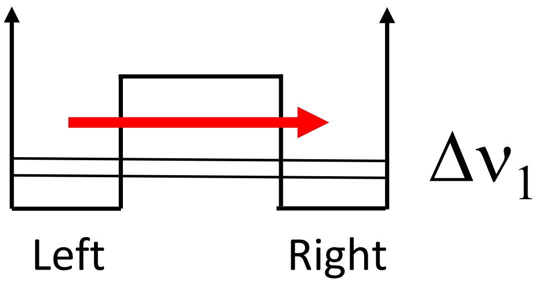
Typical one-dimensional tunneling problem

1-D 2-well potential curve V(x):
L(eft), R(ight) 2-fold degeneracy



Typical one-dimensional tunneling problem

1-D 2-well potential curve V(x):
L(eft), R(ight) 2-fold degeneracy
is split by tunneling L → R
$\Delta\nu_1$ = fitting parameter



1-D 2-well tunneling splitting $\Delta\nu_1 \propto$ overlap integral in the tunneling region: $\Delta_{LR} \equiv \int \psi_L(x)^* \, \psi_R(x)\, dx$

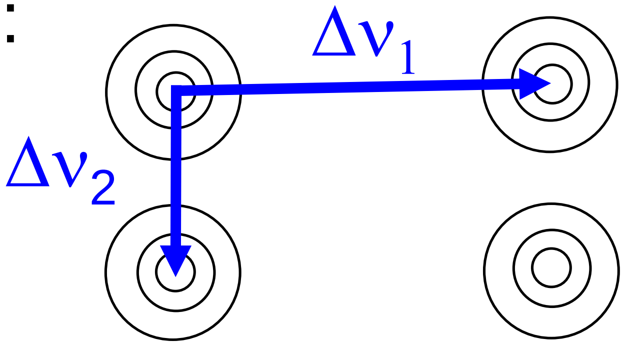
Example of two-dimensional tunneling problem

2-D 4-well potential surface V(x,y):

4-fold degeneracy – – – –

Split by tunneling along arrows

Two different tunneling paths



Define hypothetical $\Delta\nu_1$ and $\Delta\nu_2$ = “1-path splittings”

= fitting parameters (1 for each blue-arrow path).

4 energy levels = $f_{1,2,3,4}(\Delta\nu_1,\Delta\nu_2)$ (f_i from group theory)

3,4,5-D Tunneling Surfaces: Harder to draw & discuss.

The question for today's talk is:

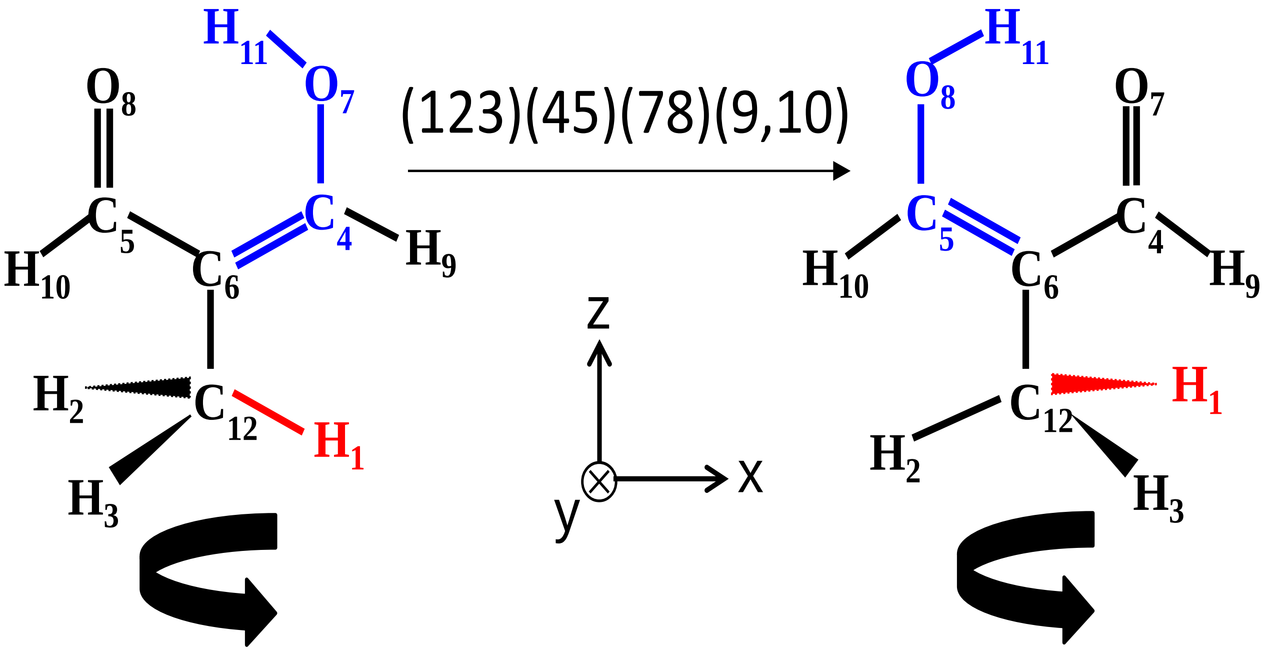
How clear is the physical meaning of the tunneling splittings $\Delta\nu_1,\Delta\nu_2,\ldots,\Delta\nu_n$ obtained from a multi-D tunneling-Hamiltonian fit???

For about 20 years Ohashi-san and I thought:
Physical meaning is only a little unclear.

But problem is much worse than we thought.
We learned this 10 years ago from studying 2-methyl malonaldehyde:

2-D tunneling: H transfer + internal rotation

2 1-path splitting parameters $\Delta\nu_H$ and $\Delta\nu_{torsion}$



(L)

$\gamma = -\gamma_o < 0$

(R)

$\gamma = +\gamma_o > 0$

OH → OD makes $\Delta\nu_{torsion}$ splitting increase by a factor of 3, when we expect no change

The problem is caused by a mathematical inconsistency in our previous tunneling treatments. Summarize 51 equations in our paper in 2 slides:

We explicitly assume a non-orthogonal basis set when setting up the tunneling H matrix, BUT we implicitly assume an orthogonal basis set when diagonalizing the tunneling H matrix.

This is related to the Löwdin transformation (1950), which makes use of $(\Delta^{-1/2})_{ij}$ = inverse square-root of basis-function overlap integral matrix $\Delta_{ij} \equiv \int \phi_i^* \phi_j \, d\tau$.

Result of the present work is two correction factors, called "cross-contamination" or "leakage". Define Δ_H^{fit}, Δ_H^{true}, $\Delta_{torsion}^{fit}$, $\Delta_{torsion}^{true}$. Then we find:

$\Delta_H^{fit} = \Delta_H^{true} - (\Delta_{LR})\Delta_{tor}^{true} \Rightarrow$ small change in Δ_H^{fit}

"Leakage" $\uparrow\downarrow$

$\Delta_{tor}^{fit} = \Delta_{tor}^{true} - (\Delta_{LR})\Delta_H^{true} \Rightarrow$ large change in Δ_{tor}^{fit}

BECAUSE basis-set overlap integral $\Delta_{LR} << 1$ (assumed), AND $\Delta_H \approx 60\ \Delta_{tor}$ in 2-methyl malonaldehyde.

Comparison of -OH and -OD values suggests that

$\Delta(OH)_{tor}^{true} \approx 3\Delta(OH)_{tor}^{fit}$, but

$\Delta(OD)_{tor}^{true} \approx \Delta(OD)_{tor}^{fit}$ for 2-methyl malonaldehyde.

Conclusions

1. There is a general problem in trying to get physical information from “raw” tunneling splitting parameters obtained from multi-dimensional tunneling Hamiltonian fits.
2. We believe the problem has a clear mathematical cause, even though our approximate treatment corrects for only about half of the discrepancy.
3. There are other ways of dealing with the 2-D problem in 2-methyl malonaldehyde:

Gulaczyk & Kręglewski (JMS 2013):	H = T + V method
Kleiner & Hougen (JPCA 2015):	hybrid H method