Recent Advances in Treatment of Multiple Large Amplitude Motions in Gas Electron Diffraction Studies Guided by Quantum Chemistry

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ESGED 16

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Theoretical description of small vibrations

Write Shroedinger's equation for electrons and nuclei

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Apply adiabatic perturbation theory (Born, Oppenheimer).

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Introduce adiabatic potential.

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Write Shroedinger's equation for nuclei in the effective potential field.

Writing a Hamiltonian for nuclear subsystem did not have to wait until strict deduction (E. B. Wilson Jr., J. B. Howard. – J. Chem. Phys., 1936)

$$\hat{H}_{nuc} = \frac{1}{2} \sum_{kl} \hat{p}_k G_{kl} \hat{p}_l + \frac{1}{2} \left(\hat{\mathbf{M}} - \hat{\mathbf{M}}^{(v)} \right)^* \sigma \left(\hat{\mathbf{M}} - \hat{\mathbf{M}}^{(v)} \right) + V(q)$$

GED of small vibrations

Experiment processing used only a portion of these results.

- **Stage 1: just fund maxima on radial distribution plot.**
Advantages: don't need to know nearly anything about the molecule.

- **Stage 2: $sM(s)$ fitting by parameter optimization.**

- **Stage 3: adding harmonic and anharmonic corrections, using compatible geometries.**

- **Stage 4: Potential approach.**
Parameters are calculated from r_e and force fields.
Advantages: compatibility with spectroscopy.
Difficulties: need force matrices.

GED of small vibrations

Limitations:

- Non-adiabatic effects ignored.
- Scattering theory limitations.
- Vibrational displacements are small (series by Δr rapidly converge).

$$M(s) = \sum g(s) \left\langle \frac{\sin sr}{sr} \right\rangle = \sum g(s) \int P(r) \frac{\sin sr}{sr} dr$$
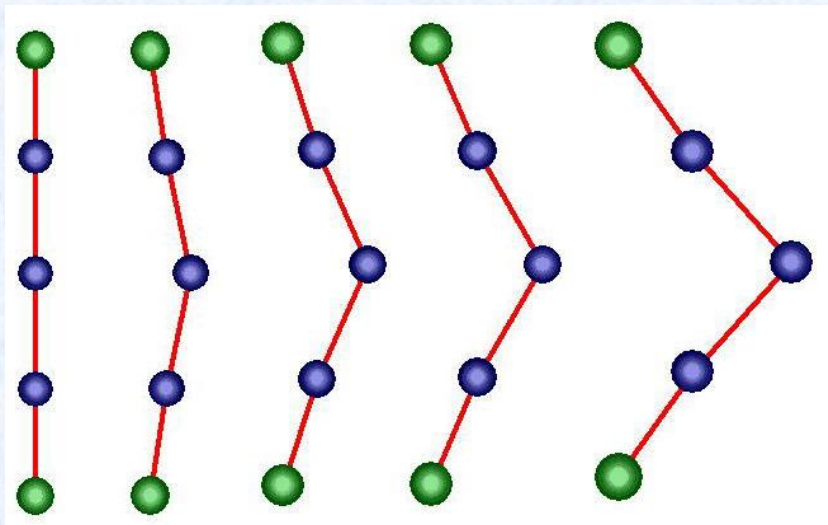
$$M(s) = \sum \frac{g(s)}{sr_a} \exp(-l^2 s^2 / 2) \sin(sr_a - \kappa s^3)$$

- Usually underdetermined:
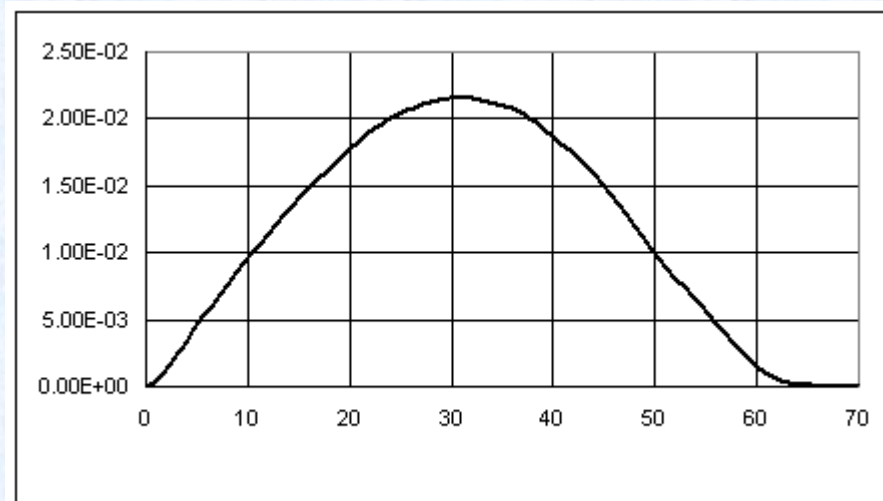Impossible to find close distances in a multi-atomic molecule.

One-Dimensional Large Amplitude Motion

- The use of dynamic molecular model based on the concept of pseudo-conformers has been successfully applied to GED investigations for many years.

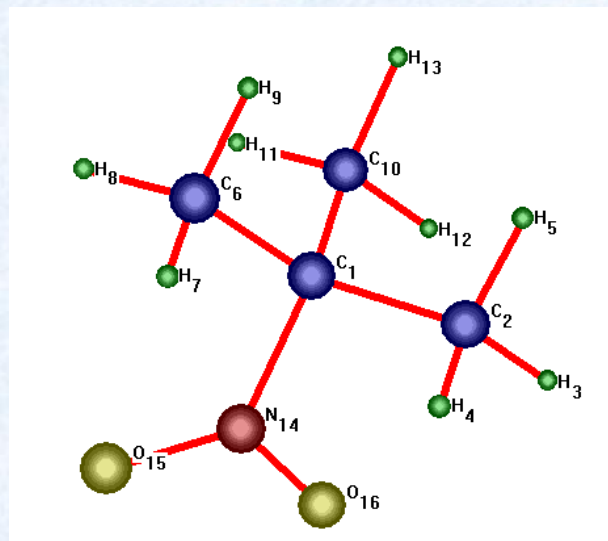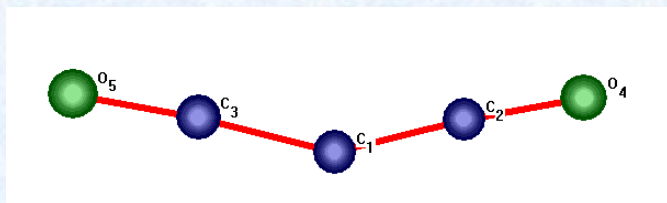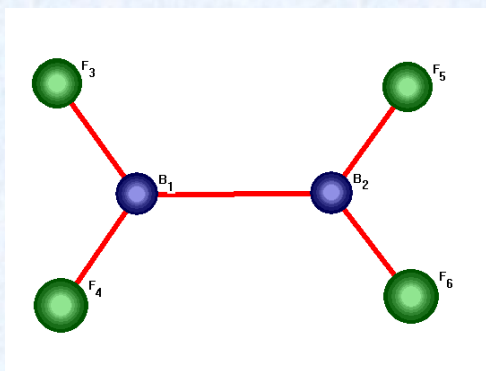Deformation of C_3O_2 molecule

Density distribution (CCC angle)

One-Dimensional Large Amplitude Motion

- However, until recently most research done in this area was limited to the molecules possessing only one large-amplitude degree of freedom (usually internal rotation).
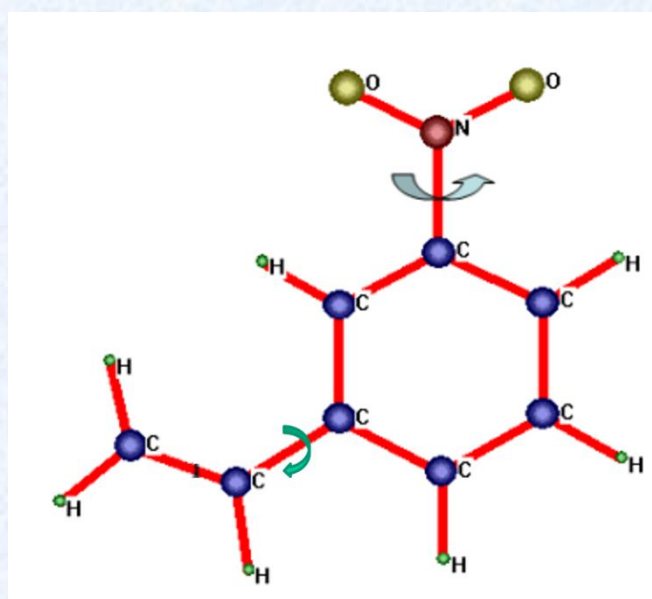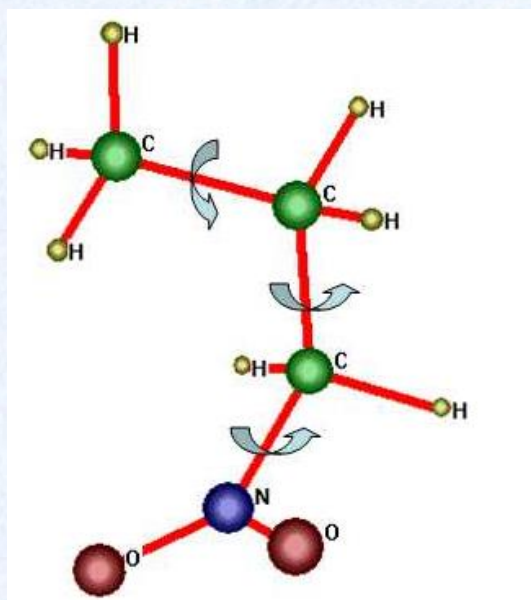

Was already used in 1970s; widely applied since 1990 (J. Laane, K. Hedberg, …).

Multi-Dimensional Large Amplitude Motion

- In many cases the low-energy molecular motions are dependent and numerous.
- Though it's still impossible to handle a general problem, recent advances in QC and computing facilities allowed treatment of up to 3 large-amplitude degrees of freedom.

Multiple rotors

Theoretical background of LAM

Original adiabatic perturbation theory:

| Electron | — | Nuclear | — | Rotation |

Modified version (for LAM):

| Electron | — | Nuclear "fast" | — | Nuclear "slow" | — | Rotation |

> 300   20 – 100   0.2 cm^{-1}
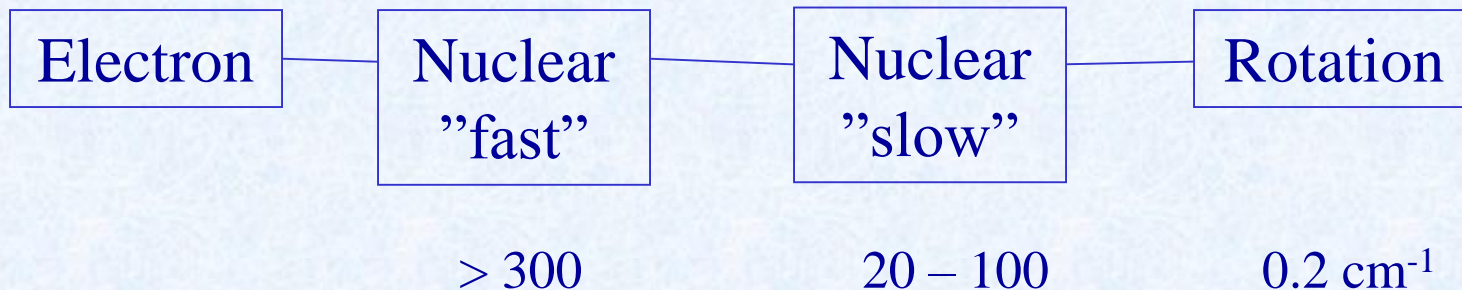
Adiabatic separation minimizes cross-term energy.

Hamiltonian in case of Large amplitude motion

$$\hat{H} = \frac{1}{2m}\sum_k \hat{\mathbf{p}}_k^2 + \frac{1}{2M}\left(\hat{\mathbf{P}} - \hat{\mathbf{P}}_e\right)^2 + \frac{1}{2}\hat{p}^*G\hat{p} + \frac{1}{2}\left(\hat{\pi} - \hat{b}\right)^* S\left(\hat{\pi} - \hat{b}\right) +$$

$$+ \frac{1}{2}\left(\hat{\mathbf{M}} - \hat{\mathbf{M}}_e - \hat{\mathbf{M}}_\rho - \hat{\mathbf{M}}_v\right)^* \sigma\left(\hat{\mathbf{M}} - \hat{\mathbf{M}}_e - \hat{\mathbf{M}}_\rho - \hat{\mathbf{M}}_v\right) + U + F(\rho, q)$$

where additional terms $\hat{\pi}$ and $\hat{\mathbf{M}}_\rho$ are momentum and angular momentum for large-amplitude coordinate(s), $\hat{b}$ describes interaction between small- and large-amplitude coordinates.

In the 1st order of perturbation theory

$$\hat{H}_q \psi(q, \rho) = E(\rho)\psi(q, \rho)$$
Small-amplitude

$$\hat{H}_\rho \Phi(\rho) = E\Phi(\rho)$$
Large-amplitude

Interaction between Large and Small coordinates

- **SA -> LA:**

Potential surface is changed:

$$V_v(\tau) = V_0(\tau) + \sum_{k=1}^{m} \hbar\omega_k(\tau)(v_k + \tfrac{1}{2})$$

May also be taken as a temperature average

$$V(\tau) = V_0(\tau) + \frac{1}{2}\sum_{k=1}^{m} \hbar\omega_k(\tau)\coth\frac{\hbar\omega_k(\tau)}{2kT}$$

- **LA->SA:**

Each conformer is a system with constraints, resulting in smaller number of degrees of freedom. Force constant matrices are not just reduced in size, they are modified.

Averaging formulas

1st order wavefunction

$$\Psi(\rho, q) = \Phi(\rho)\psi(q, \rho)$$

1st order probability density

$$P(\rho, q) = P_{\text{LAM}}(\rho)P_{\text{SAM}}(q, \rho)$$

Any average value (e. g. r_g or $sM(s)$

$$\langle x \rangle = \int P_{\text{LAM}}(\rho)d\rho \int P_{\text{SAM}}(q, \rho)x(q, \rho)d\rho = \int P_{\text{LAM}}(\rho)\langle x \rangle_q(\rho)d\rho$$
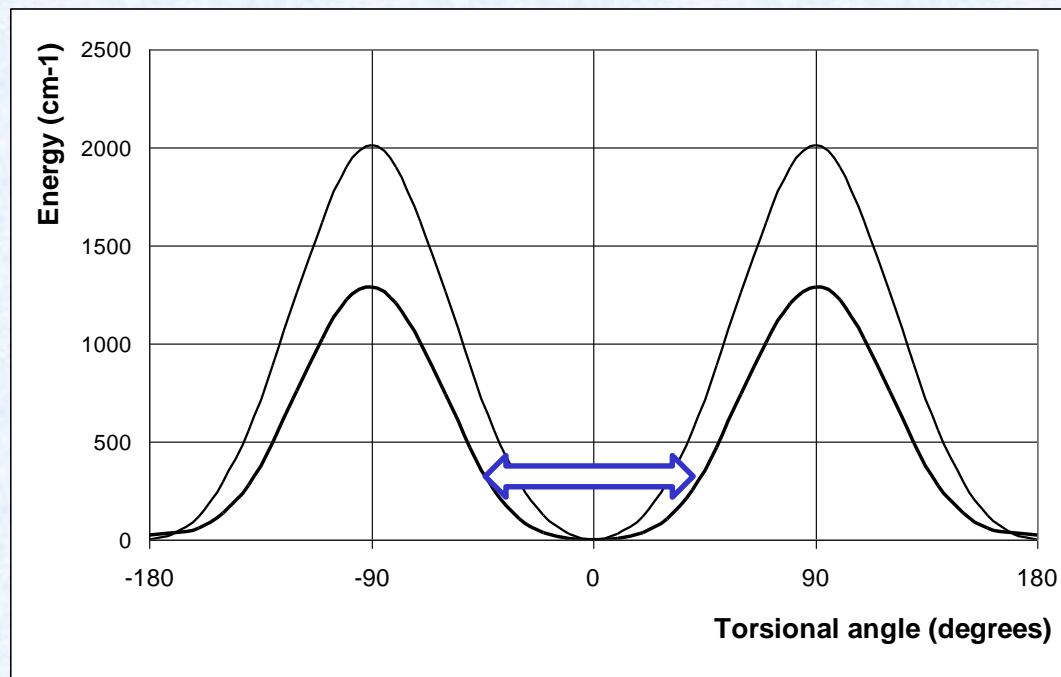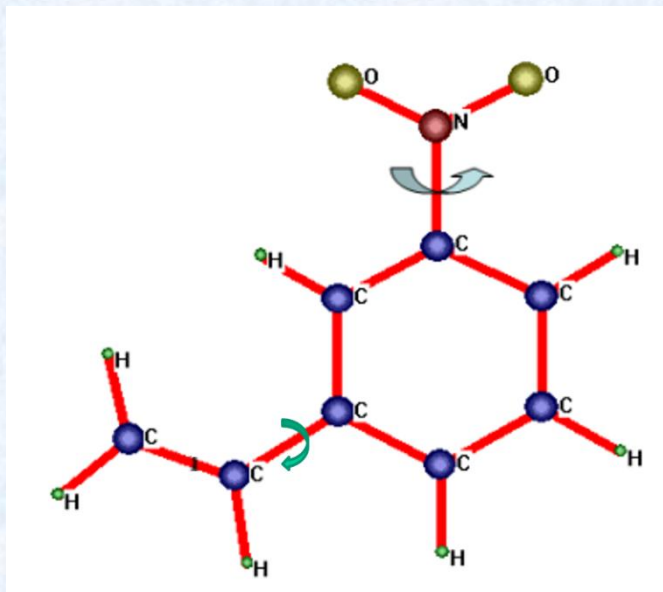
This provides the foundation for the procedure used in the pseudo-conformer approach.

Theoretically speaking, LAM approach is as well-defined as SA approach, provided that separation conditions are met (that is, 1st order approximation is dominating).
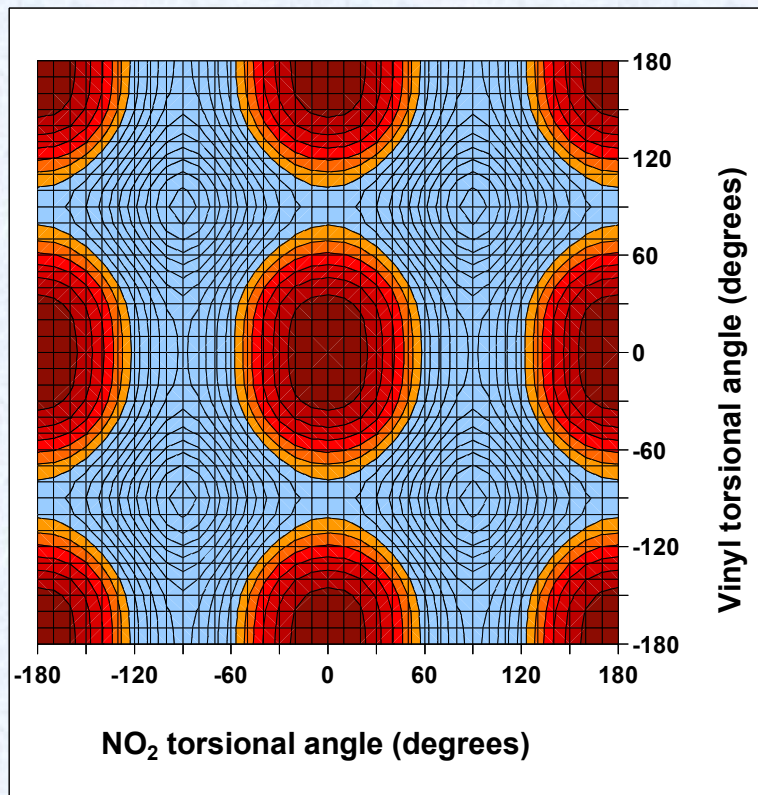
Examples of multi-LAM treatment

Little or no interaction between the rotors: 3-Nitrostyrene

2D Potential Energy Surface cross-sections: rotation of NO_2 group in syn-conformer (thin line) and vinyl group (thick line).

Examples of multi-LAM treatment

Little or no interaction between the rotors: 3-Nitrostyrene

NO$_2$ torsional angle (degrees)

Vinyl torsional angle (degrees)

2D Potential Surface

	10-deg. step	15-deg. step	30-deg. step
Total number	1296	576	144
Unique configurations	342	156	42
Populated configurations	122	58	16
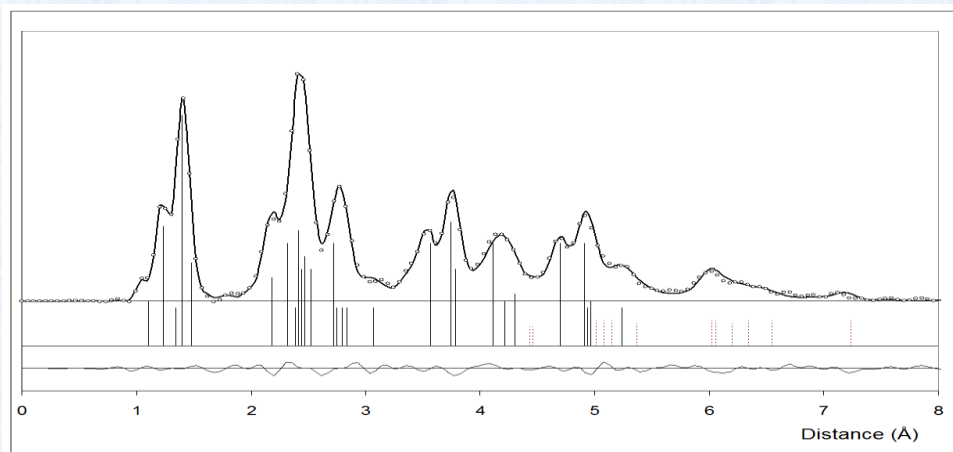
Distance (Å)

Examples of multi-LAM treatment

Significant interaction between the rotors: 1-Nitropropane
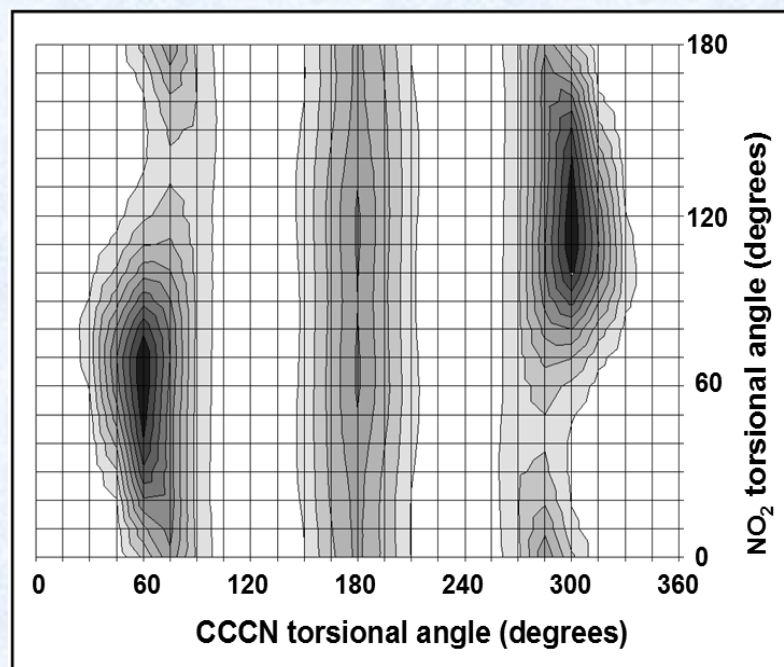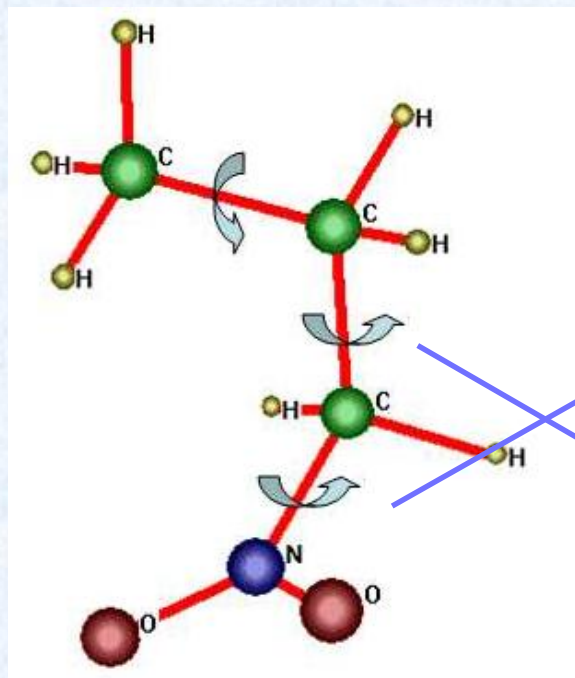
1. NO_2 group rotation (est. 30-50 cm^{-1})
2. CCCN torsion: results in two conformers (~117 cm^{-1})
3. CH_3 group rotation (~212 cm^{-1})

Examples of multi-LAM treatment

Significant interaction between the rotors: 1-Nitropropane

```
Pure terms
V[ 0] 1              =      2040.2335
V[ 2] cos(y)         =      1088.0240
V[ 5] cos(2x)        =       628.9567
V[ 8] cos(2y)        =       875.2758
V[18] cos(3y)        =      1806.4051
V[19] sin(3y)        =         4.7205

Mixed terms
V[14] cos(2x)*cos(y)  =       717.4381
V[23] sin(2x)*sin(y)  =      -342.6595
V[28] cos(2x)*cos(2y) =       470.0349
V[37] sin(2x)*sin(2y) =      -486.4706
V[46] cos(2x)*cos(3y) =       133.4013
V[55] sin(2x)*sin(3y) =      -277.4141
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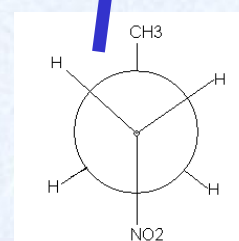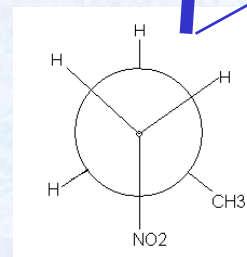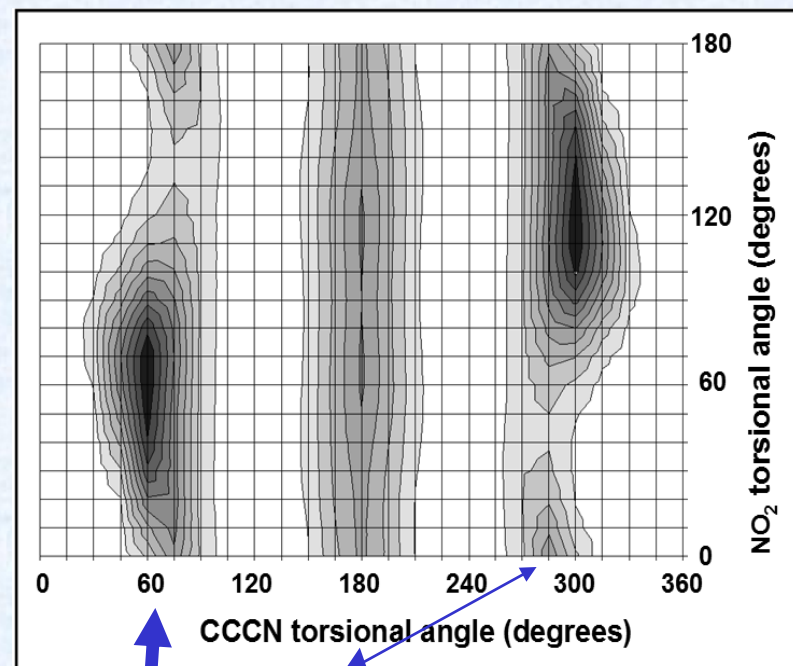

Fragment of potential function expansion
x = NO$_2$ torsional angle
y = CCCN torsional angle

Examples of multi-LAM treatment

Significant interaction between the rotors: 1-Nitropropane

Was originally treated as a mixture of 2 conformers, each with a single LAM coordinate.

Now trying 2D approach. The results are already superior to the first approach.

It's tempting to see whether account for CH_3 rotation (as a LAM) will make noticeable difference.

Need more advanced QC calculations.

Features and problems of multi-LAM treatment

Large number of pseudo-conformers to calculate

For each configuration, we need a QC structure:

- 1D : 10 – 30 configurations are usually good
- 2D: 100 – 1000 unique configurations
- 3D: 1000 – 10000 configurations

Quantum Chemistry becomes expensive

- Have to use lower levels of quantum-chemical calculation because of huge number of conformers.
- Often only calculations on the levels MP2(full)/cc-pVTZ and B3LYP/6-311+G* are feasible, and that's too weak.

Features and problems of multi-LAM treatment
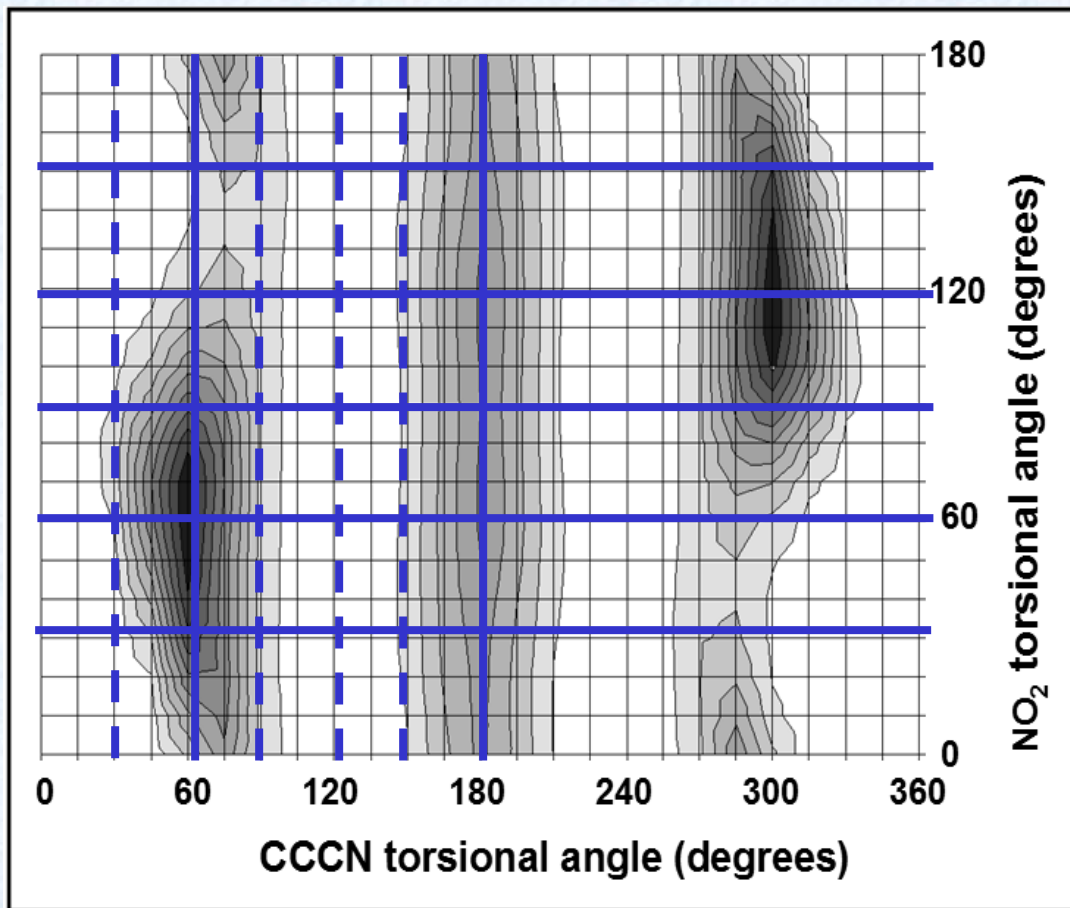
For this molecule, 30-degree grid is too rough, at least by CCCN angle.

Features and problems of multi-LAM treatment

Interpolation procedures

- Interpolate configuration geometries and potential surface, create new pseudo-conformers – more accurate (and expensive)
- Calculate sM(s) at rough grid, then interpolate it to the dense grid – simple and often sufficiently accurate

Force Matrix interpolation

Quadratic and cubic force constants are usually calculated only in a subset of the large grid. Then all elements are interpolated to the rest of the grid.

High density area

Multi-dimensional Shroedinger's Equation

$$\hat{H}_v \Psi = -\frac{\hbar^2}{2} \sum_{kl} \frac{\partial}{\partial \tau_k} G(\tau) \frac{\partial}{\partial \tau_l} \Psi + V(\tau)\Psi = E\Psi$$

- 1D case : can easily solve on a uniform grid (100-200 points).
- 2D-3D: grids become too large.

Alternative way: introduce basis and expand.

However, number of basis functions is still too large (grows as N^M where M is number of coordinates).
In both cases, should expect 10^4 to 10^6 matrix size. Need to use special procedures for sparse matrices (Lanczos algorithm and its modifications).

Features and problems of multi-LAM treatment

Multi-dimensional Shroedinger's Equation

Simplifications to make life easier:

- Don't need to solve equation at all when energy levels are not needed (no comparison with spectra).
- In case of weakly interacting coordinates, may use 1D solutions and apply 1st order perturbation corrections.

3-Nitrosyrene example: represent PES as

$$V(x, y) = V_1(x) + V_2(y) + v(x, y) + \text{const}$$

Mixed term responsible for interactions $v(x,y)$ does not exceed 20 cm^{-1} in the whole range of parameters, and is under 10 cm-1 in the most populated areas.

Features and problems of multi-LAM treatment

Summary:

- Theoretical background is sufficiently well established, and applicability limits may be evaluated.
- There's no big difference in general processing procedure compared to 1D LAM case.
- However, calculation technique is by far more complex.

There remains a question: when this procedure is worth the troubles.

Why multi-LAM treatment has sense?

Cannot fit experimental data with reasonable accuracy (or amplitudes don't fit spectroscopy data, or fitted configuration has unexpected symmetry, etc.)?

What we usually hear (and say)?

1. May happen due to anharmonicity. If we account for it (using 2^{nd}-3^{rd}-4^{th} order), it will be better.
2. Some motions may be too large to be described by the small-amplitude model. If we described it better, will fit.
3. The basics are wrong (non-adiabatic effects, etc.). This can often be excluded.
4. Experimental data may contain noticeable systematic error.
5. …

Using complex methods, we can answer at least some questions.

Why multi-LAM treatment has sense?

Used pseudo-conformer model but it did not help.

What we usually hear (and say)?

1. It's oversimplified and does not have solid theoretical background.
2. We may lose some aspects of Small-to-Large coordinate interaction.
3. We take only one LAM but there are other floppy deformations.
4. The rest: see previous page.

Again, we can answer the questions (1) – (3).

But probably the main reasons are…

Why multi-LAM treatment has sense?

It's interesting.

To what extent can we go in modeling and understanding molecular dynamics?

It's new.

Multi-LAM approach has not yet been used in GED.

It's a challenge

Multi-LAM approach is associated with non-trivial technical problems and requires significant effort.

Acknowledgements

Thanks for your attention!