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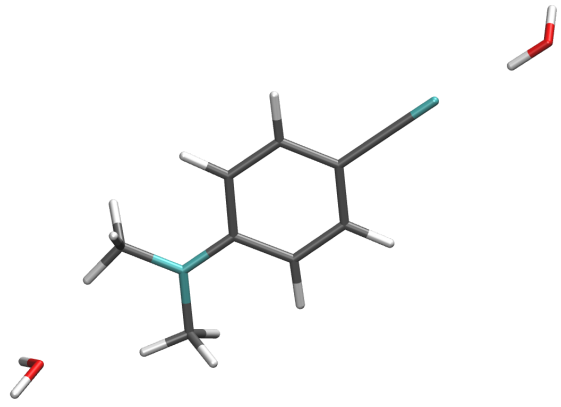
Chemistry Light & Dynamics

Quantum trajectories (DD-vMCG) for DMABN non-adiabatic dynamics

Sandra Gómez

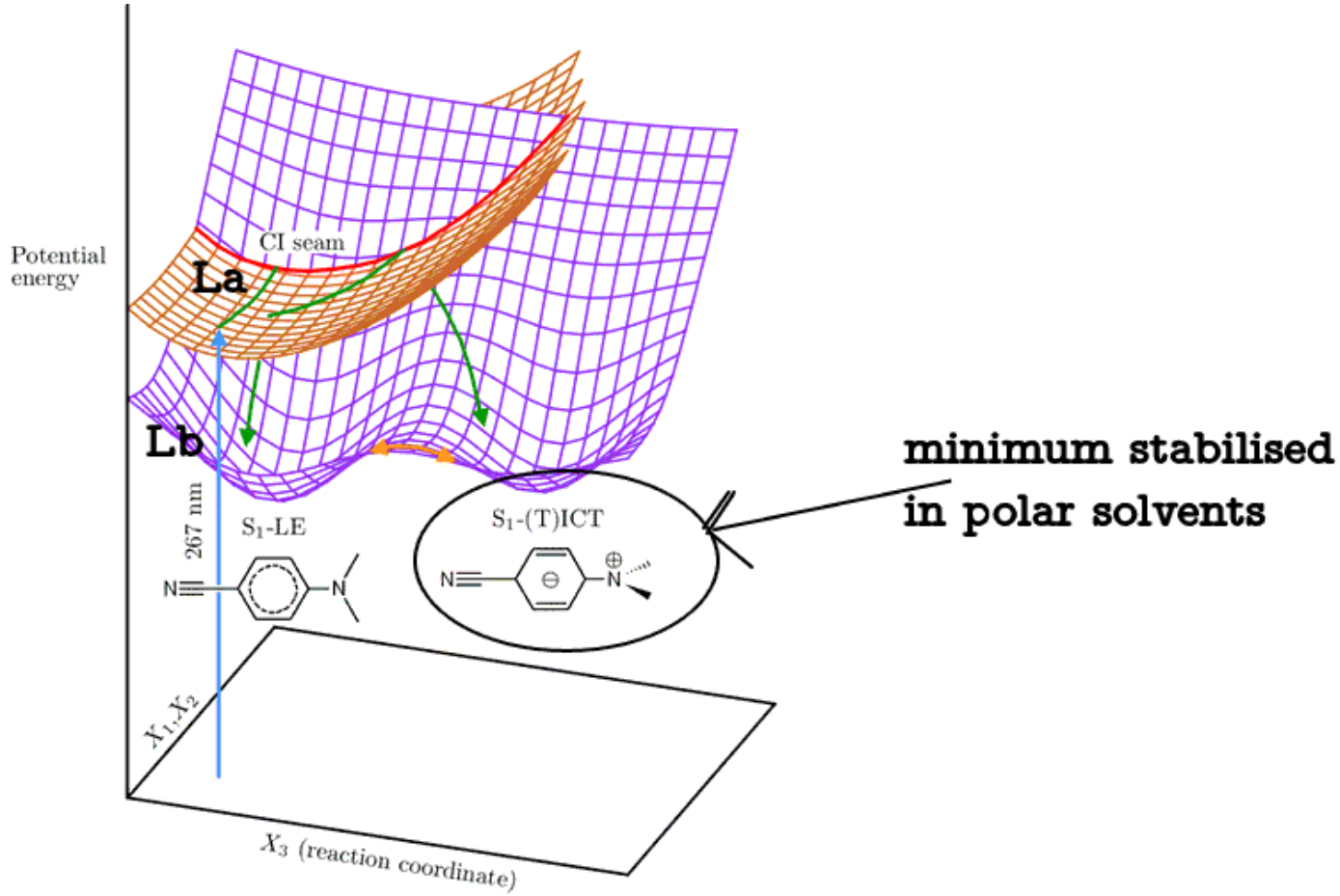
Virtual International Seminar on Theoretical Advancements

May 12, 2021



Why is DMABN interesting?

presents double fluorescence - that does not happen in gas phase



M. A. Kochman, A. Tajti, C. A. Morrison and R. J. D. Miller, J. Chem. Theory Comput. 2015, 11, 1118-1128

Experimental evidence - we went to the lab!

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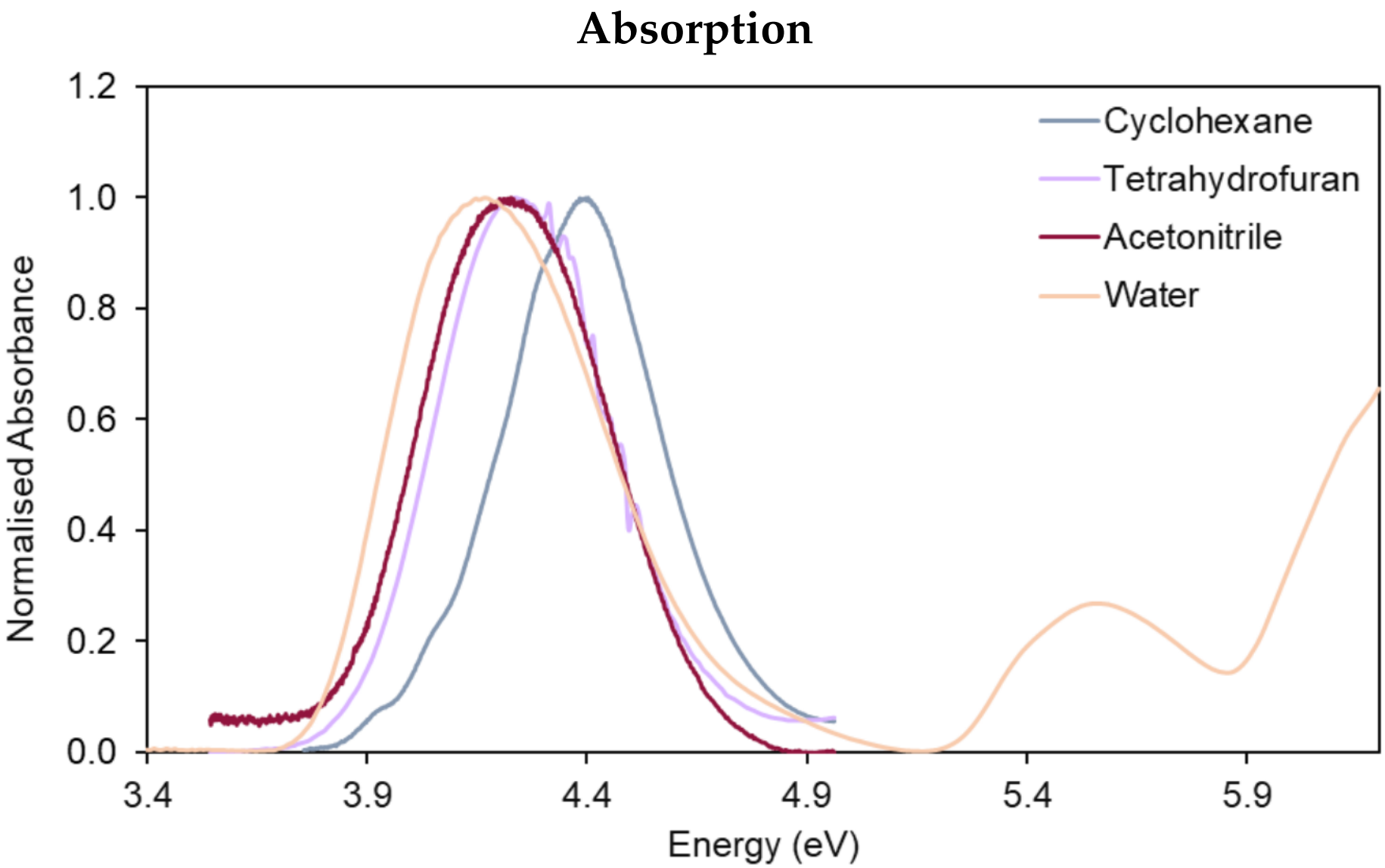

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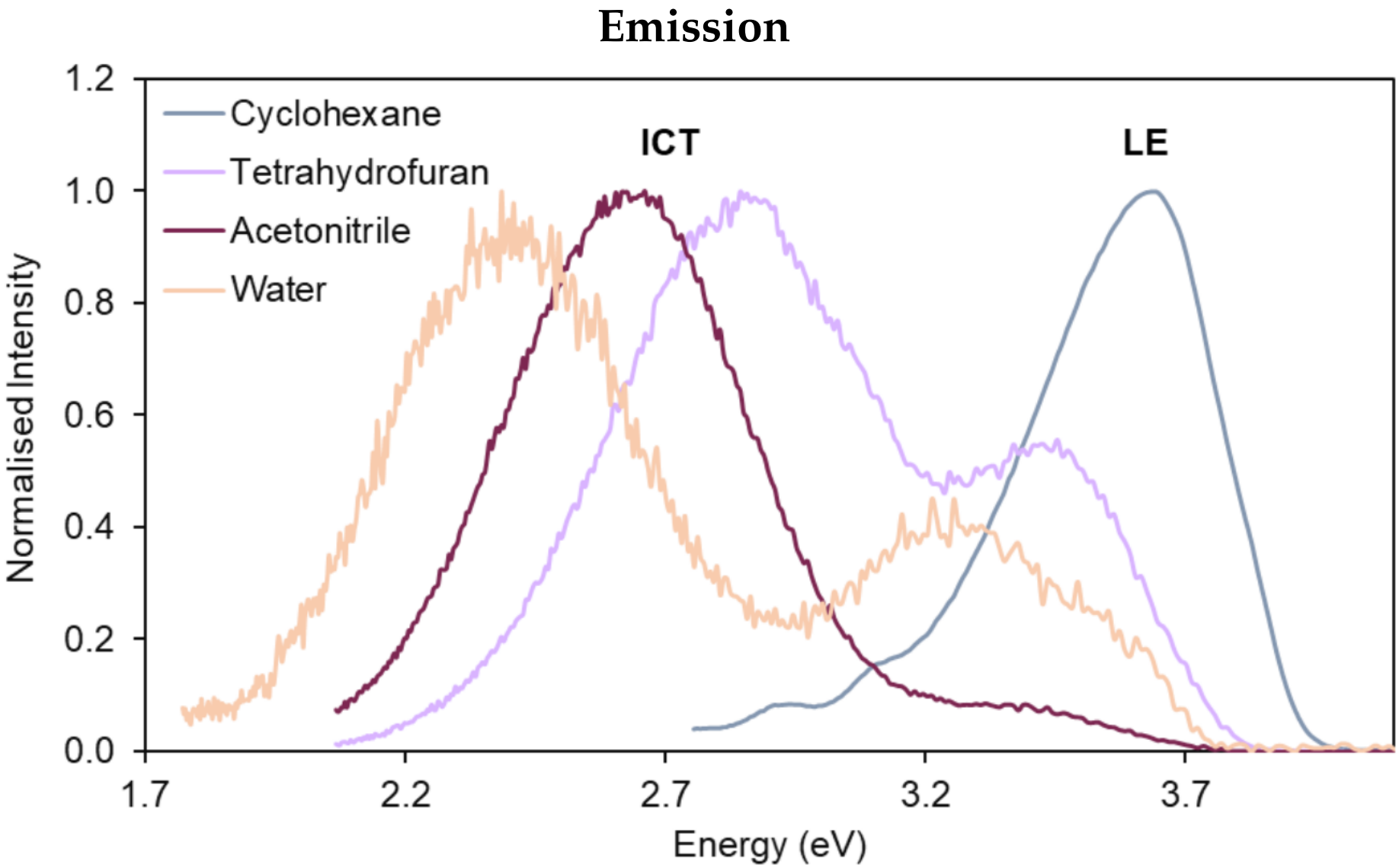

Back to work - no more playing

* frame from the film 300

Questions we would like to answer

- How is the geometry of ICT state minimum? torsionated?
- How/when is it formed?
- How the different solvents (gas/THF/acetoN/water) affect this?

- Can we theoretically predict the absorption and emission spectra in the different solvents?

Electronic Structure results - Esra's master thesis

- Benchmark TDDFT scans vs CASPT2/EOM-CCSD in gas phase
- Benchmark of many TDDFT functionals and basis sets in solution
- Structure optimisations, LE and ICT in 4 diff solvents

Solvent	Solvent Method	Basis Set	Absorption		Emission	
			^1L_b	^1L_a	LE	CT
Gas		cc-pVDZ	4.86	5.23	4.51	3.02
Tetrahydrofuran	PCM	cc-pVDZ	4.72	4.79	4.27	3.32
	Two explicit solvent molecules + PCM	cc-pVDZ	4.69 (4.58)	4.73 (4.63)	4.21	2.95
	Two explicit solvent molecules	cc-pVDZ	4.76 (4.64)	4.97 (4.88)		
	One explicit solvent molecule + PCM	cc-pVDZ	4.73 (4.60)	4.77 (4.67)		
	One explicit solvent molecule	cc-pVDZ	4.81 (4.68)	5.05 (4.95)		
Acetonitrile	PCM	cc-pVDZ	4.72	4.78	4.19	3.28
	Two explicit solvent molecules + PCM	cc-pVDZ	4.71 (4.59)	4.74 (4.62)	4.16	3.21
	Two explicit solvent molecules	cc-pVDZ	4.77 (4.63)	4.97 (4.86)		
	One explicit solvent molecule + PCM	cc-pVDZ	4.73 (4.60)	4.75 (4.63)		
	One explicit solvent molecule	cc-pVDZ	4.82 (4.69)	5.03 (4.93)		
Water	PCM	cc-pVDZ	4.72	4.78	4.18	3.27
	Two explicit solvent molecules + PCM	cc-pVDZ	4.71 (4.59)	4.71 (4.59)	4.12 (4.00)	3.15 (3.14)
	Two explicit solvent molecules	aug-cc-pVDZ	4.64	4.88	4.34	3.28

Next: non-adiabatic dynamics with TDDFT/wB97X/cc-pvDZ

DMABN dynamics on the Literature

Paper	Dyn Method	QC Method	InitConds	phase
Lan2015	FSSH	TDDFT/CAM-B3LYP/6-31G*	50 traj / Wigner / from S2	gas
Kochman2015	FSSH	ADC(2)/cc-pvDZ	24 traj / Wigner / from S2	gas
Martinez2016	AIMS	LR-TDDFT/wPE/6-31G	21 traj / Wigner / from S2	gas
Subotnik2017	A-FSSH	TDDFT/ωB97X/cc-pvDZ	200 traj /AIMD / from S2	gas/MECN
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Paper	S2→S1 time	torsion needed?	ICT detected?
Lan2015	80 fs	X	X
Kochman2015	25 fs	X	√ 500fs
Martinez2016	50 fs	X	√ S1 dyn → 90°torsion at 1ps
Subotnik2017	50fs	X	X
Durbeej2020	30 fs	X	√ in water, 1ps

- solvent does not influence the early dynamics
- ICT happens on the S1 BO surface at at least 500 fs

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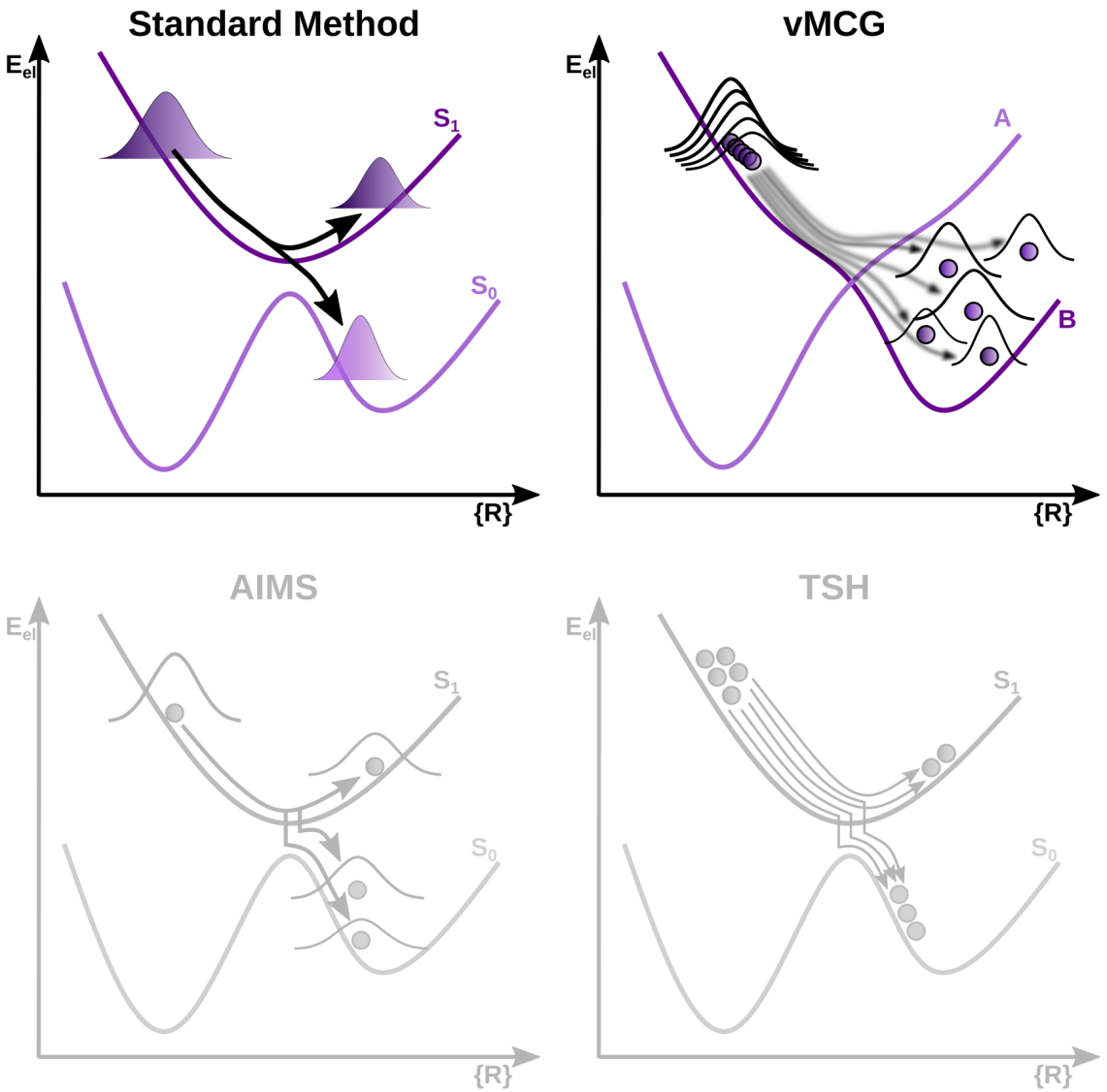

Credit: Lea Ibele

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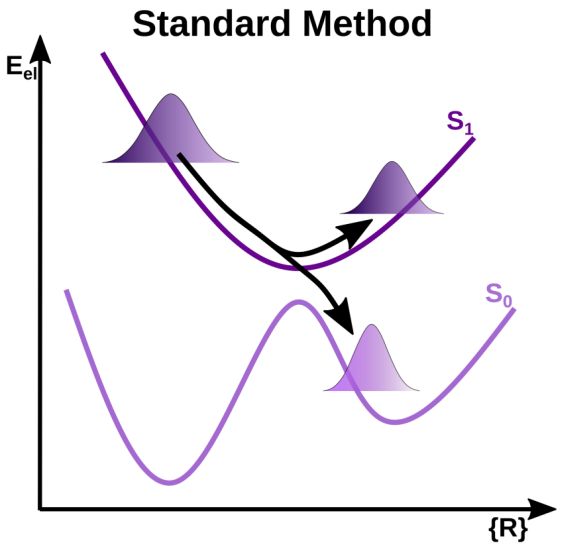

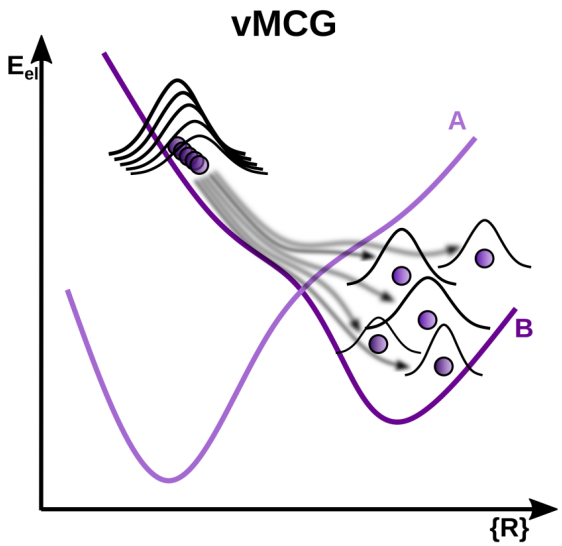

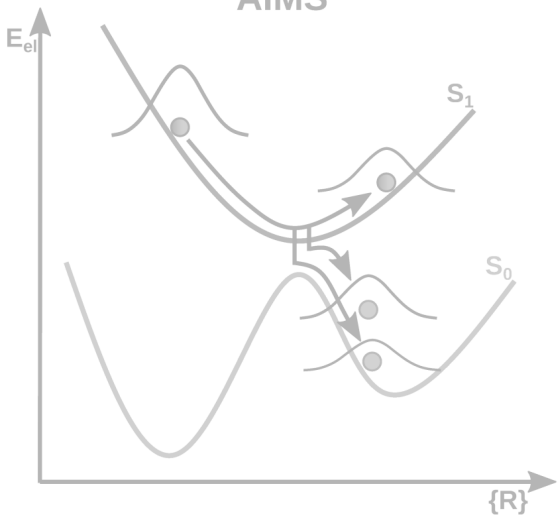

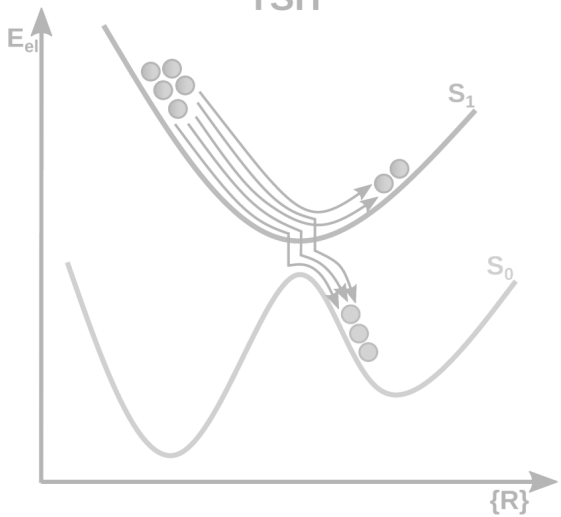

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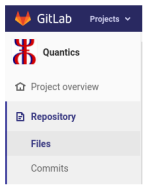
QUANTICS

A suite of programs for molecular QUANTum dynamICS simulations.



G.W. Richings, I. Polyak, K.E. Spinlove, G.A. Worth, I. Burghardt & B. Lasorne
International Reviews in Physical Chemistry, 34:2, 269-308 (2015)

G. Christopoulou, A. Freibert, and Graham A. Worth
J. Chem. Phys. 154, 124127 (2021)

What makes DD-vMCG special?

Variational trajectories

from the Dirac-Frenkel variational principle:

$$i\dot{A}_j = \sum_{lm} [S_{jl}]^{-1}(H_{lm} - i\tau_{lm})A_m,$$

$$i\dot{\mathbf{\Lambda}} = \boldsymbol{X} + \boldsymbol{C}^{-1}\boldsymbol{Y}_R$$

optimal set of gaussian parameters and coefficients

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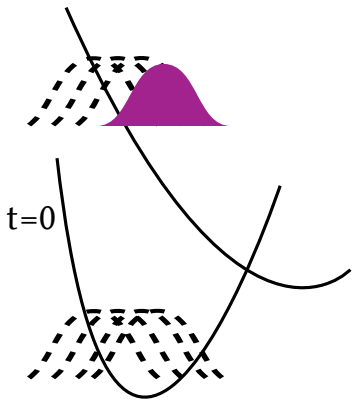

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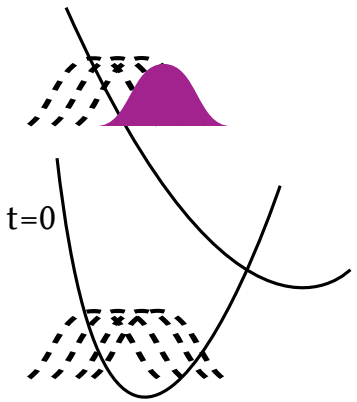

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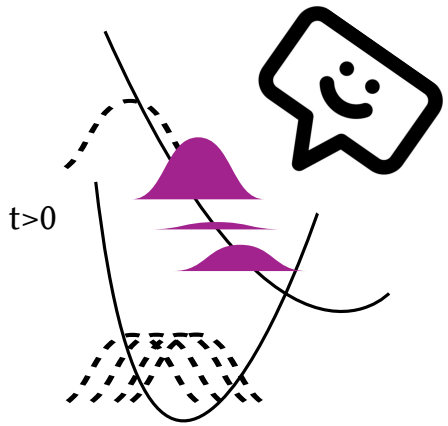
Not adaptive nor independent gaussian basis



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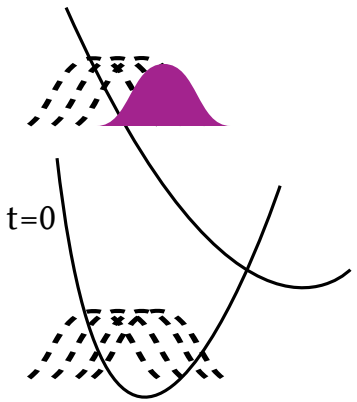

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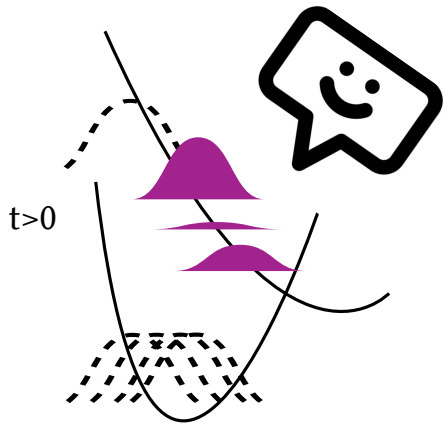
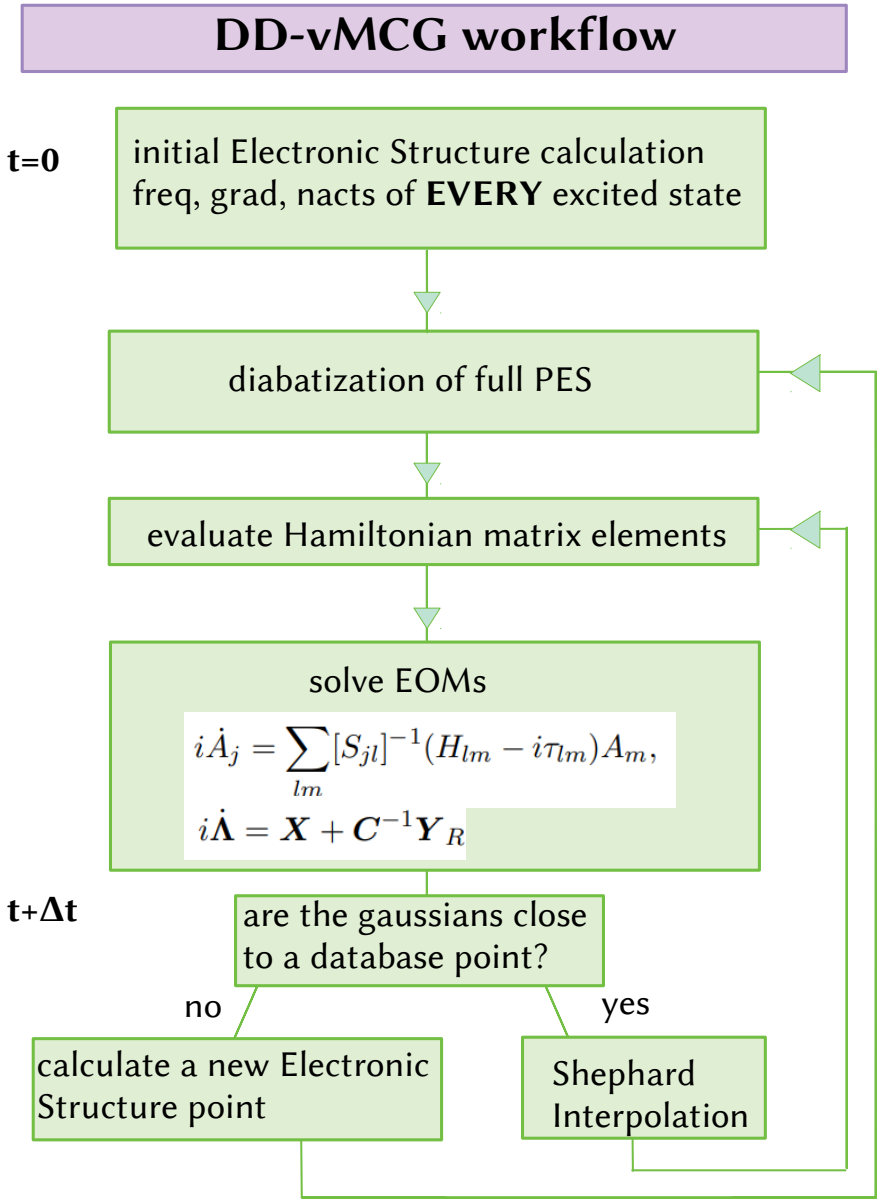


Database of Electronic Structure points

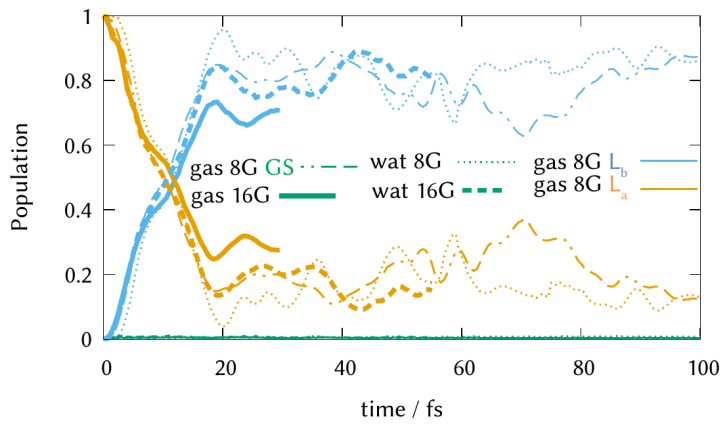
- No need to repeat time-consuming QC calculations
- Interpolation between points, Hessian Update
- Allows faster convergence towards number of gaussians

How does it work in practice?



Analysis tools applied to DMABN dynamics

diabatic populations



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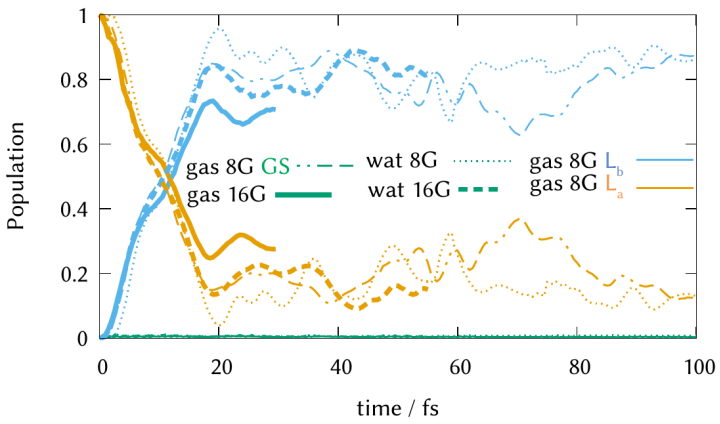
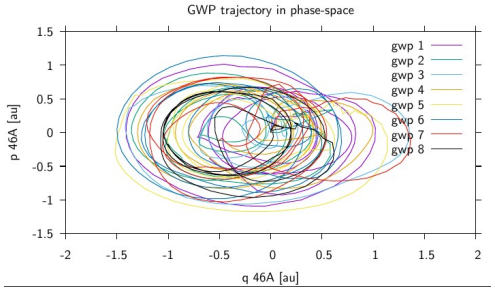
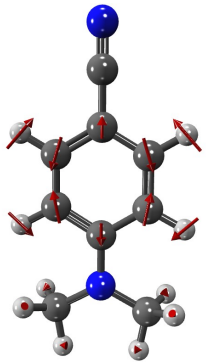


Evolution of gaussian centers in normal mode basis



we can still think in symmetry terms!



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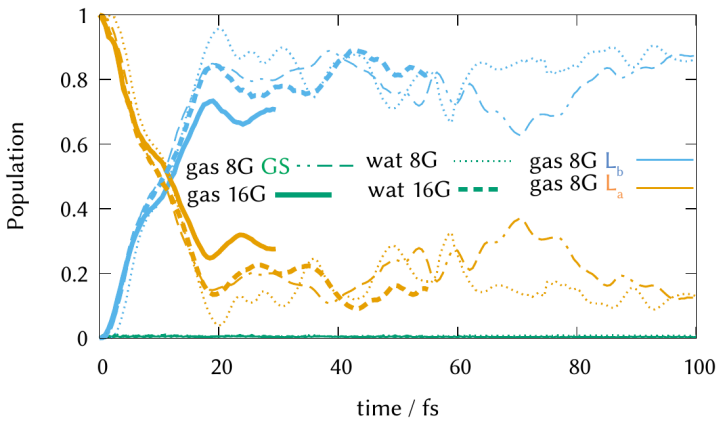

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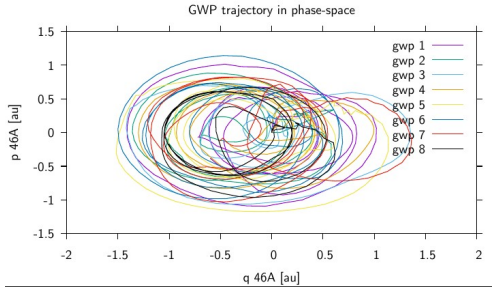

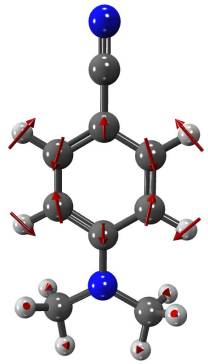

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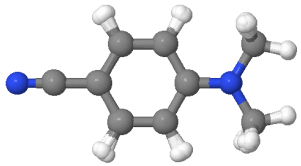
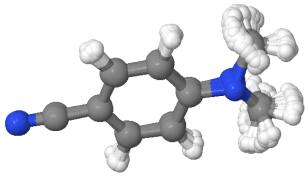
molecular movies



200 frames, fairly harmonic movement

Database geometries



78 points for gas phase simulation

Analysis tools applied to DMABN dynamics

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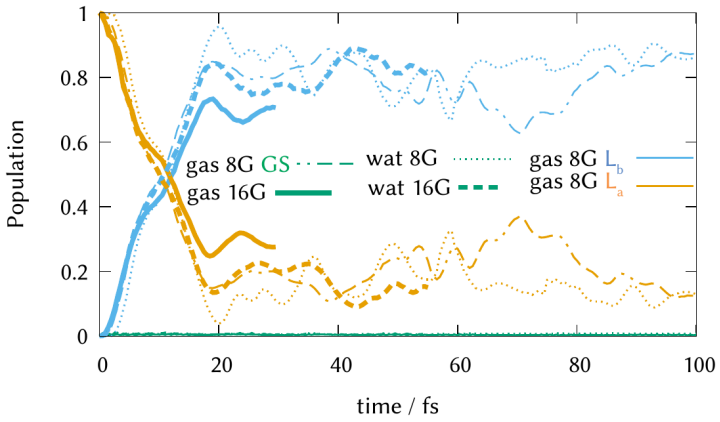

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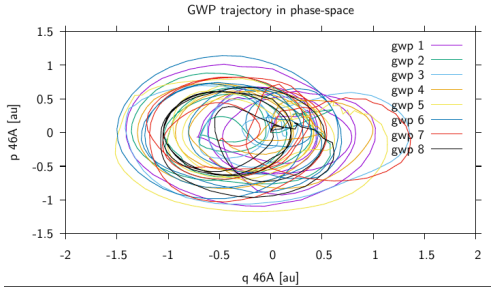

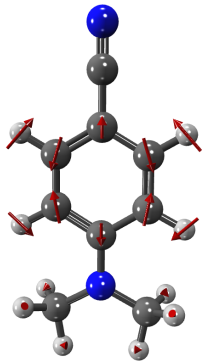

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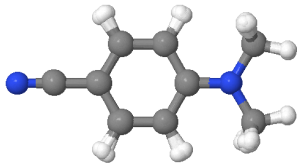

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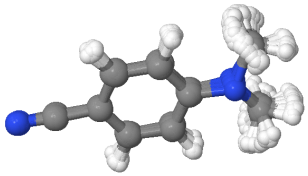
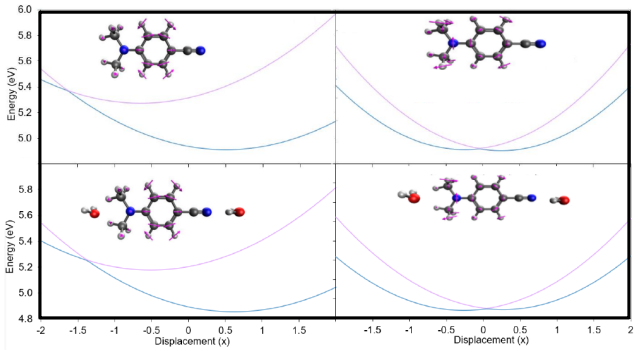


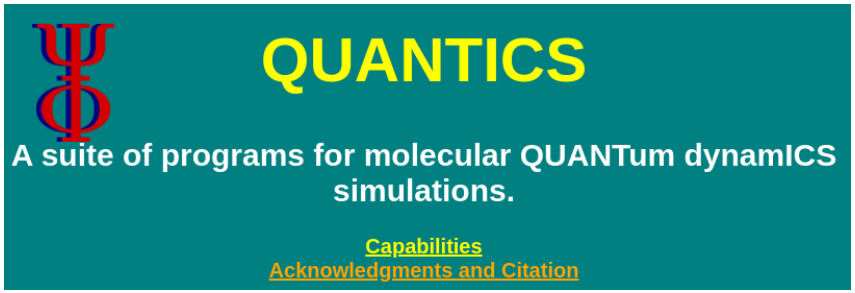
78 points for gas phase simulation

taking a look at full dimensional PES



Summary

- Theoreticians can measure their own spectra
- DD-vMCG can reproduce early non-adiabatic dynamics results in DMABN
- slight differences in gas/water



- Quantics is a very powerful tool to run and analyse on-the-fly dynamics

Acknowledgements

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UCL Chemistry Light & Dynamics

EPSRC Engineering and Physical Sciences Research Council