FULL-DIMENSIONAL AMMONIA VIBRATIONAL SPECTRUM FROM A HANDFUL OF CLASSICAL TRAJECTORIES

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The accurate description of quantum properties in real molecules is a major computational task, due to the growing efforts required as the number of degrees of freedom of the system increases. Different semiclassical methods have been adopted in the attempt to gather quantum properties from computationally cheap classical-trajectories simulations. However, issues related to possible chaotic behavior and classical integrator instability at long simulation times, together with large number of classical trajectories required, often limit the success of basic semiclassical approaches to model systems.

In the present work, we demonstrate that the multidimensional double well full vibrational spectrum, including tunnel splitting, can be described quite accurately by generating only 8 classical trajectories if Multi Coherent States Time Averaging SemiClassical Initial Value Representation (MC-TA-SCIVR) is used [**1-3**]. The first promising results are obtained on a 1D double-well potential aimed at describing the umbrella motion in ammonia; then, the full-dimensional vibrational spectrum of ammonia is presented, computed on both a high-level fitted PES and ab-initio on-the-fly simulations.

For the first time in classical-trajectories based methods, both tunnel splitting amplitudes and quantum vibrational frequencies are simultaneously reported. Moreover, the exiguous number of trajectories needed makes the present approach reliable for ab-initio on-the-fly approaches, thus avoiding the request for multidimensional PES calculations.

Theoretical definition of the quantum vibrational spectrum — 1

Vibrational spectral density

$$I(E) = \langle\chi|\delta(\hat{H}-E)|\chi\rangle = \sum_n |\langle\chi|\psi_n\rangle|^2\delta(E-E_n)$$

$$I(E) = \frac{Re}{\pi\hbar}\int_0^\infty \langle\chi|e^{-i\hat{H}t/\hbar}|\chi\rangle e^{iEt/\hbar}\,dt$$

The SemiClassical Initial Value Representation (SC-IVR) approximates the quantum propagator by running classical trajectories from sampled initial conditions in phase space and calculating related quantities.

Semiclassical approximation to the propagator

$$\langle\chi|e^{-i\hat{H}t/\hbar}|\chi\rangle = \frac{1}{(2\pi\hbar)^F}\int d\mathbf{p}_0 d\mathbf{q}_0\, C_t(\mathbf{p}_0,\mathbf{q}_0) e^{iS_t(\mathbf{p}_0,\mathbf{q}_0)/\hbar}\langle\chi|\mathbf{p}(t),\mathbf{q}(t)\rangle\langle\mathbf{p}_0,\mathbf{q}_0|\chi\rangle$$

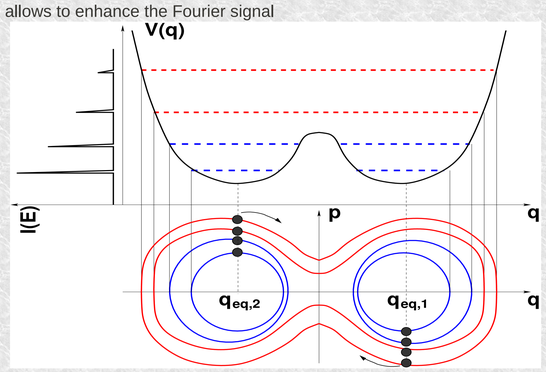
Time Averaging SCIVR [**4**] smoothes the oscillatory behavior of the integrand, permitting to slash the number of trajectories required. This feature is further enhanced by using the separable approximation for the prefactor, which leads to a positive-definite integrand.

$$I(E) = \frac{1}{(2\pi\hbar)^F}\frac{1}{2\pi\hbar T}\int d\mathbf{p}_0\int d\mathbf{q}_0 \left|\int_0^T dt\langle\chi|\mathbf{p}(t),\mathbf{q}(t)\rangle e^{i(S_t(\mathbf{p}_0,\mathbf{q}_0)+Et+\phi_t(\mathbf{p}_0,\mathbf{q}_0))/\hbar}\right|^2$$

$$\phi_t(\mathbf{p}_0,\mathbf{q}_0) = \text{phase}[C_t(\mathbf{p}_0,\mathbf{q}_0)]$$

Multi Coherent states Time Averaging SemiClassical Initial Value Representation (MC-TA-SCIVR) — 2

A sensible choice of the reference state and associated initial conditions allows to enhance the Fourier signal



The reference state is a sum over multiple coherent states at energies next to the vibrational frequency.

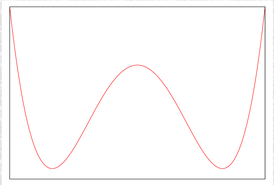
$$|\chi\rangle = \sum_{i=1}^{Nstates} |\mathbf{p}^i_{eq},\mathbf{q}^i_{eq}\rangle$$

Symmetry can be selected by appropriate linear combinations of states centered at symmetric points in phase space.

Duplication of states to choose simmetry

$$|\chi\rangle = \sum_{k=1}^{2Nstates}\prod_{j=1}^{F}\epsilon_k(j)|p^k_{eq,j},q^k_{eq,j}\rangle$$

A 1D double well potential model for the umbrella inversion motion in ammonia — 3



The barrier height is about 2000 cm^{-1} and the two equilibrium configurations may interchange via tunneling. Tunnel effect is also responsible for the overlap of eigenfunctions centered on different wells and the related tunnel splitting in the eigenvalues.

Lin's Potential [**5**]

$$V(Q) = \tfrac{1}{2}\omega^2Q^2 + A\exp(-\alpha Q^2)$$

The frequency of the wells depends on the frequency of the barrier

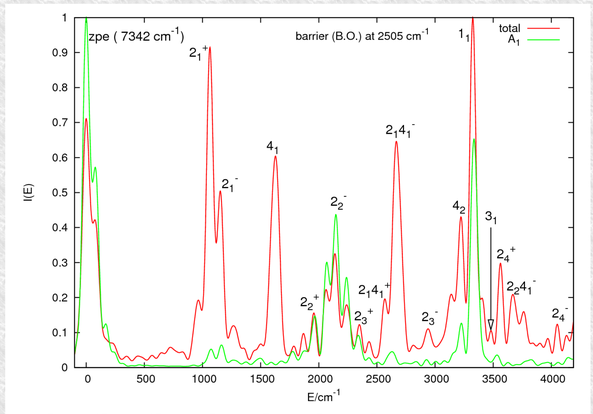
$$\omega_w = \omega\sqrt{2\rho}\quad \rho = \log(2\alpha A/\omega^2)$$

Quantum calculations have been performed on Lin's potential by means of the DVR technique. The calculated eigenenergies have been used as starting kinetic energies for classical trajectories in MC-TA-SCIVR simulations. A further semiclassical calculation has been performed starting from a harmonic distribution of the kinetic energies based on the frequency of the well.

	1 (g)	2 (u)	3 (g)	4 (u)	5 (g)	6 (u)	7 (g)	8 (u)
DVR	509.7	510.5	1442	1477	2111	2392	2894	3401
MC-TA (DVR)	515	515	1472	1534	2033	2358	2876	3401
MC-TA (Harm)	515	515	1471	1550	1997	2358	2867	3398

The results obtained via harmonic approximation look promising and not far off the mark. They represent a viable route to extend further investigations to full-dimensional ammonia.

Ammonia spectrum from ab-initio on-the-fly trajectories — 5

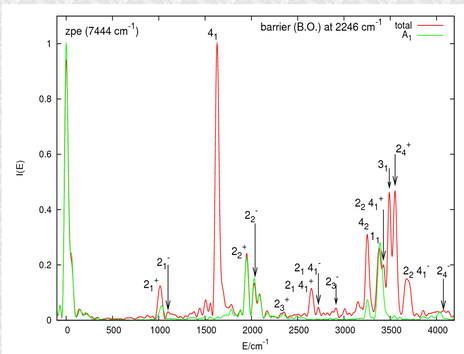


The results in section 4 have been obtained by running just 8 trajectories. This is an amount of molecular dynamics simulations small enough to permit to evaluate step by step along the trajectory the electronic potential energy, gradients and all the other quantities required by the implementation of the MC-TA-SCIVR approach. In this way, the determination of the full PES is no longer necessary, since the underlying electronic problem is solved only for nuclear configurations spanned by the actual nuclear motion.

For the above ammonia spectrum, DFT calculations have been performed using the B3LYP functional with cc-pvdz basis set. The red line represents the total spectrum, while the green one shows peaks of A_1 symmetry. Tunnel splitting is clearly detected also by the on-the-fly simulation and so are the most of the peaks. Differences in frequencies from the PES-based results in panel 4 are due to the different potential energy data.

Full-Dimensional ammonia vibrational spectrum — 4

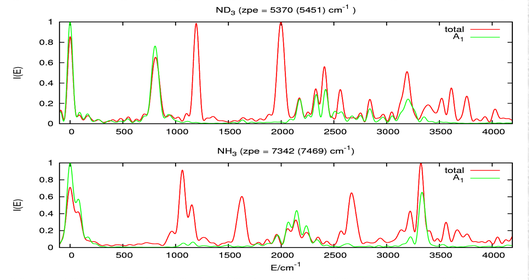
MC-TA-SCIVR has been applied to the full-dimensional problem. The classical dynamics was performed over Martin's high-accuracy PES for ammonia [**6**]. The initial conditions in phase space were chosen according to the harmonic approximation for the kinetic energies, based on the normal-mode frequency analysis at the equilibrium geometry. Just 8 trajectories, integrated for a total time of about 700 fs, were needed to resolve the spectrum.



Vibr.	Handy Morse V [**7**]	Kaledin [**8**]	This work [**9**]	Gatti (QM) [**10**]	Exp [**11**]
zpe	7444.8	7464	7442	7460.9	
A_1 $2_1(+)$	1019.3	1003	1014	1018.3	932.4
A_1 $2_1(-)$	1030.9		1100	1030.3	968.1
E $4_1(+)$	1637.5	1619	1630	1639.5	1626.3
E $4_1(-)$	1637.7		1630	1639.8	1627.3
A_1 $2_2(+)$	1811.0	2073	1950	1805.3	1597.5
A_1 $2_2(-)$	1975.9		2030	1975.5	1882.2
A_1 $2_3(+)$	2501.6		2352	2500.5	2384.2
E $2_14_1(+)$	2644.9	2612	2648	2645.7	2540.4
E $2_14_1(-)$	2660.1		2724	2661.8	2586.0
A_1 $2_3(-)$	2954.7		2914	2957.8	2895.6
A_1 $4_2(+)$	3232.7		3252	3244.7	3216.1
A_1 $4_2(-)$	3233.4		3252	3246.2	3217.8
E $4_2(+)$	3261.2	3239		3268.6	3240.4
E $4_2(-)$	3261.6			3269.1	3241.6
A_1 $1_1(+)$	3326.9	3389	3380	3369.8	3336.1
A_1 $1_1(-)$	3327.5		3380	3370.4	3337.1
E $2_24_1(+)$	3411.0		3426	3407.0	
E $3_1(+)$	3422.7		3490	3474.9	3444.0
E $3_1(-)$	3422.8	3449	3490	3474.9	3443.6
A_1 $2_4(+)$	3498.3		3552	3504.0	3448.0
E $2_24_1(-)$	3601.7	3597	3676	3604.9	
A_1 $2_4(-)$	4070.2		4074	4078.6	4045.0

The calculated spectrum and data demonstrate that both tunnel splitting in the umbrella inversion mode and localization of the peaks (i.e. the vibrational excitations) are determined with good accuracy, even when compared to the Lanzos-based quantum calculations by Gatti. VCI calculations by Handy and Carter were performed with a different implemenation of Martin's potential.

The reported tunnel splitting is not an artifact of the MC-TA-SCIVR procedure — 6



A comparison between the on-the-fly spectra for ammonia (lower panel) and deuterated ND_3 shows that the latter does not present the tunnel-splittings found for the former, as it is expected from the fact that tunnel effect is less effective for heavier atoms. It is possible to conclude, then, that the NH_3 splittings were not an artifact introduced by the MC-TA-SCIVR approach. The ND_3 spectrum has its peaks shifted to lower frequencies as well. The zpe values in parenthesis are the harmonic approximation values.

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