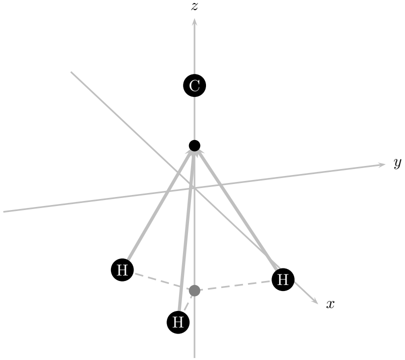
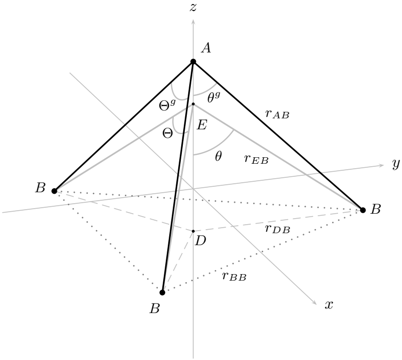
Discrete orthogonal basis sets in quantum chemistry: applications to large amplitude umbrella modes

Ana Carla P. Bitencourt[1], Mirco Ragni[2], Frederico V. Prudente[2], Patricia R. P. Barreto[3] and Andrea Lombardi[4]

[1]Universidade Federal do Recôncavo da Bahia (UFRB) - Brasil
[2]Universidade Federal da Bahia (UFBA) - Brasil
[3]Instituto Nacional de Pesquisas Espaciais (INPE) - Brasil
[4]Università di Perugia (UNIPG) - Italia

C_{3v} symmetry conservation





Coordinates and Hamiltonian for the AB_3 umbrella inversion problem.

In spherical coordinates, $\mathbf{x}_l = (r_l, \vartheta_l, \varphi_l)$:

$$
\begin{aligned}
\hat{T}(\mathbf{x}) &= -\frac{\hbar^2}{2m}\sum_{l=1}^{3}\left[\frac{1}{r_l^2}\frac{\partial}{\partial r_l} r_l^2 \frac{\partial}{\partial r_l} + \frac{1}{r_l^2}\Upsilon_l\right] , \\
\Upsilon_l &= \frac{1}{\sin\vartheta_l}\frac{\partial}{\partial \vartheta_l}\sin\vartheta_l \frac{\partial}{\partial \vartheta_l} + \frac{1}{\sin^2\vartheta_l}\frac{\partial^2}{\partial \varphi_l^2} ,
\end{aligned}
\tag{1}
$$

where $r_l = |\mathbf{x}_l| \geq 0$, $0 \leq \vartheta_l \leq \pi$, $0 \leq \varphi_l < 2\pi$.

Parametrization of the Radau-Smith vectors:

$$\begin{aligned} r_1 &= \rho\cos(\chi_2)\cos(\chi_1)\ , \\ r_2 &= \rho\cos(\chi_2)\sin(\chi_1)\ , \\ r_3 &= \rho\sin(\chi_2)\ , \end{aligned} \tag{2}$$

$$\begin{aligned} \vartheta_1 &= \theta\cos(\chi_4)\cos(\chi_3)\sqrt{3}\ , \\ \vartheta_2 &= \theta\cos(\chi_4)\sin(\chi_3)\sqrt{3}\ , \\ \vartheta_3 &= \theta\sin(\chi_4)\sqrt{3}\ . \end{aligned} \tag{3}$$

$$\begin{aligned} \varphi_1 &= \phi\cos(\chi_6)\cos(\chi_5)\ , \\ \varphi_2 &= \phi\cos(\chi_6)\sin(\chi_5)\ , \\ \varphi_3 &= \phi\sin(\chi_6)\ . \end{aligned} \tag{4}$$

The inversion angle:

$$\theta = \sqrt{\frac{\vartheta_1^2 + \vartheta_2^2 + \vartheta_3^2}{3}} \qquad 0 \le \theta \le \pi\ . \tag{5}$$

C_{3v} Hamiltonian

Kinetic energy operator:

$$\hat{T}(\mathbf{x}) = -\frac{\hbar^2}{2m}\left[\rho^{-8}\frac{\partial}{\partial\rho}\rho^8\frac{\partial}{\partial\rho} + \rho^{-2}\Delta(\Omega)\right] \ , \qquad (6)$$

where $\Delta(\Omega)$ is the so called "Grand Angular Operator" and Ω represents all the hyper-angles.

Reduced Hamiltonian (constraints):

$$\hat{H}(\rho,\theta) = \hat{T}(\rho,\theta) + V(\rho,\theta)$$

$$\hat{T}(\rho,\theta) = -\frac{\hbar^2}{2m}\left[\rho^{-8}\frac{\partial}{\partial\rho}\rho^8\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\Delta(\theta)\right]$$

$$\Delta(\theta) = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

Hyperquantization algorithm

Discrete analogous of the Legendre polynomials $P_l(\cos\theta)$ and

$$-\cos(\theta) = \frac{2\xi}{M+1} = x \ , \tag{7}$$

where $\xi = -M/2, -M/2+1, \ldots, M/2-1, M/2$ and M is the number of discretization intervals.

Principal characteristics

- Kinetic matrix tridiagonal
- Potential matrix diagonal
- No integrals need to be calculated

Applicability

Studied

- NH_3
- H_3O^+
- CH_3^+, CH_3, and CH_3^-

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Table: Geometry parameters, energies and normal mode frequencies (MP2 level) for the equilibrium and barrier configurations of NH_3, from MP2 and CCSD(T) level calculations. Values from the literature are between brackets. Assignment of normal modes of vibrations to our coordinates is reported.

MP2/aug-cc-pVQZ			
Geometry	Equilibrium	Barrier	Barrier Height (cm^{-1})
r_{NH} (Å)	1.008 (1.0124)	0.993	
θ^g (degrees)	68.240 (67.85)	90.000	
Energy (u.a.)	-56.50818360	-56.50062321	1659.314
Normal modes (cm^{-1})	Equilibrium	Barrier	Associated coordinate
A1, A2"	1028.67 (1022)	-826.46	θ
2E, 2E'	1673.19 (1691)	1585.69	χ_5, χ_6
A1, A1'	3527.02 (3506)	3664.49	ρ
2E, 2E'	3676.50 (3577)	3889.68	χ_1, χ_2
CCSD(T)/aug-cc-pVQZ level			
Geometry	Equilibrium	Barrier	Barrier Height (cm^{-1})
r_{NH} (Å)	1.013 (1.0124)	0.996	
θ^g (degrees)	67.733 (67.85)	90.000	
r_{EH} (Å)	1.000	0.996	
θ (degrees)	69.629	90.000	
Energy (u.a.)	-56.4957326	-56.4872261	1866.961 (1845.6±46.8)

Potential energy profiles as a function of the θ^g angle for the NH_3 system.

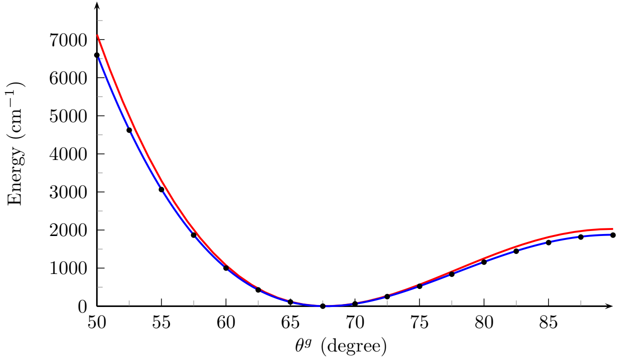


Figure: Dots represent the values optimized with respect to the hyperradius ρ. The blue curve is obtained for with ρ at the equilibrium value. The red curve is obtained setting r_{NH} at the equilibrium.

Table: Umbrella inversion energy levels of NH_3. An hyperquantization grid of 3601 interpolated points has been used.

	Our	Our-PES	Halonen *et al*	Exp.(Spirko)
GS^+	0.000	0.000	0.00	0.00
GS^-	1.257	1.258	0.96	0.793
ν_2^+	904.523	904.504	922.92	932.43
ν_2^-	956.521	956.527	964.74	968.12
$2\nu_2^+$	1545.695	1545.693	1577.97	1598.47
$2\nu_2^-$	1877.746	1877.792	1882.32	1882.18
$3\nu_2^+$	2388.918	2388.998	2387.96	2384.17
$3\nu_2^-$	2925.279	2925.404	2909.76	2895.61
$4\nu_2^+$	3512.634	3512.787	3485.55	
$4\nu_2^-$	4136.877	4137.072	4093.93	

Table: Umbrella inversion energy levels for the H_3O^+ system.

	Our-PES	Halonen *et al*	Exp.
GS^+	0.000	0.00	0.000
GS^-	59.196	52.29	55.3484
ν_2^+	584.979	588.31	581.18
ν_2^-	972.321	959.75	954.40
$2\nu_2^+$	1502.023	1482.12	1475.44
$2\nu_2^-$	2086.903	2056.61	
$3\nu_2^+$	2724.585	2683.15	
$3\nu_2^-$	3406.702	3352.54	
$4\nu_2^+$	4127.287		
$4\nu_2^-$	4882.156		

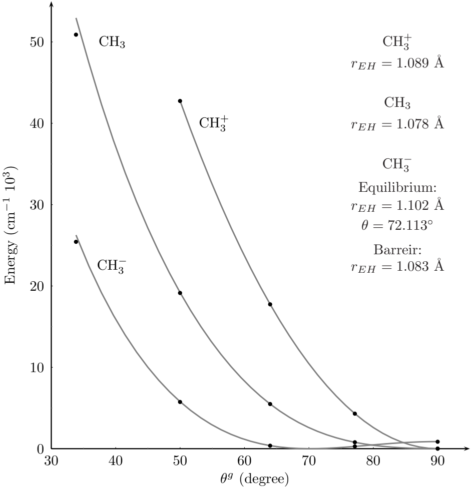


Figure: Umbrella inversion potential energy profiles of CH_3, CH_3^+, and CH_3^- systems.

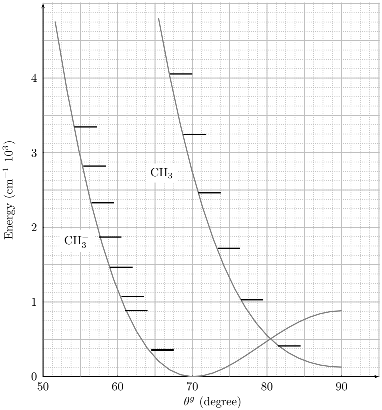
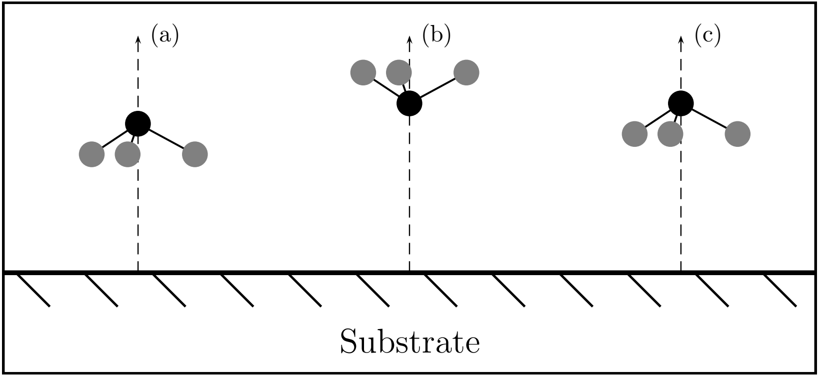


Figure: Umbrella energy levels of CH_3 and CH_3^- systems. The energy of the minimum configuration of the CH_3 radical is above 127.515 cm^{-1} of that of the anion, which presents two near degenerate energy levels under the barrier.

Possible approach to the substrate



Time Evolution

Temporal evolution operator

$$\Psi(\theta, t) = \hat{\mathbf{S}}\Psi(\theta, 0) \qquad \hat{\mathbf{S}} = e^{-i\,t\,\hat{\mathbf{H}}/\hbar}$$

$$\Psi(\theta, 0) = \sum c_n \Theta_n(\theta)$$

Evolution shape

$$\Psi(\theta, t) = \sum_n e^{-iE_n t/\hbar} c_n \Theta_n(\theta)$$

Level distribution with the temperature

$$c_n^2 = \frac{e^{-\beta E_n}}{\sum_j e^{-\beta E_j}}$$

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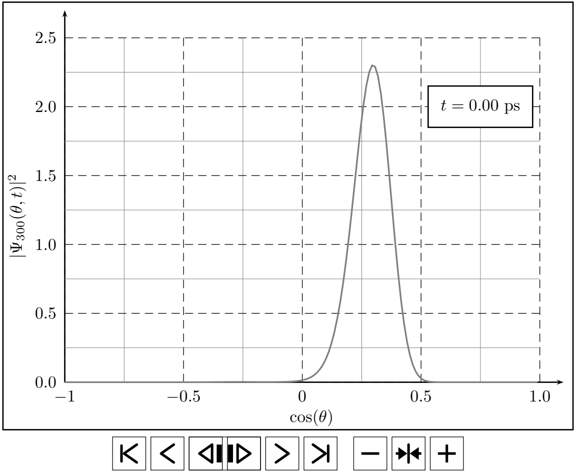
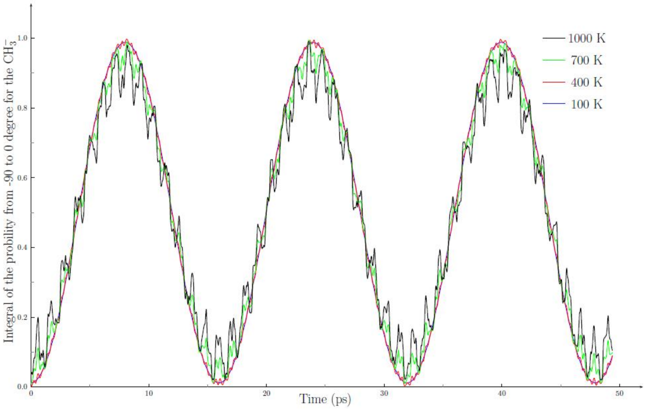
Time Evolution for the CH_3^-



Integral Time Evolution



CH_3^+, $CH_3\cdot$, and CH_3^-

	Temperatures (K)					
	100	200	300	400	500	1000
	Velocity of the CH_3 in km/s					
$v_z = (RT/m)$	0.235	0.333	0.407	0.470	0.526	0.744
$v = (3RT/m)$	0.407	0.576	0.705	0.815	0.911	1.288
	Distance ran in one umbrella inversion cycle (nm)					
CH_3^+ 148 fs	0.060	0.085	0.104	0.121	0.135	0.191
$CH_3\cdot$ 341 fs	0.139	0.196	0.241	0.278	0.311	0.439
CH_3^- 16.2 ps	6.598	9.332	11.429	13.197	14.755	20.866

J. Phys. Chem. A **2009**, *113*, 15355–15365 **15355**

Orthogonal Coordinates and Hyperquantization Algorithm. The NH_3 and H_3O^+ Umbrella Inversion Levels[†]

M. Ragni,[‡] A. Lombardi,[‡] P. R. Pereira Barreto,[§] and A. C. Peixoto Bitencourt[*,⊥]

Thank you.

FAPESB

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