

Computing spectra with an Eckart frame to refine and test a methane potential

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Calculating spectra is useful because it enables spectroscopists to

- verify the accuracy of or refine potential energy surfaces
- predict the position (and intensity) of unobserved transitions
- assign observed spectra

Spectroscopists often use a zeroth-order harmonic model and perturbation theory

- For low-lying levels of semi-rigid molecules it works pretty well.
- Methane vibrational levels in the Octad ($\sim 4000 \text{ cm}^{-1}$ above the ZPE) computed with fourth and sixth order perturbation theory differ by about 8 cm^{-1} .
- Most ab initio programs use second order perturbation theory.
- Nearly degenerate levels cause perturbation theory to break down.
- The density of states increases with energy.

For

- high-lying states
- molecules in which coupling and anharmonicity are important

one, instead, needs numerically accurate solutions to the Schroedinger equation

$$\hat{H}\psi_n = E_n\psi_n$$

How does one solve the Schrodinger equation ?

- represent wavefunctions with basis functions

$$\psi_n(\mathbf{r}, \boldsymbol{\theta}) = \sum_k c_k^n f_k(\mathbf{r}, \boldsymbol{\theta})$$

- compute eigenvalues and eigenvectors of the Hamiltonian matrix

Fundamental Recipe

$$\hat{K} + \hat{V} \rightarrow \hat{H} \xrightarrow{\text{basis}} \mathbf{H} \rightarrow \begin{matrix} \text{eigenvalues,} \\ \text{eigenvectors} \end{matrix} \rightarrow \begin{matrix} \text{energies,} \\ \text{wavefunctions} \end{matrix}$$

→ Spectrum

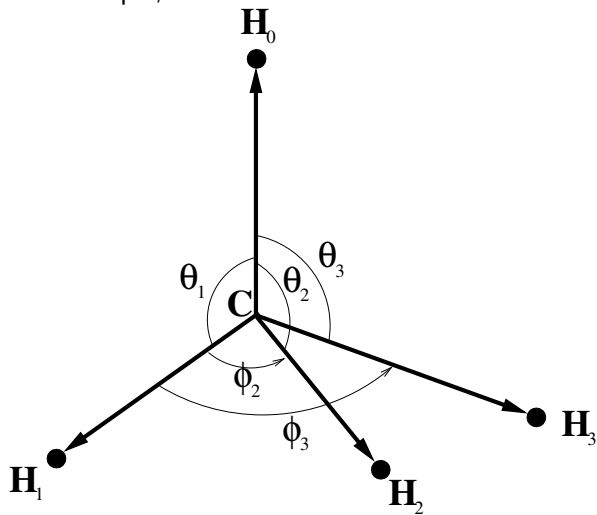
We want to be able to deal with large amplitude motion

Normal coordinates are not appropriate for molecules with large amplitude motion

For large amplitude motion it is best to :

- choose $N - 1$ vectors to describe the shape and orientation
- use the lengths of the vectors and the associated spherical polar angles as vibrational coordinates

For example,



Consider first the $J = 0$ problem

The general KEO is

$$T = T_s + T_b$$

with

$$T_s = - \sum_{k=0}^{N-2} \frac{1}{2\mu_k} \frac{\partial^2}{\partial r_k^2}$$

and

$$T_b = T_{b,\text{diag}} + T_{b,\text{off}} .$$

$$\begin{aligned}
T_{\text{b,diag}} &= [B_0(r_0) + B_1(r_1)] \left[-\frac{1}{\sin \theta_1} \frac{\partial}{\partial \theta_1} \sin \theta_1 \frac{\partial}{\partial \theta_1} + \frac{1}{\sin^2 \theta_1} L_z^2 \right] \\
&\quad + \sum_{k=2}^{N-2} [B_0(r_0) + B_k(r_k)] l_k^2 \\
&\quad + B_0(r_0) \left[2L_z^2 + 2 \sum_{k \neq k'=2}^{N-2} l_{kz} l_{k'z} \right] \\
T_{\text{b,off}} &= B_0(r_0) \left[(L_+) a_1^- + (L_-) a_1^+ + \sum_{k \neq k'=2}^{N-2} (l_{k+} l_{k'-} + l_{k-} l_{k'+}) \right]
\end{aligned}$$

A convenient basis is

$$f_{k_1, l_1, k_2, l_2, m_2 \dots} = \chi_{k_1}(r_1) \Theta_{l_1}^{m_1}(\theta_1) \chi_{k_2}(r_2) \Theta_{l_2}^{m_2}(\theta_2) \Phi_{m_2}(\phi_2) \dots$$

with $m_1 = -m_2 - m_3 - \dots$

In this basis

- there are simple equations for all KEO matrix elements
- singularities in the KEO cause no trouble.

Between 10 and 100 1-d functions required for each coordinate.

$\Rightarrow > 10^{3N-6}$ multi-d basis functions required.

The Hamiltonian matrix is

- too large to calculate
- too large to store in memory
- too large to diagonalise

How large is too large?

To calculate only the $J = 0$ levels of H_2O , one requires a $\sim 10^3 \times 10^3$ matrix, ~ 0.008 GB

Add a single atom :

to calculate only the $J = 0$ levels of CH_2O , one requires a $\sim 10^6 \times 10^6$ matrix, ~ 8000 GB

For methane, to calculate the $J = 0$ levels, one requires a $\sim 10^9 \times 10^9$ matrix, $\sim 8 \times 10^9$ GB

Lanczos Algorithm

$$\mathbf{H} = \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} \rightarrow \begin{pmatrix} \cdot & \cdot & 0 & 0 \\ \cdot & \cdot & \cdot & 0 \\ 0 & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & \cdot \end{pmatrix} = \mathbf{T}$$

- Among the eigenvalues of \mathbf{T} are eigenvalues of \mathbf{H}
- Eigenvectors of \mathbf{H} are obtained from those of \mathbf{T}

Limitations of a product basis

Even for $J = 0$ methane, a product basis calculation is large

$$|\alpha_0 \alpha_1 \alpha_2 \alpha_3\rangle |l_1 l_2 m_2 l_3 m_3\rangle$$

It would be necessary to use $\sim 20^9$ basis functions (4000 GB for one vector)!

Contracted basis functions

It is better to use products of eigenfunctions of reduced-dimension Hamiltonians.

E.g.,

$$H = H_{bend} + H_{stretch} + \Delta_{coupling}$$

$$H_{bend} b(\boldsymbol{\theta}) = E_b b(\boldsymbol{\theta})$$

$$H_{stretch} s(\mathbf{r}) = E_s s(\mathbf{r})$$

$s(\mathbf{r})b(\boldsymbol{\theta})$ is a contracted basis function.

A small number of the $s(\mathbf{r})b(\boldsymbol{\theta})$ are retained.

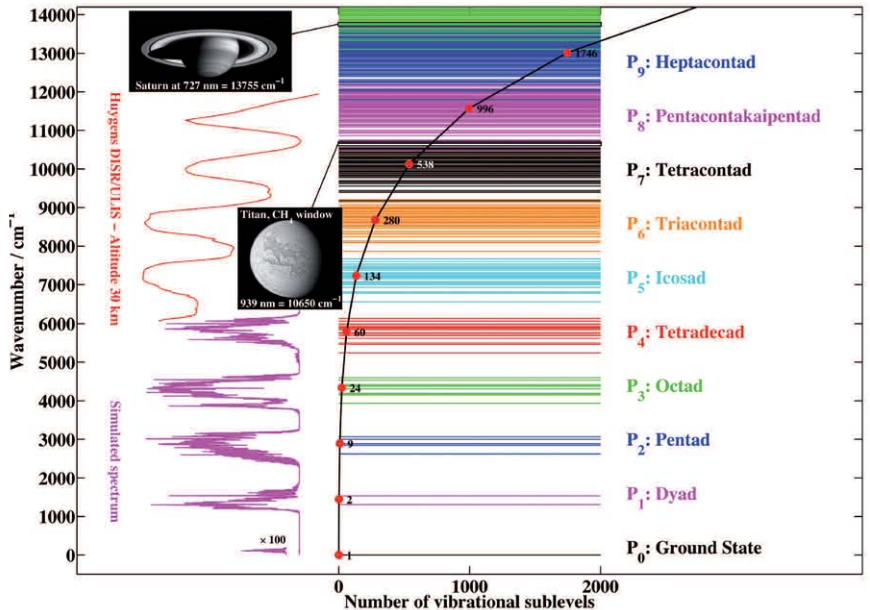
Basis	$l_{max} = m_{max}$	n_{bend}	E_b^{cut}	n_b	n_i	$n_{stretch}$	E_s^{cut}	n_s
Basis I	25	3.26M	8090	280	10	5049	20000	260

$$33 \times 10^9 \rightarrow 72 \times 10^3$$

reduction of six orders of magnitude

Methane is important

- A greenhouse gas
- Determining the chemical composition and physical conditions of atmospheres of Jupiter, Saturn, Uranus, Neptune, Titan, etc
- Modelling brown dwarfs



$$J > 0$$

If the molecule-fixed axes are attached to two vectors the KEO is still compact :

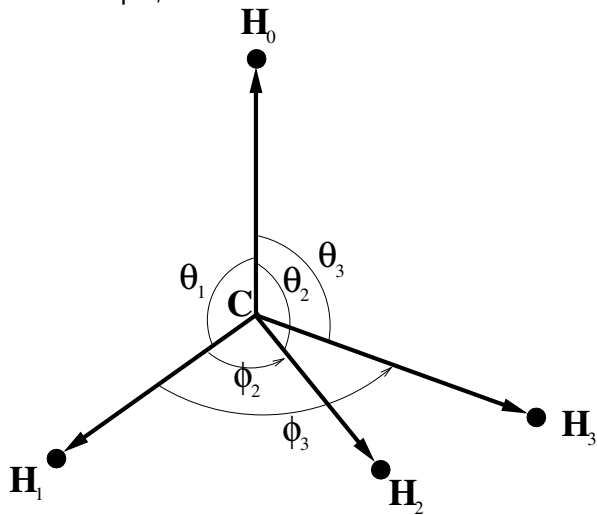
$$T = T_s + T_{\text{br}} + T_{\text{cor}}$$

with

$$T_{\text{br}} = T_{\text{br,diag}} + T_{\text{br,off}} .$$

$$\begin{aligned}
T_{\text{br,diag}} &= [B_0(r_0) + B_1(r_1)] \left[-\frac{1}{\sin \theta_1} \frac{\partial}{\partial \theta_1} \sin \theta_1 \frac{\partial}{\partial \theta_1} + \frac{1}{\sin^2 \theta_1} (J_z - L_z)^2 \right] \\
&\quad + \sum_{k=2}^{N-2} [B_0(r_0) + B_k(r_k)] l_k^2 \\
&\quad + B_0(r_0) \left[J^2 - 2(J_z - L_z)^2 - 2J_z(L_z) + 2 \sum_{k \neq k'=2}^{N-2} l_{kz} l_{k'z} \right] \\
T_{\text{br,off}} &= B_0(r_0) \left[(L_+) a_1^- + (L_-) a_1^+ + \sum_{k \neq k'=2}^{N-2} (l_{k+} l_{k'-} + l_{k-} l_{k'+}) \right] \\
T_{\text{cor}} &= -B_0(r_0) [J_-(a_1^+ + L_+) + J_+(a_1^- + L_-)]
\end{aligned}$$

For example,



$$f_{k_1, l_1, k_2, l_2, m_2 \dots, J, K, M} = \chi_{k_1}(r_1) \Theta_{l_1}^{m_1}(\theta_1) \chi_{k_2}(r_2) \Theta_{l_2}^{m_2}(\theta_2) \Phi_{m_2}(\phi_2) \cdots \\ \times D_{MK}^{J*}(\alpha, \beta, \gamma)$$

with $m_1 = K - m_2 - m_3 - \cdots$

With $m_1 = K - m_2 - m_3 - \dots$

- all matrix elements of the KEO are known in closed form
- singularities in the KEO cause no trouble

However, the basis is a factor of $2J + 1$ larger than the already huge product vibrational basis !

An obvious strategy is to use a basis of products of D_{MK}^{J*} and vibrational eigenfunctions

The Hamiltonian may be written

$$H = H_{vib} + H_{rv} .$$

The basis is $|v\rangle D_{MK}^{J*}$.

Eigenfunctions of H_{vib} , $|v\rangle$, are, in turn, computed in a $s(\mathbf{r})b(\boldsymbol{\theta})$ basis.

The $b(\boldsymbol{\theta})$ are computed in a basis of products of angular functions.

I am using nested contractions.

Two problems

- Matrix elements in the $|v\rangle$ basis are straightforward if $|v\rangle$ (i.e. $b(\theta)$) is known in the basis in which the KEO matrix is simple ($m_1 = K - m_2 - m_3 - \dots$), however, this requires recomputing $|v\rangle$ many times, for each K
- In the two-vector embedded KEO, coupling between rotation and vibration can be so large that the $D_{MK}^{J*}|v\rangle$ basis is too big

A K -independent bend basis

We use $m_1 = -m_2 - m_3 - \dots$

rather than $m_1 = K - m_2 - m_3 - \dots$

Some of the matrix elements required to compute $|v\rangle$ in this basis may be infinite

For example, those involving the factor

$$\langle \Theta_{l_1}^{m_2} | \frac{1}{\sin^2 \theta_1} | \Theta_{l_1'}^{m_2} \rangle ,$$

are infinite if $m_2 = 0$,

θ_1 is the angle between \vec{r}_0 and \vec{r}_1 .

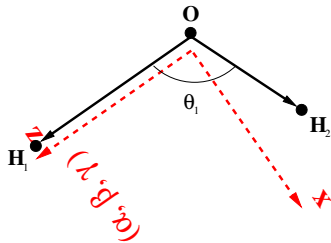
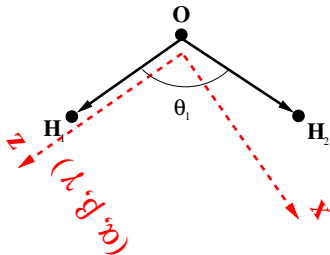
As long as all wavefunctions are tiny near $\theta_1 = 0, \pi$
the infinite integrals cause no trouble

Ro-vibrational coupling is too strong

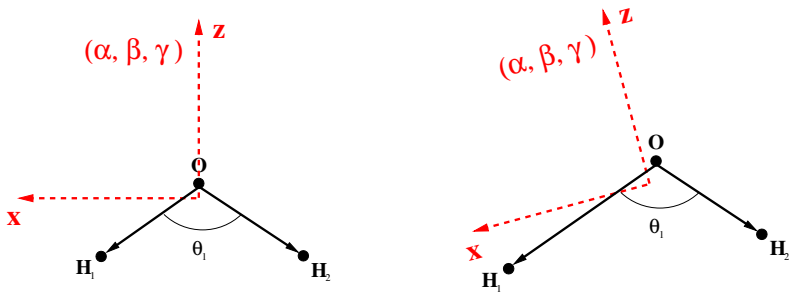
Although the contracted basis is much smaller,
the size of the contracted bend-stretch basis
required for $J > 5$ is too big.

For many molecules, ro-vibrational coupling is smaller in an Eckart frame.

The orientation of a frame with the z axis along a bond does not change when a bond is stretched.



The orientation of an Eckart frame does change when a bond is stretched



It is straightforward to use an Eckart frame with normal coordinates.

How does one use an Eckart frame with polyspherical coordinates?

The best of both worlds : vibrational coordinates that enable one to deal with large-amplitude motion AND an Eckart frame that minimizes ro-vibrational coupling

For a 3-atom molecule it is possible to derive the Eckart frame - Radau coordinate KEO

H. Wei and T. Carrington, Chem. Phys. Lett. **287**, 289-300 (1998)

$$T = T^{\text{vib}} + T^{\text{rot}} + T^{\text{cor}},$$

where

$$\begin{aligned} T^{\text{vib}} &= -\frac{1}{2m_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2m_2} \frac{\partial^2}{\partial R_2^2} \\ &\quad - \left(\frac{1}{2m_1 R_1^2} + \frac{1}{2m_2 R_2^2} \right) \frac{\partial}{\partial c} (1 - c^2) \frac{\partial}{\partial c}, \\ T^{\text{rot}} &= \frac{1}{2} [G_{xx} J_x^2 + G_{yy} J_y^2 + G_{zz} J_z^2 + G_{xy} (J_x J_y + J_y J_x)], \\ T^{\text{cor}} &= -\frac{i}{2} \sum_{v=R_1, R_2, c} \left[G_{vz} \frac{\partial}{\partial v} + \frac{\partial}{\partial v} G_{vz} \right] J_z, \end{aligned}$$

$$\begin{aligned}
G_{R_1 z} &= -\Lambda \epsilon \rho R_2 \sin(\theta - \theta_e), \\
G_{R_2 z} &= \Lambda \rho R_1 \sin(\theta - \theta_e), \\
G_{cz} &= \Lambda \sin \theta [1 - \epsilon \rho^2 - \rho(R_1/R_2 - \epsilon R_2/R_1) \cos(\theta - \theta_e)], \\
G_{xx} &= \Lambda(1 - c^2)^{-1} [S_1^2 + S_2^2/\epsilon], \\
G_{yy} &= \Lambda(1 - c^2)^{-1} [C_1^2 + C_2^2/\epsilon], \\
G_{xy} &= \Lambda(1 - c^2)^{-1} [-S_1 C_1 + S_2 C_2/\epsilon], \\
G_{zz} &= \Lambda[1 + \epsilon \rho^2],
\end{aligned}$$

where

$$\begin{aligned}
S_1 &= \sin(\theta - \eta_e) + \epsilon \rho (R_2/R_1) \sin(\theta_e - \eta_e), \\
C_1 &= \cos(\theta - \eta_e) + \epsilon \rho (R_2/R_1) \cos(\theta_e - \eta_e), \\
S_2 &= \epsilon \rho \sin(\theta - \theta_e + \eta_e) + (R_1/R_2) \sin \eta_e, \\
C_2 &= \epsilon \rho \cos(\theta - \theta_e + \eta_e) + (R_1/R_2) \cos \eta_e, \\
1/\Lambda &= m_1 [R_1^2 + (\epsilon \rho R_2)^2 + 2\epsilon \rho R_1 R_2 \cos(\theta - \theta_e)],
\end{aligned}$$

- difficult to use
- almost impossible to derive for a larger molecule

We want to use

- a vibrational KEO in polyspherical coordinates
- the volume element $\sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \cdots d\phi_2 \cdots dr_1 \cdots$
- a $\Theta_{l_1}^{m_1}(\theta_1)\Theta_{l_2}^{m_2}(\theta_2)\Phi_{m_2}(\phi_2) \cdots$ bend basis.

This enables us to deal with large amplitude vibrational motion

For any molecule-fixed axis system, the classical kinetic energy is,

$$K_{class} = \frac{1}{2} \begin{pmatrix} J & p \end{pmatrix} \begin{pmatrix} G_{rr} & G_{rv} \\ G_{rv}^t & G_{vv} \end{pmatrix} \begin{pmatrix} J \\ p \end{pmatrix}$$

How does one compute G_{rv} and G_{rr} in an Eckart frame?

- We do not have expressions for the elements.
- We can calculate the value of G_{rv} and G_{rr} at each polyspherical point.
- $G_{rr} = \mathbf{I}^{-1} + \mathbf{C}\mathbf{G}_{\mathbf{vv}}\mathbf{C}^T$
- For \mathbf{I}^{-1} this is done by finding the orientation of the Eckart frame and using the Cartesian coordinates of the nuclei.
- The orientation of the Eckart frame is found from a singular value decomposition (SVD)

For H₂O numerical and analytic G matrix elements agree well

At $r_1 = 1.7$ bohr, $r_2 = 1.5$ bohr, $\theta = 100^\circ$

gv(1,1)	4×10^{-14}
gv(1,2)	$< 10^{-14}$
gv(1,3)	$< 10^{-14}$
gv(3,3)	2×10^{-13}
grv(2,1)	$< 10^{-14}$
grv(2,2)	1×10^{-14}
grv(2,3)	$< 10^{-14}$
grr(1,1)	$< 10^{-14}$
grr(3,3)	1×10^{-14}
grr(1,3)	$< 10^{-14}$
grr(2,2)	$< 10^{-14}$

Good convergence for $J = 1$ levels of methane

TABLE I: $J = 1$: convergence and comparison with previous calculations. N_b

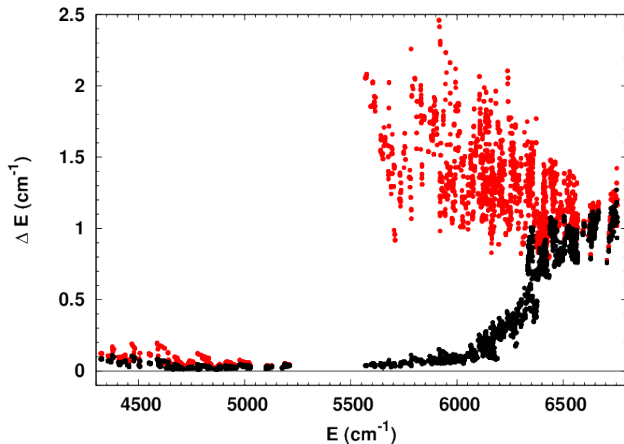
$P = 2$	$P = 3$	$P = 4$	$P = 5$		
$N_{vib} = 25$	$N_{vib} = 80$	$N_{vib} = 220$	$N_{vib} = 551$	Theory	Expt.
$E_v^{\text{cut}}=3100.$	$E_v^{\text{cut}}=4600.$	$E_v^{\text{cut}}=6200.$	$E_v^{\text{cut}}=7800.$	WC2004	Albert2009
cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}		
.014	.001	.001	10.429	10.43	10.48 (F1)
.022	.022	.000	1312.410	1312.41	1311.43 (A2)
.014	.014	.000	1317.250	1317.25	1316.30 (F2)
.020	.018	.000	1326.727	1326.73	1325.82 (F1)
.019	.018	.000	1327.030	1327.03	1326.13 (E)
.015	.014	.000	1543.788	1543.79	1543.93 (F2)
.017	.017	.000	1543.910	1543.91	1544.05 (F1)
.122	.025	.023	2600.011	2600.02	2597.37 (F1)
...
.131	.020	.018	3075.813	3075.82	3076.01 (F1)
N.A.	.293	.006	3875.859	3875.95	3871.56 (A2)
N.A.
N.A.	.160	.002	4606.426	4606.50	4606.55 (F1)

- Good convergence with N_{vib} , 200 is enough for $J = 1$
- Good agreement with our previous calculations
- 75 basis functions are sufficient for the 75 states in $P = 2$
- 4 cm^{-1} errors (wrt expt) for Octad

TABLE I: $J = 10$ lowest and highest Octad levels, lowest and highest Tetradecad levels, and lowest Icosad levels of CH_4 . The first two columns are errors wrt column 3.

$N_{vib} = 1210$	$N_{vib} = 1939$	$N_{vib} = 2949$
P=3, Octad		
0.12	0.08	4322.89 (F2)
0.12	0.08	4323.66 (E)
...
0.04	0.04	5211.71 (E)
0.04	0.03	5211.74 (F2)
P=4, Tetradecad		
2.05	0.04	5568.11 (A)
2.05	0.04	5568.77 (F)
2.06	0.04	5569.54 (F)
...
1.20	1.08	6755.08 (E)
1.16	1.05	6755.26 (F)
P=5, Icosad		
2.92	2.40	6810.87
2.96	2.41	6811.19
3.06	2.44	6814.01

Convergence of $J = 10$ tetradecad levels



- Red Nvib = 1210
- Black Nvib = 1939
- Benchmark Nvib = 2949

Determine a methane PES

- Levels computed on pure ab initio surfaces are not accurate enough
- For spectroscopic purposes the best pure ab initio surfaces are those of Schwenke
 - Schwenke and Partridge (SP), Spectrochim. Acta A, 57, 887(2001) CCSD(T) + cc-pVTZ
 - Schwenke, Spectrochim. Acta A, 58, 849 (2002) FCI extrapolation, CBS, all-electron, relativistic, Lamb shift, BODC, non-adiabatic

Ab initio surfaces are not good enough

TABLE I: o. – c. errors in cm^{-1}

	ν_1	ν_2	ν_3	ν_4
Schwenke & Partridge 2001	+2.79	+0.09	+5.90	-0.98
Schwenke 2002	-2.77	-0.52	-4.58	-0.28
NRT 2011 (unadjusted)	-3.54	-1.56	-2.44	-2.57

Fit with the contracted Lanczos method

- An efficient variational method makes it possible to refine a PES
- We adjust 5 parameters of the SP PES, using only vibrational levels.

Do not adjust the reference potential

- To calculate vibrational levels we use a basis of products of stretch and bend functions.
- The stretch potential is $V_s(\theta^{ref}, r)$ and the bend potential is $V_b(\theta, r^{ref})$.

- Adjusting the parameters makes minor changes in the shape of the potential and therefore it is not necessary to adjust the reference V_s and V_b .
- During the fit only

$$\langle s' b' | \Delta V(\lambda_1, \lambda_2, \dots) | s b \rangle$$

needs to be recomputed.

- Obtaining the $|b\rangle$ functions takes about five times as long as computing the eigenvalues in the contracted basis.

What are the parameters ?

The SP potential is a sum of two terms

$$V = V_0 + V_{crxn}$$

$$V_0 = \sum_{i=1}^4 V_s(R_i) + \sum_{i<j}^4 V_b(R_i, R_j, \theta_{ij})$$

$$V_s(R_i) = \sum_k C_k y_i^k \quad ; \quad y_i = 1 - e^{-\alpha(R_i - R_e)}$$

$$V_b(R_i, R_j, \theta_{ij}) = e^{-\beta_b[(R_i - R_e)^2 + (R_j - R_e)^2]} \sum_{k=2} D_k \left(\cos \theta_{ij} + \frac{1}{3} \right)^k$$

We optimize stretch parameters C_1 , C_2 and bend parameters D_1 , D_2 , D_3 of V_0 to 40 vibrational levels of CH_4 .

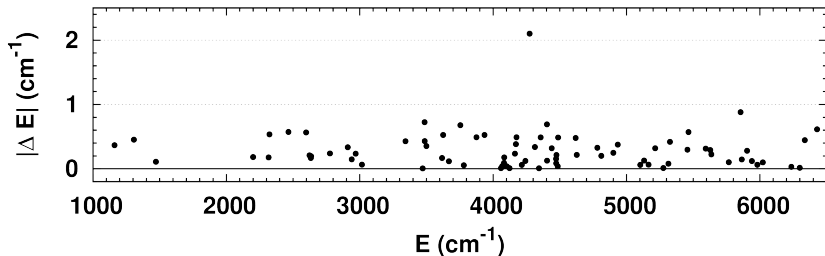
How good is the new surface?

- I: A comparison of the Schwenke-Partridge surface and the fitted surface.

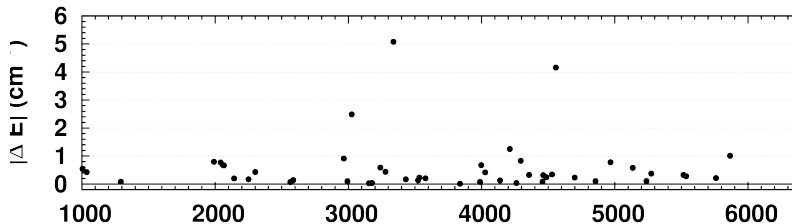
	SP PES	fitted PES
RMSD (cm^{-1})	4.80	0.28
$ \Delta E_{\text{max}} $ (cm^{-1})	13.53	0.85
R_e (\AA)	1.08900	1.08609

How good is the PES for other isotopologues?

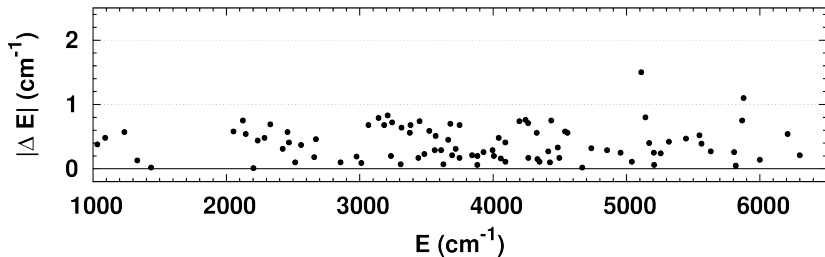
O. N. Ulenikov, E. S. Bekhtereva, S. Albert, H.-M. Niederer, S. Bauerecker, and M. Quack have studied many bands of CH_3D , CHD_3 , and CH_2D_2 .



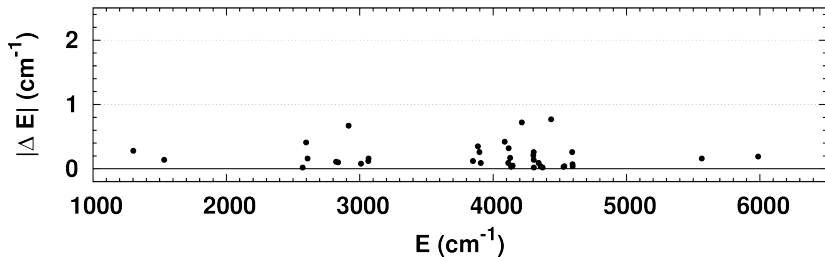
- 78 “experimental” levels (either P(1) or from a fit)
- Excluding one level : RMSD is 0.33 cm^{-1} ; $|\Delta E_{\max}| = 0.88 \text{ cm}^{-1}$.



- 46 “experimental” levels (either P(1) or from a fit)
- Excluding 3 levels : RMSD is 0.47 cm^{-1} ; $|\Delta E_{\max}| = 1.25 \text{ cm}^{-1}$.
- Possible assignment error



- 93 “experimental” levels (either P(1) or from a fit)
- RMSD is 0.47 cm^{-1} ; $|\Delta E_{\max}| = 1.25 \text{ cm}^{-1}$.



- 37 “experimental” levels (either P(1) or from a fit)
- RMSD is 0.27 cm^{-1} ; $|\Delta E_{\max}| = 0.77 \text{ cm}^{-1}$.

- Two problems impede the calculation of a ro-vibrational spectrum using a KEO in polyspherical coordinates and a contracted basis.
 - In the standard basis vibrational eigenfunctions must be computed for each K . For molecules for which vectors can be defined so that $\theta_1 = 0, \pi$ is inaccessible, this problem is solved by taking $m_1 = -m_2 - m_3 - \dots$
 - With the standard choice of molecule-fixed axes the ro-vibrational coupling is large. This problem can be solved by using Eckart axes and computing G matrix elements numerically.

- We can (finally) compute numerically exact ro-vibrational levels of methane for high J .
- A new PES is obtained by adjusting 5 parameters of SP PES
- The errors on the new PES for the vibrational levels of 5 methane isotopologues are consistently below 1 cm⁻¹.
- The same techniques can be applied to any molecule with 5 atoms.

This work has been supported by

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- The Réseau québécois de calcul de haute performance,
- The Canada Research Chairs programme

Because the basis is huge it would be far too costly to form the potential matrix and explicitly multiply the matrix with vectors.

To illustrate the computation of a matrix-vector product consider

$$w_{l'm'} = \sum_{lm} V_{l'm',lm} x_{lm}$$

replace

$$\begin{aligned} V_{l'm',lm} &= \int d\theta \int d\phi Y_{l'm'}(\theta, \phi) V(\theta, \phi) Y_{lm}(\theta, \phi) \\ &\approx \sum_{\beta\gamma} T_{l'\beta}^{m'} Q_{m'\gamma} V(\theta_\beta, \phi_\gamma) Q_{m\gamma} T_{l\beta}^m \end{aligned}$$

$$w_{l'm'} = \sum_{lm} \sum_{\beta\gamma} T_{l'\beta}^{m'} Q_{m'\gamma} V(\theta_\beta, \phi_\gamma) Q_{m\gamma} T_{l\beta}^m x_{lm}$$

$$w_{l'm'} = \sum_{\beta} T_{l'\beta}^{m'} \sum_{\gamma} Q_{m'\gamma} V(\theta_\beta, \phi_\gamma) \sum_m Q_{m\gamma} \sum_l T_{l\beta}^m x_{lm}$$

The largest vector is labelled by the grid indices.