Computing rovibrational levels of polyatomic molecules with curvilinear internal vibrational coordinates and an Eckart frame

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International Symposium on Molecular Spectroscopy
68th Meeting - - June 17-21, 2013
Columbus, Ohio, USA
Variational methods to compute rovibrational levels: normal coordinates

- For molecules with small-amplitude motion, normal coordinates and an Eckart frame are very efficient: Watson kinetic energy operator (KEO)

\[
T = -\frac{1}{2} \sum_k \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \sum_{\alpha\beta} (J_\alpha - \pi_\alpha) \mu_{\alpha\beta} (J_\beta - \pi_\beta) - \frac{1}{8} \sum_\alpha \mu_{\alpha\alpha}
\]

Eckart condition: \[\sum_{i=1}^{N} m_i a_i \times r_i = 0\]


- Normal coordinate variational calculations on CH$_4$
    M. Rey, A. V. Nikitin and V. G. Tyutereva, PCCP, 15, 10049 (2013)
Variational methods to compute rovibrational levels: internal coordinates

- For molecules with large-amplitude motion (LAM), internal coordinates are necessary: better representation of potential.

- But internal coordinates are always used with a **simple geometrical frame**: bond-z, bisector etc for 3-atom, 4-atom, 5-atom molecules

  - For example, our first rovibrational calculation of CH₄ in 2004


- Internal coordinates and Eckart frame (This talk)

A bond-z frame for CH₄: defined by two vectors

- Why bond-z frame?
- Simple analytical KEO
- Simple kinetic matrix elements in spherical harmonics basis

\[
g_{\alpha_0}(r_{\alpha_0})g_{\alpha_1}(r_{\alpha_1})g_{\alpha_2}(r_{\alpha_2})g_{\alpha_3}(r_{\alpha_3})\Theta_{l_1}^{m_1}(\theta_1)Y_{l_2}^{m_2}(\theta_2, \phi_2)Y_{l_3}^{m_3}(\theta_3, \phi_3)|JK\rangle
\]

with \(m_1 = K - m_2 - m_3\)

- Contract this basis for each \(K\) to get smaller basis \(|s(r)b(\theta)^K\rangle|JK\rangle\)
- very costly to do this for each \(K\)

Method is best for LAM molecules
Limited to small \(J\) due to coupling

**Compare bond-z frame with Eckart frame**

- When one bond is stretched, **bond-z** frame does not react. No rotation.

- Geometrical frame has large Coriolis couplings, e.g. bond-z frame for CH$_4$

\[
T_{\text{Cor}} = -2B(r_0)(l_{2x}J_x + l_{2y}J_y) \quad \text{with} \quad B(r_0) = 14.1 \, \text{cm}^{-1}
\]

- When one bond is stretched, **Eckart** frame thinks the molecule is rotated.
Internal coordinate Eckart frame KEO notoriously complicated

- Why nobody uses it before? Because the Eckart KEO is very complicated.
- Analytical KEO is only derived for H\textsubscript{2}O and planar 4-atom molecules
- Radau coordinate Eckart frame KEO for H\textsubscript{2}O:


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

where

\[ T^{\text{vib}} = -\frac{1}{2m_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2m_2} \frac{\partial^2}{\partial R_2^2} \]

\[ - \left( \frac{1}{2m_1 R_1^2} + \frac{1}{2m_2 R_2^2} \right) \frac{\partial}{\partial c} (1 - c^2) \frac{\partial}{\partial c}, \]

\[ T^{\text{rot}} = \frac{1}{2} [G_{xx} J_x^2 + G_{yy} J_y^2 + G_{zz} J_z^2 + G_{xy} (J_x J_y + J_y J_x)], \]

\[ T^{\text{cor}} = -\frac{i}{2} \sum_{v=R_1,R_2,c} \left[ G_{vz} \frac{\partial}{\partial v} + \frac{\partial}{\partial v} G_{vz} \right] J_z, \]

Analytical Radau coordinate Eckart frame KEO for H$_2$O

\[
G_{R_1z} = -\Lambda\epsilon\rho R_2 \sin(\theta - \theta_e),
\]
\[
G_{R_2z} = \Lambda\rho R_1 \sin(\theta - \theta_e),
\]
\[
G_{cz} = \Lambda \sin \theta [1 - \epsilon\rho^2 - \rho(R_1/R_2 - \epsilon R_2/R_1) \cos(\theta - \theta_e)],
\]
\[
G_{xx} = \Lambda (1 - c^2)^{-1} [S_1^2 + S_2^2/\epsilon],
\]
\[
G_{yy} = \Lambda (1 - c^2)^{-1} [C_1^2 + C_2^2/\epsilon],
\]
\[
G_{xy} = \Lambda (1 - c^2)^{-1} [-S_1 C_1 + S_2 C_2/\epsilon],
\]
\[
G_{zz} = \Lambda [1 + \epsilon\rho^2],
\]

where

\[
S_1 = \sin(\theta - \eta_e) + \epsilon\rho(R_2/R_1) \sin(\theta_e - \eta_e),
\]
\[
C_1 = \cos(\theta - \eta_e) + \epsilon\rho(R_2/R_1) \cos(\theta_e - \eta_e),
\]
\[
S_2 = \epsilon\rho \sin(\theta - \theta_e + \eta_e) + (R_1/R_2) \sin \eta_e,
\]
\[
C_2 = \epsilon\rho \cos(\theta - \theta_e + \eta_e) + (R_1/R_2) \cos \eta_e,
\]
\[
1/\Lambda = m_1[R_1^2 + (\epsilon\rho R_2)^2 + 2\epsilon\rho R_1 R_2 \cos(\theta - \theta_e)],
\]
- Difficult to use
- Almost impossible to derive for a larger molecule
- The solution is to use numerical Eckart KEO
Internal coordinate KEO for any frame

- For any molecule-fixed frame, the classical kinetic energy is

\[
T_{class} = \frac{1}{2} (P^t \ J^t) \begin{pmatrix} G_{vv} & G_{rv} \\ G_{rv}^t & G_{rr} \end{pmatrix} \begin{pmatrix} P \\ J \end{pmatrix}
\]

- \( G_{vv} \) is the Wilson G-matrix

- Its quantum mechanical form (Meyer and Gunthard 1968, Pickett 1972)

\[
T_{QM} = \left(\frac{1}{2} P^t G_{vv} P + V'\right) + \frac{1}{2} P^t G_{rv} J + \frac{1}{2} J^t G_{rv} P + \frac{1}{2} J^t G_{rr} J
\]

where

\[
P_k = -i \frac{\partial}{\partial r} \quad \text{for } k = r
\]

\[
P_k = -i \left( \frac{\partial}{\partial \theta} + \frac{1}{2} \cot \theta \right) \quad \text{for } k = \theta
\]

\[
P_k = -i \frac{\partial}{\partial \phi} \quad \text{for } k = \phi
\]

- The modified \( P_k \) for \( \theta \) is due to volume element \( \sin \theta \) (this work)

- We use a different analytical \( T_{vib} \) to compute vibrational wavefunctions.
How does one compute $G_{rv}$ and $G_{rr}$ in an Eckart frame?

- Numerical Eckart KEO was used in high order perturbative calculation of $J > 0$ levels
  - A. B. McCoy, D.C. Burleigh and E. L. Sibert, *JCP* (1991) for $\text{H}_2\text{CO} \, J > 0$ levels

\[
G_{rv} = -CG_{vv} \\
G_{rr} = \mu + CG_{vv}C^t \quad \text{with} \quad C = \mu X
\]

- $X$ is calculated from the inverse of $B$ matrix

\[
X_{\alpha,k} = \sum_{i=1}^{N} m_i \epsilon_{\alpha\beta\gamma} x_{\beta i} \frac{\partial x_{\gamma i}}{\partial Q_k}
\]

- $B$ is a $3N \times 3N$ matrix obtained by augmenting $Q_k$ (internal coord.) with 6 rows
- 3 rows are chosen to satisfy the Eckart condition (or condition for any frame).
- $B$ is computed with finite difference.
For H$_2$O numerical and analytical KEO agree well

Radau coordinates at $r_1 = 1.7$ bohr, $r_2 = 1.5$ bohr, $\theta = 100^\circ$

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$gv(1,1)$</td>
<td>$4 \times 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>$gv(1,2)$</td>
<td>$&lt; 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>$gv(1,3)$</td>
<td>$&lt; 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>$gv(3,3)$</td>
<td>$2 \times 10^{-13}$</td>
<td></td>
</tr>
<tr>
<td>$grv(2,1)$</td>
<td>$&lt; 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>$grv(2,2)$</td>
<td>$1 \times 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>$grv(2,3)$</td>
<td>$&lt; 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>$grr(1,1)$</td>
<td>$&lt; 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>$grr(3,3)$</td>
<td>$1 \times 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>$grr(1,3)$</td>
<td>$&lt; 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>$grr(2,2)$</td>
<td>$&lt; 10^{-14}$</td>
<td></td>
</tr>
</tbody>
</table>
How to use the numerical Eckart KEO?

- Use $|v\rangle|JK\rangle$ as basis (vibration basis is independent of $K$)

- First, solve the vibrational wavefunctions with contracted stretch and bend basis (Wang and Carrington 2003),

\[ |sb\rangle \rightarrow |v\rangle \]

- Compute and store two types of integrals in basis $|v\rangle$
  - For $G_{rr}$ terms
    \[
    \langle v'|G_{\alpha,\beta}|v\rangle = \sum_{s',b'} \sum_{s,b} \langle v'|s'b'\rangle \langle s'b'|G_{\alpha,\beta}|sb\rangle \langle sb|v\rangle
    \]
  - For $G_{rv}$ terms
    - If $k$ is a stretch
      \[
      \langle v'| \sum_k G_{\alpha,k} P_k |v\rangle = \sum_k \sum_{s',b'} \sum_{s,b} \sum_{s''} \langle v'|s'b'\rangle \langle s'b'|G_{\alpha,k}|s''b\rangle \langle s''|P_k|s\rangle \langle sb|v\rangle
      \]
    - If $k$ is a bend
      \[
      \langle v'| \sum_k G_{\alpha,k} P_k |v\rangle = \sum_k \sum_{s',b'} \sum_{s,b} \sum_{b''} \langle v'|s'b'\rangle \langle s'b'|G_{\alpha,k}|sb''\rangle \langle b''|P_k|b\rangle \langle sb|v\rangle
      \]
\[ \Delta V \text{ matrix : } F\text{-matrix method} \]

We do not store the \( \Delta V \) matrix, but store the F-matrix. \( |\alpha\rangle \) is the DVR basis

\[
\langle s'b'|\Delta V(r, \theta)|sb\rangle = \sum_{\alpha} \langle s'|\alpha\rangle \langle \alpha'b'|\Delta V(r_\alpha, \theta)|\alpha b\rangle \langle \alpha|s\rangle
\]

\[
F^{(\alpha)}_{b'b'}
\]

- Distribute \( \alpha \) over hundreds of processors when computing the F-matrix.
- 100% parallelization efficiency

For CH$_4$, 33 G elements to integrate (15 even G and 18 odd G)

- 6 $G_{rr}$ terms,

$$
\begin{pmatrix}
G_{xx} & G_{xy} & G_{xz} \\
G_{yx} & G_{yy} & G_{yz} \\
G_{zx} & G_{zy} & G_{zz}
\end{pmatrix}
= \begin{pmatrix}
e & o & e \\
o & e & o \\
e & e & e
\end{pmatrix}
$$

- 27 $G_{rv}$ terms.

$$
\begin{pmatrix}
G_{x,r_1} & G_{x,r_2} & G_{x,r_3} & G_{x,r_0} & G_{x,\theta_1} & G_{x,\theta_2} & G_{x,\theta_3} & G_{x,\phi_2} & G_{x,\phi_3} \\
G_{y,r_1} & G_{y,r_2} & G_{y,r_3} & G_{y,r_0} & G_{y,\theta_1} & G_{y,\theta_2} & G_{y,\theta_3} & G_{y,\phi_2} & G_{y,\phi_3} \\
G_{z,r_1} & G_{z,r_2} & G_{z,r_3} & G_{z,r_0} & G_{z,\theta_1} & G_{z,\theta_2} & G_{z,\theta_3} & G_{z,\phi_2} & G_{z,\phi_3}
\end{pmatrix}
= \begin{pmatrix}
o & o & o & o & o & o & o & e & e & e \\
e & e & e & e & e & e & e & o & o & o \\
o & o & o & o & o & o & o & e & e & e
\end{pmatrix}
$$

- Need to integrate these G elements in basis $|sb\rangle$, the F-matrix idea

- New concept: **Wilson G-matrix surface** is like potential energy surface

- We have 33 Wilson G-matrix surfaces, 33 times more work.

- All this work is parallelizable. Computing these integrals take 24 hours with 192 cores and 0.5 TB disk. It is only done once. The final stored matrices $\langle v'|G_{\alpha,\beta}|v\rangle$ and $\langle v'|\sum_k G_{\alpha,k}P_k|v\rangle$ are very small.
Basis for J = 0 calculation

Table 1: J = 0 basis sets.

<table>
<thead>
<tr>
<th></th>
<th>Bend basis</th>
<th>Stretch basis</th>
<th>→</th>
<th>full-d basis</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primitive basis</td>
<td>6.67 × 10^6</td>
<td>10^4</td>
<td>→</td>
<td>6.67 × 10^{10}</td>
<td></td>
</tr>
<tr>
<td>Contracted basis b0s1</td>
<td>280</td>
<td>260</td>
<td>→</td>
<td>72,800</td>
<td>Wang and Carrington, JCP(2003)</td>
</tr>
<tr>
<td>Contracted basis b3s1</td>
<td>954</td>
<td>260</td>
<td>→</td>
<td>248,040</td>
<td>This work, used for J &gt; 0</td>
</tr>
<tr>
<td>Contracted basis b4s1</td>
<td>1242</td>
<td>260</td>
<td>→</td>
<td>322,920</td>
<td>This work</td>
</tr>
</tbody>
</table>

- The current basis with \( N_b = 1242 \) is almost 5 times larger than our basis in 2003
- Diagonlization of a matrix of size 323,000 is done with Lanczos algorithm (the matrix has a product structure)
- The contracted J = 0 basis is larger than those used in normal coordinate approach. So we have the best converged vibrational levels and wavefunctions
Quality of vibrational levels

Table 1: The error of selected vibrational levels calculated with different bend basis sets.

<table>
<thead>
<tr>
<th>Assign</th>
<th>Basis b3s1 $N_b = 954$ $E_b^\text{cut}=10140. \text{ cm}^{-1}$</th>
<th>Basis b4s1 $N_b = 1242$ $E_b^\text{cut}=12000. \text{ cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P=4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(00)(04) A1</td>
<td>0.00</td>
<td>5128.03</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(00)(40) E</td>
<td>0.01</td>
<td>6118.41</td>
</tr>
<tr>
<td>(00)(40) E</td>
<td>0.01</td>
<td>6124.00</td>
</tr>
<tr>
<td>P=5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(00)(05) F2</td>
<td>0.07</td>
<td>6385.84</td>
</tr>
<tr>
<td>(00)(05) A1</td>
<td>0.06</td>
<td>6413.47</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(01)(30) F2</td>
<td>0.01</td>
<td>7578.18</td>
</tr>
<tr>
<td>P=6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(00)(06) A1</td>
<td>0.19</td>
<td>7615.70</td>
</tr>
<tr>
<td>(00)(50) F2</td>
<td>0.20</td>
<td>7631.85</td>
</tr>
<tr>
<td>(00)(50) E</td>
<td>0.01</td>
<td>7639.04</td>
</tr>
</tbody>
</table>

- **Quality**: the vibrational levels have small errors up to 7500 cm$^{-1}$ (about P = 5)
- $|\nu>$ basis is of high quality
Basis for $J > 0$ calculation

<table>
<thead>
<tr>
<th>Basis</th>
<th>$N_b \times N_s$</th>
<th>$\rightarrow$</th>
<th>$N_{vib}$</th>
<th>$E_{v}^{cut}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b3s1P2</td>
<td>954 $\times$ 260</td>
<td>$\rightarrow$</td>
<td>25</td>
<td>3100.</td>
</tr>
<tr>
<td>b3s1P3</td>
<td>954 $\times$ 260</td>
<td>$\rightarrow$</td>
<td>80</td>
<td>4600.</td>
</tr>
<tr>
<td>b3s1P4</td>
<td>954 $\times$ 260</td>
<td>$\rightarrow$</td>
<td>220</td>
<td>6200.</td>
</tr>
<tr>
<td>b3s1P5</td>
<td>954 $\times$ 260</td>
<td>$\rightarrow$</td>
<td>551</td>
<td>7800.</td>
</tr>
<tr>
<td>b3s1P6</td>
<td>954 $\times$ 260</td>
<td>$\rightarrow$</td>
<td>1210</td>
<td>9100.</td>
</tr>
<tr>
<td>b3s1P6x</td>
<td>954 $\times$ 260</td>
<td>$\rightarrow$</td>
<td>1939</td>
<td>10000.</td>
</tr>
<tr>
<td>b3s1P7</td>
<td>954 $\times$ 260</td>
<td>$\rightarrow$</td>
<td>2949</td>
<td>11000.</td>
</tr>
</tbody>
</table>

- Basically we truncate vibrational basis sets by the polyad

- Rotational levels up to $P = 4$ could be converged with basis $P = 5$
  - It of course depends on how high $J$ one wants

- The large basis uses about 3000 vibrational functions.
Good convergence with $N_{\text{vib}}$. About 100-200 vibrational functions are enough for $J = 1$.

Good agreement with our previous calculations Wang and Carrington, JCP(2004)
Compare bond-z frame calculations with Eckart-frame calculations

- Errors are relative to the converged Eckart frame calculations
- $J = 3$ numbers were not published in Wang and Carrington, *J. Chem. Phys.*, (2004) because we could not converge levels of $P \geq 3$
With 2949 vibrational functions, $J = 10$ levels of Tetradecad converged to within 1 cm$^{-1}$.
The convergence of $J = 10$ tetradecad levels

- Red $N_{\text{vib}} = 1210$
- Black $N_{\text{vib}} = 1939$
- Benchmark $N_{\text{vib}} = 2949$
Conclusions

- A method using internal coordinate (Radau) and Eckart frame is developed to calculate rovibrational levels:
  - Contracted stretch and bend functions used to compute vibrational wavefunctions
  - Numerical Eckart KEO
- We (finally) can compute converged high-$J$ ($J = 10$) levels of highly excited vibrational states (Tetradecad) for methane
- A better methane potential is urgently needed.
- The method's best molecule is not methane, but LAM molecules: ketene, $C_2H_3^+$, $H_3O_2^-$ etc
- The method can be used for other frames
Acknowledgment

This work has been supported by

- the Natural Sciences and Engineering Research Council of Canada
- the Réseau Québécois de Calcul de Haute Performance
- the Canada Research Chairs programme
- the Canadian Space Agency