Full-dimensional quantum translation-rotation dynamics of methane in clathrate hydrates

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1 Theory

The 6D translation-rotation (T-R) energy levels and wave functions of the methane in the small (5^{12}) cage of clathrate hydrate have been calculated by a quantum 6D bound state method presented bellow. The methodology was designed for calculating the translation-rotation levels of a complex in which a polyatomic molecule is bound to or confined in a much heavier entity, in this case different cages of a clathrate hydrate. The T-R dynamics of a methane is described in the terms of six coordinates Relative to the methane molecule the cage is assumed to be infinitely heavy which results in a final 6D T-R Hamiltonian for a spherical top

$$H = -\frac{\hbar}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + B\mathbf{j}^2 + V(x, y, z, \theta, \phi, \chi) \tag{1}$$

The computational methodology used to calculate the energy levels and wave functions of the 6D Hamiltonian in Eq.(1) is an extension of the methodology developed and used in the Prof. Bačić group to calculate the 5D T-R eigenstates of the hydrogen molecule in clathrate hydrate [1, 2, 3]. Thus, a 3D direct product discrete variable representation (DVR) is employed for the x, y, z coordinates but in the case of methane, Wigner $D^j_{k,m}(\theta, \phi, \chi)$ functions are used as the basis in the angular

θ, ϕ, χ coordinates. Together they constitute a 6D basis $\{|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jmk\rangle\}$.

1.1 DVR theory

The indices α, β, γ in the 6D basis $\{|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jmk\rangle\}$ label the grid points $\{X_\alpha\}$, $\{Y_\beta\}$, $\{Z_\gamma\}$ of the 1D DVRs in the x, y and z directions. In the 1D DVRs in the coordinates x, y, and z, $\{|X_\alpha\rangle\}$, $\{|Y_\beta\rangle\}$, and $\{|Z_\gamma\rangle\}$ are associated with the basis functions $\{\varphi_i^x(x) \mid i = 1, \ldots, N_x\}$, $\{\varphi_j^y(y) \mid j = 1, \ldots, N_y\}$ and $\{\varphi_k^z(z) \mid k = 1, \ldots, N_z\}$. In our case latter consist of the sine functions described bellow and are commonly referred to as the finite basis representation (FBR). Then,

$$\begin{aligned}
|X_\alpha\rangle &= \sum_{i=1}^{N_x} T_{i\alpha}^x \varphi_i^x(x), \\
|Y_\beta\rangle &= \sum_{j=1}^{N_y} T_{j\beta}^y \varphi_j^y(y), \\
|Z_\gamma\rangle &= \sum_{k=1}^{N_x} T_{k\gamma}^z \varphi_k^z(z)
\end{aligned} \tag{2}$$

The matrices $\mathbf{T}^x$, $\mathbf{T}^y$ and $\mathbf{T}^z$ in the Eq.(2) are the FBR-DVR transformation matrices. They diagonalize the coordinate matrices $\mathbf{X}$, $\mathbf{Y}$ and $\mathbf{Z}$, of the coordinate operators x, y and z in their respective 1D FBRs. The eigenvectors of $\mathbf{X}$, $\mathbf{Y}$ and $\mathbf{Z}$, (i.e. $\{X_\alpha\}$, $\{Y_\beta\}$, and $\{Z_\gamma\}$) are the grid points of the direct product 3D DVR.

The eigenstates of the Hamiltonian in the Eq.(1) could be solved in the above basis, however it is shown that for a variety of problems more efficient is the so-called potential optimized (PO) DVRs. PO DVRs can be constructed if, on the right-hand side of the Eq.2, we use 1D FBR functions $\{\varphi_i^{\mathrm{PO},x}(x)\}$, $\{\varphi_j^{\mathrm{PO},y}(y)\}$, and $\{\varphi_k^{\mathrm{PO},z}(z)\}$ which are the eigenstates of the appropriate chosen 1D reference Hamiltonians H_0^x, H_0^y and H_0^z,

$$H_0^x \varphi_i^{\mathrm{PO},x}(x) = \epsilon_i^x \varphi_i^{\mathrm{PO},x}(x), \tag{3}$$

and analogously for H_0^y and H_0^z. We choose out reference Hamiltonians as

$$H_0^x = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_0^x(x),$$

$$
\begin{aligned}
H_0^y &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + V_0^y(y) \\
H_0^z &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + V_0^z(z)
\end{aligned} \tag{4}
$$

The choice of the 1D potentials V_0^x, V_0^y and V_0^z in Eq.4 is dictated by the PES of the system under the study. In the case of the methane clathrate hydrate, these reference potentials are chosen as

$$
\begin{aligned}
V_0^x &= V(x,y,z,\theta,\phi,\chi)\mid_{y=z=0,\theta=\phi=\chi=0^\circ} \\
V_0^y &= V(x,y,z,\theta,\phi,\chi)\mid_{x=z=0,\theta=\phi=\chi=0^\circ} \\
V_0^z &= V(x,y,z,\theta,\phi,\chi)\mid_{z=y=0,\theta=\phi=\chi=0^\circ}
\end{aligned} \tag{5}
$$

Matrix representation of the 1D reference Hamiltonians H_0^x, H_0^y and H_0^z were constructed in the primitive 1D DVR bases associated with the sine functions which, in the x coordinate, are:

$$
\left(\frac{2}{x_l - x_0}\right)^{1/2} \sin\left[\frac{i\pi(x - x_0)}{x_l - x_0}\right], \qquad i = 1, \ldots, n_x - 1 \tag{6}
$$

with the analogous expressions for y and z. In Eq. (6), x_0 and x_l are the endpoints of the interval of interest along the x coordinate. Diagonalization of the so called coordinate matrices in the respective 1D sine bases of the Eq. (6) yields the primitive 1D DVRs whose grid points $\{x_\alpha\}$, $\{y_\beta\}$, and $\{z_\gamma\}$ are uniformly spaced, for example in x,

$$
x_\alpha = x_0 + \frac{\alpha(x_l - x_0)}{n_x}, \qquad \alpha = 1, \ldots, n_x - 1 \tag{7}
$$

The kinetic energy term of Eq.(4) in this 1D DVR is known [1], and the 1D potentials V_0^x, V_0^y and V_0^z in Eqs.(5) are diagonal on the DVR points.

Diagonalization of matrices H_0^x, H_0^y and H_0^z in sine-DVR basis gives the 1D potential-optimized bases (1D PO),$\{\varphi_i^{\mathrm{PO},x}(x)\}$, $\{\varphi_j^{\mathrm{PO},y}(y)\}$, and $\{\varphi_k^{\mathrm{PO},z}(z)\}$, respectively. One further uses this 1D PO bases to construct the coordinate matrices $\mathbf{X}^{\mathrm{PO}}$,

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[1] You can find the expressions in an appendix of D. T. Colbert *et al.* J. Chem. Phys. 96, 1982 (1992)

$\mathbf{Y}^{\mathrm{PO}}$ and $\mathbf{Z}^{\mathrm{PO}}$. Diagonalization of these coordinate matrices yields the eigenvalues, $\{X_\alpha^{\mathrm{PO}}\}$, $\{Y_\beta^{\mathrm{PO}}\}$, and $\{Z_\gamma^{\mathrm{PO}}\}$ which represent the grid points of the direct product 3D PO DVR. Note however that PO DVR points are very different from the primitive ones defined in the Eq. (7). The eigenvectors of the coordinate matrices constitute the PO transformation matrices $\mathbf{T}^x$, $\mathbf{T}^y$ and $\mathbf{T}^z$ needed in Eq. (2) to construct the basis functions in a 1D PO DVR basis i.e. $\{|X_\alpha^{\mathrm{PO}}\rangle\}$, $\{|Y_\beta^{\mathrm{PO}}\rangle\}$ and $\{|Z_\gamma^{\mathrm{PO}}\rangle\}$. The dimension of these 1D PO DVRs, N_x^{PO}, N_y^{PO} and N_z^{PO} are usually significantly smaller than the size of the corresponding 1D DVRs above.

1.2 6D bound state methodology

The 6D basis is now $\{|X_\alpha^{\mathrm{PO}}\rangle|Y_\beta^{\mathrm{PO}}\rangle|Z_\gamma^{\mathrm{PO}}\rangle|jmk\rangle\}$ where $|jmk\rangle$ are the normalized Wigner $D^j_{mk}(\mathbf{\Omega})$functions:

$$\begin{aligned} |jmk\rangle &= \left[\frac{2j+1}{8\pi^2}\right]^{\frac{1}{2}} D^{j*}_{mk}(\mathbf{\Omega}) \\ &= \left[\frac{2j+1}{8\pi^2}\right] e^{im\phi} d^j_{mk}(\theta) e^{ik\chi} \end{aligned} \tag{8}$$

The 6D TR Hamiltonian in Eq. (1) can be written as

$$H = H_0^x + H_0^y + H_0^z + B\mathbf{j}^2 + V(x,y,z,\mathbf{\Omega}) - V_0^x(x) - V_0^y(y) - V_0^z(z) \tag{9}$$

The first three terms of Eq.(9) are given in Eq.(4) and the last three are those of Eq.(5). Then, the terms constituting the general matrix element $H^{\alpha'\beta'\gamma'j'm'k'}_{\alpha\beta\gamma jmk}$ in Eq.(9) in the 6D basis $\{|X_\alpha^{\mathrm{PO}}\rangle|Y_\beta^{\mathrm{PO}}\rangle|Z_\gamma^{\mathrm{PO}}\rangle|jmk\rangle\}$ are:

$$\begin{aligned} (H_0^x)^{\alpha'\beta'\gamma'j'm'k'}_{\alpha\beta\gamma jmk} &= \delta_{\beta'\beta}\delta_{\gamma'\gamma}\delta_{j'j}\delta_{m'm}\delta_{k'k}\sum_{n=1}^{N_x^{\mathrm{PO}}} T^x_{n\alpha}T^x_{n\alpha'}\epsilon^x_n \\ (H_0^y)^{\alpha'\beta'\gamma'j'm'k'}_{\alpha\beta\gamma jmk} &= \delta_{\alpha'\alpha}\delta_{\gamma'\gamma}\delta_{j'j}\delta_{m',m}\delta_{k'k}\sum_{n=1}^{N_y^{\mathrm{PO}}} T^y_{n\beta}T^y_{n\beta'}\epsilon^y_n \\ (H_0^z)^{\alpha'\beta'\gamma'j'm'k'}_{\alpha\beta\gamma jmk} &= \delta_{\alpha'\alpha}\delta_{\beta'\beta}\delta_{j'j}\delta_{m'm}\delta_{k'k}\sum_{n=1}^{N_z^{\mathrm{PO}}} T^z_{n\gamma}T^y_{n\gamma'}\epsilon^z_n \\ (B\mathbf{j}^2)^{\alpha'\beta'\gamma'j'm'k'}_{\alpha\beta\gamma jmk} &= \delta_{\alpha'\alpha}\delta_{\beta'\beta}\delta_{\gamma'\gamma}\delta_{j'j}\delta_{m'm}\delta_{k'k}Bj(j+1)\hbar^2 \end{aligned}$$

$$
\begin{aligned}
(V_0^x)^{\alpha'\beta'\gamma'j'm'k'}_{\alpha\beta\gamma jmk} &= \delta_{\alpha'\alpha}\delta_{\beta'\beta}\delta_{\gamma'\gamma}\delta_{j'j}\delta_{m'm}\delta_{k'k}V_0^x(X_\alpha^{\mathrm{PO}}) \\
(V_0^y)^{\alpha'\beta'\gamma'j'm'k'}_{\alpha\beta\gamma jmk} &= \delta_{\alpha'\alpha}\delta_{\beta'\beta}\delta_{\gamma'\gamma}\delta_{j'j}\delta_{m'm}\delta_{k'k}V_0^y(Y_\beta^{\mathrm{PO}}) \\
(V_0^z)^{\alpha'\beta'\gamma'j'm'k'}_{\alpha\beta\gamma jmk} &= \delta_{\alpha'\alpha}\delta_{\beta'\beta}\delta_{\gamma'\gamma}\delta_{j'j}\delta_{m'm}\delta_{k'k}V_0^z(Z_\gamma^{\mathrm{PO}}) \\
V^{\alpha'\beta'\gamma'j'm'k'}_{\alpha\beta\gamma jmk} &= \delta_{\alpha'\alpha}\delta_{\beta'\beta}\delta_{\gamma'\gamma}\langle j'm'k' \mid V(X_\alpha^{\mathrm{PO}}, Y_\beta^{\mathrm{PO}}, Z_\gamma^{\mathrm{PO}}, \mathbf{\Omega}) \mid jmk\rangle \qquad (10)
\end{aligned}
$$

(11)

In Eq.(11), ϵ_n^x, ϵ_n^y and ϵ_n^z are defined in Eq.(3) and its analogs for y and z. The transformation matrices $\mathbf{T}^x$, $\mathbf{T}^y$ and $\mathbf{T}^z$ are those for the PO 1D DVRs. To calculate the potential matrix elements in Eq.(11) for every DVR point $\{X_\alpha^{\mathrm{PO}}\}$, $\{Y_\beta^{\mathrm{PO}}\}$ and $\{Z_\beta^{\mathrm{PO}}\}$ the 3D cuts of the potential in the Euler angles are expressed in the Wigner D-functions as

$$
V(X_\alpha^{\mathrm{PO}}, Y_\beta^{\mathrm{PO}}, Z_\gamma^{\mathrm{PO}}, \mathbf{\Omega}) = \sum_{jmk} c^j_{mk} D^j_{mk}(\mathbf{\Omega}) \qquad (12)
$$

the coefficients in the expansion are calculated as

$$
c^j_{mk}(X_\alpha^{\mathrm{PO}}, Y_\beta^{\mathrm{PO}}, Z_\gamma^{\mathrm{PO}}) = \frac{2j+1}{8\pi^2} \int\int\int D^{j*}_{mk}(\mathbf{\Omega}) V(X_\alpha^{\mathrm{PO}}, Y_\beta^{\mathrm{PO}}, Z_\gamma^{\mathrm{PO}}, \mathbf{\Omega}) d\mathbf{\Omega} \qquad (13)
$$

where the angle element $d\mathbf{\Omega}$ is $d\phi \sin\theta d\theta d\chi$. The three dimensional numerical integration in Eq.(13) is performed using Gauss-Legendre quadrature in θ and Gauss-Chebyshev quadrature in ϕ and χ. In this way the potential matrix elements in Eq.(11) can be computed analytically because the integral over a product of three D-functions can be expressed in the terms of Clebsch-Gordan coefficients i.e.

$$
\begin{gathered}
\langle j'm'k' \mid V(X_\alpha^{\mathrm{PO}}, Y_\beta^{\mathrm{PO}}, Z_\gamma^{\mathrm{PO}}, \mathbf{\Omega}) \mid jmk\rangle = \\
\frac{(1j'+1)^{1/2}(1j+1)^{1/2}}{8\pi^2} \sum_{j''m''k''} c^{j''}_{m''k''}(X_\alpha^{\mathrm{PO}}, Y_\beta^{\mathrm{PO}}, Z_\gamma^{\mathrm{PO}}) \int D^{j'}_{m'k'}(\mathbf{\Omega}) D^{j''}_{m''k''}(\mathbf{\Omega}) D^{j}_{mk}(\mathbf{\Omega}) d\mathbf{\Omega} = \\
\left(\frac{2j+1}{2j'+1}\right)^{1/2} \sum_{j''m''k''} c^{j''}_{m''k''}(X_\alpha^{\mathrm{PO}}, Y_\beta^{\mathrm{PO}}, Z_\gamma^{\mathrm{PO}}) \langle jk, j''k'' \mid j'k'\rangle \langle jm, j''m'' \mid j'm'\rangle \qquad (14)
\end{gathered}
$$

Although the potential-optimized 6D basis $\{|X_\alpha^{\mathrm{PO}}\rangle|Y_\beta^{\mathrm{PO}}\rangle|Z_\gamma^{\mathrm{PO}}\rangle|jmk\rangle\}$ is more compact that its unoptimized 6D counterpart $\{|X_\alpha\rangle|Y_\beta\rangle|Z_\gamma\rangle|jmk\rangle\}$, it also quickly becomes prohibitively large for our problem. In order to contract the 6D PO basis to a manageable size, we partitioned the full-dimensional Hamiltonian matrix approximately into the Hamiltonians of lower dimension. Set of eigenvectors of the lower dimensional Hamiltonians, truncated by an energy cutoff criterion, serve as the basis in which the final Hamiltonian matrix of greatly reduced size is formed. This is possible because the eigenstates of the intermediate, lower dimensional problems, are well adapted to the features of the PES and already contain a significant portion of the full solution.

In the present work we choose to solve the 3D eigenvalue problem first:

$$ {}^{3\mathrm{D}}h^{xyz}|\Phi_t^{xyz}\rangle = {}^{3\mathrm{D}}\,\epsilon_t^{xyz}|\Phi_t^{xyz}\rangle \tag{15}$$

where

$$ {}^{3\mathrm{D}}h^{xyz} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+\overline{V}(X_\alpha^{\mathrm{PO}},Y_\beta^{\mathrm{PO}},Z_\gamma^{\mathrm{PO}}) \tag{16}$$

and

$$ |\Phi_t^{xyz}\rangle = \sum_{q=1}^{N_{xyz}^{\mathrm{PO}}} {}^{3\mathrm{D}}C_{q,t}^{xyz}|X_\alpha^{\mathrm{PO}}\rangle|Y_\beta^{\mathrm{PO}}\rangle|Z_\gamma^{\mathrm{PO}}\rangle \tag{17}$$

where $N_{xyz}^{\mathrm{PO}} = N_x^{\mathrm{PO}}\times N_y^{\mathrm{PO}}\times N_z^{\mathrm{PO}}$. The 3D potential used in the Eq.(16) is chosen as the full 6D potential averaged over the angular part i.e.

$$ \overline{V}(X_\alpha^{\mathrm{PO}},Y_\beta^{\mathrm{PO}},Z_\gamma^{\mathrm{PO}}) = \int V(X_\alpha^{\mathrm{PO}},Y_\beta^{\mathrm{PO}},Z_\gamma^{\mathrm{PO}},\mathbf{\Omega})d\mathbf{\Omega} \tag{18}$$

The 3D Hamiltonian ${}^{3\mathrm{D}}h^{xyz}$ in Eq.(15) describes the translation of the methane molecule in the potential averaged over the angular part. Only the n_t^{xyz} eigenvalues with the energy lower than the defined cutoff value are kept in the final basis.

The matrix elements of the full 6D TR Hamiltonian of Eq.(9) in the contracted basis $\{|\Phi_t^{xyz}\rangle|jmk\rangle\}$, $\bar{H}$ are found to be:

$$\begin{aligned} \bar{H}_{tjmk}^{t'j'm'k'} &= \delta_{tt'}\delta_{j'j}\delta_{m'm}\delta_{k'k}\;{}^{3\mathrm{D}}\epsilon_t^{xyz} - \delta_{j'j}\delta_{m'm}\delta_{k'k}\sum_{q=1}^{N_{xyz}^{\mathrm{PO}}} {}^{3\mathrm{D}}C_{q,t'}^{xyz}\overline{V}(X_\alpha^{\mathrm{PO}},Y_\beta^{\mathrm{PO}},Z_\gamma^{\mathrm{PO}})\;{}^{3\mathrm{D}}C_{q,t}^{xyz} \\ &+ \delta_{tt'}\delta_{j'j}\delta_{m'm}\delta_{k'k}Bj(j+1)\hbar^2 \\ &+ \sum_{q=1}^{N_{xyz}^{\mathrm{PO}}} {}^{3\mathrm{D}}C_{q,t'}^{xyz}\;{}^{3\mathrm{D}}C_{q,t}^{xyz}\langle j'm'k' \mid V(X_\alpha^{\mathrm{PO}},Y_\beta^{\mathrm{PO}},Z_\gamma^{\mathrm{PO}},\mathbf{\Omega}) \mid jmk\rangle \end{aligned} \tag{19}$$

where ${}^{3\mathrm{D}}\epsilon_t^{xyz}$ are the eigenstates of the 3D Hamiltonian in Eqs.(15) and (16). The size of the final contracted basis is $n_t^{xyz} \times (j_{\max}+1)(4(j_{\max}+1)^2-1)/3$ which is much less than $N_x^{\mathrm{PO}} \times N_y^{\mathrm{PO}} \times N_z^{\mathrm{PO}} \times (j_{\max}+1)(4(j_{\max}+1)^2-1)/3$ which is the size of the uncontracted basis $\{|X_\alpha^{\mathrm{PO}}\rangle|Y_\beta^{\mathrm{PO}}\rangle|Z_\gamma^{\mathrm{PO}}\rangle|jmk\rangle\}^2$.

Note however that slightly different approach is possible, in which the angular basis is also contracted. Another 3D problem eigenvalue problem can be solved in the angular basis

$$ {}^{3\mathrm{D}}h^{\theta\phi\chi}|\Phi_r^{\theta\phi\chi}\rangle = {}^{3\mathrm{D}}\,\epsilon_r^{xyz}|\Phi_r^{\theta\phi\chi}\rangle \tag{20}$$

where

$$ {}^{3\mathrm{D}}h^{\theta\phi\chi} = B\mathbf{j}^2 + V(0,0,0,\theta,\phi,\chi) \tag{21}$$

and

$$ |\Phi_r^{\theta\phi\chi}\rangle = \sum_{w=1}^{N_{\theta\phi\chi}} {}^{3\mathrm{D}}C_{w,r}^{\theta\phi\chi}|jmk\rangle \tag{22}$$

with $N_{\theta\phi\chi} = (j_{\max}+1)(4(j_{\max}+1)^2-1)/3$. The 3D Hamiltonian ${}^{3\mathrm{D}}h^{\theta\phi\chi}$ in Eq.(20) describes the rotation of the methane molecule in the c.m. of the cage. Only the $n_r^{\theta\phi\chi}$ eigenvalues with the energy lower than the defined cutoff value are kept in the final basis. Together with the truncated translational eigenfunctions $|\Phi_t^{xyz}\rangle$, the alternative 6D basis is $\{|\Phi_t^{xyz}\rangle|\Phi_r^{\theta\phi\chi}\rangle\}$. The matrix elements of the full 6D TR Hamiltonian of Eq.(9) in this contracted basis are found to be:

$$\begin{aligned} \bar{H}_{tr}^{t'r'} &= \delta_{tt'}\delta_{r'r}\ {}^{3\mathrm{D}}\epsilon_t^{xyz} - \delta_{r'r}\sum_{q=1}^{N_{xyz}^{\mathrm{PO}}}\ {}^{3\mathrm{D}}C_{q,t'}^{xyz}\overline{V}(X_\alpha^{\mathrm{PO}},Y_\beta^{\mathrm{PO}},Z_\gamma^{\mathrm{PO}})\ {}^{3\mathrm{D}}C_{q,t}^{xyz} \\ &+ \delta_{tt'}\delta_{r'r}Bj(j+1)\hbar^2 + \sum_{q=1}^{N_{xyz}^{\mathrm{PO}}}\ {}^{3\mathrm{D}}C_{q,t'}^{xyz}\ {}^{3\mathrm{D}}C_{q,t}^{xyz} \times \\ &\left(\sum_{w=1}^{N_{\theta\phi\chi}}\sum_{w'=1}^{N_{\theta\phi\chi}}\ {}^{3\mathrm{D}}C_{w,r}^{*\theta\phi\chi}\langle jmk \mid V(X_\alpha^{\mathrm{PO}},Y_\beta^{\mathrm{PO}},Z_\gamma^{\mathrm{PO}},\mathbf{\Omega}) \mid j'm'k'\rangle\ {}^{3\mathrm{D}}C_{w',r}^{\theta\phi\chi}\right) \end{aligned} \tag{23}$$

The size of the alternative contracted basis is only $n_t^{xyz} \times n_r^{\theta\phi\chi}$. This approach can additionally reduce the size of the problem if $n_r^{\theta\phi\chi}$ is much less than $(j_{\max}+1)(4(j_{\max}+$

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[2] Note that for a spherical top, degeneracy of the level with quantum number j is $(2j+1)^2$

$1)^2 - 1)/3$. Testing this approach, it was found that the five digit accuracy of the final 6D TR eigenvalues needs $n_r^{\theta\phi\chi} \approx (j_{\max}+1)(4(j_{\max}+1)^2-1)/3$ so the full angular basis is used. The developed program includes both approaches and only a slight change in one of the subroutines is needed to include the angular basis contraction (read the comments in the tog subroutine - whh.f).

References

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