Goal

1) Do rovibrational wavepacket propagation for a nonlinear polyatomic molecule in laser field

   $\hat{H}(t) = \hat{H}_0 - \boldsymbol{\varepsilon}(t)\boldsymbol{\mu} - \frac{1}{2}\boldsymbol{\varepsilon}(t)\big(\boldsymbol{\alpha}\boldsymbol{\varepsilon}(t)\big)$ (dynamic alignment)

2) Determine time-averaged eigenstates of a „nonlinear polyatomic molecule + laser field" system

   $\hat{H}(t) = \hat{H}_0 - \frac{1}{4}\boldsymbol{\varepsilon}(\boldsymbol{\alpha}\boldsymbol{\varepsilon})$ (adiabatic alignment)

To achieve the above goals we need to construct the matrix representations of the Hamiltonians (we will use the basis of field free rovibrational eigenstates to do this), however the external field is defined in the Space Fixed cartesian coordinate system, while the molecular properties $\boldsymbol{\mu}$ and $\boldsymbol{\alpha}$ are given to us by Gaussian in a Molecule (Body) Fixed cartesian coordinate system. How to resolve this issue for polyatomic molecules? See below ☺

Notation

$\hat{J}_i^{\mathrm{SF}}, \hat{J}_i^{\mathrm{BF}}$: ith angular momentum component expressed in Space Fixed and Molecule (Body) Fixed cartesian coordinate systems, respectively.

$|JM\rangle$: angular momentum eigenstates, for which $\hat{J}^2|JM\rangle = \hbar^2 J(J+1)|JM\rangle$ and $\hat{J}_z|JM\rangle = \hbar M|JM\rangle$

Angular momentum and Wigner-matrices

Molecular angular momentum is the infinitesimal generator for the rotation of the molecule:

$$\hat{R}_{\mathrm{inf}}\Psi(\mathbf{x}) = \hat{R}(\mathbf{n}, d\varphi)\Psi(\mathbf{x}) = \Psi\big(\mathbf{R}_{\mathrm{inf}}^{-1}\mathbf{x}\big) = \Psi(\mathbf{x} - d\varphi\mathbf{n}\times\mathbf{x}) = \Psi(\mathbf{x}) - d\varphi\hat{\nabla}\Psi(\mathbf{x})\cdot(\mathbf{n}\times\mathbf{x})$$

$$= \Psi(\mathbf{x}) - d\varphi\mathbf{n}\cdot\big(\mathbf{x}\times\hat{\nabla}\big)\Psi(\mathbf{x}) = \left(\hat{I} - \frac{i}{\hbar}d\varphi\mathbf{n}\cdot\hat{\boldsymbol{J}}\right)\Psi(\mathbf{x})$$

For a finite rotation: $\hat{R}(\mathbf{n},\varphi) = \lim_{N\to\infty}\left(I - \frac{i}{\hbar}\frac{\varphi}{N}\mathbf{n}\cdot\hat{\boldsymbol{J}}\right)^N = e^{-\frac{i}{\hbar}\varphi\mathbf{n}\cdot\hat{\boldsymbol{J}}}$

Using the Euler-angles (z-y-z convention) to parametrize general 3D rotations:

$$\hat{R}(\phi,\theta,\chi) = e^{-\frac{i}{\hbar}\phi\hat{J}_z^{\mathrm{SF}}}e^{-\frac{i}{\hbar}\theta\hat{J}_y^{\mathrm{SF}}}e^{-\frac{i}{\hbar}\chi\hat{J}_z^{\mathrm{SF}}}$$

$\big[\hat{J}^2, \hat{R}\big] = 0 \quad \Rightarrow \quad \hat{J}^2$ and $\hat{R}$ have common eigensubspaces, therefore

$$\hat{R}(\phi,\theta,\chi)|JK\rangle = \sum_{M'=-J}^{J} D^J_{M'K}(\phi,\theta,\chi)|JM'\rangle$$

$$D^J_{MK}(\phi,\theta,\chi) \equiv D^J_{MK}(R) \equiv D^J_{MK} = \langle JM|\hat{R}(\phi,\theta,\chi)|JK\rangle = \langle JM|e^{-\frac{i}{\hbar}\phi\hat{J}_z^{\mathrm{SF}}}e^{-\frac{i}{\hbar}\theta\hat{J}_y^{\mathrm{SF}}}e^{-\frac{i}{\hbar}\chi\hat{J}_z^{\mathrm{SF}}}|JK\rangle =$$

$$= e^{-iM\phi}\langle JM|e^{-\frac{i}{\hbar}\theta\hat{J}_y^{\mathrm{SF}}}|JK\rangle e^{-iK\chi} = e^{-iM\phi}d^J_{MK}(\theta)e^{-iK\chi}$$

The Wigner-matrices form a representation of the rotation group, and they have many useful properties, for example:

$\sum_{K=-J}^{J} {D_{MK}^{J}}^{*}(R) D_{KM'}^{J}(R) = \delta_{MM'}$ (Unitarity)

$\int {D_{MK}^{J}}^{*}(R) D_{M'K'}^{J'}(R) d\boldsymbol{\Omega} = \frac{8\pi^2}{(2J+1)} \delta_{JJ'} \delta_{KK'} \delta_{MM'}$ (Great Orthogonality Theorem for rot. group)

$\int D_{M_1' M_1}^{J_1}(R) D_{M_2' M_2}^{J_2}(R) D_{M_3' M_3}^{J_3}(R) d\boldsymbol{\Omega} = 8\pi^2 \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1' & M_2' & M_3' \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix}$ (3-j symbols)

${D_{MK}^{J}}^{*}(R) = (-1)^{M-K} D_{-M-K}^{J}(R)$

Symmetric top eigenfunctions

For any field free molecule $\left[\hat{J}^2, \hat{H}\right] = \left[\hat{J}_z^{\mathrm{SF}}, \hat{H}\right] = 0$, additionally for a (prolate) symmetric top molecule

$\hat{H} = B\hat{J}^2 + (A-B)\hat{J}_z^{\mathrm{BF}\,2} \;\Rightarrow\; \left[\hat{J}_z^{\mathrm{BF}}, \hat{H}\right] \;\Rightarrow\; \left|\Psi^{\text{symmetric top}}\right\rangle \equiv |JKM\rangle$, for which

$\hat{J}^2|JKM\rangle = \hbar^2 J(J+1)|JKM\rangle, \qquad \hat{J}_z^{\mathrm{SF}}|JKM\rangle = \hbar M|JKM\rangle, \qquad \hat{J}_z^{\mathrm{BF}}|JKM\rangle = \hbar K|JKM\rangle$

It can be proved (see Zare or Landau) that:

$$\langle \phi, \theta, \chi | JKM \rangle \equiv \langle R | JKM \rangle = \sqrt{\frac{2J+1}{8\pi^2}} {D_{MK}^{J}}^{*}(\phi, \theta, \chi)$$

which is great, since this leads to the very useful (see later) formula

$$\int \langle JKM|R\rangle {D_{sk}^{j}}^{*}(R) \langle R|J'K'M'\rangle d\boldsymbol{\Omega} \equiv \left\langle JKM \middle| {D_{sk}^{j}}^{*} \middle| J'K'M' \right\rangle$$

$$= \frac{(2J+1)^{\frac{1}{2}}(2J'+1)^{\frac{1}{2}}}{8\pi^2} \int D_{MK}^{J}(R) {D_{sk}^{j}}^{*}(R) {D_{M'K'}^{J'}}^{*}(R) d\boldsymbol{\Omega}$$

$$= (2J+1)^{\frac{1}{2}}(2J'+1)^{\frac{1}{2}}(-1)^{s-k+M'-K'} \begin{pmatrix} J & j & J' \\ M & -s & -M' \end{pmatrix} \begin{pmatrix} J & j & J' \\ K & -k & -K' \end{pmatrix}$$

„Spherical basis" representation

We know that the $Y_{LM}(\Omega)$ spherical harmonics are angular momentum eigenfunctions, therefore

$$\hat{R}(\phi, \theta, \chi) Y_{LM} = \sum_{K=-L}^{L} D_{KM}^{L}(\phi, \theta, \chi)\, Y_{LK}$$

furthermore, $Y_{1\pm1} \propto (\mp x - iy)$, $Y_{10} \propto z$, etc., thus, based on the spherical harmonics we can define combinations of cartesian vector and tensor components such as $r^{(1,\pm1)} = \frac{1}{\sqrt{2}}(\mp x - iy)$, $r^{(1,0)} = z$, etc., with which it is easy to relate the Molecule (Body) Fixed and Space Fixed quantities using Wigner-matrices, for example:

$$r^{\mathrm{BF},(1,M)} = \hat{R}(\phi, \theta, \chi) r^{\mathrm{SF},(1,M)} = \sum_{K=-1}^{1} D_{KM}^{1}(\phi, \theta, \chi)\, r^{\mathrm{SF},(1,K)}, \quad \text{or}$$

$$r^{\mathrm{SF},(1,M)} = \hat{R}^{-1}(\phi,\theta,\chi) r^{\mathrm{BF},(1,M)} = \sum_{K=-1}^{1} {D^1_{MK}}^*(\phi,\theta,\chi)\, r^{\mathrm{BF},(1,K)}$$

(in this case ϕ, θ and χ mean the Euler angles relating the space and molecule fixed frames)

Transformation of $\boldsymbol{\mu}$ dipole moment vector and $\boldsymbol{\alpha}$ polarization tensor into „spherical basis" from Cartesian basis

$$\boldsymbol{\mu} = \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} \equiv \begin{pmatrix} \mu_1 \\ \mu_2 \\ \mu_3 \end{pmatrix}; \qquad \boldsymbol{\alpha} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \equiv \begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{pmatrix}$$

$$\mu^{(1,0)} = \mu_3$$

$$\mu^{(1,\pm1)} = \frac{1}{\sqrt{2}}(\mp\mu_1 - i\mu_2)$$

$$\alpha^{(0)} = -\frac{1}{\sqrt{3}}(\alpha_{11} + \alpha_{22} + \alpha_{33}) = -\frac{1}{\sqrt{3}}\mathrm{Tr}[\boldsymbol{\alpha}]$$

$$\alpha^{(2,\pm2)} = \frac{1}{2}[\alpha_{11} - \alpha_{22} \pm i(\alpha_{12} + \alpha_{21})]$$

$$\alpha^{(2,\pm1)} = \frac{1}{2}[\mp(\alpha_{13} + \alpha_{31}) - i(\alpha_{23} + \alpha_{32})]$$

$$\alpha^{(2,0)} = \frac{1}{\sqrt{6}}[2\alpha_{33} - \alpha_{22} - \alpha_{11}]$$

Expressing dipole- and polarizability interaction terms (with polarized external field) using Molecule (Body) Fixed components

$$\boldsymbol{\varepsilon}^{\mathrm{SF}} = (0,0,\varepsilon)$$

$$\boldsymbol{\varepsilon}^{\mathrm{SF}}\boldsymbol{\mu}^{\mathrm{SF}} = \varepsilon\mu_3^{\mathrm{SF}} = \varepsilon\mu^{\mathrm{SF},(1,0)} = \varepsilon \sum_{k=-1}^{1} {D^1_{0k}}^* \mu^{\mathrm{BF},(1,k)}$$

$$\boldsymbol{\varepsilon}^{\mathrm{SF}}\left(\boldsymbol{\alpha}^{\mathrm{SF}}\boldsymbol{\varepsilon}^{\mathrm{SF}}\right) = \varepsilon^2\alpha_{33}^{\mathrm{SF}} = \frac{\varepsilon^2}{3}\left(\alpha^{\mathrm{SF},(2,0)} - \frac{1}{\sqrt{2}}\alpha^{\mathrm{SF},(0)}\right) = \frac{\varepsilon^2}{3}\left[\sum_{k=-2}^{2} {D^2_{0k}}^* \alpha^{\mathrm{BF},(2,k)} - \frac{1}{\sqrt{2}}\alpha^{\mathrm{BF},(0)}\right]$$

Simple applications

I. Matrix representation of the Hamiltonian considering time-averaged polarisation interaction (with polarized light) in the basis of field free rovibrational eigenstates.

$$\hat{H} = \hat{H}_0 - \frac{1}{4}\boldsymbol{\varepsilon}(\boldsymbol{\alpha}\boldsymbol{\varepsilon})$$

$$\left\langle \Psi^{JMn} \middle| \hat{H} \middle| \Psi^{J'M'n'} \right\rangle = E^{Jn}\delta_{JJ'}\delta_{nn'}\delta_{MM'} - \frac{1}{4}\left\langle \Psi^{JMn} \middle| \boldsymbol{\varepsilon}(\boldsymbol{\alpha}\boldsymbol{\varepsilon}) \middle| \Psi^{J'M'n'} \right\rangle =$$

$$= E^{Jn}\delta_{JJ'}\delta_{nn'}\delta_{MM'} - \frac{\varepsilon^2}{12}\left[\sum_{k=-2}^{2} \left\langle \Psi^{JMn} \middle| {D^2_{0k}}^* \alpha^{\mathrm{BF},(2,k)} \middle| \Psi^{J'M'n'} \right\rangle - \frac{1}{\sqrt{2}}\left\langle \Psi^{JMn} \middle| \alpha^{\mathrm{BF},(0)} \middle| \Psi^{J'M'n'} \right\rangle\right]$$

I.1. „semi-Rigid" symmetric top

(v = v' would be Rigid, v ≠ v' allows for excitation onto „Rigid Rotor manifolds" in different vibr. states)

$$|\Psi^{JMn}\rangle \equiv |\Psi^{JKMv}\rangle = |v\rangle|JKM\rangle \propto \psi_v(Q_1,\dots,Q_{3N-6})D^{J}_{MK}{}^{*}(\phi,\theta,\chi)$$

$$\langle\Psi^{JKMv}|\hat{H}|\Psi^{J'K'M'v'}\rangle = E^{JKv}\delta_{JJ'}\delta_{KK'}\delta_{vv'}\delta_{MM'} -$$

$$-\frac{\varepsilon^2}{12}\left[\sum_{k=-2}^{2}\langle v|\alpha^{\mathrm{BF},(2,k)}|v'\rangle\langle JKM|D^{2}_{0k}{}^{*}|J'K'M'\rangle - \frac{\delta_{JJ'}\delta_{KK'}\delta_{MM'}}{\sqrt{2}}\langle v|\alpha^{\mathrm{BF},(0)}|v'\rangle\right] =$$

$$= E^{JKv}\delta_{JJ'}\delta_{KK'}\delta_{vv'}\delta_{MM'} -$$

$$-\delta_{MM'}\frac{\varepsilon^2}{12}\left[\sum_{k=-2}^{2}\langle v|\alpha^{\mathrm{BF},(2,k)}|v'\rangle(2J+1)^{\frac{1}{2}}(2J'+1)^{\frac{1}{2}}(-1)^{-k+M-K'}\begin{pmatrix}J & 2 & J'\\ M & 0 & -M\end{pmatrix}\begin{pmatrix}J & 2 & J'\\ K & -k & -K'\end{pmatrix} - \frac{\delta_{JJ'}\delta_{KK'}}{\sqrt{2}}\langle v|\alpha^{\mathrm{BF},(0)}|v'\rangle\right]$$

(Polarization selection rules from 3-j symbols: $\Delta J = 0,\pm2;\ \Delta K = 0,\pm1,\pm2;\ \Delta M = 0$, in the case of polarized field $\boldsymbol{\varepsilon}^{\mathrm{SF}} = (0,0,\varepsilon)$, polarisation interaction does not give coupling between states with different M values)

I.2. „semi-Rigid" asymmetric top

(v = v' would be Rigid, v ≠ v' allows for excitation onto „Rigid Rotor manifolds" in different vibr. states)

$$|\Psi^{JMn}\rangle \equiv |\Psi^{JMvn}\rangle = |v\rangle\sum_{K} C_K^{Jvn}|JKM\rangle \equiv \frac{(2J+1)^{1/2}}{8\pi^2}\psi_v(Q_1,\dots,Q_{3N-6})\sum_{K} C_K^{Jn}D^{J}_{MK}{}^{*}(\phi,\theta,\chi)$$

$$\langle\Psi^{JMvn}|\hat{H}|\Psi^{J'M'v'n'}\rangle = E^{Jvn}\delta_{JJ'}\delta_{vv'}\delta_{nn'}\delta_{MM'} -$$

$$-\frac{\varepsilon^2}{12}\left[\sum_{k=-2}^{2}\langle v|\alpha^{\mathrm{BF},(2,k)}|v'\rangle\sum_{K,K'} C_K^{Jvn}C_{K'}^{J'v'n'}\langle JKM|D^{2}_{0k}{}^{*}|J'K'M'\rangle - \frac{\delta_{JJ'}\delta_{MM'}}{\sqrt{2}}\langle v|\alpha^{\mathrm{BF},(0)}|v'\rangle\sum_{K} C_K^{Jvn}C_K^{J'v'n'}\right] =$$

$$= E^{Jvn}\delta_{JJ'}\delta_{nn'}\delta_{MM'} -$$

$$-\delta_{MM'}\frac{\varepsilon^2}{12}\sum_{k=-2}^{2}\left(\langle v|\alpha^{\mathrm{BF},(2,k)}|v'\rangle\sum_{K,K'} C_K^{Jvn}C_{K'}^{J'v'n'}(2J+1)^{\frac{1}{2}}(2J'+1)^{\frac{1}{2}}(-1)^{-k+M-K'}\begin{pmatrix}J & 2 & J'\\ M & 0 & -M\end{pmatrix}\begin{pmatrix}J & 2 & J'\\ K & -k & -K'\end{pmatrix}\right) +$$

$$+\delta_{JJ'}\delta_{MM'}\frac{\varepsilon^2}{12\sqrt{2}}\langle v|\alpha^{\mathrm{BF},(0)}|v'\rangle\sum_{K} C_K^{Jvn}C_K^{J'v'n'}$$

I.3. Nonrigid polyatomic molecule

$$|\Psi^{JMn}\rangle = \sum_{K,v} C_{Kv}^{Jn}|v\rangle|JKM\rangle \equiv \frac{(2J+1)^{1/2}}{8\pi^2}\sum_{K,v} C_{Kv}^{Jn}\psi_v(Q_1,\dots,Q_{3N-6})D^{J}_{MK}{}^{*}(\phi,\theta,\chi)$$

$$\langle\Psi^{JMn}|\hat{H}|\Psi^{J'M'n'}\rangle = E^{Jn}\delta_{JJ'}\delta_{nn'}\delta_{MM'} -$$

$$-\frac{\varepsilon^2}{12}\left[\sum_{k=-2}^{2}\left(\sum_{v,v'}\langle v|\alpha^{\mathrm{BF},(2,k)}|v'\rangle\sum_{K,K'} C_{Kv}^{Jn}C_{K'v'}^{J'n'}\langle JKM|D^{2}_{0k}{}^{*}|J'K'M'\rangle\right) - \frac{\delta_{JJ'}\delta_{MM'}}{\sqrt{2}}\sum_{v,v'}\langle v|\alpha^{\mathrm{BF},(0)}|v'\rangle\sum_{K} C_{Kv}^{Jn}C_{Kv'}^{J'n'}\right] =$$

$$= E^{Jn}\delta_{JJ'}\delta_{nn'}\delta_{MM'} -$$

$$-\delta_{MM'}\frac{\varepsilon^2}{12}\sum_{k=-2}^{2}\left(\sum_{v,v'}\langle v|\alpha^{\mathrm{BF},(2,k)}|v'\rangle\sum_{K,K'} C_{Kv}^{Jn}C_{K'v'}^{J'n'}(2J+1)^{\frac{1}{2}}(2J'+1)^{\frac{1}{2}}(-1)^{-k+M-K'}\begin{pmatrix}J & 2 & J'\\ M & 0 & -M\end{pmatrix}\begin{pmatrix}J & 2 & J'\\ K & -k & -K'\end{pmatrix}\right) +$$

$$+\delta_{JJ'}\delta_{MM'}\frac{\varepsilon^2}{12\sqrt{2}}\sum_{v,v'}\sum_{K} C_{Kv}^{Jn}C_{Kv'}^{J'n'}\langle v|\alpha^{\mathrm{BF},(0)}|v'\rangle$$

II. Matrix representation of the Hamiltonian considering dipole- and polarisation interactions (with polarized light) in the basis of field free rovibrational eigenstates.

$$\hat{H}(t) = \hat{H}_0 - \boldsymbol{\varepsilon}(t)\boldsymbol{\mu} - \frac{1}{2}\boldsymbol{\varepsilon}(t)\left(\boldsymbol{\alpha}\boldsymbol{\varepsilon}(t)\right)$$

$$\langle \Psi^{JMn}|\hat{H}|\Psi^{J'M'n'}\rangle = E^{Jn}\delta_{JJ'}\delta_{nn'}\delta_{MM'} - \langle \Psi^{JMn}|\boldsymbol{\varepsilon}(t)\boldsymbol{\mu}|\Psi^{J'M'n'}\rangle - \frac{1}{2}\langle \Psi^{JMn}|\boldsymbol{\varepsilon}(t)\left(\boldsymbol{\alpha}\boldsymbol{\varepsilon}(t)\right)|\Psi^{J'M'n'}\rangle =$$

$$= E^{Jn}\delta_{JJ'}\delta_{nn'}\delta_{MM'} - \varepsilon(t)\sum_{k=-1}^{1}\langle \Psi^{JMn}|{D^1_{0k}}^{*}\mu^{\mathrm{BF},(1,k)}|\Psi^{J'M'n'}\rangle$$

$$-\frac{\varepsilon(t)^2}{6}\left[\sum_{k=-2}^{2}\langle \Psi^{JMn}|{D^2_{0k}}^{*}\alpha^{\mathrm{BF},(2,k)}|\Psi^{J'M'n'}\rangle - \frac{1}{\sqrt{2}}\langle \Psi^{JMn}|\alpha^{\mathrm{BF},(0)}|\Psi^{J'M'n'}\rangle\right]$$

II.1. „semi-Rigid" asymmetric top

($v = v'$ would be Rigid, $v \neq v'$ allows for excitation onto „Rigid Rotor manifolds" in different vibr. states)

$$|\Psi^{JMn}\rangle \equiv |\Psi^{JMvn}\rangle = |v\rangle\sum_K C_K^{Jvn}|JKM\rangle \equiv \frac{(2J+1)^{1/2}}{8\pi^2}\psi_v(Q_1,\dots,Q_{3N-6})\sum_K C_K^{Jn}{D^J_{MK}}^{*}(\phi,\theta,\chi)$$

$$\langle \Psi^{JMvn}|\hat{H}|\Psi^{J'M'v'n'}\rangle = E^{Jvn}\delta_{JJ'}\delta_{vv'}\delta_{nn'}\delta_{MM'} -$$

$$-\delta_{MM'}\varepsilon(t)\sum_{k=-1}^{1}\langle v|\mu^{\mathrm{BF},(1,k)}|v'\rangle\sum_{K,K'}C_K^{Jvn*}C_{K'}^{J'v'n'}(2J+1)^{\frac{1}{2}}(2J'+1)^{\frac{1}{2}}(-1)^{-k+M-K'}\begin{pmatrix}J & 1 & J'\\ M & 0 & -M\end{pmatrix}\begin{pmatrix}J & 1 & J'\\ K & -k & -K'\end{pmatrix} -$$

$$-\delta_{MM'}\frac{\varepsilon^2(t)}{12}\sum_{k=-2}^{2}\left(\langle v|\alpha^{\mathrm{BF},(2,k)}|v'\rangle\sum_{K,K'}C_K^{Jvn}C_{K'}^{J'v'n'}(2J+1)^{\frac{1}{2}}(2J'+1)^{\frac{1}{2}}(-1)^{-k+M-K'}\begin{pmatrix}J & 2 & J'\\ M & 0 & -M\end{pmatrix}\begin{pmatrix}J & 2 & J'\\ K & -k & -K'\end{pmatrix}\right) +$$

$$+\delta_{JJ'}\delta_{MM'}\frac{\varepsilon^2(t)}{12\sqrt{2}}\langle v|\alpha^{\mathrm{BF},(0)}|v'\rangle\sum_K C_K^{Jvn}C_K^{J'v'n'}$$

II.2. Nonrigid polyatomic molecule

$$|\Psi^{JMn}\rangle = \sum_{K,v}C_{Kv}^{Jn}|v\rangle|JKM\rangle \equiv \frac{(2J+1)^{1/2}}{8\pi^2}\sum_{K,v}C_{Kv}^{Jn}\psi_v(Q_1,\dots,Q_{3N-6}){D^J_{MK}}^{*}(\phi,\theta,\chi)$$

$$\langle \Psi^{JMn}|\hat{H}|\Psi^{J'M'n'}\rangle = E^{Jn}\delta_{JJ'}\delta_{nn'}\delta_{MM'} -$$

$$-\delta_{MM'}\varepsilon(t)\sum_{k=-1}^{1}\left(\sum_{v,v'}\langle v|\mu^{\mathrm{BF},(1,k)}|v'\rangle\sum_{K,K'}C_{Kv}^{Jn*}C_{K'v'}^{J'n'}(2J+1)^{\frac{1}{2}}(2J'+1)^{\frac{1}{2}}(-1)^{-k+M-K'}\begin{pmatrix}J & 1 & J'\\ M & 0 & -M\end{pmatrix}\begin{pmatrix}J & 1 & J'\\ K & -k & -K'\end{pmatrix}\right) -$$

$$-\delta_{MM'}\frac{\varepsilon^2(t)}{6}\sum_{k=-2}^{2}\left(\sum_{v,v'}\langle v|\alpha^{\mathrm{BF},(2,k)}|v'\rangle\sum_{K,K'}C_{Kv}^{Jn*}C_{K'v'}^{J'n'}(2J+1)^{\frac{1}{2}}(2J'+1)^{\frac{1}{2}}(-1)^{-k+M-K'}\begin{pmatrix}J & 2 & J'\\ M & 0 & -M\end{pmatrix}\begin{pmatrix}J & 2 & J'\\ K & -k & -K'\end{pmatrix}\right) +$$

$$+\delta_{JJ'}\delta_{MM'}\frac{\varepsilon^2(t)}{6\sqrt{2}}\sum_{v,v'}\sum_K C_{Kv}^{Jn*}C_{Kv'}^{J'n'}\langle v|\alpha^{\mathrm{BF},(0)}|v'\rangle$$

Measures for alignment/orientation

$$\langle JKM|\cos^2(\delta)|J'K'M'\rangle = \cdots$$

$$\langle JKM|\cos^2(\theta_{xX})|J'K'M'\rangle = \cdots$$

$$\langle JKM|\cos^2(\theta_{yY})|J'K'M'\rangle = \cdots$$

$$\langle JKM|\cos^2(\theta_{zZ})|J'K'M'\rangle = \cdots$$

Please read *Makhija et al., Phys. Rev. A, **85**, 033425 (2012)* and references therein

Recommended literature

Richard N. Zare – Angular Momentum

Philip R. Bunker and Per Jensen – Molecular Symmetry and Spectroscopy