

# ROTATIONAL AND ROVIBRATIONAL CONSTANTS FOR TRIATOMIC MOLECULES FROM FOURTH-ORDER PERTURBATION THEORY

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# Rigid-rotor Approximation:

Inverse **moments of inertia** about  
principal axes

$$E_{RR} = E_v + \sum_{\alpha} B_e^{\alpha} \langle P_{\alpha}^2 \rangle$$

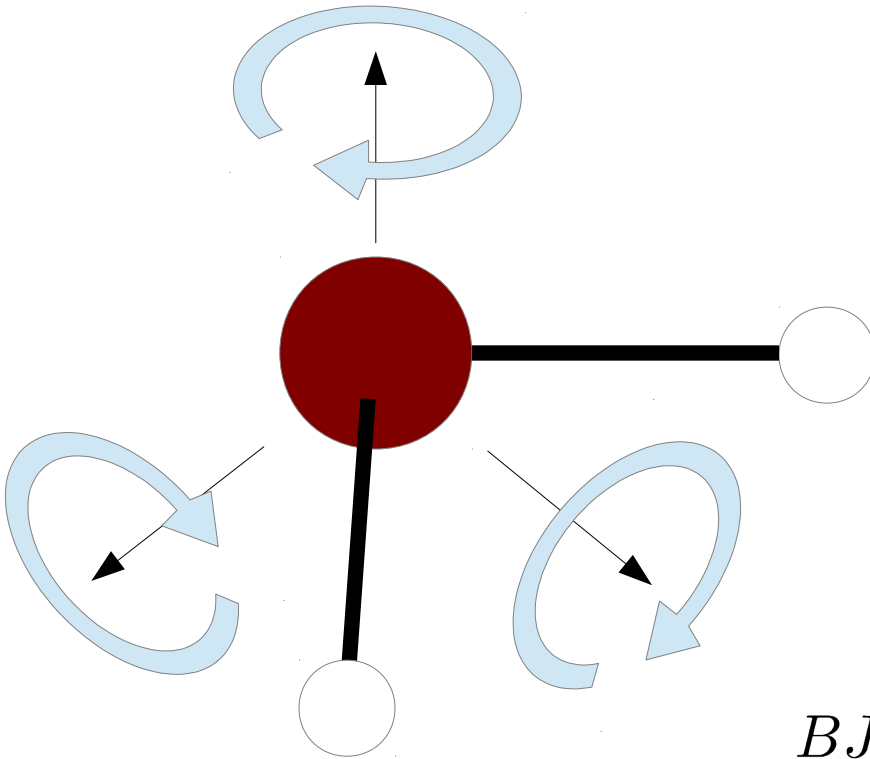
$$BJ(J + 1)$$

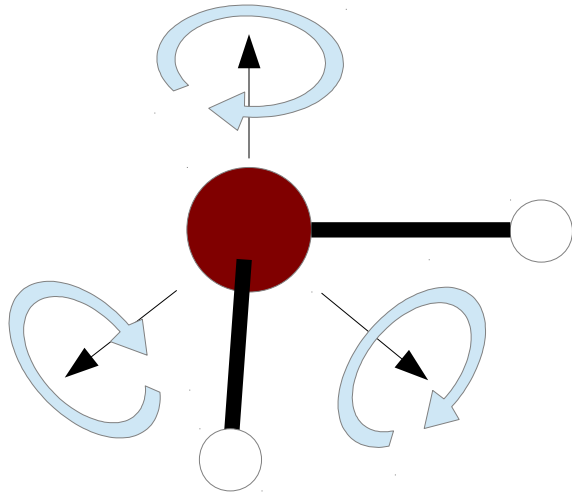
For **linear** and **spherical top** molecules

$$BJ(J + 1) + (A - B)K^2$$

For **symmetric top** molecules

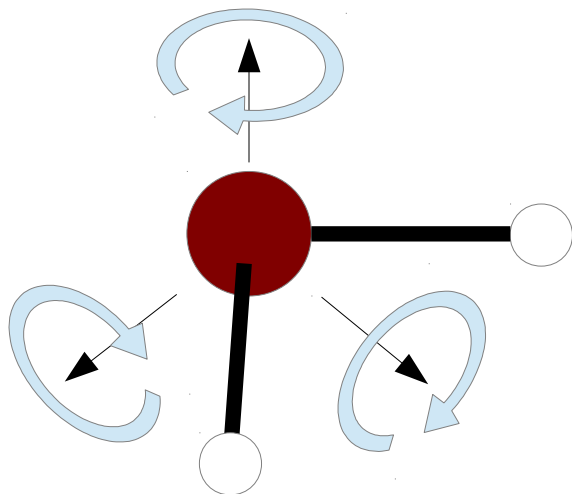
No simple form for  
**asymmetric top** molecules





For general  
(non-linear)  
molecules:

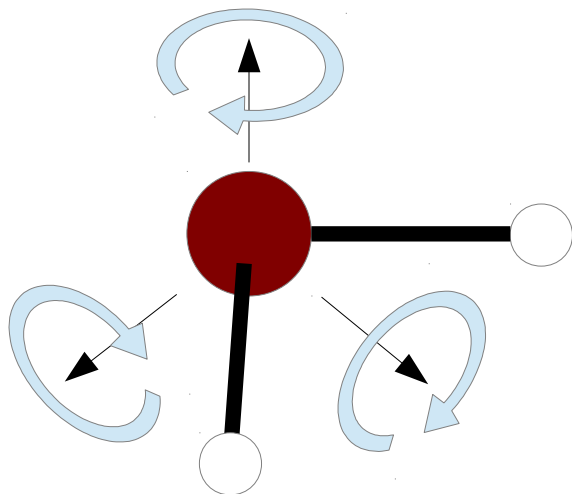
$$\begin{aligned}
 E = & E_{\text{RR}} + \frac{1}{2} \sum_{\alpha\beta} \langle P_{\alpha} P_{\beta} \rangle \left( \sum_i \sigma_{\alpha\beta}(i) \left( n_i + \frac{1}{2} \right) + \frac{1}{2} \tilde{\sigma}_{\alpha\beta} + \frac{1}{2} \sum_{i \leq j} \sigma_{\alpha\beta}(i, j) \left( n_i + \frac{1}{2} \right) \left( n_j + \frac{1}{2} \right) + \dots \right) \\
 & + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle P_{\alpha} P_{\beta} P_{\gamma} P_{\delta} \rangle \left( \tau_{\alpha\beta\gamma\delta} + \sum_i \tau_{\alpha\beta\gamma\delta}(i) \left( n_i + \frac{1}{2} \right) + \dots \right) \\
 & + \sum_{\alpha\beta\gamma\delta\epsilon\eta} \langle P_{\alpha} P_{\beta} P_{\gamma} P_{\delta} P_{\epsilon} P_{\eta} \rangle (\xi_{\alpha\beta\gamma\delta\epsilon\eta} + \dots) \\
 & + \dots
 \end{aligned}$$



For general  
(non-linear)  
molecules:

$$\begin{aligned}
 E = & E_{\text{RR}} + \frac{1}{2} \sum_{\alpha\beta} \langle P_{\alpha} P_{\beta} \rangle \left( \sum_i \sigma_{\alpha\beta}(i) \left( n_i + \frac{1}{2} \right) + \frac{1}{2} \tilde{\sigma}_{\alpha\beta} + \frac{1}{2} \sum_{i \leq j} \sigma_{\alpha\beta}(i, j) \left( n_i + \frac{1}{2} \right) \left( n_j + \frac{1}{2} \right) + \dots \right) \\
 & + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle P_{\alpha} P_{\beta} P_{\gamma} P_{\delta} \rangle \left( \tau_{\alpha\beta\gamma\delta} + \sum_i \tau_{\alpha\beta\gamma\delta}(i) \left( n_i + \frac{1}{2} \right) + \dots \right) \\
 & + \sum_{\alpha\beta\gamma\delta\epsilon\eta} \langle P_{\alpha} P_{\beta} P_{\gamma} P_{\delta} P_{\epsilon} P_{\eta} \rangle (\xi_{\alpha\beta\gamma\delta\epsilon\eta} + \dots) \\
 & + \dots
 \end{aligned}$$

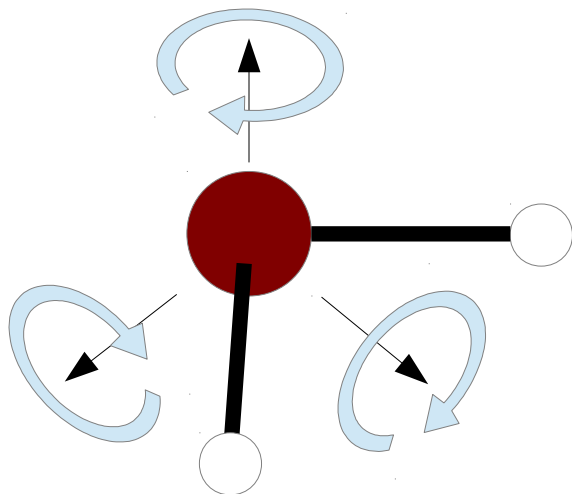
“Vibration-rotation interaction”



For general  
(non-linear)  
molecules:

$$\begin{aligned}
 E = & E_{\text{RR}} + \frac{1}{2} \sum_{\alpha\beta} \langle P_{\alpha} P_{\beta} \rangle \left( \sum_i \sigma_{\alpha\beta}(i) \left( n_i + \frac{1}{2} \right) + \frac{1}{2} \tilde{\sigma}_{\alpha\beta} + \frac{1}{2} \sum_{i \leq j} \sigma_{\alpha\beta}(i, j) \left( n_i + \frac{1}{2} \right) \left( n_j + \frac{1}{2} \right) + \dots \right) \\
 & + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle P_{\alpha} P_{\beta} P_{\gamma} P_{\delta} \rangle \left( \tau_{\alpha\beta\gamma\delta} + \sum_i \tau_{\alpha\beta\gamma\delta}(i) \left( n_i + \frac{1}{2} \right) + \dots \right) \\
 & + \sum_{\alpha\beta\gamma\delta\epsilon\eta} \langle P_{\alpha} P_{\beta} P_{\gamma} P_{\delta} P_{\epsilon} P_{\eta} \rangle (\xi_{\alpha\beta\gamma\delta\epsilon\eta} + \dots) \\
 & + \dots
 \end{aligned}$$

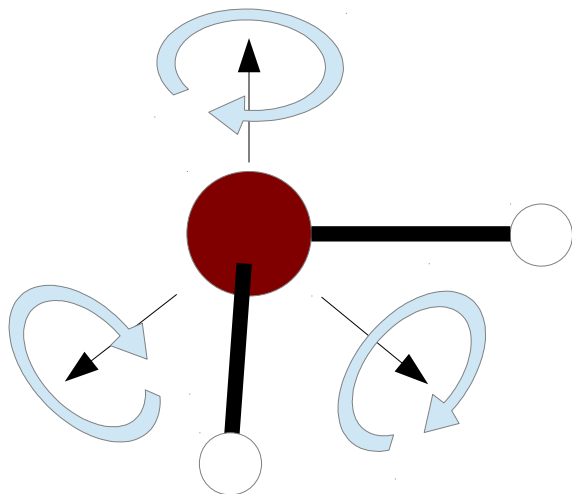
“Quartic centrifugal distortion”



For general  
(non-linear)  
molecules:

$$\begin{aligned}
 E = & E_{\text{RR}} + \frac{1}{2} \sum_{\alpha\beta} \langle P_\alpha P_\beta \rangle \left( \sum_i \sigma_{\alpha\beta}(i) \left( n_i + \frac{1}{2} \right) + \frac{1}{2} \tilde{\sigma}_{\alpha\beta} + \frac{1}{2} \sum_{i \leq j} \sigma_{\alpha\beta}(i, j) \left( n_i + \frac{1}{2} \right) \left( n_j + \frac{1}{2} \right) + \dots \right) \\
 & + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle P_\alpha P_\beta P_\gamma P_\delta \rangle \left( \tau_{\alpha\beta\gamma\delta} + \sum_i \tau_{\alpha\beta\gamma\delta}(i) \left( n_i + \frac{1}{2} \right) + \dots \right) \\
 & + \sum_{\alpha\beta\gamma\delta\epsilon\eta} \langle P_\alpha P_\beta P_\gamma P_\delta P_\epsilon P_\eta \rangle (\xi_{\alpha\beta\gamma\delta\epsilon\eta} + \dots) \\
 & + \dots
 \end{aligned}$$

“Sextic centrifugal distortion”



For general  
(non-linear)  
molecules:

Rigid-  
rotor

VPT2

$$\begin{aligned}
 E = & E_{\text{RR}} + \frac{1}{2} \sum_{\alpha\beta} \langle P_{\alpha} P_{\beta} \rangle \left( \sum_i \sigma_{\alpha\beta}(i) \left( n_i + \frac{1}{2} \right) + \frac{1}{2} \tilde{\sigma}_{\alpha\beta} + \frac{1}{2} \sum_{i \leq j} \sigma_{\alpha\beta}(i, j) \left( n_i + \frac{1}{2} \right) \left( n_j + \frac{1}{2} \right) + \dots \right) \\
 & + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle P_{\alpha} P_{\beta} P_{\gamma} P_{\delta} \rangle \left( \tau_{\alpha\beta\gamma\delta} + \sum_i \tau_{\alpha\beta\gamma\delta}(i) \left( n_i + \frac{1}{2} \right) + \dots \right) \\
 & + \sum_{\alpha\beta\gamma\delta\epsilon\eta} \langle P_{\alpha} P_{\beta} P_{\gamma} P_{\delta} P_{\epsilon} P_{\eta} \rangle (\xi_{\alpha\beta\gamma\delta\epsilon\eta} + \dots) \\
 & + \dots
 \end{aligned}$$

VPT4

# The Watson Rovibrational Hamiltonian

Rotational operators.

Neglecting all vibration gives  
RR approximation.

Vibrational “angular  
momentum”.

Vibrations combine  
and couple to rotation.

$$\hat{H} = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} (\hat{P}_{\alpha} - \pi_{\alpha})(\hat{P}_{\beta} - \pi_{\beta}) + \hat{T} + \hat{V} + \hat{U}$$

Instantaneous inverse moment-of-inertia tensor.

Vibrations change the mass distribution and hence the  
moments of inertia (and even the principal axes).

$$\frac{1}{2} \mu_{\alpha\beta} = B_e^{\alpha} \delta_{\alpha\beta} - \sum_i B_e^{\alpha} B_e^{\beta} a_i^{\alpha\beta} q_i + \frac{3}{4} \sum_{\gamma ij} B_e^{\alpha} B_e^{\beta} B_e^{\gamma} a_i^{\alpha\gamma} a_j^{\gamma\beta} q_i q_j + \dots$$



Hamiltonian expanded in perturbation series,  
order = # of P's, p's and q's – 2:

$$\begin{aligned}
 \hat{H} = & \hat{H}_v + \sum_{\alpha} \hat{H}_{\alpha} + \sum_{\alpha\beta} \hat{H}_{\alpha\beta} = \left[ \hat{H}_v^{[0]} + \sum_{\alpha} B_e^{\alpha} (P^{\alpha})^2 \right] && \text{Rigid-rotor+Harmonic Oscillator} \\
 + & \lambda \left[ \hat{H}_v^{[1]} - \sum_{\alpha ij} 2B_e^{\alpha} \sqrt{\frac{\omega_j}{\omega_i}} \zeta_{ij}^{\alpha} P^{\alpha} q_i p_j - \sum_{\alpha\beta i} B_e^{\alpha} B_e^{\beta} a_i^{\alpha\beta} P^{\alpha} P^{\beta} q_i \right] && \text{Rotation+expansion of } \mu_{\alpha\beta} \\
 + & \lambda^2 \left[ \hat{H}_v^{[2]} + \sum_{\alpha\beta ijk} 2B_e^{\alpha} B_e^{\beta} a_k^{\alpha\beta} \sqrt{\frac{\omega_j}{\omega_i}} \zeta_{ij}^{\alpha} P^{\alpha} q_k q_i p_j + \sum_{\alpha\beta\gamma ij} \frac{3}{4} B_e^{\alpha} B_e^{\beta} B_e^{\gamma} a_i^{\alpha\gamma} a_j^{\gamma\beta} P^{\alpha} P^{\beta} q_i q_j \right] \\
 + & \lambda^3 \left[ \hat{H}_v^{[3]} - \sum_{\alpha\beta\gamma ijkl} \frac{3}{2} B_e^{\alpha} B_e^{\beta} B_e^{\gamma} a_k^{\alpha\gamma} a_l^{\gamma\beta} \sqrt{\frac{\omega_j}{\omega_i}} \zeta_{ij}^{\alpha} P^{\alpha} q_k q_l q_i p_j - \sum_{\alpha\beta\gamma\delta ijk} \frac{1}{2} B_e^{\alpha} B_e^{\beta} B_e^{\gamma} B_e^{\delta} a_i^{\alpha\gamma} a_j^{\gamma\delta} a_k^{\delta\beta} P^{\alpha} P^{\beta} q_i q_j q_k \right] \\
 + & \lambda^4 \left[ \hat{H}_v^{[4]} + \sum_{\alpha\beta\gamma\delta ijk l m} \frac{1}{2} B_e^{\alpha} B_e^{\beta} B_e^{\gamma} B_e^{\delta} a_k^{\alpha\gamma} a_l^{\gamma\delta} a_m^{\delta\beta} \sqrt{\frac{\omega_j}{\omega_i}} \zeta_{ij}^{\alpha} P^{\alpha} q_k q_l q_m q_i p_j \right. \\
 + & \left. \sum_{\alpha\beta\gamma\delta\epsilon ijk l} \frac{5}{16} B_e^{\alpha} B_e^{\beta} B_e^{\gamma} B_e^{\delta} B_e^{\epsilon} a_i^{\alpha\gamma} a_j^{\gamma\delta} a_k^{\delta\epsilon} a_l^{\epsilon\beta} P^{\alpha} P^{\beta} q_i q_j q_k q_l \right] && \text{Rotation}+\pi_{\alpha}+\text{expansion of } \mu_{\alpha\beta}
 \end{aligned}$$

Vibration

[illegible]

Placement of **rotational operators** gives many terms.  
Both  $H_{\alpha\beta}$  - and  $H_{\alpha}H_{\beta}$ -type terms contribute.



$$\sigma_{\alpha\beta}(i,i)$$

[illegible]

$$\sigma_{\alpha\beta}(i,j)$$

[illegible]



$$T_{\alpha\beta\gamma\delta}(i)$$

ξ<sub>αβγδεη</sub>

$$\begin{aligned}
& + \frac{3B_e^a a_i^{ab} B_e^b B_e^c a_i^{cg} B_e^d a_i^{dg} B_e^e a_i^{ef} B_e^f B_e^g}{8\omega_i^2} + \frac{3B_e^a a_i^{ab} B_e^b B_e^c a_i^{cd} B_e^d B_e^e a_i^{eg} B_e^f a_i^{fg} B_e^g}{16\omega_i^2} + \frac{3B_e^a a_i^{ag} B_e^b a_i^{bg} B_e^c a_i^{cd} B_e^d B_e^e a_i^{ef} B_e^f B_e^g}{16\omega_i^2} + \frac{3B_e^a a_i^{ab} B_e^b B_e^c a_i^{cg} B_e^d a_i^{dg} B_e^e a_i^{ef} B_e^f B_e^g}{16\omega_i \omega_j} \\
& + \frac{3B_e^a a_i^{ab} B_e^b B_e^c a_j^{cg} B_e^d a_i^{dg} B_e^e a_j^{ef} B_e^f B_e^g}{16\omega_i \omega_j} + \frac{3B_e^a a_i^{ab} B_e^b B_e^c a_j^{cd} B_e^d B_e^e a_j^{eg} B_e^f a_j^{fg} B_e^g}{16\omega_i (\omega_j + \omega_i)} + \frac{3B_e^a a_i^{ag} B_e^b B_e^c a_j^{cd} B_e^d B_e^e a_j^{eg} B_e^f a_i^{fg} B_e^g}{16\omega_i (\omega_j + \omega_i)} + \frac{3B_e^a a_i^{ag} B_e^b a_j^{bg} B_e^c a_i^{cd} B_e^d B_e^e a_j^{ef} B_e^f B_e^g}{16\omega_j (\omega_j + \omega_i)} \\
& + \frac{3B_e^a a_i^{ag} B_e^b a_j^{bg} B_e^c a_j^{cd} B_e^d B_e^e a_i^{ef} B_e^f B_e^g}{16\omega_i (\omega_j + \omega_i)} + \frac{B_e^a a_i^{ab} B_e^b B_e^c a_i^{cd} B_e^d B_e^e a_i^{ef} B_e^f \phi_{i\eta}}{6\omega_i^3} + \frac{B_e^a a_i^{ab} B_e^b B_e^c a_j^{cd} B_e^d B_e^e a_i^{ef} B_e^f \phi_{i\eta} (\omega_j + 3\omega_i)}{4\omega_i^2 (\omega_j + \omega_i) (\omega_j + 2\omega_i)} + \frac{B_e^a a_i^{ab} B_e^b B_e^c a_i^{cd} B_e^d B_e^e a_j^{ef} B_e^f \phi_{i\eta} (\omega_j^2 + 3\omega_i \omega_j + 4\omega_i^2)}{8\omega_i^2 \omega_j (\omega_j + \omega_i) (\omega_j + 2\omega_i)} \\
& + \frac{B_e^a a_i^{ab} B_e^b B_e^c a_j^{cd} B_e^d B_e^e a_j^{ef} B_e^f \phi_{ijj} (4\omega_j^2 + 3\omega_i \omega_j + \omega_i^2)}{8\omega_i \omega_j^2 (\omega_j + \omega_i) (2\omega_j + \omega_i)} + \frac{B_e^a a_i^{ab} B_e^b B_e^c a_j^{cd} B_e^d B_e^e a_i^{ef} B_e^f \phi_{ijk} (\omega_k^2 + 2\omega_j \omega_k + \omega_i \omega_k + \omega_j^2 + 2\omega_i \omega_j + \omega_i^2)}{4\omega_i \omega_k (\omega_j + \omega_i) (\omega_k + \omega_j) (\omega_k + \omega_j + \omega_i)} - \frac{B_e^a a_i^{ab} B_e^b B_e^c a_i^{cd} B_e^d B_e^e \zeta_{ij} B_e^f \zeta_{ij}^f (\omega_j - \omega_i)}{2\omega_i^3 \omega_j} \\
& - \frac{B_e^a \zeta_{ij} B_e^b \zeta_{ij}^c B_e^c a_i^{cd} B_e^d B_e^e a_i^{ef} B_e^f (\omega_j - \omega_i)}{2\omega_i^3 \omega_j} + \frac{B_e^a a_i^{ab} B_e^b B_e^c \zeta_{ij} B_e^d \zeta_{jk}^d B_e^e a_k^{ef} B_e^f (\omega_j + \omega_i) (\omega_k + \omega_j)}{2\omega_i^{\frac{3}{2}} \omega_j^{\frac{1}{2}} \omega_k^{\frac{1}{2}}} - \frac{B_e^a a_i^{ab} B_e^b B_e^c \zeta_{jk}^c B_e^d a_i^{de} B_e^e B_e^f \zeta_{jk}^f (\omega_k - \omega_j)^2}{2\omega_i \omega_j \omega_k (\omega_k + \omega_j) (\omega_k + \omega_j + \omega_i)} + \frac{B_e^a \zeta_{ij} B_e^b a_k^{bc} B_e^c B_e^d a_k^{de} B_e^e B_e^f \zeta_{ij}^f (\omega_j - \omega_i)^2}{2\omega_i \omega_j \omega_k (\omega_j + \omega_i) (\omega_k + \omega_j + \omega_i)} \\
& - \frac{B_e^a a_i^{ab} B_e^b B_e^c \zeta_{ij}^c B_e^d a_k^{de} B_e^e B_e^f \zeta_{jk}^f (\omega_j + \omega_i) (\omega_k - \omega_j)}{2\omega_i^{\frac{3}{2}} \omega_j^{\frac{1}{2}} \sqrt{\omega_k} (\omega_k + \omega_j)} + \frac{B_e^a \zeta_{ij} B_e^b a_k^{bc} B_e^c B_e^d \zeta_{jk}^d B_e^e a_k^{ef} B_e^f (\omega_j^2 - \omega_i^2) (\omega_k + \omega_j)}{2\sqrt{\omega_i} \omega_j^2 \omega_k^{\frac{3}{2}}} - \frac{B_e^a a_i^{ab} B_e^b B_e^c \zeta_{jk}^c B_e^d \zeta_{ij}^d B_e^e a_k^{ef} B_e^f (\omega_j - \omega_i) (\omega_k - \omega_j)}{2\omega_i^{\frac{3}{2}} \omega_j \omega_k^{\frac{1}{2}} (\omega_k + \omega_j + \omega_i)} \\
& + \frac{B_e^a \zeta_{ij} B_e^b a_i^{bc} B_e^c B_e^d a_i^{de} B_e^e B_e^f \zeta_{ij}^f (\omega_j^2 - 4\omega_i^2) (\omega_j - \omega_i)^2}{2\omega_i^2 \omega_j^2 (\omega_j + \omega_i)} - \frac{B_e^a a_i^{ab} B_e^b B_e^c a_j^{cd} B_e^d B_e^e \zeta_{ik}^c B_e^f \zeta_{jk}^f (\omega_k + \omega_i) (\omega_k - \omega_j)}{2\omega_i^{\frac{3}{2}} \sqrt{\omega_j} \omega_k (\omega_j + \omega_i) (\omega_k + \omega_j)} - \frac{B_e^a a_i^{ab} B_e^b B_e^c a_j^{cd} B_e^d B_e^e \zeta_{jk}^c B_e^f \zeta_{ik}^f (\omega_k^2 - \omega_i^2) (\omega_k + \omega_j)}{2\omega_i^{\frac{3}{2}} \sqrt{\omega_j} \omega_k (\omega_j + \omega_i)} \\
& + \frac{B_e^a \zeta_{ij} B_e^b \zeta_{ik}^c B_e^c a_j^{cd} B_e^d B_e^e a_i^{ef} B_e^f (\omega_j^2 - \omega_i^2) (\omega_k + \omega_i)}{2\omega_i \sqrt{\omega_j} \omega_k^{\frac{1}{2}} (\omega_k + \omega_j)} + \frac{B_e^a \zeta_{ik} B_e^b \zeta_{ij}^c B_e^c a_j^{cd} B_e^d B_e^e a_k^{ef} B_e^f (\omega_j + \omega_i) (\omega_k - \omega_i)}{2\omega_i \sqrt{\omega_j} \omega_k^{\frac{1}{2}} (\omega_k + \omega_i) (\omega_k + \omega_j)} - \frac{B_e^a \zeta_{ij} B_e^b a_k^{bc} B_e^c B_e^d a_k^{de} B_e^e B_e^f \zeta_{ij}^f (\omega_j^2 - \omega_i^2) (\omega_k - \omega_j)}{2\sqrt{\omega_i} \omega_j^2 \sqrt{\omega_k} (\omega_k + \omega_j)} \\
& - \frac{B_e^a a_i^{ab} B_e^b B_e^c \zeta_{jk}^c B_e^d a_j^{de} B_e^e B_e^f \zeta_{ik}^f (\omega_k^2 - \omega_i^2) (\omega_k - \omega_j)}{2\omega_i^{\frac{3}{2}} \sqrt{\omega_j} \omega_k (\omega_k + \omega_j + \omega_i)} - \frac{B_e^a \zeta_{ij} B_e^b a_k^{bc} B_e^c B_e^d \zeta_{ik}^d B_e^e a_j^{ef} B_e^f (\omega_j^2 - \omega_i^2) (\omega_k - \omega_i)}{2\omega_i \omega_j^{\frac{3}{2}} \sqrt{\omega_k} (\omega_k + \omega_j + \omega_i)} - \frac{B_e^a a_i^{ab} B_e^b B_e^c \zeta_{ij} B_e^d a_i^{de} B_e^e B_e^f \zeta_{ij}^f (\omega_j^2 - \omega_i^2) (3\omega_j^2 + \omega_i \omega_j + 2\omega_i^2)}{2\omega_i^2 \omega_j^2 (\omega_j + 2\omega_i)} \\
& - \frac{B_e^a \zeta_{ij} B_e^b a_i^{bc} B_e^c B_e^d \zeta_{ij}^d B_e^e a_i^{ef} B_e^f (\omega_j^2 - \omega_i^2) (3\omega_j^2 + \omega_i \omega_j + 2\omega_i^2)}{2\omega_i^2 \omega_j^2 (\omega_j + 2\omega_i)} - \frac{B_e^a \zeta_{ij} B_e^b a_k^{bc} B_e^c B_e^d a_i^{de} B_e^e B_e^f \zeta_{jk}^f (\omega_j^2 - \omega_i^2) (\omega_k - \omega_j)}{2\sqrt{\omega_i} \omega_j \sqrt{\omega_k} (\omega_k + \omega_j) (\omega_k + \omega_j + \omega_i)} \\
& - \frac{B_e^a a_i^{ab} B_e^b B_e^c \zeta_{ij} B_e^d \zeta_{ij}^d B_e^e a_i^{ef} B_e^f (2\omega_j^2 + 3\omega_i \omega_j^3 + 10\omega_i^2 \omega_j^2 + 7\omega_i^3 \omega_j + 2\omega_i^4)}{2\omega_i^4 \omega_j^2 (\omega_j + \omega_i) (\omega_j + 2\omega_i)}
\end{aligned}$$



# Resonances

$$\sigma_{\alpha\beta}(i,j): \frac{B_e^a \zeta_{ik}^a B_e^b \zeta_{ij}^b \phi_{iij} \phi_{jjk} (20\omega_j^6 \omega_k^8 - 185\omega_i^2 \omega_j^4 \omega_k^8 - \dots + 4\omega_i^{12} \omega_j^2)}{\omega_j^{\frac{3}{2}} \omega_k^{\frac{3}{2}} (\omega_j^2 - 4\omega_i^2)(\omega_j^2 - \omega_i^2)(4\omega_j^2 - \omega_i^2)(\omega_k^2 - \omega_i^2)(\omega_k^2 - \omega_j^2) \Delta(\omega_k, \omega_j, \omega_i)}$$

**Fermi** and **Darling-Dennison/Coriolis**  
resonance denominators

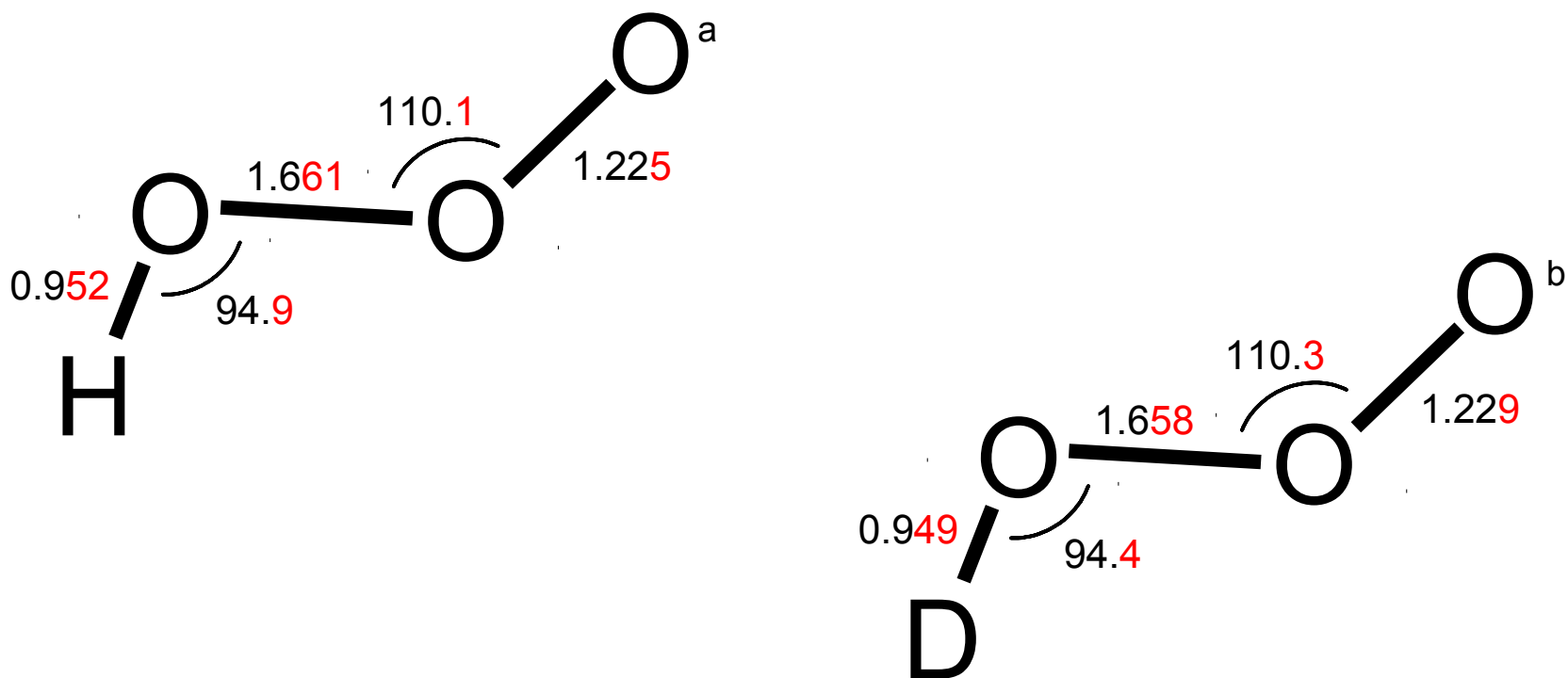
$$\xi_{\alpha\beta\gamma\delta\epsilon\eta}: \frac{B_e^a a_i^{ab} B_e^b B_e^c \zeta_{ij}^c B_e^d \zeta_{ij}^d B_e^e a_i^{ef} B_e^f (2\omega_j^4 + \dots + 2\omega_i^4)}{2\omega_i^3 \omega_j^2 (\omega_j + \omega_i)(\omega_j + 2\omega_i)}$$

**No resonance denominators!**

The ground state is **resonance-free**. Terms with no vibrational dependence have no resonance denominators, and the denominators cancel in  $\sum_{i \leq j} \sigma_{\alpha\beta}(i,j)$  and  $\sum_i \tau_{\alpha\beta\gamma\delta}(i)$ .

# Why VPT4?

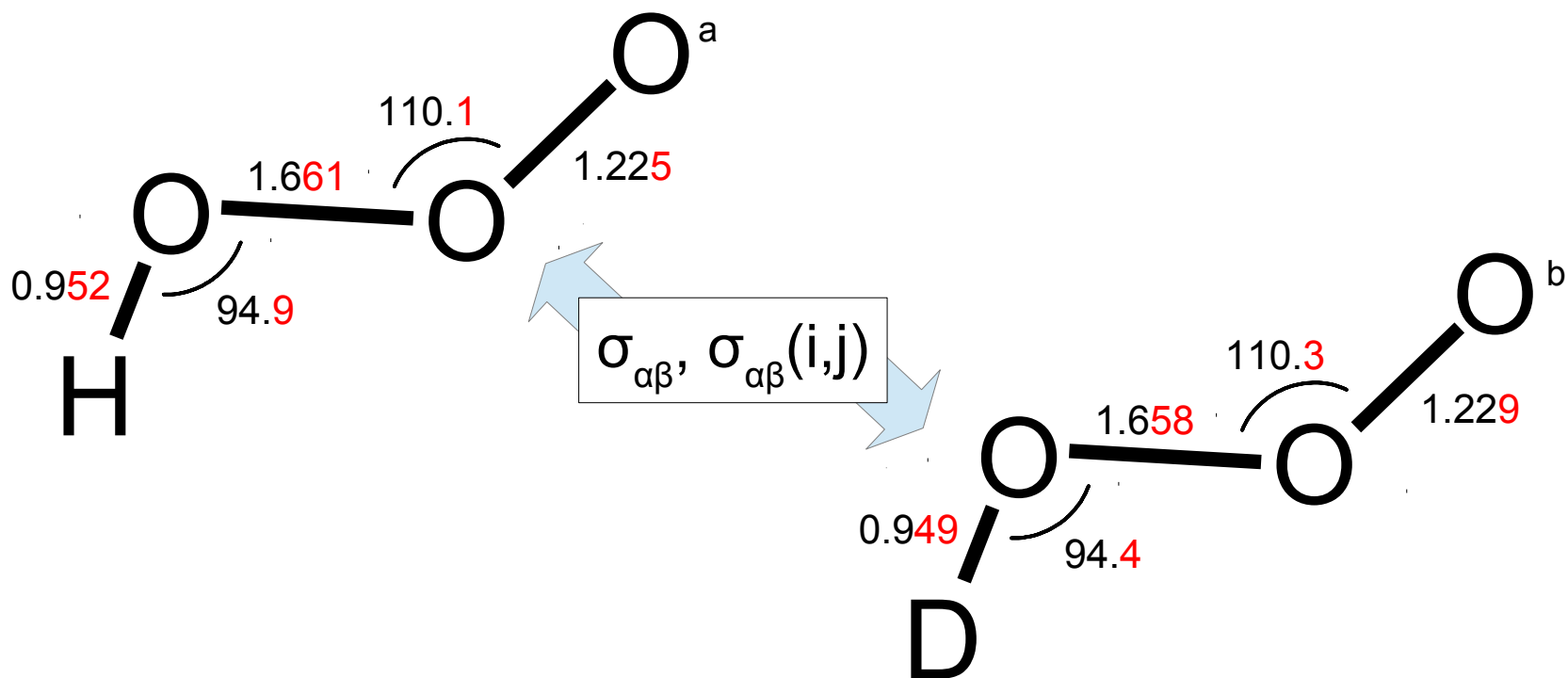
Equilibrium geometries ( $r_e$ ) from  $B_e^\gamma = B_0^\gamma + \frac{1}{2} \sum_i \alpha_i^\gamma$  ( $\sim$ VPT2).



- a) M. C. McCarthy, V. Lattanzi, D. Kokkin, O. Martinez, and J. F. Stanton, *J. Chem. Phys.* **136**, 034303 (2012).  
b) M. C. McCarthy, J. F. Stanton et al., *unpublished*.

# Why VPT4?

Equilibrium geometries ( $r_e$ ) from  $B_e^\gamma = B_0^\gamma + \frac{1}{2} \sum_i \alpha_i^\gamma$  ( $\sim$ VPT2).



- a) M. C. McCarthy, V. Lattanzi, D. Kokkin, O. Martinez, and J. F. Stanton, *J. Chem. Phys.* **136**, 034303 (2012).  
b) M. C. McCarthy, J. F. Stanton et al., *unpublished*.

	VPT2			VPT4			
	$x_{ij}$	$\sigma_{\alpha\beta}(i)$	$\tau_{\alpha\beta\gamma\delta}$	$y_{ijk}$	$\sigma_{\alpha\beta}(i,j)$	$\tau_{\alpha\beta\gamma\delta}(i)$	$\xi_{\alpha\beta\gamma\delta\epsilon\eta}$
$F_3$	$\varphi_{ijk}$	$\varphi_{iij}$	0	$\varphi_{ijk}$	$\varphi_{ijk}$	$\varphi_{ijk}$	$\varphi_{ijk}$
$F_4$	$\varphi_{iijj}$	0	0	$\varphi_{ijkl}$	$\varphi_{ijkl}$	$\varphi_{iijk}$	0
$F_5$	0	0	0	$\varphi_{iijkl}$	$\varphi_{iijjk}$	0	0
$F_6$	0	0	0	$\varphi_{iijjkk}$	0	0	0

# Future Work

- U (pseudopotential) terms missing from VPT2 may be important when going to VPT4.
- $\tilde{\sigma}_{\alpha\beta}$  equations need to be derived.
- Current constants are limited to triatomics (3 vibrational modes). The numerical implementation is not limited, however.

# Acknowledgements



Dr. John Stanton



Justin Gong



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	VPT2				VPT4		
	$x$	$\sigma_{\alpha\beta}$	$\tau_{\alpha\beta\gamma\delta}$	$y$	$\sigma_{\alpha\beta}$	$\tau_{\alpha\beta\gamma\delta}$	$\xi_{\alpha\beta\gamma\delta\epsilon\eta}$
const.		0			Not Derived		
$(n_i+1/2)$	0		0	Not Derived			
$(n_i+1/2)^2$		0	0				
$(n_i+1/2)(n_j+1/2)$		0	0				
$(n_i+1/2)^3$	0	0	0				
$(n_i+1/2)^2(n_j+1/2)$	0	0	0				
$(n_i+1/2)(n_j+1/2)(n_k+1/2)$	0	0	0				

	VPT2				VPT4		
	$x$	$\sigma_{\alpha\beta}$	$\tau_{\alpha\beta\gamma\delta}$	$y$	$\sigma_{\alpha\beta}$	$\tau_{\alpha\beta\gamma\delta}$	$\xi_{\alpha\beta\gamma\delta\epsilon\eta}$
const.		0		0	Not Derived	Not Zero!	
$(n_i+1/2)$	0		0	Not Derived	0		Not Zero!
$(n_i+1/2)^2$		0	0	0		Not Zero!	Not Zero!
$(n_i+1/2)(n_j+1/2)$		0	0	0		Not Zero!	Not Zero!
$(n_i+1/2)^3$	0	0	0		0	0	0
$(n_i+1/2)^2(n_j+1/2)$	0	0	0		0	Not Zero!	0
$(n_i+1/2)(n_j+1/2)(n_k+1/2)$	0	0	0		0	Not Zero!	0