

VHEGEN: A vibronic Hamiltonian expansion generator for trigonal and tetragonal polyatomic systems

Robert A. Lang

Riley J. Hickman

Tao Zeng

Thank you for using **VHEGEN**, the **V**-ibronic **H**-amiltonian **E**-xpansion **GEN**-erator for trigonal and tetragonal polyatomic systems. This is a **VHEGEN** output file compiled by **pdf_lat_ex**. If the **VHEGEN** package was used in research resulting in a publication, please reference the article in *Computer Physics Communications* which describes the program ([doi here]). Additional information regarding the matrix element expansion process, including the independent matrix element eigenvalues, their root formulas and constraints, and their transformation to the real basis (if applicable), can be found in the **log** output file. For questions, bugs, or comments, please contact robert.lang@mail.utoronto.ca.

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1 Vibronic interaction

$(E + E) \otimes (e + e)$ in C_3

2 Vibronic Hamiltonian operator in the complex E basis

$$\hat{H} = (|+\alpha\rangle \quad |-\alpha\rangle \quad |+\beta\rangle \quad |-\beta\rangle) \begin{pmatrix} 0 & 0 & H_{+\alpha+\beta} & H_{+\alpha-\beta} \\ 0 & 0 & H_{-\alpha+\beta} & H_{-\alpha-\beta} \\ H_{+\beta+\alpha} & H_{+\beta-\alpha} & 0 & 0 \\ H_{-\beta+\alpha} & H_{-\beta-\alpha} & 0 & 0 \end{pmatrix} \begin{pmatrix} \langle +\alpha| \\ \langle -\alpha| \\ \langle +\beta| \\ \langle -\beta| \end{pmatrix}$$

$$H_{+\alpha+\beta} = H_{+\alpha+\beta} = H_{-\alpha-\beta}^* = H_{+\beta+\alpha}^* = H_{-\beta-\alpha}^*$$

$$H_{+\alpha-\beta} = H_{+\alpha-\beta} = H_{-\alpha+\beta}^* = H_{+\beta-\alpha}^* = H_{-\beta+\alpha}^*$$

3 Matrix element expansions in the complex E basis

3.1 Order: 0

Number of fitting parameters: $H_{+\alpha+\beta}$: 2, $H_{+\alpha-\beta}$: 0.

Polar e-coordinates:

$$H_{+\alpha+\beta}^{(0)} = ia_{0,0,0,0}^i + a_{0,0,0,0}^r$$

$$H_{-\alpha-\beta}^{(0)} = -ia_{0,0,0,0}^i + a_{0,0,0,0}^r$$

$$H_{+\beta+\alpha}^{(0)} = -ia_{0,0,0,0}^i + a_{0,0,0,0}^r$$

$$H_{-\beta-\alpha}^{(0)} = ia_{0,0,0,0}^i + a_{0,0,0,0}^r$$

$$H_{+\alpha-\beta}^{(0)} = 0$$

$$H_{-\alpha+\beta}^{(0)} = 0$$

$$H_{+\beta-\alpha}^{(0)} = 0$$

$$H_{-\beta+\alpha}^{(0)} = 0$$

Cartesian e-coordinates:

$$H_{+\alpha+\beta}^{(0)} = ia_{0,0,0,0}^i + a_{0,0,0,0}^r$$

$$H_{-\alpha-\beta}^{(0)} = -ia_{0,0,0,0}^i + a_{0,0,0,0}^r$$

$$H_{+\beta+\alpha}^{(0)} = -ia_{0,0,0,0}^i + a_{0,0,0,0}^r$$

$$H_{-\beta-\alpha}^{(0)} = ia_{0,0,0,0}^i + a_{0,0,0,0}^r$$

$$H_{+\alpha-\beta}^{(0)} = 0$$

$$H_{-\alpha+\beta}^{(0)} = 0$$

$$H_{+\beta-\alpha}^{(0)} = 0$$

$$H_{-\beta+\alpha}^{(0)} = 0$$

3.2 Order: 1

Number of fitting parameters: $H_{+\alpha+\beta}$: 0, $H_{+\alpha-\beta}$: 4.

Polar e-coordinates:

$$H_{+\alpha+\beta}^{(1)} = 0$$

$$H_{-\alpha-\beta}^{(1)} = 0$$

$$H_{+\beta+\alpha}^{(1)} = 0$$

$$H_{-\beta-\alpha}^{(1)} = 0$$

$$\begin{aligned} H_{+\alpha-\beta}^{(1)} = & b_{0,0,-1,-1}^i \rho_\alpha \sin(\phi_\alpha) + ib_{0,0,-1,-1}^i \rho_\alpha \cos(\phi_\alpha) + b_{0,0,0,-1}^i \rho_\beta \sin(\phi_\beta) + ib_{0,0,0,-1}^i \rho_\beta \cos(\phi_\beta) \\ & - ib_{0,0,-1,-1}^r \rho_\alpha \sin(\phi_\alpha) + b_{0,0,-1,-1}^r \rho_\alpha \cos(\phi_\alpha) - ib_{0,0,0,-1}^r \rho_\beta \sin(\phi_\beta) + b_{0,0,0,-1}^r \rho_\beta \cos(\phi_\beta) \end{aligned}$$

$$H_{-\alpha+\beta}^{(1)} = b_{0,0,-1,-1}^i \rho_\alpha \sin(\phi_\alpha) - ib_{0,0,-1,-1}^i \rho_\alpha \cos(\phi_\alpha) + b_{0,0,0,-1}^i \rho_\beta \sin(\phi_\beta) - ib_{0,0,0,-1}^i \rho_\beta \cos(\phi_\beta) \\ + ib_{0,0,-1,-1}^r \rho_\alpha \sin(\phi_\alpha) + b_{0,0,-1,-1}^r \rho_\alpha \cos(\phi_\alpha) + ib_{0,0,0,-1}^r \rho_\beta \sin(\phi_\beta) + b_{0,0,0,-1}^r \rho_\beta \cos(\phi_\beta)$$

$$H_{+\beta-\alpha}^{(1)} = b_{0,0,-1,-1}^i \rho_\alpha \sin(\phi_\alpha) + ib_{0,0,-1,-1}^i \rho_\alpha \cos(\phi_\alpha) + b_{0,0,0,-1}^i \rho_\beta \sin(\phi_\beta) + ib_{0,0,0,-1}^i \rho_\beta \cos(\phi_\beta) \\ - ib_{0,0,-1,-1}^r \rho_\alpha \sin(\phi_\alpha) + b_{0,0,-1,-1}^r \rho_\alpha \cos(\phi_\alpha) - ib_{0,0,0,-1}^r \rho_\beta \sin(\phi_\beta) + b_{0,0,0,-1}^r \rho_\beta \cos(\phi_\beta)$$

$$H_{-\beta+\alpha}^{(1)} = b_{0,0,-1,-1}^i \rho_\alpha \sin(\phi_\alpha) - ib_{0,0,-1,-1}^i \rho_\alpha \cos(\phi_\alpha) + b_{0,0,0,-1}^i \rho_\beta \sin(\phi_\beta) - ib_{0,0,0,-1}^i \rho_\beta \cos(\phi_\beta) \\ + ib_{0,0,-1,-1}^r \rho_\alpha \sin(\phi_\alpha) + b_{0,0,-1,-1}^r \rho_\alpha \cos(\phi_\alpha) + ib_{0,0,0,-1}^r \rho_\beta \sin(\phi_\beta) + b_{0,0,0,-1}^r \rho_\beta \cos(\phi_\beta)$$

Cartesian e-coordinates:

$$H_{+\alpha+\beta}^{(1)} = 0$$

$$H_{-\alpha-\beta}^{(1)} = 0$$

$$H_{+\beta+\alpha}^{(1)} = 0$$

$$H_{-\beta-\alpha}^{(1)} = 0$$

$$H_{+\alpha-\beta}^{(1)} = ib_{0,0,-1,-1}^i x_\alpha + b_{0,0,-1,-1}^i y_\alpha + ib_{0,0,0,-1}^i x_\beta + b_{0,0,0,-1}^i y_\beta + b_{0,0,-1,-1}^r x_\alpha - ib_{0,0,-1,-1}^r y_\alpha + b_{0,0,0,-1}^r x_\beta - ib_{0,0,0,-1}^r y_\beta$$

$$H_{-\alpha+\beta}^{(1)} = -ib_{0,0,-1,-1}^i x_\alpha + b_{0,0,-1,-1}^i y_\alpha - ib_{0,0,0,-1}^i x_\beta + b_{0,0,0,-1}^i y_\beta + b_{0,0,-1,-1}^r x_\alpha + ib_{0,0,-1,-1}^r y_\alpha + b_{0,0,0,-1}^r x_\beta + ib_{0,0,0,-1}^r y_\beta$$

$$H_{+\beta-\alpha}^{(1)} = ib_{0,0,-1,-1}^i x_\alpha + b_{0,0,-1,-1}^i y_\alpha + ib_{0,0,0,-1}^i x_\beta + b_{0,0,0,-1}^i y_\beta + b_{0,0,-1,-1}^r x_\alpha - ib_{0,0,-1,-1}^r y_\alpha + b_{0,0,0,-1}^r x_\beta - ib_{0,0,0,-1}^r y_\beta$$

$$H_{-\beta+\alpha}^{(1)} = -ib_{0,0,-1,-1}^i x_\alpha + b_{0,0,-1,-1}^i y_\alpha - ib_{0,0,0,-1}^i x_\beta + b_{0,0,0,-1}^i y_\beta + b_{0,0,-1,-1}^r x_\alpha + ib_{0,0,-1,-1}^r y_\alpha + b_{0,0,0,-1}^r x_\beta + ib_{0,0,0,-1}^r y_\beta$$

3.3 Order: 2

Number of fitting parameters: $H_{+\alpha+\beta}$: 8, $H_{+\alpha-\beta}$: 6.

Polar e-coordinates:

$$\begin{aligned}
H_{+\alpha+\beta}^{(2)} = & a_{0,0,-1,0}^i \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) + ia_{0,0,-1,0}^i \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) - a_{0,0,1,0}^i \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) \\
& + ia_{0,0,1,0}^i \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) + ia_{0,2,0,0}^i \rho_\beta^2 + ia_{2,0,0,0}^i \rho_\alpha^2 - ia_{0,0,-1,0}^r \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) \\
& + a_{0,0,-1,0}^r \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) + ia_{0,0,1,0}^r \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) + a_{0,0,1,0}^r \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) + a_{0,2,0,0}^r \rho_\beta^2 + a_{2,0,0,0}^r \rho_\alpha^2
\end{aligned}$$

$$H_{-\alpha-\beta}^{(2)} = a_{0,0,-1,0}^i \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) - ia_{0,0,-1,0}^i \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) - a_{0,0,1,0}^i \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) \\ - ia_{0,0,1,0}^i \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) - ia_{0,2,0,0}^i \rho_\beta^2 - ia_{2,0,0,0}^i \rho_\alpha^2 + ia_{0,0,-1,0}^r \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) \\ + a_{0,0,-1,0}^r \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) - ia_{0,0,1,0}^r \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) + a_{0,0,1,0}^r \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) + a_{0,2,0,0}^r \rho_\beta^2 + a_{2,0,0,0}^r \rho_\alpha^2$$

$$\begin{aligned}
H_{+\beta+\alpha}^{(2)} = & a_{0,0,-1,0}^i \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) - ia_{0,0,-1,0}^i \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) - a_{0,0,1,0}^i \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) \\
& - ia_{0,0,1,0}^i \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) - ia_{0,2,0,0}^i \rho_\beta^2 - ia_{2,0,0,0}^i \rho_\alpha^2 + ia_{0,0,-1,0}^r \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) \\
& + a_{0,0,-1,0}^r \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) - ia_{0,0,1,0}^r \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) + a_{0,0,1,0}^r \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) + a_{0,2,0,0}^r \rho_\beta^2 + a_{2,0,0,0}^r \rho_\alpha^2
\end{aligned}$$

$$H_{-\beta-\alpha}^{(2)} = a_{0,0,-1,0}^i \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) + ia_{0,0,-1,0}^i \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) - a_{0,0,1,0}^i \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) \\ + ia_{0,0,1,0}^i \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) + ia_{0,2,0,0}^i \rho_\beta^2 + ia_{2,0,0,0}^i \rho_\alpha^2 - ia_{0,0,-1,0}^r \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) \\ + a_{0,0,-1,0}^r \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) + ia_{0,0,1,0}^r \rho_\alpha \rho_\beta \sin(\phi_\alpha - \phi_\beta) + a_{0,0,1,0}^r \rho_\alpha \rho_\beta \cos(\phi_\alpha - \phi_\beta) + a_{0,2,0,0}^r \rho_\beta^2 + a_{2,0,0,0}^r \rho_\alpha^2$$

$$\begin{aligned}
H_{+\alpha-\beta}^{(2)} = & -b_{0,0,0,2}^i \rho_\beta^2 \sin(2\phi_\beta) + ib_{0,0,0,2}^i \rho_\beta^2 \cos(2\phi_\beta) - b_{0,0,1,2}^i \rho_\alpha \rho_\beta \sin(\phi_\alpha + \phi_\beta) + ib_{0,0,1,2}^i \rho_\alpha \rho_\beta \cos(\phi_\alpha + \phi_\beta) \\
& - b_{0,0,2,2}^i \rho_\alpha^2 \sin(2\phi_\alpha) + ib_{0,0,2,2}^i \rho_\alpha^2 \cos(2\phi_\alpha) + ib_{0,0,0,2}^r \rho_\beta^2 \sin(2\phi_\beta) + b_{0,0,0,2}^r \rho_\beta^2 \cos(2\phi_\beta) \\
& + ib_{0,0,1,2}^r \rho_\alpha \rho_\beta \sin(\phi_\alpha + \phi_\beta) + b_{0,0,1,2}^r \rho_\alpha \rho_\beta \cos(\phi_\alpha + \phi_\beta) + ib_{0,0,2,2}^r \rho_\alpha^2 \sin(2\phi_\alpha) + b_{0,0,2,2}^r \rho_\alpha^2 \cos(2\phi_\alpha)
\end{aligned}$$

Cartesian e-coordinates:

$$H_{+\alpha+\beta}^{(2)} = ia_{0,0,-1,0}^i (x_\alpha x_\beta + y_\alpha y_\beta) - a_{0,0,-1,0}^i (x_\alpha y_\beta - x_\beta y_\alpha) + ia_{0,0,1,0}^i (x_\alpha x_\beta + y_\alpha y_\beta) + a_{0,0,1,0}^i (x_\alpha y_\beta - x_\beta y_\alpha) \\ + ia_{0,2,0,0}^i (x_\beta^2 + y_\beta^2) + ia_{2,0,0,0}^i (x_\alpha^2 + y_\alpha^2) + a_{0,0,-1,0}^r (x_\alpha x_\beta + y_\alpha y_\beta) + ia_{0,0,-1,0}^r (x_\alpha y_\beta - x_\beta y_\alpha) \\ + a_{0,0,1,0}^r (x_\alpha x_\beta + y_\alpha y_\beta) - ia_{0,0,1,0}^r (x_\alpha y_\beta - x_\beta y_\alpha) + a_{0,2,0,0}^r (x_\beta^2 + y_\beta^2) + a_{2,0,0,0}^r (x_\alpha^2 + y_\alpha^2)$$

$$H_{-\alpha-\beta}^{(2)} = -ia_{0,0,-1,0}^i (x_\alpha x_\beta + y_\alpha y_\beta) - a_{0,0,-1,0}^i (x_\alpha y_\beta - x_\beta y_\alpha) - ia_{0,0,1,0}^i (x_\alpha x_\beta + y_\alpha y_\beta) + a_{0,0,1,0}^i (x_\alpha y_\beta - x_\beta y_\alpha) \\ - ia_{0,2,0,0}^i (x_\beta^2 + y_\beta^2) - ia_{2,0,0,0}^i (x_\alpha^2 + y_\alpha^2) + a_{0,0,-1,0}^r (x_\alpha x_\beta + y_\alpha y_\beta) - ia_{0,0,-1,0}^r (x_\alpha y_\beta - x_\beta y_\alpha) \\ + a_{0,0,1,0}^r (x_\alpha x_\beta + y_\alpha y_\beta) + ia_{0,0,1,0}^r (x_\alpha y_\beta - x_\beta y_\alpha) + a_{0,2,0,0}^r (x_\beta^2 + y_\beta^2) + a_{2,0,0,0}^r (x_\alpha^2 + y_\alpha^2)$$

$$H_{+\beta+\alpha}^{(2)} = -ia_{0,0,-1,0}^i (x_\alpha x_\beta + y_\alpha y_\beta) - a_{0,0,-1,0}^i (x_\alpha y_\beta - x_\beta y_\alpha) - ia_{0,0,1,0}^i (x_\alpha x_\beta + y_\alpha y_\beta) + a_{0,0,1,0}^i (x_\alpha y_\beta - x_\beta y_\alpha) \\ - ia_{0,2,0,0}^i (x_\beta^2 + y_\beta^2) - ia_{2,0,0,0}^i (x_\alpha^2 + y_\alpha^2) + a_{0,0,-1,0}^r (x_\alpha x_\beta + y_\alpha y_\beta) - ia_{0,0,-1,0}^r (x_\alpha y_\beta - x_\beta y_\alpha) \\ + a_{0,0,1,0}^r (x_\alpha x_\beta + y_\alpha y_\beta) + ia_{0,0,1,0}^r (x_\alpha y_\beta - x_\beta y_\alpha) + a_{0,2,0,0}^r (x_\beta^2 + y_\beta^2) + a_{2,0,0,0}^r (x_\alpha^2 + y_\alpha^2)$$

$$H_{-\beta-\alpha}^{(2)} = ia_{0,0,-1,0}^i (x_\alpha x_\beta + y_\alpha y_\beta) - a_{0,0,-1,0}^i (x_\alpha y_\beta - x_\beta y_\alpha) + ia_{0,0,1,0}^i (x_\alpha x_\beta + y_\alpha y_\beta) + a_{0,0,1,0}^i (x_\alpha y_\beta - x_\beta y_\alpha) \\ + ia_{0,2,0,0}^i (x_\beta^2 + y_\beta^2) + ia_{2,0,0,0}^i (x_\alpha^2 + y_\alpha^2) + a_{0,0,-1,0}^r (x_\alpha x_\beta + y_\alpha y_\beta) + ia_{0,0,-1,0}^r (x_\alpha y_\beta - x_\beta y_\alpha) \\ + a_{0,0,1,0}^r (x_\alpha x_\beta + y_\alpha y_\beta) - ia_{0,0,1,0}^r (x_\alpha y_\beta - x_\beta y_\alpha) + a_{0,2,0,0}^r (x_\beta^2 + y_\beta^2) + a_{2,0,0,0}^r (x_\alpha^2 + y_\alpha^2)$$

$$H_{+\alpha-\beta}^{(2)} = -2b_{0,0,0,2}^i x_\beta y_\beta + ib_{0,0,0,2}^i (x_\beta - y_\beta) (x_\beta + y_\beta) + ib_{0,0,1,2}^i (x_\alpha x_\beta - y_\alpha y_\beta) - b_{0,0,1,2}^i (x_\alpha y_\beta + x_\beta y_\alpha) \\ - 2b_{0,0,2,2}^i x_\alpha y_\alpha + ib_{0,0,2,2}^i (x_\alpha - y_\alpha) (x_\alpha + y_\alpha) + 2ib_{0,0,0,2}^r x_\beta y_\beta + b_{0,0,0,2}^r (x_\beta - y_\beta) (x_\beta + y_\beta) \\ + b_{0,0,1,2}^r (x_\alpha x_\beta - y_\alpha y_\beta) + ib_{0,0,1,2}^r (x_\alpha y_\beta + x_\beta y_\alpha) + 2ib_{0,0,2,2}^r x_\alpha y_\alpha + b_{0,0,2,2}^r (x_\alpha - y_\alpha) (x_\alpha + y_\alpha)$$

$$H_{-\alpha+\beta}^{(2)} = -2b_{0,0,0,2}^i x_\beta y_\beta - ib_{0,0,0,2}^i (x_\beta - y_\beta) (x_\beta + y_\beta) - ib_{0,0,1,2}^i (x_\alpha x_\beta - y_\alpha y_\beta) - b_{0,0,1,2}^i (x_\alpha y_\beta + x_\beta y_\alpha) \\ - 2b_{0,0,2,2}^i x_\alpha y_\alpha - ib_{0,0,2,2}^i (x_\alpha - y_\alpha) (x_\alpha + y_\alpha) - 2ib_{0,0,0,2}^r x_\beta y_\beta + b_{0,0,0,2}^r (x_\beta - y_\beta) (x_\beta + y_\beta) \\ + b_{0,0,1,2}^r (x_\alpha x_\beta - y_\alpha y_\beta) - ib_{0,0,1,2}^r (x_\alpha y_\beta + x_\beta y_\alpha) - 2ib_{0,0,2,2}^r x_\alpha y_\alpha + b_{0,0,2,2}^r (x_\alpha - y_\alpha) (x_\alpha + y_\alpha)$$

$$H_{+\beta-\alpha}^{(2)} = -2b_{0,0,0,2}^i x_\beta y_\beta + ib_{0,0,0,2}^i (x_\beta - y_\beta) (x_\beta + y_\beta) + ib_{0,0,1,2}^i (x_\alpha x_\beta - y_\alpha y_\beta) - b_{0,0,1,2}^i (x_\alpha y_\beta + x_\beta y_\alpha) \\ - 2b_{0,0,2,2}^i x_\alpha y_\alpha + ib_{0,0,2,2}^i (x_\alpha - y_\alpha) (x_\alpha + y_\alpha) + 2ib_{0,0,0,2}^r x_\beta y_\beta + b_{0,0,0,2}^r (x_\beta - y_\beta) (x_\beta + y_\beta) \\ + b_{0,0,1,2}^r (x_\alpha x_\beta - y_\alpha y_\beta) + ib_{0,0,1,2}^r (x_\alpha y_\beta + x_\beta y_\alpha) + 2ib_{0,0,2,2}^r x_\alpha y_\alpha + b_{0,0,2,2}^r (x_\alpha - y_\alpha) (x_\alpha + y_\alpha)$$

$$H_{-\beta+\alpha}^{(2)} = -2b_{0,0,0,2}^i x_\beta y_\beta - ib_{0,0,0,2}^i (x_\beta - y_\beta) (x_\beta + y_\beta) - ib_{0,0,1,2}^i (x_\alpha x_\beta - y_\alpha y_\beta) - b_{0,0,1,2}^i (x_\alpha y_\beta + x_\beta y_\alpha) \\ - 2b_{0,0,2,2}^i x_\alpha y_\alpha - ib_{0,0,2,2}^i (x_\alpha - y_\alpha) (x_\alpha + y_\alpha) - 2ib_{0,0,0,2}^r x_\beta y_\beta + b_{0,0,0,2}^r (x_\beta - y_\beta) (x_\beta + y_\beta) \\ + b_{0,0,1,2}^r (x_\alpha x_\beta - y_\alpha y_\beta) - ib_{0,0,1,2}^r (x_\alpha y_\beta + x_\beta y_\alpha) - 2ib_{0,0,2,2}^r x_\alpha y_\alpha + b_{0,0,2,2}^r (x_\alpha - y_\alpha) (x_\alpha + y_\alpha)$$

4 Vibronic Hamiltonian operator in the real E basis

$$\hat{H} = (|X_\alpha\rangle \quad |Y_\alpha\rangle \quad |X_\beta\rangle \quad |Y_\beta\rangle) \begin{pmatrix} 0 & 0 & H_{X_\alpha X_\beta} & H_{X_\alpha Y_\beta} \\ 0 & 0 & H_{Y_\alpha X_\beta} & H_{Y_\alpha Y_\beta} \\ H_{X_\beta X_\alpha} & H_{X_\beta Y_\alpha} & 0 & 0 \\ H_{Y_\beta X_\alpha} & H_{Y_\beta Y_\alpha} & 0 & 0 \end{pmatrix} \begin{pmatrix} \langle X_\alpha | \\ \langle Y_\alpha | \\ \langle X_\beta | \\ \langle Y_\beta | \end{pmatrix}$$

$$H_{+\alpha+\beta} = H_{+\alpha+\beta} = H_{-\alpha-\beta}^* = H_{+\beta+\alpha}^* = H_{-\beta-\alpha}^*$$

$$H_{+\alpha-\beta} = H_{+\alpha-\beta} = H_{-\alpha+\beta}^* = H_{+\beta-\alpha}^* = H_{-\beta+\alpha}^*$$

5 Matrix element expansions in the real E basis

5.1 Order: 0

Number of fitting parameters: $H_{X_\alpha X_\beta}$: 1 (all from $H_{+\alpha+\beta}$), $H_{X_\alpha Y_\beta}$: 1 (all from $H_{+\alpha+\beta}$), $H_{Y_\alpha X_\beta}$: 1 (all from $H_{+\alpha+\beta}$), $H_{Y_\alpha Y_\beta}$: 1 (all from $H_{+\alpha+\beta}$), $H_{X_\beta X_\alpha}$: 1 (all from $H_{+\alpha+\beta}$), $H_{X_\beta Y_\alpha}$: 1 (all from $H_{+\alpha+\beta}$), $H_{Y_\beta X_\alpha}$: 1 (all from $H_{+\alpha+\beta}$), $H_{Y_\beta Y_\alpha}$: 1 (all from $H_{+\alpha+\beta}$).

Polar e-coordinates:

$$H_{X_\alpha X_\beta}^{(0)} = a_{0,0,0,0}^r$$

$$H_{X_\alpha Y_\beta}^{(0)} = a_{0,0,0,0}^i$$

$$H_{Y_\alpha X_\beta}^{(0)} = -a_{0,0,0,0}^i$$

$$H_{Y_\alpha Y_\beta}^{(0)} = a_{0,0,0,0}^r$$

$$H_{X_\beta X_\alpha}^{(0)} = a_{0,0,0,0}^r$$

$$H_{X_\beta Y_\alpha}^{(0)} = -a_{0,0,0,0}^i$$

$$H_{Y_\beta X_\alpha}^{(0)} = a_{0,0,0,0}^i$$

$$H_{Y_\beta Y_\alpha}^{(0)} = a_{0,0,0,0}^r$$

Cartesian e-coordinates:

$$H_{X_\alpha X_\beta}^{(0)} = a_{0,0,0,0}^r$$

$$H_{X_\alpha Y_\beta}^{(0)} = a_{0,0,0,0}^i$$

$$H_{Y_\alpha X_\beta}^{(0)} = -a_{0,0,0,0}^i$$

$$H_{Y_\alpha Y_\beta}^{(0)} = a_{0,0,0,0}^r$$

$$H_{X_\beta X_\alpha}^{(0)} = a_{0,0,0,0}^r$$

$$H_{X_\beta Y_\alpha}^{(0)} = -a_{0,0,0,0}^i$$

$$H_{Y_\beta X_\alpha}^{(0)} = a_{0,0,0,0}^i$$

$$H_{Y_\beta Y_\alpha}^{(0)} = a_{0,0,0,0}^r$$

5.2 Order: 1

Number of fitting parameters: $H_{X_\alpha X_\beta}$: 4 (all from $H_{+\alpha-\beta}$), $H_{X_\alpha Y_\beta}$: 4 (all from $H_{+\alpha-\beta}$), $H_{Y_\alpha X_\beta}$: 4 (all from $H_{+\alpha-\beta}$), $H_{Y_\alpha Y_\beta}$: 4 (all from $H_{+\alpha-\beta}$), $H_{X_\beta X_\alpha}$: 4 (all from $H_{+\alpha-\beta}$), $H_{X_\beta Y_\alpha}$: 4 (all from $H_{+\alpha-\beta}$), $H_{Y_\beta X_\alpha}$: 4 (all from $H_{+\alpha-\beta}$), $H_{Y_\beta Y_\alpha}$: 4 (all from $H_{+\alpha-\beta}$).

Polar e-coordinates:

$$H_{X_\alpha X_\beta}^{(1)} = b_{0,0,-1,-1}^i \rho_\alpha \sin(\phi_\alpha) + b_{0,0,0,-1}^i \rho_\beta \sin(\phi_\beta) + b_{0,0,-1,-1}^r \rho_\alpha \cos(\phi_\alpha) + b_{0,0,0,-1}^r \rho_\beta \cos(\phi_\beta)$$

$$H_{X_\alpha Y_\beta}^{(1)} = -b_{0,0,-1,-1}^i \rho_\alpha \cos(\phi_\alpha) - b_{0,0,0,-1}^i \rho_\beta \cos(\phi_\beta) + b_{0,0,-1,-1}^r \rho_\alpha \sin(\phi_\alpha) + b_{0,0,0,-1}^r \rho_\beta \sin(\phi_\beta)$$

$$H_{Y_\alpha X_\beta}^{(1)} = -b_{0,0,-1,-1}^i \rho_\alpha \cos(\phi_\alpha) - b_{0,0,0,-1}^i \rho_\beta \cos(\phi_\beta) + b_{0,0,-1,-1}^r \rho_\alpha \sin(\phi_\alpha) + b_{0,0,0,-1}^r \rho_\beta \sin(\phi_\beta)$$

$$H_{Y_\alpha Y_\beta}^{(1)} = -b_{0,0,-1,-1}^i \rho_\alpha \sin(\phi_\alpha) - b_{0,0,0,-1}^i \rho_\beta \sin(\phi_\beta) - b_{0,0,-1,-1}^r \rho_\alpha \cos(\phi_\alpha) - b_{0,0,0,-1}^r \rho_\beta \cos(\phi_\beta)$$

$$H_{X_\beta X_\alpha}^{(1)} = b_{0,0,-1,-1}^i \rho_\alpha \sin(\phi_\alpha) + b_{0,0,0,-1}^i \rho_\beta \sin(\phi_\beta) + b_{0,0,-1,-1}^r \rho_\alpha \cos(\phi_\alpha) + b_{0,0,0,-1}^r \rho_\beta \cos(\phi_\beta)$$

$$H_{X_\beta Y_\alpha}^{(1)} = -b_{0,0,-1,-1}^i \rho_\alpha \cos(\phi_\alpha) - b_{0,0,0,-1}^i \rho_\beta \cos(\phi_\beta) + b_{0,0,-1,-1}^r \rho_\alpha \sin(\phi_\alpha) + b_{0,0,0,-1}^r \rho_\beta \sin(\phi_\beta)$$

$$H_{Y_\beta X_\alpha}^{(1)} = -b_{0,0,-1,-1}^i \rho_\alpha \cos(\phi_\alpha) - b_{0,0,0,-1}^i \rho_\beta \cos(\phi_\beta) + b_{0,0,-1,-1}^r \rho_\alpha \sin(\phi_\alpha) + b_{0,0,0,-1}^r \rho_\beta \sin(\phi_\beta)$$

$$H_{Y_\beta Y_\alpha}^{(1)} = -b_{0,0,-1,-1}^i \rho_\alpha \sin(\phi_\alpha) - b_{0,0,0,-1}^i \rho_\beta \sin(\phi_\beta) - b_{0,0,-1,-1}^r \rho_\alpha \cos(\phi_\alpha) - b_{0,0,0,-1}^r \rho_\beta \cos(\phi_\beta)$$

Cartesian e-coordinates:

$$H_{X_\alpha X_\beta}^{(1)} = b_{0,0,-1,-1}^i y_\alpha + b_{0,0,0,-1}^i y_\beta + b_{0,0,-1,-1}^r x_\alpha + b_{0,0,0,-1}^r x_\beta$$

$$H_{X_\alpha Y_\beta}^{(1)} = -b_{0,0,-1,-1}^i x_\alpha - b_{0,0,0,-1}^i x_\beta + b_{0,0,-1,-1}^r y_\alpha + b_{0,0,0,-1}^r y_\beta$$

$$H_{Y_\alpha X_\beta}^{(1)} = -b_{0,0,-1,-1}^i x_\alpha - b_{0,0,0,-1}^i x_\beta + b_{0,0,-1,-1}^r y_\alpha + b_{0,0,0,-1}^r y_\beta$$

$$H_{Y_\alpha Y_\beta}^{(1)} = -b_{0,0,-1,-1}^i y_\alpha - b_{0,0,0,-1}^i y_\beta - b_{0,0,-1,-1}^r x_\alpha - b_{0,0,0,-1}^r x_\beta$$

$$H_{X_\beta X_\alpha}^{(1)} = b_{0,0,-1,-1}^i y_\alpha + b_{0,0,0,-1}^i y_\beta + b_{0,0,-1,-1}^r x_\alpha + b_{0,0,0,-1}^r x_\beta$$

$$H_{X_\beta Y_\alpha}^{(1)} = -b_{0,0,-1,-1}^i x_\alpha - b_{0,0,0,-1}^i x_\beta + b_{0,0,-1,-1}^r y_\alpha + b_{0,0,0,-1}^r y_\beta$$

$$H_{Y_\beta X_\alpha}^{(1)} = -b_{0,0,-1,-1}^i x_\alpha - b_{0,0,0,-1}^i x_\beta + b_{0,0,-1,-1}^r y_\alpha + b_{0,0,0,-1}^r y_\beta$$

$$H_{Y_\beta Y_\alpha}^{(1)} = -b_{0,0,-1,-1}^i y_\alpha - b_{0,0,0,-1}^i y_\beta - b_{0,0,-1,-1}^r x_\alpha - b_{0,0,0,-1}^r x_\beta$$

