

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

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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<sub>l</sub>at<sub>e</sub>x**. 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

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

## 2 Vibronic Hamiltonian operator in the complex $E$ basis

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

## 3 Matrix element expansions in the complex $E$ basis

### 3.1 Order: 0

Number of fitting parameters:  $H_{+A}$ : 0.

**Polar e-coordinates:**

$$H_{+A}^{(0)} = 0$$

$$H_{-A}^{(0)} = 0$$

$$H_{A+}^{(0)} = 0$$

$$H_{A-}^{(0)} = 0$$

**Cartesian e-coordinates:**

$$H_{+A}^{(0)} = 0$$

$$H_{-A}^{(0)} = 0$$

$$H_{A+}^{(0)} = 0$$

$$H_{A-}^{(0)} = 0$$

### 3.2 Order: 1

Number of fitting parameters:  $H_{+A}$ : 2.

**Polar e-coordinates:**

$$H_{+A}^{(1)} = b_{0,0,-1}^i \rho \sin(\phi) + ib_{0,0,-1}^i \rho \cos(\phi) - ib_{0,0,-1}^r \rho \sin(\phi) + b_{0,0,-1}^r \rho \cos(\phi)$$

$$H_{-A}^{(1)} = b_{0,0,-1}^i \rho \sin(\phi) - ib_{0,0,-1}^i \rho \cos(\phi) + ib_{0,0,-1}^r \rho \sin(\phi) + b_{0,0,-1}^r \rho \cos(\phi)$$

$$H_{A+}^{(1)} = b_{0,0,-1}^i \rho \sin(\phi) - ib_{0,0,-1}^i \rho \cos(\phi) + ib_{0,0,-1}^r \rho \sin(\phi) + b_{0,0,-1}^r \rho \cos(\phi)$$

$$H_{A-}^{(1)} = b_{0,0,-1}^i \rho \sin(\phi) + ib_{0,0,-1}^i \rho \cos(\phi) - ib_{0,0,-1}^r \rho \sin(\phi) + b_{0,0,-1}^r \rho \cos(\phi)$$

**Cartesian e-coordinates:**

$$H_{+A}^{(1)} = ib_{0,0,-1}^i x + b_{0,0,-1}^i y + b_{0,0,-1}^r x - ib_{0,0,-1}^r y$$

$$H_{-A}^{(1)} = -ib_{0,0,-1}^i x + b_{0,0,-1}^i y + b_{0,0,-1}^r x + ib_{0,0,-1}^r y$$

$$H_{A+}^{(1)} = -ib_{0,0,-1}^i x + b_{0,0,-1}^i y + b_{0,0,-1}^r x + ib_{0,0,-1}^r y$$

$$H_{A-}^{(1)} = ib_{0,0,-1}^i x + b_{0,0,-1}^i y + b_{0,0,-1}^r x - ib_{0,0,-1}^r y$$

**3.3 Order: 2**

Number of fitting parameters:  $H_{+A}$ : 4.

**Polar e-coordinates:**

$$H_{+A}^{(2)} = -b_{0,0,2}^i \rho^2 \sin(2\phi) + ib_{0,0,2}^i \rho^2 \cos(2\phi) + b_{1,0,-1}^i \rho z \sin(\phi) + ib_{1,0,-1}^i \rho z \cos(\phi) + ib_{0,0,2}^r \rho^2 \sin(2\phi) + b_{0,0,2}^r \rho^2 \cos(2\phi) - ib_{1,0,-1}^r \rho z \sin(\phi) + b_{1,0,-1}^r \rho z \cos(\phi)$$

$$H_{-A}^{(2)} = -b_{0,0,2}^i \rho^2 \sin(2\phi) - ib_{0,0,2}^i \rho^2 \cos(2\phi) + b_{1,0,-1}^i \rho z \sin(\phi) - ib_{1,0,-1}^i \rho z \cos(\phi) - ib_{0,0,2}^r \rho^2 \sin(2\phi) + b_{0,0,2}^r \rho^2 \cos(2\phi) + ib_{1,0,-1}^r \rho z \sin(\phi) + b_{1,0,-1}^r \rho z \cos(\phi)$$

$$H_{A+}^{(2)} = -b_{0,0,2}^i \rho^2 \sin(2\phi) - ib_{0,0,2}^i \rho^2 \cos(2\phi) + b_{1,0,-1}^i \rho z \sin(\phi) - ib_{1,0,-1}^i \rho z \cos(\phi) - ib_{0,0,2}^r \rho^2 \sin(2\phi) + b_{0,0,2}^r \rho^2 \cos(2\phi) + ib_{1,0,-1}^r \rho z \sin(\phi) + b_{1,0,-1}^r \rho z \cos(\phi)$$

$$H_{A-}^{(2)} = -b_{0,0,2}^i \rho^2 \sin(2\phi) + ib_{0,0,2}^i \rho^2 \cos(2\phi) + b_{1,0,-1}^i \rho z \sin(\phi) + ib_{1,0,-1}^i \rho z \cos(\phi) + ib_{0,0,2}^r \rho^2 \sin(2\phi) + b_{0,0,2}^r \rho^2 \cos(2\phi) - ib_{1,0,-1}^r \rho z \sin(\phi) + b_{1,0,-1}^r \rho z \cos(\phi)$$

### Cartesian e-coordinates:

$$H_{+A}^{(2)} = -2b_{0,0,2}^i xy + ib_{0,0,2}^i (x-y)(x+y) + ib_{1,0,-1}^i xz + b_{1,0,-1}^i yz + 2ib_{0,0,2}^r xy + b_{0,0,2}^r (x-y)(x+y) + b_{1,0,-1}^r xz - ib_{1,0,-1}^r yz$$

$$H_{-A}^{(2)} = -2b_{0,0,2}^i xy - ib_{0,0,2}^i (x-y)(x+y) - ib_{1,0,-1}^i xz + b_{1,0,-1}^i yz - 2ib_{0,0,2}^r xy + b_{0,0,2}^r (x-y)(x+y) + b_{1,0,-1}^r xz + ib_{1,0,-1}^r yz$$

$$H_{A+}^{(2)} = -2b_{0,0,2}^i xy - ib_{0,0,2}^i (x-y)(x+y) - ib_{1,0,-1}^i xz + b_{1,0,-1}^i yz - 2ib_{0,0,2}^r xy + b_{0,0,2}^r (x-y)(x+y) + b_{1,0,-1}^r xz + ib_{1,0,-1}^r yz$$

$$H_{A-}^{(2)} = -2b_{0,0,2}^i xy + ib_{0,0,2}^i (x-y)(x+y) + ib_{1,0,-1}^i xz + b_{1,0,-1}^i yz + 2ib_{0,0,2}^r xy + b_{0,0,2}^r (x-y)(x+y) + b_{1,0,-1}^r xz - ib_{1,0,-1}^r yz$$

### 3.4 Order: 3

Number of fitting parameters:  $H_{+A}$ : 6.

### Polar e-coordinates:

$$\begin{aligned} H_{+A}^{(3)} = & b_{0,2,-1}^i \rho^3 \sin(\phi) + ib_{0,2,-1}^i \rho^3 \cos(\phi) - b_{1,0,2}^i \rho^2 z \sin(2\phi) + ib_{1,0,2}^i \rho^2 z \cos(2\phi) + b_{2,0,-1}^i \rho z^2 \sin(\phi) \\ & + ib_{2,0,-1}^i \rho z^2 \cos(\phi) - ib_{0,2,-1}^r \rho^3 \sin(\phi) + b_{0,2,-1}^r \rho^3 \cos(\phi) + ib_{1,0,2}^r \rho^2 z \sin(2\phi) + b_{1,0,2}^r \rho^2 z \cos(2\phi) \\ & - ib_{2,0,-1}^r \rho z^2 \sin(\phi) + b_{2,0,-1}^r \rho z^2 \cos(\phi) \end{aligned}$$

$$\begin{aligned} H_{-A}^{(3)} = & b_{0,2,-1}^i \rho^3 \sin(\phi) - ib_{0,2,-1}^i \rho^3 \cos(\phi) - b_{1,0,2}^i \rho^2 z \sin(2\phi) - ib_{1,0,2}^i \rho^2 z \cos(2\phi) + b_{2,0,-1}^i \rho z^2 \sin(\phi) \\ & - ib_{2,0,-1}^i \rho z^2 \cos(\phi) + ib_{0,2,-1}^r \rho^3 \sin(\phi) + b_{0,2,-1}^r \rho^3 \cos(\phi) - ib_{1,0,2}^r \rho^2 z \sin(2\phi) + b_{1,0,2}^r \rho^2 z \cos(2\phi) \\ & + ib_{2,0,-1}^r \rho z^2 \sin(\phi) + b_{2,0,-1}^r \rho z^2 \cos(\phi) \end{aligned}$$

$$\begin{aligned} H_{A+}^{(3)} = & b_{0,2,-1}^i \rho^3 \sin(\phi) - ib_{0,2,-1}^i \rho^3 \cos(\phi) - b_{1,0,2}^i \rho^2 z \sin(2\phi) - ib_{1,0,2}^i \rho^2 z \cos(2\phi) + b_{2,0,-1}^i \rho z^2 \sin(\phi) \\ & - ib_{2,0,-1}^i \rho z^2 \cos(\phi) + ib_{0,2,-1}^r \rho^3 \sin(\phi) + b_{0,2,-1}^r \rho^3 \cos(\phi) - ib_{1,0,2}^r \rho^2 z \sin(2\phi) + b_{1,0,2}^r \rho^2 z \cos(2\phi) \\ & + ib_{2,0,-1}^r \rho z^2 \sin(\phi) + b_{2,0,-1}^r \rho z^2 \cos(\phi) \end{aligned}$$

$$\begin{aligned} H_{A-}^{(3)} = & b_{0,2,-1}^i \rho^3 \sin(\phi) + ib_{0,2,-1}^i \rho^3 \cos(\phi) - b_{1,0,2}^i \rho^2 z \sin(2\phi) + ib_{1,0,2}^i \rho^2 z \cos(2\phi) + b_{2,0,-1}^i \rho z^2 \sin(\phi) \\ & + ib_{2,0,-1}^i \rho z^2 \cos(\phi) - ib_{0,2,-1}^r \rho^3 \sin(\phi) + b_{0,2,-1}^r \rho^3 \cos(\phi) + ib_{1,0,2}^r \rho^2 z \sin(2\phi) + b_{1,0,2}^r \rho^2 z \cos(2\phi) \\ & - ib_{2,0,-1}^r \rho z^2 \sin(\phi) + b_{2,0,-1}^r \rho z^2 \cos(\phi) \end{aligned}$$

### Cartesian e-coordinates:

$$\begin{aligned} H_{+A}^{(3)} = & ib_{0,2,-1}^i x(x^2 + y^2) + b_{0,2,-1}^i y(x^2 + y^2) - 2b_{1,0,2}^i xyz + ib_{1,0,2}^i z(x-y)(x+y) + ib_{2,0,-1}^i xz^2 + b_{2,0,-1}^i yz^2 \\ & + b_{0,2,-1}^r x(x^2 + y^2) - ib_{0,2,-1}^r y(x^2 + y^2) + 2ib_{1,0,2}^r xyz + b_{1,0,2}^r z(x-y)(x+y) + b_{2,0,-1}^r xz^2 - ib_{2,0,-1}^r yz^2 \end{aligned}$$

$$\begin{aligned} H_{-A}^{(3)} = & -ib_{0,2,-1}^i x(x^2 + y^2) + b_{0,2,-1}^i y(x^2 + y^2) - 2b_{1,0,2}^i xyz - ib_{1,0,2}^i z(x-y)(x+y) - ib_{2,0,-1}^i xz^2 + b_{2,0,-1}^i yz^2 \\ & + b_{0,2,-1}^r x(x^2 + y^2) + ib_{0,2,-1}^r y(x^2 + y^2) - 2ib_{1,0,2}^r xyz + b_{1,0,2}^r z(x-y)(x+y) + b_{2,0,-1}^r xz^2 + ib_{2,0,-1}^r yz^2 \end{aligned}$$

$$H_{A+}^{(3)} = -ib_{0,2,-1}^i x (x^2 + y^2) + b_{0,2,-1}^i y (x^2 + y^2) - 2b_{1,0,2}^i xyz - ib_{1,0,2}^i z (x - y) (x + y) - ib_{2,0,-1}^i x z^2 + b_{2,0,-1}^i y z^2 \\ + b_{0,2,-1}^r x (x^2 + y^2) + ib_{0,2,-1}^r y (x^2 + y^2) - 2ib_{1,0,2}^r xyz + b_{1,0,2}^r z (x - y) (x + y) + b_{2,0,-1}^r x z^2 + ib_{2,0,-1}^r y z^2$$

$$H_{A-}^{(3)} = ib_{0,2,-1}^i x (x^2 + y^2) + b_{0,2,-1}^i y (x^2 + y^2) - 2b_{1,0,2}^i xyz + ib_{1,0,2}^i z (x - y) (x + y) + ib_{2,0,-1}^i x z^2 + b_{2,0,-1}^i y z^2 \\ + b_{0,2,-1}^r x (x^2 + y^2) - ib_{0,2,-1}^r y (x^2 + y^2) + 2ib_{1,0,2}^r xyz + b_{1,0,2}^r z (x - y) (x + y) + b_{2,0,-1}^r x z^2 - ib_{2,0,-1}^r y z^2$$

## 4 Vibronic Hamiltonian operator in the real $E$ basis

$$\hat{H} = (|X\rangle \quad |Y\rangle \quad |A\rangle) \begin{pmatrix} 0 & 0 & H_{XA} \\ 0 & 0 & H_{YA} \\ H_{AX} & H_{AY} & 0 \end{pmatrix} \begin{pmatrix} \langle X| \\ \langle Y| \\ \langle A| \end{pmatrix}$$

## 5 Matrix element expansions in the real $E$ basis

### 5.1 Order: 0

Number of fitting parameters:  $H_{XA}$ : 0,  $H_{YA}$ : 0.

**Polar e-coordinates:**

$$H_{XA}^{(0)} = 0$$

$$H_{YA}^{(0)} = 0$$

$$H_{AX}^{(0)} = 0$$

$$H_{AY}^{(0)} = 0$$

**Cartesian e-coordinates:**

$$H_{XA}^{(0)} = 0$$

$$H_{YA}^{(0)} = 0$$

$$H_{AX}^{(0)} = 0$$

$$H_{AY}^{(0)} = 0$$

### 5.2 Order: 1

Number of fitting parameters:  $H_{XA}$ : 2 (all from  $H_{+A}$ ),  $H_{YA}$ : 2 (all from  $H_{+A}$ ).

**Polar e-coordinates:**

$$H_{XA}^{(1)} = \sqrt{2} (b_{0,0,-1}^i \rho \sin(\phi) + b_{0,0,-1}^r \rho \cos(\phi))$$

$$H_{YA}^{(1)} = -\sqrt{2} (b_{0,0,-1}^i \rho \cos(\phi) - b_{0,0,-1}^r \rho \sin(\phi))$$

$$H_{AX}^{(1)} = \sqrt{2} (b_{0,0,-1}^i \rho \sin(\phi) + b_{0,0,-1}^r \rho \cos(\phi))$$

$$H_{AY}^{(1)} = -\sqrt{2} (b_{0,0,-1}^i \rho \cos(\phi) - b_{0,0,-1}^r \rho \sin(\phi))$$

**Cartesian e-coordinates:**

$$H_{XA}^{(1)} = \sqrt{2} (b_{0,0,-1}^i y + b_{0,0,-1}^r x)$$

$$H_{YA}^{(1)} = -\sqrt{2} (b_{0,0,-1}^i x - b_{0,0,-1}^r y)$$

$$H_{AX}^{(1)} = \sqrt{2} (b_{0,0,-1}^i y + b_{0,0,-1}^r x)$$

$$H_{AY}^{(1)} = -\sqrt{2} (b_{0,0,-1}^i x - b_{0,0,-1}^r y)$$

**5.3 Order: 2**

Number of fitting parameters:  $H_{XA}$ : 4 (all from  $H_{+A}$ ),  $H_{YA}$ : 4 (all from  $H_{+A}$ ).

**Polar e-coordinates:**

$$H_{XA}^{(2)} = \sqrt{2} (-b_{0,0,2}^i \rho^2 \sin(2\phi) + b_{1,0,-1}^i \rho z \sin(\phi) + b_{0,0,2}^r \rho^2 \cos(2\phi) + b_{1,0,-1}^r \rho z \cos(\phi))$$

$$H_{YA}^{(2)} = -\sqrt{2} (b_{0,0,2}^i \rho^2 \cos(2\phi) + b_{1,0,-1}^i \rho z \cos(\phi) + b_{0,0,2}^r \rho^2 \sin(2\phi) - b_{1,0,-1}^r \rho z \sin(\phi))$$

$$H_{AX}^{(2)} = \sqrt{2} (-b_{0,0,2}^i \rho^2 \sin(2\phi) + b_{1,0,-1}^i \rho z \sin(\phi) + b_{0,0,2}^r \rho^2 \cos(2\phi) + b_{1,0,-1}^r \rho z \cos(\phi))$$

$$H_{AY}^{(2)} = -\sqrt{2} (b_{0,0,2}^i \rho^2 \cos(2\phi) + b_{1,0,-1}^i \rho z \cos(\phi) + b_{0,0,2}^r \rho^2 \sin(2\phi) - b_{1,0,-1}^r \rho z \sin(\phi))$$

**Cartesian e-coordinates:**

$$H_{XA}^{(2)} = \sqrt{2} \left( -2b_{0,0,2}^i xy + b_{1,0,-1}^i yz + b_{0,0,2}^r (x-y)(x+y) + b_{1,0,-1}^r xz \right)$$

$$H_{YA}^{(2)} = -\sqrt{2} \left( b_{0,0,2}^i (x-y)(x+y) + b_{1,0,-1}^i xz + 2b_{0,0,2}^r xy - b_{1,0,-1}^r yz \right)$$

$$H_{AX}^{(2)} = \sqrt{2} \left( -2b_{0,0,2}^i xy + b_{1,0,-1}^i yz + b_{0,0,2}^r (x-y)(x+y) + b_{1,0,-1}^r xz \right)$$

$$H_{AY}^{(2)} = -\sqrt{2} \left( b_{0,0,2}^i (x-y)(x+y) + b_{1,0,-1}^i xz + 2b_{0,0,2}^r xy - b_{1,0,-1}^r yz \right)$$

## 5.4 Order: 3

Number of fitting parameters:  $H_{XA}$ : 6 (all from  $H_{+A}$ ),  $H_{YA}$ : 6 (all from  $H_{+A}$ ).

**Polar e-coordinates:**

$$H_{XA}^{(3)} = \sqrt{2} \left( b_{0,2,-1}^i \rho^3 \sin(\phi) - b_{1,0,2}^i \rho^2 z \sin(2\phi) + b_{2,0,-1}^i \rho z^2 \sin(\phi) + b_{0,2,-1}^r \rho^3 \cos(\phi) + b_{1,0,2}^r \rho^2 z \cos(2\phi) + b_{2,0,-1}^r \rho z^2 \cos(\phi) \right)$$

$$H_{YA}^{(3)} = -\sqrt{2} \left( b_{0,2,-1}^i \rho^3 \cos(\phi) + b_{1,0,2}^i \rho^2 z \cos(2\phi) + b_{2,0,-1}^i \rho z^2 \cos(\phi) - b_{0,2,-1}^r \rho^3 \sin(\phi) + b_{1,0,2}^r \rho^2 z \sin(2\phi) - b_{2,0,-1}^r \rho z^2 \sin(\phi) \right)$$

$$H_{AX}^{(3)} = \sqrt{2} \left( b_{0,2,-1}^i \rho^3 \sin(\phi) - b_{1,0,2}^i \rho^2 z \sin(2\phi) + b_{2,0,-1}^i \rho z^2 \sin(\phi) + b_{0,2,-1}^r \rho^3 \cos(\phi) + b_{1,0,2}^r \rho^2 z \cos(2\phi) + b_{2,0,-1}^r \rho z^2 \cos(\phi) \right)$$

$$H_{AY}^{(3)} = -\sqrt{2} \left( b_{0,2,-1}^i \rho^3 \cos(\phi) + b_{1,0,2}^i \rho^2 z \cos(2\phi) + b_{2,0,-1}^i \rho z^2 \cos(\phi) - b_{0,2,-1}^r \rho^3 \sin(\phi) + b_{1,0,2}^r \rho^2 z \sin(2\phi) - b_{2,0,-1}^r \rho z^2 \sin(\phi) \right)$$

**Cartesian e-coordinates:**

$$H_{XA}^{(3)} = \sqrt{2} \left( b_{0,2,-1}^i y(x^2 + y^2) - 2b_{1,0,2}^i xyz + b_{2,0,-1}^i yz^2 + b_{0,2,-1}^r x(x^2 + y^2) + b_{1,0,2}^r (x-y)(x+y) + b_{2,0,-1}^r xz^2 \right)$$

$$H_{YA}^{(3)} = -\sqrt{2} \left( b_{0,2,-1}^i x(x^2 + y^2) + b_{1,0,2}^i (x-y)(x+y) + b_{2,0,-1}^i xz^2 - b_{0,2,-1}^r y(x^2 + y^2) + 2b_{1,0,2}^r xyz - b_{2,0,-1}^r yz^2 \right)$$

$$H_{AX}^{(3)} = \sqrt{2} \left( b_{0,2,-1}^i y(x^2 + y^2) - 2b_{1,0,2}^i xyz + b_{2,0,-1}^i yz^2 + b_{0,2,-1}^r x(x^2 + y^2) + b_{1,0,2}^r (x-y)(x+y) + b_{2,0,-1}^r xz^2 \right)$$

$$H_{AY}^{(3)} = -\sqrt{2} \left( b_{0,2,-1}^i x(x^2 + y^2) + b_{1,0,2}^i (x-y)(x+y) + b_{2,0,-1}^i xz^2 - b_{0,2,-1}^r y(x^2 + y^2) + 2b_{1,0,2}^r xyz - b_{2,0,-1}^r yz^2 \right)$$