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 pdflatex. 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 jbrown88@yorku.ca.

Contents

1 Vibronic interaction **2**

2 Vibronic Hamiltonian operator in the complex E basis **2**

3 Matrix element expansions in the complex E basis **2**

3.1 Order: 0 2
3.2 Order: 1 2
3.3 Order: 2 3
3.4 Order: 3 4

4 Vibronic Hamiltonian operator in the real E basis **5**

5 Matrix element expansions in the real E basis **5**

5.1 Order: 0 5
5.2 Order: 1 5
5.3 Order: 2 6
5.4 Order: 3 7

1 Vibronic interaction

$E_1'' \otimes (e_1' + e_1'')$ in C_{5h}

$$\begin{aligned}\rho_1, \phi_1, x_1, y_1 &\rightarrow e_1' \\ \rho_2, \phi_2, x_2, y_2 &\rightarrow e_1''\end{aligned}$$

2 Vibronic Hamiltonian operator in the complex E basis

$$\hat{H} = \begin{pmatrix} |+\rangle & |-\rangle \end{pmatrix} \begin{pmatrix} H_{++} & H_{+-} \\ H_{-+} & H_{--} \end{pmatrix} \begin{pmatrix} \langle +| \\ \langle -| \end{pmatrix}$$

3 Matrix element expansions in the complex E basis

3.1 Order: 0

Number of fitting parameters: H_{++}: 2, H_{+-}: 0.

Polar e-coordinates:

$$H_{++}^{(0)} = ia^{i}_{0,0,0,0} + a^{r}_{0,0,0,0}$$

$$H_{--}^{(0)} = ia^{i}_{0,0,0,0} + a^{r}_{0,0,0,0}$$

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

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

Cartesian e-coordinates:

$$H_{++}^{(0)} = ia^{i}_{0,0,0,0} + a^{r}_{0,0,0,0}$$

$$H_{--}^{(0)} = ia^{i}_{0,0,0,0} + a^{r}_{0,0,0,0}$$

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

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

3.2 Order: 1

Number of fitting parameters: H_{++}: 0, H_{+-}: 0.

Polar e-coordinates:

$$H_{++}^{(1)} = 0$$

$$H_{--}^{(1)} = 0$$

$$H_{+-}^{(1)} = 0$$

$$H_{-+}^{(1)} = 0$$

Cartesian e-coordinates:

$$H_{++}^{(1)} = 0$$

$$H_{--}^{(1)} = 0$$

$$H_{+-}^{(1)} = 0$$

$$H_{-+}^{(1)} = 0$$

3.3 Order: 2

Number of fitting parameters: H_{++}: 4, H_{+-}: 4.

Polar e-coordinates:

$$H_{++}^{(2)} = ia^{i}_{0,0,0,1}\rho_2^2 + ia^{i}_{0,1,0,0}\rho_1^2 + a^{r}_{0,0,0,1}\rho_2^2 + a^{r}_{0,1,0,0}\rho_1^2$$

$$H_{--}^{(2)} = ia^{i}_{0,0,0,1}\rho_2^2 + ia^{i}_{0,1,0,0}\rho_1^2 + a^{r}_{0,0,0,1}\rho_2^2 + a^{r}_{0,1,0,0}\rho_1^2$$

$$H_{+-}^{(2)} = ib^{i}_{-2,0,0,0}\rho_1^2 \exp(-2i\phi_1) + ib^{i}_{0,0,-2,0}\rho_2^2 \exp(-2i\phi_2) + b^{r}_{-2,0,0,0}\rho_1^2 \exp(-2i\phi_1) + b^{r}_{0,0,-2,0}\rho_2^2 \exp(-2i\phi_2)$$

$$H_{-+}^{(2)} = -ib^{i}_{-2,0,0,0}\rho_1^2 \exp(2i\phi_1) - ib^{i}_{0,0,-2,0}\rho_2^2 \exp(2i\phi_2) + b^{r}_{-2,0,0,0}\rho_1^2 \exp(2i\phi_1) + b^{r}_{0,0,-2,0}\rho_2^2 \exp(2i\phi_2)$$

Cartesian e-coordinates:

$$H_{++}^{(2)} = ia_{0,0,0,1}^{i}(x_2^2 + y_2^2) + ia_{0,1,0,0}^{i}(x_1^2 + y_1^2) + a_{0,0,0,1}^{r}(x_2^2 + y_2^2) + a_{0,1,0,0}^{r}(x_1^2 + y_1^2)$$

$$H_{--}^{(2)} = ia_{0,0,0,1}^{i}(x_2^2 + y_2^2) + ia_{0,1,0,0}^{i}(x_1^2 + y_1^2) + a_{0,0,0,1}^{r}(x_2^2 + y_2^2) + a_{0,1,0,0}^{r}(x_1^2 + y_1^2)$$

$$H_{+-}^{(2)} = 2b_{-2,0,0,0}^{i}x_1y_1 + ib_{-2,0,0,0}^{i}(x_1 - y_1)(x_1 + y_1) + 2b_{0,0,-2,0}^{i}x_2y_2 + ib_{0,0,-2,0}^{i}(x_2 - y_2)(x_2 + y_2) - 2ib_{-2,0,0,0}^{r}x_1y_1 + b_{-2,0,0,0}^{r}(x_1 - y_1)(x_1 + y_1) - 2ib_{0,0,-2,0}^{r}x_2y_2 + b_{0,0,-2,0}^{r}(x_2 - y_2)(x_2 + y_2)$$

$$H_{-+}^{(2)} = 2b_{-2,0,0,0}^{i}x_1y_1 - ib_{-2,0,0,0}^{i}(x_1 - y_1)(x_1 + y_1) + 2b_{0,0,-2,0}^{i}x_2y_2 - ib_{0,0,-2,0}^{i}(x_2 - y_2)(x_2 + y_2) + 2ib_{-2,0,0,0}^{r}x_1y_1 + b_{-2,0,0,0}^{r}(x_1 - y_1)(x_1 + y_1) + 2ib_{0,0,-2,0}^{r}x_2y_2 + b_{0,0,-2,0}^{r}(x_2 - y_2)(x_2 + y_2)$$

3.4 Order: 3

Number of fitting parameters: H_{++}: 0, H_{+-}: 4.

Polar e-coordinates:

$$H_{++}^{(3)} = 0$$

$$H_{--}^{(3)} = 0$$

$$H_{+-}^{(3)} = ib_{1,0,2,0}^{i}\rho_1\rho_2^2\exp(i(\phi_1 + 2\phi_2)) + ib_{3,0,0,0}^{i}\rho_1^3\exp(3i\phi_1) + b_{1,0,2,0}^{r}\rho_1\rho_2^2\exp(i(\phi_1 + 2\phi_2)) + b_{3,0,0,0}^{r}\rho_1^3\exp(3i\phi_1)$$

$$H_{-+}^{(3)} = -ib_{1,0,2,0}^{i}\rho_1\rho_2^2\exp(-i(\phi_1 + 2\phi_2)) - ib_{3,0,0,0}^{i}\rho_1^3\exp(-3i\phi_1) + b_{1,0,2,0}^{r}\rho_1\rho_2^2\exp(-i(\phi_1 + 2\phi_2)) + b_{3,0,0,0}^{r}\rho_1^3\exp(-3i\phi_1)$$

Cartesian e-coordinates:

$$H_{++}^{(3)} = 0$$

$$H_{--}^{(3)} = 0$$

$$H_{+-}^{(3)} = ib_{1,0,2,0}^{i}(x_1(x_2^2 - y_2^2) - 2x_2y_1y_2) - b_{1,0,2,0}^{i}(2x_1x_2y_2 + y_1(x_2^2 - y_2^2)) + ib_{3,0,0,0}^{i}x_1(x_1^2 - 3y_1^2) - b_{3,0,0,0}^{i}y_1(3x_1^2 - y_1^2) + b_{1,0,2,0}^{r}(x_1(x_2^2 - y_2^2) - 2x_2y_1y_2) + ib_{1,0,2,0}^{r}(2x_1x_2y_2 + y_1(x_2^2 - y_2^2)) + b_{3,0,0,0}^{r}x_1(x_1^2 - 3y_1^2) + ib_{3,0,0,0}^{r}y_1(3x_1^2 - y_1^2)$$

$$H_{-+}^{(3)} = -ib_{1,0,2,0}^{i}(x_1(x_2^2 - y_2^2) - 2x_2y_1y_2) - b_{1,0,2,0}^{i}(2x_1x_2y_2 + y_1(x_2^2 - y_2^2)) - ib_{3,0,0,0}^{i}x_1(x_1^2 - 3y_1^2) - b_{3,0,0,0}^{i}y_1(3x_1^2 - y_1^2) + b_{1,0,2,0}^{r}(x_1(x_2^2 - y_2^2) - 2x_2y_1y_2) - ib_{1,0,2,0}^{r}(2x_1x_2y_2 + y_1(x_2^2 - y_2^2)) + b_{3,0,0,0}^{r}x_1(x_1^2 - 3y_1^2) - ib_{3,0,0,0}^{r}y_1(3x_1^2 - y_1^2)$$

4 Vibronic Hamiltonian operator in the real E basis

$\hat{H} = \begin{pmatrix} |X\rangle & |Y\rangle \end{pmatrix} \begin{pmatrix} H_{XX} & H_{XY} \\ H_{YX} & H_{YY} \end{pmatrix} \begin{pmatrix} \langle X| \\ \langle Y| \end{pmatrix}$

5 Matrix element expansions in the real E basis

5.1 Order: 0

Number of fitting parameters: H_{XX}: 1 (all from H_{++}), H_{XY}: 0, H_{YY}: 1 (all from H_{++}).

Polar e-coordinates:

$$H_{XX}^{(0)} = ia^{i}_{0,0,0,0} + a^{r}_{0,0,0,0}$$

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

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

$$H_{YY}^{(0)} = ia^{i}_{0,0,0,0} + a^{r}_{0,0,0,0}$$

Cartesian e-coordinates:

$$H_{XX}^{(0)} = ia^{i}_{0,0,0,0} + a^{r}_{0,0,0,0}$$

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

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

$$H_{YY}^{(0)} = ia^{i}_{0,0,0,0} + a^{r}_{0,0,0,0}$$

5.2 Order: 1

Number of fitting parameters: H_{XX}: 0, H_{XY}: 0, H_{YY}: 0.

Polar e-coordinates:

$$H_{XX}^{(1)} = 0$$

$$H_{XY}^{(1)} = 0$$

$$H_{YX}^{(1)} = 0$$

$$H_{YY}^{(1)} = 0$$

Cartesian e-coordinates:

$$H_{XX}^{(1)} = 0$$

$$H_{XY}^{(1)} = 0$$

$$H_{YX}^{(1)} = 0$$

$$H_{YY}^{(1)} = 0$$

5.3 Order: 2

Number of fitting parameters: H_{XX}: 6 (2 from H_{++}, 4 from H_{+-}), H_{XY}: 4 (all from H_{+-}), H_{YY}: 6 (2 from H_{++}, 4 from H_{+-}).

Polar e-coordinates:

$$H_{XX}^{(2)} = a_{0,0,0,1}^{r}\rho_2^2 + a_{0,1,0,0}^{r}\rho_1^2 + b_{-2,0,0,0}^{i}\rho_1^2\sin(2\phi_1) + b_{0,0,-2,0}^{i}\rho_2^2\sin(2\phi_2) + b_{-2,0,0,0}^{r}\rho_1^2\cos(2\phi_1) + b_{0,0,-2,0}^{r}\rho_2^2\cos(2\phi_2) + i(a_{0,0,0,1}^{i}\rho_2^2 + a_{0,1,0,0}^{i}\rho_1^2)$$

$$H_{XY}^{(2)} = -b_{-2,0,0,0}^{i}\rho_1^2\cos(2\phi_1) - b_{0,0,-2,0}^{i}\rho_2^2\cos(2\phi_2) + b_{-2,0,0,0}^{r}\rho_1^2\sin(2\phi_1) + b_{0,0,-2,0}^{r}\rho_2^2\sin(2\phi_2)$$

$$H_{YX}^{(2)} = -b_{-2,0,0,0}^{i}\rho_1^2\cos(2\phi_1) - b_{0,0,-2,0}^{i}\rho_2^2\cos(2\phi_2) + b_{-2,0,0,0}^{r}\rho_1^2\sin(2\phi_1) + b_{0,0,-2,0}^{r}\rho_2^2\sin(2\phi_2)$$

$$H_{YY}^{(2)} = a_{0,0,0,1}^{r}\rho_2^2 + a_{0,1,0,0}^{r}\rho_1^2 - b_{-2,0,0,0}^{i}\rho_1^2\sin(2\phi_1) - b_{0,0,-2,0}^{i}\rho_2^2\sin(2\phi_2) - b_{-2,0,0,0}^{r}\rho_1^2\cos(2\phi_1) - b_{0,0,-2,0}^{r}\rho_2^2\cos(2\phi_2) + i(a_{0,0,0,1}^{i}\rho_2^2 + a_{0,1,0,0}^{i}\rho_1^2)$$

Cartesian e-coordinates:

$$H_{XX}^{(2)} = a_{0,0,0,1}^{r}(x_2^2 + y_2^2) + a_{0,1,0,0}^{r}(x_1^2 + y_1^2) + 2b_{-2,0,0,0}^{i}x_1y_1 + 2b_{0,0,-2,0}^{i}x_2y_2 + b_{-2,0,0,0}^{r}(x_1 - y_1)(x_1 + y_1) + b_{0,0,-2,0}^{r}(x_2 - y_2)(x_2 + y_2) + i(a_{0,0,0,1}^{i}(x_2^2 + y_2^2) + a_{0,1,0,0}^{i}(x_1^2 + y_1^2))$$

$$H_{XY}^{(2)} = -b_{-2,0,0,0}^{i}(x_1 - y_1)(x_1 + y_1) - b_{0,0,-2,0}^{i}(x_2 - y_2)(x_2 + y_2) + 2b_{-2,0,0,0}^{r}x_1y_1 + 2b_{0,0,-2,0}^{r}x_2y_2$$

$$H_{YX}^{(2)} = -b_{-2,0,0,0}^{i}(x_1 - y_1)(x_1 + y_1) - b_{0,0,-2,0}^{i}(x_2 - y_2)(x_2 + y_2) + 2b_{-2,0,0,0}^{r}x_1y_1 + 2b_{0,0,-2,0}^{r}x_2y_2$$

$$H_{YY}^{(2)} = a_{0,0,0,1}^{r}(x_2^2 + y_2^2) + a_{0,1,0,0}^{r}(x_1^2 + y_1^2) - 2b_{-2,0,0,0}^{i}x_1y_1 - 2b_{0,0,-2,0}^{i}x_2y_2 - b_{-2,0,0,0}^{r}(x_1 - y_1)(x_1 + y_1) - b_{0,0,-2,0}^{r}(x_2 - y_2)(x_2 + y_2) + i(a_{0,0,0,1}^{i}(x_2^2 + y_2^2) + a_{0,1,0,0}^{i}(x_1^2 + y_1^2))$$

5.4 Order: 3

Number of fitting parameters: H_{XX}: 4 (all from H_{+-}), H_{XY}: 4 (all from H_{+-}), H_{YY}: 4 (all from H_{+-}).

Polar e-coordinates:

$$H^{(3)}_{XX} = -b^i_{1,0,2,0}\rho_1\rho_2^2\sin(\phi_1+2\phi_2) - b^i_{3,0,0,0}\rho_1^3\sin(3\phi_1) + b^r_{1,0,2,0}\rho_1\rho_2^2\cos(\phi_1+2\phi_2) + b^r_{3,0,0,0}\rho_1^3\cos(3\phi_1)$$

$$H^{(3)}_{XY} = -b^i_{1,0,2,0}\rho_1\rho_2^2\cos(\phi_1+2\phi_2) - b^i_{3,0,0,0}\rho_1^3\cos(3\phi_1) - b^r_{1,0,2,0}\rho_1\rho_2^2\sin(\phi_1+2\phi_2) - b^r_{3,0,0,0}\rho_1^3\sin(3\phi_1)$$

$$H^{(3)}_{YX} = -b^i_{1,0,2,0}\rho_1\rho_2^2\cos(\phi_1+2\phi_2) - b^i_{3,0,0,0}\rho_1^3\cos(3\phi_1) - b^r_{1,0,2,0}\rho_1\rho_2^2\sin(\phi_1+2\phi_2) - b^r_{3,0,0,0}\rho_1^3\sin(3\phi_1)$$

$$H^{(3)}_{YY} = b^i_{1,0,2,0}\rho_1\rho_2^2\sin(\phi_1+2\phi_2) + b^i_{3,0,0,0}\rho_1^3\sin(3\phi_1) - b^r_{1,0,2,0}\rho_1\rho_2^2\cos(\phi_1+2\phi_2) - b^r_{3,0,0,0}\rho_1^3\cos(3\phi_1)$$

Cartesian e-coordinates:

$$H^{(3)}_{XX} = -b^i_{1,0,2,0}(2x_1x_2y_2 + y_1(x_2^2-y_2^2)) - b^i_{3,0,0,0}y_1(3x_1^2-y_1^2) + b^r_{1,0,2,0}(x_1(x_2^2-y_2^2) - 2x_2y_1y_2) + b^r_{3,0,0,0}x_1(x_1^2-3y_1^2)$$

$$H^{(3)}_{XY} = -b^i_{1,0,2,0}(x_1(x_2^2-y_2^2) - 2x_2y_1y_2) - b^i_{3,0,0,0}x_1(x_1^2-3y_1^2) - b^r_{1,0,2,0}(2x_1x_2y_2 + y_1(x_2^2-y_2^2)) - b^r_{3,0,0,0}y_1(3x_1^2-y_1^2)$$

$$H^{(3)}_{YX} = -b^i_{1,0,2,0}(x_1(x_2^2-y_2^2) - 2x_2y_1y_2) - b^i_{3,0,0,0}x_1(x_1^2-3y_1^2) - b^r_{1,0,2,0}(2x_1x_2y_2 + y_1(x_2^2-y_2^2)) - b^r_{3,0,0,0}y_1(3x_1^2-y_1^2)$$

$$H^{(3)}_{YY} = b^i_{1,0,2,0}(2x_1x_2y_2 + y_1(x_2^2-y_2^2)) + b^i_{3,0,0,0}y_1(3x_1^2-y_1^2) - b^r_{1,0,2,0}(x_1(x_2^2-y_2^2) - 2x_2y_1y_2) - b^r_{3,0,0,0}x_1(x_1^2-3y_1^2)$$