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 robert.lang@mail.utoronto.ca.

Contents

1 Vibronic interaction

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

2 Vibronic Hamiltonian operator in the complex E basis

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

3 Matrix element expansions in the complex E basis

3.1 Order: 2

Number of terms: 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:

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

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

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

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

3.2 Order: 3

Number of terms: H_{+A}: 6.

Polar e-coordinates:

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

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

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

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

Cartesian e-coordinates:

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

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

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

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

4 Vibronic Hamiltonian operator in the real E basis

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

5 Matrix element expansions in the real E basis

5.1 Order: 2

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

Polar e-coordinates:

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

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

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

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

Cartesian e-coordinates:

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

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

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

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

5.2 Order: 3

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

Polar e-coordinates:

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

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

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

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

Cartesian e-coordinates:

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

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

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

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