Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplement to: Anharmonic excited state frequencies of para-difluorobenze, toluene and catechol using analytic RI-CC2 second derivatives

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1 Detailed formulas for the implementation

Table 1: Definitions of the different RI three-index integrals $B_{Q,pq}$. The three-index integral in the AO-basis is denoted with $(\alpha\beta|P)$, whereas $[\mathbf{V}^{-1/2}]_{PQ}$ denotes a two-index integral. The MO coefficient matrix is denoted with $\mathbf{C}$, the definitions of the $\mathbf{\Lambda}$ and λ matrices are given in table 2. The macron on the $\bar{B}_{Q,pq}$ intermediates denotes a dependency on a right vector (R^f, $R^{f,x}$, or t^x), whereas the breve denotes a dependency on a left vector (L^f or $\bar{t}^f$). Note that the intermediate $\bar{\bar{B}}^{xy}_{Q,pq}$ depends on two different right eigenvectors R^x and R^y.

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\begin{aligned}
B_{Q,pq} &= \sum_{\alpha\beta P} C_{\alpha p} C_{\beta p} (\alpha\beta|P)[\mathbf{V}^{-1/2}]_{PQ} \\
\hat{B}_{Q,pq} &= \sum_{\alpha\beta P} \Lambda^p_{\alpha p} \Lambda^h_{\beta p} (\alpha\beta|P)[\mathbf{V}^{-1/2}]_{PQ} \\
\bar{B}_{Q,pq}[R] &= \sum_{\alpha\beta P} (\bar{\Lambda}^p_{\alpha p} \Lambda^h_{\beta p} + \Lambda^p_{\alpha p} \bar{\Lambda}^h_{\beta p}) (\alpha\beta|P)[\mathbf{V}^{-1/2}]_{PQ} \\
\bar{\bar{B}}_{Q,pq}[R^x, R^y] &= \sum_{\alpha\beta P} (\bar{\Lambda}^{px}_{\alpha p} \bar{\Lambda}^{hy}_{\beta p} + \bar{\Lambda}^{py}_{\alpha p} \bar{\Lambda}^{hx}_{\beta p}) (\alpha\beta|P)[\mathbf{V}^{-1/2}]_{PQ} \\
\breve{B}_{Q,pq} &= \sum_{\alpha\beta P} (\breve{\Lambda}^p_{\alpha p} \Lambda^h_{\beta p} + \Lambda^p_{\alpha p} \breve{\Lambda}^h_{\beta p}) (\alpha\beta|P)[\mathbf{V}^{-1/2}]_{PQ} \\
\breve{\bar{\bar{B}}}_{Q,ia} &= -\sum_{kc} L_{ci} R_{ck} B_{Q,ka} - \sum_{ck} L_{ak} R_{ck} B_{Q,ic} \\
B^x_{Q,pq} &= \sum_{\alpha\beta P} \left(C^x_{\alpha p} C_{\beta p} + C_{\alpha p} C^x_{\beta p} \right) (\alpha\beta|P)[\mathbf{V}^{-1/2}]_{PQ} \\
&\quad + \sum_{\alpha\beta P} C_{\alpha p} C_{\beta p} \Big((\alpha\beta|P)^{[x]} - \tfrac{1}{2} \sum_{RQ} (\alpha\beta|R)[\mathbf{V}^{-1}]_{RS} V^{[x]}_{SP} \Big) [\mathbf{V}^{-1/2}]_{PQ} \\
\hat{B}^x_{Q,pq} &= \sum_{\alpha\beta P} \left(\Lambda^{p,x}_{\alpha p} \Lambda^h_{\beta p} + \Lambda^p_{\alpha p} \Lambda^{h,x}_{\beta p} \right) (\alpha\beta|P)[\mathbf{V}^{-1/2}]_{PQ} \\
&\quad + \sum_{\alpha\beta P} \Lambda^p_{\alpha p} \Lambda^h_{\beta p} \Big((\alpha\beta|P)^{[x]} - \tfrac{1}{2} \sum_{RS} (\alpha\beta|R)[\mathbf{V}^{-1}]_{RS} V^{[x]}_{SP} \Big) [\mathbf{V}^{-1/2}]_{PQ} \\
\bar{B}^x_{Q,ai}[R] &= \sum_b \hat{B}^x_{Q,ab} R_{bi} - \sum_j R_{aj} \hat{B}^x_{Q,ji} \\
\bar{\bar{B}}^{f,x}_{Q,ai} &= \bar{\bar{B}}_{Q,ai}[R^f, t^x] + \bar{B}^x_{Q,ai}[R^f] + \bar{B}_{Q,ai}[R^{f,x}]
\end{aligned}
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Table 2: Definitions of the transformation matrices.

$\lambda^p_{rp} = \delta_{rp} - \sum_{ai} \delta_{ri}\delta_{pa}t_{ai}$	$\lambda^h_{rp} = \delta_{rp} + \sum_{ai} \delta_{ra}\delta_{pi}t_{ai}$
$\Lambda^p_{\alpha p} = \sum_r C_{\alpha r}\lambda^p_{rp}$	$\Lambda^h_{\alpha p} = \sum_r C_{\alpha r}\lambda^h_{rp}$
$\bar{\Lambda}^p_{\alpha a} = -\sum_i C_{\alpha i}R_{ia}$	$\bar{\Lambda}^h_{\alpha i} = \sum_a C_{\alpha a}R_{ai}$
$\breve{\Lambda}^p_{\alpha i} = \sum_a \Lambda^p_{\alpha a}L_{ai}$	$\breve{\Lambda}^h_{\alpha a} = -\sum_i \Lambda^h_{\alpha i}L_{ia}$
$\Lambda^{p,x}_{\alpha p} = \sum_r C^x_{\alpha r}\lambda^p_{rp}$	$\Lambda^{h,x}_{\alpha p} = \sum_r C^x_{\alpha r}\lambda^h_{rp}$

For the two-particle terms from the derivatives of the non-separable two-particle density with the derivatives of the MO two-electron integrals:

$$\sum_{pqrs} \hat{d}^{nsep,ex,y}_{pqrs}(pq\hat{|}rs)^x = \sum_{\alpha\beta Q} \Delta^{Q,y}_{\alpha\beta}(\alpha\beta|Q)^{[x]} - \sum_{PQ} \gamma^y_{PQ}V^{[x]}_{PQ} + \sum_{pq} F^{eff,y}_{pq}U^x_{pq} \tag{1}$$

the three- and two-index two-particle densities for the contraction with the first derivatives of the three- and two-index AO integrals are defined as:

$$\Delta^{Q,y}_{pq} = \sum_{rsP} \hat{d}^{nsep,ex,y}_{pqrs}\hat{B}_{P,rs}[V^{-1/2}]_{PQ} \tag{2}$$

$$\Delta^{Q,y}_{\alpha\beta} = \sum_{pq} \Lambda^p_{\alpha p}\Lambda^h_{\beta q}\Delta^{Q,y}_{pq} \tag{3}$$

$$\gamma^y_{PQ} = \frac{1}{2}\sum_{pqR} \Delta^{Q,y}_{pq}\hat{B}_{R,pq}[V^{-1/2}]_{RP} \tag{4}$$

The effective Fock matrices needed to account for the contribution of the derivatives of the MO coefficients are:

$$F^{eff,y}_{pq} = \sum_{rst} \left(d^{nsep,ex,y}_{rstp} + d^{nsep,ex}\right)(rs|tq)^{RI} \tag{5}$$

$$d^{nsep,ex,y}_{rspq} = \sum_{r's'p'q'} \hat{d}^{nsep,ex,y}_{r's'p'q'}\lambda^p_{rr'}\lambda^h_{ss'}\lambda^p_{pp'}\lambda^h_{qq'} \tag{6}$$

For the contribution of the second derivatives of the AO integrals $\langle H^{[xy]} \rangle$ the three and two-particle densities are given by:

$$\Delta_{pq}^{Q} = \sum_{rsP} \hat{d}_{pqrs}^{nsep,ex} \hat{B}_{P,rs} [V^{-1/2}]_{PQ} \tag{7}$$

$$\Delta_{\alpha\beta}^{Q} = \sum_{pq} \Lambda_{\alpha p}^{p} \Lambda_{\beta q}^{h} \Delta_{pq}^{Q} \tag{8}$$

$$\gamma_{PQ} = \frac{1}{2} \sum_{pqR} \Delta_{pq}^{Q} \hat{B}_{R,pq} [V^{-1/2}]_{RP} \tag{9}$$

$$\Delta_{pq}^{Q,[x]} = \sum_{rsP} \hat{d}_{pqrs}^{nsep,ex} \sum_{\alpha\beta} \Lambda_{\alpha r}^{p} \Lambda_{\beta s}^{h} \Big((\alpha\beta|P)^{[x]} - \sum_{SR} (\alpha\beta|S) V_{SR}^{-1/2} V_{RP}^{[x]} \Big) V_{PQ}^{-1} \tag{10}$$

$$\Delta_{\alpha\beta}^{Q,[x]} = \sum_{pq} \Lambda_{\alpha p}^{p} \Lambda_{\beta q}^{h} \Delta_{pq}^{Q} \tag{11}$$

$$\gamma_{PQ}^{[x]} = \sum_{pqR} \Delta_{pq}^{Q,[x]} \hat{B}_{R,pq} [V^{-1/2}]_{RP} \tag{12}$$