Supporting information:

Accurate incorporation of hyperfine coupling in diabatic potential models using the Effective Relativistic Coupling by Asymptotic Representation approach

Maik Vossel, Iordanis Tsakontsis, Nicole Weike, and Wolfgang Eisfeld

Theoretische Chemie, Universität Bielefeld, Postfach 100131, D-33501 Bielefeld, Germany[a)]

[a)]Electronic mail: wolfgang.eisfeld@uni-bielefeld.de

In this supporting information we provide the representation for the hyperfine coupling matrices of dipole-dipole Eq. (12) and quadrupole Eq. (13) operators for the $^2\mathrm{P}_{3/2}$ and $^2\mathrm{P}_{1/2}$ states of the Iodine atom referenced in Sec. III.A. The matrices are given in the spinor basis $|j^I, m_j^I, i^I, m_i^I\rangle$ with $j^I = 3/2$ and $i^I = 5/2$ for the $^2\mathrm{P}_{3/2}$ state and $j^I = 1/2$ and $i^I = 5/2$ for the $^2\mathrm{P}_{1/2}$ state.

Representation of the effective hyperfine dipole-dipole operator for the $^2\mathrm{P}_{1/2}$ state.

$$\mathbf{H}^{\mathrm{md}} = A_I^{\mathrm{md}} \begin{pmatrix}
\frac{5}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -\frac{5}{4} & \sqrt{\frac{5}{4}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \sqrt{\frac{5}{4}} & \frac{3}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -\frac{3}{4} & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \sqrt{2} & \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -\frac{1}{4} & \frac{3}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{3}{2} & -\frac{1}{4} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4} & \sqrt{2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{2} & -\frac{3}{4} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{3}{4} & \sqrt{\frac{5}{4}} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{5}{4}} & -\frac{5}{4} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{5}{4}
\end{pmatrix}$$

Representation of the effective hyperfine dipole-dipole operator for the $^{2}\mathrm{P}_{3/2}$ state.

$$
\mathbf{H}^{\mathrm{md}} = A_I^{\mathrm{md}} \left(\begin{array}{cccccccccccccccccccccccc}
\frac{15}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{5}{4} & 0 & 0 & \sqrt{\frac{15}{4}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{5}{4} & 0 & 0 & \sqrt{5} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -\frac{15}{4} & 0 & 0 & \sqrt{\frac{15}{4}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \sqrt{\frac{15}{4}} & 0 & 0 & \frac{9}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \sqrt{5} & 0 & 0 & \frac{3}{4} & 0 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \sqrt{\frac{15}{4}} & 0 & 0 & -\frac{3}{4} & 0 & 0 & \sqrt{8} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{9}{4} & 0 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & 0 & \frac{3}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \sqrt{8} & 0 & 0 & \frac{1}{4} & 0 & 0 & \sqrt{\frac{27}{4}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & 0 & -\frac{1}{4} & 0 & 0 & 3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{3}{4} & 0 & 0 & \sqrt{\frac{27}{4}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{27}{4}} & 0 & 0 & -\frac{3}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 & 0 & 0 & -\frac{1}{4} & 0 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{27}{4}} & 0 & 0 & \frac{1}{4} & 0 & 0 & \sqrt{8} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{3}{4} & 0 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & 0 & -\frac{9}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{8} & 0 & 0 & -\frac{3}{4} & 0 & 0 & \sqrt{\frac{15}{4}} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 & 0 & \frac{3}{4} & 0 & 0 & \sqrt{5} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{9}{4} & 0 & 0 & \sqrt{\frac{15}{4}} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{15}{4}} & 0 & 0 & -\frac{15}{4} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{5} & 0 & 0 & -\frac{5}{4} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{15}{4}} & 0 & 0 & \frac{5}{4} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{15}{4}
\end{array}\right)
$$

Representation of the effective hyperfine quadrupole operator for the $^{2}\mathrm{P}_{3/2}$ state.

$$
\mathbf{H}^{\mathrm{eq}} = B_I^{\mathrm{eq}}
\begin{pmatrix}
\frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -\frac{1}{4} & 0 & 0 & \sqrt{\frac{3}{20}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{4} & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{3}{40}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{4} & 0 & 0 & -\sqrt{\frac{3}{20}} & 0 & 0 & \sqrt{\frac{3}{40}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \sqrt{\frac{3}{20}} & 0 & 0 & -\frac{1}{20} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{1}{20} & 0 & 0 & \sqrt{\frac{3}{50}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -\sqrt{\frac{3}{20}} & 0 & 0 & \frac{1}{20} & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{27}{200}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{20} & 0 & 0 & -\sqrt{\frac{3}{50}} & 0 & 0 & \sqrt{\frac{27}{200}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \sqrt{\frac{3}{40}} & 0 & 0 & \sqrt{\frac{3}{50}} & 0 & 0 & -\frac{1}{5} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \sqrt{\frac{3}{40}} & 0 & 0 & 0 & 0 & 0 & \frac{1}{5} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -\sqrt{\frac{3}{50}} & 0 & 0 & \frac{1}{5} & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{27}{200}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{5} & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{27}{200}} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{27}{200}} & 0 & 0 & 0 & 0 & 0 & -\frac{1}{5} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{27}{200}} & 0 & 0 & 0 & 0 & 0 & \frac{1}{5} & 0 & 0 & -\sqrt{\frac{3}{50}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{5} & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{3}{40}} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{5} & 0 & 0 & \sqrt{\frac{3}{50}} & 0 & 0 & \sqrt{\frac{3}{40}} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{27}{200}} & 0 & 0 & -\sqrt{\frac{3}{50}} & 0 & 0 & -\frac{1}{20} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{27}{200}} & 0 & 0 & 0 & 0 & 0 & \frac{1}{20} & 0 & 0 & -\sqrt{\frac{3}{20}} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{3}{50}} & 0 & 0 & \frac{1}{20} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{20} & 0 & 0 & \sqrt{\frac{3}{20}} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{3}{40}} & 0 & 0 & -\sqrt{\frac{3}{20}} & 0 & 0 & \frac{1}{4} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{3}{40}} & 0 & 0 & 0 & 0 & 0 & -\frac{1}{4} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{3}{20}} & 0 & 0 & -\frac{1}{4} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4}
\end{pmatrix}
$$