Notes on spin-orbit coupling in RbYb

We consider interaction of Rb(^2S) and Yb(^3P) atoms to form RbYb molecule. Now in absence of spin-orbit coupling (SOC) interaction of a ^2S and ^3P atomic terms will give rise to four states namely: $^2\Sigma$, $^4\Sigma$, $^2\Pi$ and $^4\Pi$.

In the presence of SOC the ^3P term of Yb atom splits into three levels, namely: $^3P_2$, $^3P_1$ and $^3P_0$. Now, atomic interaction under the SOC picture will couple the components of the angular momentum with the following rule:

$$\Omega = \Lambda + \Sigma$$

where Λ is the projection of the total orbital angular momentum of the electrons of the molecule along the internuclear axis, Σ is the projection of the total spin angular momentum of the electrons along the same axis and Ω is the projection of the resultant electron angular momentum along the internuclear axis. The term symbol being used is $^{2S+1}\Lambda_\Omega$.

So, the spin-orbit coupled states are marked by Ω or unique pairs of (Λ, Σ) with $(-\Lambda, -\Sigma)$ being degenerate with the former. Now, the four states $^2\Sigma$, $^4\Sigma$, $^2\Pi$ and $^4\Pi$ under SOC will get split into nine states and result into states identified by the following magnitudes of Ω:

$$\begin{array}{lll}
\Omega = \frac{5}{2}: & \Lambda = 1, S = \frac{3}{2}, \Sigma = \frac{3}{2} & \rightarrow \ ^4\Pi_{5/2} \\
\Omega = \frac{3}{2}: & \Lambda = 1, S = \frac{3}{2}, \Sigma = \frac{1}{2} & \rightarrow \ ^4\Pi_{3/2} \\
 & \Lambda = 1, S = \frac{1}{2}, \Sigma = \frac{1}{2} & \rightarrow \ ^2\Pi_{3/2} \\
 & \Lambda = 0, S = \frac{3}{2}, \Sigma = \frac{3}{2} & \rightarrow \ ^4\Sigma_{3/2} \\
\Omega = \frac{1}{2}: & \Lambda = 1, S = \frac{3}{2}, \Sigma = -\frac{1}{2} & \rightarrow \ ^4\Pi_{1/2} \\
 & \Lambda = 1, S = \frac{1}{2}, \Sigma = -\frac{1}{2} & \rightarrow \ ^2\Pi_{1/2} \\
 & \Lambda = 0, S = \frac{3}{2}, \Sigma = \frac{1}{2} & \rightarrow \ ^4\Sigma_{1/2} \\
 & \Lambda = 0, S = \frac{1}{2}, \Sigma = \frac{1}{2} & \rightarrow \ ^2\Sigma_{1/2} \\
 & \Lambda = -1, S = \frac{3}{2}, \Sigma = \frac{3}{2} & \rightarrow \ ^4\Pi_{1/2}
\end{array}$$

Hamiltonian and the basis functions

The total Hamiltonian of the system is:

$$\hat{H} = \frac{\hbar^2}{2\mu}\left(-\frac{d^2}{dR^2} + \frac{\hat{L}^2}{R^2}\right) + \hat{H}_{\mathrm{Rb}} + \hat{H}_{\mathrm{Yb}} + \hat{U}(R) \tag{1}$$

The atomic Hamiltonians are:

$$\hat{H}_{\mathrm{Rb}} = \zeta_{\mathrm{Rb}}\hat{i}_{\mathrm{Rb}}.\hat{s}_{\mathrm{Rb}} + (g_e\mu_{\mathrm{B}}\hat{s}_{z,\mathrm{Rb}} + g_{\mathrm{Rb}}\mu_{\mathrm{N}}\hat{i}_{z,\mathrm{Rb}})B \tag{2a}$$

$$\hat{H}_{\mathrm{Yb}} = a^{\mathrm{so}}_{\mathrm{Yb}}\hat{l}.\hat{s}_{\mathrm{Yb}} + (\mu_{\mathrm{B}}\hat{l}_z + g_e\mu_{\mathrm{B}}\hat{s}_{z,\mathrm{Yb}})B \tag{2b}$$

where $a^{\mathrm{so}}_{\mathrm{Yb}}$ is the SOC constant for Yb atom. The nuclear coordinate R-dependent potential $\hat{U}(R)$ is made up of:

$$\hat{U}(R) = V(R) + \hat{V}^{\mathrm{d}}(R) \tag{3}$$

where $V(R)$ is the interaction potential and $\hat{V}^{\mathrm{d}}(R)$ is potential due to dipolar interaction between the magnetic moments of Rb and Yb unpaired electrons.

For the time being we ignore all other interactions and consider only the SOC and write the Hamiltonian as:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}_{\mathrm{so}} \tag{4}$$

where

$$\hat{H}^{(0)} = \frac{\hbar^2}{2\mu}\left(-\frac{d^2}{dR^2} + \frac{\hat{L}^2}{R^2}\right) + V(R) \qquad \text{and} \qquad \hat{H}_{\mathrm{so}} = a^{\mathrm{so}}_{\mathrm{Yb}}\hat{l}.\hat{s}_{\mathrm{Yb}} \tag{5}$$

We want to express the matrix elements of $\hat{H}_{\mathrm{so}}$ in terms of the basis set in which the unperturbed Hamiltonian $\hat{H}^{(0)}$ is diagonal. We denote such basis set in the following way:

$$|L\,\Lambda;\,S\,\Sigma\,(s_{\mathrm{Rb}}\,s_{\mathrm{Yb}})\rangle \tag{6}$$

where $L = 1$; $\Lambda = 0, \pm 1$; $S = \frac{3}{2}, \frac{1}{2}$; $s_{\mathrm{Rb}} = \frac{1}{2}$ and $s_{\mathrm{Yb}} = 1$.

The spin-angular momenta coupled basis sets can be expressed in terms of the uncoupled basis sets as:

$$|S\,\Sigma\,(s_{\mathrm{Rb}}\,s_{\mathrm{Yb}})\rangle = \sum_{\sigma_{\mathrm{Rb}},\sigma_{\mathrm{Yb}}} C(\sigma_{\mathrm{Rb}},\sigma_{\mathrm{Yb}})|s_{\mathrm{Rb}}\,\sigma_{\mathrm{Rb}};\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle \tag{7}$$

where $C(\sigma_{\mathrm{Rb}},\sigma_{\mathrm{Yb}})$ is a Clebsch-Gordan coefficient and σ_{Rb} and σ_{Yb} are the spin projections of the individual atoms.

Since $\Sigma = \sigma_{\mathrm{Rb}} + \sigma_{\mathrm{Yb}}$, the above series [Eq. (7)] can be written in terms of a single sum as:

$$|S\,\Sigma\rangle = \sum_{\sigma_{\mathrm{Yb}}} C(\Sigma-\sigma_{\mathrm{Yb}},\sigma_{\mathrm{Yb}})|s_{\mathrm{Rb}}\,\Sigma-\sigma_{\mathrm{Yb}};\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle \tag{8}$$

Since the contribution to the total electronic angular momentum (L) is only from the Yb atom, we can write the SOC operator as $a^{\mathrm{so}}_{\mathrm{Yb}}\hat{L}.\hat{s}_{\mathrm{Yb}}$ instead of $a^{\mathrm{so}}_{\mathrm{Yb}}\hat{l}.\hat{s}_{\mathrm{Yb}}$. Thus, from Eq. (7), we have:

$$|L\,\Lambda\,S\,\Sigma\rangle = \sum_{\sigma_{\mathrm{Rb}},\sigma_{\mathrm{Yb}}} C(\sigma_{\mathrm{Rb}},\sigma_{\mathrm{Yb}})|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\,s_{\mathrm{Rb}}\,\sigma_{\mathrm{Rb}}\rangle \tag{9}$$

The SOC operator can be re-written in terms of raising and lowering operators as:

$$\begin{aligned} a^{\mathrm{so}}_{\mathrm{Yb}}\hat{L}.\hat{s}_{\mathrm{Yb}} &= a^{\mathrm{so}}_{\mathrm{Yb}}(\hat{L}_x\hat{s}_{x,\mathrm{Yb}} + \hat{L}_y\hat{s}_{y,\mathrm{Yb}} + \hat{L}_z\hat{s}_{z,\mathrm{Yb}}) && (10a)\\ &= a^{\mathrm{so}}_{\mathrm{Yb}}\left\{\frac{1}{2}(\hat{L}_+\hat{s}_{-,\mathrm{Yb}} + \hat{L}_-\hat{s}_{+,\mathrm{Yb}}) + \hat{L}_z\hat{s}_{z,\mathrm{Yb}}\right\} && (10b)\end{aligned}$$

The matrix elements of the SOC operator are thus:

$$\begin{aligned}&\langle L\,\Lambda'\,S'\,\Sigma'|a^{\mathrm{so}}_{\mathrm{Yb}}\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,S\,\Sigma\rangle = \\ &a^{\mathrm{so}}_{\mathrm{Yb}}\sum_{\sigma'_{\mathrm{Rb}},\sigma'_{\mathrm{Yb}}}\sum_{\sigma_{\mathrm{Rb}},\sigma_{\mathrm{Yb}}} C'^{*}(\sigma'_{\mathrm{Rb}},\sigma'_{\mathrm{Yb}})C(\sigma_{\mathrm{Rb}},\sigma_{\mathrm{Yb}})\langle L\,\Lambda'\,s_{\mathrm{Yb}}\,\sigma'_{\mathrm{Yb}}\,s_{\mathrm{Rb}}\,\sigma'_{\mathrm{Rb}}|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\,s_{\mathrm{Rb}}\,\sigma_{\mathrm{Rb}}\rangle \quad (11)\end{aligned}$$

Let us now consider the matrix elements inside the sum:

$$\langle L\,\Lambda'\,s_{\mathrm{Yb}}\,\sigma'_{\mathrm{Yb}}\,s_{\mathrm{Rb}}\,\sigma'_{\mathrm{Rb}}|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\,s_{\mathrm{Rb}}\,\sigma_{\mathrm{Rb}}\rangle = \langle L\,\Lambda'\,s_{\mathrm{Yb}}\,\sigma'_{\mathrm{Yb}}|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle\delta_{\sigma'_{\mathrm{Rb}}\sigma_{\mathrm{Rb}}} \tag{12}$$

Those are diagonal in σ_{Rb}. Now the diagonal elements of the resulting matrix elements are:

$$\begin{aligned}\langle L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle &= \langle L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}|\frac{1}{2}(\hat{L}_+\hat{s}_{-,\mathrm{Yb}} + \hat{L}_-\hat{s}_{+,\mathrm{Yb}}) + \hat{L}_z\hat{s}_{z,\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle\\ \Rightarrow \langle L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle &= \langle L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}|\hat{L}_z\hat{s}_{z,\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle\\ \Rightarrow \langle L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle &= \Lambda\sigma_{\mathrm{Yb}} && (13)\end{aligned}$$

Only the following off-diagonal elements will survive:

$$
\begin{aligned}
& \langle L\,\Lambda+1\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}-1|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle = \\
& \langle L\,\Lambda+1\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}-1|\frac{1}{2}(\hat{L}_+\hat{s}_{-,\mathrm{Yb}}+\hat{L}_-\hat{s}_{+,\mathrm{Yb}})+\hat{L}_z\hat{s}_{z,\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle \\
\Rightarrow\ & \langle L\,\Lambda+1\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}-1|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda+1\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}-1\rangle = \frac{1}{2}\langle L\,\Lambda+1\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}-1|\hat{L}_+\hat{s}_{-,\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle \\
\Rightarrow\ & \langle L\,\Lambda+1\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}-1|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle = \\
& \frac{1}{2}\sqrt{L(L+1)-\Lambda(\Lambda+1)}\sqrt{s_{\mathrm{Yb}}(s_{\mathrm{Yb}}+1)-\sigma_{\mathrm{Yb}}(\sigma_{\mathrm{Yb}}-1)} \qquad (14)
\end{aligned}
$$

and

$$
\begin{aligned}
\Rightarrow\ & \langle L\,\Lambda-1\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}+1|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle = \frac{1}{2}\langle L\,\Lambda-1\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}+1|\hat{L}_-\hat{s}_{+,\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle \\
\Rightarrow\ & \langle L\,\Lambda-1\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}+1|\hat{L}.\hat{s}_{\mathrm{Yb}}|L\,\Lambda\,s_{\mathrm{Yb}}\,\sigma_{\mathrm{Yb}}\rangle = \\
& \frac{1}{2}\sqrt{L(L+1)-\Lambda(\Lambda-1)}\sqrt{s_{\mathrm{Yb}}(s_{\mathrm{Yb}}+1)-\sigma_{\mathrm{Yb}}(\sigma_{\mathrm{Yb}}+1)} \qquad (15)
\end{aligned}
$$

Finding explicit matrix elements of the SOC operator

Let us now try to find out the matrix elements of the SOC operator in terms of the quantum number Ω. But before that, it is worth having the explicit expansions of the functions in Eq. (7).

$$
\begin{aligned}
\left|S=\frac{3}{2},\Sigma=\frac{3}{2}\right\rangle &= \left|\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\right\rangle && (16a)\\
\left|S=\frac{3}{2},\Sigma=\frac{1}{2}\right\rangle &= \sqrt{\frac{1}{3}}\left|\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\right\rangle+\sqrt{\frac{2}{3}}\left|\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\right\rangle && (16b)\\
\left|S=\frac{1}{2},\Sigma=\frac{1}{2}\right\rangle &= \sqrt{\frac{2}{3}}\left|\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\right\rangle-\sqrt{\frac{1}{3}}\left|\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\right\rangle && (16c)\\
\left|S=\frac{3}{2},\Sigma=-\frac{1}{2}\right\rangle &= \sqrt{\frac{2}{3}}\left|\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\right\rangle+\sqrt{\frac{1}{3}}\left|\sigma_{\mathrm{Yb}}=-1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\right\rangle && (16d)\\
\left|S=\frac{1}{2},\Sigma=-\frac{1}{2}\right\rangle &= \sqrt{\frac{1}{3}}\left|\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\right\rangle-\sqrt{\frac{2}{3}}\left|\sigma_{\mathrm{Yb}}=-1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\right\rangle && (16e)\\
\left|S=\frac{3}{2},\Sigma=-\frac{3}{2}\right\rangle &= \left|\sigma_{\mathrm{Yb}}=-1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\right\rangle && (16f)
\end{aligned}
$$

Now, let us apply the SOC operator on each the basis functions marked by Ω:

$$\begin{aligned}
|{}^4\Pi_{5/2}\rangle &\equiv \Big|\Omega=\frac{5}{2};\Lambda=1,S=\frac{3}{2},\Sigma=\frac{3}{2}\Big\rangle \\
\hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Omega=\frac{5}{2};\Lambda=1,S=\frac{3}{2},\Sigma=\frac{3}{2}\Big\rangle &= \hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
&= \hat{L}_z\hat{s}_{z,\mathrm{Yb}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
&= \Big|\Lambda=1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
&= \Big|\Omega=\frac{5}{2};\Lambda=1,S=\frac{3}{2},\Sigma=\frac{3}{2}\Big\rangle \qquad (17)
\end{aligned}$$

$$\begin{aligned}
&|{}^4\Pi_{3/2}\rangle \equiv \Big|\Omega=\frac{3}{2};\Lambda=1,S=\frac{3}{2},\Sigma=\frac{1}{2}\Big\rangle \\
&\hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Omega=\frac{3}{2};\Lambda=1,S=\frac{3}{2},\Sigma=\frac{1}{2}\Big\rangle \\
=\;& \hat{L}.\hat{s}_{\mathrm{Yb}}\Big(\sqrt{\frac{1}{3}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle+\sqrt{\frac{2}{3}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle\Big) \\
=\;& \sqrt{\frac{1}{3}}\hat{L}_z\hat{s}_{z,\mathrm{Yb}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle+\sqrt{\frac{2}{3}}\frac{\hat{L}_-\hat{s}_{+,\mathrm{Yb}}}{2}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
=\;& \sqrt{\frac{1}{3}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle+\sqrt{\frac{2}{3}}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \qquad (18)
\end{aligned}$$

$$\begin{aligned}
&|{}^2\Pi_{3/2}\rangle \equiv \Big|\Omega=\frac{3}{2};\Lambda=1,S=\frac{1}{2},\Sigma=\frac{1}{2}\Big\rangle \\
&\hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Omega=\frac{3}{2};\Lambda=1,S=\frac{1}{2},\Sigma=\frac{1}{2}\Big\rangle \\
=\;& \hat{L}.\hat{s}_{\mathrm{Yb}}\Big(\sqrt{\frac{2}{3}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle-\sqrt{\frac{1}{3}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle\Big) \\
=\;& \sqrt{\frac{2}{3}}\hat{L}_z\hat{s}_{z,\mathrm{Yb}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle-\sqrt{\frac{1}{3}}\frac{\hat{L}_-\hat{s}_{+,\mathrm{Yb}}}{2}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
=\;& \sqrt{\frac{2}{3}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle-\sqrt{\frac{1}{3}}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \qquad (19)
\end{aligned}$$

$$\begin{aligned}
|{}^4\Sigma_{3/2}\rangle &\equiv \Big|\Omega=\frac{3}{2};\Lambda=0,S=\frac{3}{2},\Sigma=\frac{3}{2}\Big\rangle \\
\hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Omega=\frac{3}{2};\Lambda=0,S=\frac{3}{2},\Sigma=\frac{3}{2}\Big\rangle &= \hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
&= \frac{\hat{L}_+\hat{s}_{-,\mathrm{Yb}}}{2}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
&= \Big|\Lambda=1,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \qquad (20)
\end{aligned}$$

$$
\begin{aligned}
&|{}^4\Pi_{1/2}\rangle \equiv \Big|\Omega = \frac{1}{2}; \Lambda = 1, S = \frac{3}{2}, \Sigma = -\frac{1}{2}\Big\rangle \\
&\hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Omega = \frac{1}{2}; \Lambda = 1, S = \frac{3}{2}, \Sigma = -\frac{1}{2}\Big\rangle \\
= \;& \hat{L}.\hat{s}_{\mathrm{Yb}}\Big(\sqrt{\frac{2}{3}}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = 0, \sigma_{\mathrm{Rb}} = -\frac{1}{2}\Big\rangle + \sqrt{\frac{1}{3}}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = -1, \sigma_{\mathrm{Rb}} = \frac{1}{2}\Big\rangle\Big) \\
= \;& \sqrt{\frac{2}{3}}\frac{\hat{L}_-\hat{s}_{+,\mathrm{Yb}}}{2}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = 0, \sigma_{\mathrm{Rb}} = -\frac{1}{2}\Big\rangle + \sqrt{\frac{1}{3}}\frac{\hat{L}_-\hat{s}_{+,\mathrm{Yb}}}{2}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = -1, \sigma_{\mathrm{Rb}} = \frac{1}{2}\Big\rangle \\
+ \;& \sqrt{\frac{1}{3}}\hat{L}_z\hat{s}_{z,\mathrm{Yb}}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = -1, \sigma_{\mathrm{Rb}} = \frac{1}{2}\Big\rangle \\
= \;& \sqrt{\frac{2}{3}}\Big|\Lambda = 0, \sigma_{\mathrm{Yb}} = 1, \sigma_{\mathrm{Rb}} = -\frac{1}{2}\Big\rangle + \sqrt{\frac{1}{3}}\Big|\Lambda = 0, \sigma_{\mathrm{Yb}} = 0, \sigma_{\mathrm{Rb}} = \frac{1}{2}\Big\rangle \\
- \;& \sqrt{\frac{1}{3}}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = -1, \sigma_{\mathrm{Rb}} = \frac{1}{2}\Big\rangle
\end{aligned} \tag{21}
$$

$$
\begin{aligned}
&|{}^2\Pi_{1/2}\rangle \equiv \Big|\Omega = \frac{1}{2}; \Lambda = 1, S = \frac{1}{2}, \Sigma = -\frac{1}{2}\Big\rangle \\
&\hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Omega = \frac{1}{2}; \Lambda = 1, S = \frac{1}{2}, \Sigma = -\frac{1}{2}\Big\rangle \\
= \;& \hat{L}.\hat{s}_{\mathrm{Yb}}\Big(\sqrt{\frac{1}{3}}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = 0, \sigma_{\mathrm{Rb}} = -\frac{1}{2}\Big\rangle - \sqrt{\frac{2}{3}}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = -1, \sigma_{\mathrm{Rb}} = \frac{1}{2}\Big\rangle\Big) \\
= \;& \sqrt{\frac{1}{3}}\frac{\hat{L}_-\hat{s}_{+,\mathrm{Yb}}}{2}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = 0, \sigma_{\mathrm{Rb}} = -\frac{1}{2}\Big\rangle - \sqrt{\frac{2}{3}}\frac{\hat{L}_-\hat{s}_{+,\mathrm{Yb}}}{2}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = -1, \sigma_{\mathrm{Rb}} = \frac{1}{2}\Big\rangle \\
- \;& \sqrt{\frac{2}{3}}\hat{L}_z\hat{s}_{z,\mathrm{Yb}}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = -1, \sigma_{\mathrm{Rb}} = \frac{1}{2}\Big\rangle \\
= \;& \sqrt{\frac{1}{3}}\Big|\Lambda = 0, \sigma_{\mathrm{Yb}} = 1, \sigma_{\mathrm{Rb}} = -\frac{1}{2}\Big\rangle - \sqrt{\frac{2}{3}}\Big|\Lambda = 0, \sigma_{\mathrm{Yb}} = 0, \sigma_{\mathrm{Rb}} = \frac{1}{2}\Big\rangle \\
+ \;& \sqrt{\frac{2}{3}}\Big|\Lambda = 1, \sigma_{\mathrm{Yb}} = -1, \sigma_{\mathrm{Rb}} = \frac{1}{2}\Big\rangle
\end{aligned} \tag{22}
$$

$$
\begin{aligned}
& |^4\Sigma_{1/2}\rangle \equiv \Big|\Omega=\frac{1}{2};\Lambda=0,S=\frac{3}{2},\Sigma=\frac{1}{2}\Big\rangle \\
& \hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Omega=\frac{1}{2};\Lambda=0,S=\frac{3}{2},\Sigma=\frac{1}{2}\Big\rangle \\
= \; & \hat{L}.\hat{s}_{\mathrm{Yb}}\Big(\sqrt{\frac{1}{3}}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle+\sqrt{\frac{2}{3}}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle\Big) \\
= \; & \sqrt{\frac{1}{3}}\frac{\hat{L}_+\hat{s}_{-,\mathrm{Yb}}}{2}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle+\sqrt{\frac{2}{3}}\frac{\hat{L}_+\hat{s}_{-,\mathrm{Yb}}}{2}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
+ \; & \sqrt{\frac{2}{3}}\frac{\hat{L}_-\hat{s}_{+,\mathrm{Yb}}}{2}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
= \; & \sqrt{\frac{1}{3}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle+\sqrt{\frac{2}{3}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=-1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
+ \; & \sqrt{\frac{2}{3}}\Big|\Lambda=-1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle
\end{aligned}
\tag{23}
$$

$$
\begin{aligned}
& |^2\Sigma_{1/2}\rangle \equiv \Big|\Omega=\frac{1}{2};\Lambda=0,S=\frac{1}{2},\Sigma=\frac{1}{2}\Big\rangle \\
& \hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Omega=\frac{1}{2};\Lambda=0,S=\frac{1}{2},\Sigma=\frac{1}{2}\Big\rangle \\
= \; & \hat{L}.\hat{s}_{\mathrm{Yb}}\Big(\sqrt{\frac{2}{3}}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle-\sqrt{\frac{1}{3}}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle\Big) \\
= \; & \sqrt{\frac{2}{3}}\frac{\hat{L}_+\hat{s}_{-,\mathrm{Yb}}}{2}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle-\sqrt{\frac{1}{3}}\frac{\hat{L}_+\hat{s}_{-,\mathrm{Yb}}}{2}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
- \; & \sqrt{\frac{1}{3}}\frac{\hat{L}_-\hat{s}_{+,\mathrm{Yb}}}{2}\Big|\Lambda=0,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
= \; & \sqrt{\frac{2}{3}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=-\frac{1}{2}\Big\rangle-\sqrt{\frac{1}{3}}\Big|\Lambda=1,\sigma_{\mathrm{Yb}}=-1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
- \; & \sqrt{\frac{1}{3}}\Big|\Lambda=-1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle
\end{aligned}
\tag{24}
$$

$$
\begin{aligned}
& |^4\Pi_{1/2}\rangle \equiv \Big|\Omega=\frac{1}{2};\Lambda=-1,S=\frac{3}{2},\Sigma=\frac{3}{2}\Big\rangle \\
& \hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Omega=\frac{1}{2};\Lambda=-1,S=\frac{3}{2},\Sigma=\frac{3}{2}\Big\rangle=\hat{L}.\hat{s}_{\mathrm{Yb}}\Big|\Lambda=-1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
= \; & \frac{\hat{L}_+\hat{s}_{-,\mathrm{Yb}}}{2}\Big|\Lambda=-1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle+\hat{L}_z\hat{s}_{z,\mathrm{Yb}}\Big|\Lambda=-1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle \\
= \; & \Big|\Lambda=0,\sigma_{\mathrm{Yb}}=0,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle-\Big|\Lambda=-1,\sigma_{\mathrm{Yb}}=1,\sigma_{\mathrm{Rb}}=\frac{1}{2}\Big\rangle
\end{aligned}
\tag{25}
$$

Now, to construct the SOC matrix we employ the expressions derived in Eqs. (17-25):

$$
\hat{H}_{\rm so} = \left|\begin{array}{c|ccccccccc}
 & {}^4\Pi_{5/2} & {}^4\Pi_{3/2} & {}^2\Pi_{3/2} & {}^4\Sigma_{3/2} & {}^4\Pi_{1/2} & {}^2\Pi_{1/2} & {}^4\Sigma_{1/2} & {}^2\Sigma_{1/2} & {}^4\Pi_{1/2} \\
\hline
{}^4\Pi_{5/2} & a_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
{}^4\Pi_{3/2} & 0 & \frac{a_3}{3} & \frac{\sqrt{2a_2a_3}}{3} & \sqrt{\frac{2a_3a_4}{3}} & 0 & 0 & 0 & 0 & 0 \\
{}^2\Pi_{3/2} & 0 & \frac{\sqrt{2a_2a_3}}{3} & \frac{2a_2}{3} & -\sqrt{\frac{a_2a_4}{3}} & 0 & 0 & 0 & 0 & 0 \\
{}^4\Sigma_{3/2} & 0 & \sqrt{\frac{2a_3a_4}{3}} & -\sqrt{\frac{a_2a_4}{3}} & 0 & 0 & 0 & 0 & 0 & 0 \\
{}^4\Pi_{1/2} & 0 & 0 & 0 & 0 & -\frac{a_3}{3} & \frac{\sqrt{2a_2a_3}}{3} & \frac{2\sqrt{2a_3a_4}}{3} & \frac{\sqrt{a_1a_3}}{3} & 0 \\
{}^2\Pi_{1/2} & 0 & 0 & 0 & 0 & \frac{\sqrt{2a_2a_3}}{3} & -\frac{2a_2}{3} & -\frac{\sqrt{a_2a_4}}{3} & \frac{2\sqrt{2a_1a_2}}{3} & 0 \\
{}^4\Sigma_{1/2} & 0 & 0 & 0 & 0 & \frac{2\sqrt{2a_3a_4}}{3} & -\frac{\sqrt{a_2a_4}}{3} & 0 & 0 & \sqrt{\frac{2a_3a_4}{3}} \\
{}^2\Sigma_{1/2} & 0 & 0 & 0 & 0 & \frac{\sqrt{a_1a_3}}{3} & \frac{2\sqrt{2a_1a_2}}{3} & 0 & 0 & -\sqrt{\frac{a_1a_3}{3}} \\
{}^4\Pi_{1/2} & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{2a_3a_4}{3}} & -\sqrt{\frac{a_1a_3}{3}} & -a_3
\end{array}\right|. \tag{26}
$$

The eigenvalues of $\hat{H}_{\rm so}$ (in units of $a^{\rm so}_{\rm Yb}$) are obtained as follows:

For $\Omega = \frac{5}{2}$: 1

For $\Omega = \frac{3}{2}$: -1, 1, 1

For $\Omega = \frac{1}{2}$: -2, -1, -1, 1, 1.

These values can be explained in the following way - at $R = \infty$ and zero field, $l_{\rm Yb} = 1$ couples to $s_{\rm Yb} = 1$ to give $j_{\rm Yb} = 0, 1, 2$ and $j_{\rm Yb}$ couples to $s_{\rm Rb} = \frac{1}{2}$ to produce J.

Now, the SO energy splittings are given by:

$$
\begin{aligned}
E_{\rm so,Yb} &= \frac{1}{2} a^{\rm so}_{\rm Yb}\{j_{\rm Yb}(j_{\rm Yb}+1) - l_{\rm Yb}(l_{\rm Yb}+1) - s_{\rm Yb}(s_{\rm Yb}+1)\} && (27)\\
&= \{-2, -1, 1\} a^{\rm so}_{\rm Yb} \quad \text{for} \quad j_{\rm Yb} = 0, 1, 2 && (28)
\end{aligned}
$$

Now, for the total angular momentum:

$j_{\rm Yb} = 0$, $s_{\rm Rb} = \frac{1}{2}$ gives $J = \frac{1}{2}$ with $\Omega = \frac{1}{2}$.

$j_{\rm Yb} = 1$, $s_{\rm Rb} = \frac{1}{2}$ gives $J = \frac{3}{2}$ with $\Omega = \frac{3}{2}, \frac{1}{2}$; $J = \frac{1}{2}$ with $\Omega = \frac{1}{2}$.

$j_{\rm Yb} = 2$, $s_{\rm Rb} = \frac{1}{2}$ gives $J = \frac{5}{2}$ with $\Omega = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$; $J = \frac{3}{2}$ with $\Omega = \frac{3}{2}, \frac{1}{2}$

So,

for $\Omega = \frac{5}{2}$, we have 1 state with $j_{\rm Yb} = 2$ and hence eigenvalue = 1.

for $\Omega = \frac{3}{2}$, we have 3 states with $j_{\rm Yb} = 1, 2, 2$ and hence eigenvalue = -1,1,1.

for $\Omega = \frac{1}{2}$, we have 5 state with $j_{\text{Yb}} = 0, 1, 1, 2, 2$ and hence eigenvalue = -2,-1,-1,1,1.

Now, the resultant potential part of the Hamiltonian is:

$$
\hat{V} + \hat{H}_{\text{so}} \;=\; \left|\begin{array}{c|ccccccccc}
 & {}^4\Pi_{5/2} & {}^4\Pi_{3/2} & {}^2\Pi_{3/2} & {}^4\Sigma_{3/2} & {}^4\Pi_{1/2} & {}^2\Pi_{1/2} & {}^4\Sigma_{1/2} & {}^2\Sigma_{1/2} & {}^4\Pi_{1/2} \\
\hline
{}^4\Pi_{5/2} & V_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
{}^4\Pi_{3/2} & 0 & V_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
{}^2\Pi_{3/2} & 0 & 0 & V_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
{}^4\Sigma_{3/2} & 0 & 0 & 0 & V_4 & 0 & 0 & 0 & 0 & 0 \\
{}^4\Pi_{1/2} & 0 & 0 & 0 & 0 & V_3 & 0 & 0 & 0 & 0 \\
{}^2\Pi_{1/2} & 0 & 0 & 0 & 0 & 0 & V_2 & 0 & 0 & 0 \\
{}^4\Sigma_{1/2} & 0 & 0 & 0 & 0 & 0 & 0 & V_4 & 0 & 0 \\
{}^2\Sigma_{1/2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & V_1 & 0 \\
{}^4\Pi_{1/2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & V_3
\end{array}\right|
$$

$$
+ \left|\begin{array}{c|ccccccccc}
 & {}^4\Pi_{5/2} & {}^4\Pi_{3/2} & {}^2\Pi_{3/2} & {}^4\Sigma_{3/2} & {}^4\Pi_{1/2} & {}^2\Pi_{1/2} & {}^4\Sigma_{1/2} & {}^2\Sigma_{1/2} & {}^4\Pi_{1/2} \\
\hline
{}^4\Pi_{5/2} & a_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
{}^4\Pi_{3/2} & 0 & \frac{a_3}{3} & \frac{\sqrt{2a_2a_3}}{3} & \sqrt{\frac{2a_3a_4}{3}} & 0 & 0 & 0 & 0 & 0 \\
{}^2\Pi_{3/2} & 0 & \frac{\sqrt{2a_2a_3}}{3} & \frac{2a_2}{3} & -\sqrt{\frac{a_2a_4}{3}} & 0 & 0 & 0 & 0 & 0 \\
{}^4\Sigma_{3/2} & 0 & \sqrt{\frac{2a_3a_4}{3}} & -\sqrt{\frac{a_2a_4}{3}} & 0 & 0 & 0 & 0 & 0 & 0 \\
{}^4\Pi_{1/2} & 0 & 0 & 0 & 0 & -\frac{a_3}{3} & \frac{\sqrt{2a_2a_3}}{3} & \frac{2\sqrt{2a_3a_4}}{3} & \frac{\sqrt{a_1a_3}}{3} & 0 \\
{}^2\Pi_{1/2} & 0 & 0 & 0 & 0 & \frac{\sqrt{2a_2a_3}}{3} & -\frac{2a_2}{3} & -\frac{\sqrt{a_2a_4}}{3} & \frac{2\sqrt{2a_1a_2}}{3} & 0 \\
{}^4\Sigma_{1/2} & 0 & 0 & 0 & 0 & \frac{2\sqrt{2a_3a_4}}{3} & -\frac{\sqrt{a_2a_4}}{3} & 0 & 0 & \sqrt{\frac{2a_3a_4}{3}} \\
{}^2\Sigma_{1/2} & 0 & 0 & 0 & 0 & \frac{\sqrt{a_1a_3}}{3} & \frac{2\sqrt{2a_1a_2}}{3} & 0 & 0 & -\sqrt{\frac{a_1a_3}{3}} \\
{}^4\Pi_{1/2} & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{2a_3a_4}{3}} & -\sqrt{\frac{a_1a_3}{3}} & -a_3
\end{array}\right| .
$$

where $V_1 \rightarrow 3^2\Sigma^+$, $V_2 \rightarrow 2^2\Pi$, $V_3 \rightarrow 1^4\Pi$ and $V_4 \rightarrow 1^4\Sigma^+$ correspond to the spin-free potential energy curves (PECs).

The above matrix is diagonalized to produce nine spin-orbit coupled PECs. Such *ab initio* calculated PECs for the system RbYb are published in a recent work [Comput. Theor. Chem. **1103**, 11 (2017)]. Our aim is to model the spin-free PECs (V_1, V_2, V_3 and V_4) such that the resulting spin-orbit PECs can mimic the published ones to a maximum extent.

Modeling the curves:

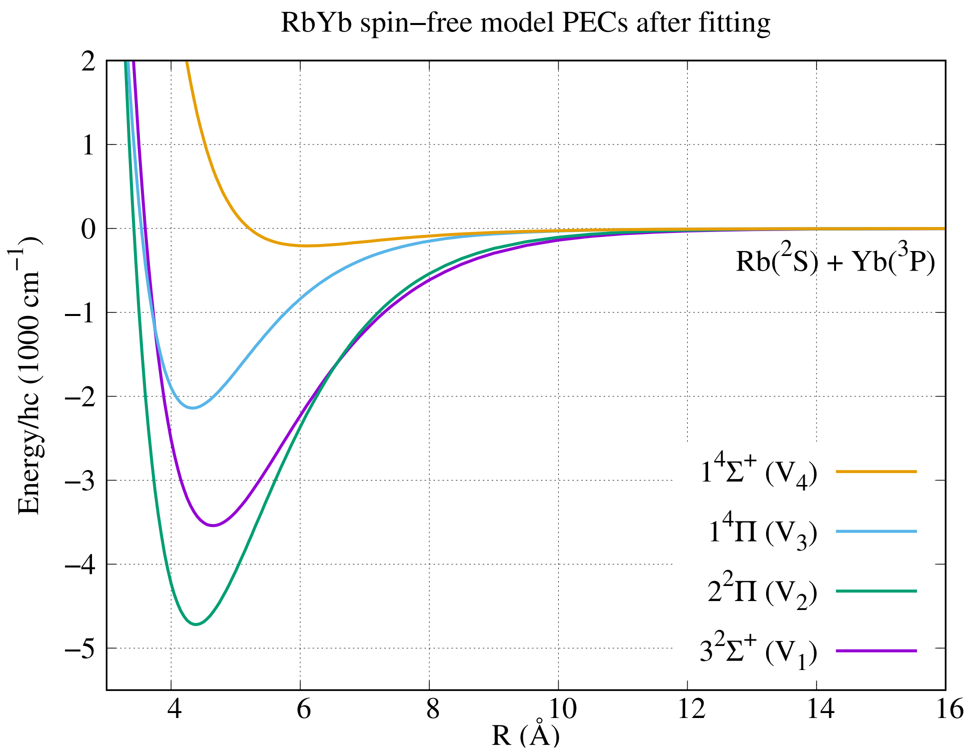

Figure 1: The model spin-free PECs.

$$
\begin{aligned}
V_i(R) &= A_i e^{-\beta_{1i}R} - B_i e^{-\beta_{2i}R} - \sum_{n=6,8} D_{n,i}(\beta_{1i}R) C_{n,i} R^{-n}, \\
D_{n,i}(\beta_{1i}R) &= 1 - e^{-\beta_{1i}R} \sum_{m=0}^{n} \frac{(\beta_{1i}R)^m}{m!}
\end{aligned}
\tag{29}
$$

Fitted parameters:

	$3^2\Sigma^+$ (V_1)	$2^2\Pi$ (V_2)	$1^4\Pi$ (V_3)	$1^4\Sigma^+$ (V_4)
A_i $(10E_h)$	2.907467	4.443079	3.446384	1.182365
B_i $(10E_h)$	2.426573	3.698275	2.264892	0
β_{1i} (a_0^{-1})	0.523439	0.569121	0.728101	0.789778
β_{2i} (a_0^{-1})	0.497607	0.541557	0.673939	0

$C_6^{\Pi} = 3915.3\ E_h a_0^6$, $C_6^{\Sigma} = 4486.9\ E_h a_0^6$ and $C_8 = 80 C_6\ a_0^2$ where E_h - Hartree, a_0 - bohr. The values of C 6 coefficients are determined in the same way as has been done for LiYb molecule in Phys. Rev. A 88, 020701(R)(2013).

Published *ab intio* PECs:

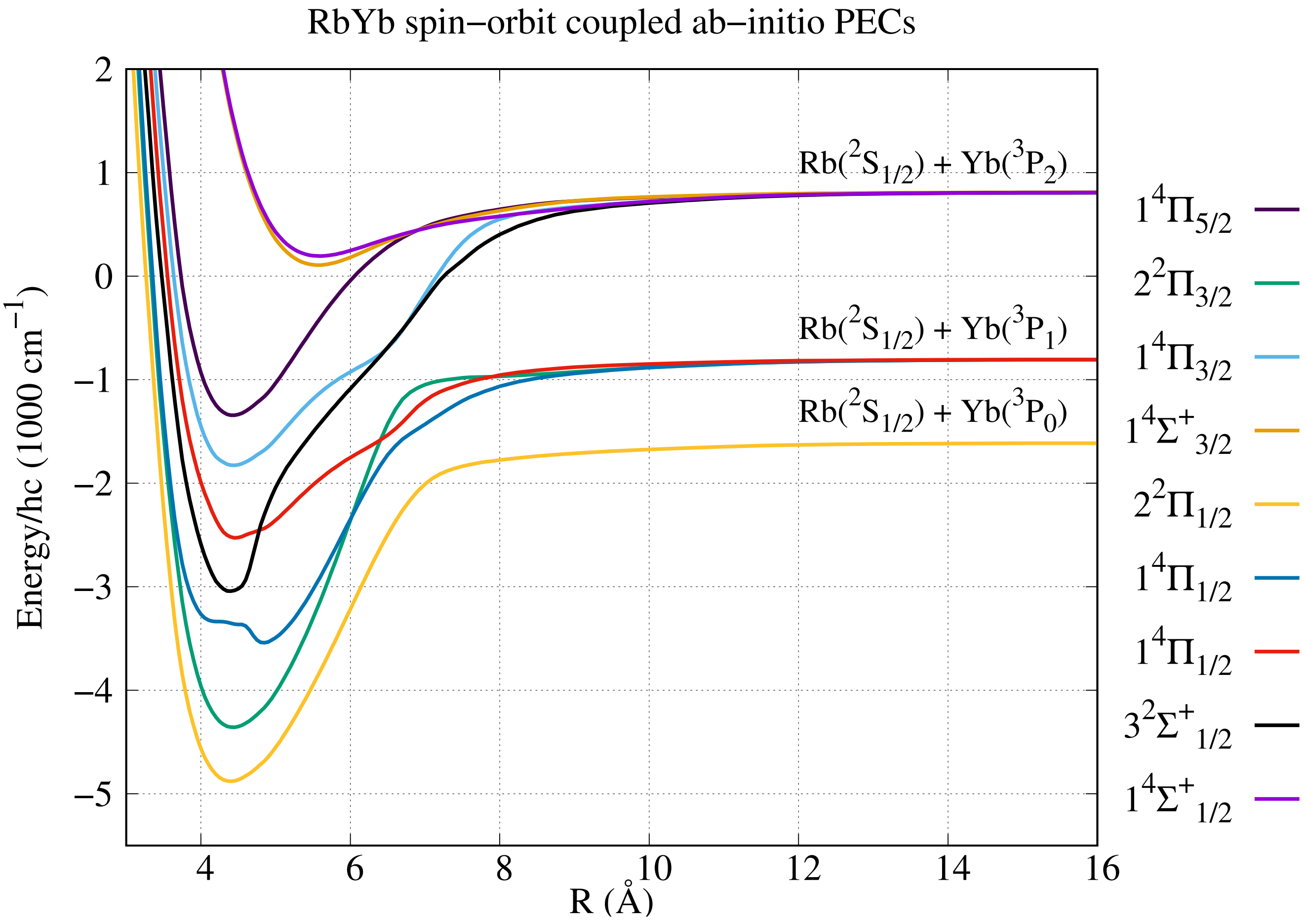

Figure 2: Spin-orbit coupled PECs as published in Comput. Theor. Chem. **1103**, 11 (2017). The zero of the energy is shifted at the spin-free energy level corresponding to the dissociation limit Rb(^2S) + Yb(^3P) atomic terms.

Resultant spin-orbit coupled curves from the model potentials:

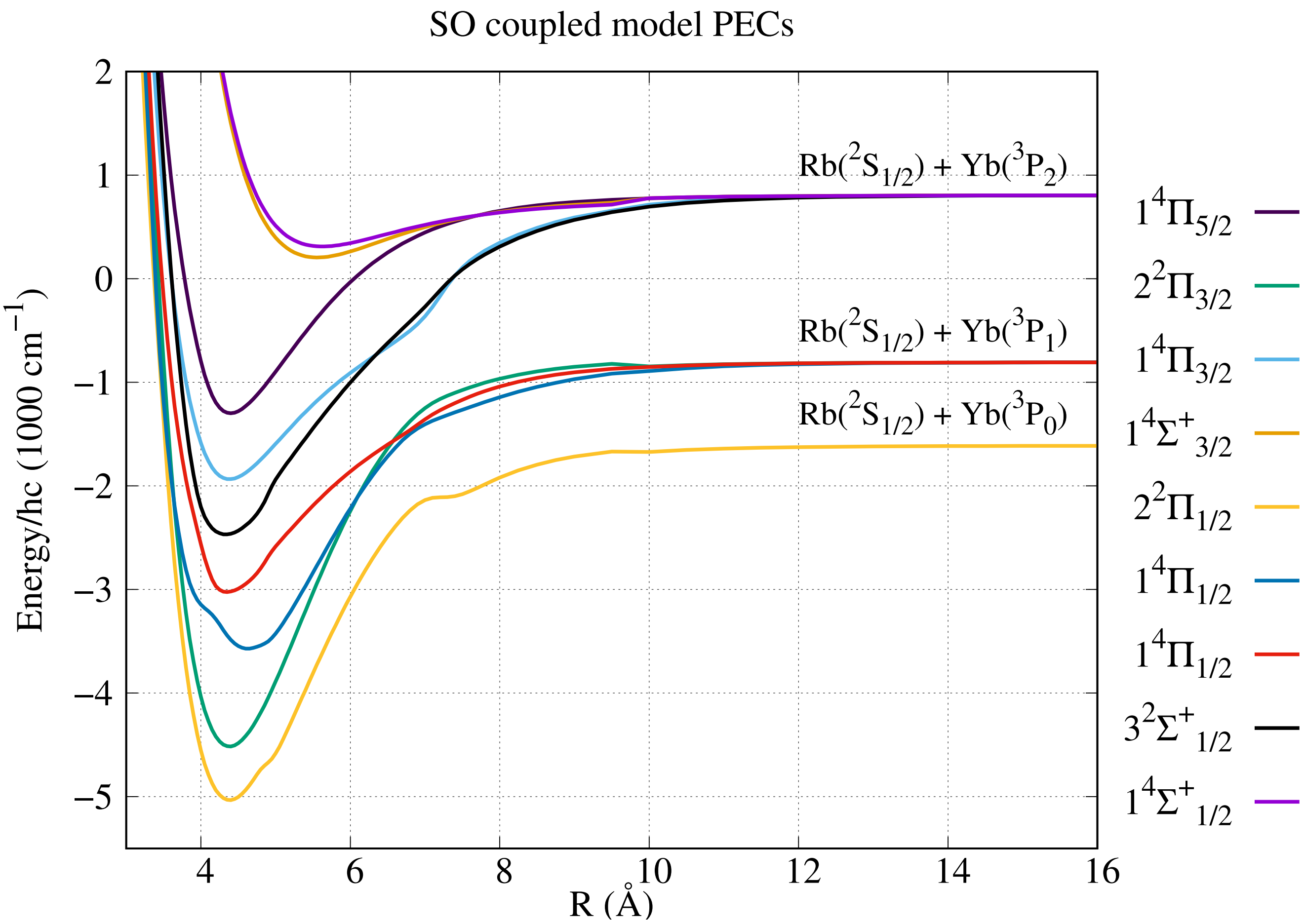

Figure 3: The spin-orbit coupled PECs as obtained by diagonalizing $\hat{V} + \hat{H}_{\rm so}$ [Eq. 29] with the model potentials as shown in Figure 1.

Comparison of the two sets of PECs:

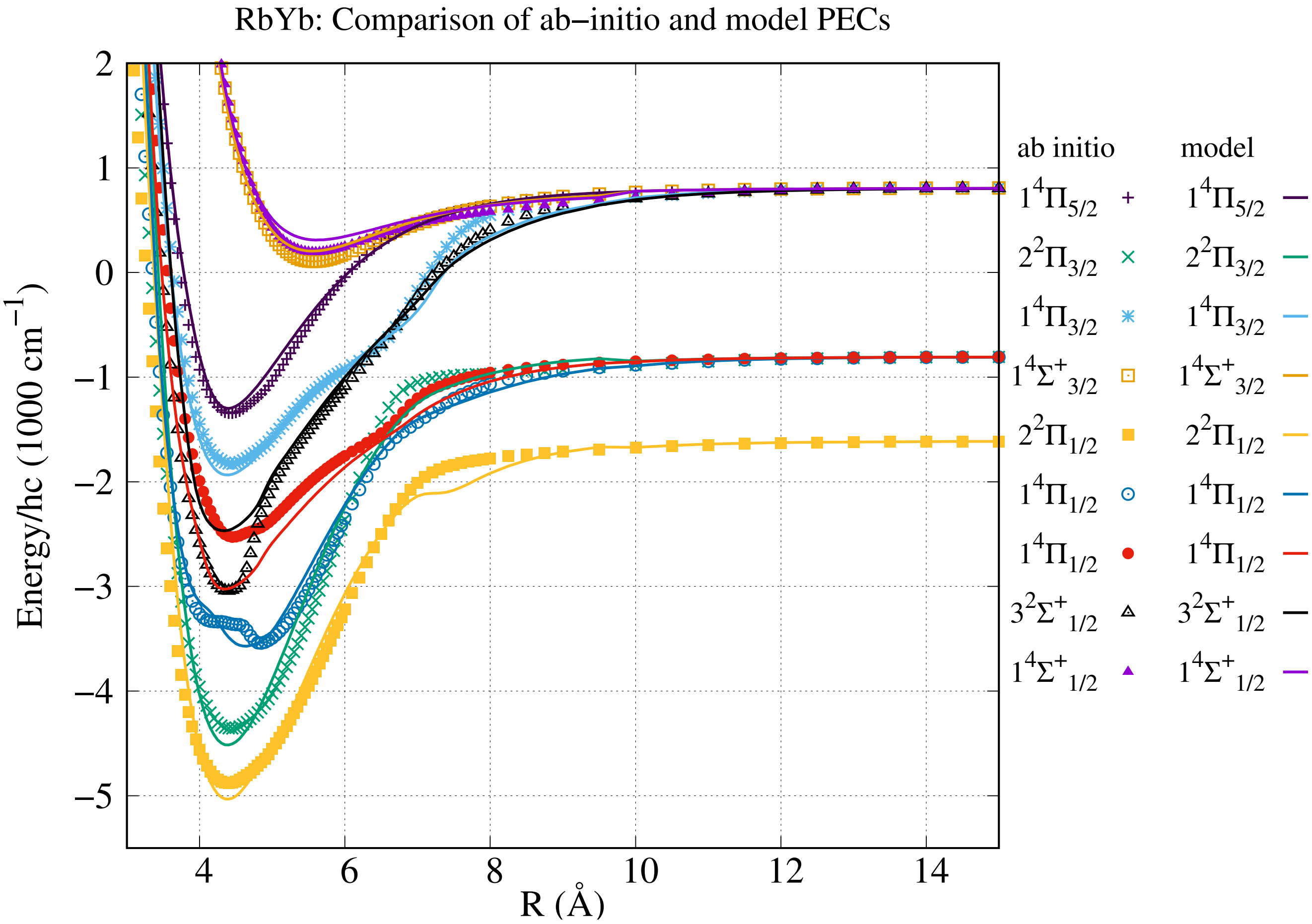

Figure 4: Comparison of the model spin-orbit coupled PECs with that of the published ones. The marker points represent *ab initio* data and the solid curves represent the model PECs.

Model functional form of $a^{\rm so}_{\rm Yb}$:

$$a_i(R) = a^{\rm so}_{\rm Yb} + \epsilon_i(1 - \tanh(\alpha_i(R - R_{0i}))) \tag{30}$$

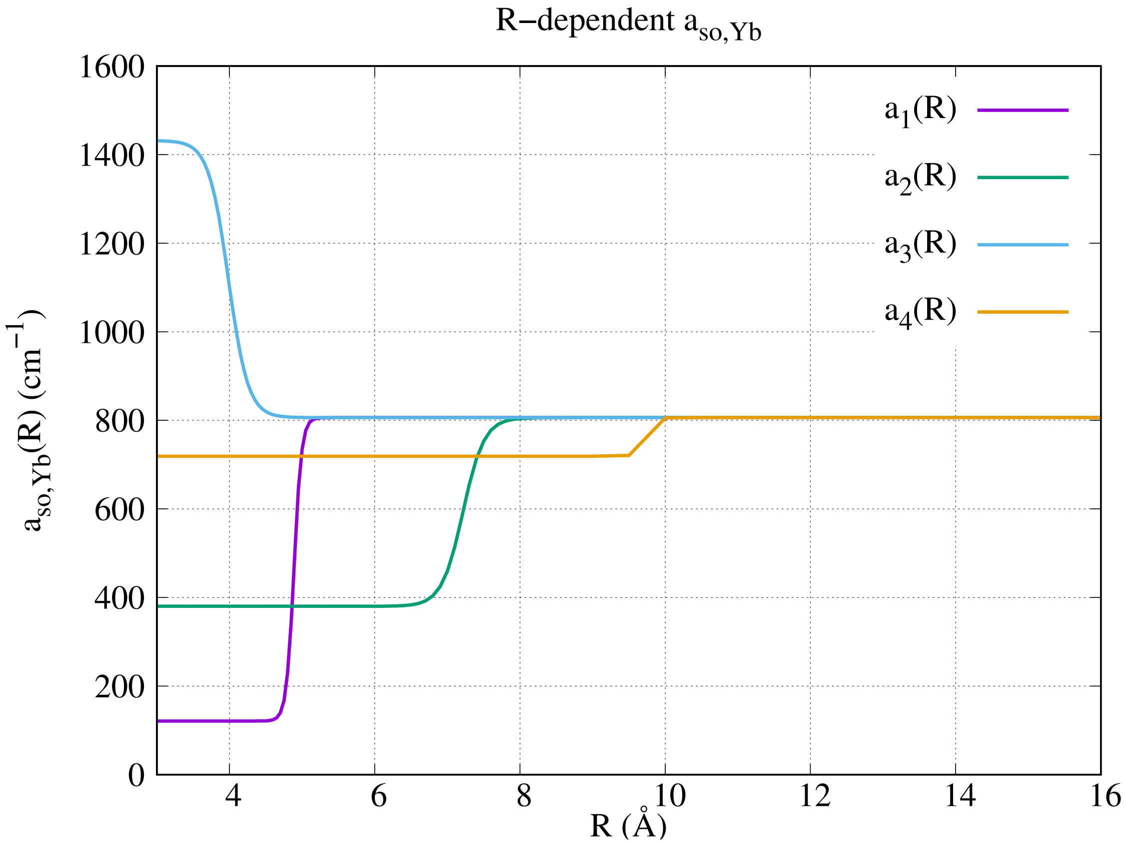

Figure 5: R-dependency of $a^{\rm so}_{\rm Yb}$.

Fitted parameters:

	a_1	a_2	a_3	a_4
$R_{0,i}$ (Å)	4.887095	7.214657	3.984396	9.726085
ϵ_i (100 cm^{-1})	-3.424339	-2.129399	3.127650	-0.435188
α_i (Å^{-1})	9.581731	3.422315	3.666937	8.704976

The following bounds are applied on the parameters:

$$\frac{a_{\mathrm{Yb}}^{\mathrm{so}}}{2} \leq \epsilon_i < \infty \quad [i = 1, 2, 3]; \quad -50\,\mathrm{cm}^{-1} \leq \epsilon_4 \leq 50\,\mathrm{cm}^{-1}$$

$$0.5\,\text{Å}^{-1} \leq \alpha_i < \infty$$

$$0\,\text{Å} \leq R_{0i} < \infty$$