Appendix B

Adiabatic FEM R-matrix

The equations for the adiabatic FEM R-matrix method can be derived by inserting the adiabatic channel decomposition (Eq. 3.20) into Eq. 3.1. Using the relationships, $H = T_R + H^{\mathrm{ad}}$, $H^{\mathrm{ad}}\Phi_\gamma(\Omega, \sigma; R) = U_\gamma \Phi_\gamma(\Omega, \sigma; R)$, Eq. 3.22 for the derivative coupling, and the orthonormality of the $\Phi_\gamma(\Omega, \sigma; R)$'s leads to the following equation for b

$$\begin{aligned} b\sum_\gamma M_\gamma(R_0)M_\gamma(R_0) &= \sum_\gamma \int 2\mu M_\gamma(E - U_\gamma)M_\gamma dR \\ &\quad - \sum_\gamma M_\gamma(R_0)M'_\gamma(R_0) \\ &\quad - \sum_{\gamma,\gamma'} M_\gamma(R_0)P_{\gamma,\gamma'}(R_0)M_{\gamma'}(R_0) \\ &\quad - \int_\Omega 2\mu\Psi^* T_R \Psi dw \end{aligned} \tag{B.1}$$

where R_0 is the internuclear separation on the boundary. In order to evaluate the last integral, I need to introduce the second derivative coupling matrix Q[78]

$$Q_{\gamma\gamma'} = \left\langle \Phi_\gamma | \frac{\partial^2}{\partial R^2} \Phi_{\gamma'} \right\rangle \tag{B.2}$$

which can be related to $\underline{P}$ using[78]

$$Q_{\gamma\gamma'} = (P^2)_{\gamma\gamma'} + \partial P_{\gamma\gamma'}/\partial R\ . \tag{B.3}$$

The last integral in Eq. B.1 becomes

$$-\int_\Omega 2\mu\Psi^* T_R \Psi dw = \sum_{\gamma,\gamma'} \int M_\gamma \left[\frac{\partial}{\partial R} + P_{\gamma\gamma'}\right]^2 M_{\gamma'} dR \tag{B.4}$$

The original diabatic equations are recovered exactly provided $\partial/\partial R$ is replaced with $\partial/\partial R + \underline{P}$. The matrix elements of Λ remain the same, however the new Γ matrix elements are given in the FEM representation by

$$\begin{aligned}\Gamma_{ij} &= 2\mu\int_{-1}^{1} u_i(x_n)(E-H)u_j(x_n)a_n dx_n \\ &\quad -\delta_{\gamma,\gamma'}\delta_{n,n_{\max}}\delta_{k,5}\delta_{k',6}/a_n \\ &\quad -\delta_{n,n_{\max}}\delta_{k,5}\delta_{k',5}P_{\gamma,\gamma'}\ .\end{aligned} \tag{B.5}$$

Again, the indices i and j include the basis function index k, the channel index γ, and the sector index n, ($i \equiv \{k\gamma n\}$ and $j \equiv \{k'\gamma' n\}$). This equation can be improved upon by first squaring the kinetic energy operator T_R and using Eq. B.3

$$(T_R)_{\gamma,\gamma'} = \delta_{\gamma\gamma'}\frac{\partial^2}{\partial R^2} + 2P_{\gamma,\gamma'}\frac{\partial}{\partial R} + \left(\frac{\partial}{\partial R}P_{\gamma,\gamma'}\right) + (P^2)_{\gamma,\gamma'}\ . \tag{B.6}$$

Plugging in the FEM basis expansion and integrating the $\underline{P}\frac{\partial}{\partial R} + \frac{\partial}{\partial R}\underline{P}$ term by parts results in the following expression for the $\underline{\Gamma}$ matrix elements

$$\begin{aligned}\Gamma_{ij} &= \int_{-1}^{1} u_k(x_n)\left[\frac{\partial^2}{\partial(a_n x_n)^2} + (P^2)_{\gamma\gamma'} + 2\mu(E-U_{\gamma\gamma'})\right]u_{k'}(x_n)a_n dx_n \\ &\quad + \int_{-1}^{1} P_{\gamma\gamma'}\left(u_k\frac{\partial u_{k'}}{\partial x_n} - \frac{\partial u_k}{\partial x_n}u_{k'}\right)dx_n \\ &\quad -\delta_{\gamma,\gamma'}\delta_{n,n_{\max}}\delta_{k,5}\delta_{k',6}/a_n\ .\end{aligned} \tag{B.7}$$

Numerical derivatives of the $\underline{P}$ matrix are no longer required in this formulation which generally improves the accuracy of the calculations. From this point on, the procedure to solve the R-matrix equations is exactly as outlined in chapter 3.1.