Problem 3: crude adiabatic basis

Consider the crossing of two electronic states along a coordinate Q. As basis functions we use two coordinate independent electronic wavefunctions which diagonalize the Born Oppenheimer Hamiltonian at the crossing point Q_0

$$(T_{el} + V(Q_0))\phi^{1,2} = E^{1,2}\phi^{1,2}$$

We use the following Ansatz functions

$$\Psi_1(r,Q) = (\cos\zeta(Q)\phi^1(r) - \sin\zeta(Q)\phi^2(r))\chi^1(Q)$$

$$\Psi_2(r,Q) = (\sin\zeta(Q)\phi^1(r) + \cos\zeta(Q)\phi^2(r))\chi^2(Q)$$

which can be written in more compact form

$$(\Psi_1, \Psi_2) = (\phi^1, \phi^2)\begin{pmatrix} c & s \\ -s & c \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix}$$

The Hamiltonian is partitioned as

$$H = T_N + T_{el} + V(Q_0) + (V(Q) - V(Q_0))$$

and the change of the potential energy is expanded in linear order

$$V(Q) - V(Q_0) = (Q - Q_0)\Delta V$$

Calculate the matrix elements of the full Hamiltonian

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} =$$

$$= \begin{pmatrix} c & -s \\ s & c \end{pmatrix}\begin{pmatrix} \Psi_1^\dagger \\ \Psi_2^\dagger \end{pmatrix}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial Q^2} + T_{el} + V(Q_0) + (Q - Q_0)\Delta V\right)\left(\Psi^1, \Psi^2\right)\begin{pmatrix} c & s \\ -s & c \end{pmatrix}$$

where $\chi(Q)$ and $\zeta(Q)$ depend on the coordinate Q whereas the basis functions $\psi^{1,2}$do not.