Section 6.5:The R matrix method*

This well-tested, frequently applied device for solving the multichannel scattering problem has first proved itself as a powerful computational tool in the context of nuclear reactions [7], and has later been adjusted to the treatment of electron-atom interactions [8] and molecular scattering [9]. To give an impression of this methodology, we present a condensed outline of the R matrix propagation scheme as developed by J.C.Light and coworkers [9, 10]. The procedure has been specifically designed to deal with inelastic as well as reactive scattering processes. The method is based on the diabatic ansatz

$$\Psi(\mathbf{Q},\rho) = \sum_{n=1}^{N} \phi_n(\mathbf{Q})\Phi_n(\rho). \tag{1}$$

for the scattering solution, involving N channel functions ϕ_n and a set of translational functions $\{\Phi_n\}$ which depend on the scattering coordinate ρ. The nature of the channel coordinates may vary from case to case. Thus, they might be chosen as purely electronic or they might involve further nuclear coordinates orthogonal to ρ. By integration over the degrees of freedom associated with the channel functions, one obtains a differential equation of second order which, in its most compact form, may be written as

$$\frac{\partial^2 \Phi_n(\rho)}{\partial \rho^2} = \sum_{m=1}^{N} W_{nm}(\rho)\Phi_m(\rho) \tag{2}$$

with a symmetric coupling matrix $\mathbf{W}$. Evidently, the system of equations (6.7) is a special case of (2). In an initial step towards R matrix propagation, one subdivides an interval $[0, \rho_{max}]$ into M segments with widths h_i and center locations ρ_i, where $i = 1, \cdots, M$. Subsequently, the coupling matrix is locally diagonalized, i.e. the operation

$$\mathbf{T}^{\dagger(i)}\mathbf{W}(\rho_i)\mathbf{T}^{(i)} = \boldsymbol{\lambda}^{2(i)} \tag{3}$$

is carried out at each ρ_i. The matrix $\boldsymbol{\lambda}^{2(i)}$ is diagonal with elements $\lambda_{mn}^{2(i)} = \delta_{mn}\lambda_n^{2\ (i)}$. As $\mathbf{W}$ is assumed to be symmetric, the transformation matrix $\mathbf{T}^{(i)}$ is orthogonal, and $\mathbf{T}^{\dagger(i)}$ is its inverse, $\mathbf{T}^{-1(i)}$. The translational functions transform according to

$$\chi_n^{(i)}(\rho) = \sum_{m=1}^{N} T_{mn}^{-1(i)}\Phi_m(\rho). \tag{4}$$

The channel functions obey the same transformation law. Negative coupling matrix eigenvalues correspond to positive kinetic energy in the considered segment, and thus to open channels, while channels with positive eigenvalues are closed. We construct a local R matrix $\mathbf{R}^{(i)}$ that connects the sector functions $\chi_n^{(i)}$ with their derivatives:

$$\boldsymbol{\chi}_r^{(i)} = \mathbf{R}^{(i)} \frac{\partial \boldsymbol{\chi}_r^{(i)}}{\partial \rho} \tag{5}$$

with $\boldsymbol{\chi}_\rho^{(i)}$ as the vector of the solution function for the sector i, evaluated at the right end of the interval: $\boldsymbol{\chi}_r^{(i)} \equiv \boldsymbol{\chi}^{(i)}(\rho = \rho_i + \frac{h_i}{2})$. At the core of the R-matrix propagation method lies a prescription for determining $\mathbf{R}^{(i)}$ recursively from $\mathbf{R}^{(i-1)}$. The procedure is continued until the location ρ_i reaches the asymptotic regime of the studied collision problem. If K matrix boundary conditions have been specified for the scattering situation, as was assumed in the preceding section, relation (5) can be used to compute the K matrix elements.

The desired recursion formula is obtained by employing a relation between the values adopted by $\boldsymbol{\chi}^{(i)}$ at the boundaries of the segment i and the derivatives of $\boldsymbol{\chi}^{(i)}$ at these places. Specifically:

$$\begin{pmatrix} \boldsymbol{\chi}_{\boldsymbol{l}}^{(\boldsymbol{i})} \\ \boldsymbol{\chi}_{\boldsymbol{r}}^{(\boldsymbol{i})} \end{pmatrix} = \begin{pmatrix} \mathbf{r}_{\mathbf{1}}^{(\mathbf{i})} & \mathbf{r}_{\mathbf{2}}^{(\mathbf{i})} \\ \mathbf{r}_{\mathbf{3}}^{(\mathbf{i})} & \mathbf{r}_{\mathbf{4}}^{(\mathbf{i})} \end{pmatrix} \begin{pmatrix} -\frac{\partial \boldsymbol{\chi}_l^{(i)}}{\partial \rho} \\ \frac{\partial \boldsymbol{\chi}_r^{(i)}}{\partial \rho} \end{pmatrix}, \tag{6}$$

with $\boldsymbol{\chi}_l^{(i)}$ referring to the left limit of the interval. The R matrix connecting the derivatives and the functions in Eq.(6) consists of four $N \times N$ submatrices. Since the differential equation

$$\frac{\partial^2 \chi_n^{(i)}(\rho)}{\partial \rho^2} = (\lambda_n^{(i)})^2 \chi_n^{(i)}(\rho) \tag{7}$$

is valid in each sector i, relation (6) can be broken down into N pseudo -one dimensional problems of the form

$$\begin{pmatrix} \chi_{n\ l}^{(i)} \\ \chi_{n\ r}^{(i)} \end{pmatrix} = \begin{pmatrix} r_1^{(i)} & r_2^{(i)} \\ r_3^{(i)} & r_4^{(i)} \end{pmatrix} \begin{pmatrix} -\frac{\partial \chi_{n\ l}^{(i)}}{\partial \rho} \\ \frac{\partial \chi_{n\ r}^{(i)}}{\partial \rho} \end{pmatrix}. \tag{8}$$

Imposing suitable boundary conditions on the two linearly independent solutions of Eq.(7) [10], one can indicate the elements $r_k^{(i)}, k = 1 - 4$, explicitly as (see exercise 6.2)

$$r_1^{(i)} = r_4^{(i)} = \begin{cases} |\lambda_n^{(i)}|^{-1} \coth |\lambda_n^{(i)}| h & \text{if } \lambda_n^2 > 0 \\ -|\lambda_n^{(i)}|^{-1} \cot |\lambda_n^{(i)}| h & \text{if } \lambda_n^2 \leq 0 \end{cases} \tag{9}$$

and

$$r_2^{(i)} = r_3^{(i)} = \begin{cases} |\lambda_n^{(i)}|^{-1} \operatorname{csch} |\lambda_n^{(i)}| h & \text{if } \lambda_n^2 > 0 \\ -|\lambda_n^{(i)}|^{-1} \csc |\lambda_n^{(i)}| h & \text{if } \lambda_n^2 \leq 0 \end{cases} \tag{10}$$

At this point, the fragment nature of the translational functions $\chi_n^{(i)}$ must be emphasized. The original ρ-dependent functions $\Phi_n(\rho)$ are continuous across the borderlines between neighboring segments i, that is

$$\Phi^{(i-1)}_{n\ r} = \Phi^{(i)}_{n\ l} \tag{11}$$

which is equivalent to

$$\hat{T}^{(i-1)}\hat{T}^{-1(i-1)}\Phi^{(i-1)}_{n\ r} = \hat{T}^{(i)}\hat{T}^{-1(i)}\Phi^{(i)}_{n\ l}, \tag{12a}$$

or, by Eq.(4)

$$\chi^{(i-1)}_{n\ r} = \hat{Q}(i-1,i)\chi^{(i)}_{n\ l}. \tag{12b}$$

The symbol $\hat{Q}(i-1,i)$ stands for the operator product $\hat{Q}(i-1,i) \equiv \hat{T}^{-1(i-1)}\hat{T}^{(i)}$ which mediates between the basis states of adjacent sectors, and a corresponding relation for the derivatives of $\chi^{(i-1)}_n$. The matrices $\mathbf{r}^{(i)}_k,\ k = 1-4$, as well as $\mathbf{Q}(i-1,i)$ are the ingredients of the R matrix recursion formula. As shown by Zvijac and Light [11], $\mathbf{R}^{(i)}$ is related to $\mathbf{R}^{(i-1)}$ by:

$$\mathbf{R}^{(i)} = \mathbf{r}^{(i)}_4 - \mathbf{r}^{(i)}_3\mathbf{Z}^{(i)}\mathbf{r}^{(i)}_2, \tag{13a}$$

$$\mathbf{Z}^{(i)} = (\mathbf{r}^{(i)}_1 + \mathbf{Q}^{-1}(i-1,i)\mathbf{R}^{(i-1)}\mathbf{Q}(i-1,i))^{-1}. \tag{13b}$$

These two statements comprise the rule for advancing the R matrix along the scattering coordinate once an initial matrix $\mathbf{R}^{(1)}$, referring to a location close to the origin $\rho = 0$ has been determined. From exercise 6.2, it may be concluded that the R matrix method does not require the eigenvalue array $\boldsymbol{\lambda}^{2\ (i)}$ of the coupling matrix $\mathbf{W}$ to be constant across the interval i.

Exercise 6.2: Let $\chi^{(i)\ I}_n$ and $\chi^{(i)\ II}_n$ be two linearly independent solutions. Solve equation (7) within the constraints

$$\chi^{(i)\ I}_{n\ r} = 1, \qquad \frac{\partial \chi^{(i)\ I}_{n\ l}}{\partial \rho} = 0,$$

$$\chi^{(i)\ II}_{n\ r} = 0, \qquad \frac{\partial \chi^{(i)\ II}_{n\ r}}{\partial \rho} = 1$$

Use the derived functions $\chi^{(i)\ I}_n$ and $\chi^{(i)\ II}_n$ as well as the fact that the Wronskian formed from them does not depend on ρ to demonstrate the validity of the expressions (9) and (11) for the pseudo–one-dimensional propagation matrix elements $r^{(i)}_l$. Discuss the cases $(\lambda^{(i)}_n)^2 \leq 0$ (open channels) and $(\lambda^{(i)}_n)^2 > 0$ (closed channels). Do your arguments have to be modified if $\lambda^{(i)}_n$ depends on ρ?

Bibliography

[1] M.S. Child, Molecular Collision Theory, Academic Press, London, 1974

[2] e.g. Arfken, Mathematical Methods for Physicists, 3rd edition p. 899; see 3.94.

[3] e.g. J.N.Murrell, S.D.Bosanac, Introduction to the theory of atomic and molecular collisions, John Wiley, Chichester, 1989, p. 91.

[4] see for instance. G.J.Tawa, S.L.Mielke, D.G.Truhlar, D.Schwenke, JCP 100, 5751 (1994).

[5] Wu, Ohmura, Quantum Theory of Scattering, Prentice Hall, 1962, Englewood Cliffs, New Jersey.

[6] E.U.Condon, G.H.Shortley, The Theory of atomic spectra, Cambridge University Press, Cambridge (1935).

[7] A.M. Lane, R.G.Thomas, Rev.Mod.Phys. 30, 257 (1958).

[8] P.G.Burke, A.Hibbert, W.D.Robb, J.Phys.B, 153 (1971).

[9] J.C.Light, R.B.Walker, JCP 65, 4272 (1976).

[10] E.B. Stechel, R.B.Walker, J.C.Light, JCP 69, 3518 (1978).

[11] D.J.Zvijac, J.C.Light, Chem.Phys.12, 237 (1976).

[12] B.R.Johnson, J.Comp.Phys.13, 445 (1973).

[13] F.Mrugala, D.Secrest, JCP 78, 5954 (1983).

[14] D.E.Manolopoulos, JCP 85, 6425 (1986).

[15] D.Secrest, B.R. Johnson, JCP 45, 4556, (1966).

[16] L.M.Delves, Nucl.Phys.9, 391 (1959).

[17] L.M.Delves, Nucl.Phys. 20, 275 (1960).

[18] F.T.Smith, Phys.Rev. 120, 1058 (1960).

[19] R.T.Pack, G.A.Parker, JCP 87, 3888 (1987).

[20] A.K.Kuppermann, P.G.Hipes, J.Chem.Phys. 84, 5962 (1986).

[21] A.T.Le, C.D.Lin, L.F.Errea, L.Mendez, A.Riera, B.Pons, PRA 69, 62703 (2004)).

[22] J.Z.H.Zhang, Theory and Application of Quantum Molecular Dynamics, World Scientific, Singapore

[23] M.Baer, ed., Theory of Cemical Reaction Dynamics, Vol.1, CRC Press, Boca Raton (1985)

[24] A.M. Arthurs, A. Dalgarno, Proc.Roy.Soc. A256, 50 (1960).

[25] J.H.Van Vleck, Rev.Mod.Phys. 23, 213 (1951).