Section 2.4:Existence of a non-trivial diabatic basis*

The diabatic condition, i.e. the identical vanishing of the vector potential in Eq.2.49, is trivially satisfied for electronic states that are independent of the nuclear coordinate $\mathbf{R}$, as discussed above. Those states, however, tend to be of very limited practical relevance. To be appropriate in an actual quantum chemical situation, a diabatic basis of the form $\{\psi_m^{(0)}(\mathbf{x})\}$ will have to be so extensive that any basis at a particular nuclear configuration $\mathbf{R}$ of the considered system can be represented by expansion into the basis functions at any other configuration $\mathbf{R}'$. This requirement is strictly met only for complete electronic bases. An approximate treatment involving a trivially diabatic basis $\phi_m(\mathbf{x})$ thus necessitates the use of a very large basis set [10]. This predicament raises the question for non-trivial diabatic states, defined as real-valued electronic basis functions $\widetilde{\psi}_n(\mathbf{x},\mathbf{R})$ that contain a parametric dependence on the nuclear coordinates and are yet compatible with a vanishing derivative coupling according to

$$\widetilde{\mathbf{A}}_{12} = \langle\widetilde{\psi}_1(\mathbf{x},\mathbf{R})|\frac{\partial}{\partial\mathbf{R}}|\widetilde{\psi}_2(\mathbf{x},\mathbf{R})\rangle = -\langle\widetilde{\psi}_2(\mathbf{x},\mathbf{R})|\frac{\partial}{\partial\mathbf{R}}|\widetilde{\psi}_1(\mathbf{x},\mathbf{R})\rangle = \mathbf{0}. \qquad (1)$$

To investigate conditions for the validity of Eq.(1) we restrict ourselves to two states $\widetilde{\psi}_1$ and $\widetilde{\psi}_2$, as in Eqns.(2.57-2.59). The matrix $\mathbf{W}$, however, connects now two pairs of functions $(\widetilde{\psi}_1(\mathbf{x},\mathbf{R}),\widetilde{\psi}_2(\mathbf{x},\mathbf{R}))$ and $(\psi_1(\mathbf{x},\mathbf{R}),\psi_2(\mathbf{x},\mathbf{R}))$ that both involve the $\mathbf{R}$ coordinate as parameters. Thus

$$\widetilde{\psi}_m(\mathbf{x},\mathbf{R}) = \sum_n W_{mn}\psi_n(\mathbf{x},\mathbf{R}) \qquad (2)$$

and

$$\widetilde{\mathbf{A}}_{12} = \mathbf{A}_{12} + \frac{\partial\theta(\mathbf{R})}{\partial\mathbf{R}} \qquad (3)$$

The latter statement follows from the explicit form of the transformation matrix $\mathbf{W}$, as given by Eq.(2.57).Combining Eq.(3) with Eq.(1), one obtains

$$\mathbf{A}_{12} = -\frac{\partial\theta(\mathbf{R})}{\partial\mathbf{R}}. \qquad (4)$$

If, therefore, the vector $\mathbf{A_{12}}$ can be represented as a field derived from a scalar potential $\theta(\mathbf{R})$, the existence of a non-trivial diabatic basis is guaranteed. A consideration based on the Helmholtz theorem [11], however, demonstrates that this condition is in general not satisfied [10]. To see this, we introduce the Fourier transform $\mathbf{A'_{12}}(\mathbf{K})$ of $\mathbf{A_{12}}(\mathbf{R})$ by

$$\mathbf{A}_{12}(\mathbf{R}) = \int d\mathbf{K}\ \mathbf{A'_{12}}(\mathbf{K})\exp(i\mathbf{K}\cdot\mathbf{R}). \qquad (5)$$

In the next step, we decompose $\mathbf{A'_{12}}(\mathbf{K})$ into a longitudinal and a transversal component:

$$\mathbf{A}'_{12}(\mathbf{K}) = \mathbf{A}'^{long}_{12}(\mathbf{K}) + \mathbf{A}'^{trans}_{12}(\mathbf{K}) \tag{6}$$

with

$$\mathbf{A}'^{long}_{12}(\mathbf{K}) = \frac{\mathbf{K}[\mathbf{K} \cdot \mathbf{A}'_{\mathbf{12}}(\mathbf{K})]}{|\mathbf{K}|^2} \tag{7}$$

and

$$\mathbf{A}'^{trans}_{12}(\mathbf{K}) = \frac{\mathbf{K} \times [\mathbf{A}'_{12}(\mathbf{K}) \times \mathbf{K}]}{|\mathbf{K}|^2} \tag{8}$$

For simplicity, we assume three spatial dimensions. The generalization of the arguments presented here to N dimensions can be found in the appendix of [10]. Setting

$$\theta(\mathbf{R}) = i \int d\mathbf{K} \; \frac{[\mathbf{K} \cdot \mathbf{A}'_{\mathbf{12}}(\mathbf{K})]}{|\mathbf{K}|^2} \exp(i\mathbf{K} \cdot \mathbf{R}) \tag{9}$$

and

$$\mathbf{C}(\mathbf{R}) = -i \int d\mathbf{K} \; \frac{\mathbf{A}'_{\mathbf{12}}(\mathbf{K}) \times \mathbf{K} \exp(i\mathbf{K} \cdot \mathbf{R})}{|\mathbf{K}|^2}, \tag{10}$$

we find the equivalent decomposition of $\mathbf{A}_{12}$ in $\mathbf{R}$ space:

$$\mathbf{A}_{\mathbf{12}}(\mathbf{R}) = -\frac{\partial \theta(\mathbf{R})}{\partial \mathbf{R}} + \bigtriangledown \times \mathbf{C}(\mathbf{R}), \tag{11}$$

where $\bigtriangledown = \bigtriangledown_{\mathbf{R}}$. The longitudinal part thus derives from a scalar potential while the transversal part is generated by a vector potential. From comparison with Eq.(4), we realize that the existence of a non-trivially diabatic basis hinges on the condition that the curl of the vector potential $\mathbf{C}(\mathbf{R})$ vanishes. This requirement may be examined more closely by using the Green's function formalism [11] in order to recast Eq.(10) as

$$\mathbf{C}(\mathbf{R}) = \frac{1}{4\pi} \int d\mathbf{R}' \frac{\bigtriangledown_{\mathbf{R}'} \times \mathbf{A}_{12}(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|}. \tag{12}$$

The curl of this vector field vanishes only if $\bigtriangledown \times \mathbf{A}_{\mathbf{12}}(\mathbf{R}) = \mathbf{0}$. This translates into the condition that

$$
\begin{aligned}
&\frac{\partial \mathbf{A}_{12,k}(\mathbf{R})}{\partial R_j} - \frac{\partial \mathbf{A}_{12,j}(\mathbf{R})}{\partial R_k} \\
&= \left\langle \frac{\partial \psi_1(\mathbf{x},\mathbf{R})}{\partial R_j} | \frac{\partial \psi_2(\mathbf{x},\mathbf{R})}{\partial R_k} \right\rangle - \left\langle \frac{\partial \psi_1(\mathbf{x},\mathbf{R})}{\partial R_k} | \frac{\partial \psi_2(\mathbf{x},\mathbf{R})}{\partial R_j} \right\rangle \\
&= \sum_n \left[\left\langle \frac{\partial \psi_1(\mathbf{x},\mathbf{R})}{\partial R_j} | \psi_n(\mathbf{x},\mathbf{R}) \right\rangle \left\langle \psi_n(\mathbf{x},\mathbf{R}) | \frac{\partial \psi_2(\mathbf{x},\mathbf{R})}{\partial R_k} \right\rangle \right. \\
&\qquad \left. - \left\langle \frac{\partial \psi_1(\mathbf{x},\mathbf{R})}{\partial R_k} | \psi_n(\mathbf{x},\mathbf{R}) \right\rangle \left\langle \psi_n(\mathbf{x},\mathbf{R}) | \frac{\partial \psi_2(\mathbf{x},\mathbf{R})}{\partial R_j} \right\rangle \right] = 0.
\end{aligned}
\tag{13}
$$

For a general polyatomic situation, however, this requirement cannot be guaranteed. An exception from this rule is given by diatomic systems with states ψ_1 and ψ_2 of equal symmetry. In these cases, $\mathbf{A_{12}}$ may be shown to depend on one parameter only [10], namely the internuclear distance, and Eq.(13) is automatically satisfied.

0.0.1 Quasidiabatic states

In general, therefore, the desired non-trivial diabatic basis $\{\widetilde{\psi}_m(\mathbf{x},\mathbf{R})\}$ that would reduce the derivative coupling to zero, does not exist. We thus ask for a second best solution and try to identify a *quasidiabatic basis* $\{\widetilde{\psi}_m(\mathbf{x},\mathbf{R})\}$ that minimizes the derivative coupling. Following Pacher et al. [8], we select a finite number of electronic states which are of importance for the problem at hand and imagine a Hilbert subspace α where these states reside. This leads to a block representation of the derivative coupling matrices $\mathbf{A_i}$ (see Eqns.(2.10, 2.46, 2.47):

$$
\mathbf{A}_i = \begin{pmatrix} \mathbf{A}_{i,\alpha\alpha} & \mathbf{A}_{i,\alpha\beta} \\ \\ \mathbf{A}_{i,\beta\alpha} & \mathbf{A}_{i,\beta\beta} \end{pmatrix} \equiv \begin{pmatrix} \mathbf{a}_i & \mathbf{c}_i \\ \\ -\mathbf{c}_i^\dagger & \mathbf{b}_i \end{pmatrix} \tag{14}
$$

where the index β stands for the complement of the subspace α. We assume that the interaction between the two subspaces, described by $\mathbf{A}_{i,\alpha\beta} = \mathbf{c}_i$, is small enough to provide a rationale for the subdivision (14). Restricting Eq.(2.49) to the subspace α, we have

$$
\left(-\sum_i \left\{ (\mathbf{I}\frac{\partial}{\partial R_i} + \mathbf{A}_i) \cdot (\mathbf{I}\frac{\partial}{\partial R_i} + \mathbf{A}_i) \right\}_\alpha + \mathbf{V}_\alpha - E\mathbf{I}_\alpha \right) \boldsymbol{\chi}_\alpha = 0, \tag{15}
$$

or, employing the block form Eq.(14):

$$
\left[-(\bigtriangledown + \mathbf{a}) \cdot (\bigtriangledown + \mathbf{a}) + \mathbf{m}_V - E\mathbf{I}_\alpha \right] \boldsymbol{\chi}_\alpha = 0, \tag{16}
$$

where we have used the definition

$$\mathbf{m}_V \equiv \mathbf{V}_\alpha + \mathbf{c}\ \mathbf{c}^\dagger \tag{17}$$

and introduced the vectorial notation $\bigtriangledown \equiv (\mathbf{I}_\alpha \frac{\partial}{\partial R_1}, ..., \mathbf{I}_\alpha \frac{\partial}{\partial R_N}), \mathbf{a} = (\mathbf{a}_1, ..., \mathbf{a}_N)$, and correspondingly for $\mathbf{c}, \mathbf{c}^\dagger$. The symbol $\mathbf{I}_\alpha$ denotes the unit matrix in the subspace α.

Our strategy for finding optimal quasidiabatic states will be to ask for conditions that minimize a suitably chosen norm of the truncated matrices $\mathbf{a}_i$. If such a minimum has been identified, applying an infinitesimal gauge transformation to $\mathbf{a}$ will not change the norm. This transformation may be expressed in the following form:

$$\mathbf{U}(\alpha) = \begin{pmatrix} \mathbf{U}_\alpha & 0 \\ 0 & \mathbf{I}_\beta \end{pmatrix} = \begin{pmatrix} \mathbf{u} & 0 \\ 0 & \mathbf{I}_\beta \end{pmatrix}. \tag{18}$$

To study the operation of $\mathbf{u}$ on $\mathbf{a}$, we write the truncated wavefunction in the subspace α in the form

$$\Psi_\alpha(\mathbf{x}, \mathbf{R}) = \sum_m \psi_{m,\alpha}(\mathbf{x}, \mathbf{R}) \chi_{m,\alpha}(\mathbf{R}) = \boldsymbol{\psi}_\alpha^T \cdot \boldsymbol{\chi}_\alpha. \tag{19}$$

The function Ψ_α remains unchanged under the action of $\mathbf{u}$. Thus

$$\bar{\boldsymbol{\psi}}_\alpha^{\mathbf{T}} = \boldsymbol{\psi}_\alpha^{\mathbf{T}} \mathbf{u} \tag{20}$$

$$\bar{\boldsymbol{\chi}}_\alpha = \mathbf{u}^\dagger \boldsymbol{\chi}_\alpha \tag{21}$$

Acknowledging a possible dependence of $\mathbf{u}$ on the nuclear coordinates, we see that the elements of the Schrödinger equation (16) transform under $\mathbf{u}$ as follows:

$$\bar{\mathbf{m}}_V = \mathbf{u}^\dagger \mathbf{m}_V \mathbf{u}, \tag{22}$$

$$\bar{\mathbf{a}} = \mathbf{u}^\dagger \mathbf{a}\ \mathbf{u} + \mathbf{u}^\dagger (\bigtriangledown \mathbf{u}). \tag{23}$$

In addition, it is readily shown that

$$\bigtriangledown \bar{\boldsymbol{\chi}}_\alpha = \mathbf{u}^\dagger\ \bigtriangledown \boldsymbol{\chi}_\alpha + (\bigtriangledown \mathbf{u}^\dagger) \boldsymbol{\chi}_\alpha. \tag{24}$$

Combining the last two equations, and exploiting that $\mathbf{u}\mathbf{u}^\dagger = \mathbf{I}$, one concludes

$$(\bigtriangledown + \bar{\mathbf{a}}) \bar{\boldsymbol{\chi}}_\alpha = \mathbf{u}^\dagger (\bigtriangledown + \mathbf{a}) \boldsymbol{\chi}_\alpha. \tag{25}$$

This latter result shows that the covariant derivative of $\boldsymbol{\chi}_\alpha$ changes under the action of the gauge transformation $\mathbf{u}$ as $\boldsymbol{\chi}_\alpha$ itself. Summarizing the relations (22-25), we infer the gauge invariance of the Schrödinger equation (16). More precisely, we have established local as opposed to global gauge invariance, since the transformation $\mathbf{u}$ is allowed to depend on the nuclear coordinates. An analogous set of arguments can be employed to prove the invariance of the unrestricted Schrödinger equation (2.49) with respect to general gauge transformations $\mathbf{U}$.

Exercise 2.4: Use the definition of the derivative coupling (2.10) to establish Eq.(23). From this result as well as the unitary property of $\mathbf{u}$, conclude that Eq.(25) is valid. Further, demonstrate that the form of Eq.(16) is invariant with respect to the local gauge transformation represented by $\mathbf{u}$.

Having clarified the transformation behavior of $\mathbf{a}$ under $\mathbf{u}$, we will now further comment on the determination of an optimal quasidiabatic basis that minimizes $\mathbf{a}$. For this purpose, we invoke the Euclidean norm of a matrix:

$$||\mathbf{a}||^2 \equiv Tr(\mathbf{a}^\dagger \mathbf{a}) = \sum_{i=1}^{M} \sum_{k,k'} (\mathbf{a}_i^\dagger)_{kk'} (\mathbf{a}_i)_{k'k}. \tag{26}$$

This norm is a function of the nuclear coordinates $R_i (i = 1, ..., M)$. Integrating over these coordinates, we generate a measure that allows minimizing the derivative coupling matrix. Thus:

$$\Xi \equiv \int ||\mathbf{a}||^2 d\mathbf{R}. \tag{27}$$

The optimal diabatic basis will be one for which Ξ adopts its minimum. This naturally presupposes that Ξ exists, which cannot be taken for granted and thus has to be secured in each individual case of interest. Implementing the search methodology mentioned above, we require the optimal matrix $\mathbf{a}$ to remain unaltered under the action of an infinitesimal gauge transformation $\mathbf{u}$, defined as

$$\mathbf{u} = \mathbf{I}_\alpha + i\boldsymbol{\varepsilon}_\alpha, \tag{28}$$

where the generator $\boldsymbol{\varepsilon}_\alpha$ is a Hermitian matrix. We obtain the transformed derivative coupling matrix $\bar{\mathbf{a}}$ by applying the prescription (23). To first order in $\boldsymbol{\varepsilon}_\alpha$, this yields

$$\bar{\mathbf{a}} = \mathbf{a} + i[\mathbf{a}, \boldsymbol{\varepsilon}_\alpha] + i(\bigtriangledown \boldsymbol{\varepsilon}_\alpha). \tag{29}$$

This makes it possible to generate an expression for the difference between $||\mathbf{a}||^2$ and $||\bar{\mathbf{a}}||^2$ and the respective measures Ξ and $\bar{\Xi}$. More specifically

$$||\bar{\mathbf{a}}||^2 - ||\mathbf{a}||^2 = iTr\left\{[\boldsymbol{\varepsilon}_\alpha, \mathbf{a} \cdot \mathbf{a}] - \boldsymbol{\varepsilon}_\alpha(\bigtriangledown \cdot \mathbf{a}) - (\bigtriangledown \cdot \mathbf{a})\boldsymbol{\varepsilon}_\alpha + \bigtriangledown \cdot (\boldsymbol{\varepsilon}_\alpha \mathbf{a} + \mathbf{a}\boldsymbol{\varepsilon}_\alpha)\right\}. \tag{30}$$

Exercise 2.5: Derive this expression, evaluating the conjugate of $\bar{\mathbf{a}}$.

The corresponding difference in the measure Ξ is

$$\delta\Xi = \bar{\Xi} - \Xi = -i \int Tr\{\boldsymbol{\varepsilon_\alpha}(\bigtriangledown \cdot \mathbf{a}) + (\bigtriangledown \cdot \mathbf{a})\boldsymbol{\varepsilon_\alpha}\} d\mathbf{R}. \tag{31}$$

In going from Eq.(30) to Eq.(31), we have used the fact that the trace over a commutator vanishes, as well as the assumption that $\boldsymbol{\varepsilon_\alpha}\mathbf{a} + \mathbf{a}\,\boldsymbol{\varepsilon_\alpha}$ disappears at infinity. Hence, the volume integral over the divergence of the latter term reduces to zero by the Gauss integral theorem. From Eq.(31), the optimal quasidiabatic basis has to satisfy the condition

$$\bigtriangledown \cdot \mathbf{a} = 0, \tag{32}$$

in accordance with the requirement that δM vanishes for arbitrary $\boldsymbol{\varepsilon_\alpha}$. The criterion (32) means that for quasidiabatic representation, $\mathbf{a}$ is to be defined in the *Lorentz gauge* which eliminates the integrable component of this quantity. This gauge consists in imposing on a gauge potential the condition of vanishing full divergence [12] which, in general, includes a time component. In the present case, however, this component is lacking, and the divergence is to be taken with respect to the full space of nuclear coordinates.

Bibliography

[1] D.R.Yarkony, Jour.Phys.Chem.A 105, 6277 (2001) -

[2] A.Szabo, N.Ostlund, Modern Quantum Chemistry, McGraw-Hill, New York 1982 –

[3] M.Born, R.Oppenheimer, Ann.Phys. (Leipzig) 84, 457 (1927) –

[4] R.L.Liboff, Quantum Mechanics, 2^{nd} edition, Addison-Wesley, Reading, MA 1992 -

[5] I.B.Bersuker, V.Z.Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, Berlin 1989 -

[6] L.I.Schiff, Quantum Mechanics, 3^{rd} edition, McGraw-Hill, New York, 1955 -

[7] M.Born, K.Huang, Dynamical Theory of Crystal Lattices, Oxford University Press, New York 1954 -

[8] T.Pacher, L.S.Cederbaum, H.Koeppel, Advances in Chemical Physics, 84, 293 (1993) -

[9] J.Z.H.Zhang, *Theory and Application of Quantum Molecular Dynamics*, World Scientific, Singapore 1999 –

[10] C.A.Mead, D.G.Truhlar, JCP 77, 6090 (1982) -

[11] G.Arfken, *Mathematical Methods for Physicists*, 3rd edition, Academic Press, San Diego, 1985 -

[12] I.J.R.Aitchinson, A.J.G.Hey, *Gauge Theories in Particle Physics*, Adam Hilger, Bristol 1982-

[13] A.Bohm, A Moustafazadeh, H.Koizumi, Q.Niu, J.Zwanziger, *The Geometric Phase in Quantum Systems*, Springer Berlin 2003-

[14] R. Englman, *The Jahn-Teller Effect in Molecules and Crystals*, Wiley, London, 1972-

[15] H.A.Jahn, E.Teller, Proc.R.Soc. London, Ser.A 161, 220 (1937)

[16] I.B.Bersuker, Jahn-Teller Effect, Cambridge University Press, Cambridge 2006 -

[17] R.Renner, Z.Phys. 92, 172 (1934) -

[18] H.C.Longuet-Higgins, Adv. Spectrosc.2, 429 (1961) -

[19] M.C.M. O'Brien, C.C.Chancey, Am.Jour.Phys. 61, 688 (1993)-

[20] M.V.Berry, Proc.Roy.Soc.London A392, 45 (1984)-

[21] Y.Aharonov, D.Bohm, Phys.Rev. 115, 485 (1959) -

[22] C.Alden Mead, Chem.Phys. 49, 23 (1980) -

[23] H.Koeppel, W.Domcke, Vibronic Dynamics of Polyatomic Molecules, in: *Encyclopedia of Computational Chemistry*; P.v.R.Schleyer, eds.; Wiley: London (1998) -

[24] J.Michl, V.Bonacic-Koutecky, *Electronic aspects of organic photochemistry*, Wiley, New York 1990-

[25] F.Bernardi, M.Olivucci, M.A.Robb, Chem.Soc.Rev. 25, 132 (1996)

[26] A.Stolow, Annu.Rev.Phys.Chem. 54, 89 (2003)

[27] L.J.Butler, Annu.Rev.Phys.Chem.49, 125 (1998

[28] D.A.Farrow, W.Qian, E.Smith, D.Jones, JCP 128, 144510 (2008

[29] C.A.Mead, Jour.Chem.Phys. 72, 3839 (1980).

[30] C.A.Mead, Rev. Mod.Phys.64, 51 (1992).

[31] I.B.Bersuker, The Jahn-Teller Effect, Cambridge University Press, Cambridge, 2006–

[32] J.W.Zwanziger, E.R.Grant, JCP 87, 2954 (1987)-

[33] D.R.Yarkony, in: Conical Intersections, eds.H.Domcke, D.R.Yarkony, H.Koeppel, Adv.Series in Physical Chemistry 15, World Scientific, New Jersey (2004)-

[34] D.R.Yarkony, Rev.Mod.Phys. 68, 985 (1996)-

[35] D.R.Yarkony,in: *Modern Electronic Structure Theory*, Part I, World Scientific, Singapore (1995)-