Existence of Strictly Diabatic Basis Sets for the Two-State Problem

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ABSTRACT: Some new properties of the nonadiabatic coupling elements are derived, in particular the orthogonality and gauge invariance of their longitudinal and transverse components. A method for constructing a strictly diabatic basis set that makes both the transverse and longitudinal components of the nonadiabatic coupling elements of the two-state problem vanish identically and is based on introducing overlap between the electronic states in the vicinity of the crossing seam is proposed. © 2002 Wiley Periodicals, Inc. Int J Quantum Chem 89: 255–259, 2002

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Introduction

Many molecular processes involve two adiabatic potential energy surfaces that get close to each other and eventually intersect along a crossing seam. Their inclusion within the Born–Oppenheimer or Born–Huang–Oppenheimer approximation [1, 2] requires us to solve separately the electronic and nuclear problems. Within such an approximation, the total Hamiltonian is split into the electronic Hamiltonian H_e and the kinetic energy operator T_n of the nuclei. The electronic problem depends parametrically on the nuclear geometry leading to the appearance in the nuclear Schrödinger equations of the so-called nonadiabatic coupling matrix elements (NACMEs) between the states of interest. These NACMEs are nonlocal and singular, giving rise to an intricate computational problem. The traditional solution consists of finding an electronic basis set that converts the NACMEs into nonsingular operators or eventually fully removes them. Such a basis set is called *diabatic* [3–19] by comparison with the former *adiabatic* one. Two types of diabatic bases are apparently possible: the *diabatic I basis* that removes only the singular part of the NACMEs, and the *strictly diabatic* [10, 11, 13, 15, 17] (*diabatic II*) *basis* that fully removes the NACMEs decoupling the nuclear equations of motion.

Adiabatic and diabatic basis sets are linked by some orthogonal transformation. Despite the wide

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use of diabatic basis sets, the existence of an orthogonal transformation leading to a strictly diabatic basis has been a problematic issue since the seminal works by McLachlan [3, 20], Mead and Truhlar [10] (see also Refs. [11, 13, 15, 17]), and Baer [7–9] (for a recent debate, see Refs. [21, 22]). In particular, Mead and Truhlar [10] (see also Ref. [17]) have shown that an orthogonal transformation of two coupled states can eliminate only the longitudinal component of the corresponding nonadiabatic coupling (NAC), leaving nonvanishing the transverse component. This might lead to fewer approximate techniques to handle the removable and nonremovable components of the nonadiabatic coupling and define most diabatic basis sets (Refs. [18, 19, 23–26] and references therein).

Nonexistence vs. Existence of Strictly Diabatic Basis Sets

The electronic eigenvalue problem assumes the form

$$H_e \Psi_k(\mathbf{r}; \mathbf{R}) = E_k(\mathbf{R}) \Psi_k(\mathbf{r}; \mathbf{R}), \qquad (1)$$

where $H_e = T_e + V_{ee} + V_{en} + V_{nn}$, and common notations are employed for the electronic kinetic energy operator, T_e, interelectronic Coulomb potential, V_{ee}, and electron–nuclear and nuclear–nuclear Coulomb potentials, respectively V_{en} and V_{nn}. In turn, $\Psi_k(\mathbf{r}; \mathbf{R})$ is the real-valued kth electronic eigenfunction of H_e associated to the E_k eigenvalue. All adiabatic basis functions $\Psi_k(\mathbf{r}; \mathbf{R})$ form a complete orthonormalized set; as usual, the parametric dependence on the nuclear configuration space is indicated by the semicolon. We reserve hereafter Roman letters for the electronic quantities while Greek letters are used for the nuclear ones.

Let us now apply the gradient operator $\nabla_{\mathbf{R}_\alpha}$ with $\mathbf{R}_\alpha \in \mathbf{R}$ to Eq. (1). The result is

$$(\nabla_{\mathbf{R}_\alpha} H_e) \Psi_k(\mathbf{r}; \mathbf{R}) + H_e[\nabla_{\mathbf{R}_\alpha} \Psi_k(\mathbf{r}; \mathbf{R})]$$
$$= [\nabla_{\mathbf{R}_\alpha} E_k(\mathbf{R})] \Psi_k(\mathbf{r}; \mathbf{R}) + E_k(\mathbf{R})[\nabla_{\mathbf{R}_\alpha} \Psi_k(\mathbf{r}; \mathbf{R})], \quad (2)$$

from which we can easily obtain

$$\mathbf{f}_{kl}^{(\alpha)} = \langle\langle \Psi_k | \nabla_{\mathbf{R}_\alpha} \Psi_l \rangle\rangle_{\mathbf{r}} = \frac{\langle\langle \Psi_k | \nabla_{\mathbf{R}_\alpha} H_e | \Psi_l \rangle\rangle_{\mathbf{r}}}{E_l - E_k}, \qquad (3)$$

where the double bracket notation in Eq. (3) implies integration over all electronic degrees of freedom $\mathbf{r}$; here and when free of ambiguity, we omit the explicit dependence on $\mathbf{r}$ and $\mathbf{R}$. By definition, $\mathbf{f}_{kl}^{(\alpha)}$ is the NAC between the electronic states k and l relative to the αth nuclear radius vector. If it vanishes identically for all pairs k and l and all $\mathbf{R}_\alpha \in \mathbf{R}$, the electronic functions form a diabatic II basis set. They will no longer be eigenfunctions of H_e.

Nonadiabatic couplings $\mathbf{f}_{kl}^{(\alpha)}$ for all pairs of electronic eigenstates Ψ_k and Ψ_l form an antisymmetrical matrix $\mathbf{F}^{(\alpha)}$ with nonzero nondiagonal NACMEs, $\mathbf{F}_{kl}^{(\alpha)} = \mathbf{f}_{kl}^{(\alpha)}$ ($k \neq l$). In fact, $\mathbf{f}_{kl}^{(\alpha)}$ is a vector field. Thus, according to Helmholtz's theorem [27, 28], it can be decomposed into two components: $\mathbf{f}_{kl}^{(\alpha)} = \mathbf{f}_{kl}^{(\alpha)\|} + \mathbf{f}_{kl}^{(\alpha)\perp}$. The component $\mathbf{f}_{kl}^{(\alpha)\|}$ of $\mathbf{f}_{kl}^{(\alpha)}$ is such that its curl, $\nabla_{\mathbf{R}_\alpha} \times \mathbf{f}_{kl}^{(\alpha)\|}$, is identically zero. This is the longitudinal or irrotational component and can be represented as $\mathbf{f}_{kl}^{(\alpha)\|} = \nabla_{\mathbf{R}_\alpha} P_{kl}^{(\alpha)\|}$, where $P_{kl}^{(\alpha)\|}$ is a scalar function of $\mathbf{R}$. The other transverse or rotational component $\mathbf{f}_{kl}^{(\alpha)\perp}$ has zero divergence: $\nabla_{\mathbf{R}_\alpha} \cdot \mathbf{f}_{kl}^{(\alpha)\perp} = 0$. Thus, $\mathbf{f}_{kl}^{(\alpha)\perp} = \nabla_{\mathbf{R}_\alpha} \times \mathbf{P}_{kl}^{(\alpha)\perp}$. This decomposition is valid if the vector field $\mathbf{f}_{kl}^{(\alpha)}$ is finite and unique if $\nabla_{\mathbf{R}_\alpha} \cdot \mathbf{P}_{kl}^{(\alpha)\perp} = 0$, $\lim_{R_\alpha \to \infty} P_{kl}^{(\alpha)\|} = 0$, and $\lim_{R_\alpha \to \infty} \mathbf{P}_{kl}^{(\alpha)\perp} = 0$ for all α. One then easily derives that

$$\nabla_{\mathbf{R}_\alpha} \cdot [P_{kl}^{(\alpha)\|} \nabla_{\mathbf{R}_\alpha} \times \mathbf{P}_{kl}^{(\alpha)\perp}] = \nabla_{\mathbf{R}_\alpha} P_{kl}^{(\alpha)\|} \cdot \nabla_{\mathbf{R}_\alpha} \times \mathbf{P}_{kl}^{(\alpha)\perp}. \qquad (4)$$

Integrating each side of Eq. (4) over all space $\mathbf{R}_\alpha^3$ and applying Gauss' theorem yields

$$\int_{\mathbf{R}_\alpha^3} d^3 \mathbf{R}_\alpha \mathbf{f}_{kl}^{(\alpha)\|} \cdot \mathbf{f}_{kl}^{(\alpha)\perp} = 0. \qquad (5)$$

Equation (5) represents an orthogonality relation between the longitudinal and transverse components of the vector field $\mathbf{f}_{kl}^{(\alpha)}$. Note that $\mathbf{f}_{kl}^{(\alpha)\perp}$ is gauge invariant: Any transformation of $\mathbf{P}_{kl}^{(\alpha)\perp}$ into $\mathbf{P}_{kl}^{(\alpha)\perp} + \nabla_{\mathbf{R}_\alpha} \Theta$ leaves $\mathbf{f}_{kl}^{(\alpha)\perp}$ unchanged for an arbitrary function Θ. A particular choice of Θ is the so-called gauge origin where $\Theta = 1/2[\mathbf{f}_{kl}^{(\alpha)\perp} \times (\mathbf{R} - \mathbf{R}')] \cdot \mathbf{R}_\alpha$. Such a gauge invariance of the transverse component is interesting in view of the recent work by Buenker and Li [29] on the independence of NAC on the choice of the origin of the coordinate frame.

Let us now apply the curl operator to $\mathbf{f}_{12}^{(\alpha)}$. The result is

$$\nabla_{\mathbf{R}_\alpha} \times \mathbf{f}_{12}^{(\alpha)} = \langle\langle \nabla_{\mathbf{R}_\alpha} \Psi_1 | \times | \nabla_{\mathbf{R}_\alpha} \Psi_2 \rangle\rangle \mathbf{r}_e = -\sum_{n \geq 3} \mathbf{f}_{1n}^{(\alpha)} \times \mathbf{f}_{n2}^{(\alpha)}.$$

$$(6)$$

This equation is readily generalized to an arbitrary nonadiabatic coupling, yielding

$$\nabla_{\mathbf{R}_\alpha} \times \mathbf{f}_{kl}^{(\alpha)} = -\sum_n \mathbf{f}_{kn}^{(\alpha)} \times \mathbf{f}_{nl}^{(\alpha)} \qquad (7)$$

or, by virtue of Eq. (3),

$$\nabla_{\mathbf{R}_\alpha} \times \mathbf{f}_{kl}^{(\alpha)} = -\sum_{m \neq k,l} \frac{\langle\langle \Psi_k(\mathbf{r}; \mathbf{R})|\nabla_{\mathbf{R}_\alpha}H_e(\mathbf{r}; \mathbf{R})|\Psi_m(\mathbf{r}; \mathbf{R})\rangle\rangle_{\mathbf{r}}}{E_m(\mathbf{R}) - E_k(\mathbf{R})}$$
$$\times \frac{\langle\langle \Psi_m(\mathbf{r}; \mathbf{R})|\nabla_{\mathbf{R}_\alpha}H_e(\mathbf{r}; \mathbf{R})|\Psi_l(\mathbf{r}; \mathbf{R})\rangle\rangle_{\mathbf{r}}}{E_l(\mathbf{R}) - E_m(\mathbf{R})}. \qquad (8)$$

Thus, $P_{12}^{(\alpha)\|}$ and $\mathbf{P}_{12}^{(\alpha)\perp}$ satisfy the following equations:

$$\nabla_{\mathbf{R}_\alpha}(\nabla_{\mathbf{R}_\alpha} \cdot \mathbf{P}_{12}^{(\alpha)\perp}) - \nabla_{\mathbf{R}_\alpha}^2 \mathbf{P}_{12}^{(\alpha)\perp} = \sum_{n \geq 3} \mathbf{f}_{1n}^{(\alpha)} \times \mathbf{f}_{n2}^{(\alpha)} \qquad (9)$$

$$\nabla_{\mathbf{R}_\alpha}^2 P_{12}^{(\alpha)\|} = \sum_{n \geq 3} \mathbf{f}_{n1}^{(\alpha)} \cdot \mathbf{f}_{n2}^{(\alpha)} + \langle\langle \Psi_1|\nabla_{\mathbf{R}_\alpha}^2 \Psi_2\rangle\rangle_{\mathbf{r}}. \qquad (10)$$

Equation (6) is actually the compact form of Eq. (19) derived by Mead and Truhlar [10]. In particular, it tells that the curl of $\mathbf{f}_{12}^{(\alpha)}$ is expressed in terms of nonadiabatic couplings of the two involved eigenstates with the rest of the eigenstates of H_e (two-state problem). If the latter are ignored, it then follows directly from Eq. (6) that the nonadiabatic coupling possesses only a longitudinal component. Moreover, it is also seen from Eq. (10) that in this case $\nabla_{\mathbf{R}}^2 P_{12}^{\|} = \langle\langle \Psi_1|\nabla_{\mathbf{R}}^2 \Psi_2\rangle\rangle_{\mathbf{r}_e}$ (the subscript α will be hereafter removed). In this case, the nonadiabatic couplings in the "old" (Ψ_1, Ψ_2) and "new" ($\tilde{\Psi}_1$, $\tilde{\Psi}_2$) 2-D basis sets satisfy the following relationship [10].

$$\tilde{\mathbf{f}}_{21} = \mathbf{f}_{21} - \nabla_{\mathbf{R}}\gamma, \qquad (11)$$

where γ is the rotation angle. The tilded NACME vanishes if γ satisfies the equation

$$\nabla_{\mathbf{R}}\gamma = \mathbf{f}_{21}, \qquad (12)$$

with γ being called the adiabatic-to-diabatic transformation (ADT) angle [7, 8, 17]. In general, when there is a coupling between the two states and the rest of the eigenstates of H_e, Eq. (12) demonstrates that the orthogonal transformation enables us to remove only the longitudinal component of the $\mathbf{f}_{12}$ NACME between the two intersecting potential energy surfaces, leaving the transverse component nonremovable. In other words, the diabatic II basis

does not in general exist [10]. It is then interesting to note from Eq. (8) that the transverse component of NAC is not singular unless there is at least an intersection of one of the coupled potential surfaces under study with a third one.

Strictly Diabatic Basis for the Generalized Two-State Problem

Starting from Eq. (1), we have always operated with the adiabatic basis set $\Psi_k(\mathbf{r}; \mathbf{R})$, which was suggested to be orthonormal:

$$\langle\langle \Psi_k|\Psi_l\rangle\rangle_{\mathbf{r}} = \delta_{kl}. \qquad (13)$$

Such a condition can be easily relaxed while keeping $\Psi_k(\mathbf{r}; \mathbf{R})$ as the kth electronic eigenfunction of the electronic Hamiltonian H_e that contains only local multiplicative $\mathbf{R}$-dependent operators. This can be done by assuming that the overlap matrix between the electronic eigenstates takes the form

$$\langle\langle \Psi_k|\Psi_l\rangle\rangle_{\mathbf{r}} = a_k(\mathbf{R})\delta_{kl}, \qquad (14)$$

which is a natural assumption in the vicinity of the crossing seam, where the degenerate electronic states are physically nonseparable.

Let us now consider the generalized two-state problem within the ansatz (14). The transformed wave functions $\tilde{\tilde{\Psi}}_1$ and $\tilde{\tilde{\Psi}}_2$ may then be represented as

$$\tilde{\tilde{\Psi}}_1 = \Psi_1\cos\tilde{\gamma} - \Psi_2\sin\tilde{\gamma}$$

$$\tilde{\tilde{\Psi}}_2 = \Psi_1\sin\tilde{\gamma} + \Psi_2\cos\tilde{\gamma}, \qquad (15)$$

where $\tilde{\gamma}$ is the new $\mathbf{R}$-dependent mixing angle. Their overlap assumes the form

$$\langle\langle \tilde{\tilde{\Psi}}_1|\tilde{\tilde{\Psi}}_2\rangle\rangle_{\mathbf{r}} = \frac{1}{2}\sin 2\tilde{\gamma}(\langle\langle \Psi_1|\Psi_1\rangle\rangle_{\mathbf{r}} - \langle\langle \Psi_2|\Psi_2\rangle\rangle_{\mathbf{r}}). \qquad (16)$$

This seems a plausible result because one may think of building the total wave function from the overlapping single-surface ones at the crossing region. However, such an overlap will vanish if $a_1(\mathbf{R}) = a_2(\mathbf{R}) \equiv a_o(\mathbf{R})$, an assumption adopted in the present work. Note that $\langle\langle \tilde{\tilde{\Psi}}_i|\tilde{\tilde{\Psi}}_i\rangle\rangle_{\mathbf{r}} = a_o(\mathbf{R})$, while

$$\langle\langle\tilde{\tilde{\Psi}}_i|\nabla_{\mathbf{R}}\tilde{\tilde{\Psi}}_i\rangle\rangle_{\mathbf{r}} = \langle\langle\Psi_i|\nabla_{\mathbf{R}}\Psi_i\rangle\rangle_{\mathbf{r}} = \frac{1}{2}\nabla_{\mathbf{R}}a_o \quad i = 1, 2. \quad (17)$$

In addition, the NACME between the new states assumes the form

$$\tilde{\mathbf{f}}_{21} = \mathbf{f}_{21} - a_o\nabla_{\mathbf{R}}\tilde{\gamma}. \quad (18)$$

Thus, the *strictly diabatic basis* for this generalized two-state problem exists if

$$\mathbf{f}_{21} = a_o\nabla_{\mathbf{R}}\tilde{\gamma}. \quad (19)$$

This implies that the transverse component of $\mathbf{f}_{21}$ should obey the equation

$$\nabla_{\mathbf{R}} \times \mathbf{f}_{21} = \nabla_{\mathbf{R}}a_o \times \nabla_{\mathbf{R}}\tilde{\gamma} \quad (20)$$

while the longitudinal component satisfies

$$\nabla_{\mathbf{R}} \cdot \mathbf{f}_{21} = a_o\nabla_{\mathbf{R}}^2\tilde{\gamma} + \nabla_{\mathbf{R}}a_o \cdot \nabla_{\mathbf{R}}\tilde{\gamma}. \quad (21)$$

Both Eqs. (20) and (21) determine the unknown functions $a_o(\mathbf{R})$ and $\tilde{\gamma}(\mathbf{R})$, which, in turn, result in the *strictly diabatic basis.* These equations can be solved in the following way: Substitution of $\nabla_{\mathbf{R}}\tilde{\gamma} = \mathbf{f}_{21}/a_o$ from Eq. (19) into Eq. (20) leads to

$$\nabla_{\mathbf{R}} \times \mathbf{f}_{21} = \frac{\nabla_{\mathbf{R}}a_o}{a_0} \times \mathbf{f}_{21}. \quad (22)$$

Without any loss of generality, we now assume that $\mathbf{f}_{21}$ is parallel to the X axis, that is, $\mathbf{f}_{21} = f(\mathbf{R})\mathbf{i}$ where $\mathbf{R} = \{X, Y, Z\}$ and $\mathbf{i}$ is the unit vector along the X-axis. It then follows from Eq. (22) that

$$\frac{\partial f}{\partial Y} = \frac{1}{a_o}\frac{\partial a_o}{\partial Y}f, \quad \frac{\partial f}{\partial Z} = \frac{1}{a_o}\frac{\partial a_o}{\partial Z}f. \quad (23)$$

These equations have the solution $a_o(X, Y, Z) = f(X, Y, Z)$. Thus, Eq. (19) rewritten now as $\partial\tilde{\gamma}/\partial X = f/a_o$, possesses the trivial solution $\tilde{\gamma}(X, Y, Z) = \tilde{\gamma}_o + X$, where $\tilde{\gamma}_o$ is an arbitrary constant. Note that the normalizing factor $a_o(\mathbf{R})$ coincides with the NAC term and hence absorbs in principle the singularity contained in its longitudinal component. This may not be recommended for practical applications. To avoid this unpleasant feature, we may think of first applying Eq. (12) to define γ, thus removing such a singularity. The functions $\{\tilde{\Psi}_i\}$ so obtained would then be taken as the set $\{\Psi_i\}$ in Eq. (13) and follow-

ing equations, leading to $\{\tilde{\tilde{\Psi}}_i\}$. This set of functions would contain the parameters a_o and $\tilde{\gamma}$ that would be extracted by solving Eq. (19), having now only the transverse nonsingular part of the NAC. In this case, Eqs. (20) and (21) are rewritten as

$$\nabla_{\mathbf{R}}a_o \times \nabla_{\mathbf{R}}\tilde{\gamma} = \nabla_{\mathbf{R}} \times \mathbf{f}_{21} \quad (24)$$

and

$$\nabla_{\mathbf{R}}a_o \cdot \nabla_{\mathbf{R}}\tilde{\gamma} = -a_o\nabla_{\mathbf{R}}^2\tilde{\gamma}. \quad (25)$$

These equations imply {see Eqs. (5.2–17) of Ref. [30]} the following relation between $\tilde{\gamma}$ and a_o:

$$(\nabla_{\mathbf{R}}\tilde{\gamma})^2\nabla_{\mathbf{R}}a_o + a_o\nabla_{\mathbf{R}}^2\tilde{\gamma}\nabla_{\mathbf{R}}\tilde{\gamma} = \nabla_{\mathbf{R}}\tilde{\gamma} \times \nabla_{\mathbf{R}} \times \mathbf{f}_{21}, \quad (26)$$

which may be useful to determine the convenient a_o and $\tilde{\gamma}$.

Conclusions

After reviewing the difficulties of constructing a strictly diabatic basis set and proving some new properties of the nonadiabatic coupling elements, a novel approach has been proposed to show the existence of such a basis within the generalized two-state problem as the cornerstone issue in non-adiabatic dynamics of molecules. An analytic procedure to derive such a basis has also been demonstrated that may, however, be difficult for implementation. Thus, both the transverse and longitudinal components of the nonadiabatic coupling element for the generalized two-state problem have been shown to vanish identically within such a basis as implied by its definition. Moreover, the overlap $a_o(\mathbf{R})$ and the ADT angle have been explicitly expressed in terms of such a nonadiabatic coupling element. To conclude, we emphasize the following points: (1) with our proposed solution for a_o, one obtains a simple expression for the ADT angle; (2) the normalization condition proposed in Eq. (14) is innovative and natural in the vicinity of the intersection because we are unable to separate there the degenerate electronic states. We also note that the proposed method for constructing a strictly diabatic basis set for the generalized two-state problem assumes nonnormalized basis functions and hence does not contradict the Mead–Truhlar theorem on the nonexistence of such a basis, which was demonstrated for the normalized case.

References

1. Born, M.; Oppenheimer, J. R. Ann Phys 1927, 84, 457.

2. Born, M.; Huang, K. Dynamical Theory of Crystal Lattices; Oxford: London, 1954.

3. McLachlan, A. D. Mol Phys 1961, 4, 417.

4. Lichten, W. Phys Rev 1965, 131, 229.

5. Lichten, W. Phys Rev A 1967, 164, 131.

6. Smith, F. T. Phys Rev 1969, 179, 111.

7. Baer, M. Chem Phys Lett 1975, 35, 112.

8. Baer, M. Chem Phys 1976, 15, 49.

9. Top, Z. H.; Baer, M. Chem Phys 1977, 25, 1.

10. Mead, C. A.; Truhlar, D. G. J Chem Phys 1982, 77, 6090.

11. Mead, C. A. J Chem Phys 1983, 78, 807.

12. Köppel, H.; Domcke, W.; Cederbaum, L. S. Adv Chem Phys 1984, 72, 59.

13. Thompson, T. C.; Mead, C. A. J Chem Phys 1985, 82, 2408.

14. Cederbaum, L. S.; Domcke, W.; Schirmer, W.; von Niessen, W. Adv Chem Phys 1986, 65, 115.

15. Mead, C. A. Rev Mod Phys 1992, 64, 51.

16. Baer, M.; Englman, R. Mol Phys 1992, 75, 293.

17. Pacher, T.; Cederbaum, L. S.; Köppel, H. Adv Chem Phys 1993, 84, 293.

18. Baer, M.; Varandas, A. J. C.; Englman, R. J Chem Phys 1999, 111, 9493.

19. Baer, M.; Englman, R.; Varandas, A. J. C. Mol Phys 1999, 97, 1185.

20. Hobey, W. D.; McLachlan, A. D. J Chem Phys 1960, 33, 1695.

21. Kendrick, B. K.; Mead, C. A.; Truhlar, D. G. Chem Phys Lett 2000, 330, 629.

22. Baer, M. Chem Phys Lett 2000, 330, 633.

23. Gadéa, F. X.; Pélissier, M. J Chem Phys 1990, 93, 545.

24. Pacher, T.; Cederbaum, L.; Köppel, H. J Chem Phys 1988, 89, 7367.

25. Pacher, T.; Cederbaum, L.; Köppel, H. J Chem Phys 1989, 91, 7057.

26. Atchity, G. J.; Ruedenberg, K. Theor Chem Acc 1997, 97, 47.

27. McQuistan, R. B. Scalar and Vector Fields: A Physical Interpretation; New York: Wiley, 1965; Section 11.6.

28. Panofsky, W. K. H.; Phillips, M. Classical Electricity and Magnetism; Addison-Wesley: Reading, MA, 1962; 2nd Ed., p. 7.

29. Buenker, R. J.; Li, Y. J Chem Phys 2000, 112, 8318.

30. Korn, G. A. Mathematical Book for Scientists and Engineers; McGraw-Hill: New York, 1968; 2nd Ed.