STATE-SELECTED AND STATE-TO-STATE ION–MOLECULE REACTION DYNAMICS
Part 2. Theory

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Part 2. Theory

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, Advances in Chemical Physics, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field which we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE
STUART A. RICE
PREFACE

This volume is composed of eight chapters all devoted to the theory of charge-transfer processes during an atom (ion)--molecule (ion) collision. In three chapters are presented different attitudes for treating the potential energy surfaces (and the corresponding coupling terms), which govern the motion of the interacting atoms and ions, and in five chapters is treated the dynamics of these particles. The range of the topics on this subject covers the pure quantum-mechanical approach, various semiclassical approaches, and several statistical approaches. The order of the chapters are as follows.

The first chapter, by Lengsfield and Yarkony, deals with the adiabatic representation of the potential energy surfaces. Special emphasis is given to the importance and the derivation of the radial nonadiabatic coupling terms. These terms represent what must be determined in order to characterize an electronically nonadiabatic process. Equally significant is the efficient determination of where it is most important to determine these quantities. Nonadiabatic effects are most important in regions of nuclear coordinate space for which the potential energy surfaces in question are in close proximity or actually touch or cross. Thus, this chapter will also discuss efficient techniques for locating actual and avoided surface crossings.

The second chapter, by Sidis, deals with the diabatic representation of the potential energy surfaces. Here are discussed the problems associated with the strict formal definitions of diabatic states and with the adiabatic-diabatic transformations when applied for reduced electronic basis sets. Next is presented in great detail a method that yields from first principles potential energy surfaces and potential coupling terms such that the corresponding nonadiabatic coupling terms are relatively small. Results for several systems are discussed.

The third chapter by Gianturco and Schneider describes a semiempirical method for the calculations of several potential energy surfaces that are usually coupled together in the case of ion--molecule interactions. The method, which is based on the diatomics-in-molecules (DIM) wave expansion, is briefly reviewed and the physical meaning of the terms included in the expansion is discussed. The rigorous handling of the nonadiabatic coupling terms between surfaces for specific geometries of the relative orientation is reduced, within their treatment, to a more simplified approach that lends itself to rather rapid evaluation via the full DIM matrix. Examples are discussed for several simple ion (atom)--diatom systems for which either
scattering experiments are available or dynamical computations have been attempted. It is shown in conclusions that the present model approach is one of the most useful and physically realistic pathways for treating ion–molecule collisions based on the general topology of the corresponding potential energy surfaces coupled with the dynamics.

The fourth chapter by Baer deals with the quantum-mechanical approach of low-energy charge-transfer processes between ions and neutrals. First is discussed the formal theory based on the Born–Oppenheimer treatment (with the emphasis on the adiabatic and the diabatic representations and the strict and approximate relations between them), which is then followed by deriving the Schrödinger equation for studying the dynamics. Special attention is given to those instances when exchange (chemical reaction) processes are competing with the charge-transfer process. Integral and differential state-to-state cross sections were calculated for several systems and compared with experiment.

The fifth chapter, by Nakamura, deals with the semiclassical approach to charge-transfer processes. Various transitions such as the Landau–Zener and the Rosen–Zener type of nonadiabatic transitions, transitions induced by Coriolis coupling, spin–orbit interaction, and the coupling due to the electron momentum transfer or the electron translation factor in charge transfer are discussed. It is shown that the semiclassical theory can be utilized to analyze all these transitions uniformly by introducing the new (dynamical-state) representation. Qualitative discussions are also presented for reactive transition or particle rearrangement by emphasizing the role of the potential ridge. Particular emphasis is given to the two-state case, which is then extended to a multistate system. Also, a simple semiclassical generalization of the trajectory-surface-hopping method is discussed.

The sixth chapter, by Gislason, Parlant, and Sizum, is devoted to classical path calculations of charge transfer for ion–molecule collisions. Inelastic processes that occur at the same time, such as fine-structure transitions and vibrational excitation, are also discussed. After a brief introduction the classical path technique is discussed in detail. In particular, the choice of basis sets, the coupled equations, and the classical trajectory are described, and the best numerical techniques to be used are summarized. The calculations of both total and differential cross sections are covered. Next are reviewed previous classical path calculations of total state-to-state cross sections and differential cross sections, and representative results are shown. Certain general features of charge-transfer collisions such as the Franck–Condon principle, the adiabatic vibronic potential energy surfaces, and the general energy dependence of charge-transfer cross sections are also discussed.

The seventh chapter, by Chapman, deals with the classical trajectory-
surface-hopping method. Here is not only described in detail the method itself and various extensions to it but also a number of procedures for locating the position for the potential hopping. The main advantage of the trajectory-surface-hopping method is that it enables one to describe relatively simply and self-consistently the wide range of processes that may occur in molecular collisions, particularly in ion-molecule reactions. These include charge transfer, chemical reaction, collision-induced dissociation, and collision-induced predissociation. With the addition of some simplifying assumptions, it is possible to include electron-detachment channels as well. Results for several ion-molecule systems are described in some detail, including \((H + H_2)^+, (Ar + H_2)^+, (He + H_2)^+, (Ne + He_2)^+, (Cl + H_2)^+.\) Electron jump reactions, including \(M + X_2 (M = \text{alkali}, X = \text{halogen})\) and \(M + O_2\) are also discussed.

The eighth chapter, by Troe, discusses the application of statistical rate theories to unimolecular and bimolecular ion-molecule reactions. Rovibrationally adiabatic channel potential curves and threshold energies are analyzed for various reactive systems. Consequently, the corresponding rate constants and cross sections for capture processes, bimolecular reactions involving predissociation of the collision complexes and unimolecular reactions are derived. Finally, also nonadiabatic corrections to these rate expressions are considered.

Michael Baer
Cheuk-Yiu Ng

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November 1991
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NONADIABATIC INTERACTIONS BETWEEN
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THEORY AND APPLICATIONS

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I. INTRODUCTION

The introduction of analytic gradient and higher-derivative techniques has had an enormous impact on the progress of \textit{ab initio} electronic-structure theory. Analytic derivative methods were first introduced as a practical computational tool for use with single configuration wavefunctions\textsuperscript{1,2} in the late 1960s as an extension of the previous work of Bratoz\textsuperscript{3} and Bishop.\textsuperscript{4} Progress in both the theory and application of these techniques has been quite rapid, so that the use of analytic first and higher derivatives at various post-Hartree–Fock levels of theory is now routine.\textsuperscript{5–13} Testimony to the importance of this area of research is given by the large number of reviews\textsuperscript{14–20} of the field. In this chapter we discuss the theory and application of analytic gradient techniques to the study of electronically nonadiabatic processes. These are processes in which the description of the nuclear motion involves more than one Born–Oppenheimer potential energy surface and include such familiar areas as electronic quenching and charge-transfer reactions, predissociation and photofragmentation, and vibronic spectroscopy. Studies of electronic quenching are frequently motivated by practical considerations such as the design of gas-phase chemical lasers and the interpretation of laser-induced-fluorescence-excitation experiments, which probe intermediate species in combustion reactions. Molecular-photodissociation processes often proceed via excitation to a bound excited state, which is predissociated by nonadiabatic coupling with a (set of) dissociative states. Alternatively, this process may involve excitation to a set of nonadiabatically coupled dissociative states corresponding to distinct exit-channel
arrangements. These situations arise in the photofragmentation of $H_3^+$, where the reactions

$$H_3^+ + h\nu \rightarrow H_2^+ + H$$

and

$$H_3^+ + h\nu \rightarrow H^+ + H + H$$

compete. Vibronic absorption spectra involving states of mixed valence-Rydberg character are strongly influenced by nonadiabatic interactions. This is clearly seen in the recent analysis\(^\text{22}\) of the $^1\Sigma^+_u$ and $^1\Pi_u$ states of $N_2$ and the kinetic energy release studies\(^\text{23,24}\) of $d^1\Pi_g$ state of $O_2$. Systems exhibiting Jahn–Teller and Renner–Teller\(^\text{25–27}\) intersections also require a knowledge nonadiabatic interactions for theoretical study. Theoretical and experimental studies of these phenomena have profitted from the work of Berry\(^\text{28}\) and Simon\(^\text{29}\) on the adiabatic evolution of the wavefunction in a region of degenerate surfaces.

Our description of these processes employs an adiabatic states approach. In this approach it is necessary to determine both the adiabatic state potential energy surfaces $E(I(R))$ as well as the first and second derivative couplings, which result in the breakdown of the single potential energy surface approximation. In this chapter it is shown how a series of recent advances in electronic-structure theory have facilitated the computation of derivative coupling matrix elements in the case where the adiabatic electronic states are represented as large-scale multireference configuration-interaction (CI) wavefunctions. The analytic derivative procedures that are discussed in this work represent a significant improvement over the finite-difference techniques that had been introduced previously to determine these quantities. In Section II these analytic-gradient-based techniques for the determination of the first
derivative (Sections II A and II B)$^{36,37}$ and second derivative (Section II C)$^{38,40}$ nonadiabatic couplings are reviewed. In Section II A a structural isomorphism between the energy gradient and the first-derivative nonadiabatic coupling matrix elements will be developed. This isomorphism is the key to the efficient evaluation of these quantities using analytic gradient methods.

Section II D discusses the additional efficiencies that can be achieved by incorporating body-fixed-frame symmetry into the evaluation of derivative couplings. In Section II F the interrelation between second-derivative couplings, $k^{II}_{s\delta}(R)$, and the absence of rigorous diabatic bases in polyatomic systems is discussed.

Derivative couplings, nonadiabatic effects, are most important in regions of coordinate space for which two or more potential energy surfaces are in close proximity or actually touch or cross. Such regions of nuclear coordinate space will frequently be characterized by actual or avoided-crossing seams of the potential energy surfaces in question. A recently introduced methodology for locating actual/avoided crossings$^{48,49}$ will be discussed in Section II E. In that subsection the isomorphism established between the energy gradient and the first-derivative nonadiabatic coupling matrix elements will be extended to include the energy-difference gradient. The method that is developed for the efficient determination of the energy-difference gradient will be essential for the determination of actual/avoided surface crossings.

Section III considers applications of the methodology discussed in Section II. As discussed in Section II the first-derivative nonadiabatic coupling matrix elements $f^{II}_{s\delta}(R)$ are responsible for transitions between potential energy surfaces, while the second-derivative nonadiabatic coupling matrix elements $h^{II}_{s\delta}(R)$ both couple and modify the potential energy surfaces. While the Born–Oppenheimer potential energy surfaces themselves are mass independent, the modifications resulting from $h^{II}_{s\delta}(R)$, referred to as the adiabatic correction or the Born–Oppenheimer diagonal correction, are mass dependent. Several groups have been interested in the Born–Oppenheimer diagonal correction.$^{39,50-60}$ Ab initio studies include those of Bishop and Cheung$^{50-52}$ who considered H$_2$, HeH$^+$, and LiH using specialized CI wavefunctions$^{50-52}$ as well as SCF level$^{58-60}$ or SCF/limited-CI treatments$^{53-57}$ of more complex molecules. In this work the second-derivative methodology is used to discuss the adiabatic correction to the $X^1\Sigma^+$ state potential energy curve of LiH. This subtle mass-dependent feature of the $X^1\Sigma^+$ potential energy curve had been the object of some controversy, since experimental and theoretical determinations of this quantity had yielded qualitatively different results. We then turn to a discussion of the electronic structure aspects of the radiationless electronic
This reaction is of particular interest since it is facilitated by a seam of actual surface crossings permitted by the multidimensional breakdown of the von Neumann-Wigner noncrossing rule. \textit{Ab initio} characterizations of an actual crossing of states of the same symmetry are rare. The characterization of an actual crossing seam using multiconfiguration self-consistent field (MCSCF)/CI wavefunctions discussed in this chapter is unique. The only previous characterization of an actual crossing seam is that of Katriel and Davidson who employed a Frost model in approximate treatment of CH$_4$$^+$. The methodology outlined in Section II E is also capable of determining seams of avoided crossings. Seams of avoided crossings represents the parametric solution of the equations defining an avoided crossing in a space of reduced dimensionality. Since an actual crossing of two states of the same symmetry is permitted, but not required, by the noncrossing rule, an actual crossing seam may merge into an avoided crossing seam when the solution permitted by the noncrossing rule ceases to exist. Thus, it is appropriate to determine avoided-crossing seams in the same parameter space used to describe an actual crossing 'seam.' In this regard the fact that both classes of solutions can be obtained from the same set of equations is particularly convenient. Although not discussed in this presentation, it is relevant to note that the role of an avoided-crossing seam, unrelated to an actual surface crossing, in the nonadiabatic reactive quenching process

\[ \text{Na}(^2P) + \text{HCl} \rightarrow \text{NaCl} + \text{H}(^2S) \]

has recently been studied using both the \textit{ab initio} techniques discussed in this work as well as the more empirical optimized diatomics-in-molecules (DIM) approach.

\section{II. THEORY}

In an electronically nonadiabatic process the rovibronic wavefunction can be expanded in a basis of Born Oppenheimer electronic states, that is the total wavefunction for the system has the form

\begin{equation}
\Psi_{\ell}(r, R) = \sum_{l, k} \Psi_{l}^\ell(r; R) \chi_{k}^\ell(R) \beta_{kl}^L
\end{equation}

\begin{equation}
= \sum_{l} \Psi_{l}^\ell(r; R) \chi_{\ell,L}^L(R),
\end{equation}
where $\mathbf{R}$ denotes the nuclear degrees of freedom and $r$ denotes the electronic degrees of freedom. Here $\Psi_i^e(r; \mathbf{R})$ is the electronic wavefunction and $\chi_{kI}^I(\mathbf{R})$ is the $K$th rovibronic wavefunction corresponding to the $I$th electronic potential energy surface. Equation 2.1 is valid for any electronic wavefunction that depends parametrically on nuclear coordinates. As a practical matter it is necessary to make a particular choice of $\Psi_i^e(r; \mathbf{R})$ in order to limit the size of the expansion in electronic states. In this work $\Psi_i^e(r; \mathbf{R})$ will be taken to be an adiabatic electronic state and denoted $\Psi_i(r; \mathbf{R})$. Thus, the electronic wavefunctions are eigenfunctions of nonrelativistic Born–Oppenheimer electronic hamiltonian,

$$H^e(r; \mathbf{R})\Psi_i(r; \mathbf{R}) = E_i^e(\mathbf{R})\Psi_i(r; \mathbf{R}) \quad (2.2)$$

and the total hamiltonian in the space-fixed coordinate frame is

$$H^T = \sum_a \frac{-1}{2M_a} \nabla_a^2 + H^e \equiv T^N + H^e \quad (2.3)$$

Inserting Eq. (2.1) into the time-independent Schrödinger $H^T\Psi^T = E^T\Psi^T$ gives the following system of coupled equations for the rovibronic functions $\chi^{I-L}(\mathbf{R})$:

$$[T^N + E_i^e(\mathbf{R}) - K^{II}(\mathbf{R}) - E] \chi^{I-L}(\mathbf{R}) = \sum_{J\neq I} \left[ -H^{IJ}(\mathbf{R}) + \sum_a \left( \frac{1}{M_a} f_{J}^{IJ}(\mathbf{R}) \frac{\partial}{\partial R_a} \right) \right] \chi^{I-L}(\mathbf{R}), \quad (2.4)$$

where the state label $L$ on $\chi^{I-L}(\mathbf{R})$ has been suppressed and

$$K^{II}(\mathbf{R}) = \sum_a \frac{-1}{2M_a} k_{aa}^{II}(\mathbf{R}), \quad (2.5a)$$

$$H^{II}(\mathbf{R}) = \sum_a \frac{-1}{2M_a} h_{aa}^{II}(\mathbf{R}), \quad (2.5b)$$

$$f_{J}^{IJ}(\mathbf{R}) = \left\langle \Psi_J(r; \mathbf{R}) \left| \frac{\partial}{\partial R_a} \Psi_J(r; \mathbf{R}) \right| r \right\rangle, \quad (2.6)$$

$$h_{J}^{IJ}(\mathbf{R}) = \left\langle \Psi_J(r; \mathbf{R}) \left| \frac{\partial^2}{\partial R_a \partial R_b} \Psi_J(r; \mathbf{R}) \right| r \right\rangle, \quad (2.7a)$$

$$k_{J}^{IJ}(\mathbf{R}) = \left\langle \frac{\partial}{\partial R_a} \Psi_J(r; \mathbf{R}) \left| \frac{\partial}{\partial R_b} \Psi_J(r; \mathbf{R}) \right| r \right\rangle. \quad (2.7b)$$
and the subscript $r$ on the matrix elements in Eqs. (2.5)–(2.7) denotes integration over all electronic coordinates. Thus, the basic matrix elements that couple adiabatic electronic states are $f_{\beta}^{J}(\mathbf{R})$ and $h_{\alpha\beta}^{J}(\mathbf{R})$. The term $-K''(\mathbf{R})$ is referred to as the adiabatic correction or the Born–Oppenheimer diagonal correction. From Eqs. (2.4) and (2.7) it is seen that $K''(\mathbf{R})$, which is a linear combination of the $k_{\alpha\beta}^{J}(\mathbf{R})$, gives rise to mass-dependent corrections to the Born–Oppenheimer potential energy surface. Note that the $k_{\alpha\beta}^{J}(\mathbf{R})$ and $h_{\alpha\beta}^{J}(\mathbf{R})$ are related as follows:

$$\frac{\partial}{\partial R_{\alpha}} f_{\beta}^{J}(\mathbf{R}) = k_{\alpha\beta}^{J}(\mathbf{R}) + h_{\alpha\beta}^{J}(\mathbf{R}). \quad (2.8)$$

This equation will provide the basis for a procedure discussed in Section II C for the evaluation of $h_{\alpha\beta}^{J}(\mathbf{R})$ using only analytic first-derivative techniques. Note, too, that in the diatomic case Romelt$^{74}$ has discussed a reformulation of the dynamical problem [Eq. (2.4)] in which $k_{\alpha\beta}^{J}(\mathbf{R})$ completely replaces $h_{\alpha\beta}^{J}(\mathbf{R})$ in the coupled electronic state equations.

The adiabatic wavefunctions considered in this chapter are multireference configuration-interaction wavefunctions, $\Psi_{J}(\mathbf{r}; \mathbf{R})$, which are given as finite (but large, on the order of $10^{4}$–$10^{6}$ terms) expansion in terms of configuration-state functions (CSFs):$^{41}$

$$\Psi_{J}(\mathbf{r}; \mathbf{R}) = \sum_{\lambda} C_{\lambda}^{J}(\mathbf{R}) \psi_{\lambda}(\mathbf{r}; \mathbf{R}), \quad (2.9)$$

where the CSF, $\psi_{\lambda}(\mathbf{r}; \mathbf{R})$, is a linear combination of Slater determinants with the appropriate spin and spatial symmetry. Inserting Eq. (2.9) into the electronic Schrödinger equation, Eq. (2.2), gives the matrix eigenvalue equation, the CI problem

$$\mathbf{H}C^{J}(\mathbf{R}) = E^{J}(\mathbf{R})C^{J}(\mathbf{R}). \quad (2.10)$$

Here the adiabatic electronic energy $E^{J}(\mathbf{R})$ in Eq. (2.2) determined from CI wavefunctions is denoted $E^{J}(\mathbf{R})$.

The molecular orbitals $\phi_{i}(\mathbf{r}; \mathbf{R})$ used to build $\psi_{\lambda}(\mathbf{r}; \mathbf{R})$ are in turn constructed from a linear combination of atomic orbitals $\chi_{i}(\mathbf{r}; \mathbf{R})$:

$$\phi_{i}(\mathbf{r}; \mathbf{R}) = \sum_{p} \tau_{pi}(\mathbf{R}) \chi_{p}(\mathbf{r}; \mathbf{R}). \quad (2.11)$$

Here and throughout this chapter the subscripts $i, j, k, l, m$ and $n$ will be used to denote molecular orbitals, and $p, q, r, s$ and $t$ will be used to label atomic orbitals.
To facilitate the evaluation of the nonadiabatic coupling matrix elements, we employ a common set of orthonormal molecular orbitals in the CSF expansion for each state. Since the use of a common set of orthonormal orbitals permits us to assure state orthogonality at the CI level, it is also key to the determination of the actual crossing seam between two states of the SAME symmetry discussed in Sections II E and III B. The common set of orthonormal molecular orbitals is determined from a quadratically convergent state-averaged MCSCF (SA-MCSCF) procedure. Although a discussion of the details of the SA-MCSCF procedure is deferred to later in the development, it is significant to note that in a well-designed calculation the quantities of interest should not be sensitive to the details of the state averaging scheme, or the reference (MCSCF) space, used in developing the CI wavefunctions. The weighting factors for the states [see Eq. (2.45)] and reference space used in the SA-MCSCF procedure should yield a multireference CI wavefunction of equivalent quality to that which would be obtained from a reliable multireference CI wavefunction based on orbitals optimized for an individual state. When it is not computationally tractable to verify or guarantee that this situation obtains, the viability of the wavefunction description will be considered by reference to the available experimental data.

A. Evaluation of the First-Derivative Nonadiabatic Coupling Matrix Elements and Energy Gradients: A Unified Approach

Differentiation of the CI wavefunction defined in Eq. (2.9) gives

$$\frac{\partial}{\partial R_a} \Psi_I(r; R) = \sum_\lambda \left[ \left( \frac{\partial}{\partial R_a} C_\lambda^I(R) \right) \psi_\lambda(r; R) + C_\lambda^J(R) \left( \frac{\partial}{\partial R_a} \psi_\lambda(r; R) \right) \right]. \quad (2.12)$$

Thus, the first derivative nonadiabatic coupling matrix element consists of two terms

$$f^{IJ}_a(R) = C^I f_a^{IJ}(R) + \text{CSF} f_a^{IJ}(R) \quad (2.13)$$

where the CI contribution is given by

$$C^I f_a^{IJ}(R) = \sum_\lambda C_\lambda^I(R) \left( \frac{\partial}{\partial R_a} C_\lambda^I(R) \right) \quad (2.14)$$

and the CSF contribution has the form

$$\text{CSF} f_a^{IJ}(R) = \sum_{\lambda, \mu} C_\lambda^I(R) \left( \psi_\lambda(r; R) \right| \frac{\partial}{\partial R_a} \psi_\mu(r; R) \right) \psi_\mu(R). \quad (2.15)$$
From Eq. (2.14) it would appear that the derivative of the CI coefficients \( \partial C'(R)/\partial R_a \equiv V'_s(R) \) would be required to evaluate the CI contribution to \( f'_s(R) \). However, this is in fact not the case since only the projection onto the state \( \Psi_s(R) \) is actually required. Equation (2.14) for \( f'_s(R) \) can be recast in a form similar to that of an energy gradient \( E'_s(R) \equiv \partial E'(R)/\partial R_a \). In the following discussion the first derivative of the CI energy with respect to a nuclear displacement \( R_a \) will be referred to as the CI gradient. The transformation of Eq. (2.14) to a form that obviates the explicit determination of \( V'_s(R) \) is key to the efficient use of analytic gradient techniques in the evaluation of \( f'_s(R) \) and provides the basis for the unified approach to the evaluation of the energy gradients, nonadiabatic coupling matrix elements, and energy difference gradients noted in the Introduction.

The manipulation of Eq. (2.14) begins with consideration of the coupled-perturbed CI (CP-CI) equations, which provide a formal expression for the derivative of the CI coefficients \( V'_s(R) \). This system of linear equations is obtained by differentiating Eq. (2.10) to give

\[
\frac{\partial}{\partial R_a} \left[ HC'(R) - E'(R)C'(R) \right] = 0
\]  
(2.16)

so that

\[
\left[ H - E'(R) \right] \frac{\partial}{\partial R_a} C'(R) = - \left[ \frac{\partial}{\partial R_a} \left[ H - E'(R) \right] \right] C'(R).
\]  
(2.17)

Taking the dot product of Eq. (2.17) with \( C'(R) \) gives

\[
f'_s(R) \equiv C'(R)^\dagger \frac{\partial}{\partial R_a} C'(R)
\]  
(2.18)

\[
= \left[ E'(R) - E'(R) \right]^{-1} C'(R)^\dagger \frac{\partial H}{\partial R_a} C'(R).
\]  
(2.19)

Note that Eq. (2.19) is not the Hellmann–Feynman theorem to which it bears a formal resemblance, since in Eq. (2.19) it is not the hamiltonian operator \( H'(r; R) \) but rather the hamiltonian matrix \( H \) that is being differentiated.

This expression will be shown to have the same form as a CI gradient but with transition density matrices replacing standard density matrices in the appropriate expressions. To see this note that the CI vectors, \( C'(R) \), are constrained to be orthonormal at all geometries, that is,

\[
C'(R)^\dagger C'(R) - \delta_{IJ} = 0.
\]  
(2.20)
Taking the dot product of Eq. (2.17) with $C'_i(R)$ and using Eq. (2.20) yields

$$E'_a(R) \equiv \frac{\partial E'_i(R)}{\partial R_a} = C'_i(R) \frac{\partial H}{\partial R_a} C'_i(R),$$

(2.21)

which has the same form as Eq. (2.19).

To demonstrate explicitly the connection between Eqs. (2.19) and (2.21) it is convenient to express the CI energy in terms of one- and two-electron integrals, CI coefficients, and coupling constants:

$$E'_i(R) \equiv C'_i(R) \frac{HC'_i(R)}{C'_i(R)}$$

(2.22a)

$$= \sum_{\lambda,\mu} C'_\lambda(R) H_{\lambda\mu} C'_\mu(R)$$

(2.22b)

$$= \sum_{\lambda,\mu} \left[ \sum_{i,j} C'_\lambda h_{ij} C'_\mu \right] + \sum_{i,j,k,l} g_{ijkl} \tilde{K}_{ijkl} C'_\mu \] + V_N$$

(2.22c)

$$= \sum_{i,j} h_{ij} C'_\lambda C'_\mu + \sum_{k,l} g_{ijkl} \tilde{K}_{ijkl} C'_\mu + V_N$$

(2.22d)

$$= \sum_{i,j} h_{ij} \psi_j^I + \sum_{i,j,k,l} g_{ijkl} \Gamma_{ijkl}^I + V_N$$

(2.22e)

where $h_{ij}$ and $g_{ijkl}$ are, respectively, the one-electron integrals and two-electron integrals in the molecular-orbital (MO) basis, $V_N$ is the nuclear repulsion energy, $\tilde{K}_{ij}$ and $\tilde{K}_{ijkl}$ are coupling constants used to construct the hamiltonian matrix element $H_{\lambda\mu}(R) = \langle \psi_j(r; R) | H^* \psi_i(r; R) \rangle$, from the MO integrals, and $\psi_j^I$ and $\Gamma_{ijkl}^I$ are one-electron and two-electron density matrices, respectively, again in the MO basis.

Thus, from Eqs (2.21) and (2.22), $E'_a(R)$ is given by

$$\frac{\partial E'_i(R)}{\partial R_a} = \sum_{i,j} \left( \frac{\partial}{\partial R_a} h_{ij} \right) \psi_j^I + \sum_{i,j,k,l} \left( \frac{\partial}{\partial R_a} g_{ijkl} \right) \Gamma_{ijkl}^I + \frac{\partial V_N}{\partial R_a}$$

(2.23)

where $\partial V_N/\partial R_a$ is the derivative of the nuclear repulsion energy. Similarly from eq. (2.19) the first derivative nonadiabatic coupling term is given by

$$\frac{\partial}{\partial R_a} \left\{ \sum_{i,j} \left( \frac{\partial}{\partial R_a} h_{ij} \right) \psi_j^I + \sum_{i,j,k,l} \left( \frac{\partial}{\partial R_a} g_{ijkl} \right) \Gamma_{ijkl}^I \right\}$$

(2.24)

where $\Delta E_{IJ}(R) \equiv E'_i(R) - E'_I(R)$ and transition density matrix elements $\psi_j^I$ and $\Gamma_{ijkl}^I$ occur in place density matrix elements, $\psi_j^I$ and $\Gamma_{ijkl}^I$, which appear in the energy gradient expression [Eq. (2.23)].
Since the molecular orbitals are linear combinations of atomic orbitals [see Eq. (2.11)], the derivatives of the molecular orbitals involve two terms:

$$\frac{\partial}{\partial R_x} \phi_i(r; R) = \sum_p \left[ \left( \frac{\partial}{\partial R_x} \tau_{pi}(R) \right) \chi_p(r; R) + \tau_{pi}(R) \left( \frac{\partial}{\partial R_x} \chi_p(r; R) \right) \right] \tag{2.25}$$

where the derivative of $\tau(R)$, the MO coefficients, is defined as follows

$$\frac{\partial}{\partial R_x} \tau_{pi}(R) = \sum_j \tau_{pj}(R) U^*_j(R)$$

$$\equiv \tau^*_p(R). \tag{2.26a}$$

Thus the derivative of $h$ and $g$, the MO integrals, also involve two terms

$$\frac{\partial}{\partial R_x} h_{ij}(R) = h^*_i(R) + h^*_j(R) \tag{2.27a}$$

$$\frac{\partial}{\partial R_x} g_{ijkl}(R) = g^*_ijkl(R) + g^*_ijkl(R). \tag{2.27b}$$

where the superscript $\alpha$ on a quantity in the MO basis indicates that the quantity in question is constructed from the derivative of the atomic integrals (here $h^*_pq$ and $g^*_pqrs$) so that we have

$$h_{ij} = \sum_{p,q} \tau_{pi} h^*_pq \tau_{qj} \tag{2.28a}$$

$$g_{ijkl} = \sum_{p,q,r,s} \tau_{pi} \tau_{qj} g^*_pqrs \tau_{rk} \tau_{sl} \tag{2.28b}$$

while the corresponding derivative quantities are given by

$$h^*_{ij} = \sum_{p,q} \tau_{pi} h^*_pq \tau_{qj} \tag{2.29a}$$

$$g^*_{ijkl} = \sum_{p,q,r,s} \tau_{pi} \tau_{qj} g^*_pqrs \tau_{rk} \tau_{sl} \tag{2.29b}$$

The remaining terms, $h^\alpha_{ij}$ and $g^\alpha_{ijkl}$ are constructed from $U^\alpha(R)$ in the following manner:

$$h^\alpha_{ij} = \sum_m \left[ U^\alpha_{mi} h_{mj} \right] + h_{im} U^*_m \tag{2.30a}$$
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\[ g_{ijkl}^{\nu} = \sum_{m} \left[ U_{mi}^a g_{mjk} + U_{mj}^a g_{imk} + g_{ijm} U_{mk}^a + g_{ijm} U_{ml}^a \right]. \] (2.30b)

The CI gradient then can be expressed as follows,

\[ \frac{\partial E_i^s}{\partial R_z} = E_i^s + \sum_{i,j} \frac{\partial E_i^s}{\partial U_{ij}} \frac{\partial U_{ij}}{\partial R_z} + \frac{\partial V_N}{\partial R_z} \] (2.31a)

\[ = \sum_{\lambda,\mu} \left[ C_i^\lambda H_{\lambda \mu}^s C_i^\mu + C_i^\lambda H_{\lambda \mu}^{\nu} C_i^\mu \right] + \frac{\partial V_N}{\partial R_z} \] (2.31b)

\[ \equiv E_i^s + E_i^{\nu s} + \frac{\partial V_N}{\partial R_z} \] (2.31c)

where

\[ E_i^s = \sum_{p,q} \gamma_{pq}^s h_{pq}^s + \sum_{p,q,r,s} \Gamma_{pqrs}^s g_{pqrs}^s \] (2.32a)

\[ E_i^{\nu s} = \sum_{i,j} L_{ij}^{\nu s} U_{ij}^s. \] (2.32b)

In Eq. (2.32a) the density matrix elements have been transformed to the atomic-orbital (AO) basis in order to avoid transforming the AO derivative integrals to the MO basis for each degree of freedom. In Eq. (2.32b) the Lagrangian, \(^1\) \( L_{ij}^{\nu s} \), has been introduced where

\[ L_{mi}^{\nu s} = \frac{\partial E_i^s}{\partial U_{mi}} \] (2.33a)

\[ = 2 \sum_j \gamma_{ij}^{s n} h_{mj} + 4 \sum_{j,k,l} \Gamma_{ijkl}^{n s} g_{mkl}. \] (2.33b)

In an analogous manner Eq. (2.24) gives the CI contribution to the first derivative nonadiabatic coupling matrix element as

\[ C_i^{\nu s} = \Delta E_j^{-1} \left[ f_{IJ}^z \right] \] (2.31c')

where

\[ f_{IJ}^s = \sum_{p,q} \gamma_{pq}^s h_{pq}^s + \sum_{p,q,r,s} \Gamma_{pqrs}^s g_{pqrs}^s, \] (2.32a')

\[ f_{IJ}^{\nu s} = \sum_{i,j} L_{ij}^{\nu s} U_{ij}^s. \] (2.32b')
and the transition Lagrangian is given by

\[ L_{m_i}^{j_1} = 2 \sum_j \gamma_j^{ij} h_{mj} + 4 \sum_{i,j,k,l} \Gamma_{ijkl} g_{mijkl} \]  

(2.33b')

Equations (2.31c) and (2.31c') provide the unified approach for the evaluation of CI gradients (Eq. (2.31)] and the CI contribution to the first-order nonadiabatic coupling elements [Eq. (2.31c')].

The evaluation of Eqs. (2.32b) and (2.32b') can be further simplified by avoiding the explicit determination of \( U^a(R) \). However, discussion of this procedure is deferred until after an expression for the CSF contribution to the first derivative nonadiabatic coupling matrix elements has been developed as the same approach can also be employed to reduce the computational effort needed to construct this term.

We now consider the CSF contribution to the first derivative nonadiabatic coupling matrix element. A CSF, \( \psi_{\lambda} \), is an antisymmetric symmetry adapted sum of products of molecular orbitals:

\[ \psi_{\lambda}(r; R) \equiv P^a \prod_i \phi_{\lambda,i}(r_i; R), \]  

(2.34)

so that its derivative has the form

\[ \frac{\partial}{\partial R_\alpha} \psi_{\lambda}(r; R) = \sum_j P^a \prod_{i \neq j} \phi_{\lambda,i}(r_i) \frac{\partial}{\partial R_\alpha} \phi_{\lambda,j}(r_j). \]  

(2.35)

Thus, the overlap between a CSF and the derivative of a CSF can be represented as the matrix element of an one-electron operator,

\[ \left\langle \psi_{\lambda}(r; R) \left| \frac{\partial}{\partial R_\alpha} \psi_{\mu}(r; R) \right. \right\rangle \right|_r = \left\langle \psi_{\lambda}(r; R) \right| D_{\alpha} \psi_{\mu}(r; R) \right\rangle \]  

(2.36)

where

\[ D_{\alpha}(r) = \sum_i d_{\alpha}(r_i) \]  

(2.37)

and

\[ d_{\alpha}(r) \phi_k(r; R) \equiv \frac{\partial}{\partial R_\alpha} \phi_k(r; R). \]  

(2.38)

The matrix element of a one-electron operator can be obtained as the trace
of the one-electron density with the appropriate integrals, thus

$$\text{CSF} f_{ij}^{\text{J}}(\mathbf{R}) = \sum_{i,j} \gamma_{ij}^{\text{J}} d_{ij}^\sigma,$$

(2.39)

where $\gamma_{ij}^{\text{J}}$ is the square one-electron transition density matrix and $d_{ij}^\sigma(\mathbf{R})$ is an antisymmetric matrix with matrix elements

$$d_{ij}^\sigma(\mathbf{R}) = \left\langle \phi_i(r; \mathbf{R}) \frac{\partial}{\partial R_a} \phi_j(r; \mathbf{R}) \right\rangle_r.$$

(2.40)

The antisymmetry of $d_{ij}^\sigma(\mathbf{R})$ is a consequence of the orthonormality of the molecular orbitals,

$$\left\langle \phi_i(r; \mathbf{R}) | \phi_j(r; \mathbf{R}) \right\rangle_r = \delta_{ij}.$$

(2.41)

Here the adjective "square" has been emphasized in reference to the one-particle transition density matrix. The one-particle transition density matrix is in general not symmetric, that is, the full or square matrix must be retained. However, in most electronic structure applications the associated one-electron integrals, for example $h$, are symmetric, permitting the off-diagonal density matrix element to be stored in folded or triangular form. Since $d_{ij}^\sigma$ is not symmetric, it is necessary to construct and store the transition density matrix in its unfolded or square form.

From Eqs. (2.25) and (2.26) $d_{ij}^\sigma$ is comprised of two terms:

$$d_{ij}^\sigma(\mathbf{R}) = \sum_{p,q} \tau_{pi}(\mathbf{R}) \left\langle \chi_p(r; \mathbf{R}) \frac{\partial}{\partial R_a} \chi_q(r; \mathbf{R}) \right\rangle_r \tau_{qj}(\mathbf{R}) + \sum_m \left\langle \phi_i(r; \mathbf{R}) | \phi_m(r; \mathbf{R}) \right\rangle_r U_{mj}^\sigma,$$

(2.42a)

so that

$$\text{CSF} f_{ij}^{\text{J}}(\mathbf{R}) = \sum_{i,j} \gamma_{ij}^{\text{J}}(\sigma_{ij}^\sigma + U_{ij}^\sigma).$$

(2.43)

Thus, the CSF contribution to the first derivative nonadiabatic coupling matrix element requires only two new quantities, $d_{ij}^\sigma$ and the square $\gamma_{ij}^{\text{J}}$, which do not appear in the formulas for a CI gradient.

Combining Eqs. (2.31c') and (2.43) we obtain the following expression for the first-order nonadiabatic coupling matrix element:

$$f_{ij}^{\text{J}}(\mathbf{R}) = \Delta E_{ij}^{-1} \left( \sum_{p,q} \gamma_{pq}^\text{J} h_{pq}^\sigma + \sum_{p,q,r,s} \Gamma_{pqrs}^\text{J} \sigma_{pqrs}^\sigma \right) + \sum_{i,j} \left[ (\Delta E_{ij}^{-1} L_{ij}^\text{J} + \gamma_{ij}^{\text{J}}) U_{ij}^\sigma + \gamma_{ij}^{\text{J}} \sigma_{ij}^\sigma \right].$$

(2.44a)