

On the quasiadiabatic description of the dynamics of electronically adiabatic chemical reactions*

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We present a description and analysis of electronically adiabatic chemical reactions in terms of nonadiabatic basis sets. By using an orthogonal transformation we separate the Hamiltonian into reactive and nonreactive parts. Explicit expressions are given for the reactive part of the interaction and some conditions are discussed for expressing it in terms of Franck-Condon type nuclear overlap. Next we derive closed formal expressions for all the various cross sections (elastic, inelastic, and reactive) in a chemically reactive system. With the present approach we make a distinction between the Franck-Condon and first-order approximation in the reactive interaction. Closed expressions for all the cross sections in terms of finite-size matrices are derived by making use of the K matrix formalism. These expressions enable us to use the Franck-Condon approximation and at the same time retain reactive interactions to infinite order.

I. INTRODUCTION

The theoretical treatment of reactive molecular collisions is considerably simplified by the possibility of "switching off" the reactive part of the Hamiltonian,¹ solving two (or more) separate nonreactive collision problems (reactantlike and productlike), and then using the formalism of scattering by two potentials^{2,3} to combine these solutions and obtain the cross section for the reactive process.

The question now arises what convenient basis set to choose for the description of reactive molecular scattering problems.

Suppose we have solved the molecular electronic problem in the Born-Oppenheimer (BO) approximation. If the reactants and products belong to different electronic BO states (i. e., a nonadiabatic reaction) then the non-BO terms in the Hamiltonian ($H - H_{BO}$) serve as the *reactive part* of the interaction and the above mentioned procedure can be carried out.⁴

In the case where the reactants and products belong to the same BO electronic state but there are other closely lying electronic states (e. g., the avoided-crossing type problem), we may use a different basis set (adiabatic,^{5,6} crude-adiabatic,⁷ etc.) which can convert the adiabatic to a nonadiabatic problem and enable us to handle the reactive part of the interaction separately.

Suppose, however, that the reaction has a BO surface ϵ_a belonging to the electronic state $|a_g\rangle$ which is well separated from all other surfaces $|b_g\rangle, |c_g\rangle, \dots$, etc. Using the BO basis set, we find the electronic and nuclear motions in this case factorized, and we can solve for a multichannel scattering wavefunction on the ϵ_a surface, ignoring the contribution of all other surfaces. A possible way in such cases for switching off the reactive part of the Hamiltonian is to add one (or more) repulsive potentials, thus defining new nonreactive scattering problems. The solutions to these problems can then be combined to give an exact formal expression for the scattering amplitudes.⁷ Such a procedure is convenient when the reactive part is treated to first order. However, since the initial and final nuclear wavefunctions are not orthogonal (solutions of different Hamiltonians), this procedure does not provide us with a convenient

complete orthonormal basis set for nuclear motion. This makes the treatments in higher orders difficult; this nonorthogonality does not allow for a complete separation of the interactions into reactive and nonreactive, as the "reactive" part also contributes to scattering within each rearrangement channel. These difficulties can be removed by including the electronic degrees of freedom in the Hamiltonian, even for purely adiabatic chemical reactions.^{6,8} Recently, the formalism was extended and applied to various systems; there were derived expressions for the reaction cross section which include explicitly the electronic wavefunctions of the molecule.⁹

The purpose of this work is to demonstrate the following: (1) Any adiabatic reaction can be treated as nonadiabatic by using an orthogonal transformation of the electronic states. This transformation (which is not unique) defies a new electronic representation (the quasiadiabatic, QA, electronic states).

(2) Due to the orthogonality of the QA states so obtained we can separate the Hamiltonian exactly into reactive (H_R) and nonreactive interactions. We then solve separately two nonreactive problems and combine them to get all the cross sections for the various possible processes (reactive, inelastic, and elastic scattering). Comparison with the two potential formalism¹⁻³ is made.

(3) The proposed method for handling adiabatic reactions does not require any additional information regarding the molecular electronic states, i. e., we need only know the ground adiabatic surface.

(4) Since the transformation (1) is not unique, we can try to choose it so that the contribution to the matrix elements of H_R will come from a very limited range of nuclear configurations. If, in addition, the reactive interaction H_R turns out to be slowly varying in that nuclear configuration domain, we may invoke a Franck-Condon (FC) type approximation and assume that the matrix elements of H_R are proportional to some appropriate nuclear overlap. We give explicit expressions for H_R and discuss the validity of the FC type expressions.⁹⁻¹³

(5) By making use of the K matrix formalism^{2,3} we derive general expressions in terms of finite-size matrices

TABLE I. Definition of the Born–Oppenheimer (BO) Hamiltonian and coupling terms.

Term		Remarks
$H = H_{\text{BO}} + H'_{\text{BO}}$	Total-molecular Hamiltonian	H_{BO} —BO (adiabatic) Hamiltonian H'_{BO} —nonadiabatic coupling
$H_{\text{BO}} = \sum_j j_e\rangle H_{\text{BO}}^{(j)} \langle j_e $	BO Hamiltonian with eigenstates	$ j_e\rangle$ —electronic states
$ j_e \omega_j^{\pm}\rangle = j_e\rangle j\omega_j^{\pm}\rangle$ $j = a, b, c$		$ j\omega_j^{\pm}\rangle$ —incoming (outgoing) nuclear states ω_j —all nuclear quantum numbers
$H'_{\text{BO}} \equiv H - H_{\text{BO}} = T' + T''$	Nonadiabatic coupling	
$T'_{ij} = -\sum_k \frac{2\hbar^2}{2M_k} \langle i_e \frac{\partial}{\partial R_k} j_e \rangle_r \cdot \frac{\partial}{\partial R_k}$		The index k extends over all nuclear coordinates (R_k). M_k is the mass associated with R_k . $\langle \rangle_r$ denotes integration over electronic coordinates
$T''_{ij} = -\sum_k \frac{\hbar^2}{2M_k} \langle i_e \frac{\partial^2}{\partial R_k^2} j_e \rangle_r$		
$H_{\text{BO}}^{(j)} = T_R + \epsilon_j(\mathbf{R}) + T'_{jj}(\mathbf{R})$	BO nuclear Hamiltonian in the j electronic state	T_R is the nuclear kinetic energy. $\epsilon_j(\mathbf{R})$ is the adiabatic surface of the $ j_e\rangle$ state.
$\epsilon_j(\mathbf{R}) = \langle j_e H - T_R j_e \rangle$	Adiabatic surface of the $ j_e\rangle$ state.	

for the various cross sections (i. e., for elastic, inelastic, and reactive processes) appearing in a chemically reactive system.

(6) In conventional spectroscopy, where the FC approximation is usually made, a first order (FO) treatment in the electromagnetic interaction is sufficient so that the FC approximation is often combined with a FO calculation to obtain a FOFC expression for the various cross sections. In this spirit, FOFC approximations have been used for chemical reactions.^{10–13} This may of course not be sufficient. Our expressions, especially with the K matrix,^{2,3} enable us to discuss separately the validity of the FC and the FO approximations and suggest ways of testing different choices of QA surfaces.

II. THE QUASIADIABATIC TRANSFORMATION

The total molecular Hamiltonian (H) is written in the form

$$H = H_{\text{BO}} + H'_{\text{BO}}, \quad (1)$$

where H_{BO} is the Hamiltonian in the Born–Oppenheimer (BO) approximation¹⁴ and H'_{BO} is the nonadiabatic coupling (nuclear kinetic energy, spin orbit coupling, etc.). The eigenstates of $H_{\text{BO}} |j_e \omega_j\rangle$ are in the form of a product of electronic $|j_e\rangle$ and nuclear $|j\omega\rangle$ states

$$|j_e \omega\rangle \equiv |j_e\rangle |j\omega\rangle, \quad (2)$$

where $j = a, b, c, \dots$ is the quantum number specifying the electronic states, whereas ω stands for all the nuclear quantum numbers. In Table I we present and define the various terms in the Hamiltonian and introduce the notation.

We now invoke the following conditions:

(1) The ground electronic state $|a_e\rangle$ is well separated in energy at all nuclear configurations from all other electronic states $|b_e\rangle, |c_e\rangle, \dots$.

(2) $|a_e\rangle$ has n different asymptotic rearrangement forms of interest corresponding to different nuclear coordinates approaching infinity. We thus define the following n different forms for partitioning $H_{\text{BO}}^{(a)}$:

$$H_{\text{BO}}^{(a)} = \hat{H}_\alpha^{(a)} + V_\alpha^{(a)} = \hat{H}_\beta^{(a)} + V_\beta^{(a)} = \dots, \quad (3)$$

where $\hat{H}_i^{(a)}$ represents the zeroth order Hamiltonian for the noninteracting fragments in the i th rearrangement configuration ($R_i \rightarrow \infty$) and

$$V_i^{(a)} \equiv H_{\text{BO}}^{(a)} - \hat{H}_i^{(a)}, \quad i = \alpha, \beta, \gamma, \dots \quad (4)$$

For the sake of simplicity we restrict the analysis for now to the two-channel problem with channels α and β . Later we suggest a method for extending the formalism to the general case.

(3) We define a unitary linear transformation on the lowest two electronic states, i. e.,

$$\begin{pmatrix} |\alpha_e\rangle \\ |\beta_e\rangle \end{pmatrix} = U(\mathbf{R}) \begin{pmatrix} |a_e\rangle \\ |b_e\rangle \end{pmatrix}, \quad (5)$$

where

$$U(\mathbf{R}) = \begin{pmatrix} \sin\eta(\mathbf{R}) & \cos\eta(\mathbf{R}) \\ -\cos\eta(\mathbf{R}) & \sin\eta(\mathbf{R}) \end{pmatrix} \quad (6)$$

is a general unitary 2×2 matrix, and \mathbf{R} denotes all the nuclear coordinates. This transformation results in two orthogonal quasiadiabatic states $|\alpha_e\rangle, |\beta_e\rangle$.

We require that $|\alpha_e\rangle$ ($|\beta_e\rangle$) reduces to $|a_e\rangle$ as $R_\alpha \rightarrow \infty$ ($R_\beta \rightarrow \infty$), i. e.,

$$\lim_{R_i \rightarrow \infty} \langle i_e | \alpha_e \rangle = 1, \quad i = \alpha, \beta. \quad (7)$$

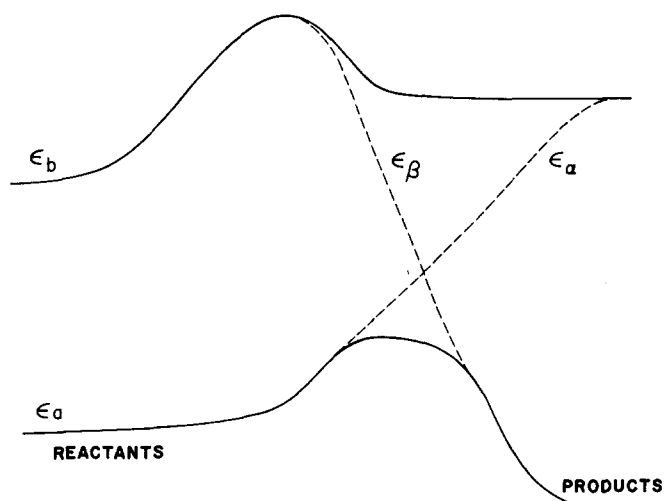


FIG. 1. Quasiadiabatic surfaces ϵ_α and ϵ_β constructed from the adiabatic surfaces ϵ_a and ϵ_b .

As a result of the conditions (7) and the unitarity of U we have the i th state orthogonal to $|\alpha_e\rangle$ as $R_j \rightarrow \infty$ ($j \neq i$)

$$\lim_{R_j \rightarrow \infty} \langle i_e | \alpha_e \rangle = \delta_{i,j}, \quad i, j = \alpha, \beta, \quad i \neq j. \quad (8)$$

These requirements are satisfied if we choose η such that

$$\begin{pmatrix} PHP & QVP \\ PVQ & QHQ \end{pmatrix} \equiv \begin{pmatrix} |\alpha_e\rangle [T_R + \epsilon_{\alpha\alpha}(\mathbf{R}) + T''_{\alpha\alpha}(\mathbf{R})] \langle \alpha_e| & |\beta_e\rangle (T'_{\beta\alpha} + T''_{\beta\alpha} + \epsilon_{\beta\alpha}) \langle \alpha_e| \\ |\alpha_e\rangle [T'_{\beta\alpha} + T''_{\beta\alpha} + \epsilon_{\beta\alpha}] \langle \beta_e| & |\beta_e\rangle [T_R + \epsilon_{\beta\beta}(\mathbf{R}) + T''_{\beta\beta}(\mathbf{R})] \langle \beta_e| \end{pmatrix}, \quad (11)$$

where we have defined the electronic projection operators

$$P = |\alpha_e\rangle \langle \alpha_e|, \quad (12)$$

$$Q = |\beta_e\rangle \langle \beta_e|.$$

The various terms appearing in Eq. (11) are defined in Table II.

We now turn to the solution of the reactive scattering problem defined by the Hamiltonian H , given that we start in channel $|\alpha_e\rangle$. For this purpose we partition the molecular Hamiltonian into

$$H = H_0 + V, \quad (13)$$

where

$$H_0 \equiv |\alpha_e\rangle \hat{H}_\alpha^{(a)} \langle \alpha_e| + |\beta_e\rangle \hat{H}_\beta^{(a)} \langle \beta_e| \quad (14)$$

and

$$V \equiv H - H_0 = PVP + QVQ + QVP + PVQ. \quad (15)$$

Comparison of Eq. (3) with (13)–(15) shows the identifications

$$\begin{aligned} PVQ &= PHQ, \\ QVP &= QHP, \\ PVP &= PHP - \hat{H}_\alpha^{(a)}, \\ QVQ &= QHQ - \hat{H}_\beta^{(a)}. \end{aligned} \quad (16)$$

$$\eta \xrightarrow{R_\alpha \rightarrow \infty} 0, \quad (9)$$

$$\eta \xrightarrow{R_\beta \rightarrow \infty} \frac{\pi}{2}.$$

We thus have two new surfaces $\epsilon_\alpha, \epsilon_\beta$ (Fig. 1) which are given in terms of the adiabatic (ϵ_a, ϵ_b) surfaces as

$$\begin{aligned} \epsilon_\alpha(\mathbf{R}) &= \sin^2 \eta \epsilon_a + \cos^2 \eta \epsilon_b, \\ \epsilon_\beta(\mathbf{R}) &= \cos^2 \eta \epsilon_a + \sin^2 \eta \epsilon_b. \end{aligned} \quad (10)$$

The following points need to be stressed:

(1) Due to our condition (1) above, the nuclear kinetic energy terms T', T'' (Table I) in the BO representation contribute only corrections

$$O\left(\frac{T' + T''}{\epsilon_a - \epsilon_b}\right) \ll 1,$$

so that we can ignore them.

(2) The nature of the excited state adiabatic surface (ϵ_b) is expectedly unimportant for our adiabatic scattering problem as long as $\epsilon_b - \epsilon_a$ is sufficiently large.

Using condition (2) we are free to choose $\epsilon_\beta(\mathbf{R}), \eta(\mathbf{R})$. However, we choose the QA surfaces $\epsilon_\alpha(\mathbf{R})$ and $\epsilon_\beta(\mathbf{R})$ at will, and express the transformed Hamiltonian in terms of these surfaces. The Hamiltonian in the QA representation takes the form

Note that V and its various projections (16) may be expressed in terms of the QA surfaces $\epsilon_\alpha, \epsilon_\beta$, which we are free to choose for our convenience (see Table II).

TABLE II. The quasiadiabatic representation.

Term	
$H = H_{QA} + QHP + PHQ$	Total molecular Hamiltonian
$H_{QA} = \alpha_e\rangle H_{QA}^{(\alpha)} \langle \alpha_e + \beta_e\rangle H_{QA}^{(\beta)} \langle \beta_e \equiv PHP + QHQ$	Quasiadiabatic Hamiltonian
$H_{QA}^{(j)} = T_R + \epsilon_j(\mathbf{R}) + T_{jj}''(\mathbf{R}), \quad j = \alpha, \beta$	The quasiadiabatic surfaces $\epsilon_\alpha(\mathbf{R}), \epsilon_\beta(\mathbf{R})$ are chosen at will.
$\eta = \text{Arctan} \sqrt{\frac{\epsilon_\beta - \epsilon_a}{\epsilon_\alpha - \epsilon_a}}; \quad \sin^2 \eta = \frac{\epsilon_\beta - \epsilon_a}{\epsilon_\alpha + \epsilon_\beta - 2\epsilon_a}$	Transformation angle
$\cos^2 \eta = \frac{\epsilon_\alpha - \epsilon_a}{\epsilon_\alpha + \epsilon_\beta - 2\epsilon_a}$	
$H_R = PHQ + QHP$	Reactive part of the Hamiltonian
$QHP = T'_{\beta\alpha} + T''_{\beta\alpha} + \epsilon_{\beta\alpha}(\mathbf{R})$	
$PHQ = -T'_{\beta\alpha} - T''_{\beta\alpha} + \epsilon_{\beta\alpha}(\mathbf{R})$	
$\epsilon_{\beta\alpha} = \sqrt{(\epsilon_\alpha - \epsilon_a)(\epsilon_\beta - \epsilon_a)}$	
$T_{\alpha\alpha}'' = T_{\beta\beta}'' = \sum_k \frac{\hbar^2}{2M_k} \left(\frac{\partial \eta}{\partial R_k}\right)^2$	
$T_{\alpha\beta}'' = -T_{\beta\alpha}'' = -\sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2 \eta}{\partial R_k^2}$	
$T_{\alpha\beta}' = -T_{\beta\alpha}' = -\sum_k \frac{\hbar^2}{M_k} \frac{\partial \eta}{\partial R_k} \cdot \frac{\partial}{\partial R_k}$	

Note also that $PVQ + QVP$ form the reactive part of the Hamiltonian H_R .

III. PROJECTIONS OF THE T MATRIX

Due to the orthogonality of the various reactive channels $|j_e\rangle$ we evaluate the cross sections using the form for the T matrix^{2,3}

$$T = V + VGV, \quad (17)$$

where

$$G = (E - H + i\epsilon)^{-1} \quad (18)$$

and V is given in Eqs. (15) and (16). The nonreactive (elastic and inelastic) cross sections are given by the projection PTP , whereas the reactive cross sections are given by QTP .

Using some formal manipulations¹⁵ (Appendix A) we obtain the following expressions for the desired projections of T :

$$\langle \beta_e \omega_\beta | QTP | \alpha_e \omega_\alpha \rangle = \langle \beta_e \omega_\beta^- | Q\tilde{T}P | \alpha_e \omega_\alpha^+ \rangle \quad (19a)$$

and

$$\langle \alpha_e v_\alpha | PTP | \alpha_e \omega_\alpha \rangle = \langle \alpha_e v_\alpha | PVP | \alpha_e \omega_\alpha^+ \rangle + \langle \alpha_e v_\alpha^- | P\tilde{T}P | \alpha_e \omega_\alpha^+ \rangle, \quad (19b)$$

where $|j\omega_j^+\rangle$ ($|j\omega_j^-\rangle$) are the outgoing (incoming) states corresponding to the nonreactive scattering problem on the j th potential surface, i. e.,

$$| \alpha_e \omega_\alpha^+ \rangle = (P + \tilde{G}_P PVP) | \alpha_e \omega_\alpha \rangle = | \alpha_e \rangle | \alpha \omega_\alpha^+ \rangle, \quad (20)$$

$$\langle \beta_e \omega_\beta^- | = \langle \beta_e \omega_\beta | (Q + QVQ\tilde{G}_Q) = \langle \beta_e^- | \langle \beta \omega_\beta^- |,$$

with the definition

$$\tilde{G}_\xi = (E - \xi H \xi + i\epsilon)^{-1} \xi, \quad \xi = P, Q. \quad (21)$$

The operators $Q\tilde{T}P$, $P\tilde{T}P$ are given by

$$Q\tilde{T}P = QVP(P - \tilde{G}_P PVPQ\tilde{G}_Q QVP)^{-1} \quad (22a)$$

and

$$P\tilde{T}P = PVPQ\tilde{G}_Q QTP. \quad (22b)$$

Similar expressions were recently obtained for the problem of photodissociation, which has a formal analogy to the problem of reaction considered here.^{16,17} Note that the states $| \alpha \omega_\alpha^+ \rangle$ ($| \beta \omega_\beta^- \rangle$) form complete sets of nuclear states within the $| \alpha_e \rangle$ ($| \beta_e \rangle$) electronic states; thus, we may write

$$\hat{P} = \sum_{\omega_\alpha} | \alpha_e \omega_\alpha^+ \rangle \langle \alpha_e \omega_\alpha^+ |, \quad (23)$$

$$Q = \sum_{\omega_\beta} | \beta_e \omega_\beta^- \rangle \langle \beta_e \omega_\beta^- |,$$

and

$$\tilde{G}_\xi = \sum_{\omega_\xi} \frac{| \xi_e \omega_\xi^+ \rangle \langle \xi_e \omega_\xi^+ |}{E - E_{\xi\omega_\xi} + i\epsilon}. \quad (24)$$

The equations just presented require some comments:

(1) $| \alpha \omega_\alpha^+ \rangle$, $| \beta \omega_\beta^- \rangle$ are solutions of the nonreactive scattering problems and they properly include (to infinite order) the "initial" and "final" state interactions, respectively.

(2) QVP is the reactive part of the interaction. It can be expressed in terms of ϵ_α , ϵ_α' , and ϵ_β . Thus, Eqs. (19), together with the definitions in Table II, provide us with exact expressions for the T matrix without any further information about the adiabatic electronic states (apart from $\epsilon_\alpha + T_{aa}''$).

(3) Equations (19) may be used for expanding the T matrix in powers of QVP . The first term in Eq. (19b) is the direct nonreactive scattering (i. e., the scattering amplitude when $QVP=0$) and the second term represents the influence of the reactive term QVP on the nonreactive scattering cross sections.

IV. K MATRIX FORMALISM

The general expressions for the T matrix (19) is the starting point for expansions to different orders in the various coupling terms. Although the first order expressions in PVQ are relatively simple, the calculations to higher orders, even in the collinear case, are extremely difficult. The higher orders involve elements off the energy shell (principal parts) and if these are approximated the S matrix becomes nonunitary. The K matrix approach^{2,3} involves exact summation of contributions on the energy shell and yields a unitary S matrix at any stage of approximation. It has been successfully applied to the problems of inelastic molecular collisions¹⁸⁻²⁰ and photodissociation¹⁷ yielding significantly better results than ordinary distorted-wave calculations and has proved to be valuable both for qualitative and quantitative purposes. In the K matrix formalism,^{2,3} the T matrix (17) is rewritten in the form

$$T = K - i\pi K \delta(E - H_0) T, \quad (25)$$

where K satisfies the relation

$$K = V + V(PPG_0)K. \quad (26)$$

(Here PP comes from the Cauchy principal part.)

Any Hermitian approximation to K results in a unitary S matrix. In Appendix B we derive expressions for the projection of T in terms of the K matrix and the results are

$$QTP = \tilde{F}_Q QKP(P + \pi^2 \tilde{F}_P PKQ\tilde{F}_Q QKP)^{-1} \tilde{F}_P, \quad (27a)$$

$$PTP = PKP\tilde{F}_P - i\pi \tilde{F}_P PKQ\tilde{F}_Q QKP(P + \pi^2 \tilde{F}_P PKQ\tilde{F}_Q QKP)^{-1} \tilde{F}_P, \quad (27b)$$

where

$$\tilde{F}_\xi = [\xi + i\pi\delta(E - H_0)\xi K \xi]^{-1} \delta(E - H_0), \quad \xi = P, Q. \quad (28)$$

We thus see that all the operators appearing in Eqs. (27) are on the energy shell, i. e., they couple only eigenstates of H_0 with the same eigenvalue E . This property enables us to expand the solutions in powers of QKP without evaluating any principal parts. Thus, the basis set required for this purpose consists of a complete set of eigenstates of H_0 with energy E . We now demonstrate a simple way of constructing an on-the-energy-shell basis of eigenstates of H_0 for the case of collinear collisions. This basis permits us to express the various transition probabilities in terms of matrices of small size. For this purpose we consider a scattering event at an energy E where the system has N differ-

ent open internal channels in the rearrangement channel $|\alpha\rangle$ and M channels corresponding to β . The transition probability from state $|\hat{i}\rangle$ to $|\hat{j}\rangle$ is given by

$$P_{\hat{i}\rightarrow\hat{j}} = |S_{\hat{j}\hat{i}}|^2 = |1 - 2\pi i T_{\hat{j}\hat{i}}|^2. \quad (29)$$

A complete solution of the scattering problem thus requires the evaluation of the $(N+M) \times (N+M)$ discrete T matrix. We now build two QA surfaces and separate the nonreactive part of the interaction V [Eq. (16)] into two components

$$\xi V \xi = \xi V_0 \xi + \xi V_1 \xi, \quad \xi = P, Q, \quad (30)$$

where V_0 consists of the diagonal part of V and is responsible for elastic scattering only. We can now solve separately the collinear elastic scattering problems on the $|\alpha_\theta\rangle$ and $|\beta_\theta\rangle$ surfaces and obtain a set of $N+M$ wavefunctions, each in the form of a product of a bound wavefunction corresponding to the internal degrees of freedom and an energy-normalized translational wavefunction which we find by integrating the one dimensional elastic problem

$$(E - PH_0P - PV_0P) |\overline{\alpha\omega_\alpha^*}\rangle = 0, \quad (31)$$

$$(E - QH_0Q - QV_0Q) |\overline{\beta\omega_\beta^*}\rangle = 0$$

(note that in this case $|\xi\overline{\omega_\alpha^*}\rangle = |\xi\overline{\omega_\beta^*}\rangle$). Using Eqs. (B20) we obtain our final expressions in terms of the finite size matrices, and we have used the first order K matrix approximations (FOKA)

$$QK'P = QVP, \quad (32)$$

$$Q\hat{T}P \equiv Q\hat{T}_1P = \hat{F}_Q \hat{W} (1 + \hat{\Phi})^{-1} \hat{F}_P \quad (M \times N), \quad (33a)$$

$$P\hat{T}P = \hat{t}_P - P\hat{T}_1P = \hat{t}_P - \frac{i}{\pi} \hat{\Phi} (1 + \hat{\Phi})^{-1} \hat{F}_P \quad (N \times N), \quad (33b)$$

where

$$\hat{\Phi} = \pi^2 \hat{F}_P \hat{W}^* \hat{F}_Q \hat{W} \quad (N \times N), \quad (34)$$

$$\hat{W}_{\omega_\beta, \omega_\alpha} = \langle \overline{\beta\omega_\beta^*} | QVP | \overline{\alpha\omega_\alpha^*} \rangle \quad (M \times N), \quad (35)$$

$$\langle \hat{V}_P \rangle_{\omega_\alpha, \omega_\alpha} = \langle \overline{\alpha\omega_\alpha^*} | PV_1P | \overline{\alpha\omega_\alpha^*} \rangle \quad (N \times N), \quad (36)$$

$$\langle \hat{V}_Q \rangle = \langle \overline{\beta\omega_\beta^*} | QV_1Q | \overline{\beta\omega_\beta^*} \rangle \quad (M \times M), \quad (37)$$

$$\hat{F}_P = (1 + i\pi \hat{V}_P)^{-1} \quad (N \times N), \quad (38)$$

$$\hat{F}_Q = (1 + i\pi \hat{V}_Q)^{-1} \quad (M \times M), \quad (39)$$

$$\langle \hat{t}_P \rangle_{\omega_\alpha, \omega_\alpha} = \langle \overline{\alpha\omega_\alpha^*} | PV_0P | \overline{\alpha\omega_\alpha^*} \rangle \delta_{\omega_\alpha, \omega_\alpha} + \hat{V}_P \quad (M \times N). \quad (40)$$

When $QV'P = 0$ we have $Q\hat{T}P = 0$ and $P\hat{T}P = \hat{t}_P$. Thus, \hat{t}_P is the scattering matrix in the absence of the reactive interaction. $Q\hat{T}_1P$ and $P\hat{T}_1P$ are the contributions of the reactive coupling \hat{W} to the reactive and nonreactive cross sections, respectively. In Eqs. (33) the T_1 matrix satisfies the optical theorem, i. e.,

$$(1 + 2\pi i \hat{T}_1)(1 - 2\pi i T_1^*) = 1. \quad (41)$$

Numerical calculations on the basis of the present formalism are under study.²¹

V. DISCUSSION

We have used two different approaches for the derivation of the transition matrix elements of a reaction on a single adiabatic surface by means of a quasiadiabatic description. Both results [Eqs. (19) and (27)] are ex-

act; however, in practice if the reactive part QVP needs to be treated approximately then the K matrix expressions are more efficient as even first order (FOKA) accounts for interactions on the energy shell to infinite order. Moreover, the first order expressions involve only on-the-energy-shell operators so that the basis set is considerably reduced in size. We saw that our final result [Eqs. (33)] can be expressed in terms of finite size matrices.

The question now arises how to construct the QA surfaces (which we are free to choose at will) such that approximate treatments will be useful. For instance, it would be convenient if one could invoke a FC type approximation^{8,9} to the reactive interaction QVP , i. e.,

$$\langle \overline{\beta\omega_\beta^*} | QVP | \overline{\alpha\omega_\alpha^*} \rangle \propto \langle \overline{\beta\omega_\beta^*} | \overline{\alpha\omega_\alpha^*} \rangle. \quad (42)$$

The validity of the FC approximation (42) depends upon the choice of the QA surfaces. A reasonable choice consists of letting the QA surfaces cross around some energy (E_c) which is close to the total energy (E) for which we calculate the cross sections. In such a way the wavefunctions $|\overline{\alpha\omega_\alpha^*}\rangle$, $|\overline{\beta\omega_\beta^*}\rangle$ overlap appreciably in a localized region of nuclear configuration lying around the crossing (R_c). This is a necessary condition for the FC approximation to hold. Let us now consider in detail the types of terms contributing to the reactive coupling QVP ($= QHP$, see Table II):

(a) Consider first the term

$$\epsilon_{\alpha\beta} = \sqrt{(\epsilon_\alpha - \epsilon_a)(\epsilon_\beta - \epsilon_a)}, \quad (43)$$

which vanishes in both asymptotic regions. Provided $E_c - E_a(R_c)$ is not too small it can be made to be nearly constant in the relevant nuclear configuration region $\epsilon_{\alpha\beta} \approx E_c$.

(b) Next we look at the kinetic energy terms.^{6,7,14} Let us define Δ to be the (nuclear) coordinate range in which η changes between 0 and $\pi/2$. We thus have

$$\frac{\partial \eta}{\partial R} \lesssim \frac{\pi}{2\Delta} \sim \frac{1}{\Delta}, \quad (44)$$

and assuming for instance the form $\eta = \pi/2 (1 - e^{-R/\Delta})$ we have also

$$\frac{\partial^2 \eta}{\partial R^2} \leq \frac{1}{\Delta^2}. \quad (45)$$

Thus (see Table II), we obtain

$$T_{j'j''}'' \sim \frac{\hbar^2}{2M\Delta^2} = \frac{m}{M} \omega_H \left(\frac{a_0}{\Delta} \right)^2. \quad (46)$$

Here $m/M < 2000$ is the ratio of electronic to nuclear mass, $\omega_H = \hbar^2/2ma_0 = 13.6$ eV, and $\Delta \sim a_0$ (we assume the slopes of the QA potential not to be too large) so that we obtain

$$[T''] \sim 50 \text{ cm}^{-1}.$$

(c) Turning now to T' we have

$$T' | \overline{\alpha\omega_\alpha} \rangle \leq \frac{1}{\Delta} \frac{\hbar^2}{M} \frac{\partial \langle R | \overline{\alpha\omega_\alpha} \rangle}{\partial R}; \quad (47)$$

since

$$\frac{\hbar^2}{2M} \frac{\partial^2 \langle R | \overline{\alpha\omega_\alpha} \rangle}{\partial R^2} = (\epsilon_\alpha - E) \langle R | \overline{\alpha\omega_\alpha} \rangle, \quad (48)$$

we write

$$\frac{\partial \langle R | \alpha \omega_\alpha \rangle}{\partial R} \approx \frac{1}{\hbar} \sqrt{2M | \epsilon_\alpha - E |} \quad (49)$$

and

$$T' | \alpha \omega_\alpha \rangle \leq \frac{a_0}{\Delta} \sqrt{\frac{m}{M}} \sqrt{\omega_H | \epsilon_\alpha - E |} | \alpha \omega_\alpha \rangle . \quad (50)$$

Thus, we have

$$T' \approx \sqrt{\frac{1}{2000}} \sqrt{10^5 | E_c - E |} \approx 6 \sqrt{E_c - E} \text{ cm}^{-1} . \quad (51)$$

In summary, the orders of magnitude of the three contributions to QVP are related by

$$T'' : T' : \epsilon_{\alpha\beta} \approx 50 \text{ cm}^{-1} : 6 \sqrt{E_c - E} : E_c , \quad (52)$$

where E and E_c are given in wavenumbers. The conclusions from these estimates are that T'' is always small and provided $|E_c - E| \ll E_c$ (i. e., the energy E is not too far from the crossing) T' will also be small relative to $\epsilon_{\alpha\beta}$. Thus, if (i) the slopes of the QA surfaces are not too steep and (ii) $|E - E_c| \ll E_c$, then we can safely neglect the T' and T'' terms in QVP and we thus get

$$\langle \beta \omega_\beta | QVP | \alpha \omega_\alpha^* \rangle \approx \langle \beta \omega_\beta | \sqrt{(\epsilon_\alpha - \epsilon_a)(\epsilon_\beta - \epsilon_a)} | \alpha \omega_\alpha^* \rangle , \quad (53)$$

which, when the $\sqrt{(\epsilon_\alpha - \epsilon_a)(\epsilon_\beta - \epsilon_a)}$ factor is made to be nearly constant, assumes the desired (FC) form

$$\langle \beta \omega_\beta | QVP | \alpha \omega_\alpha^* \rangle \approx \langle \langle \sqrt{(\epsilon_\alpha - \epsilon_a)(\epsilon_\beta - \epsilon_a)} \rangle \rangle \langle \beta \omega_\beta | \alpha \omega_\alpha^* \rangle , \quad (54)$$

where $\langle \langle \rangle \rangle$ denotes an averaged value over the relevant nuclear configuration domain which contributes to the matrix element.

This discussion is confined to the FC approximation for the reactive matrix elements but its validity goes beyond first order (FO) in QVP . In fact, substitution of the QVP matrix elements (54) in our expression for the T matrix [Eqs. (22) or (27)] results in our final expressions, which hold to any order in QVP within the FC approximation.

We are now in a position to discuss the perturbative treatment of T to first order (FO) in QVP . In this case we neglect the K matrix correction $(1 + \Phi)^{-1} \sim [1 + (QVP)^2]^{-1}$. We thus have a sufficient condition for the first order treatments after invoking the FC assumption

$$\xi \equiv (\epsilon_a - \epsilon_\alpha)(\epsilon_a - \epsilon_\beta) | \langle \beta \omega_\beta | \alpha \omega_\alpha^* \rangle |^2 \ll 1 . \quad (55)$$

Thus, we may minimize ξ by the choice of our QA surfaces to maximize the effectiveness of a FOFC treatment.

Equation (53) enables us to compare the present results with those of the common two-potential formalism.¹ We note first that the zeroth order Hamiltonian in that case

$$H_0 = | a_\alpha \rangle (T_R + \epsilon_\beta) \langle a_\alpha | \quad (56)$$

is different from the QA and hence the coupling $V = \epsilon_a - \epsilon_\beta$ is reactive and nonreactive in nature, whereas in our case the coupling (43) is purely reactive. Note, however, that Eq. (27a), to first order in the K matrix, and to first order in QVP , assumes the form

$$\langle \beta \omega_\beta | QTP | \alpha \omega_\alpha \rangle \approx \langle \beta \omega_\beta | \sqrt{(\epsilon_\alpha - \epsilon_a)(\epsilon_\beta - \epsilon_a)} | \alpha \omega_\alpha^* \rangle , \quad (57)$$

where near the crossing ($\epsilon_\alpha \approx \epsilon_\beta$) is approximately $\langle \beta \omega_\beta | (\epsilon_\beta - \epsilon_a) | \alpha \omega_\alpha^* \rangle$. Thus, in this limit both theories give practically the same first order estimates for QTP .

A final remark should be made regarding the n channel problem: We have restricted our analysis to a two channel problem; however, the method can be extended iteratively to the n channel case. This can be done in either of two ways. We can extend the 2×2 transformation (5) and define an $n \times n$ transformation to a set of n QA single channel surfaces. Another approach is iterative in nature: We first define two QA surfaces, one (P) for the incident channel and the other surface (Q) for the remaining $n - 1$ channels. The operator \tilde{F}_Q [Eq. (B6)] now to be evaluated is a Möller operator with $n - 1$ channels and we can repeat the procedure outlined here to separate the Q surface into two new surfaces again with the elimination of one channel. In such a way we can eliminate one channel at a time. This procedure is similar to the doorway-state method²² used in nuclear physics to eliminate iteratively groups of states.

APPENDIX A. DERIVATION OF THE PROJECTIONS OF THE T MATRIX

Starting from the symmetric T matrix (17) and Eqs. (13)–(15) we make use of the relation¹⁵

$$T = R + R P G P R , \quad (A1)$$

$$P G P = (E - P H_0 P - P R P)^{-1} , \quad (A2)$$

where R is the level-shift operator

$$R = V + V \tilde{G}_Q V , \quad (A3)$$

and we define

$$\tilde{G}_i = (E - \xi H \xi + i\epsilon) , \quad \xi = P, Q . \quad (A4)$$

Operating with Q on the left and P on the right of Eq. (A1) we get

$$QTP = QRP(P + P G P R P) \quad (A5)$$

and using Eq. (A2) we have

$$\begin{aligned} QTP &= QRP G P (E - P H_0 P) \\ &= QRP(E - P H P - P V Q \tilde{G}_Q QVP)^{-1} (E - P H_0 P) \\ &= QRP[(E - P H P)(P - \tilde{G}_P P V Q \tilde{G}_Q QVP)^{-1}] (E - P H_0 P) \\ &= QRP(P - \tilde{G}_P V Q \tilde{G}_Q QVP)^{-1} (P + \tilde{G}_P P V P) \\ &= (Q + Q V Q \tilde{G}_Q) QVP (P - \tilde{G}_P V Q \tilde{G}_Q QVP)^{-1} (P + \tilde{G}_P P V P) . \end{aligned} \quad (A6)$$

On defining the quantities

$$\begin{aligned} \langle \beta_e \omega_\beta | (Q + Q V Q \tilde{G}_Q) &= \langle \beta_e \omega_\beta | , \\ (P + \tilde{G}_P P V P) | \alpha_e \omega_\alpha \rangle &= | \alpha_e \omega_\alpha^* \rangle , \end{aligned} \quad (A7)$$

we obtain for the T matrix element

$$\begin{aligned} \langle \beta \omega_\beta | QTP | \alpha \omega_\alpha \rangle &= \langle \beta \omega_\beta | QVP (P - \tilde{G}_P P V Q \\ &\quad \times \tilde{G}_Q QVP)^{-1} | \alpha \omega_\alpha^* \rangle = \langle \beta \omega_\beta | (Q - QVP \\ &\quad \times \tilde{G}_P P V Q \tilde{G}_Q)^{-1} QVP | \alpha \omega_\alpha^* \rangle . \end{aligned} \quad (A8)$$

For the derivation of the other projections of T let us start again with Eq. (A1) by multiplying by Q on either side

$$QTQ = QRQ + QRPQPRQ, \quad (\text{A9})$$

$$QTQ = QVQ(Q + \tilde{G}_Q QVQ) + QRP[(E - PHP)(P - \tilde{G}_P PVQ\tilde{G}_Q QVP)^{-1}PRQ], \quad (\text{A10})$$

$$QTQ = QVQ(Q + \tilde{G}_Q QVQ) + (Q + Q\tilde{G}_Q QVQ) \times QVP\tilde{G}_P PVQ(Q - \tilde{G}_Q QVP\tilde{G}_P PVQ)^{-1} \times (Q + Q\tilde{G}_Q QVQ). \quad (\text{A11})$$

Interchanging P and Q and using the definitions (A7) we get

$$\langle \alpha v_\alpha | PTP | \alpha \omega_\alpha \rangle = \langle \alpha v_\alpha | PVP | \alpha \omega_\alpha \rangle + \langle \alpha v_\alpha | PVQ\tilde{G}_Q QVP \rangle \times (P - \tilde{G}_P PVQ\tilde{G}_Q QVP)^{-1} | \alpha \omega_\alpha \rangle. \quad (\text{A12})$$

APPENDIX B. DERIVATION OF THE PROJECTIONS QTP, PTP IN TERMS OF THE K MATRIX

Our starting equation is^{2,3}

$$T = K - i\pi K\delta(E - H_0)T \quad (\text{B1})$$

or

$$T = K \cdot F, \quad (\text{B2})$$

where

$$F = 1 - i\pi\delta(E - H_0)KF. \quad (\text{B3})$$

Multiplying Eq. (B3) on the rhs by P and the lhs by P and Q , respectively, we have

$$PFP = P - i\pi\delta(E - H_0)PKQFP - i\pi\delta(E - H_0)PKPFP, \quad (\text{B4})$$

$$QFP = i\pi\delta(E - H_0)QKQFP - i\pi\delta(E - H_0)QKQFP.$$

We solve these equations for PFP, QFP :

$$QFP = i\pi\tilde{F}_Q QKQFP, \quad (\text{B5})$$

$$PFP = (P + \pi^2\tilde{F}_P PKQ\tilde{F}_Q QKP)^{-1}\tilde{F}_P$$

where

$$\tilde{F}_\xi = [\xi + i\pi\delta(E - H_0)\xi K\xi]^{-1}\delta(E - H_0), \quad \xi = P, Q. \quad (\text{B6})$$

[We have added $\delta(E - H_0)$ on the rhs of Eq. (B6). This however does not change the operator as long as it operates on an eigenfunction of H_0 with eigenvalue E .]

From Eq. (B2) we have

$$PTP = PKPFP + PKQFP, \quad (\text{B7})$$

$$QTP = QKQFP + QKQFP.$$

Substitution of the projections (B5) in Eq. (B7) and rearranging terms results in

$$QTP = [Q - i\pi\delta(E - H_0)QKQ\tilde{F}_Q]QKQFP, \quad (\text{B8})$$

which by making use of Eqs. (B5) and (B6) leads us to the form

$$QTP = \tilde{F}_Q QKP(P + \pi^2\tilde{F}_P PKQ\tilde{F}_Q QKP)^{-1}\tilde{F}_P. \quad (\text{B9})$$

Similarly, when solving for PTP we get

$$PTP = PKPFP - i\pi PKQ\tilde{F}_Q QKQFP. \quad (\text{B10})$$

From Eq. (B5) we see that PFP satisfies the integral equation

$$PFP = \tilde{F}_P - \pi^2\tilde{F}_P PKQ\tilde{F}_Q QKQFP. \quad (\text{B11})$$

Substitution of Eq. (B11) in the first term of (B10) results in

$$PTP = PKP\tilde{F}_P - i\pi\tilde{F}_P PKQ \times \tilde{F}_Q QKP(P + \pi^2\tilde{F}_P PKQ\tilde{F}_Q QKP)^{-1}\tilde{F}_P. \quad (\text{B12})$$

Our final results for the projection of T are thus

$$QTP = \tilde{F}_Q QKP(P + \Phi)^{-1}\tilde{F}_P, \quad (\text{B13})$$

$$PTP = PKP\tilde{F}_P - \frac{i}{\pi} \Phi(P + \Phi)^{-1}\tilde{F}_P,$$

where

$$\Phi = \pi^2\tilde{F}_P PKQ\tilde{F}_Q QKP.$$

In practice it may be desirable to use a basis set of scattering wavefunctions defined by some approximate nonreactive Hamiltonian

$$(PH_0P + PV_0P) | \alpha \omega_\alpha \rangle = 0, \quad (\text{B14})$$

$$(QH_0Q + QV_0Q) | \beta \omega_\beta \rangle = 0,$$

where $\xi V_0 \xi$ are some parts of $\xi V \xi$ (e.g., the elastic part of $\xi V \xi$, which does not allow for inelastic transitions). In this case we may start from the two-potential scattering equations^{2,3}

$$\langle \beta \omega_\beta | QTP | \alpha \omega_\alpha \rangle = \langle \beta \omega_\beta | QT'P | \alpha \omega_\alpha \rangle, \quad (\text{B15a})$$

$$\langle \alpha v_\alpha | PTP | \alpha \omega_\alpha \rangle = t_P + \langle \alpha v_\alpha | PT'P | \alpha \omega_\alpha \rangle, \quad (\text{B15b})$$

where

$$t_P = \langle \alpha v_\alpha | V_0 | \alpha \omega_\alpha \rangle \quad (\text{B16})$$

is the contribution of V_0 alone

$$V_0 = PV_0P + QV_0Q \quad (\text{B17})$$

and

$$T' = V' + V'GV' \quad (\text{B18})$$

where

$$V' = V - V_0. \quad (\text{B19})$$

The operators V and G are defined by Eqs. (13)–(16) and (18), respectively. We can now work out a K matrix expansion of T' alone, analogous to the previous treatment, and obtain analogous equations to Eq. (B13); however, the operators are defined in a different way

$$\langle \beta \omega_\beta | QTP | \alpha \omega_\alpha \rangle = \langle \beta \omega_\beta | F'_Q QK'P(P + \Phi')^{-1}F'_P | \alpha \omega_\alpha \rangle, \quad (\text{B20a})$$

$$\langle \alpha v_\alpha | PTP | \alpha \omega_\alpha \rangle = t_P - \frac{i}{\pi} \langle \alpha v_\alpha | \Phi'(P + \Phi')^{-1}F'_P | \alpha \omega_\alpha \rangle, \quad (\text{B20b})$$

where

$$T' = K' - i\pi K'\delta(E - H_0 - V_0)T', \quad (\text{B21})$$

$$K' = V' + V' \left(PP \frac{1}{E - H_0 - V_0} \right) K', \quad (\text{B22})$$

$$F'_i = \xi \delta(E - H_0 - V_0) - i\pi \delta(E - H_0 - V_0) \xi V' \xi F'_i, \\ \xi = P, Q, \quad (\text{B23})$$

$$\Phi' = \pi^2 F'_P P K Q F'_Q Q K' P, \quad (\text{B24})$$

$$\hat{P} = \sum_{\omega_\alpha} |\overline{\alpha\omega_\alpha^*}\rangle \langle \overline{\alpha\omega_\alpha^*}|, \quad (\text{B25})$$

$$\hat{Q} = \sum_{\omega_\beta} |\beta\omega_\beta^*\rangle \langle \beta\omega_\beta^*|.$$

In this approximation only T' is unitary since we did not use the K matrix formalism for the whole T matrix but just for T' , which is the contribution to T due to the reactive interaction.

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