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Scattering-theory sensitivity analysis for spatial Hamiltonian variations

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An expression for the functional-derivative sensitivity density of the scattering matrix in parameter space is derived. This expression can be used to assess the effect on scattering observables of varying space-dependent quantities in the Hamiltonian (e.g., the interaction potential or the free-target portion of the Hamiltonian). This work represents the most general formulation of elementary sensitivity analysis for quantum scattering problems, and its use is demonstrated by a few sample calculations.

I. INTRODUCTION

Sensitivity analysis is a computational tool which yields information about the dependence of a system of equations on a relevant set of parameters. It has been applied to the study of quantum-mechanical scattering,[1] chemical kinetics,[2] and reaction-diffusion problems[3] as well as a variety of engineering systems. A sensitivity analysis requires the solution of a system of linear equations (i.e., differential, integral, algebraic, etc.) for the components of the solution gradient in parameter space; the components of the gradient are referred to as the sensitivity coefficients. This interpretation is valid for systems in which the parameters are constant, i.e., do not vary with space or time. If the parameters are, themselves, functions of space and/or time, the components of the gradient become functional derivatives and are referred to as sensitivity densities.

A functional sensitivity analysis has been formulated for reaction-diffusion equations.[3] In this paper we will consider a similar treatment for scattering theory in which the "parameters" are either the intermolecular potential, the internal Hamiltonian, or portions of these operators. By this approach it becomes possible to map out the manner in which the Hamiltonian influences the scattering matrix. Knowledge of this mapping would immediately lead to an understanding of the way in which various collision cross sections and other observables are related to the structure within the Hamiltonian. Concerns such as these arise under a number of circumstances in atomic and molecular scattering. A common situation occurs when the scattering potential is only approximately known. Such potentials are often generated by a combination of *ab initio* and empirical information. Although calculations based on such potentials may attempt to simulate a particular real system, the calculations should be viewed strictly as a model. An immediate, serious question arises concerning the sensitivity of the generated cross sections with respect to various features or parameters in the underlying potential function. Thus, the simplest use of sensitivity techniques would be for the generation of an error analysis of the computed results. In this way one could gain a quantitative measure for which cross sections or observables are most reliable from the calculations. At the other extreme there are situations where the potential is believed to be known accurately and, again, a sensitivity analysis could play a valuable role. In this situation the sensitivities may be used as a means of physically analyzing which aspects of the Hamiltonian are responsible for particular cross sections or S-matrix elements. This usage and interpretation can, of course, also be applied in the former case where the potential is not firmly known but is understood to be a model designed for analysis. These various circumstances are depicted in Fig. 1 where a given region on a potential surface is shown to map principally onto certain scattering matrix elements. In addition to the potential as a focus of sensitivity analysis, one may also be interested in sensitivity with respect to structure or parameters (e.g., reduced masses) in the unperturbed target portion of the Hamiltonian.

All the sensitivity issues raised in the previous paragraph are addressed by what is sometimes referred to as "elementary sensitivity coefficients." This notation follows from the fact that these coefficients are the basic or fundamental sensitivities generated by Hamiltonian variations. This paper concerns the theoretical formulation needed to calculate elementary *functional* sensitivities of this type. Beyond the elementary sensitivities one may also calculate derived sensitivities[3(b)] which can be used to address a variety of interesting physical questions. For example, one could explore the interrelationship between two different cross sections or perhaps the correlation between two regions on a potential surface in order to preserve a given cross section. Questions such as these involve an interchange of dependent and independent variables (i.e., cross sections for various parameters in the Hamiltonian, etc.) and they may be calculated by appropriate algebraic or functional manipulation of the elementary sensitivities. Another example would arise when it is desired to understand which physical aspects in the

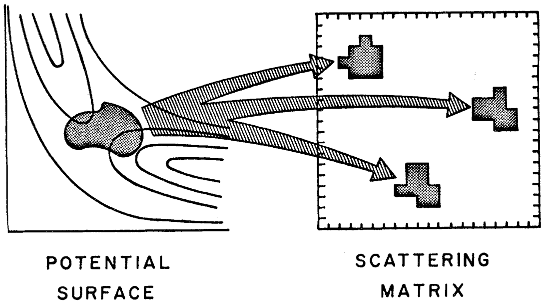

FIG. 1. A schematic illustration showing how variations in a *region* of the potential can map onto variations in the scattering matrix.

Hamiltonian contribute to observable features in the cross sections such as the location and amplitude of interference extrema. These so-called feature sensitivities may again be calculated by manipulating the elementary sensitivity coefficients. In addition to these matters certain aspects of sensitivity analysis may be useful for the design of experiments and may aid in the understanding of inverse scattering problems. The sensitivity coefficients of significance here are essentially the inverse of the elementary set; here, one would like to understand the sensitivity of parameters describing features in the Hamiltonian with respect to particular cross sections. The corresponding gradients could again be generated by an interchange of dependent and independent variables.

This paper will focus on the theoretical techniques needed to calculate elementary functional sensitivity gradients. The various interesting secondary sensitivity questions mentioned above are beyond the scope of this paper, but the techniques discussed here should have immediate use for those more refined questions of sensitivity concern. In this regard it is worth noting that mathematically parallel developments in chemical kinetics[3(b)] have already considered many of the relevant secondary or derived sensitivity questions, and some of the same techniques should be immediately transferable to problems in quantum mechanics. An important aspect of this work is that functional sensitivity analysis is valuable even for those cases in which the nominal values of the system parameters are spatially constant. This is a significant point since one may consider spatial variations around even constant reference values; the previous formulations[1,2] of scattering sensitivity analysis did not allow for such consideration.

Sensitivity analysis of quantum scattering problems is complicated by the appearance of parameters in the asymptotic boundary condition of the wave function. Because of the functional form of this boundary condition, the gradient of the wave function with respect to these parameters becomes arbitrarily large at large scattering distances—a result which is not physically meaningful. In previous work[1(b)] this problem was circumvented by calculating gradients of the system "observables" (e.g., elements of the scattering matrix or the cross section) rather than gradients of the wave function. A similar approach will be taken here. We will apply the methods of functional sensitivity analysis[3] to the calculation of gradients of the scattering matrix.

In Sec. II, we will outline the derivation of the functional derivative of the scattering matrix with respect to any parameter in the Schrödinger equation. Section III gives explicit expressions for this sensitivity density for two examples. In one example, the parameters to be varied are found in the interaction potential; in the second example, the parameters are in the internal part of the Hamiltonian. An exactly soluble model system is used to demonstrate the theory and the calculated sensitivity densities are discussed.

II. THEORY

We will consider the effect of space-dependent variations of the parameters in the time-independent Schrödinger equation:

$$\left[\nabla^2_{\vec{R}}-\frac{2\mu}{\hbar^2}[H_{\rm int}(\vec{r})+V(\vec{r},\vec{R})-E]\right]\Phi^i(\vec{r},\vec{R})=0\ , \quad (1)$$

where $\vec{R}$ is the scattering coordinate, $\vec{r}$ is the vector of internal coordinates, $H_{\rm int}(\vec{r})$ is the part of the Hamiltonian specifying the internal degrees of freedom, V is the interaction potential, E is the total energy, μ is the reduced mass, and Φ^i is the total wave function which is labeled by i, a collective index for the incident internal state of the scattering particles. For simplicity, only inelastic scattering will be treated here.

We assume that the total wave function Φ^i can be written as a linear combination of basis functions which are eigenfunctions of the internal Hamiltonian:

$$\Phi^i(\vec{r},\vec{R})=\frac{1}{R}\sum_j \phi_j(\vec{r},\hat{\Omega})\psi_{ji}(R)\ , \quad (2a)$$

where

$$H_{\rm int}(\vec{r})\phi_j(\vec{r},\hat{\Omega})=\epsilon_j\phi_j(\vec{r},\hat{\Omega})\ , \quad (2b)$$

$$\nabla^2_{\hat{\Omega}}\phi_j(\vec{r},\hat{\Omega})=\frac{l(l+1)}{R^2}\phi_j(\vec{r},\hat{\Omega})\ . \quad (2c)$$

The scattering angles are $\hat{\Omega}$ such that $\vec{R}=(R,\hat{\Omega})$ and $\nabla^2_{\hat{\Omega}}$ is the angular part of the Laplacian. The ϕ_j are therefore products, or sums of products, of the internal wave function and the angular part of the scattered wave function and are labeled by j, a collective index specifying the internal and angular momentum states. The sum in Eq. (2a) runs over a complete set of functions and the coefficients $\psi_{ji}(R)$ satisfy the radial equation, given by

$$\left[\frac{\partial^2}{\partial R^2}+k_j^2\right]\psi_{ji}(R)=\sum_{j'}U_{jj'}(R)\psi_{j'i}(R)\ , \quad (3a)$$

where

$$k_j^2=\frac{2\mu}{\hbar^2}(E-\epsilon_j)\ , \quad (3b)$$

$$U_{jj'}(R)=\frac{2\mu}{\hbar^2}\int d\vec{r}\,d\hat{\Omega}\,\phi_j^*(\vec{r},\hat{\Omega})[V(\vec{r},\vec{R})-\nabla^2_{\hat{\Omega}}]\phi_{j'}(\vec{r},\hat{\Omega})\ . \quad (3c)$$

Equation (3a) is therefore the coupled-channel formulation of the scattering problem. A complete specification of the solution to (3a) requires the asymptotic boundary condition which is of the form

$$\lim_{R\to\infty} \psi_{ji}(R) = -\delta_{ji} k_i^{-1/2} \exp(-ik_iR) + k_j^{-1/2} \exp(ik_jR) S_{ji} \ , \tag{4a}$$

where S_{ji} is an element of the scattering matrix. To simplify notation in the following treatment we introduce the functions (their asymptotic limit)

$$f_{ji}^{\pm}(R) \equiv \delta_{ji} k_i^{-1/2} \exp(\pm ik_iR) \ , \tag{4b}$$

$$\lim_{R\to\infty} \psi_{ji}(R) = -f_{ji}^{-}(R) \sum_k f_{jk}^{+}(R) S_{ki} \ . \tag{4c}$$

We will derive an expression for the gradient of the matrix $\underline{S}$ with respect to any parameter in the system. The first step gives us an explicit expression for the scattering matrix $\underline{S}$ in terms of Jost-type functions; these are Wronskian matrices of $\underline{f}^{\pm}$ and the radial wave function.

We now introduce a general solution to the Schrödinger equation, which must be a linear combination of the independent solutions $f_{ji}^{\pm}$:

$$\eta^i(\vec{r},\vec{R}) = \sum_{j,k} \phi_j(\vec{r},\hat{\Omega})[f_{jk}^{-}(R)a_{ki} + f_{jk}^{+}(R)b_{ki}] \ . \tag{5a}$$

Letting

$$\eta^i(\vec{r},\vec{R}) = \sum_j \phi_j(\vec{r},\hat{\Omega})\mu_{ji}(R) \ , \tag{5b}$$

as in Eq. (2a), we may identify

$$\mu_{ji}(R) = \sum_k [f_{jk}^{-}(R)a_{ki} + f_{jk}^{+}(R)b_{ki}] \ . \tag{5c}$$

In order to arrive at an expression for $\underline{S}$ we first calculate the matrices $\underline{a}$ and $\underline{b}$ in (5) by forming the radial Wronskian function:

$$\underline{J}^{\pm} = W_R[\underline{f}^{\pm}(R),\underline{\mu}(R)] \equiv (\underline{f}^{\pm})^T \frac{\partial \underline{\mu}}{\partial R} - \frac{\partial (\underline{f}^{\pm})^T}{\partial R} \underline{\mu} \ . \tag{6}$$

The Wronskian function, as defined in (6), is independent of R. Substituting (5c) into (6) and noting that $W_R[\underline{f}^{\pm},\underline{f}^{+}]=0$, we find

$$\underline{a} = -(2i)^{-1}\underline{J}^{+} \ , \tag{7a}$$

$$\underline{b} = +(2i)^{-1}\underline{J}^{-} \ . \tag{7b}$$

Substituting this result into (5c) we find

$$\underline{\mu}(R) = -(2i)^{-1}[\underline{f}^{-}(R) - \underline{f}^{+}(R)\underline{J}^{-}(\underline{J}^{+})^{-1}]\underline{J}^{+} \ . \tag{8}$$

Comparing the asymptotic form of (8) with (4c) we conclude that

$$\underline{S} = \underline{J}^{-}(\underline{J}^{+})^{-1} \ , \tag{9a}$$

$$\underline{\mu}(R) = (2i)^{-1}\underline{\psi}(R)\underline{J}^{+} \ . \tag{9b}$$

The gradient of $\underline{S}$ can be found by applying a small perturbation to each of the parameters. We designate the system parameters by a vector $\vec{\alpha} = \{\alpha_1, \dots, \alpha_M\}$ where each α_i may be a function of one or more of the coordinates $(\vec{r},\vec{R})$. The parameters should be considered as operators since they come from the Hamiltonian or portions of it. Designating the reference value of the parameter α_k as $\bar{\alpha}_k$, we add a small perturbation to each parameter:

$$\alpha_k(\vec{r},\vec{R}) = \bar{\alpha}_k(\vec{r},\vec{R}) + \delta\alpha_k(\vec{\gamma}_k) \ , \tag{10a}$$

where $\vec{\gamma}_k$ is a vector of the coordinates upon which $\delta\alpha_k$ depends and $\vec{\gamma}_k \subset \{\vec{r},\vec{R}\}$. The *reference value* $\bar{\alpha}_k$ may not depend on these coordinates but, for generality, we indicate that $\bar{\alpha}_k$ may be a function of $\vec{r},\vec{R}$. The perturbation $\delta\alpha_k$ induces a deviation in the scattering matrix from the reference matrix, indicated by $\bar{\underline{S}}$:

$$\underline{S} = \bar{\underline{S}} + \delta\underline{S} \ . \tag{10b}$$

Substituting (9a) into (10b) one can show

$$\delta\underline{S} = (-\bar{\underline{S}}\,\delta\underline{J}^{+} + \delta\underline{J}^{-})(\bar{\underline{J}}^{+})^{-1} \ . \tag{10c}$$

The deviations $\delta\underline{S}$ and $\delta\underline{J}^{\pm}$ are actually total variationals given by

$$\delta\underline{Q} = \sum_{k=1}^{M} \int d\gamma_1' \cdots d\gamma_{m_k}' \frac{\delta\underline{Q}}{\delta\alpha_k(\gamma_1',\dots,\gamma_{m_k}')} \times \delta\alpha_k(\gamma_1',\dots,\gamma_{m_k}') \ , \tag{11}$$

where $\underline{Q}=\underline{S}$, $\underline{J}^{+}$, or $\underline{J}^{-}$, $\vec{\gamma}_k = \{\gamma_1,\dots,\gamma_{m_k}\}$, and m_k is the number of coordinates in the set $\{\vec{r},\vec{R}\}$ upon which $\delta\alpha_k$ depends. The quantities $\delta\underline{Q}/\delta\alpha_k$ are functional derivatives. Substituting (11) into (10c) we arrive at an expression for the sensitivity density of interest:

$$\frac{\delta\underline{S}}{\delta\alpha_k(\gamma_1',\dots,\gamma_{m_k}')} = \left[-\bar{\underline{S}} \frac{\delta\underline{J}^{+}}{\delta\alpha_k(\gamma_1',\dots,\gamma_{m_k}')} + \frac{\delta\underline{J}^{-}}{\delta\alpha_k(\gamma_1',\dots,\gamma_{m_k}')} \right] (\bar{\underline{J}}^{+})^{-1} \ , \tag{12a}$$

where

$$\frac{\delta\underline{J}^{\pm}}{\delta\alpha_k(\gamma_1',\dots,\gamma_{m_k}')} = W_R\left[\bar{\underline{f}}^{\pm}(R), \frac{\delta\underline{\mu}(R)}{\delta\alpha_k(\gamma_1',\dots,\gamma_{m_k}')}\right] + W_R\left[\frac{\delta\underline{f}^{\pm}(R)}{\delta\alpha_k(\gamma_1',\dots,\gamma_{m_k}')}, \bar{\underline{\mu}}(R)\right] . \tag{12b}$$

We wish to express Eq. (12a) in terms of quantities which are explicitly known. To do so, we return to the Schrödinger equation and find expressions for the functional derivatives of the wave functions which appear in (12b).

First, let

$$G(\vec{r},\vec{R}) = \frac{2\mu}{\hbar^2}[H_{\rm int}(\vec{r}) + V(\vec{r},\vec{R})] + \nabla_{\hat{\Omega}}^2 \ , \tag{13a}$$

$$\epsilon=\frac{2\mu}{\hbar^2}E \ . \tag{13b}$$

Then, the Schrödinger equation may be written as

$$\frac{\partial^2\mathscr{F}^i}{\partial R^2}(\vec{r},\vec{R})=[G(\vec{r},\vec{R})-\mathscr{E}]\mathscr{F}^i(\vec{r},\vec{R}) \ , \tag{13c}$$

where $\mathscr{F}^i(\vec{r},\vec{R})=R\Phi^i(\vec{r},\vec{R})$ or asymptotically $\eta^i(\vec{r},\vec{R})$. We expand the Schrödinger equation around the reference system, designated again by a bar:

$$\mathscr{F}^i(\vec{r},\vec{R})=\overline{\mathscr{F}}^i(\vec{r},\vec{R})+\delta\mathscr{F}^i(\vec{r},\vec{R}) \ , \tag{14a}$$

$$G(\vec{r},\vec{R})=\overline{G}(\vec{r},\vec{R})+\sum_{k=1}^{M}\frac{\partial\overline{G}(\vec{r},\vec{R})}{\partial\alpha_k(\gamma'_1,\ldots,\gamma'_{m_k})} \times\delta\alpha_k(\gamma'_1,\ldots,\gamma'_{m_k}) \ , \tag{14b}$$

since G is a *function* of the α_k. The derivative in Eq. (14b) should be thought of as an ordinary derivative varying that portion of G controlled by α_k with the other parameters held fixed. Substituting (14a) and (14b) into (13c) and equating terms of equal order in the variation δ we have, to zeroth order,

$$\frac{\partial^2\overline{\mathscr{F}}^i}{\partial R^2}(\vec{r},\vec{R})=[\overline{G}(\vec{r},\vec{R})-\mathscr{E}]\overline{\mathscr{F}}^i(\vec{r},\vec{R}) \ , \tag{15a}$$

and to first order,

$$\frac{\partial^2}{\partial R^2}\frac{\delta\mathscr{F}^i(\vec{r},\vec{R})}{\delta\alpha_k(\gamma'_1,\ldots,\gamma'_{m_k})}=[\overline{G}(\vec{r},\vec{R})-\mathscr{E}]\frac{\delta\mathscr{F}^i(\vec{r},\vec{R})}{\delta\alpha_k(\gamma'_1,\ldots,\gamma'_{m_k})}+\frac{\partial\overline{G}(\vec{r},\vec{R})}{\partial\alpha_k(\gamma_1,\ldots,\gamma_{m_k})}\overline{\mathscr{F}}^i(\vec{r},\vec{R})\delta(\gamma_1-\gamma'_1)\cdots\delta(\gamma_{m_k}-\gamma'_{m_k}) \ , \tag{15b}$$

where we have used Eq. (11) with $\underline{Q}=\mathscr{F}^i$. Finally, to obtain an expression for the functional derivative of the radial part of the wave function we expand $\overline{\mathscr{F}}^i$ and $\delta\mathscr{F}^i$ in the complete set of basis functions $\phi_j(\vec{r},\hat{\Omega})$, which are also varied around their reference values $\overline{\phi}_j(\vec{r},\hat{\Omega})$:

$$\delta\overline{F}^i(\vec{r},\vec{R})=\sum_i\overline{\phi}_j(\vec{r},\hat{\Omega})\overline{F}_{ji}(R) \ , \tag{16a}$$

$$\delta\mathscr{F}^i(\vec{r},\vec{R})=\sum_j\overline{\phi}_j(\vec{r},\hat{\Omega})\delta F_{ji}(R)+\sum_j\delta\phi_j(\vec{r},\hat{\Omega})\overline{F}_{ji}(R) \ , \tag{16b}$$

where $F_{ji}(R)$ may be either $\psi_{ji}(R)$, $f^{\pm}_{ji}(R)$, or $\mu_{ji}(R)$. Substituting (16a) and (16b) into (15a) and (15b), multiplying both by $\overline{\phi}^*_{j'}(\vec{r},\hat{\Omega})$, and integrating over $\vec{r},\hat{\Omega}$ yields the following desired expressions:

$$\frac{\partial^2 F_{j'i}(R)}{\partial R^2}=\sum_j\overline{\mathscr{G}}_{j'j}(R)\overline{F}_{ji}(R)-\mathscr{E}\overline{F}_{j'i}(R) \ , \tag{17a}$$

$$\begin{aligned}\frac{\partial^2}{\partial R^2}\frac{\delta F_{j'i}(R)}{\delta\alpha_k(\gamma'_1,\ldots,\gamma'_{m_k})}=&\sum_j[\overline{\mathscr{G}}_{j'j}(R)-\mathscr{E}\delta_{jj'}]\frac{\delta F_{ji}(R)}{\delta\alpha_k(\gamma'_1,\ldots,\gamma'_{m_k})}\\&-\sum_{j,l'\neq j}\left[\delta_{j'l'}\mathscr{H}^k_{l'j}\left[\frac{\partial^2}{\partial R^2}+\mathscr{E}\right]-\overline{\mathscr{G}}_{j'l'}(R)\mathscr{H}^k_{l'j}\right]\overline{F}_{ji}(R)\\&+\sum_j\int d\vec{r}\,d\vec{\Omega}\,\overline{\phi}^*_{j'}(\vec{r},\hat{\Omega})\frac{\partial G(\vec{r},\vec{R})}{\partial\alpha_k(\gamma_1,\ldots,\gamma_{m_k})}\overline{\phi}_j(\vec{r},\hat{\Omega})\overline{F}_{ji}(R)\delta(\gamma_1-\gamma'_1)\cdots\delta(\gamma_{m_k}-\gamma'_{m_k}) \ ,\end{aligned} \tag{17b}$$

where

$$\overline{\mathscr{G}}_{j'j}(R)=\int d\vec{r}\,d\hat{\Omega}\,\overline{\phi}^*_{j'}(\vec{r},\vec{\Omega})\overline{G}(\vec{r},\vec{R})\overline{\phi}_j(\vec{r},\hat{\Omega}) \ , \tag{17c}$$

and

$$H^k_{l'j}=\frac{1}{\epsilon_j-\epsilon_{l'}}\int d\vec{r}\,d\hat{\Omega}\,\overline{\phi}^*_{l'}(\vec{r},\vec{\Omega})\frac{\delta H_{\text{int}}(\vec{r})}{\delta\alpha_k(\gamma'_1,\ldots,\gamma'_{m_k})}\phi_j(\vec{r},\hat{\Omega}) \ . \tag{17d}$$

This derivation makes use of Eq. (25) presented later.

We may use Eqs. (17) in evaluating the Wronskians in Eq. (12b). To do so, we first define

$$\underline{\mathscr{I}}^{\pm}_{k}(R)=W_R\left[\underline{\overline{f}}^{\pm}(R),\frac{\delta\underline{\mu}(R)}{\delta\alpha_k(\gamma'_1,\ldots,\gamma'_{m_k})}\right] , \tag{18a}$$

which is the first term of (12b). Taking the radial derivative $\partial/\partial R$ of (18a) and using the definition of W_R [Eq. (6)], we find

$$\frac{\partial \underline{\mathscr{I}}_k^{\pm}}{\partial R}=(\underline{f}^{\pm})^T\frac{\partial^2}{\partial R^2}\frac{\delta\underline{\mu}}{\delta\alpha_k(\gamma_1',\ldots,\gamma_{m_k}')}-\frac{\partial^2(\underline{f}^{\pm})^T}{\partial R^2}\frac{\delta\underline{\mu}}{\delta\alpha_k(\gamma_1',\ldots,\gamma_{m_k}')}\ . \tag{18b}$$

The radial derivatives in (18b) are given by (17a) and (17b) where $\bar{F}_{ji}=\bar{f}_{ji}^{\pm}$ and $\delta F_{ji}=\delta\mu_{ji}$. Integrating (18b) over R and substituting the result into (12b) allows for the evaluation of (12a) after some algebraic simplifications (including the symmetry assumption $S_{ij}=S_{ji}$):

$$\begin{aligned}\frac{\delta S_{ij}}{\delta\alpha_k(\gamma_1',\ldots,\gamma_{m_k}')}=\frac{1}{2i}\Bigg\{&\sum_n W_R\left[\frac{\delta f_{in}^{-}(R)}{\delta\alpha_k(\gamma_1',\ldots,\gamma_{m_k}')},\bar{\psi}_{nj}(R)\right]-\sum_k \bar{S}_{ik}W_R\left[\frac{\delta f_{kn}^{+}(R)}{\delta\alpha_k(\gamma_1',\ldots,\gamma_{m_k}')},\bar{\psi}_{nj}(R)\right]\\&-\sum_{q,s}\int d\vec{r}\,d\vec{R}\,\bar{\psi}_{qi}(R)\bar{\phi}_q^{*}(\vec{r},\hat{\Omega})\frac{\partial\bar{G}(\vec{r},\vec{R})}{\partial\alpha_k(\gamma_1,\ldots,\gamma_{m_k})}\\&\times\bar{\phi}_s(\vec{r},\hat{\Omega})\bar{\psi}_{sj}(R)\delta(\gamma_1-\gamma_1')\cdots\delta(\gamma_{m_k}-\gamma_{m_k}')\Bigg\}\ .\end{aligned} \tag{19}$$

With Eq. (19) we now have an expression for the desired sensitivity density $\delta S_{ij}/\delta\alpha_k$ in terms of known quantities.

Implicit in Eq. (19) is the evaluation of all quantities at large R, since the scattering matrix is only defined asymptotically. The functional derivatives $\delta f_{ij}^{\pm}/\delta\alpha_k(\gamma_1',\ldots,\gamma_{m_k}')$ may be evaluated directly at large values of R since explicit analytical expressions for the $f_{ij}^{\pm}$ are known there. The upper limit on the integral term is also evaluated at large R. It will be shown below that the R dependence of the Wronskian terms cancels with the R dependence of the integral term, leaving a sensitivity density that is independent of R.

Equation (19) has a simple relationship to the result of Ref. 1(b). In that work, an expression for the sensitivity coefficient $\partial S_{ij}/\partial\alpha_k$, where α_k is a constant, was derived. An integration of Eq. (19) over the range of $\{\gamma_1',\ldots,\gamma_{m_k}'\}$ reduces to the result of Ref. 1(b). We may conclude, therefore, that

$$\frac{\partial S_{ij}}{\partial\alpha_k}=\int\cdots\int d\gamma_1'\cdots d\gamma_{m_k}'\frac{\delta S_{ij}}{\delta\alpha_k(\gamma_1',\ldots,\gamma_{m_k}')} \tag{20}$$

for the case in which $\bar{\alpha}_k$ is not a function of $\{\gamma_1,\ldots,\gamma_{m_k}\}$. Analogous expressions have been obtained for chemical kinetic systems.

In Sec. III of this paper, we will evaluate Eq. (19) for specific parameters α_k and give quantitative results for a particular model system. Before proceeding to this example we consider a more general case involving variation of the full interaction potential, i.e., $V(\vec{r},\vec{R})$ as the parameter. The first two terms of Eq. (19) are zero in this case. The remaining integral term may be easily evaluated; the result is

$$\begin{aligned}\frac{\delta S_{ij}}{\delta V(\vec{r}\,',\vec{R}\,')}=-\frac{\mu}{i\hbar^2}\sum_{q,s}&[\bar{\psi}_{iq}^{\dagger}(R')\bar{\phi}_q(\vec{r}\,',\hat{\Omega}\,')]^{*}\\&\times\bar{\phi}_s(\vec{r}\,',\hat{\Omega}\,')\bar{\psi}_{sj}(R')\ ,\end{aligned} \tag{21a}$$

where $\underline{\bar{\psi}}^{\dagger}$ is the adjoint of the matrix $\underline{\bar{\psi}}$. Defining

$$\Psi_i^{\mathscr{L}}(\vec{r}\,',\vec{R}\,')=\sum_q[\bar{\psi}_{iq}(R')\bar{\phi}_q(\vec{r}\,',\hat{\Omega}\,')]^{*}\ ,$$

$$\Psi_j^{R}(\vec{r}\,',\vec{R}\,')=\sum_s\bar{\phi}_s(\vec{r}\,',\hat{\Omega}\,')\bar{\psi}_{sj}(R')\ , \tag{21b}$$

we may express (21a) the following way:

$$\frac{\delta S_{ij}}{\delta V(\vec{r},\vec{R}\,')}=-\frac{\mu}{i\hbar^2}\Psi_i^{\mathscr{L}}(\vec{r}\,',\vec{R}\,')\Psi_j^{R}(\vec{r}\,',\vec{R}\,')\ . \tag{21c}$$

The right-hand side of Eq. (21c) is *analogous* to the density, but is generally not *proportional* to the density. Notice that (21c) implies that uncertainties in the value of $V(\vec{r},\vec{R})$ in regions for which the wave-function product of (21c) is small will have little effect on the outcome of a scattering calculation (see Fig. 1). If $V(\vec{r},\vec{R})$ is to be varied in regions of space for which the wave-function product of (21c) is large, the scattering matrix will be more substantially changed. Quite naturally variations of V at large values of R will have a substantial effect. In many cases it can be more useful to consider the normalized density $\delta\underline{S}/\delta\ln V$ (or $\delta\underline{S}/\delta\ln\alpha_k$) since this will weight regions where the potential is important. The generally oscillatory nature of (21c) clearly indicates that a specific variation in S_{ij} could be achieved by a wide variety of potential alterations. This point has a direct bearing on problems in inverse scattering theory.

Next we will consider the case in which the internal part of the Hamiltonian $H_{\text{int}}(\vec{r})$ is to be varied. Variations in $H_{\text{int}}(\vec{r})$, or parameters characterizing $H_{\text{int}}(\vec{r})$, will perturb the asymptotic form of the wave function. Consequently, the first two terms of Eq. (19) will give a nonzero contribution. They will be evaluated by explicitly taking the functional derivative of $\underline{f}^{\pm}$ with respect to $H_{\text{int}}(\vec{r})$. The functional form of $\underline{f}^{\pm}$ is known only for large R, but that is sufficient for our purposes. The scattering matrix is determined for large R and we will evaluate the sensitivity density (19) at large R also.

Noting that

$$\frac{\delta f_{ij}^{\pm}(R)}{\delta H_{\text{int}}(\vec{r})}=\frac{\partial f_{ij}^{\pm}(R)}{\partial k_j}\frac{\delta k_j}{\delta H_{\text{int}}(\vec{r}\,')}\ , \tag{22a}$$

and using Eq. (46),

$$\frac{\delta f_{ij}^{\pm}(R)}{\delta H_{\text{int}}(\vec{r}\,')}=(\pm iR-\tfrac{1}{2}\bar{k}_j^{-1})\bar{f}_{ij}^{\pm}(R)\frac{\delta k_j}{\delta H_{\text{int}}(\vec{r}\,')} \tag{22b}$$

reduces the determination of the functional derivative of $\underline{f}^{\pm}$ to that of $\vec{k}$. Defining the matrix $\underline{\tilde{k}}$ as

$$\tilde{k}_{ij}=\delta_{ij}k_i\ , \tag{23a}$$

we may write

$$\underline{\tilde{k}}=\left[\frac{2\mu}{\hbar^2}(\underline{1}E-\underline{\tilde{\epsilon}})\right]^{1/2}, \tag{23b}$$

where

$$\tilde{\epsilon}_{ij}=\delta_{ij}\epsilon_j$$
$$=\int d\vec{r}\,d\hat{\Omega}\,\phi_i^*(\vec{r},\hat{\Omega})H_{\text{int}}(\vec{r})\phi_j(\vec{r},\hat{\Omega})\ . \tag{23c}$$

Taking the functional derivative of (23a) with respect to $H_{\text{int}}(\vec{r}\,')$ yields

$$\frac{\delta\tilde{k}_{ij}}{\delta H_{\text{int}}(\vec{r}\,')}=-\frac{2\mu}{\hbar^2(\bar{k}_i+\bar{k}_j)}\frac{\delta\tilde{\epsilon}_{ij}}{\delta H_{\text{int}}(\vec{r}\,')}\ , \tag{24a}$$

where

$$\frac{\delta\tilde{\epsilon}_{ij}}{\delta H_{\text{int}}(\vec{r}\,')}=\int d\vec{r}\,d\hat{\Omega}\left[\bar{\phi}_i^*(\vec{r},\hat{\Omega})H_{\text{int}}(\vec{r})\frac{\delta\phi_j(\vec{r},\hat{\Omega})}{\delta H_{\text{int}}(\vec{r}\,')}+\bar{\phi}_i^*(\vec{r},\hat{\Omega})\bar{\phi}_j(\vec{r},\hat{\Omega})\delta^3(r-r')+\frac{\delta\phi_i^*(\vec{r},\hat{\Omega})}{\delta H_{\text{int}}(\vec{r}\,')}H_{\text{int}}(\vec{r})\bar{\phi}_j(\vec{r},\hat{\Omega})\right]. \tag{24b}$$

It can be shown, by following arguments similar to first-order perturbation theory, that

$$\frac{\delta\phi_l(\vec{r},\hat{\Omega})}{\delta\alpha_k(\gamma'_1,\ldots,\gamma'_{m_k})}=\sum_{j\neq l}\mathscr{H}_{lj}^{k}\bar{\phi}_j(\vec{r},\hat{\Omega})\ , \tag{25}$$

where $\mathscr{H}_{lj}^{k}$ is given by Eq. (17d) and it is assumed that the eigenvalues ϵ_i are nondegenerate for simplicity. Substituting (25) into (24b) we find that

$$\frac{\delta\tilde{\epsilon}_{ij}}{\delta H_{\text{int}}(\vec{r}\,')}=0\quad\text{for } i\neq j\ . \tag{26a}$$

For $i=j$, the first and third terms of (24b) cancel immediately [if $H_{\text{int}}(\vec{r})$ is Hermitian], leaving

$$\frac{\delta\tilde{\epsilon}_{jj}}{\delta H_{\text{int}}(\vec{r}\,')}=\int d\hat{\Omega}\,\bar{\phi}_j^*(\vec{r}\,',\hat{\Omega})\bar{\phi}_j(\vec{r}\,',\hat{\Omega})\ . \tag{26b}$$

Substituting this result into (24a) and then (22b), we arrive at

$$\frac{\delta f_{ij}^{\pm}(R)}{\delta H_{\text{int}}(\vec{r}\,')}=-\frac{\mu}{\bar{k}_j\hbar^2}(\pm iR-\tfrac{1}{2}\bar{k}_j^{-1})f_{ij}^{\pm}(R)\int d\hat{\Omega}\,\bar{\phi}_j^*(\vec{r}\,',\hat{\Omega})\bar{\phi}_j(\vec{r}\,',\hat{\Omega})\ . \tag{27}$$

Equation (27) can be substituted into Eq. (19) which, after some simplification, yields

$$\frac{\delta S_{ij}}{\delta H_{\text{int}}(\vec{r})}=-\frac{\mu}{2i\hbar^2}\sum_l\left[-\frac{R}{\bar{k}_l^2}\frac{\partial\bar{\psi}_{il}^T}{\partial R}\frac{\partial\bar{\psi}_{lj}}{\partial R}+\frac{1}{2\bar{k}_l^2}\frac{\partial\bar{\psi}_{il}^T}{\partial R}\bar{\psi}_{lj}+\frac{1}{2\bar{k}_l^2}\bar{\psi}_{il}^T\frac{\partial\bar{\psi}_{lj}}{\partial R}-R\bar{\psi}_{il}^T\bar{\psi}_{lj}\right]\int d\hat{\Omega}\,\bar{\phi}_l^*(\vec{r}\,',\hat{\Omega})\bar{\phi}_l(\vec{r}\,',\hat{\Omega})$$
$$-\frac{\mu}{i\hbar^2}\sum_{l,l'}\int_0^R dR'\,d\hat{\Omega}\,\bar{\psi}_{il}^T(R')\bar{\phi}_l^*(\vec{r}\,',\hat{\Omega})\bar{\phi}_{l'}(\vec{r},\hat{\Omega})\bar{\psi}_{l'j}(R)\ . \tag{28}$$

This result is more complicated than that of (21c) corresponding to a variation of the potential. This is a reflection of the fact that $H_{\text{int}}(\vec{r})$ affects the boundary conditions as well as the scattering.

Equation (28) can be shown to be independent of R for large values of R; a similar analysis can be done for Eq. (21c). First, we evaluate the radial wave function and its derivative at large R:

$$\lim_{R\to\infty}\bar{\psi}_{il}^T=\sum_{l'}(\bar{S}_{il'}\bar{f}_{ll'}^{+}-\delta_{il'}\bar{f}_{ll'}^{-})\ , \tag{29a}$$

$$\lim_{R\to\infty}\frac{1}{i\bar{k}_l}\frac{\partial\bar{\psi}_{il}^T}{\partial R}=\sum_{l'}(\bar{S}_{il'}\bar{f}_{ll'}^{+}+\delta_{il'}\bar{f}_{ll'}^{-})\ . \tag{29b}$$

Substituting (29a) and (29b) into (28) and taking the derivative of (28) with respect to R we find

$$\frac{\partial}{\partial R}\left[\frac{\delta S_{ij}}{\delta H_{\text{int}}(\vec{r}\,')}\right]=0 \tag{30}$$

as expected. This result is not restricted to the parameter variation of $H_{\text{int}}(\vec{r})$, but is rather a general result for the variation of any parameter which perturbs the asymptotic form of the wave functions [i.e., which appears in k_j of Eq. (23b)].

In Sec. III, we will consider a specific example which illustrates the results of this section.

III. AN EXACTLY SOLUBLE MODEL PROBLEM

The general formulation of Sec. II can be directly applied to complex close-coupling calculations. However, since the theory is new, we choose to illustrate it with a simple, exactly soluble model that has been examined before.[4] This model will be used to illustrate some basic features of the sensitivity formulas in Sec. II. The Hamiltonian for this model includes an interaction potential that is independent of the angular variables:

$$V(r,R)=\begin{cases} v_0 V_{\text{int}}(r), & R<a \\ 0, & R>a\,. \end{cases} \tag{31}$$

The potential $V(r,R)$ is a square well with one-dimensional internal structure given by $V_{\text{int}}(r)$. It will not be necessary to explicitly specify $V_{\text{int}}(r)$ in the calculation; only matrix elements of $V_{\text{int}}(r)$ will be needed.

Since $V(r,R)$ is independent of the angle $\hat{\Omega}$, we may expand the total wave function as

$$\phi^i(r,\vec{R})=\frac{1}{R}\sum_{j,l}\chi_j(r)P_l(\theta)\psi^l_{ji}(R)\ , \tag{32}$$

where $P_l(\theta)$ are Legendre polynomials and χ_j is an eigenfunction of the internal Hamiltonian [note that $\phi_{j'}(\vec{r},\hat{\Omega})=\chi_j(r)P_l(\theta)$ where $j'=(j,l)$ in the notation of Sec. II]. The χ_j are defined by

$$H_{\text{int}}(r)\chi_j(r)=\epsilon_j\chi_j(r)\ . \tag{33}$$

Substituting (31)—(33) into (28) we arrive at the following expression for the desired sensitivity density:

$$\frac{\delta S_{ij}}{\delta H_{\text{int}}(r')}=\sum_{l,k}\left[\frac{-(2l+1)\mu}{2i\hbar^2k_k^2}\chi_k^*(r')\chi_k(r')\left[-R\frac{\partial\bar{\psi}^l_{ki}}{\partial R}\frac{\partial\bar{\psi}^l_{kj}}{\partial R}+\frac{1}{2}\frac{\partial\bar{\psi}^l_{ki}}{\partial R}\bar{\psi}^l_{kj}+\tfrac{1}{2}\bar{\psi}^l_{ki}\frac{\partial\bar{\psi}^l_{kj}}{\partial R}-k_k^2R\bar{\psi}^l_{ki}\bar{\psi}^l_{kj}\right]\right.$$
$$\left.-\sum_{k'}\frac{(2l+1)\mu}{i\hbar^2}\int_0^R dR'\bar{\psi}^l_{ki}(R')\chi_k^*(r')\chi_{k'}(r')\bar{\psi}^l_{k'j}(R')\right]\ . \tag{34}$$

Both the radial wave function $\bar{\psi}^l_{ij}(R)$ and the internal basis functions $\chi_j(r)$ appear in this expression. We have chosen a system for which both can be found analytically. If we choose $H_{\text{int}}(r)$ to be a square well describing the molecular motion, the functions $\chi_j(r)$ can be found immediately. Letting

$$H_{\text{int}}(r)=\begin{cases} -\dfrac{d^2}{dr^2}, & \dfrac{-L}{2}\le r\le\dfrac{L}{2} \\ \infty, & |r|>\dfrac{L}{2} \end{cases} \tag{35a}$$

in units of $\hbar^2/2\mu=1$, then

$$\epsilon_j=j^2\pi^2/L^2,\quad j=1,2,\ldots \tag{35b}$$

and

$$\chi_j(r)=\begin{cases} \left[\dfrac{2}{L}\right]^{1/2}\cos\dfrac{j\pi r}{L}, & j\text{ odd},\ |r|\le L/2 \\ \left[\dfrac{2}{L}\right]^{1/2}\sin\dfrac{j\pi r}{L}, & j\text{ even},\ |r|\le L/2 \\ 0, & |r|>L/2\,. \end{cases} \tag{35c}$$

The radial functions $\bar{\psi}^l$ can also be found analytically as shown in Ref. 4. The resulting expression for $\bar{\psi}^l$ can then be used to evaluate the sensitivity density $\delta\underline{S}/\delta H_{\text{int}}(r)$ in Eq. (34). We will consider a simple two-channel scattering system in which the scattered waves are s waves for simplicity (other partial waves may be similarly treated). After some straightforward algebra (see the Appendix for details) Eq. (34) reduces to

$$\frac{\delta S_{ij}}{\delta H_{\text{int}}(r')}=\sum_{k=1}^{2}\chi_k^2(r')M^k_{ij}\ , \tag{36}$$

where M^k_{ij} is a constant, complex matrix. Here we are considering a system with just two open channels. The sensitivity density $\delta\underline{S}/\delta H_{\text{int}}(r')$ is a complex, symmetric matrix. The real and imaginary parts of $\delta S_{11}/\delta H_{\text{int}}(r')$, $\delta S_{12}/\delta H_{\text{int}}(r')$, and $\delta S_{22}/\delta H_{\text{int}}(r')$ are shown in Fig. 2 as a function of r'. Here we are taking the total energy $E=5$, the potential range $a=1$, the internal Hamiltonian range $L=\pi$, the channel wave numbers $k_1=2$, $k_2=1$, and the coupling matrix elements $U_{11}=U_{12}=U_{22}=1$.

It is sometimes of use to decompose the scattering matrix into a modulus and phase

$$S_{ij}=|S_{ij}|\exp(i\eta_{ij})\ , \tag{37}$$

where $|S_{ij}|\equiv(S_{ij}S^*_{ij})^{1/2}$ is the magnitude of the scattering matrix element and $\eta_{ij}\equiv\tan^{-1}[\text{Im}(S_{ij})/\text{Re}(S_{ij})]$ is the phase of the matrix element. The functional derivative of (37) yields the desired sensitivity densities of the magnitude and phase of the scattering matrix element:

$$\frac{\delta|S_{ij}|}{\delta H_{\text{int}}(r)}=|\bar{S}_{ij}|\left[\text{Re}(\bar{S}_{ij})\text{Re}\frac{\delta\bar{S}_{ij}}{\delta H_{\text{int}}(r)}+\text{Im}(\bar{S}_{ij})\text{Im}\frac{\delta S_{ij}}{\delta H_{\text{int}}(r)}\right], \tag{38a}$$

$$\frac{\delta\eta_{ij}}{\delta H_{\text{int}}(r)}=|\bar{S}_{ij}|\left[\text{Re}(\bar{S}_{ij})\text{Im}\frac{\delta S_{ij}}{\delta H_{\text{int}}(r)}-\text{Im}(\bar{S}_{ij})\text{Re}\frac{\delta S_{ij}}{\delta H_{\text{int}}(r)}\right]. \tag{38b}$$

Figure 3 shows (38a) and (38b) on the same range of values as in Fig. 2. By comparing Fig. 2 with Fig. 3 we

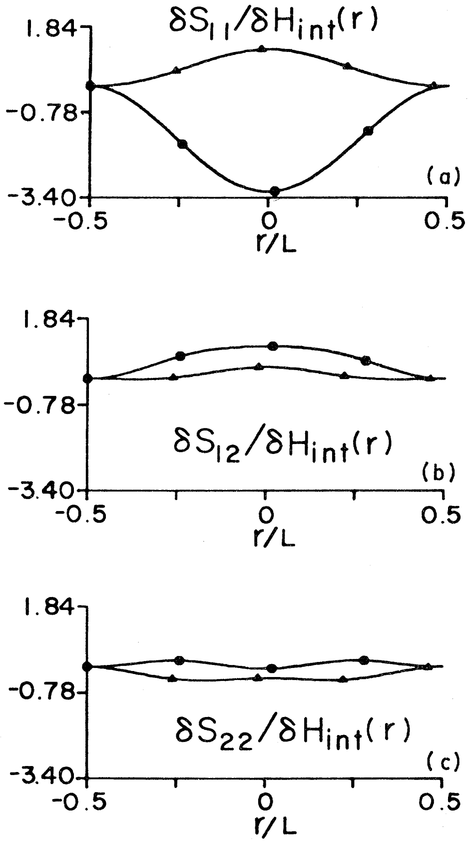

FIG. 2. Real (●—●) and imaginary (▲—▲) parts of the sensitivity densities (a) $\delta S_{11}/\delta H_{\text{int}}(r)$, (b) $\delta S_{12}/\delta H_{\text{int}}(r)$, and (c) $\delta S_{22}/\delta H_{\text{int}}(r)$ for the model system of Sec. III as a function of the dimensionless length r/L.

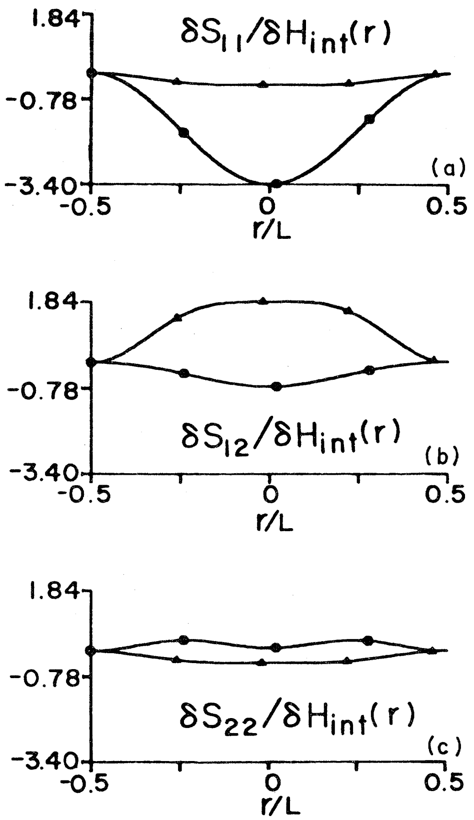

FIG. 3. The sensitivity of the magnitude $\delta|S_{ij}|/\delta H_{\text{int}}(r)$, (●—●), and the phase $\delta\eta_{ij}/\delta H_{\text{int}}(r)$, (▲—▲), given by Eqs. (38a) and (38b) for the densities of Fig. 2. [(a), (b), and (c) as in Fig. 2.]

can see that, for example, the high sensitivity of the magnitude of S_{11} [Fig. 3(a)] accounts for the large real part of $\delta S_{11}/\delta H_{\text{int}}(r)$ [Fig. 2(a)]. The correspondence between the sensitivity of the phase of S_{11} and the imaginary part of $\delta S_{11}/\delta H_{\text{int}}(r)$ is not as simple. A similar result is found for the other diagonal term S_{22} and for S_{12}.

The sensitivity of the scattering matrix to the interaction potential is given by Eqs. (21a)–(21c). For this example, the interaction potential is specified in Eq. (31) and the wave functions in Eq. (35c) and the Appendix. Elements of the sensitivity density matrix are shown in Fig. 4 and are given by

$$\frac{\delta S_{ij}}{\delta V(r,R)} = \frac{-\mu}{i\hbar^2}\sum_{k=1}^{2}\psi_{ik}^*(R)\chi_k(r)\sum_{l=1}^{2}\chi_l(r)\psi_{lj}(R) . \qquad (39)$$

The diagonal term S_{22} shows the highest sensitivity to perturbations of V and this sensitivity is largest in the region $R > a$ [see Figs. 4(e) and 4(f)]. It is also largest in the places where $\chi_2(r)^2$ is a maximum. Perturbing $V(r,R)$ in a region of r,R space where the second channel has a large density will have a large effect on S_{22}. The other diagonal term S_{11} shows a similar effect but the sensitivity of S_{11} is highest near $R = a$. Again, a perturbation of $V(r,R)$ in a region of r,R space where the first channel has a large density will result in a significant deviation of S_{11}. The imaginary parts of both S_{11} and S_{22} are about twice as sensitive to a perturbation of V as are their respective real parts.

The off-diagonal terms of the scattering matrix show a more complicated sensitivity. The real part of S_{12} will increase in response to a perturbation of $V(r,R)$, while the same perturbation will induce a decrease in the imaginary part of S_{12}. The matrix $\underline{S}$ is symmetric, as is the sensitivity density matrix, so these same observations apply to S_{21} as well. Qualitatively, the sensitivity of S_{12} is highest where the second channel has a large density. Some dependence on the density of the first channel is expected, but this dependence appears to be quite weak. In addition, the sensitivity of S_{12} is highest in the region $R > a$ as it is for S_{22}.

Some general comments can be made about the sensitivity densities $\delta\underline{S}/\delta H_{\text{int}}(r)$ and $\delta\underline{S}/\delta V(r,R)$ for the simple problem studied here; these comments will also apply to other cases. First, the sensitivity densities tend to be large where the wave function has large amplitude. Second, the densities will be oscillatory, again reflecting the nature of the wave function. This latter aspect introduces the possibility of altering the potential in a local region around a point $(\vec{r}\,',\vec{R}\,')$ in such a way as to compensate for the effects (on $\underline{S}$) of a change in the potential

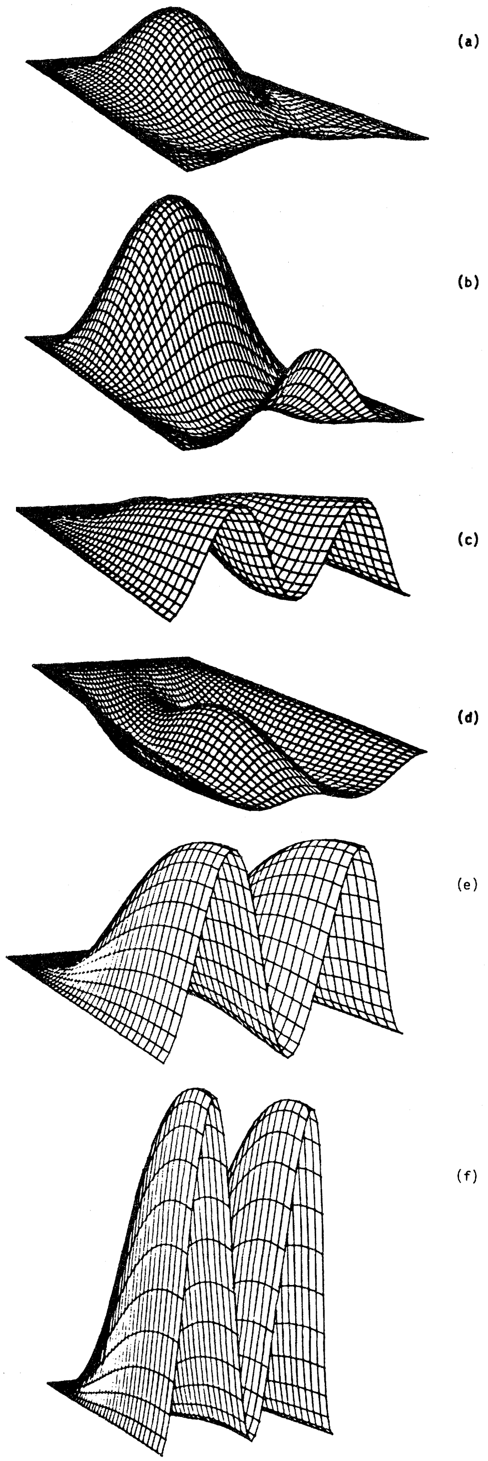

FIG. 4. The real and imaginary parts of the sensitivity densities $\delta S_{ij}/\delta V(r,R)$ for the model system of Sec. III. (a) $\mathrm{Re}(\delta S_{11}/\delta V(r,R))$, (b) $\mathrm{Im}(\delta S_{11}/\delta V(r,R))$, (c) $\mathrm{Re}(\delta S_{12}/\delta V(r,R))$, (d) $\mathrm{Im}(\delta S_{12}/\delta V(r,R))$, (e) $\mathrm{Re}(\delta S_{22}/\delta V(r,R))$, and (f) $\mathrm{Im}(\delta S_{22}/\delta V(r,R))$. All surfaces are plotted with the same scaling; the maximum plotted value is 1.7 units and the minimum plotted value is -0.3 units. The r and R axes are indicated in Fig. 4(a) and the ranges of values are $-0.5 \leq r/L \leq +0.5$, $0 \leq R \leq 2.0$. All sensitivity densities are zero for $\{r=-0.5, r=+0.5, \text{all } R\}$ and for $\{R=0, \text{all } r\}$.

around another point $(\vec{r},\vec{R})$. The best way to investigate this matter is through the *derived* sensitivity density $\delta V(\vec{r},\vec{R})/\delta V(r',R')_{\underline{S}}$ which is a measure of the correlation between points in coordinate space that preserve $\underline{S}$ or some of the matrix elements of $\underline{S}$. Derived densities similar to this have been considered previously in chemical kinetics.[3] It remains for further research to explore these matters in collision dynamics.

IV. CONCLUSIONS

The formulation presented in this paper represents the first step in the derivation of a comprehensive sensitivity theory for scattering. The discussion at the end of Sec. III hinted at the broader aspects of sensitivity analysis, such as the matter of derived densities. In practice, an entire family of sensitivity densities (including the derived densities) exist; these are useful for addressing a variety of physical questions about the scattering process. In a manner similar to that used in chemical kinetics,[3] the critical input to the calculation of these densities will be the elementary densities discussed in this paper. Ultimately, a complete map describing interrelationships between the Hamiltonian and system observables may be generated. A more complete theory and further illustrations, all based on the work in this paper, will be reported later.

ACKNOWLEDGMENT

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APPENDIX

With the expansion of the wave function given in Eq. (32) we find the following radial equation:

$$\left[\frac{\partial^2}{\partial R^2}+k_j^2-\frac{l(l+1)}{R^2}\right]\psi_{ji}^l(R) = \begin{cases} V_0\sum\limits_{j'} U_{jj'}\psi_{j'i}^l(R), & R<a \\ 0, & R>a \end{cases} \tag{A1}$$

where k_j is defined in Eq. (3b) and

$$U_{jj'}=\frac{2\mu}{\hbar^2}\int dr\,\chi_j^*(r)V_{\mathrm{int}}(r)\chi_{j'}(r)\ . \tag{A2}$$

The asymptotic boundary conditions on Eq. (A1) are

$$\lim_{R\to\infty}\psi_{ji}^l(R)=-\delta_{ji}k_i^{-1/2}\exp[-i(k_iR-l\pi/2)] +k_j^{-1/2}\exp(k_jR-l\pi/2)S_{ji}\ . \tag{A3}$$

For open channels, i.e., $E>\epsilon_j$, the appropriate outer solution (for $R>a$) is then

$$\psi_{ji}^l(R)=\delta_{ji}k_i^{-1/2}k_jRh_l^{(2)}(k_jR)+k_j^{-1/2}S_{ij}^lk_jRh_l^{(1)}(k_jR)\ , \tag{A4}$$

where $h_l^{(1),(2)}$ are spherical Hankel functions.[5]

To uncouple the equations in the interior region $(R<a)$

we first define the wave-vector matrix $\tilde{\underline{k}}$ as in Eq. (23a) and let $\underline{P}$ be a matrix which diagonalizes $\tilde{\underline{k}}^2 - V_0\underline{U}$:

$$\underline{d}^2 = \underline{P}^T(\tilde{\underline{k}}^2 - V_0\underline{U})\underline{P} \ , \tag{A5}$$

where $\underline{d}^2$ is a diagonal matrix. We next transform to a new set of wave functions

$$\tilde{\underline{\psi}}^l = \underline{P}^T\underline{\psi}^l \ . \tag{A6}$$

Then, the Schrödinger equation inside ($R < a$) is

$$\left[\frac{\partial^2}{\partial R^2} + d_j^2 - \frac{l(l+1)}{R^2}\right]\tilde{\psi}^l_{ji}(R) = 0 \ , \tag{A7}$$

where d_j^2 is a diagonal element of $\underline{d}^2$. The open-channel solutions inside (for $E > \epsilon_j$, $R < a$) are then

$$\tilde{\psi}^l_{ji}(R) = \begin{cases} C^l_{ij} d_j R j_l(d_j R), & d_j^2 > 0 \\ C^l_{ij} f_j R i_l(f_j R), & d_j^2 = -f_j^2 < 0 \end{cases} \tag{A8}$$

where j_l is a spherical Bessel function and i_l a modified spherical Bessel function of the first kind.[5] The matrix $\underline{C}^l$ is obtained by matching the inside and outside forms of the wave function [(A4) and (A8)] and its radial derivative at $R = a$.

In matching the wave function and its derivative at $R = a$ it is convenient to introduce the following notation:

$$H^{(1),(2)}_{ji} = \delta_{ji} k_j a h^{(1),(2)}_l(k_j a) \ , \tag{A9}$$

$$I_{ji} = \begin{cases} \delta_{ji} d_j a j_l(d_j a), & d_j^2 > 0 \\ \delta_{ji} f_j a i_l(f_j a), & d_j^2 = -f_j^2 < 0 \end{cases} \tag{A10}$$

where we drop the l subscript for convenience of notation. The continuity equations at $R = a$ are then

$$\underline{H}^{(2)}\underline{k}^{-1/2} + \underline{H}^{(1)}\underline{k}^{-1/2}\underline{S}^T = \underline{P}\,\underline{I}\,\underline{C}^T \ , \tag{A11}$$

$$\underline{H}^{(2)'}\underline{k}^{-1/2} + \underline{H}^{(1)'}\underline{k}^{-1/2}\underline{S}^T = \underline{P}\,\underline{I}'\underline{C}^T \ , \tag{A12}$$

where a prime indicates the radial derivative of the Hankel or Bessel function evaluated at $R = a$. Equations (A11) and (A12) comprise two simultaneous equations for the matrices $\underline{S}$ and $\underline{C}$ and, hence, can be solved for both. Doing so, substituting the result in (A8) and transforming back to the original wave function we find the following result for $R < a$:

$$\underline{\psi}(R) = \underline{P}\,\underline{I}(R)[\underline{I}(a)]^{-1}\underline{P}^T[\underline{H}^{(1)}(\underline{H}^{(1)}\underline{A} - \underline{H}^{(1)'})^{-1}(\underline{H}^{(2)'} - \underline{H}^{(2)}\underline{A}) + \underline{H}^{(2)}]\underline{k}^{-1/2} \ , \tag{A13}$$

where $\underline{A} \equiv \underline{P}\,\underline{I}'(a)[\underline{I}(a)]^{-1}\underline{P}^T$ and $\underline{I}(R)$ in Eq. (A13) is evaluated at an arbitrary R value rather than at $R = a$.

With (A13) we now have analytical expressions for all the quantities in Eq. (34). Substituting (A13) into (34) we arrive at Eq. (36) where M^k_{ij} is given by

$$M^k_{ij} = \frac{-\mu}{2i\hbar^2 k_k^2} \sum_{m=1}^{2} \sum_{n=1}^{2} [P_{km}P_{kn}C_{im}C_{jn}(-aI'_m I'_n + \tfrac{1}{2}I'_m I_n + \tfrac{1}{2}I_m I'_n - k_k^2 a I_m I_n - 2k_k^2 \mathscr{I}_{mn})] \ , \tag{A14}$$

with

$$I_{ji} = I_j\delta_{ji}, \quad I'_{ji} = I'_j\,\delta_{ji} \ , \tag{A15}$$

and

$$\mathscr{I}_{mn} = \begin{cases} \dfrac{\sin[(d_m - d_n)a]}{2(d_m - d_n)} - \dfrac{\sin[(d_m + d_n)a]}{2(d_m + d_n)}, & d_m^2 > 0, \ d_n^2 > 0, \ d_m \neq d_n \\ \dfrac{1}{2(d_m^2 + f_n^2)}\{-f_m \sin(d_m a)[\exp(-f_n a) + \exp(-f_n a)] - d_m \cos(d_m a)[\exp(-f_n a) - \exp(-f_n a)]\}, & d_m^2 > 0, \ d_n^2 < 0 \\ \dfrac{1}{4}\left[\dfrac{1}{f_m + f_n}\{\exp[(f_m + f_n)a] - \exp[-(f_m + f_n)a]\} + \dfrac{1}{f_m - f_n}\{\exp[-(f_m - f_n)a] - \exp[(f_m - f_n)a]\}\right], & d_m^2 < 0, \ d_n^2 < 0, \ d_m \neq d_n \\ \tfrac{1}{2}[d_m a - \tfrac{1}{2}\sin(2d_m a)], & d_m^2 > 0, \ d_n^2 > 0, \ d_m = d_n \\ \dfrac{1}{2}\left[\dfrac{1}{4d_m}\exp(2d_m a) - \exp(-2d_m a) - a\right], & d_m^2 < 0, \ d_n^2 < 0, \ d_m = d_n \ . \end{cases} \tag{A16}$$

In (A14)–(A16) we have considered only $l = 0$ terms as explained in the text.

If we consider also only two-channel systems, the matrices $\underline{P}$ and $\underline{C}$ can be written explicitly. Using the following notation:

$$\underline{\tilde{k}}^2-V_0\underline{U}=\begin{bmatrix} k_1^2-U_1 & -U \\ -U & k_2^2-U_2 \end{bmatrix}, \tag{A17}$$

and Eq. (A6), we see that the columns of $\underline{P}$ are simply the eigenvectors of $\underline{\tilde{k}}^2-V_0\underline{U}$. For a 2×2 matrix the eigenvectors are easily computed and we find

$$P=\begin{bmatrix} \dfrac{U}{[U^2+(k_1^2-U_1-\lambda_1)^2]^{1/2}} & \dfrac{U}{[U^2+(k_1^2-U_1-\lambda_2)^2]^{1/2}} \\ \dfrac{k_1^2-U_1-\lambda_1}{[U^2+(k_1^2-U_1-\lambda_1)^2]^{1/2}} & \dfrac{k_1^2-U_1-\lambda_2}{[U^2+(k_1^2-U_1-\lambda_2)^2]^{1/2}} \end{bmatrix}, \tag{A18}$$

where λ_1,λ_2 are the eigenvalues of $\underline{\tilde{k}}^2-V_0\underline{U}$ and are given explicitly by

$$\lambda_{1,2}=\tfrac{1}{2}(k_1^2-U_1+k_2^2-U_2)\pm\tfrac{1}{2}[(k_1^2-U_1-k_2^2+U_2)^2+4U^2]^{1/2} . \tag{A19}$$

The matrix $\underline{C}$ is also a 2×2 matrix which is found in the course of solving (A11) and (A12) to be

$$\underline{C}=\underline{k}^{-1/2}[\underline{H}^{(2)}+(\underline{H}^{(2)\prime}-\underline{H}^{(2)}\underline{A})(\underline{H}^{(1)}\underline{A}-\underline{H}^{(1)\prime})^{-1}\underline{H}^{(1)}]\underline{P} . \tag{A20}$$

This expression involves the inverse of matrix

$$\underline{Q}\equiv\underline{H}^{(1)}\underline{A}-\underline{H}^{(1)\prime} . \tag{A21}$$

Since $\underline{Q}$ is 2×2, its inverse is simply

$$\underline{Q}^{-1}=\frac{1}{\det(\underline{Q})}\begin{bmatrix} Q_{22} & -Q_{12} \\ -Q_{21} & Q_{11} \end{bmatrix}, \tag{A22}$$

where

$$Q_{ij}=-ie^{ik_ia}\left[\sum_{k=1}^{2}P_{ik}d_k\cot(d_ka)P_{jk}-ik_i\delta_{ji}\right] \tag{A23}$$

and

$$\det(\underline{Q})=e^{i(k_1+k_2)a}\Bigg[[P_{11}d_1\cot(d_1a)P_{21}+P_{12}d_2\cot(d_2a)P_{22}][P_{21}d_1\cot(d_1a)P_{11}+P_{22}d_2\cot(d_2a)P_{12}] \\ -\prod_{k=1}^{2}\left[\sum_{m=1}^{2}P_{km}d_m\cot(d_ma)P_{km}-ik_k\right]\Bigg] . \tag{A24}$$

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