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Variation-Perturbation Treatment of Scattering Problems. II. Inelastic and Rearrangement Processes*

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A variation-perturbation (VP) treatment of inelastic and rearrangement scattering processes is presented. We show that the first-order perturbation functions determine the scattering parameters through third order and develop a variation principle for the approximate calculation of these functions. It is seen how adjustable parameters in the zeroth-order potentials can be optimized separately for each scattering event by the Hulthèn variation condition, which yields a first-order function that is normalizable in the exit channel. We also propose that terms coupling different channels be included in the initial approximation. A comparison of the VP method with the usual distorted-wave Born series reveals certain practical advantages of the former, despite the formal similarity. Some of these advantages are illustrated in a sample calculation on a system characterized by a model inelastic potential.

I. INTRODUCTION

Recent experimental advances in the study of atomic and molecular collisions[1] and, especially, in electron-impact spectroscopy[2] have stimulated a number of attempts to generate quantitative methods for the calculation of scattering parameters. These include pseudoresonance variation methods,[3] Green's-function techniques,[4] semiclassical approaches,[5] an exponential form of first-order perturbation theory,[6] and others.[7] We have begun to formulate a variation-perturbation (VP) treatment of scattering problems so as to utilize some of the promising new developments[8] for bound states such as pair-function expansions[9] and exchange perturbation theories.[10] Our first paper[11] dealt with potential scattering. Here, we extend the formalism to inelastic and rearrangement processes. In doing so the most significant features of I are preserved, i.e., (i) there exists a variation condition for the first-order perturbation function ($\Psi^{(1)}$) which, in turn, determines the scattering amplitude through third order, and (ii) the unperturbed potential may contain adjustable parameters to be optimized by means of an appropriate Hulthèn[12] condition. As a consequence of this condition the first-order transition amplitude vanishes and $\Psi^{(1)}$ is normalizable in the corresponding exit channel. One new feature in our treatment of inelastic processes is the addition of terms to the zeroth-order model which couple different channels in cases where this coupling is important.

After a brief outline of the definitions and notations used in multichannel scattering theory, we derive the variation-perturbation method in Sec. III. Section IV—on optimization of the initial approximation by Hulthèn's method—completes the presentation of the VP formalism. In Sec. V the relationship of our treatment to the conventional distorted-wave Born series[13] (DWBS) is analyzed. We conclude with sample calculations for a model inelastic system. The VP reactance matrix elements, which appear to converge in each instance, compare quite favorably with those obtained from a conventional third-order DWBS. In fact, the former are accurate to 5% or less except in one case where the initial approximation is clearly inappropriate.

II. DEFINITIONS AND NOTATION

The Hamiltonian for a system of two fragments referred to a stationary over-all center of mass in an arrangement channel α may be written, in atomic units, as

$$H=H_\alpha(\vec{r}_\alpha,\vec{r})+V_\alpha(\vec{r}_\alpha,\vec{r})$$
$$=-\frac{1}{2\mu_\alpha}\nabla_\alpha^2+h_\alpha(\vec{r})+V_\alpha(\vec{r}_\alpha,\vec{r})\,, \qquad (1)$$

where $\vec{r}_\alpha$ is the vector connecting the two individual centers of mass and $\vec{r}$ designates the entire set of internal coordinates. Here $-(1/2\mu_\alpha)\nabla_\alpha^2$ is the relative kinetic energy of the fragments, V_α is the potential between these fragments, and h_α is the Hamiltonian for internal motions. We shall assume that $r_\alpha V_\alpha$ tends to zero in the asymptotic limit when $r_\alpha\to\infty$ and symbolize this by $r_\alpha V_\alpha \underset{\alpha}{\to} 0$. The internal Hamiltonian is a sum of two terms, one for each of the isolated fragments. Its eigenfunctions are, therefore, simple products that satisfy the Schrödinger relation

$$(h_\alpha - \epsilon_{\alpha i})\varphi_{\alpha i}(\vec{r}) = 0 \,, \tag{2}$$

in which i denotes the total internal state. In the asymptotic limit

$$\langle \varphi_{\alpha i} | \varphi_{\alpha j} \rangle \xrightarrow[\alpha]{} \delta_{ij} \,. \tag{3}$$

The solution of the complete Schrödinger equation

$$(H - E^{(0)})\Psi^{\pm}_{\alpha i} = 0 \tag{4a}$$

is subject to the boundary conditions (BC)[12]

$$\Psi^{\pm}_{\alpha i} \xrightarrow[\beta]{} \sum_m \Big[e^{i\vec{k}_{\beta m}\cdot\vec{r}_\beta}\delta_{\alpha\beta}\delta_{im} + r_\beta^{-1} f^{\pm}_{\beta m, \alpha i}(\vec{r}_\beta) e^{\pm i k_{\beta m} r_\beta} \Big] \varphi_{\beta m}(\vec{r}) \,, \tag{4b}$$

where + (−) indicates that just outgoing (incoming) radial waves are allowed and $\vec{k}_{\beta m}$ is the relative momentum vector. In Eq. (4b) the sum over m includes only open channels for which

$$k^2_{\beta m} = 2\mu_\beta(E^{(0)} - \epsilon_{\beta m}) \geq 0 \,. \tag{5}$$

The quantity $f^{+}_{\beta m, \alpha i}(\vec{r}_\beta)$ is the outward scattering amplitude in the direction $\vec{r}_\beta$ for transitions from the entrance channel αi to the exit channel βm. And, finally, the corresponding experimentally observable differential cross section is

$$\sigma_{\beta m, \alpha i}(\vec{r}_\beta) = \left(\frac{\mu_\alpha}{\mu_\beta}\right)\left(\frac{k_{\beta m}}{k_{\alpha i}}\right) |f^{+}_{\beta m, \alpha i}(\vec{r}_\beta)|^2 \,. \tag{6}$$

III. VARIATION-PERTURBATION METHOD

We shall now derive expressions for the scattering amplitudes through third order in terms of the initial approximation and the first-order perturbation functions. This initial approximation satisfies the Schrödinger equation

$$(H^{(0)}_\alpha - E^{(0)})\Psi^{\pm(0)}_{\alpha i} = [-(1/2\mu_\alpha)\nabla^2_\alpha + h_\alpha + V^0_\alpha - E^{(0)}]\,\Psi^{\pm(0)}_{\alpha i} = 0 \,, \tag{7a}$$

with the boundary conditions

$$\Psi^{\pm(0)}_{\alpha i} \xrightarrow[\beta]{} \sum_m \Big[e^{i\vec{k}_{\beta m}\cdot\vec{r}_\beta}\delta_{\alpha\beta}\delta_{im} + r_\beta^{-1} f^{\pm(0)}_{\beta m, \alpha i}(\vec{r}_\beta) e^{\pm i k_{\beta m} r_\beta} \Big] \varphi_{\beta m}(\vec{r}) \,. \tag{7b}$$

For convenience in comparing with the DWBS, $\varphi_{\beta m}$ is taken to be an exact internal eigenfunction of h_β. However, the treatment may be amended to accommodate an approximate eigenfunction as well. Note that the solution of Eqs. (7) yields the zeroth-order scattering amplitudes $f^{\pm(0)}_{\beta m, \alpha i}(\vec{r}_\beta)$.

As usual, we consider the Schrödinger equation

$$(H^0_\alpha + \lambda V^{(1)}_\alpha - E^{(0)})\Psi^{\pm}_{\alpha i}(\lambda) = 0 \,, \tag{8}$$

where $V^{(1)}_\alpha$ is defined as

$$V^{(1)}_\alpha \equiv V_\alpha - V^{(0)}_\alpha \,, \tag{9}$$

so that the desired wave function [cf. Eq. (4a)] is obtained when $\lambda = 1$. If $\Psi^{\pm(0)}_{\alpha i}$ is a sufficiently accurate initial approximation, then the exact solution of Eq. (8) can be expanded in a convergent power series:

$$\Psi^{\pm}_{\alpha i}(\lambda) = \sum_p \lambda^p \Psi^{\pm(p)}_{\alpha i} \tag{10}$$

for $0 \leq \lambda \leq 1$. There is, of course, a corresponding expansion

$$f^{\pm}_{\beta m, \alpha i}(\lambda; \vec{r}_\beta) = \sum_p \lambda^p f^{\pm(p)}_{\beta m, \alpha i}(\vec{r}_\beta) \tag{11}$$

for the scattering amplitude. Substituting the expression (10) into the Schrödinger relation (8), and equating like powers of λ, we obtain the perturbation equations

$$(H^{(0)}_\alpha - E^{(0)})\Psi^{\pm(0)}_{\alpha i} = 0 \tag{12a}$$

and

$$(H^{(0)}_\alpha - E^{(0)})\Psi^{\pm(p)}_{\alpha i} + V^{(1)}_\alpha \Psi^{\pm(p-1)}_{\alpha i} = 0 \quad (p > 0) \,. \tag{12b}$$

In a similar manner, the boundary conditions on $\Psi^{\pm(p)}_{\alpha i}$ are found using Eqs. (11) and (4b) to give

$$\Psi^{\pm(p)}_{\alpha i} \xrightarrow[\beta]{} \sum_m \Big[e^{i\vec{k}_{\beta m}\cdot\vec{r}_\beta}\delta_{\alpha\beta}\delta_{im}\delta_{p0} + r_\beta^{-1} f^{\pm(p)}_{\beta m, \alpha i}(\vec{r}_\beta) e^{\pm i k_{\beta m} r_\beta} \Big] \varphi_{\beta m}(\vec{r}) \,. \tag{13}$$

In order to determine the perturbation corrections to the outward scattering amplitudes we insist that

$$\langle \Psi^{-}_{\beta m} | H - E^{(0)} | \Psi^{+}_{\alpha i} \rangle = 0 \tag{14}$$

to all orders. For inelastic scattering without rearrangement the procedure is straightforward. When there is rearrangement an ambiguity in the definition or orders arises because H may be partitioned either as $H^{(0)}_\alpha + V^{(1)}_\alpha$ or $H^{(0)}_\beta + V^{(1)}_\beta$. Exactly the same type of ambiguity occurs in electron-exchange perturbation theories,[10] so we can take advantage of the lore that has been developed for the latter problem. The particular approach that will be followed here is that of the so-called *distinguishable electron method* (DEM).[14] First, let us note that Eqs. (8)–(13) are applicable with α replaced by β everywhere. Of course, there really should be two independent ordering parameters—λ_α and λ_β—but these will be restricted to the values $\lambda_\alpha = \lambda_\beta = \lambda$. The DEM partitioning convention is then quite simple—as far as the matrix element $\langle \Psi^{-(p)}_{\beta m} | H - E^{(0)} | \Psi^{+(q)}_{\alpha i} \rangle$ is concerned the $(p+q)$th-order term will be $\langle \Psi^{-(p)}_{\beta m} | H^{(0)}_\alpha - E^{(0)} | \Psi^{+(q)}_{\alpha i} \rangle$ if $q \leq p$

and $\langle\Psi_{\beta m}^{-(p)}|H_\beta^{(0)}-E^{(0)}|\Psi_{\alpha i}^{+(q)}\rangle$ otherwise. This convention appears to be the only one[15] that allows the second-order perturbation functions to be eliminated from the formula for the third-order scattering amplitude. Furthermore, the total amplitude through third order (or first order) then satisfies the reciprocity relation (see Appendix A) required for the exact result. Despite this evidence the ultimate test of our definition of orders will be the success or failure of calculations carried out on this basis for a sufficient number of cases.[16]

In first order the condition (14) becomes

$$\langle\Psi_{\beta m}^{-(0)}|H_\beta^{(0)}-E^{(0)}|\Psi_{\alpha i}^{+(1)}\rangle+\langle\Psi_{\beta m}^{-(0)}|V_\alpha^{(1)}|\Psi_{\alpha i}^{+(0)}\rangle=0\ . \tag{15}$$

The first term—$\langle\Psi_{\beta m}^{-(0)}|H_\beta^{(0)}-E^{(0)}|\Psi_{\alpha i}^{+(1)}\rangle$—is easily evaluated by means of Green's theorem using the asymptotic forms (13). Messiah[17] has discussed such integrations in detail so we give only the result here, i.e.,

$$\langle\Psi_{\beta m}^{-(0)}|H_\beta^{(0)}-E^{(0)}|\Psi_{\alpha i}^{+(1)}\rangle=(2\pi/\mu_\beta)f_{\beta m,\alpha i}^{+(1)}(\vec{r}_\beta)\ . \tag{16}$$

Thus, the first-order outward-scattering amplitude is

$$f_{\beta m,\alpha i}^{+(1)}(\vec{r}_\beta)=-(\mu_\beta/2\pi)\langle\Psi_{\beta m}^{-(0)}|V_\alpha^{(1)}|\Psi_{\alpha i}^{+(0)}\rangle\ . \tag{17a}$$

Completely analogous manipulations lead to the higher-order amplitudes

$$\begin{aligned}f_{\beta m,\alpha i}^{+(2)}(\vec{r}_\beta)&=-(\mu_\beta/2\pi)\big(\langle\Psi_{\beta m}^{-(1)}|H_\alpha^{(0)}-E^{(0)}|\Psi_{\alpha i}^{+(1)}\rangle\\&\quad+\langle\Psi_{\beta m}^{-(1)}|V_\alpha^{(1)}|\Psi_{\alpha i}^{+(0)}\rangle+\langle\Psi_{\beta m}^{-(0)}|V_\beta^{(1)}|\Psi_{\alpha i}^{+(1)}\rangle\big)\\&=-(\mu_\beta/2\pi)\langle\Psi_{\beta m}^{-(0)}|V_\beta^{(1)}|\Psi_{\alpha i}^{+(1)}\rangle\end{aligned} \tag{17b}$$

and

$$\begin{aligned}f_{\beta m,\alpha i}^{+(3)}(\vec{r}_\beta)&=-(\mu_\beta/2\pi)\big(\langle\Psi_{\beta m}^{-(2)}|H_\alpha^{(0)}-E^{(0)}|\Psi_{\alpha i}^{+(1)}\rangle\\&\quad+\langle\Psi_{\beta m}^{-(2)}|V_\alpha^{(1)}|\Psi_{\alpha i}^{+(0)}\rangle+\langle\Psi_{\beta m}^{-(1)}|H_\beta^{(0)}-E^{(0)}|\Psi_{\alpha i}^{+(2)}\rangle\\&\quad+\langle\Psi_{\beta m}^{-(0)}|V_\beta^{(1)}|\Psi_{\alpha i}^{+(2)}\rangle+\langle\Psi_{\beta m}^{-(1)}|V_\alpha^{(1)}|\Psi_{\alpha i}^{+(1)}\rangle\big)\\&=-(\mu_\beta/2\pi)\langle\Psi_{\beta m}^{-(1)}|V_\alpha^{(1)}|\Psi_{\alpha i}^{+(1)}\rangle\ .\end{aligned} \tag{17c}$$

In order to simplify these formulas as we have done it is necessary to invoke Eq. (12b) with $p=1$ so that

$$\langle\Psi_{\beta m}^{-(q)}|H_\alpha^{(0)}-E^{(0)}|\Psi_{\alpha i}^{+(1)}\rangle+\langle\Psi_{\beta m}^{-(q)}|V_\alpha^{(1)}|\Psi_{\alpha i}^{+(0)}\rangle=0 \tag{18}$$

for $q=1$ and 2. Furthermore, since the perturbation functions contain no plane-wave component,

$$\langle\Psi_{\beta m}^{-(1)}|H_\beta^{(0)}-E^{(0)}|\Psi_{\alpha i}^{+(2)}\rangle=\langle\Psi_{\alpha i}^{+(2)}|H_\beta^{(0)}-E^{(0)}|\Psi_{\beta m}^{-(1)}\rangle^*\ . \tag{19a}$$

And, since $V_\beta^{(1)}$ is assumed to be real, it also follows from Eq. (12b) (for the state βm) that

$$\langle\Psi_{\beta m}^{-(1)}|H_\beta^{(0)}-E^{(0)}|\Psi_{\alpha i}^{+(2)}\rangle+\langle\Psi_{\beta m}^{-(0)}|V_\beta^{(1)}|\Psi_{\alpha i}^{+(2)}\rangle=0\ . \tag{19b}$$

Equations (17) give the scattering amplitudes through third order in terms of the first-order perturbation functions. The latter, in turn, can be approximated through a stationary variation condition, as we now show. Consider the quantity $\tilde{J}_{\alpha i}^{+(2)}$ defined as

$$\begin{aligned}\tilde{J}_{\alpha i}^{+(2)}\equiv\langle\tilde{\Psi}_{\alpha i}^{+(1)}|H_\alpha^{(0)}-E^{(0)}|\tilde{\Psi}_{\alpha i}^{+(1)}\rangle+\langle\tilde{\Psi}_{\alpha i}^{+(1)}|V_\alpha^{(1)}|\Psi_{\alpha i}^{+(0)}\rangle\\+\langle\Psi_{\alpha i}^{+(0)}|V_\alpha^{(1)}|\tilde{\Psi}_{\alpha i}^{+(1)}\rangle\ ,\end{aligned} \tag{20a}$$

where $\tilde{\Psi}_{\alpha i}^{+(1)}$ is an arbitrary function obeying the boundary conditions

$$\tilde{\Psi}_{\alpha i}^{+(1)}\xrightarrow[\beta]{}\sum_m r_\beta^{-1}f_{\beta m,\alpha i}^{+(1)}(\vec{r}_\beta)e^{ik_{\beta m}r_\beta}\varphi_{\beta m}(\vec{r}) \tag{20b}$$

and $f_{\beta m,\alpha i}^{+(1)}$ is calculated from the zeroth-order wave functions. If

$$\tilde{\Psi}_{\alpha i}^{+(1)}=\Psi_{\alpha i}^{+(1)}+\delta\Psi_{\alpha i}^{+(1)}\ , \tag{21}$$

with $\Psi_{\alpha i}^{+(1)}$ being the exact first-order function, then the first-order change in $\tilde{J}_{\alpha i}^{+(2)}$ due to $\delta\Psi_{\alpha i}^{+(1)}$ is

$$\begin{aligned}\langle\delta\Psi_{\alpha i}^{+(1)}|(H_\alpha^{(0)}-E^{(0)})\Psi_{\alpha i}^{+(1)}+V_\alpha^{(1)}\Psi_{\alpha i}^{+(0)}\rangle\\+\langle\Psi_{\alpha i}^{+(0)}V_\alpha^{(1)}+\Psi_{\alpha i}^{+(1)}(H_\alpha^{(0)}-E^{(0)})|\delta\Psi_{\alpha i}^{+(1)}\rangle\ ,\end{aligned}$$

which vanishes by virtue of the same arguments used in connection with Eqs. (19). Therefore, $\tilde{J}_{\alpha i}^{+(2)}$ is stationary with respect to small variations about the exact value $J_{\alpha i}^{+(2)}$, and this condition may be used to optimize parameters in a variational approximation to $\Psi_{\alpha i}^{+(1)}$. This is the continuum analog of Hylleraas's familiar procedure for bound states. There is, of course, a corresponding condition for $\Psi_{\beta m}^{-(1)}$.

IV. OPTIMIZATION OF INITIAL APPROXIMATION

The selection of the initial scattering potentials $V_\alpha^{(0)}$ is governed by two criteria: (i) that exact solutions of the resulting zeroth-order Schrödinger equations are available; (ii) that $V_\alpha^{(0)}$ approximates V_α closely enough to give scattering amplitudes through third order as accurately as desired. To satisfy these conditions, we employ initial potentials which depend upon a number of adjustable parameters and, in general, support multichannel scattering. A variety of methods are available by means of which optimum values of the parameters may be chosen. We prefer the Hulthên variation condition[12] because the first-order perturbation function is then normalizable in the exit channel of interest. The derivation of this condition—given here for the sake of completeness—is very similar to the derivation at the end of Sec. III. This time, the pertinent functional is

$$\tilde{J}_{\beta m,\alpha i}=\langle\tilde{\Psi}^-_{\beta m}|H-E^{(0)}|\tilde{\Psi}^+_{\alpha i}\rangle\,, \tag{22}$$

with

$$\tilde{\Psi}^+_{\alpha i}=\Psi^+_{\alpha i}+\delta\Psi^+_{\alpha i}\,,\quad \tilde{\Psi}^-_{\beta m}=\Psi^-_{\beta m}+\delta\Psi^-_{\beta m}\,. \tag{23}$$

Since the asymptotic plane-wave term in $\tilde{\Psi}^+_{\alpha i}$ (and $\tilde{\Psi}^-_{\beta m}$) is exact, $\delta\Psi^+_{\alpha i}$ must satisfy the boundary condition

$$\delta\Psi^+_{\alpha i}\xrightarrow[r_\gamma]{}\sum_n r_\gamma^{-1}\delta f^+_{\gamma n,\alpha i}(\vec{\mathrm{r}}_{\gamma n})e^{ik_{\gamma n}r_\gamma}\varphi_{\gamma n}(\vec{\mathrm{r}})\ \ (\text{all }\gamma)\,, \tag{24a}$$

in which

$$\delta f^+_{\gamma n,\alpha i}(\vec{\mathrm{r}}_\gamma)=\tilde{f}^+_{\gamma n,\alpha i}(\vec{\mathrm{r}}_\gamma)-f^+_{\gamma n,\alpha i}(\vec{\mathrm{r}}_\gamma)\,. \tag{24b}$$

With the aid of Eqs. (23) and (24) the first-order variation in $\tilde{J}_{\beta m,\alpha i}$ is easily evaluated as

$$\delta\tilde{J}_{\beta m,\alpha i}=-(2\pi/\mu_\beta)\delta f^+_{\beta m,\alpha i}(\vec{\mathrm{r}}_\beta)\,, \tag{25}$$

leading to the variation condition

$$\delta\tilde{J}_{\beta m,\alpha i}=0=\delta\tilde{f}^+_{\beta m,\alpha i}\,; \tag{26a}$$

$$\tilde{J}_{\beta m,\alpha i}=0\,. \tag{26b}$$

If the variation functions depend upon the set of adjustable parameters a_k, then (26a) can be rewritten in the more convenient form

$$\frac{\partial\tilde{J}_{\beta m,\alpha i}}{\partial a_k}-\frac{\partial\tilde{J}_{\beta m,\alpha i}}{\partial a_1}\left(\frac{\partial\tilde{f}_{\beta m,\alpha i}}{\partial a_1}\right)^{-1}\frac{\partial\tilde{f}_{\beta m,\alpha i}}{\partial a_k}=0\quad(\text{all }k\neq 1)\,, \tag{27}$$

where a_1 is chosen so that $\partial\tilde{f}_{\beta m,\alpha i}/\partial a_1\neq 0$. Finally, in order to carry out the perturbation treatment, the wave functions $\tilde{\Psi}^+_{\alpha i}(\tilde{\Psi}^-_{\beta m})$ are restricted in form to be eigenfunctions of some convenient zeroth-order Hamiltonian $\tilde{H}^{(0)}_\alpha$ $(\tilde{H}^{(0)}_\beta)$. Thus Eqs. (26b) and (27), with

$$\tilde{J}_{\beta m,\alpha i}=\langle\tilde{\Psi}^-_{\beta m}|\,\tilde{V}^{(1)}_\alpha|\tilde{\Psi}^+_{\alpha i}\rangle\,, \tag{28}$$

provide a set of nonlinear algebraic relations for determining the optimum a_k. The resultant wave functions and corresponding potentials constitute the initial approximation. A comparison of Eqs. (28) and (26b) with (17a) shows that, by making this choice, the first-order perturbation correction to the transition amplitude vanishes. This means that the first-order wave function is normalizable in the corresponding exit channel. Of course, a separate Hulthên calculation can be carried out for each inelastic-scattering event or, for simplicity, some potentials may be transferred from one event to another.

V. COMPARISON WITH THE DISTORTED-WAVE BORN SERIES

Formally, the terms in the DWBS for the scattering amplitude are identical to those of the variation-perturbation method. There is one exception to this statement—namely, that we have resolved the ambiguity in defining orders for rearrangement processes. But the major differences lie in the practical application of the two methods. Let us begin by discussing the initial approximation which yields the scattering amplitudes through first order. In contrast to the VP treatment this is, normally, the terminal point[18] of the DWBS. Furthermore, distorted-wave calculations typically[18] employ a zeroth-order potential that makes no distinction between elastic and inelastic scattering. We propose instead to include terms that specifically couple the initial and final states. An illustration will be given in Sec. VI.

The most significant advantages of the VP method, however, are connected with the variational computation of the first-order perturbed wave functions. Our approach will, hopefully, be much easier to carry out than the usual DWBS expansion. In electron scattering, for example, we can employ the same convenient decomposition into pair functions[9] which, together with the introduction of interelectronic coordinates, has proved advantageous[19] for ordinary bound-state problems. Furthermore, the electron exchange may be simply treated using one of the new exchange perturbation theories[10] such as the *distinguishable electron method*.[14] Further details on these techniques will be saved for future papers in the series. Let us just observe here that, until now, the difficulties in determining second- and higher-order terms in the DWBS have been virtually prohibitive. And, as we shall see, these terms can be quite important.

VI. AN EXAMPLE: HUCK-TYPE EXPONENTIAL POTENTIAL

In order to illustrate the VP method for an inelastic problem (without rearrangement) we have undertaken calculations on a model system characterized by the Hamiltonian

$$H=-\frac{1}{2\mu}\frac{d^2}{dr^2}+h-Ae^{-br}(\hat{P}_{01}+\hat{P}_{10})\,, \tag{29}$$

where $\hat{P}_{ij}=|\varphi_i\rangle\langle\varphi_j|$ and the notation of previous sections remains unchanged (except for suppression of the channel index, i.e., $r_\alpha\to r$, $h_\alpha\to h$). We approximate the model potential in Eq. (29) by Huck's[20] inelastic spherical well

$$\begin{aligned}V^{(0)}&=-D(\hat{P}_{01}+\hat{P}_{10})\quad&(r\leq r_0)\\&=0&(r>r_0)\,.\end{aligned} \tag{30}$$

Both $V^{(0)}$ and V were chosen because the exact[21] eigenfunctions are readily obtained. But the usefulness of $V^{(0)}$ as an initial approximation for more complex problems such as atomic excitation by electron impact,[22] the linear atom-harmonic oscillator system,[23] etc., should also be obvious. Note that the elastic-scattering potential is zero in both cases.

It is convenient at this point to switch from transition amplitudes to the reactance, or $\underline{R}$, matrix. This involves no alteration of the method; it is accomplished merely by changing the arbitrary asymptotic boundary condition (4b) which, in the present instance, becomes[24]

$$\Psi_i(r) \to \sum_m k_m^{-1/2}(\delta_{im} \sin k_m r + R_{mi} \cos k_m r)\varphi_m . \quad (31)$$

The reason for this conversion is that recent evidence[25] indicates that probability-conserving formalisms are likely to give improved scattering parameters. Using the new boundary conditions in the derivation leading to Eq. (17) we find

$$R_{mi}^{(1)} = -2\mu \langle \Psi_m^{(0)} | V^{(1)} | \Psi_i^{(0)} \rangle , \quad (32a)$$

$$R_{mi}^{(2)} = -2\mu \langle \Psi_m^{(0)} | V^{(1)} | \Psi_i^{(1)} \rangle , \quad (32b)$$

and

$$R_{mi}^{(3)} = -2\mu \langle \Psi_m^{(1)} | V^{(1)} | \Psi_i^{(1)} \rangle . \quad (32c)$$

To determine the zeroth-, first-order, and exact wave functions for $i = 0$ and 1, we begin with the expansion

$$\Psi_i(r) = X_{0i}(r)\varphi_0 + X_{1i}(r)\varphi_1 \quad (i = 0, 1) . \quad (33)$$

Then, multiplication of the appropriate Schrödinger (or Rayleigh–Schrödinger) relation on the left by $\langle \varphi_0 |$, and by $\langle \varphi_1 |$, yields a pair of coupled second-order differential equations. The latter are derived and solved in Appendix B. Analytical solutions are obtained for the perturbation functions and numerical solutions for the model potential.

The $\underline{R}$ matrix elements reported in Table I were calculated[26] from Eqs. (32) for various values of b with $\mu = 1$, $k_0 = 1$, $k_1 = \frac{1}{2}$, and $A = 1$. Optimum values of the initial parameters D and r_0 were determined by the Hulthèn conditions on $\tilde{J}_{01}$, as given by Eqs. (26b) and (27) with f replaced by $\underline{R}$. The solution of these nonlinear equations, which we found by Newton–Raphson techniques, is not necessarily unique. In fact, near and below $b = 1$ a second solution appears. Since the original series for R_{00} seems to diverge,[27] i.e., $|R_{00}^{(3)}| > |R_{00}^{(2)}|$, we switch to the new solution. This explains the sharp change in D and r_0 at $b = \frac{4}{5}$. Finally, the transition probability P is given by[28]

$$P = \{[(\underline{R}^2 + \underline{1})^{-1}(\underline{R}^2 - \underline{1})]_{01}\}^2 + 4\{[(\underline{R}^2 + \underline{1})^{-1}\underline{R}\,]_{01}\}^2 . \quad (34)$$

For simplicity,[29] the same initial approximation was used to obtain all three matrix elements ($R_{10} = R_{01}$ by symmetry, as shown in Appendix A). It turns out that the elastic elements R_{00} and R_{11} are nearly as accurate as the inelastic element R_{01} for which the system was optimized.

The perturbation expansion of each matrix element is convergent, in the sense that $|R_{ij}^{(3)}| < |R_{ij}^{(2)}|$, for all values of the range parameter $b \geq \frac{2}{3}$. This convergence, and the accuracy through third order as well, are quite remarkable considering how poor an initial approximation we have in the case of the smaller b's. Except for R_{01} at $b = \frac{2}{3}$ all the VP matrix elements lie within 5% of the exact result. In fact, the magnitude of the error appears to be given approximately by

$$\Delta \sim \tfrac{1}{2} \left| (R_{ij}^{(3)})^2 / R_{ij}^{(2)} \right| . \quad (35)$$

It is interesting to note that the transition probability and each VP matrix element are algebraically smaller than the exact result. This suggests that a rigorous bounding principle may exist.

For comparison, we also evaluated the ordinary Born series through third order. This is the equivalent of a typical DWBS calculation since there are no elastic terms in the model potential. In every instance the values are worse than those of the VP method,[30] with the differences becoming dramatic below $b = 1$, which is the onset of strong inelastic coupling.

We are encouraged by the results of these calculations. However, a model system is not the real thing and, of course, the VP method has not been tested for rearrangement processes as yet. As indicated earlier, we plan to further develop the treatment in applications to inelastic electron scattering and to vibration-rotation-translation energy transfer as well.

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APPENDIX A

Here we prove that the VP scattering amplitudes through first and through third order satisfy the reciprocity relation

$$(\mu_\beta)^{-1} f^{+}_{\beta m, \alpha i}(\vec{r}_\beta) = (\mu_\alpha)^{-1} f^{-}_{\alpha i, \beta m}(-\vec{r}_\alpha) , \quad (A1)$$

as required for the exact result. In order to do so, it is necessary to have the VP amplitude formulas for the incoming waves. The latter are obtained by starting with the condition

$$\langle \Psi^{+}_{\alpha i} | H - E^{(0)} | \Psi^{-}_{\beta m} \rangle = 0 \quad (A2)$$

instead of (14) and following the derivation which led to Eqs. (17) in the text. These manipulations give

TABLE I. Variation-perturbation calculation of the reactance matrix for the model Hamiltonian of Eq. (29). The matrix elements were obtained for various values of the range parameter b with $\mu=1$, $k_0=1$, $k_1=\frac{1}{2}$, and $A=1$. Our zeroth-order potential $V^{(0)}$, is taken to be Huck's inelastic spherical well as given by Eq. (30). For purposes of comparison the results of a third-order Born approximation (BA) in which $V^{(0)}=0$ have also been computed. The transition probability P is determined from Eq. (34).

b		$R^{(0)}$	$R^{(1)}$	$R^{(2)}$	$R^{(3)}$	R_{VP}	R_{exact}	R_{BA}
	R_{00}	0.000 46	0.000 28	0.000 61	0.000 00	0.001 35	0.001 35	0.001 35
5	R_{01}	0.020 56	0.000 00	0.000 02	0.000 02	0.020 60	0.020 60	0.020 60
	R_{11}	0.000 02	0.000 21	0.000 36	0.000 00	0.000 59	0.000 59	0.000 59
		$D=0.010\,42$;	$r_0=1.874\,32$			P: 0.0017	0.0017	0.0017
	R_{00}	0.008 34	0.002 53	0.002 44	0.000 04	0.013 36	0.013 38	0.013 20
3	R_{01}	0.081 96	0.000 00	0.000 32	0.000 12	0.082 41	0.082 41	0.082 40
	R_{11}	0.001 30	0.001 60	0.001 47	0.000 02	0.004 39	0.004 40	0.004 34
		$D=0.052\,31$;	$r_0=1.683\,22$			P: 0.0268	0.0268	0.0268
	R_{00}	0.056 67	0.005 80	0.005 07	0.000 22	0.067 76	0.067 80	0.065 36
2	R_{01}	0.216 46	0.000 00	0.001 42	0.000 21	0.218 08	0.218 11	0.217 89
	R_{11}	0.008 05	−0.002 05	0.002 98	0.000 06	0.009 04	0.009 06	0.008 61
		$D=0.132\,49$;	$r_0=1.707\,62$			P: 0.1726	0.1727	0.1724
	R_{00}	0.430 50	0.147 52	0.017 20	−0.001 09	0.594 13	0.594 17	0.571 36
1	R_{01}	0.624 81	0.000 00	−0.033 14	−0.003 62	0.588 05	0.588 17	0.588 06
	R_{11}	0.042 57	−0.306 58	−0.027 77	0.005 50	−0.286 28	−0.285 82	−0.308 64
		$D=0.331\,10$;	$r_0=1.783\,11$			P: 0.5781	0.5784	0.5797
	R_{00}	0.364 05	0.365 13	0.150 35	0.044 14	0.923 68	0.944 42	0.997 97
$\frac{4}{5}$	R_{01}	0.340 41	0.000 00	0.085 28	0.056 33	0.482 02	0.495 48	0.457 84
	R_{11}	−0.995 82	0.288 95	0.064 61	−0.012 15	−0.654 41	−0.625 70	−0.782 18
		$D=0.215\,42$;	$r_0=3.740\,71$			P: 0.2697	0.2827	0.2092
	R_{00}	0.407 71	0.403 08	0.168 80	0.049 90	1.0295	1.0486	1.1580
$\frac{3}{4}$	R_{01}	0.241 56	0.000 00	0.098 63	0.065 03	0.405 23	0.418 87	0.342 30
	R_{11}	−1.1065	0.280 24	0.068 79	−0.019 20	−0.776 66	−0.740 82	−0.982 93
		$D=0.226\,63$;	$r_0=3.854\,94$			P: 0.1675	0.1797	0.0916
	R_{00}	0.501 42	0.451 02	0.205 10	0.065 14	1.2227	1.2306	1.4958
$\frac{2}{3}$	R_{01}	−0.021 14	0.000 00	0.138 80	0.080 58	0.198 24	0.218 04	−0.001 91
	R_{11}	−1.2941	0.247 72	0.045 38	−0.009 61	−1.0106	−0.960 04	−1.4352
		$D=0.257\,66$;	$r_0=4.005\,09$			P: 0.0301	0.0377	0.0000

$$f^{-(1)*}_{\alpha\ell,\beta m}(-\vec{r}_\alpha)=-(\mu_\alpha/2\pi)\langle\Psi^{-(0)}_{\beta m}|V^{(1)}_\beta|\Psi^{+(0)}_{\alpha\ell}\rangle, \tag{A3a}$$

$$f^{-(2)*}_{\alpha\ell,\beta m}(-\vec{r}_\alpha)=-(\mu_\alpha/2\pi)\langle\Psi^{-(0)}_{\beta m}|V^{(1)}_\alpha|\Psi^{+(1)}_{\alpha\ell}\rangle, \tag{A3b}$$

and

$$f^{-(3)*}_{\alpha\ell,\beta m}(-\vec{r}_\alpha)=-(\mu_\alpha/2\pi)\langle\Psi^{-(0)}_{\beta m}|V^{(1)}_\beta|\Psi^{+(1)}_{\alpha\ell}\rangle. \tag{A3c}$$

Taking advantage of the two alternate partitionings of the total Hamiltonian, it is trivial to show that

$$\begin{aligned}-(2\pi/\mu_\beta)f^{+(1)}_{\beta m,\alpha\ell}(\vec{r}_\beta)&=\langle\Psi^{-(0)}_{\beta m}|V^{(1)}_\alpha|\Psi^{+(0)}_{\alpha\ell}\rangle\\&=\langle\Psi^{-(0)}_{\beta m}|H^0_\beta-H^0_\alpha|\Psi^{+(0)}_{\alpha\ell}\rangle\\&\quad-(2\pi/\mu_\alpha)f^{-(1)*}_{\alpha\ell,\beta m}(-\vec{r}_\alpha).\end{aligned} \tag{A4}$$

As before, we utilize Messiah's technique[17] to evaluate the integral involving $H^{(0)}_\beta-H^{(0)}_\alpha$, which reduces to

$$\begin{aligned}&\langle\Psi^{-(0)}_{\beta m}|H^{(0)}_\beta-E^{(0)}|\Psi^{+(0)}_{\alpha\ell}\rangle-\langle\Psi^{+(0)}_{\alpha\ell}|H^0_\beta-E^{(0)}|\Psi^{-(0)}_{\beta m}\rangle^*\\&\quad=\langle\Psi^{-(0)}_{\beta m}|T_{op}|\Psi^{+(0)}_{\alpha\ell}\rangle-\langle\Psi^{+(0)}_{\alpha\ell}|T_{op}|\Psi^{-(0)}_{\beta m}\rangle^*\\&\quad=(2\pi/\mu_\beta)f^{+(0)}_{\beta m,\alpha\ell}(\vec{r}_\beta)-(2\pi/\mu_\alpha)f^{-(0)*}_{\alpha\ell,\beta m}(\vec{r}_\alpha)\end{aligned} \tag{A5}$$

with T_{op} being the total kinetic-energy operator. Substitution of (A5) into (A4) yields the desired reciprocity through first order, i.e.,

$$\begin{aligned}&(\mu_\beta)^{-1}[f^{+(0)}_{\beta m,\alpha\ell}(\vec{r}_\beta)+f^{+(1)}_{\beta m,\alpha\ell}(\vec{r}_\beta)]\\&\quad=(\mu_\alpha)^{-1}[f^{-(0)*}_{\alpha\ell,\beta m}(-\vec{r}_\alpha)+f^{-(1)*}_{\alpha\ell,\beta m}(-\vec{r}_\alpha)].\end{aligned} \tag{A6}$$

From Eqs. (17b) and (17c) the sum of the second- and third-order outward-scattering amplitudes is

$$\begin{aligned}&-(2\pi/\mu_\beta)[f^{+(2)}_{\beta m,\alpha\ell}(\vec{r}_\beta)+f^{+(3)}_{\beta m,\alpha\ell}(\vec{r}_\beta)]\\&\quad=\langle\Psi^{-(0)}_{\beta m}|V^{(1)}_\beta|\Psi^{+(1)}_{\alpha\ell}\rangle+\langle\Psi^{-(1)}_{\beta m}|V^{(1)}_\alpha|\Psi^{+(1)}_{\alpha\ell}\rangle\\&\quad=\langle\Psi^{-(0)}_{\beta m}|V^{(1)}_\beta|\Psi^{+(1)}_{\alpha\ell}\rangle+\langle\Psi^{-(1)}_{\beta m}|H^0_\beta-H^0_\alpha|\Psi^{+(1)}_{\alpha\ell}\rangle\\&\qquad+\langle\Psi^{-(1)}_{\beta m}|V^{(1)}_\beta|\Psi^{+(1)}_{\alpha\ell}\rangle,\end{aligned} \tag{A7}$$

where the two different partitionings have been used, once again, to replace the $V^{(1)}_{\alpha}$ term. The rhs of Eq. (A7) may be simplified with the aid of the first-order perturbation equations which, after appropriate multiplications (on the left-hand side) and integrations, yield

$$\langle \Psi^{-(1)}_{\beta m} | H^{(0)}_{\beta} - E^{(0)} | \Psi^{+(1)}_{\alpha i} \rangle + \langle \Psi^{-(0)}_{\beta m} | V^{(1)}_{\beta} | \Psi^{+(1)}_{\alpha i} \rangle = 0 \tag{A8a}$$

and

$$\langle \Psi^{-(1)}_{\beta m} | H^{(0)}_{\alpha} - E^{(0)} | \Psi^{+(1)}_{\alpha i} \rangle + \langle \Psi^{-(1)}_{\beta m} | V^{(1)}_{\alpha} | \Psi^{+(0)}_{\alpha i} \rangle = 0 . \tag{A8b}$$

To obtain the relation (A8a) we have employed the fact that $H^{(0)}_{\beta} - E^{(0)}$ is Hermitian with respect to the first-order wave functions since the latter have no plane-wave component. Finally, Eqs. (A7), (A8), and (A3) lead to the reciprocity formula

$$\begin{aligned}(\mu_{\beta})^{-1}[f^{+(2)}_{\beta m,\alpha i}(\vec{r}_{\beta}) + f^{+(3)}_{\beta m,\alpha i}(\vec{r}_{\beta})]& \\ = (\mu_{\alpha})^{-1}[f^{-(2)*}_{\alpha i,\beta m}(-\vec{r}_{\alpha}) &+ f^{-(3)*}_{\alpha i,\beta m}(-\vec{r}_{\alpha})] .\end{aligned} \tag{A9}$$

The symmetry of the $\underline{R}$ matrix in Sec. VI follows as a special case of the reciprocity relations. In order to convert from the scattering amplitudes to the reactance matrix (without rearrangement) we drop the channel index as well as the + or − and replace f with $\underline{R}$. Equations (A6) and (A9) then give

$$\sum_{p=0}^{3} R^{(p)}_{m} = \sum_{p=0}^{3} R^{(p)*}_{im} . \tag{A10}$$

APPENDIX B

This appendix is devoted to solving the zeroth- and first-order perturbation equations

$$(H^{(0)} - E^{(0)})\Psi^{(p)}_{i} + (1-\delta_{p0})V^{(1)}\Psi^{(p-1)}_{i} = 0 \quad (p = 0, 1) \tag{B1}$$

for the model problem of Sec. VI. The exact model Hamiltonian is given in the text as

$$H = -\frac{1}{2\mu}\frac{d^2}{dr^2} + h - Ae^{-br}(\hat{P}_{01} + \hat{P}_{10}) \tag{B2}$$

with the inelastic scattering potential being approximated, in zeroth order, by

$$\begin{aligned} V^{(0)} &= -D(\hat{P}_{01} + \hat{P}_{10}) \quad (r \leq r_0) \\ &= 0 \qquad\qquad\qquad\quad (r > r_0) . \end{aligned} \tag{B3}$$

Obviously, $V^{(1)} = -Ae^{-br}(\hat{P}_{01} + \hat{P}_{10}) - V^{(0)}$ and

$$H^{0} = -\frac{1}{2\mu}\frac{d^2}{dr^2} + h + V^{(0)} . \tag{B4}$$

The boundary conditions on the perturbation functions

$$\begin{aligned} &\Psi^{(p)}_{i}(r=0) = 0 , \\ &\Psi^{(p)}_{i} \underset{r}{\rightarrow} \sum_{m} k_m^{-1/2}(\delta_{p0}\delta_{mi}\sin k_m r + R_{mi}\cos k_m r)\varphi_m \end{aligned} \tag{B5}$$

were also specified in the text but are repeated here for completeness.

To solve Eq. (B1) for the states $i = 0$ and 1 we use the expansions

$$\Psi^{(p)}_{i}(r) = X^{(p)}_{0i}(r)\varphi_0 + X^{(p)}_{1i}(r)\varphi_1 \tag{B6}$$

and multiply on the left by $-2\mu\langle\varphi_1|$, as well as $-2\mu\langle\varphi_0|$, to obtain the coupled equations

$$\begin{pmatrix} \dfrac{d^2}{dr^2} + k_0^2 & 2\mu D \\ 2\mu D & \dfrac{d^2}{dr^2} + k_1^2 \end{pmatrix}\begin{pmatrix} X^{(p)}_{0i} \\ X^{(p)}_{1i} \end{pmatrix} = \begin{pmatrix} 0 & 2\mu(D - Ae^{-br})(1-\delta_{p0}) \\ 2\mu(D - Ae^{-br})(1-\delta_{p0}) & 0 \end{pmatrix}\begin{pmatrix} X^{(p-1)}_{0i} \\ X^{(p-1)}_{1i} \end{pmatrix} \tag{B7}$$

for $r \leq r_0$. Here $E^{(0)} = \epsilon_0 + \frac{1}{2}\mu k_0^2 = \epsilon_1 + (1/2\mu)k_1^2$ with ϵ_0 and ϵ_1 being the internal energies of the two states. For $r > r_0$, one merely sets $D = 0$ in Eq. (B7). A solution of the $p = 0$ equations for slightly different boundary conditions has been reported by Huck.[20] Following his approach we find

$$\begin{aligned} X^{(0)}_{ij}(r) &= \sum_{m=0,1} \gamma_{im} B_{mj} p_m^{-1} \sin p_m r \qquad (r \leq r_0) \\ &= k_i^{-1/2}(\delta_{ij}\sin k_i r + R^{(0)}_{ij}\cos k_i r) \quad (r > r_0) , \end{aligned} \tag{B8a}$$

where

$$\gamma_{00} = \gamma_{01} = 1 , \quad \gamma_{10} = (p_0^2 - k_0^2)/2\mu D , \quad \gamma_{11} = -(\gamma_{10})^{-1} \tag{B8b}$$

and

$$p_0^2 + p_1^2 = k_0^2 + k_1^2 , \quad p_0^2 p_1^2 = k_0^2 k_1^2 - 4\mu^2 D^2 . \tag{B8c}$$

Since the relations (B8c) are symmetric with respect to interchange of p_0^2 and p_1^2, these parameters may always be chosen so that $p_0^2 \geq p_1^2$. Thus, p_0^2 is always positive for k_0^2, $k_1^2 > 0$ but p_1^2 may be of either sign. The coefficients B_{mj} and the reactance matrix elements $R^{(0)}_{ij}$ are determined by the eight continuity conditions on the wave functions and their first derivatives at $r = r_0$.

The first-order perturbation functions may be obtained from Eq. (B7) by Laplace-transform techniques which yield

$$
\begin{aligned}
X_{ij}^{(1)}(r) = \sum_{m=0,1} (p_{m'}^2 - p_m^2)^{-1} \{ B_{mj} p_m [(k_{i'}^2 - k_i^2) \gamma_{mi'} (2\mu D (S_{m'} - S_m)(p_{m'}^2 - p_m^2)^{-1} + 2\mu A \theta^{-1} \\
\times \{ (b^2 + p_m^2 - p_{m'}^2) S_{m'} - 2b C_{m'} + e^{-br} [(b^2 + p_{m'}^2 - p_m^2) S_m + 2b C_m] \}) \\
+ 2\mu D \gamma_{mi} \{ 4\mu A [S_m - 2b^{-1} C_m + e^{-br} (S_m + 2b^{-1} C_m)] (b^2 + 4 p_m^2)^{-1} - 2\mu D p_m^{-2} (S_m - r C_m) \}] \\
+ S_m [(k_{i'}^2 - p_m^2) K_{ij} - 2\mu D K_{i'j}] \} \qquad (r \leq r_0) \\
= k_i^{-1/2} R_{ij}^{(0)} \cos k_i r - 2\mu A k_{i'}^{-1/2} e^{-br} \theta_0^{-1} [(b^2 + k_i^2 - k_{i'}^2)(\delta_{i'j} \sin k_{i'} r + R_{i'j}^{(0)} \cos k_{i'} r) \\
+ 2b k_{i'} (\delta_{i'j} \cos k_{i'} r - R_{i'j}^{(0)} \sin k_{i'} r)] \quad (r > r_0)
\end{aligned}
\tag{B9}
$$

in which $i' + i = m' + m = 1$, $S_m = p_m^{-1} \sin p_m r$, $C_m = \cos p_m r$, $\theta_0 = (b^2 + k_0^2 + k_1^2)^2 - 4k_0^2 k_1^2$, and $\theta = \theta_0 + 16\mu^2 D^2$. Note that $R_{ij}^{(1)}$ is determined by the zeroth-order functions through Eq. (32a). Finally, the constants K_{ij} can be found from the four continuity conditions on the first-order wave functions. The first derivatives will be continuous as well since this restriction was built into their original construction.

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[1] For a recent set of review articles see *Advances in Chemical Physics*, edited by J. Ross (Wiley, New York, 1966),Vol. X.

[2] See, for example, D. G. Truhlar, J. K. Rice, A. Kupperman, S. Trajmar, and D. C. Cartwright, Phys. Rev. A **1**, 778 (1970); A. Skerbele and E. N. Lassetre, J. Chem. Phys. **56**, 845 (1972); C. E. Kuyatt, G. E. Chamberlain, and S. R. Mielczarek, Phys. Rev. A **2**, 1905 (1970).

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[6] R. D. Levine, Mol. Phys. **22**, 497 (1971).

[7] See, for example, T. S. Murtaugh and W. P. Reinhardt, J. Chem. Phys. **57**, 2129 (1972).

[8] Again, especially in electron scattering.

[9] The recent revival of interest in this approach to electron correlation was initiated by Sinanoğlu's treatment in the early 1960's. The basic elements are contained in O. Sinanoğlu, Proc. R. Soc. A **260**, 379 (1960); J. Chem. Phys. 122, 493 (1961).

[10] These are reviewed in detail by D. M. Chipman, Ph.D. thesis (University of Wisconsin, 1971) (unpublished). We have been particularly interested ourselves in the *distinguishable electron method* (cf. Ref. 14).

[11] S. K. Knudson and B. Kirtman, Phys. Rev. A **3**, 972 (1971), hereafter referred to as I. See also U. Landman [Phys. Rev. A **5**, 1(1972)] for an alternate VP treatment based on the phase-amplitude method.

[12] See N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 3rd ed. (Oxford U.P., London, 1965), Chap. XIII.

[13] See, for example, A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1962). We use "series" rather than "approximation" to indicate that terms beyond first order will be considered.

[14] B. Kirtman, Chem. Phys. Lett. **1**, 631 (1968); B. Kirtman and R. L. Mowery, Chem. Phys. Lett. **55**, 1447 (1971); B. Kirtman and U. Landman (unpublished).

[15] To justify the choice for $q = p$ we point out that the opposite convention leads to the reciprocity relation [cf. Eq. (A5) in Appendix A] $(\mu_\beta)^{-1} f_{\beta m, \alpha i}^{+(0)}(\hat{r}_\beta) = (\mu_\alpha)^{-1} f_{\alpha i, \beta m}^{-(0)*}(-\hat{r}_\alpha)$, which may or may not be consistent with Eq. (12a).

[16] There is one extant confirming case [D. M. Chipman (private communication)]. In $H_2{}^+$ the DEM partitioning, together with an isolated-atoms initial approximation, gives $E^{(3)} \ll E^{(2)}$ for all R down to 2 a.u.

[17] See Ref. 13, p. 836.

[18] See, for example, K. T. Takayanagi, Adv. At. Mol. Phys. **1**, 149 (1965).

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[20] R. J. Huck, Proc. Phys. Soc. A 70, 369 (1957).

[21] That is to say, eigenfunctions of arbitrary accuracy for V as well as the exact zeroth- and first-order perturbation functions for $V^{(0)}$.

[22] Huck developed his potential as a model for excitation by electron impact from the 1*s* to 2*s* state in atomic hydrogen.

[23] Cf. D. Secrest and B. R. Johnson, J. Chem. Phys. **45**, 4556 (1966).

[24] Note that the distinction ($\pm$) between incoming and outgoing waves is no longer appropriate. Since the matrix elements of R are formally unbounded, it may be necessary to use R^{-1} when the former become very large. Or else, one might calculate phase shifts, which are also real and conserve probability (cf. Ref. 25).

[25] R. D. Levine and G. G. Balint-Kurti, Chem. Phys. Lett. **6**, 101 (1970); P. Pechukas and J. C. Light, J. Chem. Phys. **44**, 3897 (1966).

[26] By 16-point Gauss–Legendre quadrature for $r \leq r_0$, and analytically for $r > r_0$.

[27] Although the corresponding series for R_{01} and R_{11} converge.

[28] N. F. Mott and H. S. W. Massey, Ref. 12, p. 371.

[29] And to test the idea of using a single initial approimation.

[30] Except where the Born curve for R_{01} happens to cross the exact curve near $b = 1$.