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# The application of the Wigner $R$ -matrix theory to molecular collisions

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The Wigner–Eisenbud  $R$ -matrix theory is applied to molecular collisions. Previous attempts required a Buttle correction to accelerate slow convergence. The present theory makes use of radial basis functions which satisfy arbitrary conditions at the  $R$ -matrix boundary. At the same time within the boundary, the basis functions are eigenfunctions of a realistic effective radial Hamiltonian. Consequently, the radial basis set is slightly nonorthogonal. It is shown that this is sufficient to afford a rapidly convergent expansion which remains reliable both in the neighborhood of and far from resonances. The Buttle correction is no longer needed. The method is applied to a problem of collinear collisions between an atom and a diatomic molecule. Results are in excellent agreement with previous calculations.

## I. INTRODUCTION

The  $R$ -matrix theory of collisions developed by Wigner and Eisenbud<sup>1–3</sup> possesses a number of very attractive features: The energy dependence of the  $R$  matrix is simple and explicit, the  $R$  matrix is real and symmetric which alone guarantees that the collision (or  $S$ ) matrix is unitary and symmetric, and the Breit–Wigner expression for the line shape of isolated resonances appears directly from the formalism.

However, application of the theory to molecular encounters meets with a number of difficulties due essentially to the slow convergence of the  $R$ -matrix expansion. This has led to the formulation of alternative  $R$ -matrix methods,<sup>4,5</sup> of which the  $R$ -matrix propagator has established itself as a very successful procedure for solving the close-coupled equations.<sup>6–8</sup>

Nevertheless, the successful adaption of the Wigner–Eisenbud procedure to heavy particle scattering would bring with it considerable advantages: Once the eigenvalues and eigenvectors have been calculated in the inner region, the  $R$ -matrix can be very quickly assembled at any energy. Total cross sections can consequently be determined over a range of collision energies for very little extra computational effort above that required for a single energy. The  $R$ -matrix eigenvalues together with the reduced amplitudes provide an excellent diagnostic tool for the detection of even the narrowest resonances, and the structure of the corresponding eigenvector gives immediate insight into the character of the resonant state. Other advantages pertaining to both inelastic and reactive scattering will become apparent in due course.

The object of this article is to show how the Wigner–Eisenbud  $R$ -matrix theory can be applied to the description of molecular encounters in a reliable manner in a variety

of physical situations. This is achieved by the use of basis functions which do not satisfy any particular logarithmic condition at the  $R$ -matrix boundary. However, in order to provide a realistic description of the wave function in the interior region, each basis function is at the same time a solution of an effective radial Hamiltonian. These two features consequently mean that the radial functions possess a small amount of nonorthogonality among themselves. Nonorthogonal functions have previously been used in the description of collisions between nuclei.<sup>9,10</sup> They have also been employed in  $R$ -matrix theories of electron–atom and electron–molecule collisions by Schneider<sup>13</sup> and by Shimamura.<sup>11</sup> Basis functions with arbitrary derivatives at the  $R$ -matrix boundary have been utilized in collinear reactive scattering by Der *et al.*,<sup>12</sup> and an extensive formalism for treating the nonorthogonality which arises when different coordinates are used for different arrangements has been developed by Stechel *et al.*<sup>14</sup> In the present paper we introduce a small amount of nonorthogonality into basis functions of a single radial coordinate. This situation is therefore different.

If a single orthonormal set of radial basis functions  $\xi_n(R)$  is used, the convergence of the  $R$  matrix is slow because all the basis functions satisfy the same condition at the  $R$ -matrix boundary. This is usually of the form  $[d(\ln \xi_n)/dR]_{R=A} = b$ . Consequently, any finite number of  $\xi_n(R)$  functions is unable to reproduce the correct logarithmic derivative of the collision wave function. A correction due to Buttle<sup>19</sup> is often able to remedy this deficiency, but unless it is analytic, the Buttle correction frequently introduces further numerical errors. This is particularly the case in collisions between molecules since the distribution of  $R$ -matrix poles is dense and there is imperfect cancellation between Buttle poles.

The central result of this work is to show that provided the  $\xi_n(R)$  are well chosen, the introduction of just a very small amount of nonorthogonality is sufficient to afford a rapidly convergent and stable expansion. The computations remain reliable both in the neighborhood

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of and far from resonance energies. As a result we are able to dispense with the Buttle correction altogether.

That this should be so can be seen from a variation treatment of the *R*-matrix method.<sup>20-22</sup> A basis set expansion of the collision wave function must simultaneously satisfy the Schrödinger equation in the inner region and also reproduce the correct logarithmic derivative of the wave function at the boundary in order to be properly complete. Large amounts of nonorthogonality are not necessary. Indeed for rapidly oscillating functions whose wavelengths are short compared to the distance between molecules, this would quickly give rise to linear dependence.

In earlier work Gerratt and Wilson<sup>18</sup> showed that for molecular collisions it is important to place the *R*-matrix boundary at a radial distance where the interaction potential is still nonzero. This results in a relatively small inner region so that the rate of convergence of the *R*-matrix expansion is considerably enhanced. In the outer region the wave function is determined by solving the usual close-coupled equations. A particularly convenient means for this purpose is the *R*-matrix propagator method: Because the potential is now weak and slowly varying with radial distance, few steps are needed to reach the asymptotic region.

In the present paper we describe our general procedure and apply it to a collinear collision between an atom and a diatomic molecule. This particular model has previously been studied using *R*-matrix theory by Heller.<sup>15</sup> In a subsequent article we extend the method to a three-dimensional problem: that of He-H<sub>2</sub> collisions.<sup>16</sup> Finally, we have utilized our procedure to study collisions of He with H<sub>2</sub>CO at interstellar temperatures.<sup>17</sup> (Results available on request from authors.)

In Secs. II A and II B we give a fairly condensed derivation of our particular form of the *R* matrix, largely in order to establish a common notation for this and subsequent works.<sup>16,17</sup> Further details may be found in Refs. 18 and 30 and in the basic references 1-3.

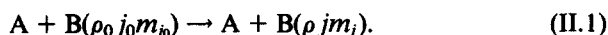
In Sec. II C we show how the basis functions are determined as eigenfunctions of a suitable effective Hamiltonian. In particular it is shown how these functions are modified so as to introduce a controlled amount of nonorthogonality between them.

The application of our method to a collinear atom-diatom problem is presented in Sec. III and the results compared to other calculations. Finally, several conclusions are drawn in Sec. IV.

## II. THEORY

### A. Basic definitions

We consider elastic and inelastic processes in which a closed shell atom A collides with a closed shell molecule B. The initial state of B is specified by quantum numbers  $\rho_0 j_0 m_{j_0}$ , where  $\rho_0$  describes the internal motion of B and  $j_0 m_{j_0}$  its rotation. As a result of the encounter B undergoes a transition to a state  $\rho j m_j$ :



We confine ourselves to collision energies sufficiently low so that electronic transitions cannot occur.

If the angular momentum of relative motion of A about B is denoted by  $l$ , an appropriate partial wave in the total angular momentum representation<sup>23</sup> is given by

$$\Phi_{\rho j l; \rho_0 j_0 l_0}^{JM}(q, R) = \frac{1}{R} F_{\rho j l; \rho_0 j_0 l_0}^J(R) \phi_{\rho j l}^{JM}(q, \Omega). \quad (\text{II.2})$$

Function  $F_{\rho j l; \rho_0 j_0 l_0}^J(R)$  describes the relative radial motion of A and B, the coordinate  $R$  measuring the distance from the center of mass of A to the center of mass of B. The channel function  $\phi_{\rho j l}^{JM}(q, \Omega)$  is given by

$$\phi_{\rho j l}^{JM}(q, \Omega) = \psi_{\rho}(q) Y_{JM}(j, l; \omega, \Omega), \quad (\text{II.3})$$

where  $\psi_{\rho}(q)$  is a wave function for the internal motion of molecule B with corresponding coordinates  $q$ . We assume a space-fixed system of axes in terms of which the angular coordinates of  $R$  are denoted by  $\Omega$ , and those pertaining to B by  $\omega$ . The function  $Y_{JM}(\dots)$  is an angular function in which the angular momentum associated with the motion of B,  $j$ , is coupled with  $l$  to form the total angular momentum  $J$ :

$$Y_{JM}(j, l; \omega, \Omega) = \sum_{m_j, m_l} u_{jm_j}(\omega) Y_{lm_l}(\Omega) \langle j l m_j m_l | J M \rangle, \quad (\text{II.4})$$

where  $u_{jm_j}(\omega)$  is a wave function describing the rotation of B, and the  $\langle \dots | \dots \rangle$  are the usual vector coupling coefficients.<sup>24</sup> We therefore use the compound index  $c$  to denote the channel quantum numbers  $\rho, j, l$  whenever possible:

$$c \equiv (\rho j l).$$

The channel functions  $\phi_c^{JM}(q, \Omega)$  are orthonormal:

$$(\phi_c^{JM} | \phi_{c'}^{JM}) = \delta_{JJ'} \delta_{MM'} \delta_{cc'}. \quad (\text{II.5})$$

It is important to note that we employ round brackets to denote integrations over all coordinates except the radial coordinate  $R$ .<sup>26</sup> The bracket notation is reserved for complete integrations over all variables.

The radial functions  $F_{cc_0}^J(R)$  satisfy the following boundary conditions:

$$F_{cc_0}^J(R) \equiv F_{\rho j l; \rho_0 j_0 l_0}^J(R) \underset{R \rightarrow \infty}{\sim} h_l^-(k_{\rho_0 j_0} R) \delta_{cc_0} - \left( \frac{k_{\rho_0 j_0}}{k_{\rho j}} \right)^{1/2} h_l^+(k_{\rho j} R) S_{\rho j l; \rho_0 j_0 l_0}^J, \quad (k_{\rho j} \geq 0; k_{\rho_0 j_0} \geq 0), \quad (\text{II.6a})$$

$$\underset{R \rightarrow \infty}{\sim} \exp(-|k_{\rho j}|R), \quad (k_{\rho j} < 0; k_{\rho_0 j_0} \geq 0), \quad (\text{II.6b})$$

$$\underset{R \rightarrow \infty}{\sim} \exp(-|k_{\rho_0 j_0}|R), \quad (k_{\rho_0 j_0} < 0). \quad (\text{II.6c})$$

In these equations the  $h_l^{\pm}(x)$  are the Riccati-Hankel functions,<sup>25</sup> and  $S_{cc_0}^J$  is an element of the collision matrix. All radial solutions are required to be regular at the origin.

The magnitude of the wave vector  $k_{\rho j}$  is given by

$$k_{\rho j}^2 = 2\mu(E - \epsilon_{\rho j})/\hbar^2, \quad (\text{II.7})$$

where  $E$  is the total energy of the system  $A + B$  (measured relative to  $A$  and  $B$  at rest in their ground states),  $\epsilon_{\rho j}$  is the energy of the isolated molecule  $B$  in state  $(\rho, j)$ , and  $\mu$  is the reduced mass for the relative motion of  $A$  and  $B$ . The energy  $\epsilon_{\rho j}$  is determined from the Schrödinger equation

$$(\mathcal{H}_T - \epsilon_{\rho j})\psi_{\rho j m_j} = 0, \quad (\text{II.8})$$

where  $\mathcal{H}_T$  is the Hamiltonian for the target molecule ( $B$ ). Energy

$$E - \epsilon_{\rho j} = \hbar^2 k_{\rho j}^2 / 2\mu$$

is therefore just the collision energy of  $A$  and  $B$ .

The total wave function for the system  $A + B$  is expanded as

$$\Psi_{\alpha}(q, \mathbf{R}) = \sum_{J, M} \sum_c \frac{1}{R} F_{c\alpha}^J(R) \phi_c^{JM}(q, \Omega). \quad (\text{II.9})$$

Each partial wave gives rise to a partial cross section

$$\sigma_{\rho j \rightarrow \rho_0 j_0}^J(E) = \frac{\pi(2J+1)}{k_{\rho_0 j_0}^2(2j_0+1)} \sum_{l=|J-j|}^{J+j} \sum_{l_0=|J-j_0|}^{J+j_0} \times |S_{\rho j l; \rho_0 j_0 l_0}^J - \delta_{\rho j l; \rho_0 j_0 l_0}|^2, \quad (\text{II.10})$$

and the total cross section is given as

$$\sigma_{\rho j \rightarrow \rho_0 j_0}(E) = \sum_J \sigma_{\rho j \rightarrow \rho_0 j_0}^J(E). \quad (\text{II.11})$$

## B. Derivation of the *R*-matrix

We consider a range of the collision coordinate  $R$  ( $0, A$ ) within which the interaction between  $A$  and  $B$  is significant and varies strongly with  $R$ . In the exterior region ( $A \leq R \leq \infty$ ) the potential is weak and varies slowly with  $R$ .

Within the interior region ( $0 \leq R \leq A$ ), we write the Schrödinger equation in the form

$$(\mathcal{H} + \hat{\mathcal{L}}_b - E)\Psi_{\alpha} = L_b \Psi_{\alpha}. \quad (\text{II.12})$$

$\mathcal{H}$  is the total Hamiltonian for the system and is given in space-fixed coordinates by

$$\mathcal{H} = \mathcal{H}(q, \mathbf{R}) = -\left(\frac{\hbar^2}{2\mu}\right) \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R}\right) + \frac{\hat{l}^2}{2\mu R^2} + \mathcal{H}_T(q) + V(q, \mathbf{R}), \quad (\text{II.13})$$

where  $V(q, \mathbf{R})$  is the potential of interaction between  $A$  and  $B$  and  $\hat{l}^2$  is the operator for the square of the relative angular momentum of  $B$  about  $A$ .

The operator  $\hat{\mathcal{L}}_b$  was introduced by Bloch<sup>26,27</sup> and for the present purposes is given by

$$\hat{\mathcal{L}}_b = \left(\frac{\hbar^2}{2\mu}\right) \delta(R-A) \sum_{JM} \sum_c |\phi_c^{JM}\rangle \times \left(\frac{1}{R} \frac{\partial}{\partial R} R - b_c\right) \langle \phi_c^{JM}|. \quad (\text{II.14})$$

The Dirac delta function ensures that the operator acts only at the *R*-matrix boundary  $R = A$ . The constants  $b_c$

are real and independent of energy but are otherwise arbitrary. The effect of  $\hat{\mathcal{L}}_b$  is to ensure that  $\mathcal{H} + \hat{\mathcal{L}}_b$  is Hermitian within the interval  $(0, A)$ ; the operator  $\mathcal{H}$  alone is not.

We now substitute the partial wave expansion (II.9) into the Schrödinger equation (II.12) to obtain

$$\begin{aligned} \sum_{JM} \sum_c R(\mathcal{H} + \hat{\mathcal{L}}_b - E) \frac{1}{R} \phi_c^{JM} F_{c\alpha}^J \\ = \sum_{JM'} \sum_c \left(\frac{\hbar^2}{2\mu}\right) |\phi_c^{JM'}\rangle \left(\frac{\partial F_{c\alpha}^{JM'}}{\partial R} - b_c F_{c\alpha}^{JM'}\right) \delta(R-A). \end{aligned} \quad (\text{II.15})$$

We expand the radial wave functions on the left-hand side of the equation as follows:

$$F_{c\alpha}^J(R) = \sum_n \xi_{cn}(R) A_{cn; \alpha}^J, \quad (\text{II.16})$$

in which the radial basis functions are arbitrary and in general nonorthogonal. These functions play a central role in this approach. They are specified below.

Combining the  $\xi_{cn}(R)$  functions with the channel functions  $\phi_c^{JM}(q, \Omega)$ , we obtain a compound basis set whose metric matrix is given by

$$\begin{aligned} \langle \xi_{c'n'} \phi_{c'n'}^{JM'} | \xi_{cn} \phi_c^{JM} \rangle \\ = \int_0^A dR \xi_{c'n'}^*(R) \xi_{cn}(R) \int d\Omega \int dq (\phi_{c'n'}^{JM'})^*(q, \Omega) \phi_c^{JM}(q, \Omega) \\ = \delta_{JJ'} \delta_{MM'} \delta_{cc'} O_{c'n'; cn}, \end{aligned}$$

where

$$O_{c'n'; cn} = \int_0^A dR \xi_{c'n'}^*(R) \xi_{cn}(R). \quad (\text{II.17})$$

Substituting Eq. (II.16) into the left-hand side of Eq. (II.15), multiplying through by  $(\xi_{c'n'} \phi_{c'n'}^{JM})^*$ , and integrating over all coordinates we obtain

$$\begin{aligned} \sum_n \langle \xi_{c'n'} \phi_{c'n'}^{JM} | R(\mathcal{H} + \hat{\mathcal{L}}_b - E) \frac{1}{R} | \xi_{cn} \phi_c^{JM} \rangle A_{cn; \alpha}^J \\ = \left(\frac{\hbar^2}{2\mu}\right) \xi_{c'n'}^*(A) \left(\frac{\partial F_{c\alpha}^J}{\partial R} - b_c F_{c\alpha}^J\right)_{R=A}. \end{aligned} \quad (\text{II.18})$$

We put

$$\begin{aligned} H = R\mathcal{H} \frac{1}{R} \\ = -\left(\frac{\hbar^2}{2\mu}\right) \frac{d^2}{dR^2} + \frac{\hat{l}^2}{2\mu R^2} + V(q, \mathbf{R}) + \mathcal{H}_T \end{aligned} \quad (\text{II.19})$$

and

$$\begin{aligned} \hat{L}_b = R\hat{\mathcal{L}}_b \frac{1}{R} \\ = \left(\frac{\hbar^2}{2\mu}\right) \delta(R-A) \sum_{JM} \sum_c |\phi_c^{JM}\rangle \left(\frac{\partial}{\partial R} - b_c\right) \langle \phi_c^{JM}|, \end{aligned}$$

and denote the matrix

$$\langle \xi_{c'n} \phi_c^{JM} | H + \hat{L}_b - E | \xi_{cn} \phi_c^{JM} \rangle$$

by

$$(H + L_b - E)_{c'n;cn}^J \quad (\text{II.20})$$

for short. It is Hermitian and nonsingular. Multiplying Eq. (II.18) through by its inverse and summing over  $c'$  and  $n'$  we have

$$A_{cn;\omega}^J = \left( \frac{\hbar^2}{2\mu} \right) \sum_{c',n'} (H + L_b - E)_{cn;c'n'}^{-1} \xi_{c'n'}^* \xi_{cn}^* (A) \times \left( \frac{\partial F_{c'\omega}^J}{\partial R} - b_{c'} F_{c'\omega}^J \right)_{R=A}.$$

The  $J$  dependence of  $(H + L_b - E)_{cn;c'n'}^{-1}$  is implicit. Finally, multiplying through by  $\xi_{cn}(A)$  and summing over  $n$  we find

$$F_{c\omega}^J(A) = \sum_{c'} R_{cc'}^J \left( \frac{\partial F_{c'\omega}^J}{\partial R} - b_{c'} F_{c'\omega}^J \right)_{R=A}. \quad (\text{II.21})$$

Equation (II.21) defines the **R** matrix as

$$R_{cc'}^J = \left( \frac{\hbar^2}{2\mu} \right) \sum_{n,n'} \xi_{cn}(A) (H + L_b - E)_{cn;c'n'}^{-1} \xi_{c'n'}^* (A). \quad (\text{II.22})$$

Equation (II.21) is the fundamental **R**-matrix relation which connects the scattering amplitudes and their derivatives at the boundary. It is given here in fairly general form for arbitrary radial basis functions. Knowledge of the **R** matrix is all that is needed in order to continue the integration of the Schrödinger equation from  $R = A$  to the asymptotic region, and hence to determine the collision matrix.

If  $N$  is the number of channels  $c$  included in the partial wave expansion (II.9),  $N_0$  of which are open (i.e., correspond to  $k_{\rho j} > 0$ ), we can arrange the radial amplitudes  $F_{c\omega}^J(A)$  in the form of an  $N \times N$  matrix as follows:

$$F^J = \begin{array}{c} \uparrow \\ N_0 \\ \downarrow \\ \left[ \begin{array}{c|c} \text{I} & \\ \hline \text{II} & \end{array} \right] \text{III} \\ \uparrow \\ N_c \\ \downarrow \end{array} \quad \begin{array}{c} \leftarrow N_0 \rightarrow \end{array}$$

where  $N_c = N - N_0$  is the number of closed channels ( $k_{\rho j} < 0$ ). All the amplitudes corresponding to a given initial state  $c_0$  lie in the same column. Block I represents incoming open channel waves with outgoing channel components [ $k_{\rho j}, k_{\rho j_0} \geq 0$ ;  $c, c_0 = 1, 2, \dots, N_0$ ; Eq. (II.6a)], block II represents incoming open channel waves with closed outgoing channel components [ $k_{\rho j_0} \geq 0$ ;  $k_{\rho j} < 0$ ;  $c_0 = 1, 2, \dots, N_0$ ;  $c = N_0 + 1, \dots, N$ ; Eq. (II.6b)], while block III represents the nonphysical incoming closed channel waves with closed or open outgoing components [ $k_{\rho j_0} < 0$ ;  $c_0 = N_0 + 1, \dots, N$ ; Eq. (II.6c)].

Correspondingly the **R** matrix is of order  $N \times N$ , and we may write Eq. (II.21) in matrix form

$$F^J = R^J (F'^J - b F^J), \quad (\text{II.24})$$

where **b** is a diagonal  $N \times N$  matrix of constants  $b_c$ :  $(b)_{cc'} = b_c \delta_{cc'}$ , and  $F'^J$  denotes the matrix of derivatives with respect to  $R$  of  $F_{c\omega}^J(R)$ .

Let the number of radial basis functions included in the expansion (II.16) be  $NM$ . The size of the compound basis set  $\xi_{cn}(R) \phi_c^{JM}(q, \Omega)$  is therefore  $N \times NM$ , and this is the order of the matrix (II.20) which we now write in the form

$$(H + L_b - OE)^J.$$

In order to obtain a more convenient expression for the **R**-matrix (II.22) in which the energy dependence occurs explicitly, we consider the following generalized eigenvalue problem:

$$U^T (H + L_b) U = \epsilon, \quad (\text{II.25a})$$

$$U^T O U = I, \quad (\text{II.25b})$$

where  $\epsilon$  is the diagonal matrix of eigenvalues of  $H + L_b$ . Superscripts  $J$  on **H**, **L**, and  $\epsilon$  have been omitted at present for clarity. The matrix **U** has indices  $U_{cn;\lambda}$  a particular column of which,  $U_\lambda$ , corresponds to an eigenvalue  $\epsilon_\lambda$ . The eigenfunctions are given by

$$\omega_\lambda^{JM}(q, R) = \sum_{c,n} \xi_{cn}(R) \phi_c^{JM}(q, \omega) U_{cn;\lambda}^J. \quad (\text{II.26})$$

It should be noted that **U** is not unitary and the superscript  $T$  in Eqs. (II.25) denotes the Hermitian transpose. (Since all quantities are in fact real,  $U^T$  is just the transpose of **U**.)

With the aid of Eq. (II.25), we may now write

$$(H + L_b - EO)_{cn;c'n'}^{-1} = \sum_\lambda \frac{U_{cn;\lambda}^J U_{\lambda;c'n'}^J}{\epsilon_\lambda^J - E},$$

and finally we have for the **R** matrix:

$$R_{cc'}^J = \sum_\lambda \frac{\gamma_{c\lambda}^J \gamma_{\lambda c'}^J}{\epsilon_\lambda^J - E}, \quad (\text{II.27})$$

where

$$\gamma_{c\lambda}^J = \left( \frac{\hbar^2}{2\mu} \right)^{1/2} \sum_n \xi_{cn}(A) U_{cn;\lambda}^J. \quad (\text{II.28})$$

The quantities  $\gamma_{c\lambda}^J$  are known as the reduced widths. From Eq. (II.26), we see that an alternative expression is

$$\gamma_{c\lambda}^J = \left( \frac{\hbar^2}{2\mu} \right)^{1/2} (\phi_c^{JM} | \omega_\lambda^{JM} \rangle_{R=A}. \quad (\text{II.29})$$

Expression (II.27) is identical in form to the original Wigner-Eisenbud expression, but has been derived here without any particular assumptions for the boundary conditions satisfied by the  $\omega_\lambda^{JM}$  at  $R = A$ . Thus in order to determine the **R** matrix it is sufficient to diagonalize  $H + L_b$  once as in Eq. (II.25) to find the eigenvalues  $\epsilon_\lambda$  and eigenvectors  $\omega_\lambda$ . Having done so, the reduced widths are found from Eq. (II.28), and the **R**-matrix (II.27) assembled at any energy  $E$ . The diagonalizing matrix **U** is obtained as shown in Appendix I.

In the outer region ( $A \leq R \leq \infty$ ), the radial wave functions satisfy the set of close-coupled equations

$$\left[ -\frac{d^2}{dR^2} + \frac{l(l+1)}{R^2} + V_{cc'}^J(R) - k_{\rho j}^2 \right] F_{c\lambda}^J(R) = -\sum_{c' \neq c} V_{cc'}^J(R) F_{c'\lambda}^J(R), \quad (\text{II.30})$$

where

$$V_{cc'}^J(R) = \left( \frac{2\mu}{\hbar^2} \right) (\phi_c^{JM} | V(q, \mathbf{R}) | \phi_{c'}^{JM}). \quad (\text{II.30})$$

A particularly convenient procedure for integrating these equations is provided by the *R*-matrix propagator method.<sup>6-8</sup> This requires as input just the *R* matrix at *R* = *A* which is then propagated to the asymptotic region where the collision matrix may be extracted by standard means.<sup>18</sup> However, it is important to note that in the outer region where the  $V_{cc'}^J(R)$  are small and vary slowly with *R*, the *R*-matrix propagator method is able to take large steps, and is consequently very effective.

The essential remaining task is the determination of optimal radial basis functions so as to ensure rapid convergence of expansion (II.27).

### C. Determination of the radial basis functions

The convergence properties of the *R*-matrix method depend heavily upon the quality of the radial functions used to represent the collision wave function in the internal region. The basis functions have to meet two separate requirements: (a) They must accurately represent the scattering wave function in the inner region, and (b) they must be able to reproduce accurately the logarithmic derivative of the collision wave function at the *R*-matrix boundary. This second requirement ensures the correct continuation of the wave function into the outer region. An *R*-matrix procedure which satisfies only the first requirement (i.e., that of Wigner and Eisenbud) leads to poor convergence. Such an *R* matrix however does converge ultimately—but nonuniformly—to the correct limit as has been shown by Jackson<sup>21,28</sup> for bounded potentials.

In order to satisfy requirement (a) for heavy particle collisions, we need to define an effective radial Hamiltonian  $H_{cc}(R)$  of which the radial basis functions  $\xi_{cn}(R)$  are eigenfunctions: This is obtained as follows: We write the exact eigenfunctions  $\omega_{\lambda}^{JM}(q, \mathbf{R})$  of  $H + \hat{L}_b$  in the form

$$\omega_{\lambda}^{JM}(q, \mathbf{R}) = \sum_c f_{c\lambda}^J(R) \phi_c^{JM}(q, \Omega), \quad (\text{II.32})$$

in which the  $f_{c\lambda}^J(R)$  functions satisfy the boundary conditions

$$\left\{ \frac{d}{dR} \ln f_{c\lambda}^J(R) \right\}_{R=A} = b_c. \quad (\text{II.33})$$

Substituting expansion (II.32) into the equation

$$(H + \hat{L}_b) \omega_{\lambda} = \epsilon_{\lambda} \omega_{\lambda}, \quad (\text{II.34})$$

multiplying through by  $\phi_c^{JM}(q, \Omega)^*$ , and integrating, we arrive at the set of equations satisfied by the  $f_{c\lambda}^J(R)$ :

$$\left[ -\frac{d^2}{dR^2} + \frac{l(l+1)}{R^2} + V_{cc}^J(R) + \frac{2\mu}{\hbar^2} (\epsilon_{\rho j} - \epsilon_{\lambda}) \right] f_{c\lambda}^J(R) = -\sum_{c' \neq c} V_{cc'}^J(R) f_{c'\lambda}^J(R). \quad (\text{II.35})$$

If we neglect the right-hand side of this equation, and replace *l* by *J*, we obtain

$$H_{cc}(R) = -\frac{\hbar^2}{2\mu} \left[ \frac{d^2}{dR^2} - \frac{J(J+1)}{R^2} + V_{cc}^J(R) \right] + \epsilon_{\rho j} \quad (\text{II.36})$$

as an effective radial Hamiltonian. The radial basis functions are determined as eigensolutions of Eq. (II.36) in an appropriate range with appropriate boundary conditions to be described below. The replacement of *l* by *J* has been discussed previously by Gerratt and Wilson<sup>18</sup>. For a given channel *c*, *l* assumes all integer values from  $|J - j|$  to  $J + j$ . Hence, the most commonly occurring value of *l* is *J*.

If the potential function  $V(q, \mathbf{R})$  is nearly isotropic, a single choice of  $V_{cc}^J(R)$  will be sufficient for all channels, and consequently  $H_{cc}(R)$  will, in this case, be independent of *c*: A single set of radial basis functions  $\xi_{cn}(R)$  is used for all channels. However, for very anisotropic potentials it is necessary to use a distinct set of radial basis functions corresponding to each level (*ρ*, *j*) considered.<sup>16,17</sup> More elaborate effective potentials can be constructed from Eq. (II.35) for use in Eq. (II.36), but so far this has not been found to be necessary.

We now turn to requirement (b). The usual method of obtaining radial basis functions  $\xi_{cn}(R)$  is to utilize a set of primitive basis functions, all of which satisfy a fixed boundary condition (this obviates the need for introducing a radial Bloch operator) and to diagonalize  $H_{cc}(R)$  in this basis. However, this automatically produces orthonormal radial functions with fixed logarithmic derivatives at the *R*-matrix boundary.

The method we use to avoid this situation is quite simple: We define a range of *R* slightly greater than the *R*-matrix region,  $0 \leq R \leq A + \delta$ , where  $\delta$  is some small positive value to be chosen. In this region we calculate the  $\xi_{cn}(R)$  from the appropriate effective Hamiltonian. The radial basis functions will be orthogonal in the extended region, but not in the *R*-matrix region and they will therefore possess arbitrary logarithmic derivatives at  $R = A$ . The advantage of this procedure is that it is quite general: The truncated radial basis functions retain their essential character as defined by  $H_{cc}(R)$  and by varying  $\delta$  we retain control over the extent of the nonorthogonality introduced. If  $\delta \rightarrow 0$ , the basis functions become orthonormal, and a Buttle correction must be included. As long as  $\delta$  is small there is no danger of linear dependence among the  $\xi_{cn}(R)$  in the range (0, *A*) even for large basis sets. In practice it is found that there is an optimum value for  $\delta$  for a given basis set and partial wave. Satisfactory results are also obtained using a  $\delta$  calculated at one value of *J* for several adjacent values of *J*. As a general guideline we have found that  $\delta$  in the range  $0.05 \times A - 0.1 \times A$  gives good results. Figure 1 shows an example of the lowest few  $\xi_{cn}(R)$ ; at  $R = A + \delta$  they have been chosen to possess zero derivatives, but at  $R = A$

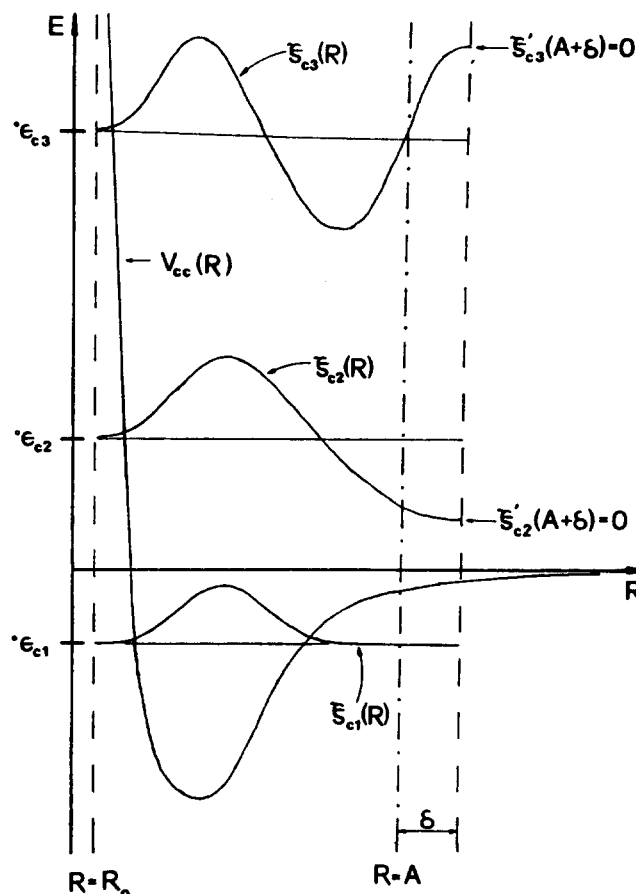


FIG. 1. The diagram shows an arbitrary effective potential  $V_{cc}(R)$  and defines the radial *R*-matrix parameters  $R_0$ ,  $A$ , and  $\delta$ . The radial functions  $\xi_{nc}(R)$  are calculated in the interval  $(R_0, A + \delta)$  and are orthonormal in that interval. They are then subsequently used in the smaller region  $(R_0, A)$  and are nonorthogonal in that region because of their arbitrary derivatives at the *R*-matrix boundary  $R = A$ .

their derivatives are arbitrary. The idea of enlarged regions has been considered before by Tobocman<sup>9,10</sup> in his extended *R*-matrix theory, but its use is different from that presented here.

The primitive basis set has the form<sup>18</sup>

$$\chi_k(R) = \left[ \frac{2}{(A + \delta - R_0)} \right]^{1/2} \sin \left[ \pi \left( k + \frac{1}{2} \right) \frac{(R - R_0)}{(A + \delta - R_0)} \right],$$

$$k = 0, 1, 2, \dots, N_R, \quad (\text{II.37})$$

so that

$$\xi_{cn}(R) = \sum_{k=0}^{N_R} \chi_k(R) D_{kn;c}, \quad R_0 \leq R \leq A + \delta. \quad (\text{II.38})$$

$R_0$  is chosen to be well inside the classically inaccessible region and is the starting point for the radial integration. The  $\chi_k(R)$  basis functions are orthonormal in the interval  $R_0 \leq R \leq A + \delta$  and have zero derivatives at  $R = A + \delta$ . If the size of the primitive basis set is  $N_R$ , diagonalization of  $H_{cc}(R)$  correspondingly produces  $N_R$  radial basis functions  $\xi_{cn}(R)$ . Of these we retain only those which correspond to the  $NM$  lowest eigenvalues for use in the expansion (II.16). (See, however, remarks in Sec. IV.)

### III. APPLICATION OF THE THEORY

The collision model to be studied is a collinear atom-diatomic oscillator as given by Diestler and Feuer.<sup>29</sup> The parameters are chosen to represent the collision of a He atom with a tungsten diatom. The model may also be used to represent the collision of a gas atom with a surface, the surface being a tungsten atom attached to a body of infinite mass by a harmonic oscillator potential. The interaction between the surface and the gas atom is described by a Morse potential. This system has also been studied by Heller<sup>15</sup> by means of an *R*-matrix calculation using orthogonal radial functions, and by Truhlar and Schwenke<sup>31</sup> using an eigenphase calculation.

The Schrödinger equation for the system is written as:

$$\left[ -\frac{\hbar^2}{2m_g} \frac{\partial^2}{\partial x_g^2} - \frac{\hbar^2}{2m_s} \frac{\partial^2}{\partial x_s^2} + 2\pi m_s \nu^2 x_s^2 + V_I(x_s, x_g) \right] \times \Psi_{\alpha}(x_s, x_g) = E \Psi_{\alpha}(x_s, x_g), \quad (\text{III.1})$$

where  $c_0$  is the initial state of the system. The interaction potential is

$$V_I(x_s, x_g) = D \{ \exp[-2a(x_g - x_s - x_0)] - 2 \exp[-a(x_g - x_s - x_0)] \}, \quad (\text{III.2})$$

where  $a$  and  $D$  are the physical inverse length and depth parameters,  $m_g$  and  $m_s$  are the masses of the gas and solid atoms, respectively,  $x_g$  and  $x_s$  are the displacements from equilibrium of the gas and solid atom, respectively. The frequency of the atomic oscillator is given by  $\nu$ ,  $x_0$  is the gas-solid separation for which  $V_I$  is a minimum, and  $E$  is the total energy. By employing a scaling factor we may write Eq. (III.2) in reduced coordinates; that is, we put

$$R = (2\pi m_s \nu / \hbar)^{1/2} x_g$$

$$q = (2\pi m_s \nu / \hbar)^{1/2} x_s. \quad (\text{III.3})$$

Equation (III.2) now becomes

$$\left[ -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + H(q) + V(R, q) - \epsilon \right] \Psi_{\alpha}(R, q) = 0, \quad (\text{III.4})$$

where

$$V(R, q) = D' \{ \exp[-2a'(R - R_m - q)] - 2 \exp[a'(R - R_m - q)] \} \quad (\text{III.5})$$

and

$$D' = D/h\nu$$

$$a' = a(\hbar/2\pi m_s \nu)^{1/2}$$

$$\epsilon = E/h\nu$$

$$\mu = m_g/m_s$$

$$R_m = x_0(\hbar/2\pi m_s \nu)^{1/2}. \quad (\text{III.6})$$

$H(q)$  is just the dimensionless harmonic oscillator Hamiltonian for the following Schrödinger equation of the target:

$$[H(q) - \epsilon_c]\phi_c(q) = \left(-\frac{1}{2}\frac{\partial^2}{\partial q^2} + \frac{1}{2}q^2 - \epsilon_c\right)\phi_c(q) = 0. \quad (\text{III.7})$$

The  $\phi_c(q)$  are the harmonic oscillator eigenfunctions:

$$\phi_c(q) = (2^c c! \pi^{1/2})^{-1/2} H_c(q) \exp(-\frac{1}{2}q^2), \quad (\text{III.8})$$

$H_c(q)$  is a Hermite polynomial, and

$$\epsilon_c = (c + \frac{1}{2}); \quad c = 0, 1, 2, \dots \quad (\text{III.9})$$

The wave function is expressed in the form of an expansion in target wave functions:

$$\Psi_\alpha(R, q) = \sum_c \phi_c(q) F_{c\alpha}(R). \quad (\text{III.10})$$

The scattering wave functions satisfy coupled equations:

$$\left[\frac{d^2}{dR^2} - V_{cc}(R) - k_c^2\right]F_{c\alpha}(R) = \sum_{c' \neq c} V_{cc'}(R)F_{c'\alpha}(R), \quad (\text{III.11})$$

where

$$V_{cc'}(R) = 2\mu(\phi_c|V|\phi_{c'}) = 2\mu \int_{-\infty}^{+\infty} dq \phi_c^*(q)V(R, q)\phi_{c'}(q), \quad (\text{III.12})$$

and

$$k_c^2 = [2\mu(\epsilon - \epsilon_c)]^{1/2}. \quad (\text{III.13})$$

The matrix elements  $V_{cc'}(R)$  are given by<sup>32</sup>

$$V_{cc'}(R) = 2\mu D' \{ \exp[-2a'(R - R_m)]f(2a', c, c') - 2 \exp[-a'(R - R_m)]f(a', c, c') \}, \quad (\text{III.14})$$

where

$$f(\alpha, c, c') = \int_{-\infty}^{\infty} dq \phi_c^*(q) \exp(\alpha q) \phi_{c'}(q) = (c!c'!)^{-1/2} \exp(\frac{1}{4}\alpha^2) \times \sum_{n=0}^{\min(c,c')} \left(\frac{\alpha}{\sqrt{2}}\right)^{c+c'-2n} \frac{c!c'!}{(c-n)!(c-n)!n!}. \quad (\text{III.15})$$

We used the following values of the reduced parameters:

$$\begin{aligned} \mu &= 0.021778 & m(\text{He}) &= 4.00 \text{ amu} \\ & & m(\text{W}) &= 183.6716 \text{ amu} \\ a' &= 0.052674 \text{ RU} \\ D' &= 0.132386 \text{ RU} \end{aligned}$$

(RU denotes reduced units). Three target states  $\phi_c$ ,  $c = 0, 1, 2$  were included in the calculations. These have energy  $\epsilon_c$  of 0.0, 1.0, and 2.0 RU, respectively. The diagonal potential functions  $V_{cc}(R)$  were examined and found to be very similar. The radial basis functions were therefore all generated from a single effective Hamiltonian

$$H(R) = \frac{d^2}{dR^2} - V_{00}(R). \quad (\text{III.16})$$

We denote this set by  $\{\xi_n^0(R)\}$  and the associated eigenvalues by  $\{\epsilon_n^0\}$ . With the values of the reduced Morse parameters given above, the interaction potential  $V_{00}(R)$  possesses a well deep enough to support a single bound state. This is shown in Fig. 2. The *R*-matrix boundary was placed at  $R = A = 6.5$  Å, which consequently includes ~85% of the coupling strength of the potential. The remainder varies slowly with *R* and becomes negligible in the neighborhood of  $R = 11$  Å. The starting point of the integration  $R_0$  was taken at  $R = 1.4$  Å, and corresponds to a point well inside the classically inaccessible region. In the outer region ( $6.5 \leq R \leq 11$  Å) the *R*-matrix propagator was used with the following parameter values<sup>7</sup>:

BETA = 0.1; FACT = 1.01; CUPMAX = 0.005.

Six types of radial basis functions  $\xi_n^0(R)$  were examined. These were obtained by diagonalizing the effective radial Hamiltonian (III.16) in the primitive sine basis (II.37) for different intervals ( $R_0 \leq R \leq A + \delta$ ) in the internal region. The values of  $\delta$  were taken as:  $\delta = 0.0, 0.1, 0.2, 0.3, 0.4$ , and  $0.5$  Å. The six sets therefore correspond to increasing extents of nonorthogonality. The radial functions for  $\delta = 0.0$  are orthogonal and a Buttle correction<sup>18,19</sup> was added to the computed *R* matrix; the same unperturbed eigenfunctions  $\xi_n^0(R)$  and their corresponding eigenvalues were used for all channels in the

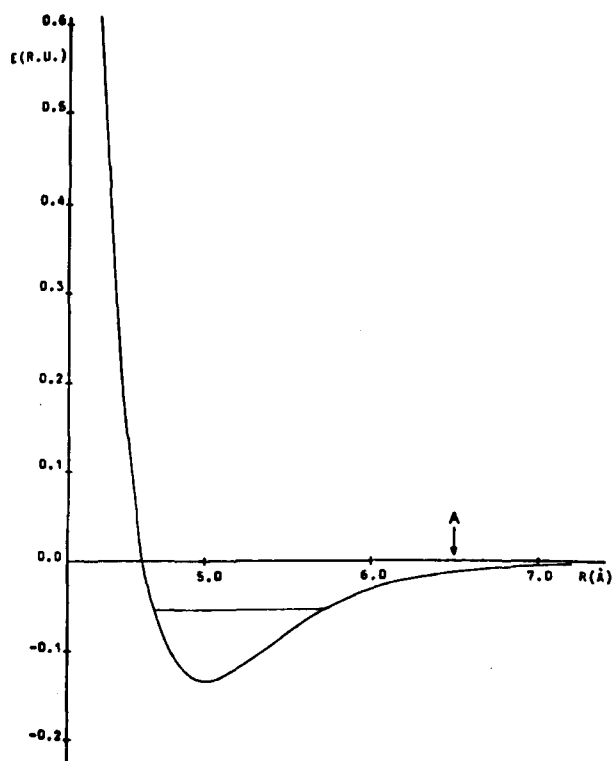


FIG. 2. The graph shows the potential matrix element  $V_{00}(R)$  as a function of the scattering coordinate *R*, used in the effective radial Hamiltonian given by Eq. (III. 16). The potential can support a bound state near  $E = -0.056$  RU. The arrow indicates the position of the *R*-matrix boundary ( $A = 6.5$  Å).



correction. Very bad results are obtained using orthogonal radial functions without the Buttle correction, as previously noted by Heller.<sup>15</sup>

Ninety primitive sine functions were used in all cases to diagonalize Eq. (III.16). From the 90  $\xi_n^0(R)$  so generated, varying numbers (*NM*) were selected for use in the *R*-matrix calculation. Table I A–C shows the rate of convergence of the opacity function  $P_{12}$  as *NM* and  $\delta$  are varied for different total energies. The opacity function is defined as

$$P_{cc'} = |S_{cc'}|^2$$

and is just the probability of transition from channel  $c'$  to channel  $c$ . Column 7 of the table shows the result of a Buttle-corrected calculation using 40 orthogonal basis functions.

It can be seen that functions with  $\delta = 0.4$  and 0.5 give results for  $P_{12}$  which have clearly converged to four to five significant figures for  $NM = 16$ . All subsequent calculations were carried out with  $\delta = 0.4$ . Convergence is seen to increase along the diagonal taken from the bottom left-hand corner to the top right-hand corner of the table.

Thus, by using a nonorthogonal set we obtain better convergence for a given *NM* than an orthogonal set plus Buttle correction. For example, in Table I B we see that  $P_{12}$  is given to three significant figures using 12 nonorthogonal radial functions when  $\delta = 0.4$  or 0.5, but to only two significant figures using orthogonal functions with Buttle correction. In fact we see from Table I A and B that even by going to 40 orthogonal functions plus Buttle correction, convergence to five significant figures is not attained.

Figure 3 shows the energy dependence (in RU) of  $P_{12}$  using three channels and 20 nonorthogonal functions per channel with  $\delta = 0.4$ . The vertical line around  $E = 1.94$  is due to a resonance (see below). Two hundred points were used to obtain the curve, each of which took 0.3 s on an IBM 360/195 computer. The curve goes to zero at threshold ( $E = 1.0$  RU). These results compare very well with those obtained by Heller<sup>15</sup> who used three channels and 61 eigenfunctions of the Morse oscillator with an analytic Buttle correction.

Since the interaction potential supports a bound state there exists the possibility of coupling between the continuum and an excited bound state of the system,

TABLE I. A–C show the convergence of the opacity function  $P_{12}$  at the total energies 1.25, 1.50, and 1.75 RU, respectively, as the number *NM* of radial functions  $\xi_n^0(R)$  per channel is varied vs the variation in the parameter  $\delta$ , when these radial functions are used in the *R*-matrix region defined by  $R_0 = 1.4$  Å to  $A = 6.5$  Å (see the text).

(A) Opacity function  $P_{12} \times 10^{-2}$  for total energy  $E = 1.25$  RU.

<i>NM</i>	$\delta$ values in Å						
	0.0	0.1	0.2	0.3	0.4	0.5	0.0
20	1.3097	1.3074	1.3102	1.3102	1.3102	1.3102	1.3101
18	1.3097	1.3054	1.3102	1.3102	1.3102	1.3102	
16	1.3100	1.3019	1.3101	1.3103	1.3102	1.3102	
14	1.3120	1.2961	1.3102	1.3105	1.3101	1.3100	
12	1.3208	1.2879	1.3117	1.3120	1.3095	1.3089	
10	1.3553	1.2838	1.3229	1.3252	1.3077	1.3008	

(B) Opacity function  $P_{12} \times 10^{-2}$  for total energy  $E = 1.50$  RU.

<i>NM</i>	$\delta$ values in Å						
	0.0	0.1	0.2	0.3	0.4	0.5	0.0
20	2.3774	2.3951	2.3797	2.3798	2.3798	2.3798	2.3793
18	2.3765	2.4062	2.3795	2.3797	2.3797	2.3797	
16	2.3741	2.4262	2.3789	2.3796	2.3797	2.3797	
14	2.3669	2.4634	2.3761	2.3789	2.3794	2.3791	
12	2.3418	2.5343	2.3630	2.3735	2.3772	2.3765	
10	2.2608	2.6917	2.2941	2.3242	2.3626	2.3723	

(C) Opacity function  $P_{12} \times 10^{-2}$  for total energy  $E = 1.75$  RU.

<i>NM</i>	$\delta$ values in Å						
	0.0	0.1	0.2	0.3	0.4	0.5	0.0
20	3.6248	3.6212	3.6259	3.6253	3.6253	3.6253	3.6253
18	3.6252	3.6178	3.6269	3.6253	3.6253	3.6253	
16	3.6275	3.6113	3.6299	3.6250	3.6250	3.6249	
14	3.6383	3.5991	3.6400	3.6235	3.6232	3.6225	
12	3.6825	3.5714	3.6757	3.6144	3.6151	3.6124	
10	3.8287	3.4114	3.8122	3.5770	3.6651	3.7165	

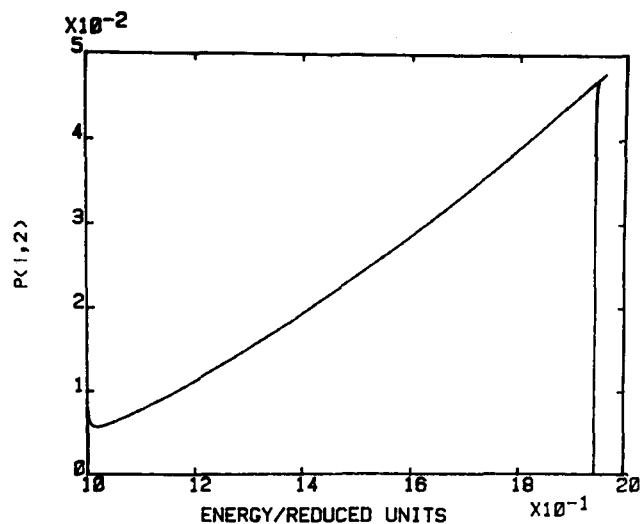


FIG. 3. The diagram shows the behavior of the opacity function  $P_{12}$  as a function of total energy. 200 separate *R*-matrix calculations were used to plot the graph. Three channels and 20 nonorthogonal radial functions ( $\delta = 0.4 \text{ \AA}$ ) were employed in the computations. The vertical line around  $E = 1.94 \text{ RU}$  is due to a Feshbach resonance. The *R*-matrix region was defined by  $R_0 = 1.4 \text{ \AA}$  and  $A = 6.5 \text{ \AA}$ .

giving rise to a Feshbach resonance.<sup>33,34</sup> Table II gives the position and width of such a resonance arising from the excitation of the target to its third vibrational state ( $c = 2$ ) while the Morse potential supports a bound state of target and projectile. Results are shown for orthogonal and nonorthogonal basis calculations with three channels and 20 basis functions per channel, together with those obtained by Heller<sup>15</sup> and in a more recent work by Truhlar and Schwenke.<sup>31</sup> We see that the nonorthogonal calculation gives results which are very close to those of Heller and Truhlar and Schwenke, whereas the orthogonal calculation does not. The resonance obtained with non-orthogonal functions is shown in greater detail in Fig. 4. A nonorthogonal calculation including five channels and  $NM = 20$  was also carried out and gave the resonance position deviating by a negligible amount from the three channel case.

In order to study the resonance in greater detail we write an element of the collision matrix as<sup>35</sup>

$$S'_{cc'} = {}^dS_{cc'} - \frac{ig_{cj}g_{jc'}}{E - E'_j + \frac{1}{2}i\Gamma_j}. \quad (\text{III.17})$$

The first term on the right is the contribution to  $S_{cc'}$  from direct (nonresonant) scattering and is presumed to vary slowly with  $E$ . The second term arises from closed channel resonant scattering. The resonance half-width is given by  $\Gamma_j$  and

$$E'_j = E_j + \Delta_j,$$

where  $E'_j$  is the resonance position,  $E_j$  the energy of the excited bound state, and  $\Delta_j$  the shift in  $E_j$  arising from the interaction between the continuum and the bound state. The quantities  $g_{cj}$  are related to the strength of this interaction and can be shown to satisfy<sup>35</sup>

$$\Gamma_j = \sum_c |g_{jc}|^2, \quad (\text{III.18})$$

TABLE II. Results are presented of the resonance position and half-width arising from a Feshbach resonance occurring when the target is excited into its closed third vibrational state ( $c = 2$ ); the projectile and target forming a compound system characterized by the vibrational quantum number  $n = 0$ . Two *R*-matrix calculations were done using 20 nonorthogonal radial functions ( $\delta = 0.4 \text{ \AA}$ ) and 20 orthogonal radial functions ( $\delta = 0.0 \text{ \AA}$ ) per channel. A Buttle correction was included in the latter case. The *R*-matrix region was defined in the interval  $R_0 = 1.4 \text{ \AA}$  to  $A = 6.5 \text{ \AA}$ . Three channels were included in both calculations.

Calculation	Resonance energy in RU	Resonance half-width in RU
Orthogonal + Buttle	1.95054	order $10^{-4}$
Nonorthogonal	1.94489	$1.26 \times 10^{-4}$
Truhlar and Schwenke	1.94415	$1.24 \times 10^{-4}$
Heller	1.944134	order $10^{-5}$

where the sum includes all open channels. Equation (III.17) may be written as

$$S_{cc'} = a_{cc'} + b_{cc'} - \frac{ib_{cc'}\Gamma_j}{E - E'_j + \frac{1}{2}i\Gamma_j}, \quad (\text{III.19})$$

with

$$\left. \begin{aligned} b_{cc'} &= g_{cj}g_{jc'}/\Gamma_j \\ a_{cc'} &= {}^dS_{cc'} - b_{cc'} \end{aligned} \right\}. \quad (\text{III.20})$$

Hence,

$$S_{cc'} = a_{cc'} + b_{cc'} \exp[2i\eta_j(E)], \quad (\text{III.21})$$

where

$$\eta_j(E) = \tan^{-1}[\frac{1}{2}\Gamma_j/(E'_j - E)]. \quad (\text{III.22})$$

Equation (III.22) shows that as the total energy  $E$  increases from far below to far above  $E'_j$ , the phase of  $S_{cc'}$  will increase by  $\pi$ . As  $E$  increases,  $S_{cc'}$  traces out a complete circle in the complex plane. The circle is centered at  $a_{cc'}$  with radius  $b_{cc'}$  and starts and finishes at  ${}^dS_{cc'}$ .<sup>37</sup> For a  $2 \times 2$  collision matrix it can be shown<sup>36</sup> that  $|a_{12}| = |b_{12}|$  so that the circle passes through the origin when  $E = E'_j$  and  $P_{12}$  is zero at the resonance energy. The computed

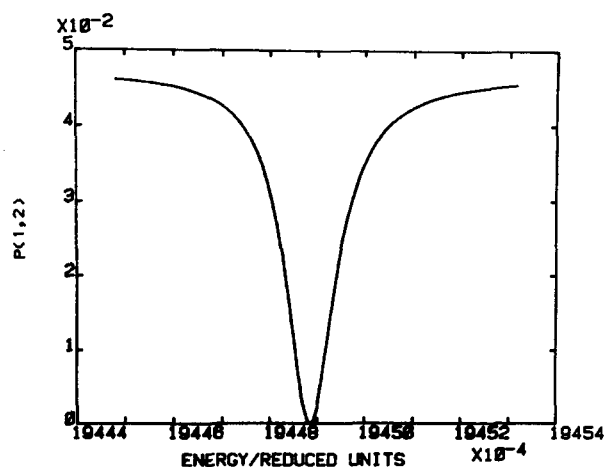


FIG. 4. The diagram shows in detail the Feshbach resonance of Fig. 3, arising from the excitation of the target into its closed third vibrational state ( $c = 2$ ), while the target and projectile form a compound system characterized by the vibrational quantum state  $n = 0$ . The resonance has a half-width of  $1.26 \times 10^{-4} \text{ RU}$ , and is situated at  $E = 1.94489 \text{ RU}$ .

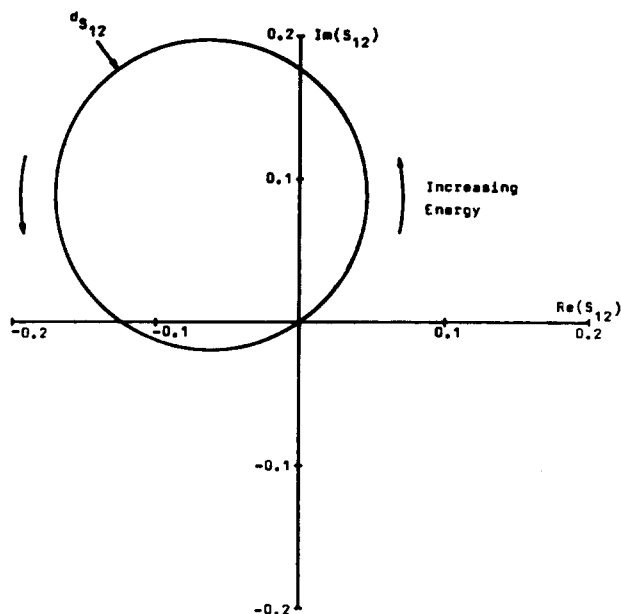


FIG. 5. The figure shows the behavior of the computed imaginary and real parts of the collision matrix element  $S_{12}$  as the total energy is varied from far below to far above the resonance. The circle begins and ends at  $dS_{12}$  and on resonance passes through the origin. Two hundred points were used to plot this curve.

Argand diagram of real  $S_{12}$  versus imaginary  $S_{12}$  is shown in Fig. 5.

The resonance energy was determined by the following procedure: Because the potentials  $V_{00}(R)$ ,  $V_{11}(R)$ ,  $V_{22}(R)$  are almost identical, the energy of the bound state of  $V_{00}(R)$  will be very close to that of the corresponding level in the other potentials. From the diagonalization of the effective Hamiltonian (III.16), the energy of this state is found at  $E_b = -0.056431$  RU. The target energy of

state  $c = 2$  occurs at 2.0 RU so we expect to find a resonance at a total energy  $E$  of approximately  $2.0 + E_b = 1.943569$  RU. We also expect to find an *R*-matrix eigenvalue  $\epsilon_\lambda$  near this energy, and indeed there are two:  $\epsilon_{14} = 1.941466$  RU and  $\epsilon_{15} = 1.951289$  RU (see Table III). We note also that the magnitude of the product of the reduced widths  $\gamma_{\lambda 1}\gamma_{\lambda 2}$  is anomalously large (0.09803 and  $-0.12859$ , respectively) for  $\lambda = 14$  and  $15$  (see below). Seventy one *R*-matrix calculations were carried out near these energies and the resonance was found at  $E = 1.944887$  RU. The opacity function  $P_{12}$  was fitted to a Fano-Beutler line shape function, the result of which is shown in Table II.

The *R*-matrix eigenfunctions are of the form

$$\begin{aligned}\omega_\lambda(q, R) &= \sum_{c,n} \phi_c(q) \xi_n^0(R) U_{cn;\lambda} \\ &= \sum_c \phi_c(q) \bar{F}_{c\lambda}(R).\end{aligned}\quad (\text{III.23})$$

The reduced widths are therefore given by

$$\gamma_{\lambda c} = (\phi_c | \omega_\lambda \rangle_{R=A} = \bar{F}_{c\lambda}(A). \quad (\text{III.24})$$

Hence, for a given *R*-matrix eigenvalue  $\epsilon_\lambda$ , there are  $N_0$  "open" reduced widths and  $N_c$  "closed"  $\gamma_{\lambda c}$ 's according to whether  $\epsilon_\lambda \geq \epsilon_c$  or  $\epsilon_\lambda < \epsilon_c$ . We expect all closed  $\gamma_{\lambda c}$ 's to be very small, and examination of Table III shows that this is indeed the case. The target excitation energies are 0.0, 1.0, and 2.0 RU. Correspondingly  $\gamma_{\lambda 1}$  is small for all  $\epsilon_\lambda < 1.0$  RU, and  $\gamma_{\lambda 2}$  is small for all  $\epsilon_\lambda < 2.0$  RU. There are, however, two exceptions in each channel ( $c = 1, 2$ ) and these occur just below threshold. These are explained by noting that there are two unperturbed energies  $\epsilon_c^{(0)} = \epsilon_c + \epsilon_n^{(0)}$  in the region. One arises from  $\epsilon_c$  ( $c = 2$ ) plus the energy of the bound state as described above, and the

TABLE III. Reduced widths  $\gamma_{\lambda c}$  for the lowest 20 eigenvalues  $\epsilon_\lambda$  obtained from an *R*-matrix calculation with an internal region defined by  $R_0 = 1.4$  Å,  $A = 6.5$  Å. Three channels and 20 nonorthogonal radial functions per channel were employed. The radial functions are defined in the interval  $R_0 = 1.4$  Å,  $A + \delta = 6.9$  Å.

$\lambda$	$\epsilon_\lambda$	$\gamma_{\lambda c}$		
		$c = 0$	$c = 1$	$c = 2$
1	-0.058 435	-4.2876 (-1)	-2.6699 (-4)	-3.0948 (-6)
2	0.017 283	1.1519 (+0)	6.9221 (-4)	8.2156 (-6)
3	0.159 665	-1.0422 (+0)	-5.7938 (-4)	-7.2414 (-6)
4	0.370 151	9.8120 (-1)	4.7330 (-4)	6.5480 (-6)
5	0.635 147	9.4815 (-1)	3.2608 (-4)	5.9008 (-6)
6	0.941 413	-2.0420 (-1)	-4.1661 (-1)	-3.6822 (-4)
7	0.949 567	9.0264 (-1)	-1.1796 (-1)	-9.8541 (-5)
8	1.017 591	2.9317 (-2)	1.1522 (+0)	9.7962 (-4)
9	1.160 252	-3.4181 (-2)	1.0415 (+0)	8.1880 (-4)
10	1.308 446	-9.0390 (-1)	-1.0688 (-1)	-8.0799 (-5)
11	1.371 795	-9.7492 (-2)	9.7632 (-1)	6.6510 (-4)
12	1.635 476	1.2031 (-1)	9.3890 (-1)	4.5697 (-4)
13	1.712 802	-8.8735 (-1)	1.4202 (-1)	5.1262 (-5)
14	1.941 466	2.1658 (-2)	2.3715 (-1)	4.1338 (-1)
15	1.951 289	-8.2545 (-2)	-8.8928 (-1)	1.4460 (-1)
16	2.017 986	4.0025 (-3)	4.1377 (-2)	1.1528 (+0)
17	2.155 109	8.7621 (-1)	-1.3203 (-1)	3.9199 (-2)
18	2.161 189	-3.9791 (-2)	-4.1748 (-2)	1.0406 (+0)
19	2.311 137	1.19421 (-1)	8.9027 (-1)	1.4909 (-1)
20	2.374 282	1.3896 (-2)	1.3526 (-1)	-9.7264 (-1)

other is due to  $\epsilon_c$  ( $c = 1$ ) plus  $\epsilon_n^{(0)}$  ( $n = 7$ ). Upon diagonalization these two states give rise to two eigenfunctions, which we may characterize as

$$\omega_{14} \simeq \phi_2 \xi_1^0 + U \phi_1 \xi_7^0$$

$$\omega_{15} \simeq U \phi_2 \xi_1^0 - \phi_1 \xi_7^0,$$

where  $U$  is a small ( $\sim 0.25$ ) positive constant [cf. Eq. (III.23)]. From this it is clear that  $\omega_{14}$  is primarily the resonant state, and that this consists largely of the target excited to its third quantum level ( $c = 2$ ) with the projectile trapped in the well of the potential. This method of analysis of *R*-matrix eigenvalues may be a fruitful way of characterising resonant states in more complicated cases.

#### IV. DISCUSSION AND CONCLUSIONS

The quality and number of radial basis functions determine the energy range over which useful results may be obtained. From present work it appears that this is approximately 75% of the energies spanned by the lowest and highest  $\epsilon_\lambda$ 's.

For higher energy ranges it is not necessary to select the first  $NM$   $\xi_{cn}(R)$  functions, but instead one can use a set with index  $n$  ranging from  $n_{\min}$  to  $n_{\max}$ . The larger the number of nodes possessed by the  $\xi_{cn}(R)$  within this set, the higher the energy range covered. However, care should be taken always to include those basis functions corresponding to bound states of the colliding system. Calculations were carried out on the W-He system in which  $\xi_1^0(R)$  was omitted, and inaccurate opacity functions were obtained at all energies.

The effective Hamiltonian used for generating the radial basis functions [Eq. (III.16)] is very simple, largely because all off-diagonal elements  $V_{cc'}(R)$  ( $c' \neq c$ ) are very small compared to the diagonal elements, and these last are practically indistinguishable. In more complicated cases where the colliding system possesses anisotropy, it is necessary to use a different effective Hamiltonian for each target state.<sup>17</sup>

In this paper we have shown that the use of slightly nonorthogonal radial basis functions provides the key to the successful application of the Wigner-Eisenbud approach to heavy particle scattering. The radial basis functions are produced by a simple but fairly general scheme. The nonorthogonality has the effect of giving rise to arbitrary derivatives at the *R*-matrix boundary while allowing for a realistic description of the wave function in the interior region. The resulting *R*-matrix procedure appears to be reliable both close to and far from resonances. The Buttle correction is no longer needed. After the initial diagonalization, the only significant computational effort is the solution of the coupled Eqs. (II.30) in the outer region. Because the potential here varies slowly with *R* and the coupling matrix  $V_{cc'}^J(R)$  is nearly diagonal, this region is quickly traversed by the *R*-matrix propagator technique. However, in molecular encounters, the explicit form of the potential in this interval is generally known:

$$V_{cc'}^J(R) = \sum_{n \geq n_{\min}} (a_n^J)_{cc'} R^{-n}, \quad (\text{IV.1})$$

where  $n_{\min} = 3, 4, 5$ , or 6 depending upon the type of leading long-range interaction, and the  $(a_n^J)_{cc'}$  are constants. Future versions of our programs will take explicit account of the form (IV.1).<sup>38</sup>

#### APPENDIX: DIAGONALIZATION OF $H + L_b$

The diagonalizing matrix  $U$  is defined by [cf. Eqs. (II.25)]:

$$\left. \begin{aligned} U^T(H + L_b)U &= \epsilon \\ U^T O U &= I \end{aligned} \right\}. \quad (\text{A1})$$

In order to determine  $U$ , we carry out a Schmidt orthonormalizing transformation<sup>39</sup> of the radial functions  $\xi_{cn}(R)$ . Because of the orthogonality of the channel functions  $\phi_c^{JM}$ , the overlap matrix  $O$  is block diagonal in the channel index, as shown in Eq. (II.17). The corresponding Schmidt transformation is therefore also block diagonal, and we need consider only the orthogonalization in the space of one channel [Eq. (II.18)]. We write the transformation as

$$\bar{\xi}_c(R) = \xi_c(R) T_{cc}, \quad (\text{A2})$$

where  $T_{cc}$  is an upper right-hand triangular matrix of dimension  $NM \times NM$ , and the row vectors  $\bar{\xi}_c(R)$ ,  $\xi_c(R)$  are of length  $NM$ . A bar over any quantity indicates an orthogonal representation. The matrix  $\bar{H} + \bar{L}_b$  is now transformed as

$$T^T(H + L_b)T = \bar{H} + \bar{L}_b, \quad (\text{A3})$$

where  $T$  is a block-diagonal matrix constructed from the blocks  $T_{cc}$  of Eq. (A2). Finally,  $\bar{H} + \bar{L}_b$  is diagonalized by the unitary matrix  $C$ :

$$C^T(\bar{H} + \bar{L}_b)C = \epsilon, \quad (\text{A4})$$

so that

$$U = TC. \quad (\text{A5})$$

It is clear that since  $T$  is not unitary, neither is  $U$ .

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