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A stable linear reference potential algorithm for solution of the quantum close-coupled equations in molecular scattering theory

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We show how the linear reference potential method for solution of the close-coupled equations, which arise in inelastic scattering theory, can be reformulated in terms of an "imbedding-type" propagator. Explicit expressions are given for the blocks of the propagator matrix in terms of Airy functions. By representing these functions in terms of moduli and phases, in both classically allowed and classically forbidden regions, one can evaluate the propagator without any numerical difficulty. The resulting algorithm is tested on a highly pathological problem—the rotationally inelastic scattering of a polar molecule by a spherical ion at extremely low kinetic energy—and found to be completely stable.

I. INTRODUCTION

There has been considerable interest[1-10] in the development of efficient algorithms for the solution of the close-coupled (CC) equations which arise in the quantum description of inelastic atomic and molecular collisions. At moderate to large interparticle distances, where the potential is slowly varying compared to the local de Broglie wavelength of the collision partners, a "potential following" algorithm is generally preferable.[1,2,8] The two most widespread potential following algorithms are the R-matrix propagator of Light and co-workers,[4-6,11] and the linear reference potential method of Gordon.[12,13] Although approximation of the potential by a series of linear segments is in principle more accurate than approximation by a series of constant segments, which underlies the R-matrix methods, the original program of Gordon[14] was hampered both by the necessity of periodically stabilizing the solution[12] in regions where some (or all) of the channels are classically forbidden as well as by the numerical difficulty in using Airy function reference solutions[12] in regions where the potential is nearly flat.

Recently, we have developed[8] a modified version of the original Gordon propagator which propagates directly the log-derivative matrix, rather than the wave function and its derivative, thus eliminating the necessity for stabilization. Since this algorithm was developed in terms of the Cauchy propagator,[3] rather than the "imbedding-type"[1,6,10,11] propagators used in the "solution following" log-derivative method of Johnson[15] and in the R-matrix method,[4,6,11] a possibility still persists of numerical inaccuracy and overflow when the potential is nearly flat or when closed channels are propagated over long distances.

In the present paper we recast the linear reference potential propagation method in terms of an imbedding-type propagator. This is reviewed briefly in Sec. II. Then, in Sec. III, we present explicit expressions for this propagator involving Airy functions evaluated at both ends of a locally adiabatic interval. It will be convenient to represent the Airy functions, for both positive and negative arguments, in terms of a modulus and a phase. In Sec. IV we demonstrate that the blocks of the imbedding propagator are numerically stable and reduce, when the potential is completely flat, to those appropriate for a constant reference potential.[11] Section V demonstrates how the new algorithm can be applied without the need for analytic evaluation of the radial derivatives of the potential matrix. Then, in Sec. VI, we discuss the application of the present propagator to a pathologically difficult scattering problem, namely the low energy collision of an ion with a polar molecule. The potential is extremely long ranged, varying asymptotically as R^{-2}, and the deep well requires a large number of rotational channels, most of which become closed as the two partners recede. A brief conclusion follows.

II. CLOSE-COUPLED EQUATIONS

Using as closely as possible the notation of Secrest[1] in his review article, we write the CC equations as

$$\left[-\frac{d^2}{dR^2}+\frac{l_i(l_i+1)}{R^2}-k_i^2\right]F_{iI}(R)$$
$$=-\sum_{i'}V_{ii'}(R)F_{i'I}(R), \tag{1}$$

where l_i and k_i designate, respectively, the orbital angular momentum quantum number and wave vector in the ith channel. Equivalently, Eq. (1) can be written in matrix notation as

$$\left[\mathbf{I}\frac{d^2}{dR^2}+\mathbf{W}(R)\right]\mathbf{F}(R)=0, \tag{2}$$

where $\mathbf{I}$ is the identity matrix and $\mathbf{W}(r)$, the wave vector matrix, is given by

$$\mathbf{W}(R)=\mathbf{k}^2-\mathbf{l}^2(R)-\mathbf{V}(R), \tag{3}$$

with $\mathbf{k}^2$ and $\mathbf{l}^2(R)$ being diagonal matrices. Rather than propagating the wave function matrix $\mathbf{F}(R)$ and its derivative, $\mathbf{F}'(R)$, it is convenient to propagate the log-derivative matrix $\mathbf{Y}(R)$ defined by[1,3,10,15]

$$\mathbf{Y}(R) = \mathbf{F}'(R)\mathbf{F}(R)^{-1}. \tag{4}$$

This eliminates the need for stabilization when some of the channels are classically inaccessible $[W_{ii}(R) < 0]$.

In a "potential following" method[1] the integration range is first partitioned into a series of intervals, the nth interval extending from $R = R_n$ to $R = R_{n+1}$. One then defines a transformation matrix, $\mathbf{T}_n$, chosen to diagonalize $\mathbf{W}(R)$ at the midpoint of the interval $R = R_{n+1/2}$. If we assume that $\mathbf{W}(R)$ is real and symmetric, as is usually the case, then $\mathbf{T}_n$ is orthogonal and we have

$$\mathbf{T}_n \mathbf{W}(R_{n+1/2})\mathbf{T}_n^T = \tilde{\mathbf{k}}_n^2, \tag{5}$$

where $\tilde{\mathbf{k}}_n^2$ is a diagonal matrix. Since $\mathbf{T}_n$ is independent of R within the interval, the solution matrix and its derivative transform into the "local basis"[1,12,13] according to

$$\mathbf{F}_n(R) = \mathbf{T}_n \mathbf{F}(R), \tag{6}$$

and

$$\mathbf{F}'_n(R) = \mathbf{T}_n \mathbf{F}'(R). \tag{7}$$

Combining these equations we see that the log-derivative matrix Eq. (4) transforms as

$$\mathbf{Y}_n(R) = \mathbf{T}_n \mathbf{Y}(R)\mathbf{T}_n^T. \tag{8}$$

One can also show that $\mathbf{F}_n(R)$ satisfies the equation[8]

$$\Big[\mathbf{I}\frac{d^2}{dR^2} + \tilde{\mathbf{k}}_n^2 + (R - R_{n+1/2})\tilde{\mathbf{W}}'_n + \frac{1}{2}(R - R_{n+1/2})^2\,\tilde{\mathbf{W}}''_n + \cdots\Big]\mathbf{F}_n(R) = 0, \tag{9}$$

where

$$\tilde{\mathbf{W}}'_n = \mathbf{T}_n\left(\frac{d\mathbf{W}}{dR}\right)_{R = R_{n+1/2}}\mathbf{T}_n^T \tag{10}$$

and

$$\tilde{\mathbf{W}}''_n = \mathbf{T}_n\left(\frac{d^2\mathbf{W}}{dR^2}\right)_{R = R_{n+1/2}}\mathbf{T}_n^T. \tag{11}$$

A propagator in the nth interval may be defined as a block matrix which connects values of any solution of Eq. (9), $\mathbf{F}_n(R)$, and its derivative, $\mathbf{F}'_n(R)$, at the end points of the interval, R_n and R_{n+1}. The standard propagator, well known from the theory of differential equations, is the Cauchy matrix, $\mathbf{C}$, defined by[3,13]

$$\begin{bmatrix}\mathbf{F}_n(R_{n+1})\\ \mathbf{F}'_n(R_{n+1})\end{bmatrix} = \begin{bmatrix}\mathbf{C}_1^{(n)} & \mathbf{C}_2^{(n)}\\ \mathbf{C}_3^{(n)} & \mathbf{C}_4^{(n)}\end{bmatrix}\begin{bmatrix}\mathbf{F}_n(R_n)\\ \mathbf{F}'_n(R_n)\end{bmatrix}, \tag{12}$$

where $\mathbf{C}_1^{(n)}$ to $\mathbf{C}_4^{(n)}$ are square matrices of order equal to the number of channels. Equation (12) implies the following propagation relation for the log-derivative matrix in the local basis[8]:

$$\mathbf{Y}_n(R_{n+1}) = [\mathbf{C}_1^{(n)} + \mathbf{Y}_n(R_n)\mathbf{C}_2^{(n)}]^{-1} \times [\mathbf{C}_3^{(n)} + \mathbf{Y}_n(R_n)\mathbf{C}_4^{(n)}]. \tag{13}$$

Note that the matrices $\mathbf{C}_1^{(n)}$, $\mathbf{C}_2^{(n)}$, $\mathbf{C}_3^{(n)}$, and $\mathbf{C}_4^{(n)}$ used here correspond, respectively, to the matrices $\mathbf{A}_n$, $\mathbf{B}_n$, $\mathbf{C}_n$, and $\mathbf{D}_n$ defined in Ref. 8.

Alternatively, one can define an imbedding-type propagator $\mathscr{Y}$, by the equation[3,10]

$$\begin{bmatrix}\mathbf{F}'_n(R_n)\\ \mathbf{F}'_n(R_{n+1})\end{bmatrix} = \begin{bmatrix}\mathscr{Y}_1^{(n)} & \mathscr{Y}_2^{(n)}\\ \mathscr{Y}_3^{(n)} & \mathscr{Y}_4^{(n)}\end{bmatrix}\begin{bmatrix}-\mathbf{F}_n(R_n)\\ \mathbf{F}_n(R_{n+1})\end{bmatrix}, \tag{14}$$

which leads to the following relation for propagation of the log-derivative matrix[10]:

$$\mathbf{Y}_n(R_{n+1}) = \mathscr{Y}_4^{(n)} - \mathscr{Y}_3^{(n)}[\mathbf{Y}_n(R_n) + \mathscr{Y}_1^{(n)}]^{-1}\mathscr{Y}_2^{(n)}. \tag{15}$$

Obviously the above approaches are equivalent, and it is easy to show from the defining relations, [Eqs. (12) and (14)] that the blocks of the propagators $\mathscr{Y}$ and $\mathbf{C}$ are related by the expressions[3]

$$\mathscr{Y}_1^{(n)} = \mathbf{C}_2^{(n)^{-1}}\mathbf{C}_1^{(n)}, \tag{16a}$$

$$\mathscr{Y}_2^{(n)} = \mathbf{C}_2^{(n)^{-1}}, \tag{16b}$$

$$\mathscr{Y}_3^{(n)} = \mathbf{C}_4^{(n)}\mathbf{C}_2^{(n)^{-1}}\mathbf{C}_1^{(n)} - \mathbf{C}_3^{(n)}, \tag{16c}$$

$$\mathscr{Y}_4^{(n)} = \mathbf{C}_4^{(n)}\mathbf{C}_2^{(n)^{-1}}. \tag{16d}$$

If the off-diagonal elements of the $\tilde{\mathbf{W}}'_n$, $\tilde{\mathbf{W}}''_n$ and higher derivative matrices are neglected, then the matrix blocks of the Cauchy propagator, $\mathbf{C}_1^{(n)}$ to $\mathbf{C}_4^{(n)}$, become diagonal. The elements of these matrices can be expressed in terms of any two linearly independent solutions to an uncoupled set of ordinary second-order differential equations, the so-called "reference equation"[11-13]:

$$\Big[\frac{d^2}{dR^2} + \tilde{\mathbf{k}}_{n_{ii}}^2 + (R - R_{n+1/2})(\tilde{\mathbf{W}}'_n)_{ii} + \frac{1}{2}(R - R_{n+1/2})^2(\tilde{\mathbf{W}}''_n)_{ii} + \cdots\Big]^{f_i^{(n)}(R)}_{g_i^{(n)}(R)} = 0. \tag{17}$$

We find[8,13]

$$(C_1^{(n)})_{ij} = \delta_{ij}[f_j^{(n)}(R_{n+1})g_j^{(n)\prime}(R_n) - g_j^{(n)}(R_{n+1})f_j^{(n)\prime}(R_n)]/w_j, \tag{18a}$$

$$(C_2^{(n)})_{ij} = \delta_{ij}[g_j^{(n)}(R_{n+1})f_j^{(n)}(R_n) - f_j^{(n)}(R_{n+1})g_j^{(n)}(R_n)]/w_j, \tag{18b}$$

$$(C_3^{(n)})_{ij} = \delta_{ij}[f_j^{(n)\prime}(R_{n+1})g_j^{(n)\prime}(R_n) - g_j^{(n)\prime}(R_{n+1})f_j^{(n)\prime}(R_n)]/w_j, \tag{18c}$$

$$(C_4^{(n)})_{ij} = \delta_{ij}[g_j^{(n)\prime}(R_{n+1})f_j^{(n)}(R_n) - f_j^{(n)\prime}(R_{n+1})g_j^{(n)}(R_n)]/w_j, \tag{18d}$$

where w_j denotes the R-independent Wronskian of the two solutions,

$$w_j = f_j^{(n)}(R)g_j^{(n)\prime}(R) - f_j^{(n)\prime}(R)g_j^{(n)}(R). \tag{19}$$

Using the definition of the Cauchy propagator [Eq. (12)], and the fact that the Wronskian is constant, one can show that the diagonal matrices $\mathbf{C}_1^{(n)}$ to $\mathbf{C}_4^{(n)}$ are related by the expression

$$\mathbf{c}_1^{(n)}\mathbf{c}_4^{(n)} - \mathbf{c}_3^{(n)}\mathbf{c}_2^{(n)} = \mathbf{I}, \tag{20}$$

where lower-case letters are used to emphasize the diagonal character of the matrices. Combining Eq. (20) with Eqs. (16), and noting that the matrix blocks of the $\mathscr{Y}$ propagator are now also diagonal, we obtain

$$\mathbf{y}_1^{(n)} = \mathbf{c}_2^{(n)^{-1}}\mathbf{c}_1^{(n)}, \tag{21a}$$

$$\mathbf{y}_2^{(n)} = \mathbf{y}_3^{(n)} = \mathbf{c}_2^{(n)^{-1}}, \tag{21b}$$

$$\mathbf{y}_4^{(n)} = \mathbf{c}_4^{(n)}\mathbf{c}_2^{(n)-1}. \tag{21c}$$

These relations, when combined with Eqs. (18), give the diagonal matrix blocks of the local basis $\mathscr{Y}$ propagator in terms of any two linearly independent solutions, $\mathbf{f}^{(n)}(r)$ and $\mathbf{g}^{(n)}(r)$, of the reference equation. Similar expressions have been given previously by Light and co-workers,[11] within the context of propagation of the R matrix, which is the inverse of the log-derivative matrix.

As discussed previously,[8] passage from the local basis in interval $n-1$ to that in interval n necessitates the following transformation of the log-derivative matrix:

$$\mathbf{Y}_n(R_n) = \mathbf{P}_n \mathbf{Y}_{n-1}(R_n)\mathbf{P}_n^T, \tag{22}$$

where

$$\mathbf{P}_n = \mathbf{T}_n \mathbf{T}_{n-1}^T. \tag{23}$$

III. LINEAR REFERENCE EQUATION

If the second (and higher) derivative terms in Eq. (17) are neglected, then the reference solutions are the Airy functions,[12,13]

$$f_i^{(n)}(R) = \mathrm{Ai}(x_i^{(n)}), \tag{24a}$$

$$g_i^{(n)}(R) = \mathrm{Bi}(x_i^{(n)}), \tag{24b}$$

where

$$x_i^{(n)} = \alpha_i^{(n)}(\rho^{(n)} + \beta_i^{(n)}) \tag{25}$$

with

$$\rho^{(n)} = R - R_{n+1/2}, \tag{26}$$

$$\alpha_i^{(n)} = -[(\tilde{W}_n')_{ii}]^{1/3}, \tag{27}$$

and

$$\beta_i^{(n)} = (\tilde{k}_n^2)_{ii}/(\tilde{W}_n')_{ii}. \tag{28}$$

Both Airy functions satisfy the equation[16]

$$\left(\frac{d^2}{dx^2} - x\right)\begin{bmatrix}\mathrm{Ai}(x)\\ \mathrm{Bi}(x)\end{bmatrix} = 0, \tag{29}$$

and the Wronskian [Eq. (19)] is equal to π^{-1}.

To evaluate the desired imbedding propagators [Eq. (21) and Eqs. (18)–(20)] it will be convenient to make use of the known expansion of the Airy functions, for *negative* argument, in terms of moduli and phases, namely[16]

$$\mathrm{Ai}(-x) = M(x)\cos[\theta(x)], \tag{30a}$$

$$\mathrm{Bi}(-x) = M(x)\sin[\theta(x)], \tag{30b}$$

$$\mathrm{Ai}'(-x) = N(x)\cos[\phi(x)], \tag{30c}$$

$$\mathrm{Bi}'(-x) = N(x)\sin[\phi(x)]. \tag{30d}$$

Obviously,

$$M(x)^2 = \mathrm{Ai}(-x)^2 + \mathrm{Bi}(-x)^2, \tag{31}$$

$$\theta(x) = \arctan[\mathrm{Bi}(-x)/\mathrm{Ai}(-x)], \tag{32}$$

and similarly for $N(x)$ and $\phi(x)$ in terms of $\mathrm{Ai}'(x)$ and $\mathrm{Bi}'(x)$. In Eqs. (30)–(32) the quantity x is a positive number; so that the argument of the Airy functions is negative.

For positive argument it is convenient to use exponentially normalized Airy functions, which we define as

$$\mathrm{ai}(x) = e^{\xi}\mathrm{Ai}(x), \tag{33a}$$

$$\mathrm{ai}'(x) = e^{\xi}\mathrm{Ai}'(x), \tag{33b}$$

$$\mathrm{bi}(x) = e^{-\xi}\mathrm{Bi}(x), \tag{33c}$$

$$\mathrm{bi}'(x) = e^{-\xi}\mathrm{Bi}'(x), \tag{33d}$$

where

$$\xi = (2/3)x^{3/2}. \tag{34}$$

These, too, can be expressed in terms of moduli and (hyperbolic) phases, namely

$$\mathrm{ai}(x) = \bar{M}(x)\sinh[\chi(x)], \tag{35a}$$

$$\mathrm{bi}(x) = \bar{M}(x)\cosh[\chi(x)], \tag{35b}$$

$$\mathrm{ai}'(x) = \bar{N}(x)\sinh[\eta(x)], \tag{35c}$$

$$\mathrm{bi}'(x) = \bar{N}(x)\cosh[\eta(x)], \tag{35d}$$

where

$$\bar{M}(x)^2 = \mathrm{bi}(x)^2 - \mathrm{ai}(x)^2 \tag{36}$$

and

$$\chi(x) = \mathrm{arctanh}[\mathrm{ai}(x)/\mathrm{bi}(x)] \tag{37}$$

and similarly for $\bar{N}(x)$ and $\eta(x)$.

With a little algebra it is possible to show that the diagonal elements of the imbedding propagators can be written, in the case where the arguments of the Airy functions are *negative* at both ends of the interval,

$$y_1^{(n)} = \alpha_n(N_1/M_1)[\sin(\phi_1 - \theta_2)/\sin(\theta_2 - \theta_1)], \tag{38a}$$

$$y_2^{(n)} = y_3^{(n)} = \alpha_n/[\pi M_1 M_2 \sin(\theta_2 - \theta_1)], \tag{38b}$$

$$y_4^{(n)} = \alpha_n(N_2/M_2)[\sin(\phi_2 - \theta_1)/\sin(\theta_2 - \theta_1)]. \tag{38c}$$

In the case where the arguments of the Airy functions are *positive* at both ends of the interval, we find

$$y_1^{(n)} = \alpha_n(\bar{N}_1/\bar{M}_1)[\sinh(\chi_2 - \eta_1) - \tanh(\xi_2 - \xi_1)\sinh(\chi_2 + \eta_1)]/D_{++}, \tag{39a}$$

$$y_2^{(n)} = y_3^{(n)} = \alpha_n/[\pi\bar{M}_1\bar{M}_2\cosh(\xi_2 - \xi_1)D_{++}], \tag{39b}$$

and

$$y_4^{(n)} = \alpha_n(\bar{N}_2/\bar{M}_2)[\sinh(\chi_1 - \eta_2) + \tanh(\xi_2 - \xi_1)\sinh(\chi_1 + \eta_2)]/D_{++}, \tag{39c}$$

where

$$D_{++} = \sinh(\chi_1 - \chi_2) + \tanh(\xi_2 - \xi_1)\sinh(\chi_1 + \chi_2). \tag{40}$$

When the arguments of the Airy functions are *positive* at $R = R_n$ and *negative* at $R = R_{n+1}$, we find

$$y_1^{(n)} = \alpha_n(\bar{N}_1/\bar{M}_1)\cosh\eta_1[\cos\theta_2(1 + \tanh\xi_1) - \tanh\eta_1\sin\theta_2(1 - \tanh\xi_1)]/\mathrm{D}_{+-}, \tag{41a}$$

$$y_2^{(n)} = y_3^{(n)} = \alpha_n/(\pi\bar{M}_1 M_2\cosh\xi_1 D_{+-}), \tag{41b}$$

and

$$y_4^{(n)} = \alpha_n(N_2/M_2)\cosh\chi_1[-\cos\phi_2(1 + \tanh\xi_1) + \tanh\chi_1\sin\phi_2(1 - \tanh\xi_1)]/D_{+-}, \tag{41c}$$

where

$$D_{+-} = \cosh\chi_1[-\cos\theta_2(1 + \tanh\xi_1) + \tanh\chi_1\sin\theta_2(1 - \tanh\xi_1)]. \tag{42}$$

Finally, when the arguments of the Airy functions are *negative* at $R = R_n$ and *positive* at $R = R_{n+1}$, we find

$$y_1^{(n)} = \alpha_n (N_1/M_1) \cosh \chi_2 [-\cos \phi_1 (1 + \tanh \xi_2) + \tanh \chi_2 \sin \phi_1 (1 - \tanh \xi_2)]/D_{-+}, \quad (43a)$$

$$y_2^{(n)} = y_3^{(n)} = \alpha_n / [\pi M_1 \bar{M}_2 \cosh \xi_2 D_{-+}], \quad (43b)$$

and

$$y_4^{(n)} = \alpha_n (\bar{N}_2/\bar{M}_2) \cosh \eta_2 [\cos \theta_1 (1 + \tanh \xi_2) - \tanh \eta_2 \sin \theta_1 (1 - \tanh \xi_2)]/D_{-+}, \quad (43c)$$

where

$$D_{-+} = \cosh \chi_2 [\cos \theta_1 (1 + \tanh \xi_2) - \tanh \chi_2 \sin \theta_1 (1 - \tanh \xi_2)]. \quad (44)$$

In the algebra involved both here in the derivation of the expressions for the imbedding propagators, as well as in the next section, we have made invaluable use of the SMP symbolic algebra program running on a VAX 11/785.

IV. ASYMPTOTIC EXPRESSIONS FOR THE LINEAR REFERENCE POTENTIAL PROPAGATORS

The weakness in previous linear reference potential propagation methods[13,17] has occurred whenever the derivative of the $W(R)$ matrix approaches zero. In this case the argument of the Airy functions becomes asymptotically large, which can lead to exponential overflow for closed (classically forbidden) channels ($x \gg 1$) or loss of accuracy for open channels ($x \ll -1$). As will be shown here, these problems are *completely eliminated* in the present development.

For x large and *negative* the known asymptotic expressions for the moduli and phases of the Airy functions are[16]

$$\lim_{x\to\infty} M^2(x) = [1/\pi x^{1/2}][1 - 5/(32x^3) + \cdots], \quad (45a)$$

$$\lim_{x\to\infty} N^2(x) = [x^{1/2}/\pi][1 + 7/(32x^3) + \cdots], \quad (45b)$$

$$\lim_{x\to\infty} \theta(x) = \pi/4 - (2/3)x^{3/2} + O(x^{-3/2}), \quad (45c)$$

$$\lim_{x\to\infty} \phi(x) = 3\pi/4 - (2/3)x^{3/2} + O(x^{-3/2}). \quad (45d)$$

Using the definition of x in terms of $(\tilde{k}_n^2)_{ii}$ and $(\tilde{W}_n')_{ii}$ [Eqs. (25)–(28)], we find, after considerable algebra,

$$\lim_{\tilde{W}_n' \to 0} \begin{bmatrix} y_1^{(n)} \\ y_4^{(n)} \end{bmatrix} = (\tilde{k}_n^2)^{1/2} \cot[\Delta_n (\tilde{k}_n^2)^{1/2}] + O(\tilde{W}_n') \quad (46)$$

and

$$\lim_{\tilde{W}_n' \to 0} \begin{bmatrix} y_2^{(n)} \\ y_3^{(n)} \end{bmatrix} = (\tilde{k}_n^2)^{1/2} \csc[\Delta_n (\tilde{k}_n^2)^{1/2}] + O(\tilde{W}_n'), \quad (47)$$

where $\Delta_n = R_{n+1} - R_n$ is the width of the nth interval. In Eqs. (46) and (47) the coefficients k_n^2 and $\tilde{W}_n'$ refer to the diagonal elements of the matrices k_n^2 *and* $\tilde{W}_n'$ [Eqs. (5) and (10)].

For x large and positive, the known asymptotic expressions for the Airy functions[16] can be used to show that

$$\lim_{x\to\infty} \bar{M}^2(x) = 3/(4\pi x^{1/2})[1 + (25/72)x^{-3/2} + O(x^{-3})], \quad (48a)$$

$$\bar{N}^2(x) = (3x^{1/2}/4\pi)[1 + (7/24)x^{-3/2} + O(x^{-3})], \quad (48b)$$

$$\chi(x) = \frac{1}{2} \ln 3 - (5/36)x^{-3/2} + O(x^{-3}), \quad (48c)$$

$$\eta(x) = -\frac{1}{2} \ln 3. \quad (48d)$$

In a similar manner to the development leading to Eqs. (46) and (47) we find, after considerable algebra,

$$\lim_{\tilde{W}_n' \to 0} \begin{bmatrix} y_2^{(n)} \\ y_3^{(n)} \end{bmatrix} = (-\tilde{k}_n^2)^{1/2} \operatorname{csch}[\Delta_n (-\tilde{k}_n^2)^{1/2}] + O(\tilde{W}_n'), \quad (49)$$

$$\lim_{\tilde{W}_n' \to 0} \begin{bmatrix} y_1^{(n)} \\ y_4^{(n)} \end{bmatrix} = (-\tilde{k}_n^2)^{1/2} \coth[\Delta_n (-\tilde{k}_n^2)^{1/2}] + O(\tilde{W}_n'). \quad (50)$$

As one might expect, Eqs. (46) and (47) or (49) and (50) are *exactly* the equations derived previously[10] for the blocks of the $\mathscr{Y}$ propagator in the case of a constant reference potential. Thus the imbedding propagator for a linear reference potential goes smoothly, *without numerical instability*, to the correct limit as the derivatives of the diagonal terms in the local wave vector matrix go to zero.

If one uses the Cauchy propagator [Eqs. (13) and (18)–(20)], then exponential overflow becomes a serious problem in the classically forbidden region. We find, for example,

$$\lim_{\tilde{W}_n' \to 0} c_1^{(n)} \sim \cosh[\Delta_n (-\tilde{k}_n^2)^{1/2}] + O(\tilde{W}_n') \quad (51)$$

and

$$\lim_{\tilde{W}_n' \to 0} c_2^{(n)} \sim \sinh[\Delta_n (-\tilde{k}_n^2)^{1/2}] + O(\tilde{W}_n'). \quad (52)$$

Overflow will occur when the interval widths are large and/or when the channels are strongly closed ($|\tilde{k}_n^2| \gg 1$). More seriously, as will be seen in Sec. VI below, linear independence problems are encountered in the Cauchy propagation of the log-derivative matrix [Eq. (13)] well before the exponential behavior of the closed channel $c_i^{(n)}$ components [Eqs. (51) and (52)] causes numerical overflow.

In all fairness we should point out that one type of numerical problem can, at least in principle, occur when the imbedding propagator, $\mathscr{Y}$ is used. The blocks of this propagator matrix may be obtained[3] by solving certain boundary value problems on the interval of interest, and it is well known that solutions to particular boundary value problems do not always exist. Hence the propagator matrix $\mathscr{Y}$ may be undefined for some intervals. In practice this can only happen in a classically allowed region when the interval width is exactly equal to a characteristic length of the reference equation. When this occurs, in the case of a linear reference potential, the difference between the phase of the Airy functions, $\theta(x)$, at the two ends of the interval will equal an integer multiple of π, so that all the blocks of the $\mathscr{Y}^{(n)}$ propagator [Eq. (38)] become infinitely large. A similar overflow will occur for a constant reference potential, when the product of a local wave vector and the width of the interval [Eqs. (46) and (47)] becomes equal to an integer multiple of π. In practice significant loss of precision due to the overflow of $\mathscr{Y}^{(n)}$ will occur only rarely and can easily be circumvented by a slight increase in the chosen interval width. Obviously, then, this problem is nowhere near as nasty as the stability problems which accompany use of the Cauchy propagator in classically forbidden regions.

V. OPTIMUM LINEAR REFERENCE POTENTIAL

In most inelastic scattering problems the potential matrix $\mathbf{V}(R)$ is expanded as

$$\mathbf{V}(R) = \sum_{\lambda} v_{\lambda}(R)\mathbf{V}_{\lambda}, \tag{53}$$

where $\mathbf{V}_{\lambda}$ is a constant matrix involving, typically, sums and products of vector coupling coefficients.[18] Thus all the dependence on the interparticle coordinate is contained in a set of multiplicative coefficients. The derivative of the transformed wave vector matrix [Eq. (10)] is then given by

$$\widetilde{\mathbf{W}}'_n = -\mathbf{T}_n\left[\sum_{\lambda} v'_{\lambda}(R_{n+1/2})\mathbf{V}_{\lambda}\right]\mathbf{T}_n^T. \tag{54}$$

In previous linear reference potential codes[8,14] the local wave vectors are obtained by evaluation of the $v_{\lambda}(R)$ expansion coefficients at $R = R_{n+1/2}$, and diagonalization of $\mathbf{W}(R_{n+1/2})$ [Eq. (5)]. The $\widetilde{\mathbf{W}}'_n$ matrix is then obtained by evaluation of the radial derivatives of the expansion coefficients, followed by the transformation in Eq. (54). Finally the local wave vectors are shifted[13] to provide an optimum choice of linear reference potential for the interval in question.

As discussed previously by Alexander and Gordon,[13,19] the optimum choice of linear reference potential can be obtained by requiring the linear reference wave vector matrix to equal the true wave vector matrix at the two-point Gauss–Legendre abscissae for the interval in question, namely[19]

$$R_{\pm}^{(n)} = R_{n+1/2} \pm \Delta_n/(2\cdot 3^{1/2}). \tag{55}$$

This choice of linear reference potential guarantees that the Airy function solutions will represent the true solutions to the untruncated reference equation [Eq. (17)] to order Δ_n^5.

It follows that the optimum choice of linear reference potential can be defined by diagonalization of the *average* of the wave vector matrices at $R_{+}^{(n)}$ and $R_{-}^{(n)}$:

$$\tilde{\mathbf{k}}_n^2 = \tfrac{1}{2}\mathbf{T}_n\left[\mathbf{W}(R_{+}^{(n)}) + \mathbf{W}(R_{-}^{(n)})\right]\mathbf{T}_n^T, \tag{56}$$

with the derivatives given in terms of the *difference* between the wave vector matrices at $R_{+}^{(n)}$ and $R_{-}^{(n)}$:

$$\widetilde{\mathbf{W}}'_n = \frac{3^{1/2}}{\Delta_n}\mathbf{T}_n\left[\mathbf{W}(R_{+}^{(n)}) - \mathbf{W}(R_{-}^{(n)})\right]\mathbf{T}_n^T. \tag{57}$$

The number of matrix operations is identical to that required in the previous method. The *advantage* of the present approach is that it is now no longer necessary to evaluate the radial derivatives of the expansion coefficients analytically.

VI. TEST CALCULATION

A program has been written[20] to carry out the linear reference potential propagation of the log-derivative matrix as described in Sec. III. To test the stability of the calculation we have performed CC calculations for a pathologically difficult problem: the rotationally inelastic scattering of a polar molecule by a spherical ion at extremely low kinetic energy. This type of system is of astrophysical importance,[21,22] and a number of previous studies of this problem have been reported.[22–24] The difficulty in treating this problem arises from: (1) A deep anisotropic well which necessitates a large number of rotational channels to describe the perturbation of the rotational motion of the molecule in the well region. (2) The low collision energy which implies that most of the rotational channels become closed as the interparticle distance increases. (3) The extreme range of the ion–dipole potential.

The model potential for this problem is described by the usual form[18]

$$v(R,\gamma) = v_0(R) + v_1(R)P_1(\cos\gamma), \tag{58}$$

where γ is the angle between the molecular axis and the vector joining the atom to the center of mass of the molecule. The radial expansion coefficients are described by Morse-spline-van der Waals functions, namely

$$\begin{aligned} v_{\lambda}(R) &= D_e \exp[-\beta(R-R_e)] \\ &\quad \times\{\exp[-\beta(R-R_e)] - 1\}, \quad R<R_e, \qquad (59a)\\ &= -D_e + A(R-R_e)^2 + B(R-R_e)^3, \quad R_e \leqslant R \leqslant R_l, \qquad (59b)\\ &= -C_n R^{-n}, \quad R>R_l \qquad (59c)\end{aligned}$$

which contains six variable parameters ($D_e, R_e, \beta, R_l, C_n$, and n). The constants A and B are fixed by requiring the potential and its derivative to be continuous at $R = R_l$. The parameters used here are given in Table I.

The scattering was treated within the standard rotationally inelastic CC framework.[18] The collision reduced mass was taken to be 2.55 amu and the molecule was treated as a rigid rotor with rotational constant 18.91 cm^{-1}. This choice of constants, and the potential chosen, would be appropriate to the scattering of OH, treated as a spin-free molecule, by H_3^+, treated as a point change. The total energy was taken to be 57.82 cm^{-1}, so that only two rotational levels ($j = 0$ and

TABLE I. Morse-spline-van der Waals parameters for model ion–dipole potential.[a]

	v_0[a]	v_1[a]
D_e (cm^{-1})	2400	5000
R_e (bohr)	4	3
β_e (bohr^{-1})	0.4	0.3
R_l (bohr)	8	8
C_n[b]	2.4(+6)	1.424(+5)
n[c]	4	2

[a] See Eq. (59).
[b] Units are $\text{cm}^{-1}\,\text{bohr}^n$, where n is the inverse power dependence of the long-range potential.
[c] The chosen inverse power dependence is appropriate to an ion–dipole interaction for the anisotropy and an ion–polarizable sphere for the isotropic term.

$j = 1$) are energetically open. The CC equations were solved for a value of the total angular momentum[18] of $J = 10$.

Under these conditions all rotational levels up to and including $j = 16$ were required in order to converge the squares of the elastic and inelastic T-matrix elements[18] to within 1%. Note that the internal energy of the $j = 16$ channel is 5144 cm^{-1}, so that all the high j channels are strongly closed in the asymptotic region. Because the anisotropic ion–dipole interaction varies as R^{-2} at long range, convergence of the squares of the inelastic T-matrix elements requires integration to a final distance of $R = 1000$ bohr.

The program used here was a modification[20] of the hybrid LOGD/AIRY code[8], specifically altered to propagate the log-derivative matrix by means of the imbedding propagators described in Sec. III. With a linear reference potential method the interval size can be continuously increased as the interparticle distance increases, and the variation in the potential decreases. In the present case only 430 steps were required to propagate from $R = 7$ to $R = 1000$ bohr; the maximum interval width was 11 bohr. The present program never displayed any numerical instabilities; convergence of the T-matrix was smooth.

By contrast, we were *unable* to treat this problem using our earlier[8] linear reference potential method, which involved Cauchy propagation. The reason is as follows: Table II lists the asymptotic values of the wave vectors (k^2) for several closed rotational channels. We see from Eqs. (51) and (52) that even for moderate interval widths ($\Delta_n = 5$–10 bohr), the diagonal propagators become so large in comparison with the terms for the open channels, which themselves are of the order of unity, that even with full precision (64 bits) all numerical significance becomes lost in the solution of the linear equation (13) for propagation of the log-derivative matrix. On the other hand, the corresponding closed channel elements of the imbedding propagator [Eqs. (49) and (50)] remain of the order of unity [$y_1^{(n)}, y_4^{(n)}$] or go to zero [$y_2^{(n)}, y_3^{(n)}$], so that numerical accuracy is not lost in propagation of the log-derivative matrix by means of Eq. (15). The instability found when the log-derivative matrix is propagated using the Cauchy propagator does not result from numerical overflow or underflow in the evaluation of the propagator matrix elements, but rather from the consequence of finite precision in solution of the propagation relation, Eq. (13).

VII. CONCLUSION

It is now widely accepted that the so-called "invariant-imbedding" approach to scattering problems is inherently more stable than the more standard initial-value approach.[1,3,6,11] In particular, propagation through extreme nonclassical regions can be accomplished directly, without the need for explicit stabilization,[12] if one employs an imbedding-type propagation method.

In this paper we have shown how the linear reference potential method, introduced originally by Gordon,[12] can be reformulated in terms of the imbedding-type $\mathscr{Y}$-matrix propagator.[10] Explicit expressions are given for the blocks of this propagator in terms of the Airy function solutions to the linear reference potential problem. By representing the Airy functions in terms of moduli and phases, in both classically allowed and classically forbidden regions, one can evaluate these propagators without any numerical difficulty.

The resulting algorithm for the propagation of the log-derivative matrix has been tested on a highly pathological problem—the rotationally inelastic scattering of a polar molecule by a spherical ion at extremely low kinetic energy—and found to be completely stable. By contrast, this problem could not be solved numerically using an earlier linear reference potential program based on the initial-value Cauchy propagator.[8]

For large numbers of coupled equations a linear, rather than constant, reference potential becomes significantly advantageous, since fewer intervals are required for an adequate representation of the potential. Thus the number of matrix (N^3) operations required will be significantly reduced.[8] Now that numerical stability can be guaranteed, with the algorithmn presented here, this method can be successfully exploited for a wide range of collision problems. In view of the conclusion of the NRCC workshop[2] on quantum scattering algorithms, it will be most efficient to combine this linear reference potential method with a "solution following" method[1] at short range. The improved log-derivative method recently developed by one of us[10] appears to be a sensible choice for the short-range region.

TABLE II. Asymptotic wave vectors of various rotational levels.[a]

j	$k^2(\text{bohr}^{-2})$
5	-21.6
7	-42.4
10	-85.7
14	-165.8

[a] The entries are defined by $k^2 = (2m/\hbar^2)\,[E_{\text{tot}} - Bj(j+1)]$, where the total energy is 57.82 cm^{-1}, the collision reduced mass is 2.55 amu, and the molecular rotational constant is 18.91 cm^{-1}.

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