Artificial boundary inhomogeneity method for quantum scattering solutions in an $\mathcal{L}^2$ basis

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A novel method for quantum reactive scattering calculations is introduced and tested for simple model problems. It is shown to be efficient and quite accurate. The method is based on a simple modification to the time independent Schrödinger equation, $(H-E)\Psi=0$. It is obtained by setting $(H-E)\Psi=B$ where $B$ is a localized boundary inhomogeneity. A necessary and sufficient number of arbitrary linearly independent wave functions represented by a real $\mathcal{L}^2$ basis set over a finite range of scattering coordinate are generated. The subsequent analysis of the wave functions using a point fitting technique or flux amplitude evaluations produces the full $S$ matrix. The real matrix representation of Green’s operator and energy independent integrals involved promise an efficient calculational method. Even for multiarrangement reactive scattering, only an $\mathcal{L}^2$ basis defined on a single coordinate system is needed. © 1994 American Institute of Physics.

I. INTRODUCTION

In this paper, we present a novel method for solving unbound scattering states of the time independent Schrödinger equation (SE). The new method involves a simple modification to the homogeneous SE resulting in a simple generic equation which can be easily applied to any scattering problem, whether multiarrangement reactive scattering, resonance, or photodissociation. Also, because it has a simple structure and the integrals involved in the calculations are energy independent, it is easy to code and efficient for many energy scattering calculations.

A set of $N_{\text{open}}$ ($N_{\text{open}}$ denotes the number of open channels for a given scattering energy) degenerate, real, regular, and arbitrary linearly independent wave functions (LIW), which are the solutions of the SE, are accurately determined in a scattering coordinate range, $R \subseteq [0,l_1]$ (here, we specialize to a radial scattering problem). The wave functions and the Green’s operators are represented by a homogeneous (i.e., vanishing at the boundaries of the radial basis set range) energy independent real $\mathcal{L}^2$ basis defined on a finite range of the scattering coordinate $[0,l_2]$ where $l_1 \leq l_2$. (It should be understood that in multidimensional problems, the $\mathcal{L}^2$ basis is augmented properly for other degrees of freedom.) Throughout the paper, we refer to this definition for an $\mathcal{L}^2$ basis. In the boundary range of $[l_1,l_2]$ where we add an artificial inhomogeneity, we do not have the solutions to the SE. The linear combination coefficients of the $N_{\text{open}}$ degenerate LIW to form a proper scattering wave function satisfying appropriate boundary conditions can be determined provided that $l_1$ lies in the asymptotic region.

Since the present method involves inverse matrices of the real representations of $(H-E)$, one may worry that some difficulty like the well known Kohn anomaly may occur. This is not the case, in fact. This point will be demonstrated in later sections.

Incidentally, we observe that several new basis set methods have been introduced recently which generate similar LIW in the first part of the calculation. The subsequent analysis of the LIW gives the desired scattering information such as the $S$ matrix. We note that the LIW generation part is completely independent of the analysis part, so that any combination of methods in each part can be used in appropriate situations. These methods can be viewed as basis set versions of the close coupling propagation methods in which arbitrary linearly independent solutions of the SE are propagated to and then analyzed in the asymptotic region to obtain the scattering information.

In Sec. II we analyze other methods with the concepts of “arbitrary LIW” and “artificial boundary inhomogeneity” in mind; in Sec. III we present the theory; in Sec. IV several model calculations demonstrating the validity of the present approach; in Sec. V brief conclusions; and in Sec. VI we examine other methods in the context of the present approach.

II. OTHER ARBITRARY LIW METHODS

The finite range scattering wave function method (FRSW) calculates the LIW which solve the SE in the whole range of the $\mathcal{L}^2$ basis set $[0,l_2]$, i.e., up to and including the boundary. They are obtained by solving the homogeneous SE with enforced boundary conditions such as

$$ \Psi_i = F_i - (H-E)^{-1}(H-E)F_i, $$

(1)

where $F_i$ is an energy dependent or energy independent auxiliary (boundary) function which vanishes at the inner boundary and does not vanish at the outer boundary ($l_2$). The full Green’s operator $(H-E)^{-1}$ is represented in the $\mathcal{L}^2$ basis, $(H-E)F_i$ is evaluated analytically and each auxiliary function ensures the linear independence of $\Psi_i$.

At this point, we differentiate two kinds of anomalies which may occur in various $\mathcal{L}^2$ basis set scattering methods which involve the full Green’s operator. The first one is the problematic “linear dependence” anomaly caused by linear dependence among the basis functions. In the conventional $K$-matrix version of the Kohn variational principle method, when the energy approaches a value where the co-
sinelike basis function becomes effectively linearly dependent on the other $\mathcal{Z}^2$ basis functions, the linear dependence anomaly occurs. In this case, the anomaly is also accompanied by a singularity of the Green’s operator. The second anomaly is the nonproblematic singular matrix anomaly which is caused by a singular matrix inversion (i.e., singular Green’s operator) with the singularity not caused by basis set linear dependence. Perhaps surprisingly, this anomaly does not pose any practical difficulty since it plagues calculations only when the scattering energy approaches the singular energy (an eigenvalue of the Hamiltonian matrix) almost within computer accuracy about one part in $10^9$ to $10^{13}$ in double precision calculations. This hardly occurs by choosing the scattering energy randomly. This aspect of the singular matrix anomaly has been demonstrated on several occasions.

It was observed that, in the version in which $F_i$ is energy dependent, the linear dependence anomaly occurs when $F_i(l_2)$ approaches zero as one scans the scattering energy (note that $l_2$ is the outer boundary at which the $\mathcal{Z}^2$ basis is zero). In other words, when $F_i$ becomes linearly dependent on the $\mathcal{Z}^2$ basis of the Green’s operator, the calculated LIW are effectively the trivial (zero) solutions of the SE resulting in the linear dependence anomaly. Obviously, no such anomaly occurs in the energy independent version in which the $F_i$ do not depend on energy $E$.

Neuhauser showed that even in the energy dependent version of the FRSW method, the linear dependence anomaly can be avoided by adding a very short range imaginary potential to the Green’s operator of Eq. (1). This imaginary potential can be viewed as a boundary inhomogeneity causing the LIW not to be the solutions of the SE in the boundary region, i.e., $[l_1,l_2]$. The LIW are now complex; however, the reward is removing any possible linear dependence among the basis functions of LIW in the valid range of $[0,l_1]$ where Eq. (1) after modification with the boundary imaginary potential still provides solutions of the SE. As an unnecessary effect, this also removes the poles of the Green’s operator away from the real energy axis. However, on the numerical side, it makes the Green’s function complex which is somewhat undesirable.

Hoffman et al. proposed the general initial wave packet method in the context of the time independent wave packet equations in which the LIW are given by

$$\Psi_i = \delta(E-H) \chi_i = \frac{i}{2\pi} (G^+ - G^-) \chi_i,$$

where $G^+$ ($G^-$) is the causal (anticausal) Green’s operator and $\chi_i$ is a complex general initial wave packet ensuring the linear independence of the LIW. In an actual implementation, $G^+$ is obtained from Legendre polynomial expansions of $(H - \iota l - E)^{-1}$ where the optical potential $-\iota l$ is assumed to be completely absorbing (so it must span a considerable fraction of basis set range). This optical potential can also be viewed as a boundary inhomogeneity with the same argument made for the Neuhauser’s method. But here, there is no issue about the linear dependence or singular matrix anomalies since it does not involve either any energy dependent basis function or real poles of the Green’s operator representation.

In a somewhat different context, Mandelshtam et al. also introduced a method generating the LIW by using an expression for the spectral density operator $\delta(E-H)$ obtained by the stabilization method$^9$; formally,

$$\Psi_i = \delta(E-H) \chi_i.$$

By generalizing the concept of the boundary inhomogeneity, we introduce a much simpler method for generating the same LIW in a finite range.

## III. ARTIFICIAL BOUNDARY INHOMOGENEITY METHOD

The basic equation of the present method is simply given by

$$(H-E)\Psi_i = B_i,$$

or,

$$\Psi_i = (H-E)^{-1} B_i,$$

which is real and obtained from the time independent SE [Eq. (3) below] by adding to the “zero” side an arbitrary real boundary inhomogeneity function $B_i$ (being nonzero and smooth only in the small range $[l_1,l_2]$). A complex $B_i$ could also be used, but we do not consider it at present. The Green’s operator is represented by a real homogeneous $\mathcal{Z}^2$ basis set defined on $[0,l_2]$. We note that Eq. (2) is subject only to the singular matrix anomaly, and is robust.

In the case of multichannel scattering, the $B_i$ must be linearly independent to ensure the linear independence of the $\Psi_i$. The $\Psi_i$ of Eq. (2) are the solutions of the SE, i.e.,

$$(H-E)\Psi_i = 0,$$

in the range $[0,l_1]$ where $B_i = 0$. Therefore, they are the proper LIW in the valid range provided that they are not zero functions. This is not the case of course unless $B_i$ is identically zero. The boundary portion of $\Psi_i$ in $[l_1,l_2]$ should not be used for the subsequent analysis since it is irrelevant to the true SE like the other methods using optical potentials. The arbitrariness of $B_i$ is restricted in that it should prevent trivial (zero) $\Psi_i$, and also should not perturb the LIW in the valid range $[0,l_1]$. Also it should ensure the linear independence of the $\Psi_i$. All of these conditions are easily realizable.

What determines $B_i$? The shapes (including the range) of the $B_i$ are calculational parameters although not their magnitudes (the $\Psi_i$ are determined with arbitrary factors). This property simplifies the convergence test procedures compared to other methods mentioned earlier. The numerical results depend on the particular shapes of the $B_i$ to some extent although accurate results can be obtained with reasonable choices. This aspect will be demonstrated (including poor choices) in the next model calculations section.

Equation (2) has a similar structure to the time independent Lippmann–Schwinger equation which was introduced by Kouri et al., in that equation the Green’s operator is the proper causal one (a complex representation) and the initial $\mathcal{Z}^2$ wave packet corresponding to the present $B_i$ is thought to be a superposition of asymptotic wave functions.
of many energies. The causal Green’s operator is capable of projecting a proper scattering wave function from a wave packet, unlike in the present method.

In the present artificial boundary inhomogeneity (ABI) method, once the $N_{\text{open}}$, $\Psi_j$, are determined from Eq. (2), we can extract the $S$ matrix in various ways. The two-point-per-channel (TPC) fitting technique was used before with the FRSW method in single arrangement scattering problems.\textsuperscript{1,10} The $S$ matrix, $\mathbf{S}$, and the expansion coefficient matrix ($\mathbf{C}$ matrix), $\mathbf{C}$, are determined as the solutions of the system of linear equations obtained by imposing scattering boundary conditions on a linear combinations of $\Psi_j$ and evaluating them in the valid asymptotic region. The proper scattering wave functions satisfying the asymptotic boundary conditions can be expanded in the LIW and may be arranged in a vector form as

$$\psi(q) \sim i(q) - o(q) \cdot \mathbf{S}, \tag{4}$$

where $\psi$, $i$, and $o$ are the vectors composed of $\Psi_j$, the open channel incoming and outgoing waves $I_i, O_i$ (normalized to unit probability flux in atomic units) augmented by the appropriate asymptotic internal states ($\phi$), respectively, and the $q$ denotes a configuration (point) in the configuration space. Below we present two schemes to construct equations for $\mathbf{S}$, and later discuss their different implications in practical applications.

Namely the two schemes are; we can project Eq. (4) either onto $N_{\text{open}}$ asymptotic open channel internal states at the corresponding $m \geq 2$ asymptotic scattering coordinates ($\{R_0, \phi_{ij}\}$) (define $M = m \times N_{\text{open}}$) or onto $M_{\text{open}}$ open configuration points ($\{q\}$) in the asymptotic region to construct at least $2N_{\text{open}}$ independent linear equations to solve for the $\mathbf{S}$ and $\mathbf{C}$. Evaluations of Eq. (4) by the above $M$ projections lead to the system of linear equations given by

$$\Psi \cdot \mathbf{C} = \mathbf{I} - \mathbf{O} \cdot \mathbf{S}, \tag{5}$$

where

$$\Psi_{ij} = \langle q_i | \Psi_j \rangle, I_{ij} = \langle q_i | i_j \rangle, O_{ij} = \langle q_i | o_j \rangle,$$

and $\Psi, \mathbf{I}$ and $\mathbf{O}$ are rectangular matrices of order of $M \times N_{\text{open}}$. The $\{q\}$ denote either $\{R_0, \phi_{ij}\}$ or $\{q\}$. It can be solved for $\mathbf{S}$ and $\mathbf{C}$ after some rearrangements as

$$\begin{bmatrix} \mathbf{S} \\ \mathbf{C} \end{bmatrix} = (\mathbf{W}^T \mathbf{W})^{-1} \cdot \mathbf{W}^T \cdot \mathbf{I}, \tag{6}$$

where

$$\mathbf{W} = [\mathbf{O}, \Psi]$$

is a composite matrix of $\mathbf{O}$ and $\Psi$ and of order of $M \times 2N_{\text{open}}$.

Alternatively Eq. (5) can be solved for only $\mathbf{S}$ as

$$\mathbf{S} = (\mathbf{\Omega}^T \mathbf{\Omega})^{-1} \cdot \mathbf{\Omega}^T \cdot \mathbf{O}, \tag{7}$$

where

$$\mathbf{\Omega} = \mathbf{O} - \Psi \cdot (\Psi^T \Psi)^{-1} \cdot \Psi^T \cdot \mathbf{O}$$

is a rectangular matrix of order of $M \times N_{\text{open}}$. We note that, using these generalized inverse matrix approaches, several different but equally valid expressions for $\mathbf{S}$ (and/or $\mathbf{C}$) may be obtained by taking the adjoint instead of the transpose of $\mathbf{W}$ or $\mathbf{\Omega}$ and/or by using the unitarity and symmetry requirement of the $\mathbf{S}$ matrix. The Eqs. (6) and (7) amounts to least squares methods for determining $\mathbf{S}$ if we choose $M \geq 2N_{\text{open}}$. If a necessary and sufficient number ($M = 2N_{\text{open}}$) of equations are used, Eq. (6), for example, reduces to the TPC fitting analysis given by

$$\begin{bmatrix} \mathbf{S} \\ \mathbf{C} \end{bmatrix} = \mathbf{W}^{-1} \cdot \mathbf{I}. \tag{8}$$

In the asymptotic internal state projection scheme, the submatrices of $\mathbf{I}$ and $\mathbf{O}$, such as for the log derivative and $R$-matrix approach, are diagonal, and the evaluation of $\Psi$ involves surface integrals for internal coordinates which can be easily calculated in a single arrangement problems. However, in multiarrangement cases, this scheme often requires cumbersome overlap integral evaluations involving two different coordinate systems, although they can be made energy independent.

We rather prefer to use the asymptotic configuration point projection scheme (projecting Eq. (4) to $\{q\}$) for multiarrangement problems. In fact, the above surface integral evaluations are completely avoided in this scheme. None of the matrices in Eqs. (5) to (8) involve integral evaluations. Only function value evaluations are needed once $\Psi_j$ are determined from the energy independent Hamiltonian matrix element integrals. Now the $\mathbf{I}$ and $\mathbf{O}$ are full matrices. We note that this does not harm any efficiency for ordinary methods of solving system of linear equations (e.g., LU decomposition) since the full matrices $\Psi$ and $\mathbf{O}$ have to be combined in some way. Therefore it does not make any significant difference whether the $\mathbf{I}$ and $\mathbf{O}$ are diagonal or not. This configuration point projection analysis is expected to be most useful in multiarrangement reactive scattering problems since it does not involve any kind of integral evaluation in the analysis procedures.

Although yet to be demonstrated, we note that this ABI method requires, at least formally (and we expect in practice), only one set of $\mathbf{C}^2$ basis defined on a single coordinate system for multiarrangement scattering problems. This differs from the log derivative Kohn variational method as presented by Manolopoulos et al.\textsuperscript{7,11} which has been very efficient and accurate but required basis functions defined on different coordinate systems in these problems, thus requiring complicated, if energy independent, overlap integrals. A limited remedy has been produced to use basis functions of a single coordinate system, but at the price of sacrificing the accuracy.\textsuperscript{12}

On the other hand, the flux amplitude evaluated at the asymptotic exit channel region also can be used to calculate the $S$ matrix as used by Neuhauser\textsuperscript{2} and Mandelshtam et al.\textsuperscript{9} In particular, the $S$ matrix can be calculated in terms of the flux amplitudes ($\mathbf{A}$) as
\[ S = A^* \cdot A^{-1}, \]
\[ A_{ij} = \langle O_i^* | F_S | \Psi_j \rangle = \frac{1}{2m} \int dS (\nabla_n O_i - O_i \nabla_n \Psi_j) = \int dq O_i V \Psi_j, \]
where \( O_i \) is the \( i \)th internal state augmented outgoing wave, \( F_S \) is the flux operator, \( m \) is the system reduced mass, and \( V \) is the interaction potential. The surface \( S \) is located in the asymptotic region corresponding to the \( i \)th channel and \( \nabla_n \) denotes that the derivative is taken normal to the surface. This equation shows that the flux amplitude can be expressed either in terms of surface integrals and derivatives or volume integrals without derivative evaluations.\(^9\) The two forms are connected by Green’s theorem. The volume integral version is valid only when the probability flux is nonzero solely in the proper exit channel.

In the ABI method, once the \( \Psi_j \) are determined from the energy independent integrals of the Hamiltonian operator, the point projection (including TPC fitting) analysis does not involve any integral evaluations, while the flux amplitude analysis requires only order of \( N_{\text{open}}^2 \times N_{\text{basis}} \) energy dependent surface (volume) integrals and/or derivatives. This favorable computational requirement facilitates many energy calculations and is in contrast to other methods like the \( S \)-matrix Kohn variational method as presented by Zhang \textit{et al.}\(^8\) which requires order of \( N_{\text{open}} \times N_{\text{basis}} \) energy dependent integrals. The TPC fitting and volume integral flux amplitude analyses will be used in the next model calculations section.

IV. MODEL CALCULATIONS

We applied the ABI method to two model systems. They are: (1) the Eckart barrier with the Hamiltonian operator given by
\[ H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{D}{\cosh^2(x/\alpha)}, \]
where \( m = 1.007 \text{ g/mol} \) (\( H_2 \) atom mass), \( D = 0.5 \text{ eV} \), \( \alpha = 0.25 \text{ Å} \), and the \( \mathcal{D}^2 \) basis is 61 discrete variable representation (DVR)\(^13\) functions based on particle-in-a-box eigenfunctions (i.e., sine functions vanishing at boundaries) defined in \([-2, 2] \text{ Å}\): and (2) a model spherical van der Waals (vdW) molecule with the Hamiltonian operator given by
\[ H = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 J(J + 1)}{2mr^2} + D \left[ \left( \frac{\alpha}{r} \right)^{12} - 2 \left( \frac{\alpha}{r} \right)^6 \right], \]
where \( m = 1.92 \text{ g/mol} \), \( J = 8 \), \( D = 60 \text{ cm}^{-1} \), \( \alpha = 3.56 \text{ Å} \), and the \( \mathcal{D}^2 \) basis set is 70 interior Lobatto shape functions\(^11\) or 50 DVR functions based on sine functions defined in \([2, 21] \text{ Å}\). We also use the same DVR quadratures of the Hamiltonian matrix elements to evaluate integrals in the case of flux amplitude analysis.

The two LIW of the Eckart barrier problem are generated in the \( \mathcal{D}^2 \) basis set in the basis set range as

![FIG. 1. Magnitude of relative errors in \( T \) for various forms of boundary inhomogeneity as a function of average distances (\( x_{\text{avg}} \)) of evaluation points using TPC fitting analysis for Eckart barrier problem. The energy is 0.5 eV with the corresponding asymptotic wavelength 0.4046 Å and transmission coefficient 0.550 619 49. Refer to Table I for the label definitions. The errors in the region less than about 1.2 Å are caused by the effect of the non-negligible potential, and not by the fault of the present method.

\[ \Psi_j = (H - E)^{-1} B_{ji}, \]
\[ \Psi_j = (H - E)^{-1} B_{ji}, \]
where \( B_{ji} \) is nonzero only in the small asymptotic region left (right) of the barrier, specifically in \([ -2, 2 ] \text{ Å} \) where \( x_i \) and \( x_j \) are calculational parameters. The center of the barrier is at the origin. For simplicity, we use \( B_l(x) = B_r(-x) \). The TPC fitting analysis requires four points to define a system of linear equations for the \( S \) and \( C \) matrices. They are chosen as \( x_i, x_{i+1}, x_j, -x_i, \) and \( -x_{i+1} \) where \( x_j \) and \( x_j+1 \) are consecutive DVR points. Again we emphasize that only the region where \( B_l \) and \( B_r \) are zero is usable for the analysis points.

Since \( B_l \) and \( B_r \) (or simply \( B \) for convenience) appear as calculational parameters, we first examine how different functional forms affect the calculational results. In Fig. 1 we show, for five different forms, the magnitude of relative errors (against exact analytical values) in the transmission coefficient \( T \), plotted as a function of the average distances of the four evaluation points from the origin using the TPC fitting analysis. The detailed definitions of \( B \) are given in Table I. Note again that the magnitude of \( B \) cannot affect the results since the \( C \) matrix renormalizes the results. For all the trial forms, we can obtain reasonably accurate results with errors less than 1% for most of the asymptotic evaluation

<table>
<thead>
<tr>
<th>( B(x) ) (^a)</th>
<th>( B(x) ) (^b)</th>
</tr>
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<tbody>
<tr>
<td>1 (^b)</td>
<td>( B(1.953) = 1.75 )</td>
</tr>
<tr>
<td>2IL</td>
<td>( B(1.953) = 1.65, B(1.870) = 0.593 )</td>
</tr>
<tr>
<td>2DL</td>
<td>( B(1.953) = 1.06, B(1.870) = 2.12 )</td>
</tr>
<tr>
<td>2HS</td>
<td>( B(1.953) = 2.72, B(1.870) = 2.72 )</td>
</tr>
<tr>
<td>3IL</td>
<td>( B(1.953) = 1.95, B(1.870) = 1.19, B(1.806) = 0.431 )</td>
</tr>
</tbody>
</table>

\(^a\) The unit is Å. Same for other entries.
\(^b\) The unit is 10\(^{-4}\) eV. Same for other entries.
points at the energy 0.5 eV where \( T = 0.550 \times 10^{-9} \). Preliminary investigations of the convergence properties like Fig. 1 for many energies revealed that the range of \( B \) must be at least some fraction (say, about a quarter) of the de Broglie wavelength to obtain very accurate results and also that a linear form increasing toward the boundary appeared to be better than the decreasing linear or Heaviside forms. We observed that as the range of \( B \) becomes smaller, the magnitude of \( \Psi_i (\Psi_r) \) also becomes smaller, so the error increases.

In Fig. 2, the relative and absolute errors in \( T \) are examined as a function of energy ranging from 0.1 eV (where \( T \approx 1.7 \times 10^{-9} \)) to 1.1 eV (where \( T \approx 9.999 \times 10^{-9} \)). The \( T \) were calculated using the TPC fitting analysis adopting a two point linear form for \( B_l \) and \( B_r \) ("2IL" in Table I). To minimize further the perturbation caused by \( B \), we used the second and the third points (skipping the first point) from the last point with \( B \neq 0 \). Note that, for all calculations below, we used the same form of \( B \) except for Figs. 3 and 4 (which make different comparisons), and the same prescription regarding evaluation points for the TPC fitting analysis for all calculations. These fixed \( B \) calculations again reflect that the relative errors at low energies are bigger than those at higher energies as discussed above. However, the relative errors less than 0.02% are achieved for the whole energies considered.

In Fig. 3, the phase shifts of the spherical vdW molecule problem are presented, which are obtained by the TPC fitting and the volume integral flux amplitude analyses. Both analyses agree to 3 to 4 significant figures for most of the energies considered, thereby, demonstrating that any appropriate analysis of the \( \Psi_i \) can be used to obtain accurate scattering information. Since, in the volume integral flux amplitude analysis, the amplitude density \( V \Psi_i \) may contribute to the flux amplitude mostly from the high potential or classically forbidden region, one needs fairly accurate quadratures and also accurate \( \Psi_i \) especially in the high potential energy region in order to calculate the flux amplitude accurately. In some cases, it was observed that the flux amplitude was not accurately determined either because the quadratures were not dense enough or the \( \Psi_i \) are not sufficiently accurate in that region. However, even in these cases, the TPC fitting or the surface integral flux amplitude analyses could give reasonable results since they only use the \( \Psi_i \) in the asymptotic region where the interaction potential is negligible.

Finally, note that Figs. 2 and 3 demonstrate that the ABI method is free of problematic linear dependence anomaly which is obvious because no basis function linear dependence can occur.

V. CONCLUSIONS FOR THE ABI METHOD

We proposed a novel calculational method which generates \( N_{open} \) real degenerate linearly independent wave functions (LIW) which are accurate over a subrange of the finite range scattering coordinate spanned by a real \( 2 \times 2 \) basis set, and we demonstrated that they can be used to extract the desired scattering information accurately. The simple structure of the method produces several favorable features. They are: (1) formally, only a real \( 2 \times 2 \) basis of a single coordinate system is sufficient even for multiarrangement scattering problems (although yet to be demonstrated); (2) all integrals involved in determining LIW are energy independent; (3) real representations of the Green’s operator and the boundary inhomogeneities are used; (4) scattering information can be extracted in various ways, e.g., through the configuration point projection, or surface (or volume) integral flux amplitude analyses, all of which are easily applicable to multiarrangement scattering; (5) the overall magnitude of the boundary inhomogeneity does not affect the results, thus reducing the number of calculational parameters.

Also the method is automatically free of problematic linear dependence anomalies. Preliminary investigation showed that if the range of the artificial inhomogeneity is larger than some fraction (say, about a quarter) of the de Broglie wavelength, the present method’s fitting of LIW are very accurate for the whole valid region.

VI. FINAL COMPARISONS

The success of the present ABI method suggests that we may also use a real boundary inhomogeneity in the place of the very short range imaginary potential in Neuhauser’s method, thus saving the costs of complex arithmetic computation. In Fig. 4, we tested this idea. The phase shifts of the spherical vdW molecule are calculated near a difficult linear dependence anomaly energy which is obviously visible by the energy dependent integral FRSW calculation.\(^1\) The two other calculations are done by the original complex Green’s function method of Neuhauser\(^2\) using

\[
\Psi = S - (H + iB - E)^{-1} V S,
\]

and by a new modification replacing the complex representation of the Green’s operator with two real representations of the Green’s operator as

\[
\Psi = [S - (H - E)^{-1} V S] + i [S - (H + B - E)^{-1} V S],
\]

where \( S \) is the Riccati–Bessel function which is the regular solution of the free radial Hamiltonian, \( V \) is the vdW potential, \(-iB \) is Neuhauser’s very short range imaginary potential, and \( B \) is a real boundary inhomogeneity \( [\text{note that the} \]

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**FIG. 2.** Relative (R) and absolute (A) errors in \( T \) as a function of energy using TPC fitting analysis for Eckart barrier problem. The boundary inhomogeneity is the "2IL" of Table I. 101 equally spaced energies from 0.1 eV to 1.1 eV are considered.
same $B$’s are used in Eqs. (10) and (11) for calculations]. It is readily seen in Fig. 4 that both expressions of Eqs. (10) and (11) give results of about the same accuracy and that the anomalous results of the (energy dependent integral) FRSW method are replaced by somewhat more accurate ones. Incidentally, in these expressions in which $B$ enters the Green’s operator, the overall magnitude of $B$ affects the results. Therefore, an optimum $B$ should be determined large enough to avoid the anomaly, also, small enough not to perturb the $\Psi$ in the valid region. Interestingly, each of the real and imaginary parts of Eq. (11) has its own separate anomaly energy (but at different energies) where the amplitude of one part of the wave function becomes effectively zero, but by combining them as in Eq. (11) we can avoid any linear dependence anomaly due to generating the trivial solution $\Psi=0$.

Similar arguments can be applied to the general initial wave packet method of Hoffman et al.3 We consider the same Eckart barrier problem discussed in Sec. IV where we can use Neuhauser’s very short range imaginary potential ($-iB$) in the place of the completely absorbing imaginary potential in the casual Green’s operator as

$$\Psi = [(H - iB - E)^{-1} - (H + iB - E)^{-1}]\chi.$$  \hfill (12)

Alternatively we can use two different real Green’s operators modified with real boundary inhomogeneity functions (potentials) as

$$\Psi = [(H + B_I - E)^{-1} - (H + B_r - E)^{-1}]\chi.$$  \hfill (13)

In Eqs. (12) and (13) we use $B = B_I + B_r$ [$B_I$ and $B_r$ are defined in Eq. (9) for Eckart barrier problem], and $\chi$ is a complex $\mathcal{S}^2$ initial wave packet. The real and imaginary parts of $\Psi$ provide the necessary two LIW for analysis.

Both expressions save the computation by reducing the region which must be spanned by the $\mathcal{S}^2$ basis set and/or by using real matrices compared with the form of Hoffman et al.

![FIG. 3. Phase shifts of vdW molecule as a function of energy using TPC fitting and volume integral flux amplitude (VFA) analyses. The boundary inhomogeneity is an increasing linear function spanning the range of [20.5 Å, 21.0 Å] encompassing 7 DVR points. The basis set is 70 interior Lobatto shape functions. A shape resonance around 9.5 cm$^{-1}$ is visible as the phase shift is rapidly rising by $\pi$.](Image 324x126 to 552x263)

![FIG. 4. Phase shifts of vdW molecule around a linear dependence anomaly energy using TPC fitting analysis. “F” denotes the results of the energy dependent version of FRSW method, “VSRI” for the Neuhauser’s method [Eq. (10)], “B” for the present real modification [Eq. (11)]. The boundary inhomogeneity is $4.47 \times 10^{-3}$ cm$^{-1}$ at the last DVR point. The basis set is 50 sine DVR functions.](Image 73x126 to 276x269)

![FIG. 5. Relative (R) and absolute (A) errors in $T$ as a function of energy using TPC fitting analysis. The results of using Eq. (12) are denoted by the suffix “IB” and Eq. (13) by the suffix “B.” The same energies as in Fig. 2 are considered. The boundary inhomogeneity is the “2LI” of Table I. The initial wave packet $\chi$ is given by $Ve^{ik_0x}$ with $k_0$ of $(\hbar^2k_J^2/2m)=E_0$ where $E_0=0.1$ eV.](Image 20.5 Å, 21.0 Å)
efficiency and simplicity for variety of scattering problems.

It is quite striking that if the linear combination of linearly independent wave function (LIW) analysis is done for “interior” points, one has enormous flexibility in artificial potentials, real or imaginary, and artificial boundary inhomogeneities, while still generating accurate results.

Note added in proof. At the Harvard–Smithsonian Workshop on Reactive Scattering, Cambridge, MA 30 June, 1994, V. A. Mandelshtam and H. S. Taylor presented a number of options for solving the Schrödinger equation including Eq. (2) above, using the standard Jost form, $S + A^*A^{-1}$. They noted that accurate results were obtained on the collinear H+H$_2$ reactive scattering problem.

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2 D. Neuhauser (private communication).