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Discrete variational quantum reactive scattering method with optimal distorted waves. I. Theory

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The size of the interaction region grid in a discrete Kohn variational reactive scattering calculation may be minimized by using distorted waves (DWs) in the trial wave function. Fully converged state-to-state results may be obtained with a small grid if (1) closed channels are included in the coupled channels expansion of the DWs and (2) asymptotically vanishing DWs are included in the trial wave function. This may be done without spoiling the sparsity of the interaction region Hamiltonian, which allows the use of an iterative method for solving the linear equations. We define boundary conditions for the regular, irregular, and asymptotically closed DWs, that minimize the number of DWs needed for convergence. The application to the reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, is given in part II. © 1998 American Institute of Physics. [S0021-9606(98)01514-1]

I. INTRODUCTION

Many reactive scattering problems have been solved accurately with variational methods in the last decade. A common feature of these methods, whether based on the S -matrix version of the Kohn variational principle (SKVP),¹ its log-derivative version,² the (Generalized) Newton variational principle³ or the outgoing wave variational principle,⁴ is the use of some n -dimensional square integrable ($\mathcal{L}^2$) basis set to represent the interaction region part of the scattering wave function. The main computational effort in these methods is the construction of the Hamiltonian matrix and the subsequent solution of a set of linear equations. Several attempts have been made to reduce the core-memory requirements and the n^3 scaling of the cpu-time of the standard approach. We mention the use of a collocation approach,⁵ a block Lanczos method,⁶ the generalized minimal residual method⁷ and finite element methods.⁸ The present author and Colbert proposed a method based on the SKVP in which a discrete variable representation (DVR) was used in combination with an iterative method (SYMMLQ⁹).

Yet for a reaction involving two heavier atoms, such as the $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ reaction, no variational calculation has been attempted, even though it has been studied with other methods. In the present paper we report considerable progress made in our DVR-SKVP method, in particular with the construction of the distorted waves (DWs), which enables us to obtain very well converged state-to-state variational results for this reaction. The method is described in the present paper and its application will be given in paper II.¹⁰ The unimolecular dissociation $\text{HO}_2 \rightarrow \text{H} + \text{O}_2$ has been studied previously with the log-derivative KVP method.¹¹ In that study an optimized basis of about 9000 functions was used to describe the resonances up to about 0.4 eV above the dissociation threshold.

A grid representation greatly reduces the core-memory requirements that are associated with a delocalized basis set. However, a grid representation tends to be less compact than

a well contracted basis set. Our strategy for minimization of the size of the interaction region grid is the use of DWs which are well converged solutions of the Schrödinger equation in the external region (the region outside the grid). For this purpose we represent the DWs with a coupled channels expansion including closed channels, and we retain full coupling when solving the coupled channels equation.

Due to the presence of the closed channels in the expansion, the usual incoming wave boundary conditions of the “free” waves in the SKVP formalism no longer uniquely define the DWs. In particular, for every closed channel in the expansion, there is an asymptotically vanishing solution of the coupled channels equation, which we will refer to as a “closed DW.” Any linear combination of closed DWs may be added to the asymptotically open (i.e., non-diverging and non-vanishing) DWs. Furthermore, asymptotically open DWs may become locally closed, diverge exponentially, and cause serious numerical problems in the subsequent variational calculation. Here, we derive boundary conditions that define a set of DWs which lead to a completely stable, rapidly converging, variational calculation.

In the next section we introduce a matrix notation for the Wronskian relations between sets of DWs. This notation is very convenient in the multichannel formulation of the variational principle in Sec. III, since only the Wronskian relations, rather than the precise asymptotic form of the DWs enter the variational formalism. We will use the T -matrix KVP, which is almost identical to the SKVP, but has slight numerical advantages, as we will argue below. Another new aspect of our (re)derivation is that we explicitly include closed DWs. Although (regularized) closed DWs are formally equivalent to $\mathcal{L}^2$ basis functions, we treat them on equal footing with the open DWs, since otherwise they would spoil the sparsity of the interaction region hamiltonian matrix. Only a few (properly chosen) closed DWs are required to reduce the size of the interaction region grid considerably. We emphasize that closed DWs, which are defined

to be asymptotically vanishing solutions of the Schrödinger equation, must not be confused with closed channels, which are used in the coupled channels expansion of the DWs and which have been used as such before.^{3,4,9}

In Sec. IV A we consider all possible orthogonal transformations of the boundary conditions of the DWs that leave the Wronskian relations unchanged, i.e., that allow us to use the variational principle. Then, we present a singular value decomposition technique to determine the optimal choice. Section V gives a few details on the implementation. The application to the H+O₂ reaction is given in paper II.

II. THEORY

Our starting point for the description of a general bimolecular reaction is the division of the nuclear configuration space into internal and external regions. The internal region is also referred to as the interaction region. A detailed description of this concept can be found in the original paper by Wigner and Eisenbud¹² or in a very clear review by Manolopoulos, D'Mello, and Wyatt.² In these papers it is assumed that in the external region only elastic events may occur, and no inelastic or reactive events. However, since we want to minimize the size of the interaction region, we will allow inelastic events in the external region. These events will be described by (inelastically) DWs.

In the external regions we use the Jacobi coordinates ($R_\alpha, \mathbf{q}_\alpha$), where α labels the arrangements, R_α is the distance between the fragments and $\mathbf{q}_\alpha = (q_\alpha^{(1)}, \dots, q_\alpha^{(n)})$ are all the other coordinates. We define the (real) channel eigenfunctions $\phi_{i,\alpha}(\mathbf{q}_\alpha)$ by

$$(\hat{H}_\alpha - \epsilon_{i,\alpha})g_\alpha^{-1/4}\phi_{i,\alpha}(\mathbf{q}_\alpha) = 0, \quad (1)$$

where $\hat{H}_\alpha$ is the sum of the Hamiltonians of the separate fragments and g_α is the determinant of the metric tensor of the Jacobi coordinates. Because of the $g_\alpha^{-1/4}$ we have the simple orthogonality relations

$$\int \phi_{i,\alpha}(\mathbf{q}_\alpha)\phi_{j,\alpha}(\mathbf{q}_\alpha)dq_\alpha^{(1)} \dots dq_\alpha^{(n)} = \delta_{ij}. \quad (2)$$

The full Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu_\alpha R_\alpha} \frac{\partial^2}{\partial R_\alpha^2} R_\alpha + \hat{H}_\alpha(\mathbf{q}_\alpha) + \hat{V}_\alpha(R_\alpha, \mathbf{q}_\alpha), \quad (3)$$

where μ_α is the reduced scattering mass and $\hat{V}_\alpha$ includes the interaction potential and the centrifugal term. Below, we will drop the arrangement label α , except to distinguish between the Hamiltonian $\hat{H}$ and the arrangement Hamiltonian $\hat{H}_\alpha$. For large scattering coordinate R the solutions may be written as

$$\psi_i(R, \mathbf{q}) = g^{-1/4} h_i(R) \phi_i(\mathbf{q}). \quad (4)$$

For the open channels, i.e., those for which ϵ_i is less than the total energy (E), the functions $h_i(R)$ are linear combinations of the regular and irregular solutions of the radial Schrödinger equation, denoted by $f_i(R)$ and $g_i(R)$, respectively. One may or may not include the centrifugal term in the defi-

nition of the (ir)regular radial functions, but in either case they may be normalized such that the Wronskian relation between f and g is equal to $1/\hbar$,

$$f_i(R)g'_i(R) - f'_i(R)g_i(R) = \hbar^{-1}. \quad (5)$$

The prime indicates differentiation with respect to R . The radial parts of the asymptotically vanishing solutions corresponding to the closed channels ($\epsilon_i > E$) will be denoted by $c_i(R)$. The above Wronskian relation is important because it enters into the surface term in Green's symmetrical theorem: for two sufficiently smooth, complex functions U and V we have

$$\langle U | \hat{H} - E | V \rangle - \langle V | \hat{H} - E | U \rangle = -\frac{\hbar^2}{2} W(U, V), \quad (6)$$

where

$$W(U, V) = \int_S \mu^{-1} (UV' - U'V) g^{1/2} dq^{(1)} \dots dq^{(n)}. \quad (7)$$

The bracket notation denotes integration, without complex conjugation in the bra or the ket, over the region enclosed by the surface S . The surface term $W(U, V)$, which we will refer to as the Wronskian integral, may have contributions from several arrangements. Note, however, that DWs of different arrangements are constructed such that they do not overlap and their Wronskian integrals involve only a single arrangement coordinate system.

We now introduce the coupled channels expansion

$$U = \sum_{i=1}^{n_o + n_c} \mu^{1/2} g^{-1/4} u_i(R) \phi_i(\mathbf{q}), \quad (8)$$

where the summation runs over n_o open and n_c closed channels. We introduce a vector notation by arranging the expansion coefficients $u_i(R)$ in a column vector $\mathbf{u}$ (and similarly for the function V). Using the orthogonality of the channel eigenfunctions $\phi_i(\mathbf{q})$ we find

$$W(U, V) = \mathbf{u}^T \mathbf{v}' - \mathbf{u}'^T \mathbf{v}. \quad (9)$$

In the multi-arrangement case the vectors $\mathbf{u}$ and $\mathbf{v}$ consist of expansion coefficients for all the arrangements. Below, we will use calligraphic characters to indicate a set of (N) functions, e.g., $\mathcal{U} = \{U_1, U_2, \dots, U_N\}$. The corresponding set of coupled channels expansion coefficients is arranged in a matrix $\mathbf{U} = [\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_N]$. A matrix of Wronskian integrals will be denoted by $\mathbf{W}(\mathcal{U}, \mathcal{V})_{ij} = W(U_i, V_j)$, so that we have

$$\mathbf{W}(\mathcal{U}, \mathcal{V}) = \mathbf{U}^T \mathbf{V}' - \mathbf{U}'^T \mathbf{V}. \quad (10)$$

We also extend the bracket notation to denote a matrix of integrals with the elements

$$\langle \mathcal{U} | \hat{H} - E | \mathcal{V} \rangle_{ij} = \langle U_i | \hat{H} - E | V_j \rangle. \quad (11)$$

We define the set of n_o asymptotic regular solutions $\mathcal{F}$ with the expansion coefficients

$$\mathbf{F} = \begin{bmatrix} \mathbf{F}_o \\ \mathbf{0}_{n_c \times n_o} \end{bmatrix}, \quad (12)$$

where $\mathbf{0}$ is the null matrix of the indicated dimension, and $\mathbf{F}_o$ is a diagonal matrix containing the previously defined regu-

lar solutions, multiplied by a cutoff function $f_{\text{cut}}(R)$ that switches smoothly from zero to one in the interaction region

$$(\mathbf{F}_o)_{ii} = f_{\text{cut}}(R)f_i(R). \quad (13)$$

The set of n_o irregular asymptotic solutions $\mathcal{F}$ and the set of n_c asymptotically closed functions $\mathcal{C}$ are defined similarly, except that the matrix $\mathbf{C}$ is partitioned as

$$\mathbf{C} = \begin{bmatrix} \mathbf{0}_{n_o \times n_c} \\ \mathbf{C}_c \end{bmatrix}. \quad (14)$$

III. GENERALIZED KOHN VARIATIONAL PRINCIPLE

We will now show how the closed functions may be treated on an equal footing with the free waves, even though formally the (regularized) closed functions belong to the set of square integrable functions. In this derivation we only use the Wronskian relations between the functions, rather than their specific form. This will make it more transparent what freedom we have in the choice of the boundary conditions when switching to DWs. It is well established that the $\mathbf{S}$ -matrix version of the Kohn variational principle is to be preferred over the $\mathbf{K}$ -matrix version, which gives rise to the so called ‘‘Kohn anomalies.’’¹³ Here, we will use the $\mathbf{T}$ -matrix version, which is more stable than the $\mathbf{S}$ -matrix version when (locally) strongly closed DWs are used, as we will explain at the end of this section.

We define a set of n_o trial functions by

$$\tilde{\Psi}_T = \mathcal{F} + \mathcal{T}\tilde{\mathbf{T}} + \mathcal{L}\mathbf{X}, \quad (15)$$

where

$$\mathcal{T} = \{(\mathcal{F} + i\mathcal{F}), \mathcal{C}\}. \quad (16)$$

The sets $\mathcal{F}$, $\mathcal{C}$, and $\mathcal{L}$ are defined in the previous section. The set $\mathcal{L}$ consists of $n_b \times \mathcal{L}_2$ interaction region functions which may be replaced by a discrete representation (see Ref. 9) and $\mathbf{X}$ is a $n_b \times n_o$ dimensional matrix of expansion coefficients. The trial $\tilde{\mathbf{T}}$ -matrix may be partitioned in two blocks,

$$\tilde{\mathbf{T}} = \begin{bmatrix} \tilde{\mathbf{T}}_o \\ \tilde{\mathbf{T}}_c \end{bmatrix}, \quad (17)$$

where $\tilde{\mathbf{T}}_o$ is the $n_o \times n_o$ dimensional ‘‘physical’’ part. All functions are assumed to be sufficiently smooth and regularized by means of a cutoff function. The variational principle is derived by considering the first order variation

$$\delta \langle \tilde{\Psi} | \hat{H} - E | \tilde{\Psi} \rangle = \langle \delta \tilde{\Psi} | \hat{H} - E | \tilde{\Psi} \rangle + \langle \tilde{\Psi} | \hat{H} - E | \delta \tilde{\Psi} \rangle \quad (18)$$

with

$$\delta \tilde{\Psi} = \mathcal{T} \delta \tilde{\mathbf{T}} + \mathcal{L} \delta \mathbf{X}. \quad (19)$$

Using Green’s theorem [Eq. (6)], we find for the second term in the right hand side of Eq. (18)

$$\langle \tilde{\Psi} | \hat{H} - E | \delta \tilde{\Psi} \rangle = \langle \delta \tilde{\Psi} | \hat{H} - E | \tilde{\Psi} \rangle^T - \frac{\hbar^2}{2} \mathbf{W}(\tilde{\Psi}, \delta \tilde{\Psi}). \quad (20)$$

For the Wronskian integral term we have

$$\mathbf{W}(\tilde{\Psi}, \delta \tilde{\Psi}) = c_T \delta \tilde{\mathbf{T}}_o; \quad c_T = \hbar^{-1} \quad (21)$$

because

$$\mathbf{W}(\mathcal{F}, \mathcal{G}) = \hbar^{-1} \mathbf{1}_{n_o \times n_o} \quad (22)$$

and all other Wronskian relations involving the sets $\mathcal{F}$, $\mathcal{C}$, and $\mathcal{L}$ give zero. Combining these results we obtain the $\mathbf{T}$ -matrix version of the Kohn variational principle

$$\mathbf{T} = \text{stat} \left[\tilde{\mathbf{T}}_o + \frac{2}{\hbar^2 c_T} \langle \tilde{\Psi} | \hat{H} - E | \tilde{\Psi} \rangle \right]. \quad (23)$$

Following Zhang, Chu, and Miller (ZCM)¹ we arrive at the algebraic equations by substituting the trial wave function into this variational principle. In the matrix-partitioning step of the derivation we keep the set of functions $\mathcal{T}$ together, which gives

$$\mathbf{T} = \frac{2}{\hbar^2 c_T} [\mathbf{B}_{0,0} - \mathbf{C}_{1,0}^T \mathbf{D}_{1,1}^{-1} \mathbf{C}_{1,0}], \quad (24)$$

where

$$\mathbf{B}_{0,0} = \mathbf{M}_{0,0} - \mathbf{M}_0^T \mathbf{M}^{-1} \mathbf{M}_0 \quad (25)$$

$$\mathbf{C}_{1,0} = \mathbf{M}_{1,0} - \mathbf{M}_1^T \mathbf{M}^{-1} \mathbf{M}_0 \quad (26)$$

$$\mathbf{D}_{1,1} = \mathbf{M}_{1,1} - \mathbf{M}_1^T \mathbf{M}^{-1} \mathbf{M}_1 \quad (27)$$

and

$$\mathbf{M}_{0,0} = \langle \mathcal{F} | \hat{H} - E | \mathcal{F} \rangle \quad (28)$$

$$\mathbf{M}_{1,0} = \langle \mathcal{T} | \hat{H} - E | \mathcal{F} \rangle \quad (29)$$

$$\mathbf{M}_{1,1} = \langle \mathcal{T} | \hat{H} - E | \mathcal{T} \rangle \quad (30)$$

$$\mathbf{M}_0 = \langle \mathcal{L} | \hat{H} - E | \mathcal{F} \rangle \quad (31)$$

$$\mathbf{M}_1 = \langle \mathcal{L} | \hat{H} - E | \mathcal{T} \rangle \quad (32)$$

$$\mathbf{M} = \langle \mathcal{L} | \hat{H} - E | \mathcal{L} \rangle. \quad (33)$$

For the wave function we obtain

$$\tilde{\mathbf{T}} = -\mathbf{D}_{1,1}^{-1} \mathbf{C}_{1,0} \quad (34)$$

$$\mathbf{X} = -\mathbf{M}^{-1} \mathbf{M}_0 + \mathbf{M}^{-1} \mathbf{M}_1 \mathbf{D}_{1,1}^{-1} \mathbf{C}_{1,0}. \quad (35)$$

Finally, the $\mathbf{T}$ -matrix may be transformed to the $\mathbf{S}$ -matrix, defined by the asymptotic form

$$\Psi_S = (\mathcal{F} + i\mathcal{F}) + (-\mathcal{F} + i\mathcal{F})\mathbf{S}, \quad (36)$$

using

$$\mathbf{S} = -\mathbf{W}(\mathcal{F} + i\mathcal{F}, \Psi) \mathbf{W}(-\mathcal{F} + i\mathcal{F}, \Psi)^{-1} = \mathbf{1} - 2i\mathbf{T}. \quad (37)$$

Note that for the wave functions we have $\Psi_S = 2i\Psi_T$.

Thus, we see that when using a discrete representation for the interaction region basis functions $\mathcal{L}$, the sparsity of the matrix $\mathbf{M}$ is not destroyed by the delocalized functions $\mathcal{C}$.

The numeric advantage of the $\mathbf{T}$ matrix formalism can now be understood. If the functions $\mathcal{F}$ become locally strongly closed, the corresponding matrix elements in $\mathbf{M}_{0,0}$ and $\mathbf{B}_{0,0}$ may become very small, and the corresponding $\mathbf{T}$ -matrix element, which should also be very small, is computed as the difference of small numbers. In the $\mathbf{S}$ -matrix

formalism however, the S -matrix element, which should be close to one, would be computed as the difference between two large numbers.

ZCM already point out that in the SKVP the (ir)regular functions may be replaced by the (ir)regular solutions of a distorting potential, multiplied by a cutoff function, as long as the asymptotic form is unchanged. Here, we note that it is actually sufficient that the (regularized) DWs satisfy the same Wronskian integral relations asymptotically [Eq. (22)]. This gives additional freedom in the choice of the asymptotic boundary conditions, which we exploit in the next section.

IV. DISTORTED WAVES

We minimize the size of the interaction region by replacing the sets of free waves $\mathcal{F}$, $\mathcal{G}$, and $\mathcal{C}$ by, respectively, a set of regular DWs $\tilde{\mathcal{F}}$, a set of irregular DWs $\tilde{\mathcal{G}}$ and a set of closed DWs $\tilde{\mathcal{C}}$, satisfying the same Wronskian integral relations. We require the DWs to be well converged solutions of the Schrödinger equation in the external region. Therefore, we use a coupled channels expansions including closed channels. The expansion coefficients [see Eq. (8)] must satisfy the well known coupled channels equation¹⁴

$$U''(R) = W(R)U(R), \quad (38)$$

where

$$\begin{aligned} W_{ij}(R) = & \frac{2\mu}{\hbar^2} \int \phi_i(\mathbf{q}) [\hat{H}_\alpha + V(R, \mathbf{q}) - E] \\ & \times \phi_j(\mathbf{q}) d\mathbf{q}^{(1)} \dots d\mathbf{q}^{(n)}. \end{aligned} \quad (39)$$

In order to use the variational formalism without modification, one might imagine matching the DWs and their derivatives to the free waves at some point $R=C$ in the external region and propagating inward. Because of the closed channels in the expansion, however, the solutions would diverge exponentially. Instead, we will specify boundary conditions for the DWs that will lead to a stable method and that will also minimize the number of DWs needed for convergence. In the end, the S -matrix is transformed to the physical boundary conditions.

The boundary conditions for the DWs will be specified at a point $R=A$ inside the interaction region, such that the DWs may be regularized by a cutoff function that switches from zero at $R=A$ to one at the boundary of the interaction region ($R=B$). The boundary conditions at some point $R=C$ far enough into the external region will be chosen such that the DWs satisfy the same Wronskian integral relations as the free waves. This ensures that the variational formalism can be applied without modification.

A. Open distorted waves

First, we determine a linearly independent set of functions that are zero at $R=A$. This is a standard inelastic scattering problem which we may solve by enforcing, e.g., K -matrix boundary conditions at $R=C$,

$$\Psi_K(A) = 0 \quad (40)$$

$$\Psi_K(C) = \mathcal{F} - \mathcal{G}K + \mathcal{C}C_K. \quad (41)$$

Any non-singular linear combination of these functions could serve as regular DWs. For numerical stability, we require the asymptotic boundary conditions for the open DWs to differ from the free waves $\mathcal{F}$ and $\mathcal{G}$ by at most a real, orthonormal transformation $\mathbf{Q}$. Thus, at $R \geq C$ we have

$$[\tilde{\mathcal{F}} \tilde{\mathcal{G}}] = [\mathcal{F} \mathcal{G}] \begin{bmatrix} \mathbf{Q}_1 & \mathbf{Q}_2 \\ -\mathbf{Q}_2 & \mathbf{Q}_1 \end{bmatrix} + \mathcal{C}[C_F C_G]. \quad (42)$$

In Appendix A we show that the supermatrix $\mathbf{Q}$ must have the above block structure and that, in addition, $\mathbf{Q}_1 + i\mathbf{Q}_2$ must be unitary if we require the sets $\tilde{\mathcal{F}}$ and $\tilde{\mathcal{G}}$ to satisfy the same Wronskian relations as the sets $\mathcal{F}$ and $\mathcal{G}$.

Since the regular DWs $\tilde{\mathcal{F}}$ must be some linear combination of the set Ψ_K we have

$$\begin{aligned} \mathbf{K} = & -W(\mathcal{F}, \tilde{\mathcal{F}})W(-\mathcal{G}, \tilde{\mathcal{F}})^{-1} \\ = & \mathbf{Q}_2 \mathbf{Q}_1^{-1}. \end{aligned} \quad (43)$$

This equation, together with the unitarity condition for $\mathbf{Q}_1 + i\mathbf{Q}_2$, has the non-unique solution

$$\mathbf{Q}_1 = (\mathbf{1} + \mathbf{K}^2)^{-1/2} \mathbf{Q}_0 \quad (44)$$

$$\mathbf{Q}_2 = (\mathbf{1} + \mathbf{K}^2)^{-1/2} \mathbf{K} \mathbf{Q}_0, \quad (45)$$

where $\mathbf{Q}_0$ is an arbitrary orthonormal matrix. In order to determine the optimal choice for $\mathbf{Q}_0$ we define the auxiliary sets of (ir)regular DWs, $\tilde{\mathcal{F}}$ and $\tilde{\mathcal{G}}$, that arise from the choice $\mathbf{Q}_0 = \mathbf{1}$. Thus, for the—not yet determined—optimal $\mathbf{Q}_0$ we have

$$\tilde{\mathcal{F}} = \mathcal{F} \mathbf{Q}_0, \quad \tilde{\mathcal{G}} = \mathcal{G} \mathbf{Q}_0. \quad (46)$$

The additional boundary conditions $\tilde{\mathcal{F}}(A) = 0$ for the regular DWs now fully define the set $\tilde{\mathcal{F}}$. To determine the boundary conditions for $\tilde{\mathcal{G}}$ at $R=A$ we use the Wronskian relations [setting $\hbar = 1$ and using $\tilde{\mathcal{F}}(A) = 0$]

$$\begin{aligned} W(\tilde{\mathcal{F}}, \tilde{\mathcal{G}}) = & \tilde{\mathbf{F}}(A)^T \tilde{\mathbf{G}}'(A) - \tilde{\mathbf{F}}'(A)^T \tilde{\mathbf{G}}(A) \\ = & -\tilde{\mathbf{F}}'(A)^T \tilde{\mathbf{G}}(A) = \mathbf{1}_{n_o \times n_o}. \end{aligned} \quad (47)$$

Since $\tilde{\mathbf{F}}'(A)$ and $\tilde{\mathbf{G}}(A)$ are $(n_o + n_c) \times n_o$ dimensional matrices, the equation still leaves n_c degrees of freedom for each column of $\tilde{\mathbf{G}}(A)$. We expect the numerically most favorable choice for $\tilde{\mathbf{G}}(A)$ to be the one with minimal norm. This solution may be found from the singular value decomposition¹⁵ of $\tilde{\mathbf{F}}(A)'$

$$\tilde{\mathbf{F}}'(A) = \mathbf{P}_F \mathbf{\Lambda} \mathbf{Q}_F^T, \quad (48)$$

where, by definition

$$\mathbf{P}_F^T \mathbf{P}_F = \mathbf{Q}_F^T \mathbf{Q}_F = \mathbf{1}_{n_o \times n_o} \quad (49)$$

and where $\mathbf{\Lambda}$ is a diagonal matrix with the so called singular values on the diagonal, ordered such that

$$\Lambda_{1,1} \geq \dots \geq \Lambda_{n_o, n_o} > 0. \quad (50)$$

The singular values are real and non-negative by definition and, in this case, they cannot be zero because that would

correspond to a linearly dependent set of free waves. We may now solve Eq. (47) by taking $\tilde{G}(A)$ to be minus the generalized inverse of $\tilde{F}'(A)$,

$$\tilde{G}(A) = -P_F \Lambda^{-1} Q_F^T. \quad (51)$$

Equations (48) and (51) clearly suggest that we should use the freedom in the choice of the boundary conditions for $\tilde{\mathcal{F}}$ and $\tilde{\mathcal{G}}$ by setting $Q_0 = Q_F$, since this gives

$$\tilde{F}'(A) = P_F \Lambda \quad (52)$$

$$\tilde{G}(A) = -P_F \Lambda^{-1}. \quad (53)$$

Thus, the norm of the i th columns of $\tilde{F}'(A)$ and $\tilde{G}(A)$ are, respectively, $\Lambda_{i,i}$ and $\Lambda_{i,i}^{-1}$. Hence, every regular DW with small derivative at $R=A$ corresponds to an irregular DW with large amplitude at $R=A$. Neither of these are expected to contribute much in the variational calculation and we only include DWs for which the singular value $\Lambda_{i,i}$ is larger than a certain threshold. In paper II we show that there is a rapid convergence if we systematically decrease this threshold.

Now that we have formally defined the boundary conditions at $R=A$ and $R=C$ we proceed as follows. First, we compute the propagator Y^{AB} for the interval $[A,B]$ (i.e., the part of the interval inside the internal region), defined by

$$\begin{bmatrix} -U'(A) \\ U'(B) \end{bmatrix} = \begin{bmatrix} Y_1^{AB} & Y_2^{AB} \\ Y_3^{AB} & Y_4^{AB} \end{bmatrix} \begin{bmatrix} U(A) \\ U(B) \end{bmatrix}. \quad (54)$$

A fairly straightforward imbedding type propagator technique is used to compute this propagator. In Appendix B a few details are given of the actual algorithm. During the propagation in the interval $[A,B]$ we store the information on disk that allows us compute the wave function once the boundary conditions are found. Next, we compute the propagator Y^{BC} for the external region (omitting the BC superscript)

$$\begin{bmatrix} -U'(B) \\ U'_o(C) \\ U'_c(C) \end{bmatrix} = \begin{bmatrix} Y_{1,1} & Y_{1,2} & Y_{1,3} \\ Y_{2,1} & Y_{2,2} & Y_{2,3} \\ Y_{3,1} & Y_{3,2} & Y_{3,3} \end{bmatrix} \begin{bmatrix} U(B) \\ U_o(C) \\ U_c(C) \end{bmatrix}, \quad (55)$$

where we partitioned the matrix to distinguish between the open and the closed channels at $R=C$. Since we do not need the wave function in the external region we do not have to store any intermediate information during the propagation. For the closed channel part we have

$$U'_c(C) = K^{cc} U_c(C), \quad (56)$$

where K^{cc} is a diagonal matrix defined by the asymptotically closed functions $K_{i,i}^{cc} = c'_i(C)/c_i(C)$. We may now define an effective propagator $\bar{Y}$ for the interval $[B,C]$ by eliminating the closed channel parts

$$\begin{bmatrix} -U'(B) \\ U'_o(C) \end{bmatrix} = \begin{bmatrix} \bar{Y}_1 & \bar{Y}_2 \\ \bar{Y}_3 & \bar{Y}_4 \end{bmatrix} \begin{bmatrix} U(B) \\ U_o(C) \end{bmatrix}. \quad (57)$$

By substituting Eq. (56) into Eq. (55) we find

$$\bar{Y}_1 = Y_{1,1} + Y_{1,3}(K^{cc} - Y_{3,3})^{-1} Y_{3,1}$$

$$\bar{Y}_2 = Y_{1,2} + Y_{1,3}(K^{cc} - Y_{3,3})^{-1} Y_{3,2} \quad (58)$$

$$\bar{Y}_4 = Y_{2,2} + Y_{2,3}(K^{cc} - Y_{3,3})^{-1} Y_{3,2}.$$

Note that the propagators are symmetric and we have $\bar{Y}_3 = \bar{Y}_2^T$. By combining Y^{AB} and $\bar{Y}$ we find the effective propagator for the entire interval $[A,C]$,

$$\begin{bmatrix} -U'(A) \\ U'_o(C) \end{bmatrix} = \begin{bmatrix} \bar{Y}_1^{AC} & \bar{Y}_2^{AC} \\ \bar{Y}_3^{AC} & \bar{Y}_4^{AC} \end{bmatrix} \begin{bmatrix} U(A) \\ U_o(C) \end{bmatrix}, \quad (59)$$

with

$$\bar{Y}_1^{AC} = Y_1^{AB} - Y_2^{AB} [Y_4^{AB} + \bar{Y}_1]^{-1} Y_3^{AB}$$

$$\bar{Y}_2^{AC} = -Y_2^{AB} [Y_4^{AB} + \bar{Y}_1]^{-1} \bar{Y}_2 \quad (60)$$

$$\bar{Y}_4^{AC} = \bar{Y}_4 - \bar{Y}_3 [Y_4^{AB} + \bar{Y}_1]^{-1} \bar{Y}_2.$$

The inelastic K -matrix is found by matching Ψ_K to the free waves at $R=C$,

$$K = [G'_o - \bar{Y}_4^{AC} G_o]^{-1} [F'_o - \bar{Y}_4^{AC} F_o]. \quad (61)$$

Using the Wronskian relations this may be rewritten in a symmetric form

$$K = G_o^{-1} F_o + \hbar^{-1} G_o^{-1} [\bar{Y}_4^{AC} - G_o' G_o^{-1}]^{-1} G_o^{-T}, \quad (62)$$

where the superscript $-T$ refers to the inverse of the transpose of the matrix. The K -matrix fixes the boundary conditions for $\tilde{\mathcal{F}}$ [using Eqs. (44) and (45) with $Q_0 = \mathbf{1}$] and we may compute

$$\tilde{F}'(A) = -\bar{Y}_2^{AC} \tilde{F}_o(C). \quad (63)$$

The singular value decomposition of this matrix [see Eq. (48)] fully determines the boundary conditions for the open DWs at $R=A$ and $R=C$ via $Q_0 = Q_F$ and Eqs. (52) and (53).

B. Closed distorted waves

For the closed DWs, defined by the expansion coefficients

$$\bar{C}(R) = \begin{bmatrix} \bar{C}_o(R) \\ \bar{C}_c(R) \end{bmatrix}, \quad (64)$$

we have the following conditions at $R=C$

$$\bar{C}_o(C) = \bar{C}'_o(C) = \mathbf{0}_{n_o \times n_c}, \quad (65)$$

where the overline indicates that the coefficient matrix is some—as yet undetermined—linear transformation of the matrix defined in Eq. (14) for $R > C$. Substituting these conditions into Eq. (59) gives

$$\bar{Y}_3^{AC} \bar{C}_o(A) = \mathbf{0}_{n_o \times n_c}. \quad (66)$$

Again, these are only n_o constraints, which leave us with n_c degrees of freedom for each of the n_c closed DWs. This time, minimizing the amplitude is useless, since the normalization of the closed DWs is arbitrary.

First, we observe that $\bar{C}(A)$ must span the null-space of the matrix $\bar{Y}_3^{AC}$. An orthogonal basis for the null-space of a

matrix may be found by using the singular value decomposition (SVD) of this matrix (which is the most reliable way) or by its QR factorization (which is twice as fast, see Ref. 15). We use the SVD based method. Let C_1 be this orthogonal basis for the null-space. We now select a specific basis by diagonalizing the $\mathbb{W}(A)$ -matrix projected onto this space, i.e., we solve the eigenvalue problem

$$[C_1^T \mathbb{W}(A) C_1] Q_c = Q_c \Lambda_c \quad (67)$$

and we take as the boundary conditions for the closed DWs at $R=A$,

$$\bar{C}(A) = C_1 Q_c. \quad (68)$$

In part II of the paper we show that we only need a few of the closed DWs corresponding to the smallest (most negative) eigenvalues Λ_c to converge the calculation. This can be easily understood, since the small eigenvalues correspond to a small internal energy and thus a large (less negative) translational kinetic energy. Thus, these DWs extend further into the external region, which is precisely what is needed to complete the set of (discrete) $\mathcal{L}^2$ interaction region functions.

V. IMPLEMENTATION

In the previous section we have specified the boundary conditions for the DWs in a point $R=A$ inside the interaction region and at some point $R=C$ in the external region. Since in the variational calculation we only need to evaluate the DWs in the interaction region, i.e., in the interval $[A, B]$, we compute the boundary conditions at $R=B$ using

$$U(B) = -[Y_4^{AB} + \bar{Y}_1^{BC}]^{-1} [Y_3^{AB} U(A) + \bar{Y}_2^{BC} U_o(C)]. \quad (69)$$

In order to evaluate the M_0 and M_1 matrix elements the DWs and their first and second derivative are computed at the sector boundaries that were used during the propagation (see Appendix B). The DWs are interpolated by fitting the expansion coefficients with piecewise eleventh degree Chebyshev polynomials spanning three adjacent sectors at a time by the use of the NAG library routine E01AEF.¹⁶

We found that with the present formalism a single cutoff function suffices to regularize all DWs. We use a polynomial of degree $2N+1$ (with $N=10$) that switches from zero to one in the interval $[A_\alpha, B_\alpha]$, for the arrangement α . The polynomial is determined by the requirement that its derivatives up till the N th order are zero in A_α and B_α . The parameters B_α , which determine the extent of the internal region, are chosen such that there is no overlap between the DWs of different arrangements. The parameters A_α are chosen such that $B_\alpha - A_\alpha$ is equal to three times the corresponding de Broglie wavelength.

Summarizing, the first step in the calculation is choosing the intervals $[A_\alpha, B_\alpha]$ and $[B_\alpha, C_\alpha]$ for which the propagators are computed. Subsequently, these propagators are used to construct the boundary conditions for the open and closed DWs as described in the previous section. To evaluate the matrix elements required for the variational calculation (see Sec. III), the DWs only have to be evaluated in the intervals $[A_\alpha, B_\alpha]$. The Kohn calculation employing the DWs results

in the $\bar{T}$ - and $\bar{S}$ -matrices associated with the DWs. Finally, the $\bar{S}$ -matrix must be transformed to the physical boundary conditions by the transformation

$$S = Q \bar{S} Q^T, \quad (70)$$

where $Q = (Q_1 + iQ_2)Q_0$.

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APPENDIX A: FORM OF SUPERMATRIX Q

In order to prove that the supermatrix Q must have the specified form replace the matrix Q in Eq. (42) by the general form

$$Q = \begin{bmatrix} Q_1 & Q_2 \\ Q_3 & Q_4 \end{bmatrix}. \quad (A1)$$

By working out the orthogonality condition

$$Q^T Q = 1 \quad (A2)$$

and the Wronskian integral relations

$$\begin{aligned} W(\mathcal{F}, \mathcal{F}) &= \hbar^{-1} \mathbf{1} \\ W(\mathcal{F}, \mathcal{F}) &= W(\mathcal{F}, \mathcal{F}) = 0, \end{aligned} \quad (A3)$$

we may verify that

$$(Q_1 - Q_4)^T (Q_1 - Q_4) + (Q_2 + Q_3)^T (Q_2 + Q_3) = 0, \quad (A4)$$

which shows that we must have

$$\begin{aligned} Q_4 &= Q_1 \\ Q_3 &= -Q_2. \end{aligned} \quad (A5)$$

If we substitute this back into the orthogonality condition Eq. (A2) we get

$$\begin{aligned} Q_1^T Q_1 + Q_2^T Q_2 &= 1 \\ Q_1^T Q_2 - Q_2^T Q_1 &= 0. \end{aligned} \quad (A6)$$

These real conditions are equivalent to the condition that $(Q_1 + iQ_2)$ is unitary, i.e.,

$$(Q_1 + iQ_2)^{-1} = (Q_1 - iQ_2)^T. \quad (A7)$$

APPENDIX B: ALGORITHM TO COMPUTE PROPAGATORS

In order to compute the propagators defined in Eqs. (54) and (55) the intervals $[A, B]$ and $[B, C]$ are divided in sectors. In each sector $[a, b]$ the Cauchy matrix,¹⁴ defined by

$$\begin{bmatrix} U(b) \\ U'(b) \end{bmatrix} = \begin{bmatrix} C_1^{ba} & C_2^{ba} \\ C_3^{ba} & C_4^{ba} \end{bmatrix} \begin{bmatrix} U(a) \\ U'(a) \end{bmatrix} \quad (B1)$$

is computed by solving the coupled channels equation in the interval $[a, b]$ with the initial conditions

$$\begin{bmatrix} U(a) \\ U'(a) \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \quad (\text{B2})$$

For this purpose we use the high order Runge–Kutta Nystrom algorithm from the NAG routine D02LAF,¹⁶ which is especially designed for second order differential equations. The sectors must be chosen small enough to prevent the norm of the solutions to become too large, which would cause numerical instability. The Cauchy matrices are subsequently transformed to the imbedding type propagator Y for each interval via

$$\begin{aligned} Y_1 &= C_2^{-1} C_1 \\ Y_2 &= -C_2^{-1} \\ Y_3 &= C_3 - C_4 C_2^{-1} C_1 \\ Y_4 &= C_4 C_2^{-1}. \end{aligned} \quad (\text{B3})$$

The propagators for the sectors $[a,b]$ and $[b,c]$ are combined via

$$\begin{aligned} Y_1^{ac} &= Y_1^{ab} - Y_2^{ab} [Y_4^{ab} + Y_1^{bc}]^{-1} Y_3^{ab} \\ Y_2^{ac} &= -Y_2^{ab} [Y_4^{ab} + Y_1^{bc}]^{-1} Y_2^{bc} \\ Y_3^{ac} &= -Y_3^{bc} [Y_4^{ab} + Y_1^{bc}]^{-1} Y_3^{ab} \\ Y_4^{ac} &= Y_4^{bc} - Y_3^{bc} [Y_4^{ab} + Y_1^{bc}]^{-1} Y_2^{bc}. \end{aligned} \quad (\text{B4})$$

In our present implementation the Cauchy matrices are computed in a basis of asymptotic channel eigenfunction. A well known technique in inelastic scattering calculations is the

use of a “local basis” of eigenfunctions of the $\mathbb{W}[(a+b)/2]$ matrix, which might be used to reduce the number of coupled equations in each sector.¹⁴

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