Reconciling semiclassical and Bohmian mechanics. VI. Multidimensional dynamics

Bill Poirier

Citation: J. Chem. Phys. 129, 084103 (2008); doi: 10.1063/1.2969102
View online: http://dx.doi.org/10.1063/1.2969102
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v129/i8
Published by the American Institute of Physics.

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Instruments for advanced science
Reconciling semiclassical and Bohmian mechanics. VI. Multidimensional dynamics

Bill Poirier

Department of Chemistry and Biochemistry and Department of Physics, Texas Tech University, Box 41061, Lubbock, Texas 79409-1061, USA

(Received 12 May 2008; accepted 17 July 2008; published online 26 August 2008)

In previous articles [J. Chem. Phys. 121, 4501 (2004); J. Chem. Phys. 124, 034115 (2006); J. Chem. Phys. 124, 034116 (2006); J. Phys. Chem. A 111, 10400 (2007); J. Chem. Phys. 128, 164115 (2008)] an exact quantum, bipolar wave decomposition, \( \psi = \psi_+ + \psi_- \), was presented for one-dimensional stationary state and time-dependent wavepacket dynamics calculations, such that the components \( \psi_\pm \) approach their semiclassical WKB analogs in the large action limit. The corresponding bipolar quantum trajectories are classical-like and well behaved, even when \( \psi \) has many nodes or is wildly oscillatory. In this paper, both the stationary state and wavepacket dynamics theories are generalized for multidimensional systems and applied to several benchmark problems, including collinear \( \text{H}+\text{H}_2 \). © 2008 American Institute of Physics. [DOI: 10.1063/1.2969102]

I. INTRODUCTION

This paper is the final installment in a series of six articles,1–5 dedicated to the development of bipolar counterpropagating wave methods1–6 for solving both the time-independent Schrödinger equation (TISE) and time-dependent Schrödinger equation (TDSE) exactly. The basic idea is to decompose the wave function into a two-term, or “bipolar,” form, 
\[
\psi = \psi_+ + \psi_-(\text{or } \phi^E = \phi^E_+ + \phi^E_-),
\]
(1)
such that \( \psi_\pm \) represent the two wave “components,” moving in opposite directions. In this paper, \( \psi \) denotes a localized wavepacket solution of the TDSE, whereas \( \phi^E \) is a stationary state solution of the TISE with definite energy \( E \).

The original motivation for the bipolar ansatz of Eq. (1) (Ref. 1) came from the desire to reconcile a seemingly profound contradiction between the two dynamical theories of Bohmian mechanics8–14 and semiclassical mechanics15–18—namely, that the exact quantum trajectories of the former often bear no qualitative resemblance to the approximate classical trajectories of the latter, even in the classical limit, in which semiclassical mechanics is supposed to become increasingly accurate. This apparent violation of the correspondence principle can be resolved by acknowledging the key difference between the two theories, i.e., that the Bohmian mechanical field functions are necessarily single valued,8,14 whereas those of semiclassical mechanics can be multivalued due to caustics and turning points.15–18 A proper comparison between the two theories thus generally requires a multipolar expansion, such as that of Eq. (1). A more detailed exposition may be found in the introductory sections of the previous papers in the series, especially Paper I,1 Paper II,2 and Paper V.5

For stationary states of one-dimensional (1D) systems,1–3,6,15–18 momentum symmetry implies that a multipolar expansion of the Eq. (1) form is appropriate, with the \( \phi^E_\pm \) component corresponding to the positive (right-moving) momentum contribution and the \( \phi^E_\mp \) component to the negative (left-moving) momentum contribution. The exact TISE solution \( \phi^E \) is thus regarded as a linear superposition of left and right traveling waves. As was observed in the previous papers1–3,6 the bipolar traveling wave components \( \phi^E_\pm \) are exact quantum analogs of the corresponding approximate semiclassical WKB wave components,16–18 and the resultant Bohmian mechanical exact quantum trajectories are indeed now found to approach classical trajectories in the classical limit. The bipolar densities, \( \rho^E_\pm = |\phi^E_\pm|^2 \), are smooth and well behaved, even when \( \rho^E = |\phi^E|^2 \) itself exhibits substantial interference and nodes. This was shown for 1D stationary bound states in Paper I and for scattering states in Papers II and III.5 Later bipolar generalizations for 1D multisurface and wavepacket dynamics applications were presented in Paper IV (Ref. 4) and Paper V, respectively.

In this, the final paper of the series, we consider the multidimensional generalization of both the TISE and TDSE bipolar decomposition methodologies. Obviously, the existence and feasibility of a multidimensional generalization are crucial if the bipolar approach is to be applied to real molecular systems; establishing that this is indeed the case is therefore the central goal of this paper. In addressing the question of the multidimensional generalization, the first and most important question that arises is this: How many components should be required? If \( D \) is the number of degrees of freedom (DOF), then consideration of a separable Hamiltonian might lead one to conclude that \( 2^D \) wave function components is appropriate, stemming from a separate bifurcation along each DOF. On the other hand, the Paper I bipolar decomposition for bound DOFs—though perhaps fundamentally important—may not be very practical for real calculations as the \( \phi^E_\pm \) are delocalized (and non-\( L^2 \) inte-
grable). Thus, provided \( \phi^E \) (or \( \psi \)) itself is free of nodes in the bound DOFs (see below), a sensible strategy is to bifurcate only along the scattering DOFs.

For reactive scattering systems in chemical dynamics, this approach is particularly well suited because the number of scattering DOFs can be quite small, even for large systems. Indeed, in the ideal case—which is in fact very common—there is just a single scattering DOF, known as the “reaction coordinate.”\(^{13}\) By bifurcating along the reaction coordinate only, the worst form of interference—i.e., from reaction barrier reflection (as opposed to inelastic transitions)—can be accommodated with just two wave function components, regardless of system dimensionality. There is an appealing intuitive aspect to this type of bipolar decomposition as well, with the + component corresponding to the forward reaction and the − component to the reverse reaction. Interference oscillations in \( \psi \) or \( \phi^E \) then arise naturally from the superposition of (presumably smooth) forward and reverse reaction contributions. The reaction coordinate concept is of course far from original, and is ubiquitous in the field of chemical dynamics. The bipolar methodology developed here will thus be more useful and accessible, to the extent that it readily incorporates familiar and time-honored constructions such as curvilinear reaction paths. Conversely, in situations where the reaction coordinate picture breaks down or becomes more complicated—e.g., three-dimensional (3D) scattering of a single particle from an external central force potential—the bipolar approach will be more difficult to apply without further theoretical developments.

An allusion was made above to classical and quantum trajectories associated, respectively, with semiclassical and Bohmian mechanics. Although this paper does not directly concern itself with trajectories, a trajectory-based implementation of the relevant bipolar dynamical equations would be straightforward, at least in principle. In general, trajectory-based methods for solving the exact TDSE, based on a Bohmian or similar formulation, are referred to as “quantum trajectory methods” (QTMs).\(^{8,20–35}\) QTMs have experienced rapid growth of interest in the chemical dynamics field since they were introduced nine years ago.\(^{20,21}\) The great promise of QTMs is not only pedagogical, i.e., by providing classical-like dynamical insight, but also practical, enabling accurate quantum dynamics calculations to be performed for large systems in a manner similar to classical simulations. QTMs appear to be able to defeat exponential scaling of computational effort with system dimensionality, as suggested by calculations on model systems with up to 200 DOFs (Refs. 8, 25, and 33) provided linear reaction paths are assumed, and reflection interference is ignored.

However, owing to the “node problem”\(^{8,24,32–35}\)—numerically unstable quantum trajectories in the presence of nodes or oscillatory probability densities—standard unipolar QTMs invariably fail when there is substantial interference unless approximations are used, such as linearized quantum force\(^{36,37}\) or artificial viscosity.\(^{30,31}\) Consequently, no exact QTM calculation has previously been achieved for a real molecular system, not even for collinear H+H\(_2\). As discussed above, bipolar QTMs can get around the node problem difficulty—at least for barrier reflection interference—via a natural superposition of (presumably) node-free components. The numerical applications presented in this paper, in which the \( \phi^E \) and \( \psi \) components are determined via nontrajectory-based means, may therefore be regarded as a feasibility study to demonstrate that multidimensional bipolar QTM calculations would be successful if performed for real molecular applications.

The remainder of this paper is organized as follows. Section II discusses the theoretical developments needed to generalize both the stationary state (TISE) and wavepacket dynamics (TDSE) bipolar decompositions for multidimensional systems of arbitrary system dimensionality. The conceptually simplest case of linear reaction paths and symmetric potentials is considered first (Sec. II A). More complicated situations, including the important case of curvilinear reaction paths, are considered in Sec. II B. In Sec. II B 4, a curious universality relation is discussed; one ramification is that the precise definition of the reaction coordinate is immaterial, provided it is defined properly in the asymptotic regions. The \( \phi^E \) and \( \psi \) bipolar components computed in this paper are obtained using fixed-grid algorithms, as discussed in Sec. III. This section also addresses bipolar QTM implementations and how these would likely scale with increasing system dimensionality. Results, primarily of TDSE wavepacket dynamics calculations, are presented for a variety of two-dimensional (2D) applications in Sec. IV. The first of these are simple model calculations, designed to investigate various multidimensional dynamical effects in relative isolation. Section IV D then examines the more complicated and realistic collinear H+H\(_2\) reaction. Concluding remarks, including future prospects for the bipolar QTM approach, are provided in Sec. V.

II. THEORY

A. Linear reaction paths and asymptotically symmetric potentials

Consider a multidimensional quantum scattering system of the form

\[
\hat{H} = -\left(\frac{\hbar^2}{2m}\right) \nabla^2 + V(\bar{x}),
\]

where

\[
\bar{x} = (x_1, x_2, \ldots, x_D)
\]

denotes all \( D \) system DOFs and

\[
\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \cdots + \frac{\partial^2}{\partial x_D^2}
\]

is the \( D \)-dimensional Laplacian.

Assume further that the coordinate \( x = x_1 \) is singled out as the reaction coordinate for some asymptotically symmetric process, so that in both \( x \) asymptotes, the potential behaves as

\[
V(\bar{x}) = V(x, y) \rightarrow V^0(y) \quad \text{as} \quad x \rightarrow \pm \infty,
\]

with
\[ y = (x_2, \ldots, x_D). \]

The vector \( y \) denotes all of the \((D-1)\) nonreaction DOFs, referred to collectively as the “perpendicular modes.” Perpendicular vector quantities shall be denoted using boldface, whereas arrow superscripts shall be used for vectors over the full \( D \)-dimensional configuration space—i.e., including the reaction coordinate \( x \). Thus, \( \vec{x} = (x, y) \), as used in Eq. (3) above.

Equation (2) may serve as a simple reaction-path Hamiltonian model (without curvature) for an exchange scattering system, as has been done previously in the quantum trajectory context,\(^{22,30,32} \) or it might represent an actual physical system with confinement. In either case, the primary reaction path—taken to be defined by \( y = 0 \)—is linear. Let us further assume that the positive reaction direction corresponds to \( x > 0 \).

1. Stationary states

For a given energy \( E \), Eq. (2) has \( n_{\text{max}} \) linearly independent left-incident stationary eigenstates, where \( n_{\text{max}} \) is the number of open channels available among the perpendicular modes. These eigenstates will be labeled \( \phi_{E,n}^{L}(x, y) \), with \( 0 \leq n < n_{\text{max}} \) denoting a particular channel. Each channel, in turn, is associated with a particular eigenstate \( \phi_0(y) \) (with energy \( E_0 < E \)) of the left-asymptotic Hamiltonian,

\[ \tilde{H}^L = -\left( \frac{\hbar^2}{2m} \right) \nabla_y^2 + V(y), \]

(4)

where

\[ \nabla_y^2 = \frac{\partial^2}{\partial x_2^2} + \cdots + \frac{\partial^2}{\partial x_D^2} \]

is the perpendicular Laplacian.

The left-asymptotic incident wave contribution to \( \phi_{E,n}^{L}(x, y) \) is

\[ \phi_{E,n}^{L}(x, y) \rightarrow \phi_0(y) \exp \left[ \frac{ip_0^L x}{\hbar} \right] \text{ as } x \rightarrow -\infty, \]

(5)

where \( p_0^L = \sqrt{2m(E-E_0)} \). We shall henceforth consider only single-channel incident wave functions, so that the super-/ subscript \( n \) will be dropped, except when needed.

Since \( \phi_E = (\phi_L - \phi_R) \) by Eq. (1), Eq. (5) implicitly provides the correct bipolar decomposition in the left-asymptotic limit, in accord with expectations of the prior work\(^{2,3,6}\) and standard scattering theory.\(^{38} \) Similarly, in the right asymptote, one should find that \( \lim_{y \rightarrow \infty} \phi_E(x, y) = 0 \)—at least for “elastic scattering,” by which we mean scattered channels with the same perpendicular energy \( E_0 \) as the incident channel. To determine how the \( \phi_{E,n}^{L}(x, y) \) interpolate smoothly through the interaction region, we develop a multidimensional generalization of the constant-velocity Fröman approach used previously in one dimension.\(^ {3-6,16} \) Please consult these references for further details.

In one dimension, the constant-velocity Fröman decomposition of Eq. (1) is uniquely determined from the TISE [Eq. (2)] and the relation\(^ {3,5,6,16} \),

\[ \phi_{E,n}^{L} = \frac{i \hbar}{p_0^L} \int \phi_0 \left( \phi_E - \phi_R \right). \]

(6)

In the present multidimensional context, for which \( x \) has been singled out as the sole reaction coordinate, it seems eminently sensible to apply precisely the same Eq. (6) condition—with the prime interpreted to mean the partial derivative with respect to \( x \). It is easy to demonstrate that regardless of system dimensionality, no additional conditions are required to uniquely determine the resultant \( \phi_{E,n}^{L}(x, y) \).

Moreover, this choice is consistent with the desired \( x \)-asymptotic \( \phi_{E,n}^{R} \) boundary conditions, as discussed above.

Note that although the Eq. (6) condition above is the same as for the 1D case, the TISE itself is not, because of the perpendicular contribution to the kinetic energy. This has an effect on some of the bipolar solutions as derived in the previous work, but not on others. For instance, the multidimensional generalization of Eq. (7) in Ref. 5 becomes

\[ \phi_{E,n}^{L} = \pm \frac{i \hbar}{2p_0^L} \nabla_y^{2} (\phi_L^{E} + \phi_R^{E}) \]

(7)

Note that for the incident channel value of \( n \) (i.e., for elastic scattering) Eq. (4) implies that the coupling in Eq. (7) vanishes in both \( x \) asymptotes, as it should. Only the first, plane wave term in Eq. (7), contributes asymptotically.

In contrast to Eq. (7), the action of the Hamiltonian operator is essentially unchanged from the 1D case, i.e., the multidimensional generalization of Eq. (9) in Ref. 5 is still

\[ \hat{H} \phi_{E,n}^{L} = E \phi_{E,n}^{L} \pm \frac{i \hbar}{2p_0^L} V_i (\phi_L^{E} + \phi_R^{E}). \]

(8)

Also, Eqs. (1) and (6) can be combined to obtain a direct expression for \( \phi_E^{L} \) in terms of \( \phi_E \) and its \( x \) derivative, that is unchanged from the 1D form:

\[ \phi_{E,n}^{L} = \frac{1}{2} \left( \phi_E^{L} + \frac{i \hbar}{p_0^L} \phi_E^{R} \right). \]

(9)

In Sec. IV, a variation of Eq. (9) [Eq. (16)] will be used to compute \( \phi_E^{L} \) functions from known \( \phi_E \) TISE solutions. This will be the primary focus of the current paper insofar as stationary state solutions are concerned; we leave to a future paper the development of a trajectory-based time-dependent relaxation algorithm to actually compute multidimensional \( \phi_E \), analogous to previous 1D algorithms.\(^ {2,3,6} \) Nevertheless, the stationary state time-evolution equations will be briefly considered here to verify that (like the previous 1D work) the total combined probability is conserved over time, i.e.,

\[ \int \left( \frac{\partial \rho_{E}^{L}}{\partial t} + \frac{\partial \rho_{E}^{R}}{\partial t} \right) dx dp^{D-1} y = 0, \]

(10)

where \( \rho_{E}^{L} = |\phi_{E,n}^{L}|^2 \) are the bipolar component densities.

Equation (10) implies that suitable flux fields \( \vec{J}_{\pm} \) can be constructed that satisfy a multidimensional combined flux continuity relation, i.e.,
field

To a unique specification of the multidimensional velocity as represented schematically in Fig. 1. This in turn gives rise to a pair of incident and reflected wavepackets; this

ability that leaves the component (lower box) must flow into the \( \psi^\pm \) component (upper box). Consequently, \( \int [\rho^E(x,y) + \rho^F(x,y)] dx dy \) is conserved for all time.

\[
\frac{\partial \psi^E}{\partial t} - \frac{i}{\hbar} \bar{H} \psi^E = \frac{1}{2 \rho^0} (\psi^E + \psi^F).
\]

As in Eq. (10) of Ref. 5, Eq. (12) above satisfies the TDSE at all times \( t \) (for \( \phi^E = \psi^E + \psi^F \), unlike the relaxation equations of Eq. (A1). Recall that Eq. (12) is associated with a particular incident channel \( n \) via the specific value of \( \rho^0 \). For a given channel, therefore, the energy \( E \) uniquely specifies \( \phi^E \) and \( \psi^E \). We can therefore define a unique multidimensional wavepacket bipolar decomposition as an orthonormal expansion in the \( \phi^E \) exactly as in the 1D case, i.e., Eq. (11) of Ref. 5:

\[
\psi(x,y,t) = \int_{E^0}^\infty a(E) \phi^E(x,y,t) dE,
\]

\[
\psi^\pm(x,y,t) = \int_{E^0}^\infty a(E) \phi^\pm(x,y,t) dE.
\]

Continuing the analysis in Ref. 5, Eq. (12) is replaced by an equivalent expression that removes the explicit dependence on \( \rho^0 \) but replaces the \( (\psi^E + \psi^F) \) factor in the final term

with a (line) integration of this quantity over \( dx \) at constant \( y \)—in effect, by relying on the \( x \) integral of Eq. (6). The result is Eq. (13) of Ref. 5. The final step is to substitute both sides of this equation into Eq. (13) to obtain time-evolution equations for the bipolar components \( \psi^\pm \). Once again, the result is identical in form to the 1D case [Ref. 5, Eq. (14)]:

\[
\frac{\partial \psi^\pm}{\partial t} = -\frac{i}{\hbar} \bar{H} \psi^\pm + \frac{V'}{2} (\psi^+ - \psi^-),
\]

where

\[
\psi^\pm(x,y,t) = \int_{-\infty}^t \psi^\pm(x',y,t) dx'.
\]

With respect to the incident channel \( n \) value, Eq. (14) above exhibits all of the desirable conditions discussed in Sec. IIC of Ref. 5, including \( \psi^\pm \) localization and perfect asymptotic separation (at large \( t \), \( \psi^\pm \) is vanishingly small in the left \( x \) asymptote and \( \psi^- \) is vanishingly small in the right \( x \) asymptote). However, the incident channel \( \rho^0 \) value will not result in perfect asymptotic separation for the \( \psi^\pm \) contribution from other channels, to which the single-channel incident wavepacket may scatter inelastically. The situation is reminiscent of the asymmetric and/or multisurface 1D potentials considered in Ref. 5, except that in multidimensions, the effect can be observed even for symmetric, single surface systems. As in the previous work, two approaches naturally present themselves: (1) propagate multiple \( \psi^\pm \) decompositions, one for each available channel \( \rho^0 \); (2) propagate only the single decomposition corresponding to the incident channel \( \rho^0 \) value. The former, explicit multichannel approach (1) satisfies perfect asymptotic separation and also avoids possible interchannel interference effects in the final transmitted and reflected (reacting and nonreacting) wavepackets; this approach will be explored in a later paper.

The simpler approach (2) will not exhibit perfect asymptotic separation, but as in Ref. 5, is nevertheless likely to result in very well-behaved \( \psi^\pm \) components. In particular, interchannel interference often manifests in wavepacket dynamics as a gentle “snaking motion” in the transmitted or reflected wavepackets (Sec. IV C). This type of interference—associated with waves that are traveling at different speeds but in the same direction—is much less problematic numerically than reflection interference associated with waves traveling in opposite directions, which the bipolar \( \psi^\pm \) decomposition is designed to ameliorate. In any case, Eq. (14) satisfies the most important property, i.e., that all couplings vanish in both asymptotic limits, even when there is inelastic scattering. In fact, at large \( \pm t \), one finds that \( \psi^\pm \) independently evolve in accord with the usual TDSE for the asymmetric \( \bar{H}^0 \) Hamiltonian of Eq. (4). Note also that like the 1D case, Eq. (14) does not depend on the particular value of \( \rho^0 \), even though the resultant \( \psi^\pm \) decomposition itself does.

B. Curvilinear reaction paths and asymptotically asymmetric potentials

Our next task is to extend the above to more general potentials that exhibit different asymmetric potentials in the two \( x \) asymptotes, and/or curvilinear reaction paths. The lat-
ter is an important consideration if exact multidimensional QTM applications are to be extended beyond model reaction-path Hamiltonians. In particular, a QTM is desired that may be applied to scattering problems represented in conventional Cartesian Jacobi coordinate systems, and that can accommodate direct (single barrier) reactions, as well as reaction intermediates. One presumption we will make for the present paper is that the potential has a single reaction pathway, linking a single reactant and a single product arrangement. This is done for convenience, rather than because multiple pathways and arrangements are beyond the reach of the present methodology, which is not the case (Sec. V). In any event, such a further generalization will be explored in a future paper.

1. Asymptotically asymmetric potentials

First, let us consider the linear reaction-path case in Sec. II A but with asymptotically asymmetric potentials. In other words, the left-asymptotic ($x \to -\infty$) and right-asymptotic ($x \to +\infty$) potentials $V^0$ are presumed to be different. We shall refer to these, respectively, as $V^0_{\text{reac}}$ and $V^0_{\text{prod}}$. [Note the switch in notations from the “L” (left) and “R” (right) of Ref. 5 to the more general “reac” (reactant) and “prod” (product) forms used here.] These, in turn, give rise to completely different asymmetric Hamiltonians and sets of reactant and product channels, corresponding to channel energies $E^0_{\text{reac}}$ and $E^0_{\text{prod}}$, respectively. The situation is very reminiscent of the asymmetric multisurface 1D bipolar wavepacket decomposition considered in Ref. 5, except that there is no one-to-one correspondence between individual reactant and product channels. Every $E^0_{\text{reac}}$ and $E^0_{\text{prod}}$ value gives rise to a different $\phi^E_{\text{reac}}$ and $\psi^E_{\text{reac}}$ decomposition, for which perfect asymptotic separation is (generally) only satisfied for the corresponding channel and arrangement. All such decompositions, though $p^0$ value dependent (with $p^0$ obtained from the corresponding $E^0_{\text{reac}}$ or $E^0_{\text{prod}}$ channel energies) satisfy the same bipolar wavepacket evolution equations, i.e., Eq. (14).

For a given calculation, which value of $p^0$ should be used? Certainly, the incident channel value, $p^0 = p^0_{\text{reac}}$, is ideal for the reactant valley asymptote, as it gives rise to perfect asymptotic separation. Moreover, based on 1D results from Ref. 5, this choice is expected to yield solutions that are well behaved throughout space, albeit not perfectly separated in the product asymptote. Similarly, if there is scattering into only a single product channel, then the corresponding product channel value, $p^0_{\text{prod}}$, will yield perfect asymptotic separation of products but not of reactants, except in the elastic case where $p^0_{\text{reac}} = p^0_{\text{prod}}$. For the inelastic case, if perfect asymptotic separation is desired in both asymptotes, this can be achieved by discontinuously fusing together the $p^0_{\text{reac}}$ and $p^0_{\text{prod}}$ solutions at a dividing surface, $x = x_D$, as discussed in Ref. 5. Note that the choice of the $p^0_{\text{prod}}$ value is less straightforward if there is substantial scattering into multiple product channels, as no choice will yield perfect asymptotic separation for products; in such cases, it may be best to simply use the $p^0_{\text{prod}} = p^0_{\text{reac}}$ solutions throughout.

2. Curvilinear reaction paths: Dividing surface approach

We now explicitly consider the general case where the Hamiltonian of Eq. (2) need not adhere to the linear reaction-path constraint in Sec. II A, so that the reaction path may curve around a bend in position space. In the equations that follow, mass-weighted Jacobi coordinates are assumed, so that all dot products and gradients have their standard Cartesian meanings. More generally, non-Cartesian coordinate systems could also be employed, though this may necessitate more complicated expressions than those provided here.

In Sec. II B 1 above, regardless of the particular choice of $p^0$ used, it is clear that any positive value gives rise to a different $\phi^E$ or $\psi^E$, bipolar decomposition for the same $\phi^E$ or $\psi$. For the generalization to curvilinear reactive systems, it is useful to broaden the range of available bipolar decompositions with respect to the choice of momentum vector, $\vec{p} = (p_1, \ldots, p_D)$ rather than just the magnitude, $p^0 = |\vec{p}|$—regardless of channel energy or whether the direction of $\vec{p}$ coincides with the reaction path in reactant or product asymptotic limits. In this subsection, we shall first derive the formulas of Sec. II A for a completely arbitrary choice of momentum vector $\vec{p}$ and then apply these formulas to specific $\vec{p}$ choices, so as to yield appropriate bipolar decompositions.

Specifically, the basic conceptual idea is that there is now one momentum vector, $\vec{p} = \vec{p}_{\text{reac}}$, that is natural to use in the reactant valley (i.e., will lead to perfect asymptotic separation there), and (ideally) one other momentum vector, $\vec{p} = \vec{p}_{\text{prod}}$, that is natural for products. These vectors are associated with motion along the reaction-path direction in each of these two asymptotic regions; thus, for the reactant case, $|\vec{p}_{\text{reac}}| = p^0_{\text{reac}} = p^0$ is determined from the incident channel energy. The two momentum vectors and their corresponding bipolar decompositions are generally not identical owing either to different reactant and product channel energies (i.e., vector magnitudes) or to curvilinear reaction paths (leading to different vector directions). As discussed in Sec. II B 1 and Ref. 5, the strategy will thus be to solve the dynamical equations for both $\vec{p} = \vec{p}_{\text{reac}}$ and $\vec{p} = \vec{p}_{\text{prod}}$ independently, and to merge the two sets of solutions together at a dividing surface. For example, Fig. 2(a) indicates the situation for the collinear H+H2 system (Sec. IV D).

The starting point is the vector generalization of Eq. (6), leading [with Eq. (1)] to

$$
\phi^E_{\vec{p}_{\text{reac}}} = \frac{1}{2} \left( \phi^E \mp \left( \frac{i \hbar}{\vec{p} \cdot \vec{\hat{p}}} \right) \vec{p} \cdot \vec{\nabla} \phi^E \right),
$$

(16)

where the momentum dependence of the decomposition is now explicitly suggested by the $\vec{p}$ subscript in the left-hand side. In essence, Eq. (16) is no different than Eq. (9), except that the $x$ derivative of $\phi^E$ is replaced with a derivative in the momentum vector direction, $\vec{p}$. For an arbitrary function $f(x)$, we introduce the following notation:

\[ f(x) \]
should be well behaved over time, i.e., are well localized, etc., even when applied to the “wrong” part of space (e.g., product decomposition in the reactant well, etc.). Composite solutions are then constructed by joining reactant and product results at the dividing surface, as per the discussion above and Eq. (21) of Ref. 5.

3. Curvilinear reaction paths: Reaction-path approach

In all of the discussion in Sec. II B 2, the momentum vector $\vec{p}$ is constant over position space, thus necessitating propagation of two different decompositions, one for $\vec{p}_{\text{reac}}$ and one for $\vec{p}_{\text{prod}}$. In many respects, it would be much nicer if only a single bipolar decomposition were required, corresponding to a momentum field that follows the reaction path around from reactant to product arrangement valleys. Such a decomposition would automatically provide the most appropriate decomposition in both the reactant and product asymptotes. However, it also requires a further generalization of the previous discussion to allow for momentum fields $\vec{p} = p(\vec{x})$ that explicitly depend on position.

Note that even in 1D, we have not as yet generalized the derivation of the bipolar wavepacket evolution equations to accommodate position-dependent $p^0$ fields,5 though we certainly intend to do so in the future. That being the case, we are ill equipped at present to handle the even more general case of completely arbitrary $\vec{p}(\vec{x})$ fields in multiple dimensions. In addition to position-dependent momentum vector magnitudes $p^0$, there are nontrivial operator-ordering effects associated with position-dependent vector directions, $\vec{p}(\vec{x})$, that manifest in the equations as extra commutator terms. It turns out, however, that we can indeed accommodate arbitrarily changing momentum vector directions provided that the magnitude $p^0$ is held constant throughout position space—an option discussed at the end of Sec. II B 1 and in Ref. 5. Moreover, this can be done in a manner that is completely independent of the particular $\vec{p}(\vec{x})$ field used—provided this field coincides with the natural reaction directions in both reactant and product asymptotes [Sec. II B 4 and Fig. 2(b)].

We therefore take the momentum vector direction field, $\vec{p}(\vec{x})$, to define the forward reaction direction at every point in position space. This is expected to vary smoothly between the natural reaction directions in the reactant and product asymptotic valleys—defined by $\vec{p}_{\text{reac}} = \partial_x V_{\text{reac}} = 0$ and $\partial_y V_{\text{prod}} = 0$, respectively. The momentum vector magnitude, $|\vec{p}| = p^0$, is taken, as in Sec. II A 1, to correspond to the incident channel energy in the reactant asymptote, i.e., $p^0 = p_{\text{reac}}$.

Note that the form of all single-$\partial$-derivative expressions is unaffected by the generalization for position dependence. The first condition defining the bipolar decomposition is therefore still the vector version of Eq. (6), i.e.,

$$\partial_\nu \Phi^\nu = \frac{i}{\hbar} p^0 \left( \phi^E_{\nu+} - \phi^E_{\nu-} \right).$$

The second condition is of course the TISE itself. As in the previous examples, these two conditions (and appropriate
boundary conditions) uniquely determine the resultant bipolar decomposition, \( \phi^E_{\rho \pm} \).

In reworking the derivations of Sec. II A 1, one finds that Eq. (7) is replaced with

\[
\partial_t \phi^E_{\rho \pm} = \pm \frac{i}{\hbar} \rho^0 \phi^E_{\rho \pm} + \frac{i}{\hbar} \left( \frac{m}{p^0} \right) (V - E^0) \phi^E_{\rho \pm} + \frac{i}{\hbar} \frac{\hbar^2}{2m} \left( \partial^2_{\rho \pm} - \partial^2_{\rho} \right) \phi^E_{\rho \pm}.
\]  

(20)

Equations (7) and (20) look very similar; however, it should be noted that \( \left[ \nabla^2 - \partial^2_{\rho} \right] \) is not the perpendicular Laplacian, owing to commutator corrections associated with position dependence, which arise whenever there are two or more factors of \( \partial_\rho \). The commutator correction is more explicit in the position-dependent Hamiltonian action expression, i.e.,

\[
\hat{H} \phi^E_{\rho \pm} = E \phi^E_{\rho \pm} + \frac{i \hbar}{2\rho^0} \left( \partial_\rho \psi^E_{\rho \pm} - \frac{\hbar^2}{2m} \left[ \partial^2_\rho, \nabla^2 \right] \right) \phi^E_{\rho \pm}.
\]  

(21)

Note that the final, \( \partial_\rho \) and \( \nabla^2 \) commutator term, vanishes when \( \rho(\vec{x}) \) is constant—e.g., for the dividing surface approach in Sec. II B 2.

In generalizing for wavepacket dynamics, the final step prior to the expansion integration of Eq. (13) is to remove all explicit \( \rho^0 \) and \( E \) dependence from Eq. (21). Note that \( \rho^0 \) depends on \( E \) but is unique for a given \( E \) value. It is essential, however, that \( \rho(\vec{x}) \) be chosen to be the same for all \( E \).

The \( \rho^0 \) term in Eq. (21) can then be removed as before, i.e., via substitution using the spatial integration of Eq. (19). This results in the following bipolar wavepacket evolution equations:

\[
\frac{\partial \psi^E_{\rho \pm}}{\partial t} = \frac{i}{\hbar} \left( \hat{H} \psi^E_{\rho \pm} \pm \frac{1}{2} \left( \partial_\rho \psi^E_{\rho \pm} - \frac{\hbar^2}{2m} \left[ \partial^2_\rho, \nabla^2 \right] \right) \psi^E_{\rho \pm} \right),
\]  

(22)

where

\[
\Psi^E_{\rho \pm}(\vec{x}, t) = \int_{-\infty}^{\infty} \psi^E_{\rho \pm}(\vec{x}(s), t) ds.
\]  

(23)

The prime above now denotes a vector function in the parameter \( s \), rather than an \( x \) spatial derivative. Note that as in Eq. (14), the coupling term in Eq. (22) vanishes in both reactant and product asymptotic limits, provided that the asymptotic reaction directions are properly chosen, as described above.

Equation (23) above is a 1D line integral, taken along a reaction path, \( \vec{x}(s) \), that passes through the given point \( \vec{x} = \vec{x}(0) \) when \( s = 0 \). The reaction path is defined so as to be everywhere tangent to the reaction direction field, \( \hat{\rho}(\vec{x}) \). The parameter \( s \) is the reaction coordinate along the path, equal to the arc length for Cartesian coordinate systems such as those used here, but determined more generally from the form of the gradient. Figure 2(b) indicates several parallel reaction paths for collinear \( \text{H} + \text{H}_2 \).

4. Universality of \( (\Psi_{\rho^+} - \Psi_{\rho^-}) \)

From the discussion above, it is clear that the bipolar wavepacket components \( \psi_{\rho \pm} \) depend on the particular choice of the reaction direction field \( \hat{\rho}(\vec{x}) \). However, consider the spatially integrated difference quantity

\[
\Psi_\Delta = (\Psi_{\rho^+} - \Psi_{\rho^-})
\]  

(24)

that appears in Eq. (22) above. Perhaps remarkably, it can be shown that \( \hat{\rho}(\vec{x}) \) yields the same \( \Psi_\Delta(\vec{x}, t) \) provided that \( \rho^0 = |\vec{p}| \) is constant. It is for this reason that we state that the precise details of the \( \hat{\rho}(\vec{x}) \) field are immaterial.

Perhaps even more surprisingly, it can be shown that

\[
\frac{\partial \Psi_\Delta}{\partial t} = -\frac{i}{\hbar} \hat{H} \Psi_\Delta,
\]  

(25)

i.e., like \( \psi \) itself, \( \Psi_\Delta \) independently satisfies the TDSE. This suggests that a fundamental importance be attributed to \( \Psi_\Delta \) (more so than for \( \psi_{\rho \pm} \)), the significance of which will be discussed in more detail in future papers. Equation (25) also has important numerical ramifications, implying that both \( \psi \) and \( \Psi_\Delta \) can be propagated using standard fixed-grid TDSE methods (Sec. III). At any desired later time, \( \psi_{\rho \pm} \) can then be reconstructed via

\[
\psi_{\rho \pm} = \frac{1}{2} (\psi \pm \partial_\rho \Psi_\Delta).
\]  

(26)

Indeed, one can reconstruct a host of separate \( \psi_{\rho \pm} \) bipolar decompositions for different \( \hat{\rho} \) fields, all from a single \( \psi \) and \( \Psi_\Delta \) propagation.

Equation (25) is obtained by subtracting the \( \pm \) expressions in Eq. (22) and rewriting as

\[
\frac{\partial \psi_{\rho \pm}}{\partial t} = -\frac{i}{\hbar} \left( \hat{H} \psi_{\rho \pm} + [\partial_\rho, \hat{H}] \Psi_\Delta \right) = -\frac{i}{\hbar} \partial_\rho \hat{H} \Psi_\Delta.
\]  

(27)

Taking the line integral over reaction paths on both sides of Eq. (27) then leads directly to Eq. (25).

The universality of \( \Psi_\Delta \), as discussed above, may be proved by taking the line integral over reaction paths on both sides of Eq. (19). Rewriting the result slightly yields

\[
\Phi^E_{\rho \pm} = -\left( \frac{i \hbar}{\rho^0} \right) \phi^E.
\]  

(28)

In the left-hand side of Eq. (28) above, the reaction direction field \( \hat{\rho}(\vec{x}) \) is completely arbitrary, yet the right-hand side is always the same [for fixed, constant \( \rho^0 = |\vec{p}^0(\vec{x})| \)]. Consequently, substituting both sides of Eq. (28) into the expansion integration of Eq. (13) yields \( \Psi_\Delta \) on the left and an expression on the right that is independent of \( \hat{\rho}(\vec{x}) \). Thus, \( \Psi_\Delta \) is universal for all reaction direction fields \( \hat{\rho}(\vec{x}) \), though it does depend on \( \rho^0(E) \), which in turn depends on the incident channel energy \( E^0 \).

Note that the above conclusions apply equally well to the curvilinear momentum vector fields in Sec. II B 3 as to the constant momentum vector fields in Sec. II B 2. For the latter, \( \Psi_{\rho \pm}^{\text{react}} \neq \Psi_{\rho \pm}^{\text{prod}} \) in general, although the equality holds if \( \rho_{\text{react}} = \rho_{\text{prod}} \). Note also that at any given position \( \vec{x} \), the local bipolar decomposition \( \psi_{\rho \pm}(\vec{x}, t) \) for an arbitrary curvilinear \( \hat{\rho}(\vec{x}) \) is identical to that associated with the constant field \( \hat{\rho} = \rho^0 \).
From a numerical perspective, all that is required to propagate \( \psi_{\pm,\pm} \) as described above is a specification of the initial values, \( \psi(0,x) \) and \( \Psi_{\Delta,\pm}(x) \). Without loss of generality, we assume as in Sec. II A that the reaction direction in the reactant valley asymptote points along the \( x \) axis. Then the initial wavepacket is of the form

\[
\psi(0,x) = g(x) \phi_0^E(y),
\]

where \( \phi_0^E(y) \), as discussed, is the channel eigenstate, and \( g(x) \) is a localized 1D wavepacket centered in the reactant valley asymptote, heading toward the interaction region.

More specifically, the function \( g(x) \) should satisfy all of the same properties as does the 1D \( \psi(0,x) \) function in Ref. 5. In particular, this will guarantee perfect reactant asymptotic separation, i.e., Eq. (18). This in turn implies \( \psi_{\pm,\pm}^0 = \psi_0 \), so that the initial \( \Psi_{\Delta,\pm}^0 \) is just the line integral over \( x \) of Eq. (29), i.e.,

\[
\Psi_{\Delta,\pm}^0(x) = G(x) \phi_0^E(y),
\]

with

\[
G(x) = \int_{-\infty}^{\infty} g(x') dx'.
\]

III. COMPUTATIONAL DETAILS

A. Overview

The eventual goal is to use quantum trajectories to propagate bipolar wavepacket components \( \psi_{\pm,\pm} \) “synthetically”—i.e., without \textit{a priori} knowledge of the wave function. Prospects for such calculations, even at high dimensionality, are very favorable provided that the \( \psi_{\pm,\pm} \) are nodeless (or nearly so), as intended. Note that qualitatively, \( \Psi_{\Delta,\pm}(x) \) behaves much like \( \psi(x) \) itself (i.e., can exhibit substantial reflection interference) and is therefore unsuitable for synthetic QTM calculation—even though it is of greater fundamental significance than the \( \psi_{\pm,\pm} \). In practice, therefore, we envision synthetic propagation of the \( \psi_{\pm,\pm} \) via Eq. (22), using either the constant reaction direction fields of Sec. II B 2 or the reaction-path approach of Sec. II B 3. The latter is expected to yield smoother \( \psi_{\pm,\pm} \) components, but requires explicit calculation of the final commutator correction term. For smoothly varying \( \hat{p} \) fields, however (which should be adopted whenever possible, even when the minimum energy path \textit{per se} is erratic), this term is quite small. In any case, ignoring this term altogether gives rise to an exact propagation scheme for \( \psi \) with similarly well-behaved \( \psi_{\pm,\pm} \) components, so in practice, this may be the simplest and most effective route vis-à-vis numerical implementation. Note that apart from standard spatial derivatives already implemented in traditional QTM applications, the only new numerical operation is the line integration which—being a 1D operation—does not become the bottleneck for large system dimensionality. Additional discussion of the numerical integration procedure may be found in Ref. 5.

The goal of the present paper is quite different, however; as in Ref. 5, we seek here merely to demonstrate that the \( \psi_{\pm,\pm} \) (and \( \phi_{\pm,\pm}^E \)) components determined as per Sec. II are indeed well behaved for realistic multidimensional systems. To this end, it is far more effective to obtain \( \psi_{\pm,\pm} \) by first computing \( \psi \) and \( \Psi_{\Delta} \), as discussed in Sec. II B 4, using standard fixed-grid TDSE propagation methods—specifically, a variant of the Crank–Nicholson algorithm, discussed below. Such methods do not scale well with increasing system dimensionality but are very well suited to the present purpose, for which only 2D systems are considered. For the \( \phi_{\pm,\pm}^E \), the exact solution \( \phi^E \) is first computed using standard sinc-function discrete variable representation (DVR) techniques, and then \( \phi_{\pm,\pm}^E \) is obtained using Eq. (16).

B. Multidimensional Crank–Nicholson propagation scheme

For 1D systems, an extremely efficient algorithm for TDSE propagation is the Cayley version of Crank–Nicholson, which is stable, unitary, and second-order accurate in space and time. This method allows for extremely large time-step sizes \( \Delta \) to be used—on the order of hundreds of a.u., as compared to the \( \Delta=0.1 \) value required by the first-order propagation method used in Ref. 5 for the 1D examples considered therein. Difficulties arise when applying the basic Crank–Nicholson algorithm for multidimensional systems, however—namely, that the central processing unit (CPU) effort per time step is proportional to \( N^2 \) rather than \( N \), where \( N \) is the number of grid points. A standard fix is the so-called alternating-direction implicit method—an \( O(N) \) split-operator approach, which in its standard implementation, is neither unitary nor applicable to nonseparable Hamiltonians.

Instead, we use a different split-operator scheme to remedy the above defects. For notational convenience, we assume a 2D Eq. (2) Hamiltonian, \( \hat{H} = \hat{T}_x + \hat{T}_y + V(x,y) \), and discretized time but not space. If \( \psi(k)(x,y) \) represents the wave function (or \( \Psi_{\Delta}(x,y) \)) at the \( k \)th time step, then the wave function at the \((k+1)\)th time step is given by

\[
\psi(k+1) = \left[ 1 + \frac{i}{\hbar} \left( \frac{\Delta}{2} \hat{T}_x \right) \right]^{-1} \frac{1 - \frac{i}{\hbar} \left( \frac{\Delta}{4} \hat{V} \right)}{1 + \frac{i}{\hbar} \left( \frac{\Delta}{4} \hat{V} \right)} \left[ 1 + \frac{i}{\hbar} \left( \frac{\Delta}{2} \hat{T}_y \right) \right]^{-1} \times \left[ 1 - \frac{i}{\hbar} \left( \frac{\Delta}{2} \hat{T}_y \right) \right]^{-1} \left[ 1 - \frac{i}{\hbar} \left( \frac{\Delta}{4} \hat{V} \right) \right] \psi(k).
\]

Numerically, the wave functions and operators in Eq. (31) above are implemented in the standard manner using Eulerian fixed-grid discretization of the spatial DOFs, \( x \) and \( y \), with uniform grid spacings \( \Delta x \) and \( \Delta y \), respectively. The \( \hat{T}_{x,y} \) spatial derivatives are represented using symmetric second-order finite difference. Each square-bracketed quantity in Eq. (31) above can be regarded as a separate sparse matrix.

\[
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\]
C. Initial conditions

For all of the calculations performed in this paper, the initial wavepackets \( \psi^0(x,y) \) are of the Eq. (29) form, with \( g(x) \) taken to be Gaussian:

\[
g(x) = \left( \frac{2\gamma}{\pi} \right)^{1/4} \exp[-\gamma(x-x_0)^2] \exp \left( \frac{ip_0x}{\hbar} \right). \tag{32}
\]

The initial \( \Psi_{\Delta}(x,y) \) is then determined via analytic integration of Eq. (32), which yields

\[
G(x) = \left( \frac{\pi}{2\gamma} \right)^{1/4} \sqrt{\frac{1}{2}} \exp \left( \frac{-p_0^2}{4\gamma^2} \right) \exp \left[ \frac{ip_0 x_0}{\hbar} \right] \times \text{erfc} \left[ -\frac{\sqrt{\gamma(x-x_0)} + \frac{i}{2\sqrt{\gamma}} p_0}{\sqrt{2}} \right]. \tag{33}
\]

The incident channel state \( \phi^0(y) \) is always taken to be the ground state of the reagent Hamiltonian \( \hat{H}^{\text{reac}} \)—i.e., \( n=0 \). For all but the collinear \( \text{H}^++\text{H}_2 \) application, \( \hat{H}^{\text{reac}} \) is a harmonic oscillator, and so \( \phi^0(y) \) and \( E_0^0 \) are known analytically. For collinear \( \text{H}^++\text{H}_2 \), a different procedure is used. A propagation identical to Eq. (31) is performed, except that (1) the \( \hat{T}_x \) contribution is ignored, (2) time is replaced with imaginary time, (3) \( V(x,y) \) is evaluated at the extremal grid value for \( x \) in the reactant valley asymptote, and (4) the initial \( \psi^0(y) \) is uniform. After a sufficiently large number of time steps, the resultant \( \psi^0(y) \) converges to \( \phi^0(y) \) in a way that is numerically consistent with the grid and time-step parameters used for the final 2D propagation.

For all of the 2D calculations performed here, the numerical parameters \( \Delta, \Delta_t, \Delta_y, x_{\text{min}} \) (i.e., left grid edge), \( x_{\text{max}} \), \( y_{\text{min}} \), \( y_{\text{max}} \), and \( x_0 \) are chosen so as to converge the final reflection and transmission probabilities [i.e., integral of final \( |\psi(x,y)|^2 \) over reactant and product valley asymptotes, respectively] to around \( 10^{-5} \) or \( 10^{-6} \). Values for \( \gamma \) and \( p_0 \) are chosen to satisfy certain additional conditions, as discussed in Ref. 5. The mass is taken to be \( m=2000 \) a.u. in all but the collinear \( \text{H}^++\text{H}_2 \) application, for which mass weighting yields \( m=\frac{3}{2} m_H \), where \( m_H=1837.1527 \) a.u. is the mass of the hydrogen atom.

Computer animations (.wmv file format) for all of the unipolar and bipolar multidimensional wavepacket dynamics calculations presented in this paper are available as EPAPS supplements and by direct request from the author.

IV. RESULTS

We have applied the methods described above to a variety of model 2D applications and to the 2D collinear \( \text{H}^++\text{H}_2 \) system. The model systems chosen are useful because they present a variety of different dynamical effects that can be examined in isolation. All of these factors come into play for the more realistic collinear \( \text{H}^++\text{H}_2 \) application, for which the present work provides the first indication of the viability of an exact QTM treatment.

A. Uncoupled Eckart+harmonic oscillator system

The uncoupled 2D Eckart+harmonic oscillator system, i.e.,

\[ V(x,y) = V_0 \text{sech}(\alpha x)^2 + \frac{1}{2} k_0 y^2, \tag{34} \]

was chosen as a test case because the correct dynamical behavior is known a priori. Specifically, at all times \( t, \psi(x,y,t) \) is a separable product of the \( x \) and \( y \) functions, as follows:

\[ \psi(x,y,t) = \psi_x(x,t) \left( \frac{2\gamma}{\pi} \right)^{1/4} \exp[-\gamma y^2] \exp[-(i/\hbar)E_0^0], \tag{35} \]

where \( \psi_x(x,t) \) is just the 1D wavepacket associated with the \( x \) Eckart barrier system alone (as in Ref. 5), \( \gamma = \sqrt{k_0 m/2 \hbar} \), and \( E_0^0 = (\hbar/2) \sqrt{k_0}/m \). Similar separability characterizes \( \Psi_{\Delta}(x,y,t) \) and \( \psi_x(x,y,t) \). Note that \( \psi_x(x,y) = \delta \), with the reaction path being \( y=0 \) and the reaction profile just the Eckart barrier itself.

This system was also chosen as a "calibration" run to obtain reasonable convergence parameters for the related bottleneck potential system (Sec. IV B). The system parameters used are \( V_0 = 0.004, \alpha = 1.0, k_0 = 0.005 \) 12, and \( m = 2000 \), in a.u. The initial \( \psi_x(x,x_0) = g(x) \) Gaussian parameters are provided in column 2 of Table I. The resultant perpendicular energy is \( E_0^0 = 0.0008 \) a.u., whereas the \( p^2 \) value corresponds to an incident kinetic energy of 0.006 a.u., which is substantially above the Eckart barrier energy \( V_0 \).

Exploiting separability of the Hamiltonian, convergence parameters were obtained from separate Cayley Crank–Nicholson calculations for Eckart \( (x) \) and harmonic oscillator \( (y) \) systems. Convergence for the former, 1D wavepacket dynamics calculation is achieved as per Ref. 5. Convergence for the \( \hat{H}_y \) calculation is signaled by numerical stationarity of the computed \( |\psi^0(y,t)|^2 \) density over time. The two 1D calculations led to convergence parameter values as reported in column 2 of Table I, with \( \Delta = 50 \) a.u. being the smaller of the two time-step sizes. The final time \( \tau_{\text{max}} \), corresponding to reasonable reactant and product separation, was determined from the \( \hat{H}_y \) calculation. Only 160 total time steps were required owing to the remarkably large \( \Delta \) value required of the Cayley Crank–Nicholson algorithm. This is typical for all calculations reported in this paper, for which the .wmv files never required more than one time step per animation frame; indeed, in some cases, we were obliged to reduce \( \Delta \) in order to obtain smoother animations.

As the first test for the multidimensional wavepacket propagation codes, the above parameter values were also used in a full 2D calculation—as per Sec. III B but using \( \hat{H}_x + \hat{H}_y \) as well as \( \hat{T}_x + \hat{T}_y + \hat{V} \) split-operator schemes (numerical differences between the two were negligible). The resulting wavepacket dynamics were stable, accurate, and consistent with Eq. (35) to a level of numerical error commensurate with the above 1D calculations, as expected. The total CPU time required on a 2.60 GHz Pentium CPU was less than 1 s.

B. Bottleneck potential system

The 2D bottleneck potential system is similar to the uncoupled Eckart+harmonic oscillator system, except that the
TABLE I. Parameters used for all multidimensional bipolar wavepacket scattering calculations. All units are a.u., except for the last row, the required CPU time in seconds on a 2.60 GHz Pentium CPU. Final reflection and transmission probabilities are converged to around $10^{-5}$ or $10^{-6}$.

| Quantity and symbol | Uncoupled Eckart+harmonic oscillator | Bottleneck potential | Curvilinear Eckart+harmonic oscillator | Collinear H+H$_2$ |
|---------------------|-------------------------------------|----------------------|---------------------------------------|------------------|
| Initial Gaussian    | 1                                   | 1                    | 1                                     | 0.75             |
| Width $\gamma$      | 1                                   | 1                    | 1                                     | 0.75             |
| Center $x_0$        | $-6.5$                              | $-6.5$               | $-8.2$                                | +9.0             |
| Momentum $p_0$       | 4.898 98                            | 4.898 98             | 4.898 98                              | $-5.750$ 54      |
| $x$ parameters       |                                     |                      |                                       |                  |
| Grid size $N_x$     | 111                                 | 111                  | 301                                   | 301              |
| Left edge $x_{\text{min}}$ | $-11.0$                           | $-11.0$             | $-20.0$                               | 1.33             |
| Right edge $x_{\text{max}}$ | 13.0                           | 13.0                 | 0                                     | 23.0             |
| Grid spacing $\Delta x$ | 0.218 182                        | 0.218 182            | 0.066 667                             | 0.072 233        |
| $y$ parameters       |                                     |                      |                                       |                  |
| Grid size $N_y$     | 30                                  | 30                   | 361                                   | 301              |
| Bottom edge $y_{\text{min}}$ | $-1.677$ 05                    | $-1.677$ 05                  | 0                                     | 0.43             |
| Top edge $y_{\text{max}}$ | 1.677 05                          | 1.677 05             | 24                                    | 22.1             |
| Grid spacing $\Delta y$ | 0.115 659                        | 0.115 659            | 0.066 667                             | 0.072 233        |
| Time parameters      |                                     |                      |                                       |                  |
| Time step $\Delta$  | 50                                  | 50                   | 50                                    | 10               |
| Maximum time $t_{\text{max}}$ | 8 000                           | 8 000                 | 6 350                                 | 4 600            |
| No. of steps $t_{\text{max}}/\Delta$ | 160                               | 160                   | 127                                   | 460              |
| CPU time (s)         | $<1$                                | $<1$                 | 16                                    | 58               |

y harmonic oscillator constant, $k=k(x)$, is allowed to vary with $x$, thus introducing nontrivial coupling. The general bottleneck potential is given by

$$V(x,y) = V_0 \text{sech}(ax)^2 + \frac{1}{2}k(x)y^2,$$  \hspace{1cm} (36)

where for the present paper, we take $k(x)$ to be of the form

$$k(x) = k_0[1 + C \text{ sech}(ax)^2].$$  \hspace{1cm} (37)

In Eq. (37) above, the unitless constant $C$ measures the extent of coupling, with the choice $C=0$ restoring the uncoupled Eckart+harmonic oscillator system. We shall use $C=2.00$, representing a rather large amount of coupling, with all other system parameter values identical to those used in Sec. IV A.

The bottleneck potential model is based on the natural collision coordinate reaction-path Hamiltonian approach of Marcus.\textsuperscript{30} A more general version includes curvature effects of the underlying reaction path (in Jacobi coordinates), which are ignored here. The reaction path and profile are identical to those in Sec. IV A. However, “bottleneck” narrowing near the transition state increases the perpendicular zero point energy [due to increased $k(x)$ values], which effectively raises the activation barrier height and reduces the resultant transmission/reaction probability. The 2D bottleneck potential, as well as higher-dimensional forms, have been considered previously in QTM treatments,\textsuperscript{22,30,32} albeit with a slightly different $k(x)$ functional form and with much smaller, negative coupling ($C=-0.15$), resulting in (slight) barrier lowering rather than raising.

All initial Gaussian and Crank–Nicholson convergence parameters are also identical to those used in Sec. IV A, as indicated in column 3 of Table I. In addition to reduced transmission/enhanced reflection, the dynamical coupling and large initial incident kinetic energy in $x$ now allow for inelastic transitions to several excited perpendicular harmonic oscillator channels in both the transmitted and reflected waves, at least in principle. This calculation therefore serves as a useful test of the quality of the resultant $\psi_\pm(x,y,t)$ bipolar wavepacket components vis-à-vis the desired criteria as discussed in Sec. II and in Ref. 5.

Figure 3 shows the resultant wavepacket dynamics for $\psi_\pm(x,y,t)$ at four representative time slices, including $t=t_0=0$ and $t=t_f=t_{\text{max}}$. The bipolar decomposition has been carefully inspected at all intermediate times to ensure that Fig. 3 captures all of the relevant dynamics. The plots are rescaled over time for visual clarity, although at any given time, the $\psi_+$ and $\psi_-^\star$ plots are correctly scaled relative to each other. Note the sharp “slices” or “gouges” evident in the left edge of both $\psi_\pm$ components in Fig. 3(c). It has been established that these are not present in the true $\psi_\pm$ functions but constitute a numerical artifact due to the calculation of $\psi_\pm$ using $\psi$ and $\Psi_\Delta$, which exhibit reflective interference/nodes. If Eq. (14) were used directly, as in a synthetic QTM propagation, these glitches would disappear, and the resultant computed $\psi_\pm$ would (correctly) be smooth throughout. Similar comments characterize the other wavepacket dynamics plots of this paper. A more detailed discussion of this issue will be presented in an upcoming paper.

The computed $\psi_\pm(x,y,t)$ are found to be well behaved and, in particular, seem to exhibit perfect or nearly perfect asymptotic separation despite the fact that inelastic transitions are evident. The latter are suggested by the transmitted $\psi_+$ wavepacket at $t=t_{\text{max}}$, which appears to be just beginning to separate into its constituent channel components, each of which is propagating at a different mean translational velocity. Also, $\psi_-$ at $t=t_{\text{max}}$ has a very small peak following just
behind the main peak, which presumably corresponds to the first excited perpendicular channel. These features can be seen in Fig. 3.

Although the above features at \( t = t_{\text{max}} \) would also be evident in a plot of \( \psi \) itself (not indicated here, though an animation file is available)\(^{42} \) at intermediate times, the latter is complicated by interference fringes, not found in \( \psi_n \). Following the notation of Ref. 5, both type I and type II interferences are observed, meaning that \( \psi_n(x,y,t) \) leaves behind a “spur,” \(^{42} \) evident in Fig. 3(c) \) which “heals” nodes in the reflected wavepacket, and eventually dissipates away over time as the nodes are healed. As a result, the \( \psi_n(x,y,t) \) are both smooth and reflection-interference-free at all times. An additional feature of the \( \psi_n(x,y,t) \) dynamics is the narrowing of the wavepacket in the perpendicular direction as the transition state is traversed, due to the bottleneck effect discussed above \([\text{Fig. 3(b)}]\). We also note that bottleneck narrowing does indeed lead to enhanced total reflection probability, relative to the corresponding uncoupled calculation in Sec. IV A, as expected.

To ensure that there is nothing special about a 2D calculation, we have also performed a 3D bottleneck potential calculation, with two perpendicular modes identical to that described above, and identical numerical parameters. The total CPU time required to perform the propagation was a few
minutes. The resultant $\psi_\pm(x,y,z,t)$ are similar to the 2D results described above, and equally well behaved.

C. Curvilinear Eckart+harmonic oscillator system

A major goal of this paper is to develop a QTM technique that may be applied directly to systems with curvilinear reaction paths in mass-weighted Jacobi coordinates. Such a development is vital for exact QTM treatments that circumvent the approximations inherent in the natural collision coordinate reaction-path Hamiltonian approach. In particular, since curvature effects are ignored in the reaction-path Hamiltonians of Secs. IV A and IV B, in this section we explore a curvilinear version of the Eckart+harmonic oscillator system in Sec. IV A. Bottleneck narrowing in the perpendicular direction is deliberately not included, in order that we may consider in isolation the two dynamical factors that contribute to inelastic transitions, i.e., perpendicular narrowing/widening (Sec. IV B) versus reaction-path curvature (this subsection).

For simplicity, a 90° elbow-bend primary reaction path is adopted, corresponding to a collinear light-heavy-light three-atom reactive scattering system. The bend in the primary reaction path is a quarter circle, with radius $R$; this is joined to horizontal and vertical straight lines, denoting minima for the reactant and product valley asymptotes, respectively. As in the previous examples, the reaction profile is a symmetric Eckart barrier potential; however, to avoid potential surface discontinuities, this contribution must now be reduced with increasing perpendicular distance from the reaction path, $q$, via the scale factor $(1-q^2/R^2)$. The perpendicular, harmonic oscillator contribution to the potential is identical to that in Sec. IV A, however.

The curvilinear Eckart+harmonic oscillator potential surface is therefore given by

$$V(x,y) = \left[1 - q(x,y)^2/R^2\right]V_0 \text{sech}[\alpha s(x,y)]^2$$

$$+ (1/2)\hbar^2\omega^2 q(x,y)^2,$$

where $q(x,y)$ is the shortest distance to the primary reaction path from the point $(x,y)$, and $\vec{V} q$ points along the contours of the reaction coordinate, $s(x,y)$. A contour plot and the primary reaction path are presented in Fig. 4.

The reaction direction points along the contours of $q(x,y)$ or the gradient of $s(x,y)$, i.e., $\vec{p}(x,y) = \vec{\nabla} s(x,y)/|\vec{\nabla} s(x,y)|$. The function $s(x,y)$ is further defined by the following:

1. Along the dividing surface, $x=-y$, $s(x,y)$ is zero.
2. Along the primary reaction path, $q=0$, $s(x,y)$ is equal to the arc length.

The arc-length property is also true everywhere in the reactant and product valley asymptotes, but off of the primary reaction path in the bend region, $s(x,y)$ is rescaled relative to the true arc length, so that the same “distance” is covered by all 90° bend segments. Finally, to ensure that the numerical grid has sufficient extent in the perpendicular direction, the top left corner of the bend region (i.e., the center of the quarter circle) is positioned at $[x=-(R+y_{\text{unc}}), y=(R+y_{\text{unc}})]$, where $y_{\text{unc}}=1.677$ a.u. is the $y$ value from Sec. IV A. The other system parameters are chosen as follows: $V_0 = 0.006$, $\alpha=1.0$, $k_0=0.005$ 12, $R=6.0 - y_{\text{unc}}$, and $m=2000$, in a.u.

Wavepacket propagation calculations were performed for the curvilinear Eckart+harmonic oscillator system described above, using a Gaussian initial wavepacket similar to that in Secs. IV A and IV B but centered a bit further back in the reactant valley (Table I, column 4). Initially, we used similar Crank–Nicholson parameters as well; however, these were found to lead to (slight) unphysical reflections from the grid edges, particularly for the $\Psi_\Delta$ propagation. In order to be sure of our dynamical interpretation of the $\psi_\pm$ bipolar wavepacket component densities, and not just the integrated reflection and transmission probabilities, a comprehensive convergence test was performed for the former, leading to the remaining parameter values as presented in column 4 of Table I. Though the number of grid points is greatly increased relative to the previous calculations, a similarly large $\Delta=50$ a.u. value was found to be sufficient, leading to a propagation with just 127 total time steps. The resultant CPU time was only 16 s.

Figure 5 shows the resultant wavepacket dynamics for $\psi_\pm(x,y,t)$ at four representative time slices, including $t_0 = 0$ and $t=t_f=t_{\text{max}}$. As in the previous calculations, the computed $\psi_\pm(x,y,t)$ are well behaved—apart from the inconsequential glitches (Sec. IV B) evident in Fig. 5(b)—and exhibit perfect asymptotic separation. There is both substantial reflection and transmission, with a transient $\psi_\pm$ spur [Fig. 5(b)], as in the other examples. Note that the system and initial Gaussian parameters are such as to allow inelastic transitions to the same excited channels as for the bottleneck potential—indeed, such transitions are evident in the figure. Here, though, they manifest in a completely different manner than in Sec. IV B, via a snaking motion of both the reflected and transmitted wavepackets. The different behaviors are perhaps not surprising, given that the dynamical source of the inelastic transitions is completely different in each case, as discussed above. Transmitted wavepacket snaking is clearly visible in the figure by comparing Fig. 5(c) to Fig. 5(d).
D. Collinear H+H₂ system

The 2D collinear H+H₂ system is a standard benchmark problem that is commonly used for evaluating theoretical reactive scattering methods, as applied to "realistic" molecular systems. It has particular relevance as a benchmark for QTMs in the sense that to date, no exact QTM calculations for this system have yet been achieved, owing to reflection interference. However, approximate QTM treatments on similar systems can be found in the literature.

The collinear H+H₂ system has further interest for this paper because it combines together all of the various dynamical coupling effects treated individually in the previous examples, i.e., curvature, bottleneck narrowing/widening, inelastic transitions, snaking, etc. As in previous computational work, the Liu, Siegbahn, Truhlar, and Horowitz potential energy surface (PES) is used here. This PES exhibits a barrier height of ~0.016 hartree. Ordinary mass-weighted Jacobi coordinates are used, in terms of which the reaction path undergoes a 120° kinematic bend from the reactant to the product valley. We take the former to lie along the x coordinate, as in the other examples, but the initial wavepacket is now incident from the right.

In essence, the reaction direction at any point (x, y) is obtained by translating the primary reaction path up or down along the dividing surface. This implies that the reaction direction, \( \hat{\rho} = (\cos \theta, \sin \theta) \), depends only on the perpendicular distance from the dividing surface, which is defined by \( y = x/\sqrt{3} \). Instead of using the minimum energy path as the primary reaction path, a smoother curve is used—although the precise choice is not expected to be very important, as discussed previously. Specifically, we use

\[ y = \frac{x}{\sqrt{3}} \]

FIG. 5. (Color online) Wavepacket dynamics for the curvilinear Eckart+harmonic oscillator system described in Sec. IV C. Each plot represents a snapshot for a specific time \( t \), as listed. Each plot consists of two surfaces, indicating bipolar component wavepacket densities as a function of position; see Fig. 3 caption for explanation. In (b), the \( \psi_+ (x,y) \) peak has just passed that of \( \psi_- (x,y) \). Snaking of the transmitted wavepacket can be observed by comparing the upper surfaces in (c) and (d). In (c), the \( \psi_- (x,y) \) peak extends beyond the range of the plot owing to a time-dependent plot rescaling that has been introduced here (and in the other figures) for improved visual clarity at later times. At any given time, the \( \rho_+ (x,y) \) and \( \rho_- (x,y) \) plots are rendered to scale relative to each other.
\[ \theta(x, y) = \frac{\pi}{3} \left[ 2 - \tanh \left( -\frac{\beta}{2} (x - \sqrt{y}) \right) \right], \]  
(39)

with \( \beta = 2.5 \). The corresponding reaction paths are presented in Fig. 2(b). Note that the above scheme for selecting \( \theta \) is also particularly well suited to heavy-light-heavy three-atom systems, for which tunneling and the extreme kinematic bend angle can lead to substantial reactive crossing of the dividing surface far in advance of the transition state.

Although several wavepacket calculations were performed for the collinear \( \text{H} + \text{H}_2 \) system, displaying all of the dynamical effects described previously, we focus here in a single calculation for a rather low-energy wavepacket, exhibiting little, if any, inelastic transition. Since the resultant transmitted and reflected wavepackets should occupy only the ground perpendicular channel for products and reactants, respectively, this calculation serves as a good numerical test of perpendicular stationarity at large times.

As described in column 5 of Table I, the initial wavepacket is similar to those used for the previous calculations, but has a higher incident kinetic energy of 0.009 hartree. This is less than the reaction barrier; nevertheless, the initial momentum spread, bottleneck widening, and perhaps tunneling conspire to achieve a very substantial transmission/reaction probability. The \( E^0 \) value for the reactant and product channel ground states is found via the procedure described in Sec. III C to be around 0.013 hartree. The first excited state is at \( E^1_y \approx -0.029 \) hartree—beyond the range of relevant initial momentum values considered.

The Crank–Nicholson convergence parameters are also presented in column 5 of Table I and found to be comparable to those in Sec. IV C, except for the greatly reduced mean-step size of \( \Delta = 10 \) a.u. In part, the reduced time-step size can be attributed to the higher velocities, which also account for the significantly smaller \( t_{\text{max}} \) value. However, the primary reason for the \( \Delta \) reduction—and the main difference from the Sec. IV C calculation—are the enormous potential energy values found in the physically unimportant region where \( x \) is small and \( y \) is large. For \( \Delta = 20 \) a.u. or larger, unphysical numerical instabilities form in these regions and grow exponentially—even when the maximum potential energy value is capped at \( E_{\text{cut}} = 0.25 \) hartree. It is likely that smaller \( E_{\text{cut}} \) values will allow substantially larger time-step sizes than \( \Delta = 10 \) a.u. to be used without significantly reducing the accuracy. However, as the entire \( \Delta = 10 \) a.u. calculation still only required less than 1 min of CPU time—and is as well converged as for the previous examples, with no indication of numerical instability—we did not bother to explore this conjecture.

Figure 6 shows the resultant bipolar wavepacket dynamics for \( \psi_{-}(x, y, t) \) at four representative time slices. At the two intermediate times, the unipolar density plots for \( \psi(x, y, t) \) itself are also presented. Dynamical features are similar to what have been observed and discussed for the previous systems. Note the highly pronounced \( \psi(x, y, t) \) interference in Fig. 6(e); this comes about because the corresponding \( \psi_{-}(x, y, t) \) densities [Fig. 6(b)]—though themselves very well behaved—are nearly identical in this region. Less obvious from the figure but very clear in the animation is the fact that there is no longer any indication of inelastic transitions. Indeed, the perpendicular dynamics at large times appears to be completely stationary and stable, as desired.

A time-independent, multidimensional stationary state calculation was also performed for the collinear \( \text{H} + \text{H}_2 \) system in order to assess the behavior of the resultant \( \phi^E_{\pm}(x, y) \) decomposition. The reaction-path approach of Sec. II B 3 was used, with the reaction direction defined by Eq. (39), as for the wavepacket calculation. The incident kinetic energy and momentum values, i.e., 0.009 hartree and \( p_x^0 = -5.750 \) 54 a.u., also correspond to those of the wavepacket calculation. At this energy, only the ground state is energetically open in both the reactant and product channels, i.e., inelastic transitions are forbidden. The stationary eigenstate solution \( \phi^E \) and corresponding bipolar components \( \phi^E_{\pm} \) were obtained as per the discussion at the end of Sec. III A; note that Eq. (16) is still valid even for position-dependent \( p(x) \) fields, as can easily be verified by combining Eqs. (1) and (19).

The stationary state results are presented in Fig. 7. As expected, the \( \phi^E_{\pm}(x, y) \) densities are smooth (nonoscillatory) and well behaved in both asymptotes, whereas \( |\phi^E_{\pm}(x, y)|^2 \) exhibits oscillatory interference in the reactant valley asymptote [right side of Fig. 7(b)]. This interference is fairly pronounced, even though the \( |\phi^E_{\pm}(x, y)|^2 \) reflection contribution in this region is so small that it is difficult to make out in the plot [right side of Fig. 7(a) bottom]. Such behavior has been observed previously and is essentially due to the square-root relationship between amplitudes and densities. Magnification of the \( |\phi^E_{\pm}(x, y)|^2 \) plot does reveal that this density goes to zero in the product asymptote, as required. The \( |\phi^E_{\pm}(x, y)|^2 \) density appears to be nearly symmetric, consistent with the near-complete transmission/reaction exhibited by this particular solution \( \phi^E \). We note that some variation of the reaction direction field, away from Eq. (39), was also applied in order to determine the resultant effect on the \( \phi^E_{\pm} \) densities. These were found to be fairly insensitive to such variation, which in any case did not change the basic qualitative properties, as discussed above.

V. SUMMARY AND CONCLUSIONS

The primary goal of this paper has been to generalize the bipolar methodologies—developed in the previous five papers for 1D systems—in a manner suitable for application to realistic, multidimensional molecular systems. Although no QTM calculations are performed here, the aim is to demonstrate that such a calculation would be feasible, and moreover, could be applied to exact quantum Hamiltonians using any reduced configuration space or coordinate system of interest. In particular, this requires that that the method easily accommodates curvilinear reaction paths and that the bipolar components, if not perfectly asymptotically separate, satisfy the other important properties discussed in Sec. II C of Ref. 5—notably, a lack of interference nodes. For the full promise of QTMs to be realized, it is also crucial that the numerical algorithm scale well with system dimensionality.
The results as presented here are very favorable on all counts described above. The prognosis is very positive vis-à-vis the likelihood that bipolar QTMs will be useful for performing exact quantum wavepacket dynamics calculations for large multidimensional systems. That is not to say that they will be universally applicable to all such problems; as discussed below, there will certainly be situations where the bipolar wavepacket method as presented here is expected to fail. Moreover—like all stationary state methods—the bipolar version will never be feasible for very large systems.
owing to the fact that stationary states are delocalized over a many-dimensional space.

From both a theoretical and practical standpoint, a key premise of the present approach is that a bipolar decomposition—i.e., only two components—is necessary, no matter how large the system dimensionality. Ultimately, this hinges on the chemical dynamics (and thermodynamical) notion that a single reaction coordinate is needed to monitor the “extent of reaction,” no matter how complicated the process, or how many molecular species are involved. This picture works well for bimolecular exchange reactions—even with intermediates if the reaction steps are sequential—provided overall translation and rotation are not explicitly considered, as is often the case. In such situations, it is completely natural and desirable to associate with every point in configuration space a “reaction direction” $\hat{r}(\vec{x})$—which is really nothing but the gradient of the reaction coordinate. The two bipolar components, $+$ and $-$, then represent forward and reverse reaction contributions.

To be of practical utility, $\hat{r}(\vec{x})$ must be allowed to vary through space—either smoothly (Sec. II B 3) or discontinuously (Sec. II B 2). Despite complications that this lends to some of the dynamical equations (none of which pose a serious practical drawback, as per Sec. III A), it is a compelling aspect of this theory that the precise details of this variation are unimportant in the sense described in Sec. II B 4. This depends on the fact that the asymptotic reaction directions are known a priori, and can be thought of as the directions in which the coupling ($\Psi_\Delta$) term vanishes in Eq. (22). This interpretation/definition also establishes a nice link between the present formalism and traditional multichannel scattering theory in that in both cases, it is the interaction potential $(V-V^0)$ that induces transitions, rather than $V$ itself. Note that despite the fact that only Cartesian coordinates are considered here, the theory can be easily extended to any non-Cartesian coordinate system, as the kinetic energy operator automatically provides the necessary distance metric.

For three or more reactant or product molecules (as in three-body formation or collision-induced dissociation), the reaction coordinate idea breaks down somewhat. In particular, in one or both asymptotes, the reaction direction as determined by the condition described above is no longer unique, but corresponds to a continuous range of possibilities. Actually, a similar situation arises for bimolecular systems if rotational coordinates are retained, as in the more physics-oriented treatments of scattering. In such cases, one simple strategy would be to employ a “multisurface” theory over partial waves, following a procedure analogous to that in Refs. 4 and 5 (as was also suggested for dealing with interchannel interference in Sec. II A 2). However, we will also explore some ideas for implementing bipolar wavepacket dynamics directly on the full rovibrational configuration space, starting with 3D scattering of a single particle off of a central force potential. Note that the above situation is to be contrasted with that of multiple product arrangements, or more generally, of parallel reaction pathways. Although the latter case may give rise to a measure-zero set of reaction paths that split or fork (much like separatrices), at all other points in configuration space, the general reaction direction is unambiguous. The bipolar methodology of this paper should thus be readily applicable as is to parallel reaction systems.

The most important area for future work is obviously the synthetic QTM propagation of bipolar wavepackets; a first

FIG. 7. (Color online) Wave densities as a function of position for right-incident stationary state of the collinear H+H$_2$ system with incident kinetic energy of 0.009 hartree: (a) bipolar component wave densities, $\rho^\pm(x,y)=|\phi^\pm(x,y)|^2$ (upper surface) and $\rho^\mp(x,y)$ (lower surface); (b) unipolar density $\rho(x,y)$. Visual perspective is shifted, so that one is peering straight down the dividing surface. The $\rho^\pm(x,y)$ magnitudes are quite small in the reactant valley asymptote—implying little reflection but enough to induce substantial $\rho^\mp(x,y)$ interference oscillations in the right side of (b).
publication on this subject will be submitted in the near future. For reasons discussed in Sec. III A, the scaling of computational effort with system dimensionality is expected to be excellent—certainly on par with other QTM s that have been applied to model systems with up to 200 DOFs. In certain situations, however, poor dimensional scaling is unavoidable—e.g., weakly bound clusters, with vibrational states delocalized over $N!$ equivalent potential well minima. The multidimensional synthetic bipolar QTM approach may also not work well for initial wavepackets that occupy a single excited reactant channel $n>0$, as these will necessarily exhibit nodes in the perpendicular coordinates. More generally, if the asymptotic channel distribution is highly vibrationally excited—as might be the case, for example, for the products of a highly exothermic reaction—the resultant perpendicular interference might be problematic for quantum trajectories.

On the other hand, interchannel interference in the reaction direction does not appear to be problematic at all—at least not for any examples considered thus far, which include a number in addition to those discussed explicitly in Sec. IV—nor does kinematic bending of the reaction path appear to pose any difficulty, so the method (at least the reaction-path approach of Sec. II B 3) should be able to handle any combination of fragment masses, e.g., light-heavy-light, heavy-light-heavy, etc., even with substantial tunneling.

In addition to the future work ideas already discussed, several other avenues will also be explored. In particular, the dividing surface approach of Sec. II B 2 may be further developed—particularly for highly exo- or endothermic reactions where the mean translational kinetic energy is very different between reactants and products. Ideally, this would require propagation of only a single discontinuous bipolar decomposition pair rather than both the reactant and product $\phi_\pm$ over all $t$. Alternatively, a generalization of the reaction-path approach in Sec. II B 3, for which $p^0$ is not presumed constant (the analog of the 1D $V_{eff}$ method for stationary states, discussed in Ref. 6), could also be quite useful. As discussed in Ref. 5, both of these ideas will require some further theoretical developments.

The multidimensional bipolar decomposition for stationary states will also be explored further—in particular, we will generalize the time-dependent relaxation equations of the previous papers in the series to obtain an algorithm for actually computing stationary scattering solutions. For relatively few DOFs, this approach is expected to be very efficient numerically—similar to DVR calculations but without the need for absorbing potentials and absorbing regions. This algorithm per se will not scale effectively to very large dimensionalities. However, we are currently exploring a promising new statistical implementation based on trajectory surface hopping ideas that may indeed allow transmission/reaction probabilities to be computed for very large systems, at least approximately.

ACKNOWLEDGMENTS

This work was supported by a grant from The Welch Foundation (Grant No. D-1523) and by a Small Grant for Exploratory Research from the National Science Foundation (Grant No. CHE-0741321). The author wishes to express gratitude to Alon Faraggi, Yair Goldfarb, Marco Matone, Salvador Miret-Artés, Angel Sanz, Jeremy Schiff, David Tannor, and Robert Wyatt for many interesting discussions. Corey Trahan is especially acknowledged for being the first to write computer codes for the multidimensional stationary state bipolar decomposition, and for creating Fig. 1.

APPENDIX: TIME-DEPENDENT ASPECTS OF STATIONARY STATE BIPOLAR COMPONENTS

For reasons discussed in Sec. II A 1, it is of interest to consider time-dependent aspects of the bipolar decomposition for multidimensional stationary states. Following a procedure analogous to that used for previous Fröman-based decompositions, Eq. (7) can be used to derive the following time-evolution equations:

$$
\frac{\partial \phi^E \pm}{\partial t} = \frac{p^0}{m} \phi^E \pm \frac{i}{\hbar}(E-E^0-V)\phi^E \pm + \frac{i}{\hbar}(E^0-V)\phi^E \mp \\
+ \frac{i\hbar}{2m} \nabla^2 \phi^E \pm \phi^E \mp.
$$

(A1)

The above are relaxation equations, for which the $\phi^E \pm$ correspond to the actual stationary state decomposition (as considered elsewhere in this paper) only in the large time limit. Thus in general, the corresponding $\frac{\partial \rho \pm}{\partial t}$ need not be zero.

Equation (A1) above is the multidimensional generalization of Eq. (3) of Ref. 5. The first term is a convective-canceling term, associated with the presumed constant-velocity motion along the reaction coordinate $x$. Thus, the $x$ velocity is taken to be $v_x = \pm v_x = \pm \frac{p^0}{m}$, so that the $x$ part of the flux divergence is $j_x = \pm \frac{p^0}{m} \rho^0 \pm$. In terms of this substitution, the expression for $\frac{\partial \rho \pm}{\partial t}$ as obtained from Eq. (A1) [compare to Eq. (13) of Ref. 3] becomes

$$
\frac{\partial \rho \pm}{\partial t} = -j_{\pm,x} \frac{\hbar}{m} \text{Im} \left[ \phi^E \pm \nabla^2 \left( \phi^E \pm + \phi^E \mp \right) \right] \\
\pm \frac{2}{\hbar} (V-E^0) \text{Im} \left[ \phi^E \pm \phi^E \mp \right].
$$

(A2)

Next we relate the terms in Eq. (A2) above to corresponding quantities from $\phi^E$ itself. For instance, the flux of $\phi^E$ is $j = (\hbar/m) \text{Im} \left[ \phi^E \nabla \phi^E \right]$, where $j = (j_x,j_y)$, with $j_x = (\hbar/m) \text{Im} \left[ \phi^E \nabla \phi^E \right]$ and $j_y = \frac{\hbar}{m} \text{Im} \left[ \phi^E \nabla \phi^E \right]$. Substituting Eq. (6) into the above,

$$
j_x = \frac{p^0}{m} \text{Im} \left[ i(\phi^E \pm + \phi^E \mp) (\phi^E \pm - \phi^E \mp) \right] = j_{+,x} + j_{-,x}.
$$

(A3)

We have not yet specified $j_{\pm,y}$, though we can nevertheless now demonstrate that

$$
\left( \frac{\partial \rho_x}{\partial t} + \frac{\partial \rho_y}{\partial t} \right) = -j_x - \nabla \cdot j_y = -\nabla \cdot j = \frac{\partial \rho}{\partial t}.
$$

(A4)

Since total probability from $\rho(\vec{r})$ itself is conserved over time, Eq. (A4) implies Eq. (10).
In comparing Eq. (11) with the above equations, it is clear that the desired perpendicular flux field must satisfy $\nabla_y \cdot \mathbf{j}_y = \nabla_y \cdot (\mathbf{j}_{x,y} + \mathbf{j}_{y,-y})$. This in turn implies the vector relation

$$\mathbf{j}_y = \mathbf{j}_{x,y} + \mathbf{j}_{y,-y} \tag{A5}$$

apart from an arbitrary additive (vector) function of $x$, which is taken to be zero. Equation (A5) serves as one of two conditions needed to specify the perpendicular flux fields $\mathbf{j}_{x,y}$ and $\mathbf{j}_{y,-y}$. For the second condition, it is natural to presume that the perpendicular velocity fields for the two bipolar components are equal and opposite, i.e., $\mathbf{v}_{x,y} = \pm \mathbf{v}_y$. Together, these conditions lead to a unique specification of the perpendicular velocity field:

$$\mathbf{v}_y = \frac{p^0 (\mathbf{j}_y)}{m (\mathbf{j}_y)}. \tag{A6}$$

The Eq. (A6) result is a vector relation that holds for any number of DOFs. Note also that both $\mathbf{v}_x$ and $\mathbf{v}_y$ are proportional to $p^0$, so that for all $p^0$ values, the resultant trajectory orbits are identical. This is an important consideration, say, for inelastic scattering applications.

For the stationary solutions themselves (i.e., the large time limit), we have, in addition to all of the above, that $\partial p / \partial t = \partial p_z / \partial t = 0$, and thus, $\nabla \cdot \mathbf{j} = \nabla \cdot \mathbf{j}_x + \nabla \cdot \mathbf{j}_y = 0$. Note that unlike the 1D case, $j_{x,y} \neq 0$ in general, so that $p_{x,y} \neq p_{x,y}$. 

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