

LETTERS TO THE EDITOR

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COMMUNICATIONS

A reactant-product decoupling method for state-to-state reactive scattering

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We propose a general and computationally attractive method that decouples the reactant from the product for state-to-state dynamics calculation in quantum reactive scattering with multiproduct arrangements. In this decoupled approach, the full wave function is divided into the reactant and product components that are connected through absorbing potentials. Using this method, the overall computational effort for state-to-state calculation is essentially the sum of those for the reactant and product arrangements separately. This method solves, to a large extent, the notorious problem of the choice of coordinates in quantum reactive scattering. Although the application of this decoupling method is specifically presented for time-dependent implementation in this communication, the basic methodology should also be applicable in the time-independent application as well. © 1996 American Institute of Physics. [S0021-9606(96)03838-X]

Recently, the time-dependent (TD) wave packet approach has provided new hope for accurate quantum reactive scattering calculations of chemical reactions involving more than three atoms.¹⁻⁷ The TD method is especially efficient when applied to the calculation of initial state-selected but final state summed dynamical quantities such as total reaction probabilities and cross sections. As shown in Ref. 2, one can calculate the total reaction probability by evaluating the reactive flux at a dividing surface and simply uses an absorbing potential to absorb the wave function beyond the transition state region.^{8,9} Thus, one can choose the Jacobi coordinates corresponding to the reactant arrangement to propagate the time-dependent wave function and avoid the need to deal with the wave function entering into the product arrangement space. However, if state-to-state dynamics information such as individual S matrix element or reaction probability is desired, the problem facing the choice of coordinates surfaces again. Although one could still use a single set of Jacobi coordinates to carry out the state-to-state calculation, it can only be done at an immense computational cost as demonstrated in recent state-to-state calculations for $\text{H}_2 + \text{OH}$ reaction.¹⁰⁻¹²

In this communication, we present a general reactant-product decoupling (RPD) approach to treat state-to-state reactive scattering problems in the spirit of divide and conquer. In our approach the wave function is partitioned into reactant and product components that are confined roughly to each arrangement channel space. The reactant and product components are connected through the absorbing potentials but the calculation of each component can be carried out separately in each arrangement channel. Although the idea of wave-function partitioning in reactive scattering is not new, the current approach is significantly different from previous

attempts. In the following, we discuss this method in the time-dependent framework although the basic methodology can be easily implemented in the time-independent framework as well.

Let us first partition the full wave function into the reactant and a sum of all product components:

$$\Psi(t) = \Psi_r(t) + \sum_p \Psi_p(t), \quad (1)$$

where r and p are labels of reactant and product arrangements, respectively. Since we only require the full wave function $\Psi(t)$ to satisfy the TD Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle, \quad (2)$$

there is considerable freedom in choosing the individual component. The main criterion is to confine each component to its corresponding arrangement space. The conventional wisdom is to devise coupled equations that determine all components of the wave function simultaneously.¹³⁻¹⁵ However, the coupled equation approach leads to the full overlap matrix between basis functions of different arrangements. The handling of the overlap matrix can be computationally overwhelming in terms of computer memory and CPU time even in the time-dependent approach.^{16,17} Another potential problem of the coupled equation approach is related to the over-completeness of nonorthogonal basis functions defined in different arrangement channels that are used to simultaneously expand different components of the full wave function. Also, artificially designed coupled equations can lead to unphysical behavior of the component wave function in the interaction region.¹⁶

In our present approach, we try to avoid all of the above-mentioned problems and instead design the following *uncoupled* equations,

$$i\hbar \frac{\partial}{\partial t} |\Psi_r(t)\rangle = H |\Psi_r(t)\rangle - i \sum_p V_p |\Psi_r(t)\rangle, \quad (3)$$

$$i\hbar \frac{\partial}{\partial t} |\Psi_p(t)\rangle = H |\Psi_p(t)\rangle + i V_p |\Psi_r(t)\rangle,$$

where $-iV_p$ is the negative imaginary potential (absorbing potential) used to block the wave function $\Psi_r(t)$ from entering the p product arrangement space. One can see immediately that the first equation in (3) is exactly the same equation that has been successfully employed to calculate the total reaction probability for four-atom reactions using the reactant Jacobi coordinates.¹⁻⁷ The solution of $\Psi_r(t)$ is completely independent of those of $\Psi_p(t)$. If the absorbing potential V_p is chosen smooth enough to absorb the $\Psi_r(t)$ perfectly without any appreciable reflection, then $\Psi_r(t)$ will be the correct representation of the full scattering wave function in the reactant and strong interaction regions where $V_p=0$. Thus the product component wave function $\Psi_p(t)$ needs to be nonzero only in the corresponding p th product space starting from where V_p is turned on. In other words, the $\Psi_p(t)$ only covers the inelastic region in the p th product arrangement and its calculation involves essentially an inelastic propagation only. The $\Psi_p(t)$ satisfies an inhomogeneous equation with a source term $iV_p\Psi_r(t)$ that provides the driving force towards the asymptotic region in the p th product space. If we sum over the equations for all the component wave functions in (3), we recover the original Schrödinger equation (2) for the full wave function. Thus, we still solve the Schrödinger equation correctly for the full wave function. The main attraction of this approach is that the overall computational cost is divided into that for each arrangement channel and the dynamics calculation for each arrangement component wave function can be carried out individually using the Jacobi coordinates of the correspond arrangement channel. The exchange of information between the reactant and product component wave functions is real-

ized through the absorbing potential for the particular product channel of interest, independent of the rest of the product channels.

In practice, one first carries out the scattering calculation for $\Psi_r(t)$ using the reactant Jacobi coordinates in much the same way as in the calculation of total reaction probabilities without final state resolution.^{1,2} This part of the calculation requires essentially the same computational effort as in the calculation of total reaction probability, and $\Psi_r(t)$ spans a space in the reactant arrangement just beyond the transition state region.^{1,2} The only extra effort required here is to write out the quantity $V_p\Psi_r(t)$ on the strip of absorbing potential to a computer disk for later use. The second part of the calculation is to carry out an essentially inelastic propagation of the wave function $\Psi_p(t)$ for the desired product channel p in Eq. (3) using the p th product Jacobi coordinates. The formal solution for $\Psi_p(t)$ can be written as

$$|\Psi_p(t+\Delta)\rangle = e^{-(i/\hbar)H\Delta} |\Psi_p(t)\rangle + \frac{1}{\hbar} e^{-(i/\hbar)H\Delta} \times \int_t^{t+\Delta} e^{-(i/\hbar)H(t-t')} V_p |\Psi_r(t')\rangle dt'. \quad (4)$$

If we use the trapezoidal rule to evaluate the integral for a short time step Δ , we obtain a propagation equation

$$|\Psi_p(t+\Delta)\rangle = e^{-(i/\hbar)H\Delta} [|\Psi_p(t)\rangle + \frac{\Delta}{2\hbar} V_p \Psi_r(t)\rangle] + \frac{\Delta}{2\hbar} V_p |\Psi_r(t+\Delta)\rangle. \quad (5)$$

If we define a new product wave function $\tilde{\Psi}_p(t) = \Psi_p(t) + (\Delta/2\hbar)V_p\Psi_r(t)$, which is everywhere the same as $\Psi_p(t)$ except in the absorption region, we obtain the simplified propagation equation for $\tilde{\Psi}_p(t)$

$$|\tilde{\Psi}_p(t+\Delta)\rangle = e^{-(i/\hbar)H\Delta} |\tilde{\Psi}_p(t)\rangle + \frac{\Delta}{\hbar} V_p |\Psi_r(t+\Delta)\rangle \quad (6)$$

which is the final working formula for $\tilde{\Psi}_p(t)$. Using Eq. (6), one carries out the standard split-operator propagation for $\tilde{\Psi}_p(t)$ and simply adds the second term in Eq. (6) afterwards.

TABLE I. State-to-state reaction probabilities $P_{00 \rightarrow v'j'}$ at $E=1.0$ eV. SKVP: the results of Zhang and Miller (Ref. 19) using S -matrix Kohn variational principle method. JKNB: the results of Judson, Kouri, Neuhauser, and Baer (Ref. 20).

(v',j')	SKVP	Present work	JKNB	(v',j')	SKVP	Present work	JKNB
(0,0)	8.0E-2	8.0E-2	8.4E-2	(1,0)	2.1E-2	2.1E-2	2.2E-2
(0,1)	1.4E-1	1.4E-1	1.5E-1	(1,1)	3.5E-2	3.3E-2	3.4E-2
(0,2)	7.4E-2	7.7E-2	7.5E-2	(1,2)	1.8E-2	1.7E-2	1.8E-2
(0,3)	1.7E-2	1.7E-2	1.8E-2	(1,3)	3.2E-3	3.3E-3	3.3E-2
(0,4)	2.4E-2	2.2E-2	2.2E-2	(1,4)	1.2E-4	1.2E-4	1.2E-4
(0,5)	3.1E-2	3.4E-2	3.2E-2	(1,5)	4.9E-9	3.3E-9	3.5E-8
(0,6)	1.6E-2	1.5E-2	1.5E-2				
(0,7)	2.6E-3	2.5E-3	3.3E-3				
(0,8)	1.7E-4	2.3E-4	2.0E-4				
(0,9)	6.9E-7	7.2E-7	1.4E-6				

Since $\tilde{\Psi}_p(t)$ is only nonzero in the product arrangement space starting from where V_p is turned on, the calculation of $\tilde{\Psi}_p(t)$ is a much simpler inelastic scattering problem. Although the coordinate transformation is still required to generate $V_p\Psi_r(t)$ in the proper representation, this is much easier than the calculation of the full-blown overlap matrix because $V_p\Psi_r(t)$ is only nonzero in a very small region of space.

Application of this RPD (reactant–product decoupling) method to the state-to-state reactive scattering calculation for three-dimensional H+H₂ reaction in time-dependent implementation is currently in progress. The preliminary result is very encouraging. As shown in Table I, these state-to-state probabilities for 3D H+H₂ reaction calculated by the TD RPD method are in excellent agreement with those from the *S* matrix Kohn variational calculation. We used a quadratic absorbing potential defined in terms of the product translational coordinate in the range of [3.5, 5.5]*a*₀ to obtain these results. More detailed numerical aspects of application to 3D state-to-state H+H₂ reactive scattering as well as detailed results of application will be reported in a follow-up paper.¹⁸

Finally, we note that the same idea can be implemented in the time-independent framework as well. For this purpose, one can straightforwardly write down the time-independent versions of Eqs. (1) and (3) as

$$\Psi(E) = \Psi_r(E) + \sum_p \Psi_p(E) \quad (7)$$

and

$$\begin{aligned} E|\Psi_r(E)\rangle &= H|\Psi_r(E)\rangle - i\sum_p V_p|\Psi_r(E)\rangle, \\ E|\Psi_p(E)\rangle &= H|\Psi_p(E)\rangle + iV_p|\Psi_r(E)\rangle. \end{aligned} \quad (8)$$

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