Coherent Control of Reactive Scattering

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(Received 11 December 1997)

Coherent control of bimolecular reactions is demonstrated for 3D atom-diatom reactive scattering. In particular, a superposition of initial degenerate \(vjk\) diatomic states is used to control reactive integral and differential cross sections in \(D + H_2(vjk) \to H + HD\), where \(v, j\) are the vibrational and rotational quantum numbers of \(D\) and \(k\) is the projection quantum number of the diatomic angular momentum onto the initial relative translational velocity vector. Control over the ratio of reactive to nonreactive scattering is extensive.

\[ |\mathbf{n}, \alpha\rangle = \sum_{i=1,2} a_i |\alpha v j k_i\rangle |E^\text{kin}_\alpha(i)\rangle |E^\text{cm}(i)\rangle, \]

where \(\mathbf{n}\) encapsulates all the state labels other than \(\alpha\), \(|E^\text{kin}_\alpha(i)\rangle\) are plane waves describing the free motion of the atom relative to the diatom for the \(\alpha\) arrangement and \(|E^\text{cm}(i)\rangle\) describes the motion of the atom-diatom center of mass. The superposition state \(|\mathbf{n}, \alpha\rangle\), assumed normalized, is therefore composed of two degenerate eigenstates \(|\alpha v j k_i\rangle |E^\text{kin}_\alpha(i)\rangle\) of the asymptotic \(\alpha\)-channel Hamiltonian, where the quantum numbers \(v, j, k_i\) denote the vibrational, rotational, and angular momentum projection quantum numbers of the diatomic. The latter, \(k_i\), is taken as the helicity, i.e., the angular momentum projection along the relative initial translational velocity vector, and the diatomic states \(|\alpha v j k_i\rangle\) are of energy \(E^\text{kin}_{\alpha v j}\).

Traditional time independent scattering theory deals with asymptotic states where one of the \(a_i = 0\), so that scattering correlates with one asymptotic state. The equations below are a direct, but significant, extension of these traditional results. In particular, the differential cross section for forming the \(\alpha'\) arrangement at scattering angle \(\theta\), having started from the \(|\mathbf{n}, \alpha\rangle\) superposition state \[\text{Eq. (1)}\], is given by

\[ \sigma^R(\theta) = \sum_{v',j',k'} \left| \sum_{m=1,2} E^\text{cm}(m) \right| \sum_{i=1,2} a_i f_{\alpha' v' j' k' \to \alpha v j k}(\pi - \theta) \left| E^\text{cm}(i) \right|^2, \]

where the superscript \(R\) denotes reactive scattering into a specific final arrangement channel \(\alpha' \neq \alpha\) and where the scattering amplitude is

\[ f_{\alpha' v' j' k' \to \alpha v j k}(\theta) = (2i k_{\alpha v j})^{-1} \sum_J (2J + 1) d_{\alpha k_{\alpha v j}}^J(\theta) \times [S^J_{\alpha' v' j' k' \to \alpha v j k} - \delta_{\alpha' \alpha} \delta_{v' v} \delta_{j' j} \delta_{k' k}], \]

Here \(S^J_{\alpha' v' j' k' \to \alpha v j k}\) are the elements of the scattering matrix in the helicity representation, \(J\) is the total angular momentum, \(k'\) is the helicity of the product diatom (i.e., the projection of the diatomic angular momentum onto the final relative translational velocity vector), \(d_{\alpha k_{\alpha v j}}^J(\theta)\) are the reduced rotation matrices [6], and \(k_{\alpha v j} = \sqrt{2} \mu_a (E - E_{\alpha v j}) / \hbar\), with \(\mu_a\) being the...
atom-diatom reduced mass in the $\alpha$ channel. Expanding
the square in Eq. (2) gives the reactive differential
scattering cross section as
\[ \sigma^R(\theta) = |a_1|^2 \sigma^R_{11}(\theta) + |a_2|^2 \sigma^R_{22}(\theta) + 2 \text{Re}[a_1^* a_2 \sigma^R_{12}(\theta)], \]
where
\[ \sigma^R_{ii}(\theta) = \sum_{v',j,k'} |f_{a'v'j'k'}(\pi - \theta)|^2, \quad i = 1, 2, \]
\[ \sigma^R_{12} = \frac{\pi}{2k^2_{\alpha v j}} \sum_{v',j',k'} (2J + 1) |S^J_{a'v'j'k',\alpha v j k}|^2, \quad i, j = 1, 2, \]
\[ \sigma^R_{12} = \frac{\pi}{2k^2_{\alpha v j}} \sum_{v',j',k'} (2J + 1) (2J' + 1) S^J_{a'v'j'k',\alpha v j k} S^J_{a'v'j'k',\alpha v j k} \]
\[ \times \int_0^{\pi} \sin \theta d\theta \alpha \neq \alpha'. \]

Note that $\sigma^R_{ii}(\theta)$ and $\sigma^R_{12}$ in Eqs. (5) and (7) are
the differential and integral cross sections that appear
in standard scattering theory, while $\sigma^R_{11}(\theta)$ and $\sigma^R_{12}$
in Eqs. (6) and (8) are new types of interference terms which
allow for control through the $a_i$ over the atom-diatom
collision process. Note further that significant control
requires substantial $\sigma^R_{12}$ and, by the Schwartz inequality
[$|\sigma^R_{12}| \leq \sqrt{|\sigma^R_{11}| \sigma^R_{22}}$], large $\sigma^R_{11}$ and $\sigma^R_{22}$. Significantly
then, extensive control is not limited to regions near the
reactive threshold [7]. Further, although Eqs. (4), (7), and
(8) indicate that the differential and total reactive cross
sections are controllable, removing the sums over $v', j'$,
and $k'$ shows that detailed cross sections to product states
$|\alpha', v', j', k'\rangle$ can also be controlled.

Thus, by varying the coefficients $a_i$ in Eq. (1) through
an initial preparation step, we can directly alter the inter-
ference term $\sigma^R_{12}$ and hence control the scattering
cross sections. Such a preparation might be carried out, for
example, by a suitably devised molecular beam experiment
where the diatomic is excited, via elliptically polarized
light to a collection of well defined $m_j$ states. Alterna-
tively, the preactive step may consist of coherently con-
trolling the photodissociation of a polyatomic molecule
[1] to produce the diatom in a controlled superposition of
$k$ states relative to an incoming scattering partner. For
example, in the D + H$_2$ case considered below we can
subject H$_2$S to a coherently controlled preparatory step
producing H$_2$. Aiming the D atom exactly antiparallel to
the direction of motion of the H$_2$ will then produce the
desired scattering of a $k$ superposition.

To examine the extent of control it is useful to rewrite
the total reactive cross section in the form
\[ \sigma^R = \sigma^R_{11} + x \sigma^R_{12} + 2x |\phi_{12}|, \]
where $x = |a_2/a_1|$, $\phi_{12} = \text{arg}(a_2/a_1)$, and
\[ \sigma^R_{12}(\theta) = \sum_{v',j',k'} \langle E_{\text{cm}}(1) | E_{\text{cm}}(2) \rangle_{v'} f_{a'v'j'k'\rightarrow avj k}(\pi - \theta) \]
\[ \times f_{a'v'j'k'\rightarrow avj k}(\pi - \theta) \]
In the cases considered here, i.e., a superposition of
degenerate diatomic states, the overlap $\langle E_{\text{cm}}(1) | E_{\text{cm}}(2) \rangle_{v'}$
of the center of mass wave functions over the scattering
volume $V$, which appears in Eq. (6), is unity.

Integration of Eq. (4) over angle $\theta$ gives the integral
reactive cross section $\sigma^R$. This can also be written as
three terms, as in Eq. (4), but with $\sigma^R_{ii}(\theta)$ replaced by $\sigma^R_{ij}$
where
\[ \sigma^R_{ij} = \frac{2k^2_{\alpha v j}}{\pi} \sum_{v',j',k'} (2J + 1) |S^J_{a'v'j'k',\alpha v j k}|^2, \quad i, j = 1, 2, \]
\[ \sigma^R_{12} = \frac{2k^2_{\alpha v j}}{\pi} \sum_{v',j',k'} (2J + 1) (2J' + 1) S^J_{a'v'j'k',\alpha v j k} S^J_{a'v'j'k',\alpha v j k} \]
\[ \times \int_0^{\pi} \sin \theta d\theta \alpha \neq \alpha'. \]

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\[ \sigma^R_{ij} = \frac{2k^2_{\alpha v j}}{\pi} \sum_{v',j',k'} (2J + 1) |S^J_{a'v'j'k',\alpha v j k}|^2, \quad i, j = 1, 2, \]
\[ \sigma^R_{12} = \frac{2k^2_{\alpha v j}}{\pi} \sum_{v',j',k'} (2J + 1) (2J' + 1) S^J_{a'v'j'k',\alpha v j k} S^J_{a'v'j'k',\alpha v j k} \]
\[ \times \int_0^{\pi} \sin \theta d\theta \alpha \neq \alpha'. \]
\[ \sigma^R_{12} = \frac{2k^2_{\alpha v j}}{\pi} \sum_{v',j',k'} (2J + 1) (2J' + 1) S^J_{a'v'j'k',\alpha v j k} S^J_{a'v'j'k',\alpha v j k} \]
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to demonstrate substantial control in the presence of a significant natural reactive cross section.

Consider first the range of coherent control over the differential cross sections. Initial numerical tests showed that the best control over the \( \sigma^R(\theta)/\sigma^{NR}(\theta) \) differential cross section ratio for transitions from initial states with \( v = 0, j = 2, \) and \( k_1, k_2 \) in the range \(-2, -1, \ldots, 2\) occurred at \( \theta \approx 60^\circ \). Figure 1a shows results for this ratio and scattering angle as a function of relative phase \( \phi_{12} \) and the amplitude parameter \( s = x^2/(1 + x^2) \), for \( k_1 = 1, k_2 = 0 \). Varying \( s \) from zero to one corresponds to changing the initial superposition from scattering out of state one (\( s = 0 \), corresponding to \( a_1 = 1, a_2 = 0 \)) to scattering out of the second state (\( s = 1 \) corresponding to \( a_1 = 0, a_2 = 1 \)). The results clearly show substantial control over \( \sigma^R(\theta)/\sigma^{NR}(\theta) \). That is, varying \( s \) and \( \phi_{12} \) allows a change in the ratio from 0.23 to 1.01, compared with the uncontrolled ratio of \( \sim 0.55 \). Similarly, for example, the \( \sigma^R(\theta)/\sigma^{NR}(\theta) \) ratio can be increased by a factor of 4.4 just by changing the phase angle \( \phi_{12} \) from 260° to 67° at \( s = 0.49 \).

Figures 1b and 1c show the \( \sigma^R \) and \( \sigma^{NR} \) corresponding to Fig. 1a. Control over both \( \sigma^R(\theta = 60^\circ) \) and \( \sigma^{NR}(\theta = 60^\circ) \) is clearly seen, with \( \sigma^R \) ranging from \( 0.10a_0^2 \text{sr}^{-1} \) to \( 0.32a_0^2 \text{sr}^{-1} \) as \( s \) and \( \phi_{12} \) are varied. This compares, for example, to the uncontrolled values of \( \sigma^R(\theta = 0.21 \text{ sr}^{-1} \) and \( \sigma^{NR}(\theta = 0.22a_0^2 \text{ sr}^{-1} \) at \( s = 0 \) and \( s = 1 \). Similar control can be seen in \( \sigma^{NR} \). Indeed, both the constructive enhancement of \( \sigma^R \) and the destructive depletion of \( \sigma^{NR} \) are seen to be responsible for the controlled \( \sigma^R/\sigma^{NR} \) maximum.

Also of interest is the \( \theta \) dependence of \( \sigma^R(\theta)/\sigma^{NR}(\theta) \) as a function of \( s \) and \( \phi_{12} \). Figure 2 shows the \( \theta \) dependence of this ratio, for scattering from a superposition state composed of \( v = 0, j = 2, k_1 = 2, k_2 = 0 \) at \( \phi_{12} = 157^\circ \) and at four different values of \( s \). [Note that these results also show, for limits \( s = 0 \) and \( s = 1 \), the dependence of the ratio on the initial \( k \) state, the first such data of its kind. That is, \( s = 0 \) corresponds to scattering out of the initial state (\( v = 0, j = 2, k = 2 \)), and \( s = 1 \) corresponds to scattering from (\( v = 0, j = 2, k = 2 \)).]
the ratio of integral cross sections. Figure 3 shows a contour plot of

\[ \frac{\sigma^R}{\sigma^{NR}} \times 10^3 \]

integral cross section ratio as a function of \( \phi_{12} \) and \( s \); for the case of

\( k = 0 \).] For this transition the controlled ratio of differential cross sections is seen to be considerably different from the uncontrolled ratio. For example, the controlled \( \frac{\sigma^R(\theta)}{\sigma^{NR}(\theta)} \) for \( s = 0.748 \) is about twice as large as the uncontrolled ratios at \( \theta = 91^\circ \). Analysis of Fig. 2 shows that maxima and minima of the controlled \( \frac{\sigma^R}{\sigma^{NR}} \) ratio in the region between 50° and 120° are achieved at the corresponding minima and maxima of uncontrolled ratios. That is, quantum interference leads to constructive enhancement of the \( \frac{\sigma^R}{\sigma^{NR}} \) ratio at minima of uncontrolled ratios and to destructive depletion of controlled ratios at their maxima. Exactly the opposite behavior is observed in the outer \( \theta \) regions. Hence coherent control changes both the magnitude and the structure of the differential cross section. Note also that the maxima of the controlled differential cross sections far exceed those for \( s = 0 \) and \( s = 1 \), confirming that the changes are due to quantum interference effects, as opposed to an interpolation between the \( s = 0 \) and \( s = 1 \) curves.

Of great interest as well is the extent of control over the integral cross sections. Figure 3 shows a contour plot of the ratio of integral cross sections \( \frac{\sigma^R}{\sigma^{NR}} \) for scattering from \( \nu = 0, j = 2, k_1 = 2, k_2 = 1 \) as a function of the control parameters \( \phi_{12} \) and \( s \). The ratio is seen to vary from 0.032 to 0.113, showing maxima and minima that are well outside the range of the results for scattering from a single \( k_1 \) state. Greater control is anticipated at higher energies where the uncontrolled \( \sigma^R \) and \( \sigma^{NR} \) become comparable.

In this Letter we have demonstrated that one may obtain considerable control over differential and integral cross sections branching ratios for realistic atom-diatom reactive scattering by preparing, and varying the characteristics of, a superposition of degenerate scattering states. Further, although not explored here, we expect similar control over detailed cross sections to specific product states.

Since the results of molecular beam experiments are well represented by time independent scattering theory and since our computations are state of the art, we anticipate that observed results will be in accord with our computations. Further, additional computations suggest that the control is not very sensitive to small changes in total energy so that one would anticipate little effect due to velocity distributions, etc. However, control is always sensitive to dephasing effects, e.g., external collisions, a feature to be examined in future papers.

This study opens a vast new area of application for coherent control. Work currently underway will extend studies to atom-heteronuclear diatom scattering to results at higher collision energies [12] and will incorporate specific scenarios to prepare the initial superposition state.

We thank Dr. B. Ramachandran for providing us with the REACT scattering code and for useful comments on its use. This work was supported in part by the U.S. Office of Naval Research, Photonics Research Ontario and by a grant of HPC time on the CRAY C-90 and the SGI Origin 2000 from the DoD ASC MSRC Center, and the CRAY T-90 and the SGI PCA from the DoD NAVOCEANO MSRC Center.

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