

Coherent Control of Resonance-Mediated Reactions: F + HD

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Cross sections resulting from scattering that proceeds via an intermediate resonance are shown to be exceptionally controllable using a coherent superposition of only two initial states. Full quantum computations on $F+HD(v=0; j=0, 1) \rightarrow H+DF, D+HF$, which exhibits a resonance in one of the reactive channels, support the formal arguments, showing that control is indeed vast. In this case the ratio of reactive integral cross sections can be altered by a factor of 62 (compared to a noncoherent factor of only 3.3), while the ratio of reactive differential cross sections can be altered by a factor of over 6000 (compared to a noncoherent factor of less than 7). These results constitute the first prediction of extensive quantum control in a collisional process.

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Coherent control is a rapidly developing method for controlling atomic and molecular processes. Recent experimental and theoretical developments in this area have been extensively summarized in Refs. [1,2]. In this approach one manipulates, through laboratory parameters, quantum interference contributions that arise when a final state is reached by two or more coherent routes. Although initially introduced for unimolecular processes, coherent control has been extended formally to collisions [3–6] and has been numerically studied for reactive scattering of the isotopic variants of $H+H_2$ [3] and for H_2+H_2 [6]. All of the established principles apply equally well to atomic, molecular, and nuclear processes.

There are very few general results known for control of scattering. We previously showed that complete control, i.e., the ability to completely suppress or maximally enhance a particular product arrangement channel, is achieved in collision processes when the number of reactant states used in an initial coherent superposition is greater than the number of open final product states in that product channel [5]. In this article we show that final product channels that arise via the formation of a resonance can be completely controlled via a superposition of *only two initial states, regardless of the number of open product states*. We provide, as a numerical example, results of a full 3D quantum computation of control through the recently discovered reactive resonance in $F+HD \rightarrow D+HF$ [7–9]. Even though this resonance is short lived [8], and direct reactive scattering occurs as well, we find that a very large range of control is possible.

Control of a collisional process is achieved [3] by constructing an initial state $|\Psi\rangle$ in the initial arrangement channel composed of a superposition of N energetically degenerate asymptotic states $|q, m\rangle$. Here q denotes the arrangement channel and m indicates all state labels; the energy label is dropped for convenience. For the case of $N = 2$:

$$|\Psi\rangle = c_1|q, 1\rangle + c_2|q, 2\rangle. \quad (1)$$

The cross section $\sigma_{q'}$ for scattering into final arrangement channel q' , starting from state $|\Psi\rangle$, is given by

$$\sigma_{q'} = \sum_n \left| \sum_{i=1}^2 c_i \langle q', n | T | q, i \rangle \right|^2, \quad (2)$$

where T is the transition operator. For notational convenience we drop the q' subscript unless necessary.

Equation (2) can be rewritten as

$$\sigma_{q'} = |c_1|^2 \sigma_{q'}(11) + |c_2|^2 \sigma_{q'}(22) + 2\text{Re}[c_1^* c_2 \sigma_{q'}(12)], \quad (3)$$

where

$$\sigma_{q'}(ij) = \sum_n \langle q, i | T | q', n \rangle \langle q', n | T | q, j \rangle. \quad (4)$$

To produce the integral cross section, the sum over n includes an integral over the product scattering angles as well as a sum over all final diatom states.

Equation (3) can be rewritten by defining the relative amplitude $s = |c_2|^2 / [|c_1|^2 + |c_2|^2]$, $0 \leq s \leq 1$, and the relative phase between the two coefficients as $\phi_{12} = \text{Arg}[c_2/c_1]$. The cross section then becomes

$$\begin{aligned} \sigma_{q'} = & (1-s)\sigma_{q'}(11) + s\sigma_{q'}(22) \\ & + 2\sqrt{s(1-s)}|\sigma_{q'}(12)|\cos(\text{Arg}[\sigma_{q'}(12)] + \phi_{12}), \end{aligned} \quad (5)$$

indicating that control is achieved experimentally by varying s and ϕ_{12} . Note that $\sigma_{q'}(11)$ and $\sigma_{q'}(22)$ are real, corresponding to the cross sections for initial states 1 and 2, respectively, while $\sigma_{q'}(12)$ is complex, corresponding to quantum interference between the two reaction pathways. Since ϕ_{12} can always be chosen so that $\text{Arg}[\sigma_{q'}(12)] + \phi_{12}$ is a multiple of 2π , the extent of control over $\sigma_{q'}$ is determined by $|\sigma_{q'}(12)|$, which is seen to satisfy the Schwartz inequality $|\sigma_{q'}(12)| \leq \sqrt{\sigma_{q'}(11)\sigma_{q'}(22)}$. Maximum control therefore occurs when $|\sigma_{q'}(12)| = \sqrt{\sigma_{q'}(11)\sigma_{q'}(22)}$. The value of the

cross section can be controlled within the range $\sigma_{q'}(\min) \leq \sigma_{q'} \leq \sigma_{q'}(\max)$, where the limiting values and corresponding control parameters are [assuming $\sigma_{q'}(22) > \sigma_{q'}(11)$]

$$\begin{aligned}\sigma_{q'}(\min) &= 0, & \sigma_{q'}(\max) &= \sigma_{q'}(11) + \sigma_{q'}(22), \\ s(\min) &= \frac{\sigma_{q'}(11)}{\sigma_{q'}(11) + \sigma_{q'}(22)}, & s(\max) &= \frac{\sigma_{q'}(22)}{\sigma_{q'}(11) + \sigma_{q'}(22)}, \\ \phi_{12}(\min) &= \pi - \text{Arg}[\sigma_{q'}(12)], & \phi_{12}(\max) &= -\text{Arg}[\sigma_{q'}(12)].\end{aligned}$$

Note that $\sigma_{q'}(\max)$ is twice that achievable in the absence of the interference term.

We show below that the Schwartz equality is satisfied for scattering into a particular arrangement channel if it occurs through a resonance at all scattering angles and for all product states, a situation that we term an ideal resonance. By comparison, the limits of noncoherent control (i.e., when no quantum interference occurs) are the cross sections corresponding to the two initial states $\sigma_{q'}(11)$ and $\sigma_{q'}(22)$ (corresponding to $s = 0$ and $s = 1$).

Consider a system displaying an isolated Feshbach resonance [10]. In this case the T matrix elements at scattering energy E are of the general form [10,11]

$$\langle q', n | T | q, j \rangle = \gamma'_r(q', n) \gamma_r(q, j) / [E - E_r], \quad (6)$$

where $\gamma'_r(q', n)$ and $\gamma_r(q, j)$ are matrix elements of the Hamiltonian coupling the product state to the resonance state (denoted by the subscript r) and coupling the resonance to the initial state, respectively. E_r is the complex energy associated with the resonance. If the form of Eq. (6) holds, for all final states and all scattering angles at the energy of interest, we have

$$\sigma_{q'}(kk) = \frac{|\gamma_r(q, k)|^2}{|E - E_r|^2} \sum_n |\gamma'_r(q', n)|^2, \quad k = 1, 2, \quad \sigma_{q'}(12) = \frac{\gamma_r^*(q, 1) \gamma_r(q, 2)}{|E - E_r|^2} \sum_n |\gamma'_r(q', n)|^2 \quad (7)$$

so that

$$\sigma_{q'} = \frac{\sum_n |\gamma'_r(q', n)|^2}{|E - E_r|^2} \times [(1-s)|\gamma_r(q, 1)|^2 + s|\gamma_r(q, 2)|^2 + 2\sqrt{s(1-s)}|\gamma_r^*(q, 1)\gamma_r(q, 2)| \cos(\text{Arg}[\sigma_{q'}(12)] + \phi_{12})]. \quad (8)$$

Under these circumstances the magnitudes of the $\sigma_{q'}(ij)$ satisfy the Schwartz equality and complete control over $\sigma_{q'}$ is possible.

Control via a resonance over the *ratio* of cross sections into different arrangement channels q' , q'' requires that at least one of these channels have a direct scattering component, or that they arise by scattering through different ideal resonances. If this is not the case, i.e., if both final arrangements q' and q'' are accessible only via the same ideal resonance, then, as is evident from Eq. (8), the ratio $\sigma_{q'}/\sigma_{q''}$ no longer depends upon the control parameters s and ϕ_{12} .

The above argument is general and the recently observed reactive resonance in $\text{F} + \text{HD} \rightarrow \text{D} + \text{HF}$ scattering [7–9] provides an opportunity for a challenging numerical test within the framework of molecular scattering. The FHD resonance, corresponding to a collinear arrangement with quantum numbers ($v_{\text{FH}} = 3$, $v_{\text{HD}} = 0$, $v_{\text{bend}} = 0$) is short lived, with a lifetime of 109 fs. In the low energy regime, where the resonance dominates the reactive scattering, the rotational period is ≈ 1420 fs, and the contributions from several total angular momentum values overlap one another [8]. Advantageously, the collinear FHD complex is much more likely to decay to $\text{D} + \text{HF}$ than to $\text{H} + \text{DF}$, so that complete control over the resonant mechanism should allow large control over both the $\text{D} + \text{HF}$ cross sections as well as over the ratio of

$\text{D} + \text{HF}$ to $\text{H} + \text{DF}$ reactive cross sections. Deviations of control from the maximum value can also be enlightening, being attributable to nonresonant, direct reactive scattering contributions.

Control results shown below were obtained using a converged full three-dimensional quantum coupled-channel hyperspherical coordinate approach [12] on the Stark-Werner potential energy surface [13], using an available code [14]. Results were obtained for a variety of energies over the range 0.25–0.31 eV (relative to the HD minimum) in increments of 0.005 eV. A basis set containing all three channels with maximum diatomic energy levels of 1.7 eV, maximum rotational quantum number $j_{\text{max}} = 15$, and maximum total angular momentum and helicity $J_{\text{max}} = 31$ and $K_{\text{max}} = 4$ were used. S -matrix elements for all possible combinations of energetically available initial and final states were calculated.

Control was studied for the case where the initial state was comprised of a superposition of the $(v_1, j_1, m_1) = (0, 0, 0)$ and $(v_2, j_2, m_2) = (0, 1, 0)$ states of HD, which have internal energies of $e_1 = 0.23252$ and $e_2 = 0.24358$ eV, and with k_1 and k_2 satisfying the conditions [4]

$$\mathbf{K}_1 = \mathbf{K}_2; \quad E = \hbar^2 k_1^2 / 2\mu + e_1 = \hbar^2 k_2^2 / 2\mu + e_2. \quad (9)$$

Here $\hbar \mathbf{k}_i$ and $\hbar \mathbf{k}_i$ are the center of mass and relative momenta, respectively, and $\mu = M_{\text{F}} M_{\text{HD}} / M_{\text{FHD}}$ is the

reduced mass. For the case we have considered the kinetic energies of the two coherent components, defined as $E_{k_j} = \hbar^2 k_j^2 / 2\mu$ are related by $E_{k_2} = E_{k_1} - 0.01106$ eV.

Most relevant is the ratio of product cross sections. Figure 1(a) shows the maximum and minimum values of the ratio of integral reactive cross sections, $r = \sigma[\text{D}+\text{HF}]/\sigma[\text{H}+\text{DF}]$ attainable at each energy. Results using coherent control are shown as solid lines while those without control [i.e., resulting from $\sigma_{q'}(11)$ and

$\sigma_{q'}(22)$] are shown as dashed lines. Clearly, r peaks near the resonance ($E = 0.2550$ eV) with the ratio controllable, at resonance, over a huge range: 2.60 to 161, a factor of 62. This range is far greater than the analogous noncoherent control factor of 3.3. Further, the coherent control parameters resulting in the minimum ratio (2.60) are $s = 0.7027$ and $\phi_{12} = 185.1^\circ$, while for the maximum (161) they are $s = 0.9344$ and $\phi_{12} = 352.9^\circ$, sufficiently far apart to allow easy discrimination.

These results are shown in a somewhat different way in Fig. 1(b), where the ratio of maximum and minimum ratios r , i.e., $R = \max[r]/\min[r]$ attainable via coherent control are compared to those attainable without coherent control. Three features are evident: coherent control affords a vastly larger range of control, the best ratio control is seen at the resonance, and R for the coherent control case remains greater than 20 at energies up to 0.31 eV, where the cross section is no longer dominated by the resonant process. However, as seen in Fig. 1(a), in this higher energy region the actual value of r is quite small.

Figures 1(c) and 1(d) provide the cross sections from which the earlier panels are constructed. Figure 1(c) shows that the D+HF cross section can be coherently controlled at the resonance from a minimum of $0.0850 \text{ \AA}^2$ to a maximum of $2.193 \text{ \AA}^2$. This is to be compared to the ideal case of complete control with a minimum of 0 and a maximum, corresponding to $\sigma_{q'}(11) + \sigma_{q'}(22)$, of $2.278 \text{ \AA}^2$. Alternatively, we can gauge the “quality” of the resonance from the deviation of $\sigma_{q'}(12)/[\sigma_{q'}(11)\sigma_{q'}(22)]^{1/2}$, from unity. This ratio peaks, at the resonance energy, at a value of 0.906. As a general observation we note that this ratio is far larger than that seen in previous studies, such as those of the isotopic analogs of $\text{H}+\text{H}_2$ [4]. Hence control is far more extensive in this case than in any collisional process previously studied.

Results were also obtained for control of the differential cross section. In this case the sum in Eq. (4) does not contain an integral over scattering angle. Results at the resonant energy show that the greatest control occurs for backward scattering ($\theta = 180^\circ$). There the ratio of reactive cross sections can be coherently controlled from a minimum of 0.236 (at $s = 0.6469$ and $\phi_{12} = 167.0^\circ$) to a maximum of 1455 (at $s = 0.8097$ and $\phi_{12} = 331.1^\circ$), a factor of over 6000. By contrast, the noncoherent control factor never rises above 7 at this energy. At this scattering angle the Schwartz ratio $\sigma_{q'}(12)/[\sigma_{q'}(11)\sigma_{q'}(22)]^{1/2} = 0.984$. Such near-unity values are consistent with the fact that much of the averaging is eliminated in examining the differential cross section.

We have shown above that if there is an ideal resonance then complete control is possible using a superposition of two initial states. We note further that the behavior of the Schwartz ratio at the resonance energy provides a useful theoretical test for the contrapositive. That is, if the Schwartz equality does not hold at a particular energy then the dynamics must have a nonresonant component. Thus, for example, information regarding the

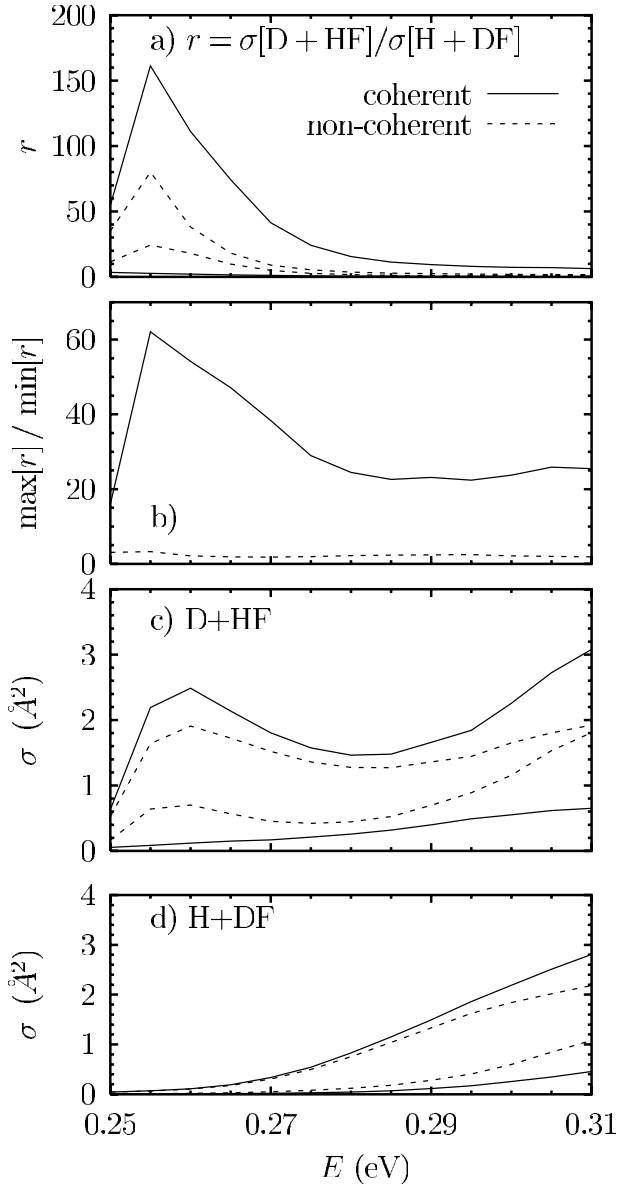


FIG. 1. Maximum and minimum values through which integral cross sections can be coherently (solid line) or non-coherently (dashed line) controlled using the initial state described in the text. (a) The ratio of the cross sections into the D+HF channel to that in the H+DF channel. Note that the minimum values are very close to the $r = 0$ line; (b) The ratio of the maximum to minimum r at each energy; (c) the cross section for the resonant D+HF channel; (d) the cross section for the nonresonant H+DF channel.

resonant (or nonresonant) behavior of $H + HD$ scattering in the forward direction, a subject of recent debate [15], can be augmented by computing the Schwartz ratio in that direction. Doing so using the same initial superposition as for the $F + HD$ above and the established BKMP2 potential surface [16] gives us $\sigma_{q'}(12)/\{\sigma_{q'}(11)\sigma_{q'}[1,2](22)\}^{1/2} = 0.850$, indicating that the dynamics does not go solely through a resonance.

In conclusion, we have shown that scattering through a resonance allows for a vast range of control over product cross sections using an initial state comprising a superposition of as few as two states. Preparing this superposition for atom-diatom scattering does present a challenge since the terms in the superposition comprise wave functions where the translational and the internal diatom wave functions are correlated [4]. However, significant advances have been made in experimental coherent control studies for unimolecular problems [1,2] and there are a number of possible approaches to preparing the states required for bimolecular control. These include extending a method successfully applied [17] to atoms in order to prepare the required correlated initial states, or state-selectively accelerating or decelerating molecules [18] that are in different internal state to achieve this result. Alternatively, we note that, for the case of the scattering of identical particles, preparation of the required states is straightforward [6]. Since the discussion in this Letter applies equally well to such cases we suggest that the effect described here may well be first observed, in molecular physics, in the scattering of identical diatomic molecules, e.g., $OH + OH$.

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