

Rotational Feshbach Resonances in Ultracold Molecular Collisions

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In collisions at ultralow temperatures, molecules will possess Feshbach resonances, foreign to ultracold atoms, whose virtual excited states consist of rotations of the molecules. We estimate the mean spacing and mean widths of these resonant states, exploiting the fact the molecular collisions at low energy display chaotic motion. As examples, we consider the experimentally relevant molecules O₂, OH, and PbO. Especially for polar species, the density of *s*-wave resonant states is quite high, implying potentially disastrous consequences for trapped molecules.

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Scattering resonances are of great importance in ultracold collisions. Feshbach resonances occur when the energy of a pair of free atoms (or molecules) is nearly degenerate with that of a quasibound state of the pair. The quasibound state is characterized by the promotion of one or both atoms to an excited internal state, for example, an excited hyperfine state [1]. External magnetic fields can then shift these states in or out of resonance, giving the experimenter direct control over interparticle interactions [2]. In this way, Bose-Einstein condensates of ⁸⁵Rb have been made stable or unstable on command, leading to novel many-body effects [3]. It is, moreover, predicted that this kind of control will be useful in preparing degenerate Fermi gases in “resonant superfluid” states with any desired interaction strength [4,5]. Magnetic field Feshbach resonances have now been observed in the alkali atoms ²³Na [6], ⁸⁵Rb [7,8], ¹³³Cs [9], and ⁴⁰K [10]. While not uncommon, these resonances are far from ubiquitous in ultracold alkali atoms. This is largely due to the relatively small number of atomic hyperfine states available to form resonances.

Ultracold molecules, by contrast, offer a far greater number of resonances than alkali atoms, because rotational excitations can also contribute to resonant states [11]. In contrast to the two hyperfine states in an alkali atom, a molecule can possess a large number of energetically available rotational states. Considering that “typical” rotational energy splittings are of order 1–10 K, while the well depths of intermolecular potential energy surfaces (PESs) can be hundreds or thousands of K, it is clear that tens of rotational states may contribute, including their degeneracies arising from magnetic quantum numbers.

Identifying the number and properties of these resonances is important for understanding the behavior of a molecular gas reduced to extremely low temperatures. Of greatest immediate importance is the fact that a resonance near threshold can greatly enhance the occurrence of two- and three-body inelastic collisions, which can lead to unacceptably large heating and/or trap loss,

thereby undermining the stability of the trapped sample [6,9,12]. In planning an experiment, it is therefore important to know whether it will even be possible to avoid these resonances, or whether they inevitably lie close enough to threshold to have an influence on the gas’ stability. For heavy polar molecules, it is likely that the latter will occur, as we will see below.

In addition, careful mapping of the resonances in cold collision experiments will provide invaluable information for constraining potential energy surfaces to accurately reproduce threshold scattering phase shifts. In turn, this will enable theory to assess the effect of magnetic and electric fields on the resonances, just as is the case in ultracold atom physics. This could lead to resonant field control of molecular collisions, perhaps even of chemical reactions [13], in the ultracold environment. Moreover, a high density of near-threshold resonances will influence elastic scattering and, thus, the mean-field energy in ultracold clouds.

In this Letter, we estimate the most basic properties of molecule-molecule rotational Feshbach resonances, namely, how many we can expect, and what their widths might be. We are interested here in molecules produced in their rovibrational ground states by buffer-gas cooling [14] or Stark slowing [15] techniques. However, vibrationally excited cold molecules produced by photoassociation of cold atoms will also exhibit rich resonant dynamics [16].

Classical chaos at low energies has been studied extensively in molecular scattering problems [17]. Of greatest relevance to our present purposes are multiple-collision events: It is possible that a collision deposits sufficient energy in internal molecular degrees of freedom (e.g., rotations and vibrations) that there is not enough translational energy left to allow the molecules to separate. The molecules may therefore collide many times before finally shedding enough energy to separate. Multiple collisions are increasingly likely as the collision energy is lowered, and, in fact, are useful in quantifying the onset of chaos in this regime [18].

Our classical calculations verify that multiple-collision resonances persist at ultracold temperatures. We consider scattering of $^{17}\text{O}_2$ molecules, using the singlet rigid rotor potential energy surface of Ref. [19]. To simplify the calculation, we constrain all the coordinates to fixed values except the intermolecular distance R and the orientations of the molecules in the scattering plane, as shown in the inset of Fig. 1. The main part of the figure shows a slice through a sample phase space trajectory for collision energy 1 mK. The axes are R and the angular momentum P_{θ_1} (in units of \hbar) of one of the molecules. As a guide, the heavy solid line indicates the allowed region of phase space. The trajectory eventually fills the allowed phase space, by scrambling the available energy in rotational degrees of freedom.

Chaotic motion in the classical realm leaves its signature in the quantum-mechanical spectrum as well. We have computed the quantum-mechanical elastic scattering cross section for the $|N=0, J=1, M_J=1\rangle$ fine-structure state of $^{17}\text{O}_2$ [Fig. 2(a)], following the model described in Ref. [20]. This model includes rotational levels up to $N=2$, and the partial waves $L=0, 2, \dots, 14$, where L is defined as the orbital angular momentum of the two molecules about their common center of mass. Treating the resulting 33 resonances as bound states of the $(\text{O}_2)_2$ collision complex, we expect to find evidence of quantum chaos in statistical measures of the energy level distributions. A glance at the spectrum in Fig. 2(a) suggests that there is no clustering of levels, but rather that they are roughly evenly spaced. This “rigidity” of level spacings is characteristic of the quantum-mechanical spectrum of a system that displays classical chaos, and is usually quantified in terms of the spectral rigidity function $\Delta(x)$ introduced by Dyson and Mehta [21]. If the number of states with energy less than or equal to E is denoted $N(E)$, then $\Delta(x)$ represents the root-mean-squared deviation of $N(E)$ from a straight line over an energy range x , where x is measured in units of the mean level spacing. Figure 2(b) shows this function, computed using the resonances from Fig. 2(a). A spectrum consisting of uncorrelated energy levels would yield a rigidity

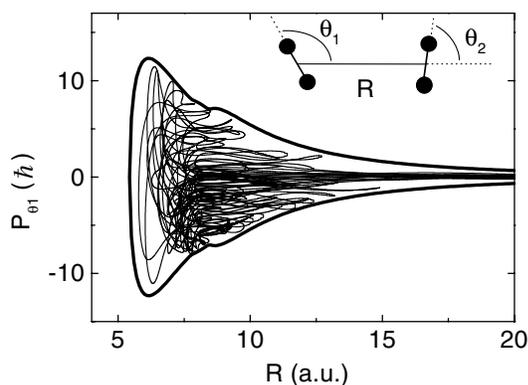


FIG. 1. A single classical trajectory for O_2 - O_2 scattering at a collision energy 1 mK. See text for details.

$\Delta(x) = x/15$, as shown with the dashed line. A spectrum generated in the Gaussian orthogonal ensemble (GOE) approximation, representing a chaotic system, yields instead the solid line. The $\Delta(x)$ computed from the spectrum in Fig. 2(a) more closely resembles the GOE result, suggesting that this system is chaotic. A similar analysis has been applied to the eigenphase shifts in reactive scattering processes [22].

Given that the classical trajectories can fill phase space (Fig. 1), each energetically allowed state is equally likely to be populated during a resonant collision. This observation has been exploited in the theory of unimolecular chemical reactions [23]. We use the same idea here to estimate the total number of resonant states available in a given energy range. To this end, we separate the molecule-molecule Hamiltonian into three independent terms:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{\text{int}}, \quad (1)$$

where \hat{H}_1 and \hat{H}_2 represent the rotational fine structure of each individual molecule, and \hat{H}_{int} is an effective intermolecular potential that depends only on R . Each Hamiltonian is represented by a set of independent energy eigenvalues E_1 , E_2 , and E_{int} . During a resonant collision, any partition of the total energy $E = E_1 + E_2 + E_{\text{int}}$ is equally likely, provided that angular momentum is conserved. Estimating the number of states $N(E)$ at or below energy E is then a simple counting

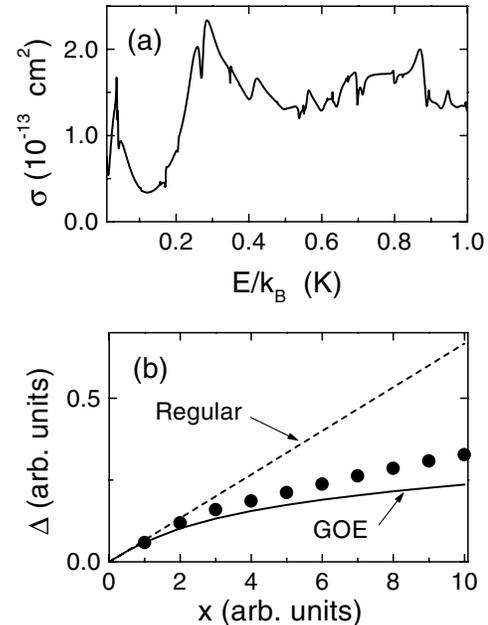


FIG. 2. Evidence of chaos in quantum mechanical scattering of oxygen molecules. (a) shows the complete elastic scattering cross section, computed as in Ref. [20]. In (b) the Dyson rigidity function (points) is computed for the energy spacings of the 33 resonances in (a). Our results are much more closely related to the results of a Gaussian orthogonal ensemble (GOE) approximation to a chaotic system than to a nonchaotic regular system.

TABLE I. Number of resonances in a 1 K energy interval above threshold for cold collisions of $^{17}\text{O}_2$ molecules in their $J = M_J = +1$ state, neglecting nuclear spin. These results are determined from a quantum mechanical calculation. Various levels of completeness of this calculation are specified by the maximum value of rotational quantum number N_{\max} and maximum partial wave L_{\max} . For each such calculation, the table gives the number of resonances found separately in each incident partial wave L .

N_{\max}	L_{\max}	$L = 0$	$L = 2$	$L = 4$	$L = 6$	$L = 8$	$L = 10$
2	2	1	4
2	4	2	7	8
2	6	2	7	9	8
2	8	2	10	14	9	10	...
2	10	3	10	14	11	11	6
4	4	3	11	15

exercise. The density of states, $\rho(E) = dN/dE$, is also easily computed.

To illustrate that this is a reasonable estimate of the density of states, we compare the results to those of a fully quantum-mechanical calculation for $^{17}\text{O}_2$ - $^{17}\text{O}_2$ scattering [20]. Table I tabulates, for the quantum-mechanical calculation, the number of resonances in each partial wave L in an energy range 1 K above the incident threshold. Each row in the table represents a separate calculation, characterized by the maximum number of molecular rotation states (N_{\max}) and partial wave states (L_{\max}) included in the basis set.

Table II reports the same information, but this time estimated from the statistical model. Fluctuations in the density of states function $\rho(E)$ in the relevant energy range correspond to uncertainties of $\sim 50\%$ in the numbers given. Within this uncertainty, the agreement with the quantum-mechanical calculation in Table I is quite good, giving us further confidence that the statistical estimate is reasonable for this purpose.

A clear advantage of the statistical model over the full quantum-mechanical calculation is that it can easily be calculated including *all* allowed values of N and L consistent with conservation of energy and angular momentum. The result is given by the final row in Table II, for small values of the incident partial wave. Considering all partial waves yields a total number of resonances in this

1 K interval of order $\sim 10^3$. However, in ultracold collisions, we are limited to low values of L , typically $L = 0$ alone, barring occasional shape resonances with higher values of L . We therefore conclude from Table II that the mean density of s -wave rotational resonances in O_2 is on the order of 10 K^{-1} . For comparison, alkali atoms typically exhibit on the order of one s -wave Feshbach resonance per 1 K energy interval. Thus, rotational Feshbach resonances are slightly more numerous than atomic hyperfine Feshbach resonances, but not strikingly so, at least for nonpolar molecules.

This simple statistical theory can also estimate the widths of these resonances. Again borrowing from the theory of unimolecular dissociation, the resonance width may be approximated in the Rice-Ramsperger-Kassel-Marcus (RRKM) approximation [23]. Here the energy width is approximately $\bar{\Gamma} = W(E^+)/2\pi\bar{\rho}$, where $W(E^+)$ denotes the number of states that permit the molecules to actually escape to infinite separation. For sufficiently low collision energies, we must have $W(E^+) = 1$, i.e., both molecules must return to their rotational ground states to be energetically able to separate.

We can check this estimate using the set of quantum-mechanical resonances from Fig. 2(a). The 33 resonances that appear in this 1 K energy interval imply a mean width of 5 mK. The actual widths span several orders of magnitude, from 70 μK up to 40 mK, but their geometric

TABLE II. Number of resonances for $^{17}\text{O}_2$ cold collisions, as in Table I. Here, however, the resonances are estimated using the statistical counting model described in the text. In addition, the final row gives the result for $N_{\max} = 8$ and $L_{\max} = 36$, thus including all possible energetically allowed states of the $(^{17}\text{O}_2)_2$ dimer.

N_{\max}	L_{\max}	$L = 0$	$L = 2$	$L = 4$	$L = 6$	$L = 8$	$L = 10$
2	2	2	5
2	4	3	8	11
2	6	3	10	15	11
2	8	3	10	16	14	9	...
2	10	3	10	16	16	12	9
4	4	5	15	24
All	All	14	45	78	83	85	84

mean is 2.4 mK, comparable to the RRKM result. As noted above, in a complete calculation that could include all rotational states up to $N_{\max} = 8$ and $L_{\max} = 36$, we would find $\bar{\rho} \approx 10^3 \text{ K}^{-1}$, dropping the mean width down to $\bar{\Gamma} \approx 10^{-4} \text{ K}$ for realistic O_2 cold collisions. The RRKM approximation is, unfortunately, unable to predict the variation of the widths in this case.

The situation is dramatically different for polar molecules, whose long-range dipole-dipole interaction potential, proportional to $1/R^3$, holds many more intermolecular bound states near threshold. To illustrate this point, we consider two examples: OH, which is suitable for Stark slowing [15]; and the $a(1)$ state of PbO, which is a leading candidate in which to measure the electric dipole moment of the electron [24,25]. Both molecules possess, in addition to a dipole moment, a pair of closely spaced states of opposite parity: a Λ doublet of splitting $\Delta = 0.081 \text{ K}$ in OH [26], and an Ω doubling of splitting $\Delta = 260 \mu\text{K}$ in PbO [27]. Intermolecular potential curves correlating to these thresholds will hold a large number of dipole-bound resonant states.

For the OH-OH interaction, an approximate PES exists [28]. We include the long-range part of this interaction, which has a minimum at $R \approx 6 \text{ a.u.}$ that arises from hydrogen bonding forces. We approximate this surface with a single curve by fixing the two OH molecules in their linear geometry. For PbO-PbO, the PES is entirely unknown; however, since the bound states near threshold depend primarily on the long-range potential, we estimate the PbO-PbO PES by multiplying that of OH-OH by the appropriate ratio of squared dipole moments, $[d_{\text{PbO}}/d_{\text{OH}}]^2 \approx 7.7$. Then, using the same statistical model, we estimate the density of states in a 2Δ energy interval near threshold, 240 K^{-1} for OH and $2 \times 10^5 \text{ K}^{-1}$ for PbO, significantly larger than for the nonpolar O_2 .

The result for the heavier species PbO is particularly striking: We expect to find an s -wave resonance, on average, every $5 \mu\text{K}$ in collision energy. In such a gas, Feshbach resonances are the rule rather than the exception, with many resonances accessible within the kinetic energy spread of the trapped molecules. Apart from increased opportunities for resonant trap loss, such a gas will have new properties arising from extremely strongly energy-dependent scattering lengths. For example, the influence of resonant scattering on the mean-field energy of a Bose-Einstein condensate of these molecules may have to be reconsidered, perhaps using semiclassical methods that are applicable in the realm of dense resonant spectra [29,30].

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