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 O$_2$, OH, and PbO. The density of s-wave resonant states for these species is quite high, implying that a large number of narrow resonant states will exist.

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 quasi-bound state of the pair. The quasi-bound state is characterized by the promotion of one or both atoms to an excited internal state, for example an excited hyperfine state. External magnetic fields can then shift these states in or out of resonance, giving the experimenter direct control over interparticle interactions. In this way, Bose-Einstein condensates of $^{85}$Rb have been made stable or unstable on command, leading to novel many-body effects. 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. Magnetic field Feshbach resonances have now been observed in the alkali atoms $^{23}$Na, $^{85}$Rb, $^{133}$Cs, and $^{40}$K. While not uncommon, these resonances are far from ubiquitous in ultracold alkali atoms. This is largely due to the relatively small number of 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. 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 (PES’s) 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. These resonances may be useful as tools for pinning down the details of multidimensional PES’s. They may also imply resonant control over cold molecular collisions, including, possibly, control over chemical reactions. In addition, the scattering dynamics is chaotic, implying that ultracold resonances will form a new laboratory for studying quantum chaos. In this Letter we estimate the most basic properties of these resonances, namely, how many we can expect, and what their widths might be. We are interested here in molecules produced in their ro-vibrational ground states by buffer-gas cooling or Stark slowing techniques. However, vibrationally excited cold molecules produced by photoassociation of cold atoms will also exhibit rich resonant dynamics.

Classical chaos at low energies has been studied extensively in molecular scattering problems. 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.

Our classical calculations verify that multiple-collision resonances persist at ultracold temperatures. We con-
sider scattering of $^{17}$O$_2$ molecules, using the singlet rigid rotor potential energy surface of Ref. [18]. At the collision energies considered, vibrational excitation is not energetically allowed. 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 to Figure 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 $P_{01}$ (in units of $\hbar$) of one of the molecules. As a guide, the heavy solid line indicates the allowed region of phase space. For the molecules to separate at this energy, the greatest angular momentum either molecule could have is $0.027\hbar$. Instead, the molecules can exchange several $\hbar$ of angular momentum in each collision, and the trajectory eventually fills the allowed phase space.

![Graph of elastic scattering cross section](image)

**FIG. 2.** Evidence of chaos in quantum mechanical scattering of oxygen molecules. (a) shows the complete elastic scattering cross section, computed as in Ref. [19]. 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.

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 $|N = 0, J = 1, M_J = 1|$ fine-structure state of $^{17}$O$_2$ [Fig. 2(a)], following the model described in Ref. [19]. As in Ref. [19], we have neglected the nuclear spin of the $^{17}$O atoms, to emphasize the effect of from rotational motion. This model includes rotational levels up to $N = 2$, and the partial waves $L = 0, 2, ... 14$, and finds 33 resonances in this energy range. Treating these levels as bound states of the (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. 2a) 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 $\Delta(x)$ of Dyson and Mehta [20]. 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 $\Delta(x) = x/15$, 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 [21].

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, which considers the breakup of a large molecule under the influence of random collisions with other molecules in a solution [22]. 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:

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

where $\hat{H}_1$ and $\hat{H}_2$ represent the rotational fine structure of each individual molecule, and $\hat{H}_{\text{int}}$ 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 $E_{\text{int}}$. 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 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 \([14]\). Table I tabulates, for the quantum mechanical calculation, the number of resonances in each partial wave \(L\) in an energy range 1K above the incident threshold. Each row in the table represents a separate calculation, characterized by the maximum number of molecular rotation states \((N_{\text{max}})\) and partial wave states \((L_{\text{max}})\) included in the basis set.

Table II reports the same information, but this time estimated from the statistical model. Statistical 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 calculation is that it can easily be extrapolated to include all allowed values of \(N\) and \(L\) consistent with conservation of energy and angular momentum, as well as Bose symmetry. 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 1K 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 \(\text{O}_2\) is on the order of 10 K\(^{-1}\). For comparison, alkali atoms typically exhibit on the order of 1 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. (In practice the numerous hyperfine levels in \(^{17}\text{O}_2\) will play a role also, but we are concerned here strictly with rotation.)

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 as \([22]\)

\[
\tilde{\Gamma} = \frac{W(E^+)}{2\pi \rho},
\]

where \(\rho\) is the mean density of states we have been considering, and \(W(E^+)\) is the number of states that permit the molecules to actually escape to infinite separation. For the low collision energies considered here, both molecules must return to their ground state to separate, so that \(W(E^+) = 1\). In the quantum mechanical calculation in Fig. 2(a), there are 33 resonances in a 1 Kelvin interval, implying a mean width in this approximation of \(\tilde{\Gamma} \approx 5\) mK. For comparison, the arithmetic mean of the quantum mechanical resonance widths is 8 mK. Note that the quantum mechanical widths span several orders of magnitude; their standard deviation is not given by the RRKM result \([23]\).

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 \([14]\); and the \(a(1)\) state of PbO, which is a leading candidate in which to measure the electric dipole moment of the electron \([23,24]\). Both molecules possess, in addition to a dipole moment, a pair of closely-spaced states of opposite parity: a \(\Lambda\) doublet of splitting \(\Delta = 0.081\) K in OH, and an \(\Omega\)-doubling of splitting \(\Delta = 260\) \(\mu\)K in PbO. Intermolecular potential curves correlating to these thresholds will hold a large number of dipole-bound resonant states. Details of the fine structure of OH is given in \([27]\, and that of PbO in \([28]\).

For the OH-OH interaction an approximate PES exists \([24]\. We include the long-range part of this interaction, which has a minimum at \(R \approx 6\) a.u. that arises from hydrogen bonding forces. For the sake of our statistical model, we approximate this surface with a single curve by fixing the two OH molecules in their linear geometry. The intermolecular bound state energies \(E_{\text{int}}\) are then simply the bound states of this potential, for each of the partial waves considered. We ignore for our present purposes an even deeper part of the PES corresponding to chemical binding of hydrogen peroxide, \(\text{H}_2\text{O}_2\). For PbO-PbO the PES is entirely unknown; however, since the bound states of interest 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, \([d_{\text{PbO}}/d_{\text{OH}}]^2 \approx 7.7\). Table III tabulates the number of s-wave resonances to be expected for each species. These numbers refer to the important energy range \(2\Delta\) above threshold, where the number of resonances is greatest. Expressed as a mean density-of-states over this range, the densities are 240 K\(^{-1}\) for OH and 2 \times 10^9 K\(^{-1}\) for PbO, significantly larger than for the nonpolar \(\text{O}_2\).

In general, the resonances shift when an external electric field is applied, so that one after the other can be brought into resonance with the essentially zero-energy molecules. Given a mean density of states \(\approx 10^9\) K\(^{-1}\) for OH, and given the OH dipole moment (=1.67 D), the mean spacing of these resonances as a function of field would be of order \(\sim 250\) V/cm. This means that, in contrast to the magnetic field resonances in alkali atoms, there will be many available resonances in ultracold polar molecule collisions.

We conclude by sketching the implications of this work for the theory of ultracold collisions. As is well-known, ultracold collision theory requires a certain level of experimental input to fine-tune the scattering Hamiltonian. It is not yet clear how much or what kind of information is required to perform this fine-tuning for molecules \([29]\). Knowing roughly how many resonances to expect can greatly simplify theory, by providing an estimate of how many parameters are strictly necessary to reproduce the data. With this information theory could then turn
around and predict how these resonances evolve with applied external electric and magnetic fields.

A second, equally important implication concerns experiments at temperatures where $kT$ is large compared to the mean spacing between resonances. In this case individual resonances are not resolved, and only the overall modulation of the spectrum matters. It is then likely that semiclassical methods should prove insightful.

This work was supported by the NSF and by the OSEP program at the University of Colorado. We acknowledge an allocation of parallel computer time by NPACI, and useful discussions with D. Nesbitt.

*email address: bohn@murphy.colorado.edu

[1] W. C. Stwalley, Phys. Rev. Lett. 37, 1628 (1976).
[2] E. Tiesinga, B. J. Verhaar, and H. T. C. Stoof, Phys. Rev. A 47, 4114 (1993).
[3] J. L. Roberts et al., Phys. Rev. Lett. 86, 4211 (2001).
[4] M. Holland, S. J. J. M. Kokkelmans, M. L. Chiofalo, and R. Walser, Phys. Rev. Lett. 87, 120406 (2001).
[5] E. Timmermans, K. Furuya, P. W. Milloni, and A. K. Kerman, Phys. Lett. A 285, 228 (2001).
[6] S. Inouye et al., Nature 392, 151 (1998).
[7] Ph. Courteille et al., Phys. Rev. Lett. 81, 69 (1998).
[8] J. L. Roberts et al., Phys. Rev. Lett. 81, 5109 (1998).
[9] V. Vuletić, A. J. Kerman, C. Chin, and S. Chu, Phys. Rev. Lett. 82, 1406 (1999).
[10] T. Loftus et al., Phys. Rev. Lett. 88, 173201 (2002).
[11] That chemical reactions may occur at ultralow temperatures is suggested by N. Balakrishnan and A. Dalgarno, Chem. Phys. Lett. 341, 652 (2001).
[12] M. C. Gutzwiller, Chaos in Classical and Quantum Mechanics (New York, Springer-Verlag, 1990).
[13] J. D. Weinstein et al., Nature 395, 148 (1998).
[14] H. L. Bethlem et al., to appear in Phys. Rev. A.
[15] R. C. Forrey et al., Phys. Rev. Lett. 82, 2657 (1999).
[16] K. M. Atkins and J. M. Hutson, J. Chem. Phys. 103, 9218 (1995), and references therein.
[17] P. E. S. Wormer and A. van der Avoird, J. Chem. Phys. 81, 1929 (1984).
[18] T. Pattard and J. M. Rost, Chem. Phys. Lett. 291, 360 (1998).
[19] A. V. Avdeenkov and J. L. Bohn, Phys. Rev. A 64, 052703 (2001).
[20] F. J. Dyson and M. L. Mehta, J. Math. Phys. 4, 701 (1963).
[21] P. Houvaut and J.-M. Launay, Chem. Phys. Lett. 329, 233 (2000).
[22] R. G. Gilbert and S. C. Smith, Theory of Unimolecular and Recombination Reactions (Blackwell Scientific, 1990).
[23] In addition, resonance widths can display signatures of quantum chaos, but the limited statistics of this sample prevent us from drawing any conclusions in this regard.
[24] B. Kuhn et al., J. Chem. Phys. 111, 2565 (1999).

TABLE I. Number of resonances in a 1K energy interval above threshold for cold collisions of $^{17}$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 $N_{\text{max}}$ and maximum partial wave $L_{\text{max}}$. For each such calculation, the table gives the number of resonances found separately in each incident partial wave $L$.

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

TABLE II. Number of resonances for $^{17}$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 extrapolates to the limit where $N_{\text{max}} = 8$ and $L_{\text{max}} = 36$, thus including all possible energetically allowed states of the $^{(17)}$O$_2$ dimer.

| $N_{\text{max}}$ | $L_{\text{max}}$ | $L = 0$ | $L = 2$ | $L = 4$ | $L = 6$ | $L = 8$ | $L = 10$
|-----------------|-----------------|--------|--------|--------|--------|--------|--------|
| 2               | 2               | 2      | 5      | –      | –      | –      | –      |
| 2               | 4               | 3      | 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     | –      | –      | –      |

TABLE III. Summary of s-wave resonances for two polar molecules. $\rho_\Delta$ is the average density of states consistent with s-wave initial conditions, over an energy range $2\Delta$ above threshold, where $\Delta$ refers to the $\Lambda (\Omega)$-doublet of OH (PbO). Using the RRKM result, this density translates into the mean energy width $\Gamma_\Delta$.

| Molecule | $\Delta$ (K) | $\rho_\Delta$ (K$^{-1}$) | $\Gamma_\Delta$ ($\mu$K) |
|----------|--------------|--------------------------|-------------------------|
| OH       | 0.081        | 240                      | 660                     |
| PbO      | $2.6 \times 10^{-4}$ | $1.9 \times 10^{5}$ | 5                      |