

Polar molecules in the quantum regime

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With molecular gases so cold that collisions must be described quantum mechanically, researchers are studying chemical reactions as they've never been seen before.

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Molecules at ultralow temperatures represent an exciting new frontier for atomic, molecular, and optical physics; that frontier is endowed with a strong interdisciplinary character and connections to other scientific fields, including chemistry, quantum information, condensed-matter physics, and astrophysics.¹ The connections, and many possibilities for technological advances, arise naturally, as molecules are the ubiquitous building blocks of materials. Control of molecular interactions has thus been an outstanding scientific quest for generations.

In the past three decades, researchers have been tremendously successful in creating ultracold atomic gases, in which atoms brought to a near standstill exhibit striking quantum behaviors. Bringing molecules into the ultracold regime, in which interaction dynamics are fully quantum mechanical, opens up exciting new opportunities. Reaching the ultracold regime with molecules has long been hindered by the many molecular internal degrees of freedom, such as vibrational and rotational levels, fine and hyperfine structure, and symmetry-breaking doublets, but the situation is now changing rapidly.

In this article we present an overview of some of the techniques involved in creating, controlling, and understanding ultracold molecules; we also describe the first set of experiments that demonstrate ultracold molecular collisions and chemical reactions in the regime where collisions must be described in terms of quantum wavefunctions. Those efforts serve as an important staging ground for the next step of exploring collective quantum effects in an ultracold gas of molecules.

Why cold molecules?

Figure 1 shows the various energy scales involved in an ultracold molecular gas. For a gas cooled to an ultralow translational temperature, the internal excitation energies can be up to 10 orders of magnitude larger than typical kinetic energies. Control of the internal quantum states, and of the energy flow from internal states to translation, is thus of paramount importance when preparing a molecular gas in the quantum regime. At the same time, molecules' rich internal structure gives rise to a diverse set of scientific opportunities if one can prepare an ultracold molecular gas.

First, experiments on molecules represent a natural extension of our capabil-

ity to control and precisely measure quantum systems. Thanks to their internal structure, molecules provide a testing ground for some of the fundamental laws of nature: fundamental constants, symmetry and parity, extensions of the standard model, and so forth.^{2,3} At low temperatures, motional effects can be carefully studied and controlled, allowing for high-resolution spectroscopy of molecular structure at an unprecedented level of precision, which is crucial in the search for symmetry violations.

Second, polar molecules also provide new opportunities for the study of novel many-body quantum systems.⁴ Many-body systems are characterized by their interparticle interactions, and cold polar molecules, like cold atoms, allow tunable interactions between particles. Furthermore, the anisotropic interactions between polar molecules are significant at the typical interparticle separations in a quantum gas, whereas the interactions between atoms, including the dipolar interactions between magnetic atoms, operate over a much shorter range.⁵ Polar molecules are easily manipulated by external electric fields, so their dipole moments can be tuned in the laboratory frame. Scientific opportunities with quantum gases of ultracold molecules include creating novel molecular superfluids that rely on the dipole-dipole interaction between ultracold fermionic molecules, studying quantum magnetism using the many internal degrees of freedom in molecules to engineer effective spin-spin interactions, and implementing novel quantum phases with polar molecules confined in optical lattices.

Third, molecular quantum gases allow the study of chemical reactions at ultralow energies.⁶ As recent work at JILA demonstrates, the ultracold reaction rate is dictated largely by quantum statistics and the long-range intermolecular interactions and can be surprisingly large.⁷ Areas for

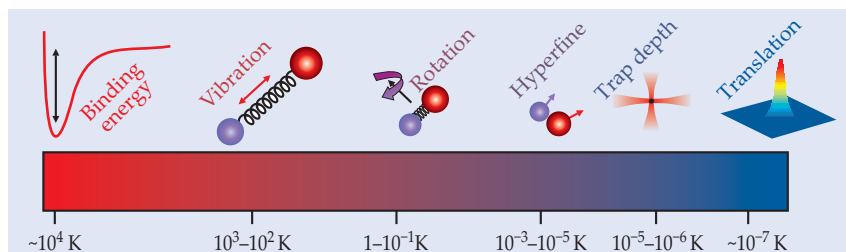


Figure 1. The many molecular degrees of freedom and their corresponding energy scales. Molecules' complex internal structure provides unique advantages and challenges for precision measurement, quantum science, and ultracold chemistry.

future study include electric-field-controlled collisions, resonance-mediated reactions, and collective many-body effects in chemistry.

Cooling molecules—or making them cold

The scientific research directions outlined above present demanding requirements on the preparation of ultracold molecular gases. For precision spectroscopy, control of molecular motional states permits the most accurate measurement, and low temperatures facilitate long coherence times. For the study of novel quantum systems, the ultracold molecular gas must be dense, stable, and easily polarized. For the study of cold chemical reactions, a variety of chemically interesting molecules in single quantum states is highly desirable.

Over the past decade, several methods have been developed to produce cold polar molecules.¹ One is to cool molecules through thermal contact with a cold atomic gas, such as cryogenically cooled helium. That general approach works with many different molecular species and can be used for either trapping a cold molecular gas or extracting a cold molecular beam.⁸ A second approach is to take advantage of molecular-beam technology, which has a strong tradition in chemical physics, and slow the beam down to rest in the lab frame. That method has been implemented using spatially inhomogeneous and synchronously switched electric, magnetic, or optical fields.⁹ In a third approach, molecules, like atoms, may be laser cooled, although such cooling is difficult because of the many molecular energy levels; a molecule typically scatters only a few photons before it is pumped into an internal state that is dark to the cooling laser light. Recent work has shown that laser cooling can be feasible for carefully chosen molecules¹⁰ (see also PHYSICS TODAY, January 2010, page 9), but many challenges remain.

So far, cooling techniques have produced molecular gases with fewer than 10^{-12} molecules per phase-space state; in contrast, a quantum gas requires a phase-space density of order 1. Nevertheless, directly cooled molecules have already been used in high-resolution spectroscopy and low-energy collisional studies. For example, a recent experiment combining Stark deceleration and buffer-gas cooling led to a direct measurement of electric-field effects on bimolecular collisions.¹¹ But the observed collision dynamics were in the semiclassical, not the quantum, regime.

An alternative to direct cooling is to start with ultracold atoms, such as the readily cooled alkali metal atoms, and form them into molecules.² The atoms can be joined by photo-association, in which a laser drives an optical transition from the free state of two unbound atoms to an electronically excited molecular state, which then decays by spontaneous emission. However, spontaneous emission is a random process that leaves the molecules in a wide distribution of states. Moreover, conversion of atom pairs into ground-state molecules is inefficient, and typical molecular phase-space densities are below 10^{-12} .

The efficiency can be increased by making the process fully coherent. A coherent state-transfer process, illustrated in figure 2, preserves the atomic gas's initial phase-space density and makes it feasible to directly produce a molecular quantum gas. Such a scheme is now possible thanks to recent experimental advances in ultracold atomic gases and precision laser tools.^{12,13} Starting from a quantum gas of two types of atoms—potassium and rubidium, for example—extremely weakly bound molecules (which only exist at ultracold temperature) can be efficiently produced in a single internal state. The association does not use lasers but instead takes advantage of a Fano–Feshbach scattering resonance, which

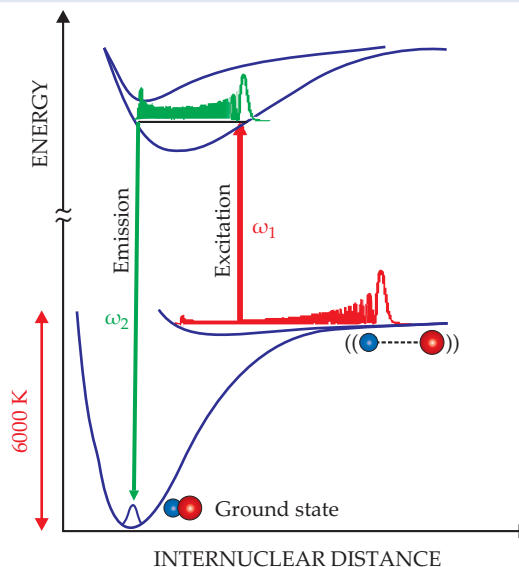


Figure 2. The current state of the art in creating ultracold polar molecules involves first forming exotic, weakly bound molecules near a Fano–Feshbach resonance. Then two phase-coherent optical lasers, whose frequencies ω_1 and ω_2 are precisely tuned so that their difference matches the molecular binding energy, coherently transfer the molecules to the rotational and vibrational ground state by way of an electronic excited state. (Adapted from ref. 2.)

occurs when the energy of a weakly bound molecular state is equal to the kinetic energy of a colliding pair of atoms. Experimentally, the resonance can be accessed by using a magnetic field to tune the relative energies of the atom pair and the weakly bound molecule. A pair of Raman lasers, phase locked to a common optical frequency comb, then coherently transfer the molecules to their ground state by way of an electronic excited state. The coherent-transfer technique has produced a gas of fermionic $^{40}\text{K}^{87}\text{Rb}$ molecules with a temperature of a few hundred nanokelvin and a spatial density of 10^{12} molecules per cubic centimeter, corresponding to a phase-space density of about 0.1.

The molecules are detected via the unlikely route of first reversing the coherent optical transfer step—taking the molecules from their ground state back to the weakly bound state—and then imaging them using light resonant with an atomic absorption.¹² That light first dissociates the weakly bound molecules and then scatters off the free atoms. The detection scheme works well because of the efficiency of the coherent state transfer and the high signal-to-noise ratio of absorption imaging of ultracold trapped atoms. The molecules can also be imaged directly, but with a reduced signal-to-noise ratio, using light resonant with a molecular transition; one such image is shown in figure 3.

Collisions and chemistry

Although the actual density of the ultracold KRb gas is still very low—one-millionth that of air at room temperature and pressure—its high phase-space density makes the creation of quantum molecular gases seem imminent. Particularly exciting is the prospect of a quantum gas of polar molecules with strong anisotropic interactions between the particles. Indeed, the temperature of the KRb gas is only 1.5 times the Fermi

temperature, which marks the onset of the quantum regime.¹²

A prerequisite for creating a quantum dipolar gas is an understanding of ultracold molecular collisions. The rate of inelastic collisions determines the lifetime of the trapped gas, and the rate of elastic collisions determines the time required for rethermalization following any perturbation. Cooling the gas any further—by forced evaporation, for example—will require a favorable ratio of those rates. Furthermore, collisions between molecules can be chemically reactive. Ultracold molecules access a new and different regime for chemistry, in which long-range physics, threshold laws, and the quantum statistics of the molecules themselves govern how two molecules collide.

Hyperfine, or nuclear, states of molecules ordinarily are not important in a chemical reaction. But at ultralow temperatures, collision energies can easily be much smaller than the hyperfine splitting in a modest magnetic field. Moreover, any internal degree of freedom, even a nuclear spin that couples extremely weakly to the molecular state's electronic degrees of freedom, can significantly affect the outcome of an ultracold reaction because of the importance of quantum statistics.

The hyperfine state of the fermionic KRb molecules can be precisely controlled.¹⁴ The excellent energy resolution of the coherent two-photon transfer process in figure 2 ensures that molecules are created in just one (but not the lowest) of the 36 possible hyperfine states. The hyperfine state can then be controlled by using microwaves to drive the transition between the rotational ground state and the first rotational excited state. Interaction of the rotation and the nuclear quadrupole moments leads to a small mixing of hyperfine states, so when the molecules are driven back to the ground rotational state, they can be placed in the lowest-energy hyperfine state or any other desired hyperfine state.

When two ultracold KRb molecules in their lowest-energy hyperfine state collide, only one reaction is possible,¹⁵ the atom-exchange reaction $\text{KRb} + \text{KRb} \rightarrow \text{K}_2 + \text{Rb}_2$. The easiest way, if not the most direct, to detect that reaction is to monitor the loss of KRb molecules from the trap.⁷ Because the loss is observed to follow the expected time dependence for two-body collisions, it can't result from collisions with background gas in the vacuum chamber, which would yield a density-independent exponential decay. And because the same loss rate was observed even when all the molecules were transferred into the lowest-energy hyperfine state, the loss cannot be due to nonreactive inelastic collisions, but must be due to chemical reactions. Because the loss rate is reasonably large in the ultracold regime, we can deduce that the atom-exchange reaction has no chemical reaction barrier—or, more precisely, that the maximum energy of any such barrier must be smaller than the thermal energy $k_B T$, where k_B is Boltzmann's constant and T is the temperature of the gas.

The role of quantum statistics

A remarkably simple picture of the KRb reaction has emerged through the joint efforts of experiment and theory.¹⁶ It is assumed that when two molecules get close enough that chemical forces are relevant, they always react. The long-range part of the collision, in which the molecules approach each other but are still far apart compared to the range of chemical forces, must be treated quantum mechanically in

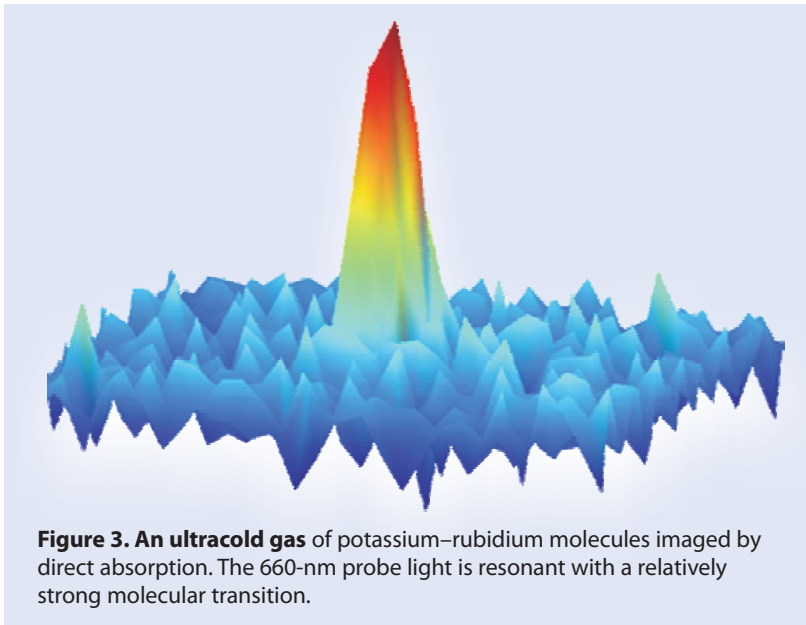


Figure 3. An ultracold gas of potassium–rubidium molecules imaged by direct absorption. The 660-nm probe light is resonant with a relatively strong molecular transition.

the ultracold regime. (In the typical chemistry picture at higher temperatures, trajectories are treated classically.) Instead of discussing impact parameters, we describe ultracold collisions in terms of the individual partial-wave components of the relative orbital angular momentum of the colliding molecules; reactions typically occur in only one partial-wave collision channel. These ideas are familiar to the ultracold atomic gas community in describing cold collisions in Bose and Fermi atomic gases.

Just as in Bose and Fermi atomic gases, quantum statistics of colliding particles play a critical role. Since the KRb molecules are fermions, their wavefunction must be antisymmetric with respect to the exchange of identical molecules. Because the wavefunction of two molecules is the direct product of a component describing the internal states and a component describing the relative motion, the required antisymmetry of the total wavefunction couples the internal states and the relative motion of the colliding molecules.

When all the molecules are in the same internal state, the relative-motion wavefunction must be antisymmetric. The lowest-energy antisymmetric partial wave is the p -wave, with one quantum of relative angular momentum. But the p -wave channel has a centrifugal barrier that is much higher than the collision energy in the ultracold gas. Molecules must tunnel through that barrier, and the reaction rate therefore scales linearly with temperature in a threshold behavior that is characteristic for inelastic p -wave collisions. The measured loss rate, shown by the black and blue data in figure 4, agrees well with calculations based on rate of quantum mechanical tunneling through a p -wave centrifugal barrier.

On the other hand, if the molecules are created in a mixture of hyperfine states, the relative-motion wavefunction need not be antisymmetric, and collisions can proceed via the s -wave channel with zero angular momentum and no centrifugal barrier. One expects the reaction rate to be much higher and independent of temperature, and indeed it is, as shown by the green data in figure 4. The reaction can thus be controlled by a flip of a nuclear spin.

Dipolar interactions

A gas of polar molecules is a unique and interesting quantum system because of its dipole–dipole interactions, which can be turned on by applying an external electric field to orient

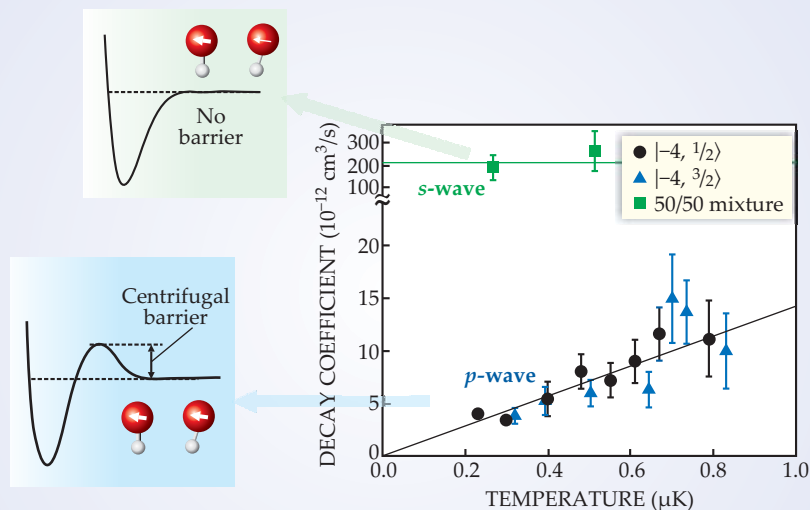


Figure 4. Quantum statistics in ultracold chemistry. In a gas of fermionic $^{40}\text{K}^{87}\text{Rb}$ molecules, when all the molecules are in the same internal state $|m^{\text{K}}, m^{\text{Rb}}\rangle$, the relative wavefunction of two reacting molecules must be antisymmetric, so the reaction must proceed via a p -wave channel, in which the reacting molecules must tunnel through a centrifugal barrier. The reaction rate as measured by the decay coefficient of the number of atoms in the trap (blue triangles and black circles) is therefore low and proportional to temperature. On the other hand, when the molecules are in a mixture of hyperfine states, the reaction can proceed via the barrierless s -wave channel, and the reaction rate (green squares) is much higher and independent of temperature. In both cases, experimental data agree well with theory (black and green lines). (Adapted from ref. 7, Ospelkaus et al.)

the molecules in the lab frame. Although experiments exploring molecular dipolar interactions have not yet reached the quantum gas regime, they are well into the quantum regime of collisions.⁷ When a modest electric field of a few kilovolts per centimeter is applied to a KRb gas, a significant net dipole moment of up to 0.22 debye per molecule ($1 \text{ D} = 3.3 \times 10^{-30} \text{ C}\cdot\text{m}$, a typical dipole moment for an isolated polar molecule) is observed. Even though KRb's dipole moment is small compared to other alkali species, its effect on collisions is already dominant.

In the KRb system, the primary effect of dipole-dipole interactions comes from the attraction of molecules oriented head to tail, which can facilitate reactions by lowering the p -wave centrifugal barrier. As shown by the blue data in figure 5, at induced dipole moments above 0.1 D the rate coefficient for the chemical reactions increases as the sixth power of the dipole moment, and by 0.22 D, the centrifugal barrier has almost entirely disappeared for head-to-tail collisions and the reaction rate is nearly 100 times faster.

From the point of view of ultracold chemistry, the data represent a remarkable demonstration of control over the bimolecular reaction rate. But from the point of view of creating

novel quantum matter, the rapid increase in reaction rate presents a serious obstacle, since the desired quantum gas of oriented molecules becomes unstable. In principle, the simplest solution is to use a molecule that cannot undergo chemical reactions. Indeed, recent calculations predict that several alkali dimer species do not have any exothermic bimolecular chemical reaction channels, and experiments are under way to create ultracold polar molecules using those species.

In the JILA KRb experiments we instead took the approach of placing fermionic polar molecules in a confined geometry.¹⁷ Specifically, confinement in a two-dimensional geometry can prevent the head-to-tail collisions that would otherwise result in chemical reactions. True 2D confinement, in which the size of the cloud in the third dimension is smaller than the interaction length scale, requires an extremely tight trap and a large dipole moment. But it turns out that quasi-2D confinement is sufficient to suppress chemical reactions for fermionic polar molecules, because quantum statistics and dipolar interaction both help to prevent molecules from reaching short range. As shown by the black data in figure 5, when molecules are confined in a 1D optical lattice (a stack of pancake-shaped traps created by counterpropo-

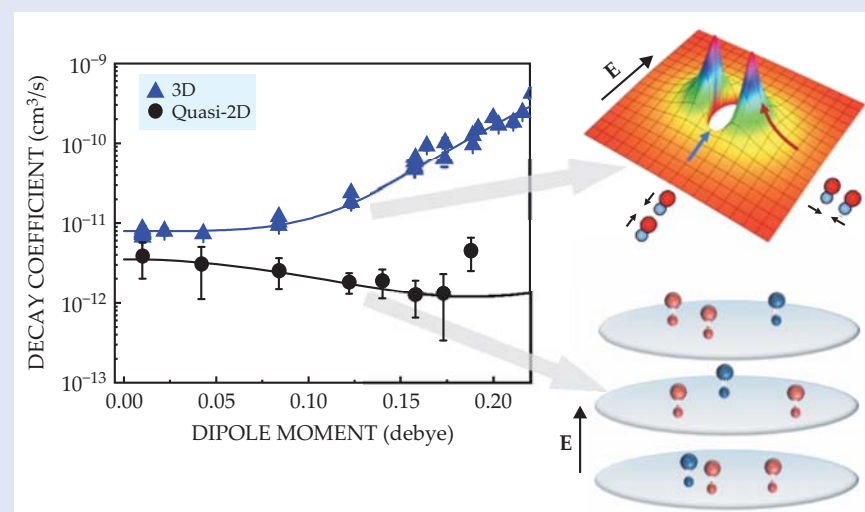


Figure 5. Anisotropic dipolar interactions are revealed by confining molecules in different geometries. In three dimensions, the attractive head-to-tail collisions are allowed, so increasing the dipole moment in the laboratory frame with an applied electric field increases the reaction rate. In a quasi-2D geometry, when the molecules are confined to a stack of pancake-shaped optical-lattice traps, oriented molecules can undergo only the repulsive side-by-side collisions, so there is no increase in reaction rate. (Adapted from ref. 7, Ni et al., and ref. 17, de Miranda et al.)

agating laser beams), the loss rate remains suppressed even as the dipole moment is increased.

Outlook

The study of ultracold molecules is an emerging research direction of interdisciplinary interest. Fundamentally, the work represents the continued advance of our capabilities to precisely control and measure increasingly complex quantum systems. It has the potential both to provide basic physical insight and to yield practical applications. The techniques used to produce cold and ultracold molecules have advanced tremendously in the past few years, and one can expect that in the near future more molecular species will be available in the ultracold regime.

Recent results have shown how the ultracold regime can simplify chemical reactions by limiting the available collision channels and, moreover, how the reactions can be controlled through quantum statistics, threshold laws, electric fields, and trapping geometry. In the exploration of ultracold chemistry, direct detection of the products and their quantum states would provide a much more detailed look at the reactions. In addition, we must explore elastic collisions and the possibility of collision resonances as a function of applied electric and magnetic fields. As has been amply seen in ultracold atomic gases, elastic scattering resonances can be an extremely important tool for creating and probing novel quantum-gas physics.

With an understanding of inelastic and elastic collisions, one can tackle the goal of creating and studying novel quantum matter with ultracold polar molecules. The next steps include evaporative or sympathetic cooling to create a quantum degenerate gas and investigation of many-body or collective effects in the gas. (It will also be interesting to look at chemistry in quantum molecular gases.) In particular, studying polar molecules in 3D optical lattices—arrays of pointlike trapping potentials formed by optical standing waves—opens new opportunities because the dipole–dipole interaction can extend between neighboring sites; in contrast, atoms in optical lattices exhibit interactions only among particles on the same site. Moreover, molecules' long-range interactions are spatially anisotropic and can be tuned with an applied electric field.

A tantalizing prospect is to use stacked multilayer pancakes of polar molecules, which have already been realized in our experiment, for investigation of novel many-body physics. The interplay between the intralayer repulsive and the interlayer attractive interactions can give rise to exotic, strongly correlated quantum phases.¹⁸ For example, molecules from different layers may form dipolar chains, composite objects whose structure, stability, and thermodynamics will be intriguing to explore. Going beyond the quasi-2D system by adding another pair of optical beams along the perpendicular direction will confine molecules in one dimension. Another rich set of problems exists with 1D confinement of strongly interacting quantum gases, and introducing long-range and anisotropic interactions will no doubt present new challenges and excitement. Going then to a fully 3D optical lattice will allow the study of extended Bose– or Fermi–Hubbard Hamiltonians. Finally, another exciting possibility is that even in the absence of optical lattices as external confinement potentials, polar molecules can self-assemble into crystalline structure when their long-range interactions are sufficiently strong and repulsive.⁴

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