

REFERENCE FRAME

The Most Tenuous of Molecules

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Although molecules lie only one small step beyond atoms along the path of complexity that leads from physics to the world about us, many a physicist—molecular physicists excepted—secretly suffers from molecule anxiety. Even the lowly diatomic molecule can be threatening. Arthur Schawlow has neatly summarized the situation: “A diatomic molecule,” he has declared, “is a molecule with one atom too many.”

Happily, we now have a molecule that is so simple that even physicists can understand it. The most tenuous of molecules, its atoms linger far from each other, bound merely by light. More prosaically, the molecule consists of two identical atoms that share a photon. Although it rapidly radiates and falls apart, on the molecular scale of times it leads a long and productive life. What sets this molecule apart from an everyday diatomic molecule is its size—more than a hundred times larger than normal. Its size is the secret of its simplicity: The atoms are so far apart that they hardly know they are parts of a molecule.

The force that binds atoms at such colossal distances goes by various names: the resonance dispersion force, the first-order van der Waals interaction, the superradiant force or, more simply, the very-long-range force. In spite of this confusion of names, the force itself is so simple that one can understand it using only a few ideas from elementary quantum mechanics.

The molecule is composed of identical atoms that have a ground state S and an electronically excited state P , separated in energy by $h\nu_0 = E_p - E_s$. Suppose two atoms in their ground state happen to be close to each other in a spatial state that is symmetric with respect to atom interchange. (To satisfy the Pauli principle, the angular momentum state must be either symmetric or antisymmetric, depending on the nuclear statistics.) If the system absorbs a photon at frequency ν_0 the state of the system, which must continue to be symmetric with respect to atom interchange, is $(S_1P_2 +$

$P_1S_2)/\sqrt{2}$, where the subscripts refer to the two atoms. Because each atom is then in a superposition of its excited and ground states, it possesses an electric dipole moment that oscillates at frequency ν_0 . The two dipoles oscillate in phase, generating a net oscillating moment and a large interatomic force.

The dipoles attract or repel each other depending on whether they are oriented end-to-end along the interatomic axis R or side-by-side, respectively. The orientation is determined by the angular momentum selection rules that govern the photon absorption. In the case of attraction the force is so large that the atoms can be bound at enormous distances, forming what is called a long-range molecule.

A long-range molecule spontaneously radiates, resulting in either two unbound ground-state atoms or, in some cases, two atoms bound in their ground state—the molecular dimer. The dimer's oscillating dipole moment is $\mathbf{p}_1 + \mathbf{p}_2 = \sqrt{2}\mathbf{p}$, where $\mathbf{p}$ is the dipole moment for a single atom. Because the radiation rate is proportional to the square of the moment, the molecule radiates twice as fast as a single atom.

A few comments to put this in perspective: The long-range molecule is essentially a two-atom superradiant system; the giveaway is the factor-of-two enhancement of the radiation rate. (An N -atom superradiant system radiates N times as fast as a single atom.) Hence the attraction is really a superradiant force. A bound excited system could also exist in an antisymmetric state with the two dipoles out of phase. However, lacking a net dipole moment, it would neither radiate nor absorb. It would be subradiant.

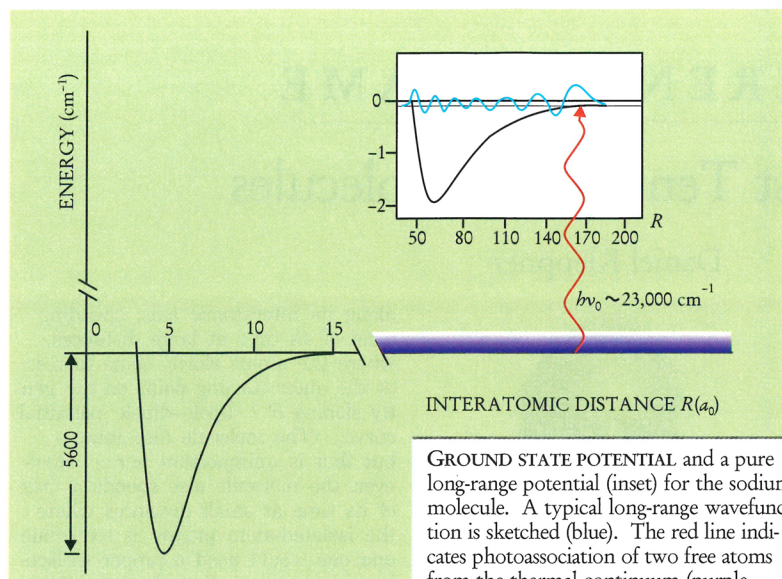
The long-range molecule vibrates

along its interatomic axis, spending most of its time at large distances, where the atoms slowly come to rest at the outer turning point on the gently sloping R^{-3} dipole-dipole potential curve. (The molecule also rotates, but that is unimportant here.) However, the molecule also spends a little of its time at small distances where the isolated-atom picture is too crude and one would need a proper molecular calculation to find the potential. For some states, however, the atoms never get that close. What happens is this: The atoms are actually excited into one of the fine structure components of the P state, for instance $P_{1/2}$ or $P_{3/2}$. As R decreases, the dipole-dipole interaction grows until it becomes larger than the fine-structure interval. When this happens, the angular momentum becomes recoupled, changing the relative orientation of the dipoles. For a few states, this causes the attraction to become a repulsion, and this change occurs while R is still relatively large. A molecule in such a state is dubbed a pure long-range molecule.

Some potentials and a wavefunction for the diatomic sodium system are sketched in the drawing on page 12. In a pure long-range state for which the outer turning point is more than $200 a_0$, the atoms never get closer than about $60 a_0$. ($a_0 = 5.3 \times 10^{-11}$ m is the atomic unit of distance, the bohr.) In contrast, the ground-state sodium dimer, bound by the usual relatively short-range molecular forces, has a potential minimum at about $6 a_0$. The drawing also shows why it is not so easy to make a pure long-range molecule. Its spatial overlap with the ground-state dimer is essentially zero, making it impossible to photoexcite the dimer. However, one can make a pure long-range molecule by directly exciting a pair of free atoms into a bound molecular state—photoassociation.

A pair of atoms can photoassociate only if they happen to be at the same distance from each other and moving with the same relative speed as they would in the molecule. Only for such a pair do the initial and final nuclear wavefunctions overlap sufficiently to allow a large transition dipole moment. Such pairs are rare. The problem is that the kinetic energy of a

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GROUND STATE POTENTIAL and a pure long-range potential (inset) for the sodium molecule. A typical long-range wavefunction is sketched (blue). The red line indicates photoassociation of two free atoms from the thermal continuum (purple area). At room temperature this continuum has an energy spread of about 200 cm^{-1} , but for a gas that has been cooled into the millikelvin regime the continuum can be 10^{-3} cm^{-1} or less, giving it many of the properties of a single sharp state.

room temperature gas of atoms is spread over a huge range, typically 200 cm^{-1} . (Apologies if the energy unit looks strange: Spectroscopists generally measure energy in units of cm^{-1} corresponding to about 10^{-4} eV or a frequency of 30 GHz .) As a result, the number of atom pairs that are eligible for photoassociation is vanishingly small. To make matters worse, the vibrational states of a long-range molecule are typically separated in energy by a few cm^{-1} or less. This is so small compared to the thermal energy spread that there could be no hope of resolving the individual vibrational states.

I feel a personal affinity with long-range molecules, because many years ago I set out to make them. The goal was not to study them in detail but merely to witness superradiance in a two-atom system—to see the factor-of-two enhancement in the radiation rate. Although my students and I measured some useful molecular lifetimes, from the point of view of demonstrating superradiance the project was pretty much of a fizzle. I recall consoling myself with a hortatory verse that somebody—not my mother—taught me:

They said it couldn't be done,
But he set out with a will to
do it.

He tried that thing that couldn't
be done . . .

And found that he couldn't do it.
As it happened, however, the venture turned out to be ultimately rewarding for me. It got my research group started in laser spectroscopy, and it gave me a splendid appreciation for what happened later when laser cooling suddenly opened the way to the world of long-range molecules.

Atoms can be cooled by laser light

to temperatures in the millikelvin regime (and below) and confined by optical or magnetic fields. At a temperature of 1 mK the thermal energy spread is narrower than 10^{-3} cm^{-1} . From a spectroscopist's point of view, atoms in such a narrow thermal continuum behave almost as if they were in a single discrete state. Compared with room temperature, the experiment is improved by a factor of about a million, enough to create the molecules in abundance and study them in exquisite detail.

Some brief history:¹ The field of long-range molecules was founded about 20 years ago by William C. Stwalley, who recognized that highly lying vibrational states of diatomic molecules have unusual properties. With Yea-Hwang Uang and Goran Pichler, he pointed out the exotic features of the pure long-range state. What moved the field into high gear experimentally was a 1987 paper by Helen R. Thorsheim, John Weiner and Paul S. Julienne who pointed out that laser-cooled atoms created fantastic opportunities for photoassociation spectroscopy. Within the past couple of years, long-range molecules, and in some cases pure long-range molecules, have been studied by groups led by Phillip Gould and Stwalley at the University of Connecticut, Daniel Heinzen at the University of Texas, Randall G. Hulet at Rice University, Paul D. Lett and William D. Phillips at the National Institute of Standards and Technology, and Weiner and Vanderlei Bagnato at

the University of Maryland.

In these days of sophisticated science it is natural to be suspicious of anything so simple you can really understand it. Then why bother with long-range molecules? There are two answers. The first is that the study of a simple system that one way or another is off the scale of things previously studied invariably yields surprises and rewards. Photoassociation spectroscopy, for instance, is providing information that is crucial to the pursuit of Bose-Einstein condensation in a gas and helping out the quest for atomic tests of the standard model of particle physics. Many groups are working to achieve Bose-Einstein condensation by laser-cooling alkali atoms. A crucial question is whether the condensate is actually stable. Stability requires that the low-energy scattering length be positive. The scattering length depends critically on the location of the highest vibrational state of the dimer molecule, which can be found from measurements of low-temperature photoassociation spectroscopy. With respect to atomic tests of the standard model—measurements of parity-violating effects due to neutral currents (see my Reference Frame column in *PHYSICS TODAY*, October 1994, page 9)—interpretation of the tests is limited by uncertainties in many-body atomic theory. Photoassociation spectroscopy of laser-cooled atoms has provided new tests of that theory and spurred a resurgence of interest in the interactions and dynamics of ultracold atoms.

The second answer is that simple systems are usually not really simple when you look at them in detail. The cavalier description of a long-range molecule invoked here—two-level atoms in a symmetric state—overlooks a few complications due to electron spin, fine structure and hyperfine structure. Taking these into account requires dealing with hundreds of states. Furthermore, the description overlooks some subtle effects due to molecular perturbations and nonadiabatic interactions. To molecular physicists, such problems are all in day's work. However, if you, like me, suffer from molecule anxiety, it is better not to think about them.

I thank Daniel Heinzen, Randall Hulet, William D. Phillips and William C. Stwalley for helpful conversations.

Reference

1. A number of publications by the authors mentioned have appeared in *Physical Review Letters* during the past two years. A review will appear shortly: P. D. Lett, P. S. Julienne, W. D. Phillips, in *Annual Review of Physical Chemistry*, vol. 46, H. L. Strauss, ed., Annual Reviews, Palo Alto, Calif. (1995), in press. ■