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A new perspective on the binding power of an electron

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When chemists describe the bonds that hold atoms together in molecules, they rely on a classification of the binding mechanisms as covalent, ionic and van der Waals. In the first case, the atoms bind to form molecules by sharing some of their valence electrons which occupy molecular orbitals. In the second case, encountered for instance in NaCl, the bond can be thought of as resulting from an electron transfer from Na to Cl and the attractive electrostatic interaction between the Na⁺ and Cl⁻ ions. In the last case, the atoms or molecules are held together by weak long-range electrostatic interactions, while each retains its chemical identity. These three types of bond represent idealized limiting cases, and any given molecule represents an intermediate situation.

Very recently, Bendkowsky et al. [1] have observed and characterized by high-resolution spectroscopy long-range Rb₂ molecules that cannot be described in terms of these three binding mechanisms. Instead they arise from the scattering of a slow electron in a diffuse Rydberg orbital of high principal quantum number n with a ground-state neutral atom. This binding mechanism had been predicted theoretically before its observation [2] and is rather unusual for chemists as it gives rise to extraordinarily weak bonds, with binding energies on the order of 10-100 MHz (i.e., $4 \cdot 10^{-6}$ - $4 \cdot 10^{-5}$ kJ/mol, to be compared with binding energies often larger than 200 kJ/mol for covalent bonds) and bond lengths easily exceeding 1000 a_0 (a_0 is the Bohr radius). In their experiments, Bendkowsky et al. have observed the vibrational structure associated with these weak bonds.

The basis for the understanding of the long-range molecules observed by Bendkowsky et al. was laid by Fermi in 1934 [3] who proposed a theoretical model to explain surprising observations made by Amaldi and Segrè when measuring spectra of Rydberg states of the alkali metal atoms Na and K in gas cells containing different gases such as argon, molecular hydrogen and helium [4]. They had found that (1) lines corresponding to transitions to individual Rydberg states of high principal quantum number ($n \approx 30$) could be spectrally resolved even though the pressure in the cell containing the alkali metal atoms was such that several thousand ground-state atoms or molecules were located within a sphere of radius equal to the classical orbit of the Rydberg electron, (2) the spectral positions of the lines depended on the chemical identity of the main component of the gas mixture, (3) both positive and negative frequency shifts of the lines could be observed - the positive shift was particularly difficult to explain because the charge-induced-dipole interaction between the positively charged ion core and the neutral atoms within the electron orbit was known to be attractive, and (4) the shifts were proportional to the pressure.

To explain these results, Fermi analyzed in detail the interaction of slow electrons with neutral atoms in their ground state [3]. An electron in a diffuse Rydberg orbital has a very low average velocity because it is primarily located in the region of the last lobe of the

radial wave function where the total energy is dominated by the potential energy. The electron in this region can be approximated as a free electron of very low kinetic energy. In the limit of zero kinetic energy, only two contributions are sufficient to describe the interaction between a Rydberg atom and a neutral ground-state atom (see Fig. 1a for a definition of the relevant coordinates): The first contribution comes from the attractive charge-induced-dipole interaction between the ion core and the ground-state atom mentioned above, which scales as R^{-4} . At low densities, R is large and this contribution negligible. The second contribution originates from the interaction of the slow electron with the ground-state atom, which is dominated by the effects of the charge distribution near the nucleus, causing a “hole” in the potential of the ground-state atom (“buca di potenziale” in Fermi’s words). At very low electron kinetic energies, the centrifugal barrier in the scattering potential of the ground-state atom prevents partial wave components of the electron with non-zero angular momentum from approaching the region of the potential hole, and only s-wave scattering need be considered.

Depending on the sign of the phase shift in the radial wave function of the s electron partial wave as the electron scatters in the potential of the neutral atom, the interaction with this atom is either attractive or repulsive. When the slow electron is in a Rydberg orbital Ψ_{nlm} with principal, orbital and magnetic quantum numbers n , l , and m , the interaction potential can be described by what is called today a Fermi-pseudo-potential (It is important to distinguish the orbital angular momentum l of the Rydberg electron from the orbital angular momentum l' of the collision between the electron and the ground state atom (l' is 0 in the case of s-wave scattering at the ground state atom)) as [5,2]:

$$V_{\text{FPP}} = 2\pi a |\Psi_{nlm}|^2. \quad (1)$$

The remarkable property of Equation (1) is that it describes a *molecular* binding potential between the Rydberg and the ground-state atom solely in terms of the Rydberg electron wave function Ψ_{nlm} and the s-wave scattering length a , which is weakly energy dependent and can be positive or negative. Comparisons of pseudo-potentials calculated with Equation (1) with potential energy curves calculated ab initio have confirmed its validity. In the case of the interaction between a 5s and a 35s Rubidium atom, the potential calculated by Bendkowsky et al. [1] is represented in Fig. 1b together with the electron probability density distribution of the 35s Rydberg electron in Rb. The potential wells, though very shallow, are broad enough to sustain several vibrational levels of the long-range molecule made of the Rydberg atom and the ground-state atom. Also shown in the figure are the positions and wave functions of the first two vibrational levels.

Fermi’s model has been elegantly implemented by Masnou-Seeuws and her coworkers in the theoretical description of the potential energy curves HeK, NeK, HeNa and NeNa and of their spectroscopic and collisional properties [6]. Because the scattering length of electron – alkali-metal-atom collisions is negative, minima in the interaction potential arise when the Rydberg electron radial wave function exhibits maxima or minima. In the case of the rare gas atoms He and Ne in their ground state, the scattering length is positive, and potential maxima arise at the maxima of the Rydberg electron probability

density [7]. The scattering length for the heavier rare gas atoms becomes progressively more negative with increasing size.

Expression (1) is only strictly valid for slow electrons and thus at large distances from the ion core. At smaller distances, the electron accelerates in the potential of the ion core, gains kinetic energy, and the electron-ground-state-atom interaction can no longer be described by s-wave scattering only. Greene and his coworkers [2] have examined situations where Eq. (1) can be used to describe the interaction potential between a ground-state atom and a Rydberg atom and were the first to describe in detail, and draw attention to, the unusual properties of the resulting long-range molecules and their vibrational quantum states.

They predicted two types of long-range molecules bound by Fermi-pseudo-potentials (Eq. (1)): (i) Molecules in which the Rydberg electron is in a state of low- l , high- n value and which correspond to those observed by Bendkowsky et al. [1]. (ii) Molecules in which the Rydberg electron is in one of the degenerate non-penetrating states of high angular momentum quantum number ($l > 3$). In this case, the interaction with the neutral atom mixes all degenerate high- l states of the same n value. The effect is similar to that of a weak electric field, which leaves the non-degenerate low- l states unaffected, but efficiently mixes all degenerate high- l states. In the presence of the ground state atom, the wave functions of the Rydberg electron thus become linear combinations of $l > 3$ functions and show complex patterns of angular nodes. In particular, one of these linear combinations is such that it gains a very large dipole moment and has a large maximum of its electron density at the position of the perturbing neutral atom. This situation leads, via Eq. (1), to a larger binding energy (up to several GHz) compared to the binding energies of only several MHz typical of the first type of long-range molecules. The electron density distribution of this l -mixed state in any plane containing the ion core and the ground-state atom shows a striking resemblance with fossils known as trilobites (see Fig. 1 of Ref. [2]) and led Greene et al. to describe it as “trilobite resembling”. The resulting molecular states possess a very large dipole moment, and the similarity of these molecules with Rydberg Stark states implies that they should be as easily confined in electrostatic traps as atoms in Rydberg Stark states [8]. Such “trilobite” molecules remain to be observed experimentally.

The work of Greene et al. highlighted the unusual binding mechanism described by Eq. (1) and stimulated experimental searches for spectral signatures of the corresponding molecular quantum states beyond pressure shifts in Rydberg spectra. It also stimulated theoretical predictions, by Rost and his coworkers, of the formation of polyatomic molecules based on the same principles [9], and even of the existence of trimers composed solely of atoms having a positive scattering length [10].

Whereas a careful analysis, by Greene and his coworkers [11], of the line shapes in older spectroscopic data indirectly pointed at the existence of long-range molecules, it is the high-resolution spectroscopic study of Bendkowsky et al. [1] which, for the first time, revealed the quantized vibrational energy level structure of these molecules. In their study, they also measured the first vibrational energy interval and the binding energy (13

MHz and 25 MHz, respectively) of the long-range molecule made of a 5s and a 35s Rb atom, and found its lifetime to be about four times shorter than that of the 35s atomic Rydberg state. This breakthrough was made possible by their ability to generate very dense, ultracold samples of Rb atoms (temperature 3.5 μ K, number density $1.5 \cdot 10^{13} \text{ cm}^{-3}$) in a magnetic trap and to excite these atoms to high Rydberg states with narrow-bandwidth (< 1 MHz) laser radiation. Under these experimental conditions, the kinetic energy associated with the relative motion of the atom pairs is less than the binding energy of the long-range molecules, collisions are suppressed, and the probability of pairs of atoms separated by distances corresponding to the electron orbit radius of a 35s Rydberg state is sufficiently high to permit the efficient formation of long-range dimers.

The work of Bendkowsky et al. [1] will undoubtedly have a significant impact on chemistry and physics, for the following reasons:

- (1) The identification and spectroscopic characterization of a new type of long-range molecules is in itself a significant contribution to chemistry and physics.
- (2) A rapidly increasing number of research groups worldwide are attempting to study chemical processes at (ultra)cold temperatures, i.e. much below 1 K, but, so far, only very few observations have been made that are specific to the very low temperatures. Along with the demonstration of molecule formation in well-defined high vibrational levels by photoassociation of ultra-cold alkali metal atoms by Pillet and his coworkers [12], the association of alkali metal atoms in BECs by tuning magnetic fields across Feshbach resonances [13,14], and the observation of Efimov resonances corresponding to alkali metal trimers [15], the results of Bendkowsky et al. may be regarded, in our opinion, as one of the most important products of ultracold chemistry so far.
- (3) High-resolution spectroscopic measurements of binding energies and vibrational frequencies enable the determination of the scattering lengths for collisions between low-energy electrons and atoms and molecules and precise tests of the underlying scattering theory.
- (4) The extreme weakness of the bonds implies that neither the Rydberg, nor the ground state atoms are substantially modified by the formation of the long-range molecule. One may therefore envisage using the weak bond as a way to non-invasively tag a ground state neutral atom or a Rydberg atom with its long-range binding partner or to trap the ground state atom by trapping the Rydberg atom or vice versa.
- (5) The observation of long-range molecules of a new kind opens many perspectives for future fundamental research. For instance, one should look for effects beyond the s-wave scattering approximation and search for the real trilobite molecular states. Future experiments are likely to lead to the formation of long-range molecules containing more diverse atoms than alkali metal atoms. Moreover, the “synthesis” of trimers consisting of two ground state atoms bound to a Rydberg atom, or of an atom bound to a diatomic Rydberg molecule, or of a ground state diatomic molecule bound to a Rydberg atom, the synthesis of tetramers, etc., will broaden the scope of the investigations. The observation of the rotational energy level structure of these long-range molecules is a tantalizing prospect because it

could provide structural and dynamical information, e.g., concerning the neutral atom probability distribution and its evolution in the three dimensional Fermi-pseudo-potential (see Fig. 1b). However, measuring the rotational structure of molecules of the type discussed here, which have rotational constants in the kHz range, will necessitate ultra-narrow-bandwidth radiation sources to resolve the very dense spectral structures. It is also not clear at present whether the natural lifetimes of the corresponding quantum states are long enough for such measurements to be at all possible. Finally, it would be interesting to characterize the decay of these molecules, in particular to understand why their lifetimes differ so substantially from the lifetimes of the isolated Rydberg atoms. Indeed, it is very difficult to imagine any molecular decay mechanism that would not rely on a short-range interaction.

In the same way that Fermi did not consider the possible existence of long-range molecules on the basis of his model, it is possible that unanticipated discoveries will add further significance to the work on long-range molecules briefly summarized here. In any case, curiosity-driven research aiming at improving our current understanding will undoubtedly continue to stimulate efforts toward generating ultra-cold and dense samples of other atoms and also of molecules.

References:

- [1] V. Bendkowsky, B. Butscher, J. Nipper, J. P. Shaffer, R. Löw, and T. Pfau, *Nature* **2009**, 458, 1005.
- [2] C. H. Greene, A. S. Dickinson, and H. R. Sadeghpour, *Phys. Rev. Lett.* **2000**, 85, 2458.
- [3] E. Fermi, *Nuovo Cimento*, **1934**, 11, 157.
- [4] E. Amaldi and E. Segrè, *Nuovo Cimento*, **1934**, 11, 145.
- [5] A. Omont, *J. Phys. France*, **1977**, 38, 1343.
- [6] F. Masnou-Seeuws, M. Philippe, and P. Valiron, *Phys. Rev. Lett.* **1978**, 41, 395.
- [7] E. Kleimenov, O. Zehnder, and F. Merkt, *J. Mol. Spectrosc.* **2008**, 247, 85.
- [8] S. D. Hogan and F. Merkt, *Phys. Rev. Lett.* **2008**, 100, 043001.
- [9] I. C. H. Liu and J. M. Rost, *Eur. Phys. J. D* **2006**, 40, 65.
- [10] I. C. H. Liu, J. Stanojevic, and J. M. Rost, *Phys. Rev. Lett.* **2009**, 102, 173001.
- [11] C. H. Greene, E. L. Hamilton, H. Crowell, C. Vadla, and K. Niemax, *Phys. Rev. Lett.* **2006**, 97, 233002.
- [12] A. Fioretti, D. Comparat, A. Crubellier, O. Dulieu, F. Masnou-Seeuws, and P. Pillet, *Phys. Rev. Lett.* **1998**, 80, 4402.
- [13] S. Jochim, M. Bartenstein, A. Altmeyer, G. Hendl, S. Riedl, C. Chin, J. Hecker Denschlag, and R. Grimm, *Science* **2003**, 302, 2101.
- [14] M. W. Zwierlein, C. A. Stan, C. H. Schunck, S. M. F. Raupach, S. Gupta, Z. Hadzibabic, and W. Ketterle, *Phys. Rev. Lett.* **2003**, 91, 250401.
- [15] T. Kraemer, M. Mark, P. Waldburger, J. G. Danzl, C. Chin, B. Engeser, A. D. Lange, K. Pilch, A. Jaakkola, H.-C. Nägerl, and R. Grimm, *Nature* **2006**, 440, 315.

Figure caption:

Fig. 1. (a) Definition of the internal coordinates relevant for the description of long-range molecules composed of a ground-state atom and a Rydberg atom. (b) Rb(35s) Rydberg electron probability density in a plane containing the Rb^+ ion core and the Rb(5s) ground-state atom. The inverted trace represents the attractive part of the interaction potential and the horizontal lines the vibrational energy levels measured experimentally. Reproduced with the permission of Bendkowsky et al. [1].

