

# MOLECULES IN STRONG MAGNETIC

In quantum chemistry, we apply the methods of quantum mechanics to the study of chemistry. This field of chemistry can trace its origins to the early decades of the twentieth century, when it was discovered that molecules consist of positively charged, heavy nuclei and negatively charged, light electrons in relative motion, governed by the laws of quantum mechanics.

At the same time, it was also recognized that the underlying many-particle problem was computationally intractable as even a moderately sized molecule consists of hundreds of interacting particles. Indeed, in 1927, P. A. M. Dirac, one of the founding fathers of quantum mechanics, famously stated that [1] "The underlying physical laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations that are much too complicated to be soluble."

However, at the time Dirac could not foresee the spectacular emergence and development of electronic computer in the second half of the twentieth century, which revolutionized much of chemistry by making molecules amenable to accurate quantum-mechanical simulations. As a result of Moore's law, first-principles simulations of chemical systems and processes have now become commonplace and are today being performed by non-specialists more often than by specialists, in support of experimental activities and measurements. Indeed, a perusal of the most general journal of chemistry, *Journal of American Chemical Society*, reveals the ubiquity of computation in modern chemistry: about 40% of its articles are today supported by computation,

mostly quantum mechanical. At the Department of Chemistry, University of Oslo, about one third of the scientific staff have authored publications supported by quantum-chemical simulations. This is an astonishing transformation of a science that only a few years ago was considered to be archetypically experimental and empirical in nature. Nowadays, computation is an integral part of chemistry and is widely perceived as the "third way": simulations not only play an important role in the interpretation and prediction of experimental observations, they are in fact more and more often viewed as an alternative to experimental work, which may be dangerous, expensive, difficult or even impossible to carry out.

For example, in molecular clouds of the interstellar medium, a wide variety of molecules have been observed by spectroscopic techniques. Many of these molecules are too reactive to be studied in laboratories on earth, making their identification and characterization impossible by experimental techniques alone. In such cases, advanced quantum-mechanical simulations may be performed on a set of candidate molecules and their identity confirmed by comparing observed and simulated spectra. Once identified in this manner, further calculations may be carried out to establish the chemistry and properties of the detected molecules.

While the molecules inside interstellar molecular clouds exist under conditions of extreme low pressure and temperature, entirely different conditions are experienced by atoms and molecules in the atmospheres of fast-rotating compact stellar objects such as white dwarves and neutron stars, whose magnetic fields may be as strong as  $10^5$  and  $10^8$  T, respectively – that is, orders of magnitude stronger than the fields generated by the earth (typically 30–50  $\mu$ T) or in laboratories (up to about 100 T). In such extreme magnetic fields, chemistry changes and becomes unfamiliar [2]. This 'alien' chemistry can only be explored by performing simulations, using the advanced methods of quantum chemistry developed since the 1920s. Such simulations provide information that may help in the interpretation of spectra from these stellar objects. Particularly relevant is the study of molecules consisting of hydrogen and helium, by far the most abundant elements in the universe.

We have recently undertaken an extensive quantum-chemical study of atoms and molecules in strong magnetic fields, for which a special computer program LONDON has been developed in our group [3]. Previous such simulations have either been carried out for two-electron systems or at lower levels of theory, revealing a less detailed picture of molecules in

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# FIELDS

strong magnetic fields. In particular, our calculations are unique in that they are not restricted to special orientations of the field relative to the molecules, being rigorously gauge-origin invariant. In the following, we describe some results of our investigations.

Our first simulations concern the changes that occur in the electronic energy as a magnetic field is applied to closed-shell molecules – that is, to molecules that have only paired electrons and therefore possess no permanent magnetic moment [4]. According to Lenz's law, the applied external field induces a net rotation of the electrons about the direction of the field, thereby increasing their kinetic energy and generating a local magnetic field that opposes the applied field. As a result of this increased electronic energy, the molecule escapes from the field to lower its energy. Most closed-shell molecules behave in this classically expected *diamagnetic* manner but a few behave non-classically, entering into the field rather than escaping from it. In these *paramagnetic* closed-shell molecules, the induced rotation reduces the kinetic energy of the electrons and enhances the applied field rather than opposing it.

However, as we found numerically with our LONDON code, all such paramagnetic

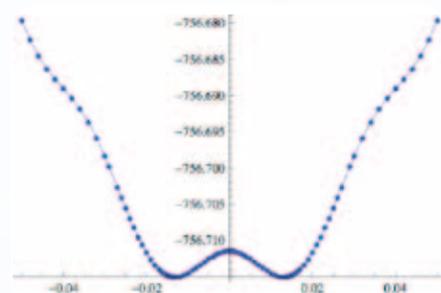


Fig. 1. The energy of the cyclic  $C_{20}$  molecule in a magnetic field perpendicular to the molecular plane.

molecules become diamagnetic at a critical field strength  $B_c$  characteristic of each molecule [4] – see Figure 1, where we have plotted the energy of the cyclic  $C_{20}$  compound in a field perpendicular to the molecular plane. We here and elsewhere use atomic units, in which the magnetic field is measured in units of  $B_0 = 2.35 \times 10^5$  T and the energy in units of  $E_h = 2625.5$  kJ/mol. As illustrated in this figure, the energy of  $C_{20}$  has a local maximum at  $B = 0$  and a double global minimum at  $B = \pm B_c = \pm 0.013B_0$ . As the magnetic field is slowly turned on, the electrons begin to rotate against the field, reducing their energy paramagnetically until rotation comes to rest at the critical field strength  $B_c$ . As the field is increased further, rotation occurs in the opposite direction, increasing the energy diamagnetically rather than reducing it. Previously, molecular paramagnetism had only been studied perturbatively, by expanding the energy in low orders in  $B$  around zero field strength, not revealing the full picture. Guided by our numerical simulations, we were able to construct an analytical model for the diamagnetic transition, predicting that it should be observable in laboratories for large paramagnetic closed-shell molecules such as  $C_{72}H_{72}$  [4].

The transition from paramagnetism to diamagnetism discussed above has not yet been detected experimentally but should nevertheless be observable in laboratories. We now turn to molecules of astrophysical interest, in fields far stronger than those obtainable in laboratories. We begin with  $H_2$ , the most abundant molecule in the universe, consisting of two protons and two electrons.

Like all molecules,  $H_2$  exists in (infinitely many) discrete electronic states of different energy, between which it may perform transitions accompanied by the emission or absorption of radiation. The state of lowest energy is called the ground state; all other states are said to be excited. To understand the interaction of molecules with radiation in stellar atmospheres, it is important to know these states as precisely as possible. Here, our interest concerns the evolution of the electronic states with increasing magnetic fields [5].

The most important electronic states are those of lowest energy. In  $H_2$ , we consider two states: the lowest *singlet* and the lowest *triplet* state. These states differ in the arrangement of the spins of the electrons. Spin is a property of the electron that may be thought of as rotation about its own axis. Each electron may rotate in one of two ways: spin up (alpha spin) or spin down (beta spin). Moreover, since the electron is negatively charged, its spin generates a magnetic moment. In the singlet state of  $H_2$ , the two spins are oppositely directed and the electrons have no net magnetic moment; in the triplet state, the spins are parallel and the electrons have a net magnetic moment.

In Figure 2, we have plotted the energy of the lowest singlet state (red curves) and the lowest triplet state (blue curves) of  $H_2$  as a function of the internuclear separation  $R$  (in units of  $a_0 = 52.9$  pm) and in the two magnetic fields  $0B_0$  and  $2.25B_0$ . A minimum in such a potential energy curve at a given distance  $R$  shows that the molecule is stable at this bond distance; the absence of a minimum shows that the molecule is unstable, dissociating into separate atoms to reduce its energy.

In the absence of a magnetic field, the singlet state (red curve) is the molecular ground state, with a minimum at  $R = 1.4a_0$ , whereas the triplet is dissociative and higher in energy. In the strong field  $B = 2.25B_0$ , the situation is reversed and the triplet state has now become the ground

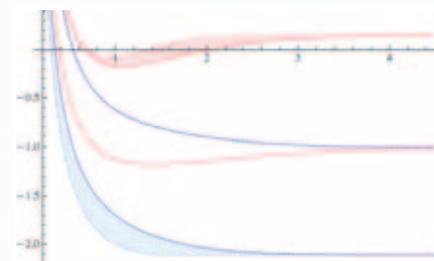


Fig. 2. Potential energy curves of  $H_2$  in the lowest singlet state (red) and the lowest triplet state (blue). Full lines represent the energy with the molecule oriented parallel to the field; dashed lines represent the energy with the molecule oriented perpendicular to the field.

state. In both states, the electrons rotate diamagnetically, raising their energy but in the triplet state this increase is more than compensated for by the alignment of its net spin magnetic moment with the field, lowering the energy of the electrons. No such lowering occurs for the singlet state, which has no net magnetic moment.

In a magnetic field, the energy of a molecule depends also on its orientation relative to the field. In the singlet state, the energy is lowest when the molecule is parallel with the field (full red line) and highest when it is perpendicular to the field (dashed red line). The shaded area between the full and dashed line represents orientations intermediate between parallel and perpendicular. We also note that the singlet  $H_2$  molecule is shorter in the field than outside the field (in particular, in the perpendicular orientation) and that the energy minimum is deeper in the field, generating a more stable molecule. These changes can be rationalized by noting that the atoms from which the molecule is formed become smaller in a magnetic field (following the induced rotation) and slightly elongated in the direction of the field.

By contrast and somewhat counter-intuitively, the triplet  $H_2$  molecule has its lowest energy in the perpendicular orientation (dashed blue line) rather than in its parallel orientation (full blue line). Interestingly, this triplet state now has a shallow minimum of about 38 kJ/mol at a bond distance of  $1.75a_0$ , unlike the dissociative triplet state in the absence of a field. Previously, only the parallel orientation of  $H_2$  had been investigated and the molecule was assumed to be dissociative at this field strength. Only with the development of the LONDON program has it been possible to explore all orientations reliably and to identify  $H_2$  as a bound molecule also at these field strengths.

The second most abundant element in the universe is helium. It is an elementary fact of chemistry that helium and all other noble gas atoms such as neon and argon do not form bonds and are therefore only very loosely attached to each other, by

weak dispersion forces. Indeed, it is their inability to form chemical bonds that has given these atoms their name: noble gas atoms. However, our calculations have shown that the situation is very different in strong magnetic fields.

In Figure 3, we have plotted the potential energy curves of the helium dimer in various magnetic fields, in the three possible spin states of this molecule: the lowest *singlet state* (to the left) with no net spin magnetic moment, the lowest *triplet state* (in the middle) with a net spin magnetic moment equal to that of  $H_2$ , and the lowest *quintet state* (to the right) with a net spin magnetic moment twice that of the triplet state. As for  $H_2$  in Figure 2, full and dashed curves correspond to parallel and perpendicular orientations in the field, respectively.

In the absence of a magnetic field, the singlet state  $He_2$  is lowest in energy but only weakly bound. As the field increases, the singlet  $He_2$  increases in energy, becoming smaller and more strongly bound (in the perpendicular orientation). However, this singlet state is no longer the ground state in strong magnetic fields. In fact, in the magnetic fields  $0.5B_0$  and  $1.0B_0$ , the very strongly bound triplet state is the ground state (in the parallel orientation), whereas the [less strongly bound] quintet state becomes the ground state in fields stronger than  $1.0B_0$  (in the perpendicular orientation). The helium atom is thus not so 'noble' in magnetic fields, forming strong bonds with other atoms.

Our calculations are the first studies of the helium molecule in strong magnetic fields, revealing a complicated evolution of the electronic states with increasing magnetic field strength. We will continue to explore the chemistry of these and other species in magnetic fields. Such calculations reveal a fascinating chemistry, different from that experienced on earth, where noble gas atoms form chemical bonds and molecules align themselves in unexpected ways relative to the field. In fields even stronger than those explored by us, chemistry becomes stranger still, molecules forming long chains of atoms

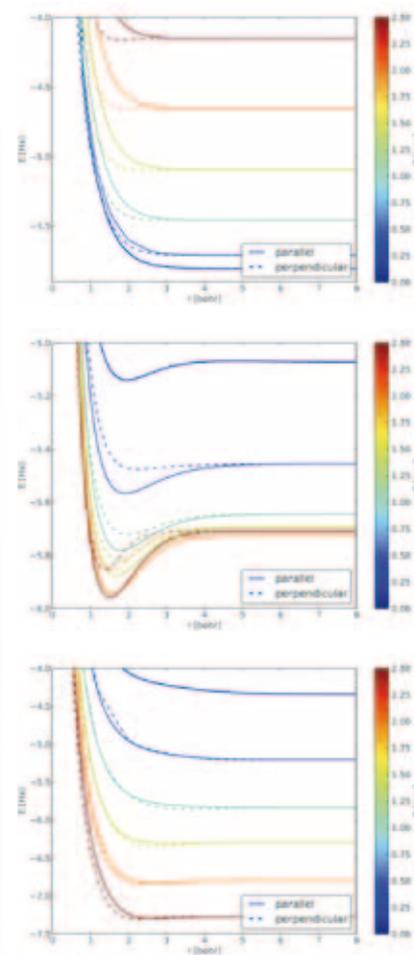


Fig. 3. Potential energy curves of  $He_2$  in the lowest singlet state (left), the lowest triplet state (middle) and the lowest quintet state (right). For each state, the energy has been plotted at magnetic field strengths  $B = 0, 0.5, 1.0, 1.5, 2.0, 2.5B_0$ , in parallel (full) and perpendicular (dashed) orientations relative to the field.

parallel to the field, with all electrons in beta spin and all orbitals singly occupied.●

## Bibliography

1. P. A. M. Dirac. Proc. R. Soc. London Ser. A 123, 714 (1929).
2. D. Lai, Rev. Mod. Phys. 73, 629 (2001)
3. E. I. Tellgren, A. Soncini, and T. Helgaker, J. Chem. Phys. 129, 154114 (2008)
4. E. I. Tellgren, T. Helgaker, and A. Soncini, Phys. Chem. Chem. Phys. 11, 5489 (2009)
5. K. K. Lange, E. I. Tellgren, T. Helgaker and M. Hoffmann in preparation.