Molecules in strong magnetic fields

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In strong magnetic fields, chemistry changes: electronic states change character, molecules change their shape, and their interactions with radiation are affected, often in a dramatic manner. Such magnetic-field induced changes are not only fascinating as a contrast to the chemistry observed on the earth, they are also relevant to astrophysics, where molecules in stellar atmospheres are subject to strong magnetic fields.

We have undertaken a quantum-mechanical study of molecules in strong magnetic fields, using a recently developed computer code for the calculation of many-electron molecules at the Hartree–Fock, Kohn–Sham, full-configuration-interaction (FCI) and complete-active-space multiconfigurational self-consistent-field (CASSCF) levels of theory. Moreover, implementations of molecular gradients and linear-response theory allow molecular structures and excitation energies to be studied in strong fields. Gauge-origin invariance is ensured by the use of London atomic orbitals.

Our calculations on molecular systems in strong magnetic fields have revealed and highlighted many interesting phenomena, such as the transition to diamagnetism of paramagnetic molecules in strong fields, changes in molecular structure such as the squeezing and flattening of ammonia, and large changes in excitation energies and oscillator strengths in strong fields. Typically, the most dramatic changes are observed at field strengths of about one atomic unit; in weaker fields, chemistry is dominated by electrostatics; in stronger fields, by magnetic interactions.

In the present talk, we concentrate on the role of electron correlation in magnetic fields, as described at the FCI and CASSCF level of theories, for small molecules. In particular, we shall study how the electronic states of small molecules change character with increasing magnetic field—resulting, for example, in a strongly bound He_2 molecule in the electronic ground state. In the future, our FCI and CASSCF code will be used to elucidate the role of the current dependence in the exchange–correlation functional of Kohn–Sham theory; our plans for such studies are outlined.