Current-density-functional theory of molecules in weak and strong magnetic fields

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Abstract. We have undertaken a quantum-mechanical study of molecules in finite magnetic fields, using a recently developed computer code London for the calculation of many-electron molecules with wave-function theory [Tellgren *et al.*, *J. Chem. Phys.* **129**, 154114 (2008)] and more recently with Kohn–Sham density-functional theory (DFT) and current-density-functional theory (CDFT). These two approaches to electronic-structure theory are connected by an implementation of the Lieb variation principle [Teale *et al.*, *J. Chem. Phys.* **130**, 104111 (2009); **132**, 164115 (2010)], allowing us to study the exchange-correlation functional of DFT at different levels of ab initio theory.

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 at a critical field strength [Tellgren *et al.*, *Phys. Chem. Chem. Phys.* **11**, 5489 (2009)]. Perhaps most interestingly, antibonding molecular orbitals are stabilised in the field, leading to strongly bound triplet H_2 and singlet He_2 molecules [Lange *et al.*, *Science* **337**, 327 (2012)] and helium clusters [Tellgren *et al.*, *Phys. Chem. Chem. Phys.* 14, 9492 (2012)] at field strengths of about 10^5 Tesla.

The application of DFT to magnetic fields requires modifications of the standard theory, by introducing a field- or current-dependence in the exchange-correlation functional. However, essentially all applications of Kohn–Sham theory to study magnetic phenomena ignore these modifications—yielding, for example, NMR shielding constants that are unreliable [Teale *et al.*, *J. Chem. Phys.* **138**, 024111 (2013)]. We discuss here some aspects of DFT in magnetic fields, including the Hohenberg–Kohn theorem and the choice of variables in DFT [Tellgren *et al.*, *Phys. Rev.* A **86**, 062506 (2012)]. Kohn–Sham calculations with different parameterisations of the Vignale–Rasolt–Geldart (VRG) functional in finite magnetic fields are presented. The results demonstrate that this functional form does not provide improvements in practical calculations and highlight the need for the development of new current-dependent approximations. On the other hand, the TPSS meta-generalised-gradient-approximation (meta-GGA) with a dependence on the kinetic energy density provides a natural framework for introducing a current dependence [Dobson, *J. Chem. Phys.* **98**, 8870 (1993)], giving good results in comparison with high-level many-body methods (FCI and CCSD(T)). In the figure below, dissociation curves of Ne_2 in a strong magnetic field have been plotted. The Tao-Perdew-Staroverov-Scuseria (TPSS and TPSSh) curves with current dependence compare well with CCSD(T) curve.