Reduced Density Matrix inspired approaches to electronic structure theory

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SUMMARY

Chemistry can be characterized as a branch of science studying the composition, structure, properties and transformations of matter. Although 118 different elements are identified and only first 98 occur naturally on earth the number of possible molecules coming from their combinations is overwhelming. Therefore studying how molecules can form, break apart and change into one another is a crucial mission of chemistry. The molecular changes are described in terms of chemical reactions during which existing chemical bonds can be rearranged or dissociated and new bonds can be created. Modern description of chemical bonds relies heavily on the concepts from electronic structure theory rooted in quantum mechanics. A quantum chemical description of chemical reaction energetics can be considered from the perspective of electronic energy changes upon atomic rearrangements. Variations of the electronic energy with the geometry of the system are a consequence of a delicate balance of different physical interactions between the elementary particles composing the system. All of the mutual physical interactions among nuclei and electrons and between electrons and protons depend only on the mutual distance of the interacting particles.

Although the theory of chemical bonding follows from quantum chemistry only a limited number of available electronic structure methods can accurately predict the energy changes upon bond elongation for a wide range of distances. Except for the prohibitively expensive FCI or full couple cluster expansions usually multireference methods are employed for this purpose.

An alternative approach presented in this thesis is one-body reduced density matrix functional theory (1RDMFT) where the electronic energy is given as a functional of the one-body reduced density matrix and the approximations for the unknown electron-electron interaction potential are developed. The great advantage of density matrix functionals, as opposed to density functionals, is their ability to describe chemical bonding since they naturally cover both nondynamical and dynamical correlation. Although as discussed in chapter 4 not all of the 1RDM functionals can describe bond dissociation accurately there are promising examples that might be treated as guidelines for improvement. The obvious benchmark is the Löwdin-Shull functional, which is the exact natural orbital functional for two-electron systems presented in section 4.4.1. In chapter 5 an extensions of this functional for the breaking of a single electron pair bond in N-electron molecules, using LiH, BeH^+, and Li_2 molecules as prototypes is presented. Attention was given to the proper formulation of the functional in terms of not just J and K integrals but also the two-electron L integrals (K integrals with a different distribution of the complex conjugation of the orbitals), which is crucial for the calculation of response functions. Accurate energy curves are obtained with extended Löwdin-Shull ELS functionals along the complete dissociation coordinate using FCI calculations as benchmark.

In Part II the developments towards a 1RDM functional capable of correctly describing the intermolecular interactions are presented. Chapter 7 investigates the errors in super-molecule calculations for the Helium dimer. In a FCI calculation there are two errors. One is the basis set superposition error (BSSE), the other is the basis set convergence error (BSCE). Both of the errors arise from the incompleteness of the basis set. These two errors make opposite contributions to the interaction energies. The BSCE is the by far the largest error in the short range, and larger than (but much closer to) BSSE around the van der Waals minimum. Only at the long range the BSSE becomes the larger error. The BSCE and BSSE largely cancel each other over the van der Waals well. The proposed recommendation is to not include the BSSE correction for the calculation of the potential energy curve from short distance till well beyond the van der Waals minimum, but it may be recommended to include the BSSE correction if an accurate tail behavior is required.

Chapter 8 gives a natural orbital (NO) based analysis of the van der Waals interaction in H_2 in singlet and triplet states at long distance. In the triplet state of H_2 the van der Waals interaction results in a shallow minimum at 7.8 bohr that can be accounted for by a configuration interaction expansion containing just 3 CSFs. The corresponding pair density can be formulated using the NOs and ONs however the resulting functional contains the non-primitive terms. In the case of the singlet state although the van der Waals interaction does not lead to a distinct van der Waals well, it affects the shape of the interaction potential in the distance range of 5–9 bohr and can be clearly distinguished from chemical bonding effects. In the NO basis the van der Waals interaction can be quantitatively covered with, apart from the ground state configurations $(1\sigma_g)^2$ and $(1\sigma_u)^2$, just the 4 configurations $(2\sigma_g)^2$ and $(2\sigma_u)^2$, and $(1\pi_u)^2$ and $(1\pi_g)^2$. The physics of the dispersion interaction requires and explains the peculiar relatively large positive CI coefficients of the doubly excited electron configurations $(2\sigma_u)^2$ and $(1\pi_g)^2$ (the occupancy amplitudes of the $2\sigma_u$ and $1\pi_{gx,y}$ NOs) in the distance range 5-9 bohr, which have been observed before by Cioslowski and Pernal [202]. We show in section 8.5 that such positive occupancy amplitudes do not necessarily lead to the existence of zero occupation numbers at some H-H distances.

In chapter 9 an attempt to extend the treatment of the van der Waals interaction in terms of RDMs beyond the 2-electron systems is made. In section 9.1 a detailed analysis of the FCI wave function of the He_2 dimer is given. Then from selected excitations the dispersion part of the two-particle density matrix is obtained. It emerges that the entirely different physics embodied in the dispersion interaction leads to an essentially different type of exchange-correlation orbital functional for the dispersion energy (non-JK). This can be contrasted with various types of non-dynamical correlation like the left-right correlation in a (dissociating) bond that can be described accurately with an NO functional employing only J and K integrals (JK-only functional, see chapter 5. The distinct NO integrals for the different types of correlation imply that they can be used in conjunction without problems of double counting. The general form of the functional being able to account for the dispersion interaction is given in section 9.7. Moreover it is established that the requirements on the (primitive) basis set for vdW bonding appear to be more modest than for other types of correlation.

Additional important conclusions from chapter 9 that only certain type of double excitations are crucial for the van der Waals interaction and that they can be readily identified by examining the 2RDM led us to propose a scheme for computing dispersion energy that can be considered as a generalization of the procedure presented in chapter 9. The scheme is based on the expansion of the wave function and corresponding 2RDM in localized molecular orbitals where the benefit is that in such a basis the van der Waals terms can be recognized from the form of 2RDM and used to calculate the binding energy directly. A proof of principle application to He_2 provided promising results but the method requires further investigations.