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A possible valence-bond approach to symmetry-adapted perturbation theory

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Abstract

The multi-configurational ansatz of valence-bond theory may serve as basis for calculating intermolecular interaction energies in a non-orthogonal basis. We look in the present contribution at the possibility to obtain the 1st-order electrostatic interactions from breathing-orbital valence-bond densities, and the 2nd-order dispersion energy from dipole-dipole interactions. The discussion is based on numerical results for the interaction of two N₂O molecules.

1. Introduction

Since the beginnings of describing electronic structure in terms of orbitals, the two pictures of completely localized bonds or completely delocalized molecular orbitals compete [1, 2, 3]. Both pictures have their advantages and shortcomings, and obvious applications. From molecular orbitals we have Hartree-Fock theory and beyond all the methods for describing dynamical electron correlation. In cases of bond breaking, multi-reference methods have been developed, adding non-dynamical electron correlation in situations where relying on a single reference is not any more justified. This machinery becomes very demanding on computer resources for handling immense amounts of data due to the large number of Slater determinants or Configuration State Functions (CSF) involved, and their interactions.

In a chemist's language this apparently brute-force approach is difficult to treat — bonds, bond formation, bond breaking and electron rearrangement need only few electrons involved in a picture, despite the indiscernibility of elementary particles and long-range Coulomb interactions between them.

Valence Bond theory tries to describe these essentials of a chemist's view on molecules and matter. It relies on one or several Lewis structures (i.e. electron pairs assembled in bonds or lone pairs, or left alone in singly occupied orbitals). Each of these structures may be developed in a common (localized) orbital set, or in a more modern formulation [4], in orbital sets for each involved structure, the Breathing Orbitals Valence Bond (BOVB) approach. The main obstacle for routine calculations in this type of development is the inherent non-orthogonality of the orbital sets. All expressions have to carry overlap matrix elements throughout, rendering calculations much heavier to be executed than expansions in determinants in common orthogonal orbitals, where today one may handle dimensions of millions or even several billions of determinants.

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