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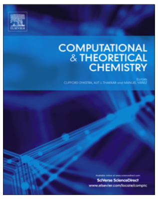

Assessing the performance of ab initio classical valence bond methods for hydrogen transfer reactions

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ABSTRACT

Ab initio classical valence bond theory in terms of localized orbitals has several advantages over electronic structure methods based on canonical delocalized Hartree-Fock molecular orbitals, with two key distinctions being greater applicability to inherently multiconfigurational systems (also called multireference systems or strongly correlated systems) and great interpretability in terms of covalent and ionic valence bond configurations (also called valence bond structures). This can be especially advantageous for applications to chemical reactions. However, until now only limited work tested the quantitative accuracy for the energetics of chemical reactions. The present study provides such tests and validations for a representative test set of six barrier heights corresponding to forward and reverse barriers of three hydrogen transfer reactions. In particular, we test the valence bond self-consistent-field theory (VBSCF) and three post-VBSCF methods that use VBSCF as a reference function for adding dynamic correlation, in particular valence bond configuration interaction (VBCI), breathing orbital valence bond (BOVB), and valence bond second-order perturbation theory (VBPT2). The VBSCF method itself is, as expected, not quantitatively accurate, with a mean unsigned error (MUE) for the six barrier heights of $\sim$17 kcal/mol. But the post-VBSCF methods are found to be quite successful. Depending on the basis set, and valence bond structure selection we obtain MUEs (in kcal/mol) as low as 3.7 for VBCI, 4.5 for BOVB, and (using a bigger basis-set) 1.3 for VBPT2. These compare well, on the same data set, with 1.6 for coupled clusters with singles and doubles (CCSD) and 1.5 for multireference second order perturbation theory based on a complete active space self-consistent field reference function (MRPT2). We discuss the results in terms of the pros and cons of each of these methods.

1. Introduction

Classical valence bond (VB) theory, which was first formulated in 1927 by Heitler and London [1,2] to describe the bond in a hydrogen molecule, served chemists for many years mainly as a qualitative tool. However, in the past three decades the theory has progressed considerably and become a quantitative tool, comparable to molecular orbital (MO)-based methods. Important milestones in the development of quantitative VB methodology include three classes of methods. One class is based on fully delocalized orbitals, also called overlap-enhanced orbitals (OEOs); in this class, the contributions from ionic VB structures are implicitly involved in covalent structures. This class includes, for example the generalized valence bond scheme (GVB) [3–6], the spin-coupled VB scheme (SCVB) [7,8], and the complete active space VB method [9]. The second class is based on strictly localized fragment orbitals, including the valence bond self-consistent field (VBSCF) method [10] and various recent developments of higher-level ab initio VB methods such as the breathing orbitals valence bond (BOVB) method [11,12], the VB configuration interaction (VBCI) method [13,14], the VB-second-order perturbation theory (VBPT2) [15,16], density-functional-based VB (DFVB) [17,18], and the VB-Quantum Monte Carlo method [19]. Since nonorthogonal localized orbitals are used in this class of methods, one is able to represent the classical VB theory faithfully. Thus, these methods are regarded as ab initio classical VB, and they are the subject of the present article. The third class is the block localized wave function (BLW) approach [20–23], and its extension to the MOVB approach

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[23–27], which can be considered to be a hybrid of the first two classes.

In recent years, VB theory and especially ab initio classical VB methods have proved to be very useful for understanding bonding and reactivity in chemistry due to the simple and unique insights they provide. A partial list of successes includes improving the understanding of how enzymes work [28–33], resolving misconceptions regarding VB [34], elucidating new bonding concepts such as charge shift bonding [35], predicting structures of transition metal complexes (e.g., [36]), and providing new insights into bonding (for a partial list, see e.g., [37–46]).

The significant developments of ab initio classical VB methodology have involved both accuracy and efficiency, particularly due to the use of nonorthogonal orbital based reduced density matrix in VB theory [16,47–49]. Consequently, a wide range of systems and challenges are now addressable by these methods. This notable progress now allows us to assess the performance of these methods not only against a particularly difficult problem as was the case so far (see e.g., dissociation of the F_2 molecule [11], or the barrier height of the hydrogen exchange reaction [50]) but rather against a well-defined benchmark set. VB is particularly suited to studies of bonding and reactivity. Yet, the majority of the quantitative VB studies to date have involved bonding, with a lesser number of studies involving quantitative studies of reactivity. In this paper we examine the latter issue by using a set of benchmark reactions.

Hydrogen transfer reactions are known to be challenging [50]. Here we study this class of reactions using a small yet diverse and representative data set [51]. The data set (referred to as HTBH6), is a statistically representative subset of a larger database (Database/3) [52]. Considering both the forward and reverse reactions the data set involves 6 barrier heights. This data set serves here for assessment of the performance of various ab initio classical VB approaches.

2. Methodology

In the present work we assessed the performance of the most practical ab initio classical VB methods, including VBSCF, BOVB, VBPT2, and three variants of VBCI [53,54]. Specific details on the particular methods can be found elsewhere [53,54]. Here we only briefly describe the main points.

In VB methods, the many-electron wave function involves a linear combination of all the possible VB functions (also called VB configurations or VB structures) in the system as indicated in Eq. (1).

$$\Psi^{VBSCF} = \sum_{K} C_K \Phi_K \tag{1}$$

where Φ_K is the Kth VB structure. Orbitals that are doubly occupied in all configurations are called inactive orbitals; orbitals with variable occupancy in the various configurations are called active. The inactive orbitals include all core orbitals and some valence orbitals. The electrons that are not in inactive orbitals are called active electrons. In ab initio classical VB calculations, all the active orbitals are required to be localized on one or another of the fragments (which may be atoms or groups of atoms; the definition of the fragments is dictated by what one is interested in studying, and the choices made for the present work will be explained in Section 3). Each structure in Eq. (1) is defined by a particular distribution of active electrons among the active orbitals (which are nonorthogonal), and C_K are the corresponding coefficients.

VBSCF is the basic method of ab initio classical VB where one set of orbitals is common to all the VB structures [10]. Hence, the calculation involves simultaneous optimization of the coefficients of all the VB orbitals (sometimes termed VB vectors) that construct the VB structures as well as the structure coefficients (C_K) leading to a self-consistent field type wave function. We note that in the present VBSCF calculations, the structure list used in Eq. (1) includes all possible ways to distribute the active electrons among the active orbitals. The VBSCF method accounts for static correlation but has only a limited amount of dynamic correlation; however, dynamic correlation is usually very important for quantitative work. Various methods that expressly incorporate dynamic correlation are available [54]. Those whose performance is studied here are described next.

The BOVB method is one approach for including more dynamic correlation. It removes the same-orbitals-in-every-structure restriction of the VBSCF method by using a different set of orbitals for each VB structure [11,12]. In other words, each Φ_K in Eq. (1) is described by its own set of orbitals. These sets of orbitals are then allowed to optimize simultaneously. Each set of orbitals thereby accommodates the particular charge distribution of the structure it describes [11,12].

Another approach to including more dynamic correlation is VBCI, where the configuration interaction procedure follows a VBSCF calculation. That is, excited configurations are produced by replacing occupied VB orbitals by virtual VB orbitals that are localized on the same fragments [13,14]. Three levels of VBCI are currently available, differing by the type of excitations. VBCIS involves only single excitations of both active and inactive electrons; VBCIDS involves single excitations for both active and inactive electrons and double excitation only for active electrons; and VBCISD involves single and double excitations for both active and inactive electrons. The wave function is a linear combination of the fundamental structures Φ_K^0 and the corresponding excited structures:

$$\Psi^{VBCI} = \sum_{K}\sum_{i} C_K^i \Phi_K^i \tag{2}$$

where the index K represents the fundamental structures, and the index i stands for the different possible excitations. The coefficients C_K^i and the overall energy are determined by solving the secular equations without further optimization of the VB orbitals (which are based on the VBSCF calculation).

Another post-VBSCF method is the VBPT2 method. This method incorporates perturbation theory where the wave function is given as the sum of the zeroth-order wave function obtained at the VBSCF level and the first-order wave function given as a linear combination of the singly and doubly excited structures [15]. We note however, in contrast to VBCI, the currently available version of VBPT2 involves virtual orbitals that are not strictly localized [53]. This greatly enhances the efficiency of the method yet results with excited VB structures which are not necessarily physically meaningful and do not belong to any specific fundamental structure. An improved version of VBPT2 that will allow interpretation of the wave function based on the specific structures is currently under development by one of us.

3. Computational details

Ab initio VB calculations were performed with the XMVB program, version 2.1 [55–57]; MO-based calculations were performed with both the *Gaussian 09, revision D.01* [58] and the *GAMESS US*, version R1 [59] packages. Core orbitals were frozen at the spin-restricted Hartree-Fock level, and spin-restricted Hartree-Fock calculations were carried out to obtain these frozen-core orbitals and the integrals.

The VB methods tested include VBSCF [10,48,49], BOVB [11,12], VBCI (including VBCIS, VBCIDS, VBCISD) [13,14] and VBPT2 [15,16], and their performance was compared to that of the coupled-cluster

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