An Accurate Barrier for the Hydrogen Exchange Reaction from Valence Bond Theory: Is this Theory Coming of Age?

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Abstract: One of the landmark achievements of quantum chemistry, specifically of MO-based methods that include electron correlation, was the precise calculation of the barrier for the hydrogen-exchange reaction (B. Liu, *J. Chem. Phys.* **1973**, *58*, 1925; P. Siegbahn, B. Liu, *J. Chem. Phys.* **1978**, *68*, 2457). This paper reports an accurate calculation of this barrier by two recently developed VB methods *that use only the eight classical VB structures.* To our knowledge, the present work is *the first accurate ab initio VB barrier that matches an experimental value.* Along with the accurate barrier, the VB method provides accurate bond energies and diabatic quantities that enable the barrier height to be analyzed by the VB state correlation diagram approach, VBSCD (S. Shaik, A. Shurki, *Angew. Chem.* **1999**, *111*, 616; *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 586). This is a proof of principal that VB theory with appropriate account of dynamic electron correlation can achieve quantitative accuracy of reaction barriers, and still retain a compact and interpretable wave function. A sample of S_N2 barriers and dihalogen bonding energies, which are close to CCSD(T) and G2(+) values, show that the H_3 problem is not an isolated case, and while it is premature to conclude that VB theory has come of age, the occurrence of this event is clearly within sight.

Keywords: ab initio calculations · reaction barrier · transition states · valence bond theory

Introduction

The acceptance of quantum mechanics by chemists was aided, among other events, by a few landmark achievements. In 1927 Heitler and London (HL) published their seminal paper[1] on the origins of the chemical bond in the H_2 molecule, using Heisenberg's resonance approach.[2] Even though not quantitatively accurate, the HL wave function for the first time provided a physical mechanism for bond formation between two neutral atoms, due to the quantum-mechanical interference effect called resonance energy. The HL wave function formed the foundation of the valence bond (VB) theory of Slater[3] and Pauling[4] and, especially due to the work of the latter, it became a powerful tool that explained most of the known chemistry of the time.[5] At about the same time, Hund[6] and Mulliken[7] formulated a spectroscopy-based method, called molecular orbital (MO) theory, which accounted for a multitude of spectral observations: the magnetic properties of the dioxygen molecule,[8] the rotational barriers of olefins,[9] the properties of conjugated molecules,[10] and so on. These pioneering VB and MO treatments suggested that the whole of chemistry would naturally emerge from quantum mechanical principles. However, the quantitative aspects of the methods were still unsatisfactory, and a quantitative proof of the validity of quantum mechanics was required.

The H_2 molecule was a good benchmark case. VB theory could be improved by adding ionic structures to the HL wave function,[11] but the results were still some way from quantitative accuracy. MO theory with a single determinant gave even worse results than the HL wave function, but it could be improved by configuration interaction (CI). CI brought to the fore the notion of electron correlation, which eventually culminated in the wave function of James and Coolidge (JC),[12] giving highly accurate results for the bond energy and other properties of the H_2 molecule. This second landmark achievement demonstrated that a quantum mechanical method that accounts properly for electron correlation is capable of predicting molecular properties with an accuracy that

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matches, if not surpasses, experimental accuracy. This was a proof of principle that quantum mechanics correctly and accurately describes the nature of the chemical bond.

The next landmark was the calculation of the barrier for the simplest chemical reaction that describes bond exchange, the identity hydrogen transfer [Eq. (1)].

$$\text{H–H} + \text{H}^{\bullet} \rightarrow \text{H}^{\bullet} + \text{H–H} \qquad (1)$$

An early VB treatment of this reaction by London[13a] showed that VB theory can account qualitatively for the entire potential surface. This VB treatment was generalized by Eyring and Polanyi,[13b] and eventually led to the development of a useful parametrization scheme for generating potential energy surfaces. Still, though, quantitative accuracy of reaction barriers was beyond the reach of VB theory. By contrast, MO-based treatments with extensive CI, initially by Liu et al.[14] and by Truhlar and Horowitz,[15] gave a highly accurate barrier for the hydrogen-exchange reaction. Liu's computational data are still widely used for global analytical potential energy surfaces. Subsequent computational work by Peterson et al.,[16] Bauschlicher et al.,[17] Anderson et al.,[18] and again Peterson et al.[19] further substantiated the results of this pioneering study. This work demonstrated that quantum mechanics was also able to account most accurately for a key quantity that determines the speed of a chemical reaction. With these three landmarks it has become apparent that, in principle, chemistry has entered under the sovereignty of quantum mechanics.

In the interim, MO and MO-CI theories have been going from one achievement to another and establishing the validity of quantum mechanics. It is unanimously accepted that MO-based theory with electron correlation correction is the method of choice for the calculation of molecular properties and especially of reaction barriers. In contrast, VB theory, the one that was the first to achieve the landmarks of describing the chemical bond and the reaction barrier, has been receding and almost fading out as a quantitative method. Despite the resurgence of VB methods since the early 1980s,[20] and the insight this theory provides into chemical reactivity,[21] it is still considered to be inferior to MO-based methods, primarily due to quantitative aspects. The bond energy challenge has already been met by VB theory, and accurate bond energies may be obtained by VB treatments such as the breathing orbital VB method (BOVB).[22] However, highly accurate reaction barrier calculations are still challenging for VB theory. When this challenge is met, VB theory will finally come of age, and the addition of quantitative accuracy to its chemical lucidity will form a formidable theoretical tool in the service of chemistry. Meeting this challenge is an important goal of modern quantum chemistry, and is part of our own program. This work represents a step towards this goal.

The most valuable feature of a VB wave function is its chemical lucidity: the fact that it maintains a very clear correspondence between the VB eigenfunctions and the chemically common Lewis structures for a given electronic system. For this correspondence to hold, it is necessary to employ VB methods that make use of pure AOs that are strictly localized on a single atom or fragment, without any delocalization tails to other atoms. This feature is also required for the calculation of the diabatic curves used in the VBSCD diagrams (vide infra). The VBSCF method of Balint-Kurti and van Lenthe[23] is appropriate for this purpose, but its accuracy is still wanting. The BOVB method,[22] devised to improve the accuracy of VBSCF while keeping its conceptual simplicity and interpretability, is also appropriate. Finally, some of us recently introduced a VB-based method, called VBCI, that incorporates the CI technique and philosophy into VB wave functions, while conserving the lucidity of the wave function, in terms of a minimal set of constituent VB structures.[24] In this form, the method enables quantitative accuracy to be obtained with a wave function based on the classical VB structures. While BOVB has already been tested for its ability to reproduce bond energies, and similar tests are reported in this work for the VBCI method (vide infra), the question is whether the BOVB and/or VBCI methods can also *meet the greater challenge of an accurate calculation of a reaction barrier with a minimal set of VB structures.*

To answer this question we decided to compute the barrier of the hydrogen exchange reaction,[14–19, 25–33] in Equation (1), in an attempt to duplicate the landmark achievement of Liu,[14] and to analyze the constitution of the thus calculated precise barrier by use of the VB state correlation diagram model, at a highly accurate level.[21] Although this challenge may seem unimpressive in comparison with the current capabilities of MO-based methods, this is not the case for VB theory. Thus, an earlier VB study by Harcourt and Ng,[34] used the STO-6G basis set, and arrived at a barrier of 23.6 kcal mol^{-1}. Our own BOVB study,[35] with the 6–31G basis set, gave a barrier of 18.7 kcal mol^{-1}, almost twice the true classical barrier of around 9.8 kcal mol^{-1}.[14–19] The challenge of accuracy facing the VBCI and BOVB methods is therefore not trivial. As shall be seen, the VBCISD method meets the quantitative challenge, and at the same time provides the means to produce basis set-independent diabatic energy curves and accurate VB parameters of VB state correlation diagram for the hydrogen exchange reaction.[21] The computational results show that VB theory is not only a powerful tool for qualitative understanding but also able to a good approach for quantitative applications.

Results and Discussion

Methodology

The VBCI method: The VB calculations use a spin-free formulation of VB theory, which has been fully described elsewhere.[36, 37] In spin-free VB theory, a many-electron wave function is expressed in terms of spin-free function Φ_K. Φ_K

$$\Psi = \sum_K C_K \Phi_K \qquad (2)$$

may be a bonded tableau (BT)[37] state that maintains a one-to-one correspondence with the chemical VB structures.

In the VBSCF method,[23] both the VB orbitals and the structural coefficients are optimized simultaneously to minimize the total energy. The VBSCF method takes care of the static electron correlation. However, it lacks dynamic correlation,[22] which is absolutely essential for the goal of quantitative accuracy. The VBCI method[24] uses a configuration interaction technique to improve the energetics after a VBSCF calculation in which all the fundamental VB structures are involved [Eq. (3)].

$$\Psi^{VBSCF} = \sum_K C_K^{SCF} \Phi_K^0 \tag{3}$$

A subsequent VBCI calculation[24] involves all the fundamental and the excited VB structures. This includes double excitations on each atom, plus products of single excitations of two atoms. In Equation (4), the structures are indexed by the superscript *i*, which can correspond to a fundamental ($i = 0$) or a virtual VB structure ($i \neq 0$).

$$\Psi^{VBCI} = \sum_K \sum_i C_{Ki} \Phi_K^i \tag{4}$$

Here, excited structures are nascent from their fundamental structure through replacement of occupied orbital(s) with virtual orbital(s), keeping the same spin-pairing. To preserve the interpretability of the final wave function, the virtual orbitals are defined, by use of a projector, so as to be *strictly localized on precisely the same atom as the corresponding occupied orbitals.* This form of the virtual orbitals conserves the nature of the fundamental VB structures. In this manner, *one does not add new VB structures*, but rather dresses the fundamental structures, found at the VBSCF stage, with dynamic correlation. The total VBCI energy of the system is given by Equation (5).

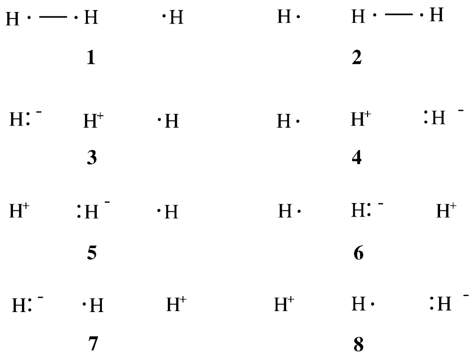
$$E^{VBCI} = \frac{\sum_{K,L} \sum_{i,j} C_{Ki} C_{Lj} \langle \Phi_K^i | \mathrm{H} | \Phi_L^j \rangle}{\sum_{K,L} \sum_{i,j} C_{Ki} C_{Lj} \langle \Phi_K^i | \Phi_L^j \rangle} \tag{5}$$

Since the virtual orbitals for each fundamental structure are localized on the same atoms as in the fundamental structure, the entire VBCI wave function can be written in terms of the fundamental structures. The weight of a given VB structure is given by the usual Coulson–Chirgwin formula[38] in Equation (6).

$$w_K = C_K^2 + \sum_{K \neq L} C_K C_L \langle \Phi_K | \Phi_L \rangle \tag{6}$$

The CI can be truncated at any desired level. Thus, single excitation of all the fundamental orbitals leads to the VBCIS method, while double excitation corresponds to VBCISD. Thus, the method can be gradually improved to the desired accuracy. Practical experience with the method shows that going beyond double excitation is usually not necessary. For this purpose one may resort to perturbational summations, but that is beyond the scope of the present paper. Fortunately, unlike the MO-based CISD, the VBCISD method is free of size inconsistency effects.[24]

The BOVB method: The BOVB method is another way of improving VBSCF by accounting for some dynamic correlation. Relative to the minimal set of VB structures of the VBSCF wave function [Eq. (3)], BOVB does not perform any extra CI, but improves the description of the VB structures by allowing different orbitals for different structures. The method has been described in detail elsewhere[22] and is only very briefly summarized here. The basic principle is that each VB structure is allowed to possess its specific set of orbitals, different from one VB structure to the other, during the optimization process. The orbitals and coefficients of the VB structures are optimized simultaneously so as to minimize the total energy of the multistructure wave function. In this manner, the orbitals can fluctuate in size and shape so as to fit the instantaneous charges of the atoms on which these orbitals are located. In this work, the BOVB method is used at two levels of accuracy. The most basic level, L-BOVB, displays a very compact three-configuration wave function for H_2, just involving the three classical VB structures—one covalent and two ionic—and each ionic structure is described as a unique doubly occupied AO on the anionic center. Extension of this description to the H_3 system yields an eight-configuration wave function, each configuration (spin eigenfunction) corresponding to one of the VB structures **1**–**8** displayed in Scheme 1.



Scheme 1. The VB structure set for H_3.

With respect to this simple level, the more sophisticated SL-π-BOVB level brings two improvements: 1) an ionic structure is now described as two singly occupied AOs that are singlet-coupled, but localized on the same ionic fragment, this improvement bringing radial correlation energy to the ionic structures, and 2) VB structures corresponding to the π bonding of H_2 are added to provide some angular correlation. Previous experience has shown us that such VB structures are not entirely negligible in diatomic molecules such as H_2, Li_2, etc.

The VB structure set: The minimal set of VB structures required to describe the hydrogen exchange reaction is shown in Scheme 1. These structures involve all the modes of distribution of three electrons among the three hydrogen atoms. Structures **1**, **3**, and **5** correspond to the reactants (H_a–H_b + H_c), and structures **2**, **4**, and **6** correspond to the products (H_a + H_b–H_c). Structures **7** and **8** are excited states that can mix only into the TS but do not contribute to the reactants and products.[35]

The VB state correlation diagram (VBSCD) method: The VBSCD[21] method uses VB theory to provide chemical insight into the barrier and other features of a chemical reaction. The diagram, shown in Figure 1, is composed of three curves: one is the adiabatic energy profile of the ground state involving all eight structures in Scheme 1, and the other two are the reactant and product curves, also called diabatic curves. The diabatic curves are variational within the subset of VB structures,[22f] structures **1**, **3**, and **5** for reactants and **2**, **4**, and **6** for products.[35] In a nutshell, after construction of these three curves, the barrier can then be analyzed in terms of the diabatic quantities. These are the promotion gap, G, the height of the crossing point, ΔE_c, given as a fraction of the gap, fG, and the resonance energy of the transition state, B, which results from avoided crossing and VB mixing.[21, 35, 39]

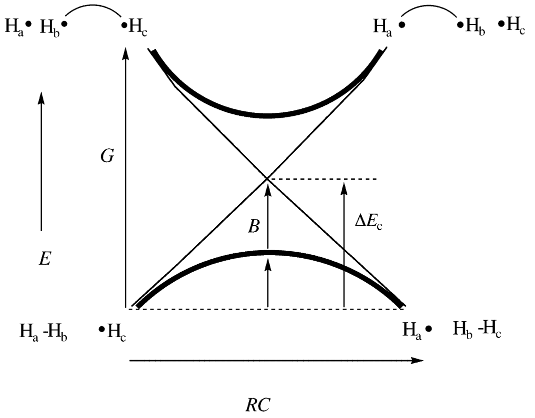


Figure 1. VBSCD for the hydrogen exchange reaction.

While full variation is suitable for the adiabatic curve that obeys the variational theorem, this may not necessarily be the case for the diabatic curves. Except for their asymptotic points, the diabatic curves are not physical states, and therefore a straightforward variational procedure may result in a wrong description of the diabatic curve. Thus, in a fully variational treatment, with a large basis set, the diabatic curve may try to mimic the full adiabatic and collapse to the ground state.[40] Many test calculations show that such a problem is not serious for a moderate basis set, but deterioration is rapidly incurred with improvement of the basis set; this is especially pronounced when the basis set includes diffuse functions. This will create a serious basis set dependence of the parameters—G, B, and f of the diagram—and this is precisely what we wish to avoid. *The way to solve the problem is to optimize only the orbitals of the bonded fragment, while the orbitals of the unbound fragment are kept in their optimized situation for the free fragment.* By following this procedure, for the H_3 system, full variational procedure is used for R (reactants at the reactant geometry), while atomic orbitals naturally become the orbitals of P* (reactant at the product geometry). The computational results shown later demonstrate that *the diabatic curves generated with this definition are independent of basis sets, and give a consistent set of parameters G, f, and B.*

To avoid artificial bonding interaction between the spin-paired fragment and the uncoupled one during the VBCI procedure for the diabatic state (e.g., P*), we use a "partial" CI procedure. Thus, a VBCI calculation is carried out on the spin-paired fragment by itself, to provide the coefficients of the participating VB structures. Subsequently, the energy of the whole system is computed by bringing in the uncoupled fragment while using the same VB structures and coefficients as in the spin-paired fragment. Such a technique prevents undesired bonding interactions from taking place between the bonded fragment and the uncoupled fragment, which would have artificially caused the diabatic excited state wave function to collapse to the adiabatic ground state below it.

Basis sets, geometries, and computational levels: Five different basis sets were used for this study: the three Pople basis sets[41] 6–31G, 6–31G**, and 6–31++G**, and two correlation-consistent ones,[42] cc-pVTZ and aug-cc-pVTZ. Initially, the geometries used in the VB calculations are taken from CCSD(T)/aug-cc-pVTZ calculations. Subsequently, geometries are optimized at the VBCISD/aug-cc-pVTZ level. The Gaussian98 package[43] is used for the MO-based calculations, while the VB calculations are carried out with the Xiamen package.[44] The calculations are done at the following VB levels: VBSCF, L-BOVB, SL-π-BOVB, VBCIS, and VBCISD.

Computational results

To determine the barrier height of the hydrogen exchange reaction, corresponding results for the H_2 molecule are required. Table 1 shows the bond energy of H_2 obtained by various methods. It can be seen that the VBSCF bond energy is ca. 94–95 kcal mol^{-1} and almost independent of basis set. L-BOVB and VBCIS results do not improve the results compared with VBSCF. The VBCISD bond energy is slightly improved from the VBSCF results in the 6–31G basis set. As the basis set increases, both the SL-π-BOVB and VBCISD bond energies increase and depart from the VBSCF, L-BOVB, and VBCIS results. The SL-π-BOVB values reach about 105 kcal mol^{-1} in the 6–31G** and 6–311++G** basis sets, and about 107 kcal mol^{-1} in the correlation-consistent basis sets. The VBCISD results are always slightly better than BOVB, reaching about 106 kcal mol^{-1} for the 6–31G**/6–311++G**, and converging to about 108.6 kcal mol^{-1} for the correlation-consistent basis sets. The larger the basis set, the more significant the BOVB-VBCISD difference. This is explained by the fact that VBCISD can use the extra basis functions of the large basis set to account for angular correlation. This could also be done at the BOVB level, but only at the price of adding further VB structures. We note that the VBCISD results are exactly the same as those of MO-based CCSD(T). This is because, for H_2, VBCISD is indeed a full CI calculation that covers all electron correlations as CCSD(T). Both VBCISD and CCSD(T) results match the experimentally determined value very well.

Table 2 displays the barriers of the hydrogen exchange reaction. It is apparent that VBSCF barriers for all basis sets are too high and do not get significantly lower with basis set improvement. The BOVB calculations have been restricted to

Table 1. The bond energy of H_2 by various methods

Basis set	Method	$E(H_2)$ (a.u.)	$E(H+H)$ (a.u.)	D [kcal mol^{-1}]
6–31G	VBSCF	– 1.14627	– 0.99647	94.0
	L-BOVB	– 1.14627	– 0.99647	94.0
	VBCIS	– 1.14628	– 0.99647	94.0
	VBCISD	– 1.15169	– 0.99647	97.4
	CCSD(T)	– 1.15169	– 0.99647	97.4
6–31G**	VBSCF	– 1.14926	– 0.99647	95.9
	L-BOVB	– 1.14946	– 0.99647	96.0
	SL-π-BOVB	– 1.16452	– 0.99647	105.5
	VBCIS	– 1.14955	– 0.99647	96.1
	VBCISD	– 1.16514	– 0.99647	105.8
	CCSD(T)	– 1.16514	– 0.99647	105.8
6–311++G**	VBSCF	– 1.15045	– 0.99964	94.6
	L-BOVB	– 1.15085	– 0.99964	94.9
	SL-π-BOVB	– 1.16758	– 0.99964	105.4
	VBCIS	– 1.15096	– 0.99964	95.0
	VBCISD	– 1.16838	– 0.99964	105.9
	CCSD(T)	– 1.16838	– 0.99964	105.9
cc-pVTZ	VBSCF	– 1.15080	– 0.99962	94.9
	L-BOVB	– 1.15121	– 0.99962	95.1
	SL-π-BOVB	– 1.69968	– 0.99962	106.9
	VBCIS	– 1.15142	– 0.99962	95.3
	VBCISD	– 1.17234	– 0.99962	108.4
	CCSD(T)	– 1.17234	– 0.99962	108.4
aug-cc-pVTZ	VBSCF	– 1.15098	– 0.99964	95.0
	L-BOVB	– 1.15133	– 0.99964	95.2
	SL-π-BOVB	– 1.17078	– 0.99964	107.4
	VBCIS	– 1.15148	– 0.99964	95.3
	VBCISD	– 1.17264	– 0.99964	108.6
	CCSD(T)	– 1.17264	– 0.99964	108.6
experimental[45]				109.5

Table 2. The barriers of the hydrogen exchange reaction.

Basis set	Method	$E(H_3)$ (a.u.)	$E(H_2+H)$ (a.u.)	Barrier (kcal mol^{-1})
6–31G	VBSCF	– 1.60481	– 1.64450	24.9
	L-BOVB	– 1.61471	– 1.64451	18.7
	VBCIS	– 1.61428	– 1.64451	19.0
	VBCISD	– 1.62160	– 1.64992	17.8
	CCSD(T)	– 1.62625	– 1.64992	14.9
6–31G**	VBSCF	– 1.60705	– 1.64750	25.4
	L-BOVB	– 1.62086	– 1.64769	16.8
	VBCIS	– 1.62044	– 1.64779	17.2
	VBCISD	– 1.63827	– 1.66338	15.8
	CCSD(T)	– 1.64275	– 1.66338	12.9
6–31++G**	VBSCF	– 1.61267	– 1.65027	23.6
	L-BOVB	– 1.62694	– 1.65067	14.9
	VBCIS	– 1.62729	– 1.65077	14.7
	VBCISD	– 1.64775	– 1.66819	12.8
	CCSD(T))	– 1.65048	– 1.66819	11.1
cc-pVTZ	VBSCF	– 1.61275	– 1.65062	23.8
	L-BOVB	– 1.62925	– 1.65103	13.7
	VBCIS	– 1.62819	– 1.65123	14.5
	VBCISD	– 1.65451	– 1.67215	11.1
	CCSD(T)	– 1.65619	– 1.67215	10.0
aug-cc-pVTZ	VBSCF	– 1.61804	– 1.65081	20.6
	L-BOVB	– 1.63485	– 1.65115	10.2
	VBCIS	– 1.63149	– 1.65130	12.4
	VBCISD	– 1.65655	– 1.67246	10.0
	CCSD(T)	– 1.65689	– 1.67246	9.8

Table 3. The geometries of H_2 and H_3 at the TS with aug-cc-pVTZ basis set [Å].

Method	R(H_2)	R(H_3)
BOVB	0.743	0.932
VBCISD	0.743	0.932
CCSD(T)	0.743	0.931
experimental[46]	0.741	0.930

the simple L-BOVB level. Some preliminary tests showed that use of the more sophisticated SL-π-BOVB level did not change the barriers since it resulted in the same energy reduction for the ($H_3^\bullet$) transitions state and the (H_2 + $H^\bullet$) reactants. Thus, even at this lower level, the L-BOVB barriers are much better than those of VBSCF, due to dynamic correlation imparted by the BOVB method.[22] As noted before,[24] L-BOVB and VBCIS are approximately equivalent, and this equivalency is projected both from the total energies and from the barriers of the two methods, which are extremely close. Nevertheless, the L-BOVB and VBCIS barriers are still higher than the experimental values in small or medium-sized basis sets, while VBCISD is better and partly compensates for basis set deficiency. The L-BOVB results are rather sensitive to the quality of the basis set and gradually improve as the size of the basis set increases, to reach the fairly accurate value of 10.2 kcal mol^{-1} in the best basis set. Once again, the VBCISD barriers are consistently slightly better than BOVB, and reach the value of 10.0 kcal mol^{-1} with the correlation consistent aug-cc-pVTZ basis set. This latter value is in very good agreement with the value of 9.8 kcal mol^{-1} derived from previous MO-based CI methods[14–16] and CCSD(T) calculations, and with the experimental estimate of 9.8 ± 0.2 kcal mol^{-1} cited in [14]. The CCSD(T) method is one of the most reliable MO-based methods for barrier calculation. In this respect, not only are the BOVB and VBCISD barriers in very good agreement with that of CCSD(T), but the total VBCISD energy at the TS also matches the CCSD(T) result at the aug-cc-pVTZ level. *Thus, valence bond theory clearly meets the challenge of reproducing the landmark barrier of the hydrogen exchange reaction.*

Table 3 shows the optimized bond lengths of H_2 and of H_3 at the TS at the BOVB/aug-cc-pVTZ and VBCISD/aug-cc-pVTZ levels. Again, the BOVB and VBCISD bond lengths for both the reactants and the transition state are precisely the same as those derived from CCSD(T), and previous ab initio values,[14–16] within 0.001–0.002 Å.

Clearly, the above results demonstrate that a properly designed VB method that brings in dynamic correlation in full can result in accurate estimates of bond energies, bond lengths, and—most importantly—of a reaction barrier. This successful calculation of the barrier is not an isolated event, and occasionally one does not even need a large basis set as in the hydrogen exchange reaction. Table 4 displays central barriers for identity S_N2 reactions [Eq. (7)].

$$X{:}^- + CH_3{-}X \rightarrow X{-}CH_3 + {:}X^- \qquad (7)$$

These barriers are calculated with the 6–31G* basis set for X = F, Cl, or its effective core potential equivalent, LANL2DZ* for Br and Cl. In the CCSD(T) method all electrons are correlated, while in the VBCISD method only

Table 4. Central barriers for identity S_N2 reactions $X^- + CH_3X \rightarrow XCH_3 + X^-$ (kcal mol^{-1})

Method	F	Cl	Br	I
VBCISD	13.3	14.2	12.2	11.6
CCSD(T)	11.2	13.6	10.4	9.2
G2(+)	11.6	13.2	10.8	9.6

the four valence electron pairs, which have σ-symmetry with respect to the X-C-X axis, are correlated. Nevertheless, the VBCI barriers are close to the CCSD(T) data and to earlier G2(+) data.[47]

Bonding energies of the dihalogen molecules pose difficult test cases, and require high levels of CI in MO-based theory.[22f] Table 5 displays a sample of bond energies calculated at the VBCISD level by use of moderate basis sets and only the three classical structures—one covalent and two ionic. Alongside these quantities we present the bond energies calculated with the coupled cluster method CCSD(T). Quite large basis sets are normally required for such molecules to approach the experimentally measured bonding energies, and the CCSD(T) results vary from poor to quite good as the size of the basis set is increased. The VBCI method, with merely the three classical structures, follows the same behavior and yields bonding energies with an accuracy comparable to that of the extensive MO-based CCSD(T) method. The ability of the BOVB method to yield good bonding energies has also proved satisfactory, as discussed in previous papers.[22]

Table 5. Bond energies calculated with CCSD(T)[a] and VB methods [kcal mol^{-1}].

Molecule/Basis	D_e[CCSD(T)]	D_e[VBCISD]
Cl–Cl (LANL2DZ)		39.35
Cl–Cl (6–31G*)	40.52	41.55
Cl–Cl (6–311G*)	39.96	40.38
Cl–Cl (cc-pVDZ)	41.78	45.02
Cl–Cl (cc-pVTZ)	52.08	56.12
Cl–Cl (cc-pVQZ)	55.90	
Cl–Cl (cc-pV5Z)	58.09	
Exp.	57.8	
F–F (6–31G*)	32.84	32.25
F–F (6–311G*)	26.80	29.75
F–F (cc-pVDZ)	27.14	28.46
F–F (cc-pVTZ)	34.76	36.12
F–F (cc-pVQZ)	36.64	
F–F (cc-pV5Z)	37.48	
Exp.	38.3	
Br–Br (LANL2DZ)		41.06
Br–Br (6–31G*)	41.18	44.09
Br–Br (cc-pVDZ)		41.35
Br–Br (cc-pVTZ)	47.97	49.99
Br–Br (cc-pVQZ)	51.74	
F–Cl (6–31G*)	50.23	49.31
F–Cl (cc-pVDZ)	43.17	45.61
F–Cl (cc-pVTZ)	55.0	58.84
F–Cl (cc-pVQZ)	59.18	
F–Br (6–31G*)	52.20	52.48
Cl–Br (6–31G*)	41.84	43.89

[a] CCSD(T) calculations were done with frozen core approximation.

Valence bond state correlation diagrams (VBSCDs)

Having demonstrated that VB theory can lead to correct barrier data, we now turn to analysis of the origins of this barrier, in order to emphasize the second aspect of VB theory: its conceptual lucidity. Table 6 shows the VB-computed parameters of the VBSCD (Figure 1).[21]

Table 6. VB parameters of H_3 [kcal mol^{-1}].

Basis set	Method	ΔE^*	ΔE_c	B	G	f
6–31G	VBSCF	24.9	62.7	37.8	163.3	0.38
	L-BOVB	18.7	62.7	44.0	163.3	0.38
	VBCISD	17.8	63.9	46.2	166.7	0.38
6–31G**	VBSCF	25.4	64.0	38.6	165.9	0.39
	L-BOVB	16.8	64.0	47.1	166.0	0.39
	VBCISD	15.8	66.8	51.0	175.8	0.38
6–311++G**	VBSCF	23.6	64.9	41.3	163.6	0.40
	L-BOVB	14.9	64.9	50.0	163.9	0.40
	VBCISD	12.8	67.7	54.9	174.9	0.39
cc-pVTZ	VBSCF	23.8	64.9	41.1	163.8	0.40
	L-BOVB	13.7	64.9	51.3	164.1	0.40
	VBCISD	11.1	68.0	57.0	177.7	0.38
aug-cc-pVTZ	VBSCF	20.6	65.1	44.5	164.0	0.40
	L-BOVB	10.2	65.2	54.9	164.2	0.40
	VBCISD	10.0	68.1	58.1	177.6	0.38

It can be seen from the table that the promotion gap, G, the height of the crossing point, ΔE_c, and the curvature parameter, f, are virtually independent of the VB method. The promotion gap G converges at the VBSCF/BOVB levels to 164.2–164.0 kcal mol^{-1} and is almost independent of basis sets. However, at the VBCISD levels, the value of G is somewhat higher and converges quickly to 177.0 kcal mol^{-1}. This value is close to a theoretical estimate—182.7 kcal mol^{-1}—based on the approximate formula that relates the promotion gap to the singlet-to-triplet excitation energy of the ground state H–H bond [Eq. (8)].[35, 39]

$$G \approx 0.75\Delta E_{ST} \tag{8}$$

This equation, the derivation of which was elaborated in previous treatments of the VBSCD,[35, 39] is a good approximation to G. However, a *precise estimate* of G is given in Equation 7, as the average of the singlet-to-triplet excitation and the corresponding bond energy [Eq. (9)] where D is the bond energy of H_2. Using this equation and the computed values for these physical quantities, one obtains G = 176.5 kcal mol^{-1}, which shows a perfect agreement with the VBCISD/aug-cc-pVTZ result. This gives us confidence in the other reactivity factors.

$$G = 0.5(\Delta E_{ST} + D) \tag{9}$$

The height of the crossing point, ΔE_c, is approximately constant: about 62.7–65.2 kcal mol^{-1} for the VBSCF/BOVB methods and 63.9–68.1 kcal mol^{-1} for the VBCISD method. These values are again close to the semiempirical estimate of this quantity, 61.5 kcal mol^{-1}, as a sum of the bond distortion energy ($\Delta D^{\neq}$) and the averaged triplet repulsion across the short $H_a \cdots H_b$ and long $H_a \cdots H_c$ distances in the TS [Eq. (10)].[39]

$$\Delta E_c = \Delta D^{\ddagger} + 0.5[{}^3E(\mathrm{a,b})^{\ddagger} + {}^3E(\mathrm{a,c})^{\ddagger}] = fG \qquad (10)$$

Since the factor f is simply the ratio $\Delta E_c/G$, and neither quantity varies much, this factor itself is approximately constant (ca. 0.38–0.40), in agreement with results of other identity hydrogen abstraction reactions,[35] as well as with a semiempirical estimate of this quantity.[35]

What appears to make the barrier in Table 6 so small is B, the resonance energy of the transition state, which varies from 37.8 at the VBSCF level with the smallest basis set, all the way to 57.1–58.0 kcal mol^{-1} at the VBCISD level with the correlation consistent basis sets. It therefore seems that the resonance energy of the transition state is optimum when dynamic electron correlation is accounted for in a precise manner. The value of B is extremely close to the semiempirical estimate of B, as one half of the bond energy of the ground state molecules [Eq. (11)].

$$B = 0.5\,\mathrm{D} \qquad (11)$$

By use of the bond energy calculated in Table 2, the estimated value of B is 54.5 kcal mol^{-1}, in good agreement with the best VBCISD values. A previously recommended simple expression for the barrier, Equation (12), gives a barrier of 12.5 kcal mol^{-1}, which is not a bad estimate.

$$\Delta E = fG - 0.5D; f = 0.38 \qquad (12)$$

Moreover, this equation, based on the VBSCD model,[21] provides a very clear mechanism for barrier formation; the barrier is a balance between, on the one hand, the total deformation and repulsion energies, required to achieve resonance between the reactant and product boding schemes, and on the other hand, the resonance energy lowering due to the delocalization of the electrons, which are reorganized during the transformation.

Conclusion

The calculation of the barrier for the hydrogen exchange reaction[14] in the 1970s constituted a landmark achievement of quantum chemistry and specifically of MO-based methods that include electron correlation. In this paper we report an accurate calculation of this barrier by use of recently developed VB methods, BOVB and VBCI, that incorporate the necessary dynamic correlation. As expected for any well behaved computational method, the VB barriers are too high when small basis sets are used and gradually converge to the experimentally determined or best MO-based values as the quality of the basis set is increased. In our case the VB convergence is rather fast and occurs in a medium-sized basis set, aug-cc-pVTZ. This is achieved with VB wave functions that deal *with only the eight classical VB structures.* With the BOVB method, the wave function is extremely compact, as each VB structure is described by the appropriate determinant spin eigenfunction. In the VBCI framework, each VB structure is described by several spin eigenfunctions, which are condensed into a single structure. In that sense, the VBCI wave function should be regarded as a function that deals with a minimal set of VB structures, eight in the current case, that are dressed with dynamic correlation. As such, VBCI does not lose any advantage relative to BOVB and even tends to be more accurate in medium-sized basis sets. Both the BOVB and VBCI methods, while for the moment still being computationally more costly than, for example, CCSD(T), are suitable for the calculation of diabatic states and for the many applications that are specific to VB.

To the best of our knowledge, this work is the first accurate VB barrier that matches an experimental value. This is a proof of principal that VB theory with appropriate accounting for dynamic electron correlation can achieve quantitative accuracy of reaction barriers, and still retain a compact and "very chemical" wave function. The sample of S_N2 barriers shows that this is not an isolated case.

In addition, the paper presents a new strategy for computing diabatic energy curves that are independent of the basis set. This enables the generation of quantitatively accurate VB state correlation diagrams (VBSCD). Thus, the VB method can attain high accuracy and still retain relatively simple and straightforward interpretability. In this respect, while announcing the coming of age of VB theory is still somewhat premature, this event is certainly within close reach.

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