

The generalized resonating valence bond method: Barrier heights in the HF + D and HCl + D exchange reactions

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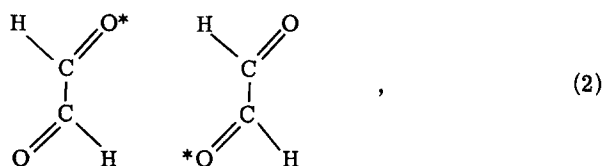
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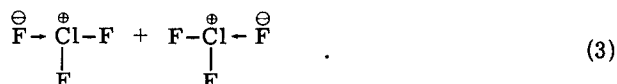
There are many molecules that are best described as linear combinations of localized bonding structures. Examples include conjugated organic molecules such as benzene:



systems with coupled localized excitations as in glyoxal:



and hypervalent compounds such as ClF₃:



However, actually solving for such a wave function has been impractical due to the nonzero overlap between the different resonance structures.

In the self-consistent generalization of valence bond theory¹ (GVB), the wave function for a single localized form can be optimized, but this formalism does not allow mixing of different resonance structures. We have now developed a method that allows self-consistent optimization of a resonating wave function such as (1), (2), or (3). Herein this generalized resonating valence bond (GRVB) method is described and applied to the calculation of the barrier heights in the HF + D and HCl + D exchange reactions.

We wish to minimize the energy of a wave function of the form

$$\Psi_{\text{tot}} = c_A \Psi_A + c_B \Psi_B + \dots, \quad (4)$$

where each Ψ_A or Ψ_B is a correlated multiconfigurational (e.g., GVB) wave function. The difficulty in solving for such a wave function is that an orbital in Ψ_A may overlap any number of orbitals in Ψ_B . We have recently presented a method² for evaluating the total energy of a wave function such as (4). This consists of evaluating the interaction between each pair of wave functions Ψ_A and Ψ_B by expanding each in terms of determinants and transforming the orbitals to obtain biorthogonalization. In order to optimize the orbitals, we evaluate the first derivative for each possible rotation between each occupied orbital and every other occupied or virtual orbital. This is accomplished by evaluating the total energy of the new wave function resulting from an incre-

mental orbital rotation and numerically calculating the energy derivative. The second derivatives may be calculated for each pair of orbital rotations, but we found that considerable computational savings are realized by calculating only the diagonal second derivatives to find an initial solution vector, and then performing a fully quadratic search (including off-diagonal second derivatives) within the two-dimensional space defined by this solution vector and the solution from the previous iteration. The orbitals in each sub-wave function Ψ_A or Ψ_B are optimized in this manner. Each energy evaluation allows relaxation of the configuration coefficients of (4) and the configuration interaction coefficients internal to each sub-wave function, so that all coefficients are optimized simultaneously with the orbital shapes, leading to rapid convergence.

The HF + D \rightleftharpoons H + FD exchange reaction has generated considerable experimental^{3,4} and theoretical^{5,6} interest in recent years. Inclusion of electron correlation has been found to be very important in calculating the barrier height accurately. Simple wave functions such as Hartree-Fock (HF) and GVB-perfect pairing [GVB(PP)] (hereafter referred to as GVB) yield a barrier 15–20 kcal/mole higher than high-quality configuration interaction (CI) calculations. Thus the barrier in the HF + D exchange reaction provides a critical test of the accuracy of the GRVB method.

In the resonating valence bond formalism, the HF + D exchange is viewed as a continuously varying linear combination of the two possible bonding structures,

$$\Psi_{\text{HFD}} = c_{\text{HF}} \Psi_{\text{HF}} + c_{\text{FD}} \Psi_{\text{FD}}, \quad (5)$$

where one structure (Ψ_{HF}) has a bond between H and F (and an unpaired electron on the D atom), and the other has an F–D bond (Ψ_{FD}). Each of the reaction limits (products or reactants) is perfectly described by only one of these structures, while all other points along the surface require a resonance of the two. At the saddle point, Ψ_{HF} will be the mirror image of Ψ_{FD} , and c_{HF} and c_{FD} will have equal magnitude.

The GRVB wave function, which simultaneously optimizes the shapes of Ψ_{HF} and Ψ_{FD} and the coefficients c_{HF} and c_{FD} , is appropriate for describing all points along the reaction coordinate and is equivalent to a GVB wave function at each limit. The GVB(1/2) wave function for HF has a sigma bond consisting of two one-electron orbitals that are spin paired, allowing the molecular wave function to dissociate properly into ground state H and F atoms. The GRVB(1/2) wave function is the resonance of two GVB(1/2) sub-wave functions, but with both sets of orbitals optimized for the resonating

wave function (5). Flexible contracted Gaussian basis sets [$H(6s1p/3s1p)$, $F(9s5p1d/3s2p1d)$] were employed and (except for the $F 1s$ orbital whose shape was obtained from an $\mathcal{R}\mathcal{F}$ calculation at the saddle point) all orbitals were fully optimized in the GRVB(1/2) calculation. The collinear barrier height at this level is 47.7 kcal/mole, in excellent agreement with the best CI results of Wadt and Winter⁵ (47.6) and Bender *et al.*⁶ (49.0). Experimentally, the barrier is thought to be between 42 and 53 kcal/mole.⁴ In contrast, $\mathcal{R}\mathcal{F}$ and GVB calculations lead to barriers of 67.8 and 69.5 kcal/mole, respectively. We also find that increasing the level of correlation in the bond pairs from (1/2) to (1/5) (the bond pair correlated with five natural orbitals) yields a collinear barrier height of 48.3 kcal/mole, essentially unchanged from the GRVB(1/2) level.

We have also examined the $HCl + D$ exchange reaction using a GRVB(1/2) wave function. Using a valence double zeta plus polarization basis, we find a barrier of 25.5 kcal/mole at the collinear geometry optimized by Dunning.⁷ This is in agreement with the barriers of 24.5⁷ and 22.1⁸ obtained by other workers and adds to the body of evidence indicating a barrier much higher than previously thought.⁹

The advantage of the GRVB approach is that the wave function is conceptually simple yet provides a quantitatively accurate description of the exchange process. One-electron orbitals for each of the sub-wave functions may be examined to provide a simple interpretation of the wave function (generally not possible or not useful for normal CI wave functions). In fact, the GRVB orbitals at the $HF + H$ saddle point bear a striking resemblance to those of an HF molecule next to an H atom, showing the validity of the resonating VB picture of the exchange reaction. These plots also show that there is a large Pauli-induced orthogonality between the incoming hydrogen and the fluorine $2s$ pair. This interaction explains why the barrier for this "allowed" reaction is so high (e.g., the $H_2 + H$ barrier is only 9.8 kcal/mole¹⁰).

We can also understand why the barrier in $HCl + H$ is only one half as high since the size of the chlorine $3s$ relative to the $3p$ is much less than the $2s$ to $2p$ size ratio in fluorine.

We believe that the GRVB method will be useful both for quantitative and conceptual progress in studying chemical bonding and reactions. With this method, many complicated electronic states that previously required extensive CI calculations may be adequately described in terms of a small number of meaningful resonance contributors, a picture that is conceptually simple and chemically appealing.

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^aContribution No. 6434.

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Observation of magnetic vibrational circular dichroism^{a)}

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In recent years instrumentation development has made possible the detection of "natural" vibrational circular dichroism in the near- and mid-IR for chiral molecules.^{1,2} The analogous magnetic circular dichroism experiment has been proposed, based on theoretical predictions; but has not yet been measured.³⁻⁵ Herein are reported the first observations of magnetic vibrational circular dichroism (MVCD) spectra for the fundamental CH stretching vibrations of several high symmetry organic compounds in dilute CCl_4 solution. These

MVCD spectra, while weak, are in several cases easily detectable and may provide a new tool for the analysis of vibrations of the ground electronic state and of their interaction with excited molecular vibronic states.

MVCD spectra were measured using an infrared circular dichroism instrument constructed at UICC, which has been detailed separately.² In order to adequately shield from the magnetic field effects, the InSb detector was moved away from the sample by ~60 cm and encased