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Valence Bond Formulations of the Identity Hydrogen Abstraction Reaction, $X^\bullet + H{-}X' \rightarrow X{-}H + X'^\bullet$, with Reactantlike and Productlike Complexes

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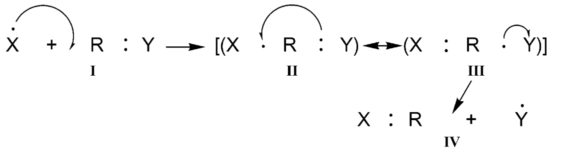
Connections are made between two valence bond studies of hydrogen atom abstraction reactions: (a) *J. Phys. Chem. A* **2001**, *105,* 8226 and (b) *J. Phys. Chem.* **1993**, *97,* 12210; corrections **1994**, *98,* 3226. At each stage along the reaction coordinate, the variational-best valence bond formulation for the reacting system of (b) can be described in terms of resonance between valence bond structures for a reactantlike complex and a productlike complex. It is demonstrated that the (a) and (b) descriptions of the transition states are equivalent. Further development for (b) is presented, to compare expressions for the promotion gap (*G*) and the resonance energy at the avoided crossing (*B*) with those that arise in (a). By use of a triple-ζ 1s atomic orbital (AO) basis set to formulate the wave functions for the reactantlike and productlike complexes, it is demonstrated how these wave functions are constructed as linear combinations of localized molecular orbital (MO) configurations, each of which involves one AO per atomic center. Similar procedures that include 2p AOs as polarization functions in the treatment are also described. The results of valence bond calculations that use these two types of AO basis sets provide illustrative examples of how the formulation of (b) provides a compact valence bond representation for the electronic reorganization that is involved in the conversion of reactants into products.

Introduction

Shaik et al.[1] have provided valence bond (VB) studies of identity hydrogen atom transfer reactions of the type $X^\bullet + H{-}X' \rightarrow X{-}H + X'^\bullet$, with $X = X' = CH_3$, SiH_3, GeH_3, SnH_3, and PbH_3. Attention was given to both quantitative estimates of reaction parameters and the construction of state correlation diagrams via the use of Lewis-type VB structures. After the publication of ref 1, Shaik et al.[2] contrasted their model with the Z model of Zavitsas,[3] to respond to a criticism that was provided by Zavitsas.[4] In ref 5, a different type of quantitative VB study for $H^\bullet + H{-}H' \rightarrow H{-}H + H'^\bullet$ was also presented. Although ref 5 involved an extensive list of corrections, the treatment provided is relevant for the provision of compact qualitative VB representations for $X^\bullet + H{-}X' \rightarrow X{-}H + X'^\bullet$ radical transfer reactions. In particular, Scheme A of ref 5, or more generally **I** → [**II** ↔ **III**] → **IV** here[6] with X = R = Y = H, does indicate clearly how reactants are converted into products via the formation of reactantlike (RC) and productlike (PC) complexes. The VB structures **II** and **III**, with fractional X−R and R−Y bonding, are examples of "increased-valence" structures.[5−8]



In this paper, extensions to the treatment provided in ref 5 will be developed in order to demonstrate how extended atomic orbital (AO) basis sets can be incorporated into this type of VB formulation. With both triple-ζ and 1s−2p basis sets used to construct the wave functions for the reactantlike and productlike complexes of the $H^\bullet + H{-}H' \rightarrow H{-}H + H'^\bullet$ reaction, it will be demonstrated, with illustrative calculations for the transition state, how these wave functions can be expressed as linear combinations of increased-valence configurations, each of which involves one nonhybrid or hybrid AO per atomic center. The purpose is to show how the theory for **I** → [**II** ↔ **III**] → **IV** is appropriate for all types of AO basis sets, rather than an attempt to provide fairly accurate values for the transition-state barrier height and geometry via the illustrative calculations, which use only small AO basis sets.

Initially in this paper, some comparisons will be made with the theory that has been provided in ref 1.

Wave Functions for VB Structures

To establish the VB formulation, we redescribe the orbitals and orbital occupancies for the mechanism of **I** → [**II** ↔ **III**] → **IV**. At intermediate stages along the reaction coordinate, the electrons are accommodated in six (nonorthogonal) two-center molecular orbitals (MOs)—three for **II** and three for **III**. Therefore the mechanism differs from a generalized VB (GVB) formulation[9] for the $H^\bullet + H{-}D \rightarrow H{-}H + D^\bullet$ reaction, in which the electrons occupy three-center MOs at intermediate stages along the reaction coordinate. Although the GVB formulation could provide a more convenient algorithm for calculations, the three-center nature of its orbitals does not provide a localized "picture" of how electronic reorganization might proceed as reactants are converted into products.At all stages of **I** → [**II** ↔ **III**] → **IV**, the orbitals that accommodate the electrons are either AOs or localized two-center MOs. With configuration interaction (CI), the GVB and the **I** → [**II** ↔ **III**] → **IV** formulations can generate the same energy.

With a, b, and c as the overlapping (nonhybrid or hybrid) AOs located on the atomic centers X, R, and Y, the orbital

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TABLE 1: Weights for H_3 VB Structures 1−8 for the H_3 Transition State, with Triple-ζ 1s Basis Set[a]

VB structure	AO configuration	$\zeta_a = 1.0$, $\zeta_b = \zeta_c = 1.193$	$\zeta_a = \zeta_b = 1.0$, $\zeta_c = 0.6875$	$\zeta_a = \zeta_c = 1.0$, $\zeta_b = 0.6875$	$\zeta_c = \zeta_b = 1.0$, $\zeta_a = 0.6875$	$\zeta_a = \zeta_b = 1.193$, $\zeta_c = 1.0$	sum of weights
1	a(bc)	0.179	0.004	0.003	0.002	0.001	0.189
2	a(bb)	0.066	0.011	0.009	0.001	0.053	0.140
3	a(cc)	0.009	0.018	0.116			0.143
4	c(ba)	0.001	0.002	0.003	0.004	0.179	0.189
5	c(bb)	0.053	0.001	0.009	0.011	0.066	0.140
6	c(aa)			0.116	0.018	0.009	0.143
7	b(cc)	0.008	0.008	0.010			0.026
8	b(aa)			0.010	0.008	0.008	0.026

[a] The AO exponents ζ_a, ζ_b, and ζ_c obtain to the AO configurations for the VB structures. The two electrons that occupy the AOs in parentheses are singlet-spin paired. The remaining electron is assumed to have $m_s = +^1/_2$ spin.

occupancies for the X + RY reactants of **I** and the XR + Y products of **IV** are $(a)^1(\phi'_{bc})^1(\phi''_{cb})^1$ and $(\phi'_{ba})^1(\phi''_{ba})^1(c)^1$, respectively, in which $\phi'_{bc} = b + k'c$, $\phi''_{cb} = c + k''b$, $\phi'_{ba} = b + \kappa' a$, and $\phi''_{ab} = a + \kappa'' b$ are Coulson−Fischer[10]-type bonding MOs; cf. eqs 3 and 4 of ref 5. As the reactants approach, and the a and b AOs overlap, the X electron delocalizes into the X−R bonding MO, $\phi_{ab} = a + lb$, to give the orbital occupancies of $(\phi_{ab})^1(\phi'_{bc})^1(\phi''_{cb})^1$ for the reactantlike complex **II**. Electronic reorganization of **II** occurs via the delocalization of an electron from an R−Y bonding MO into an X−R bonding MO to generate the productlike complex **III** with MO occupancies of $(\phi'_{ba})^1(\phi''_{ab})^1(\phi_{cb})^1$ and $\phi_{cb} = c + \lambda b$. Formation of the product **IV** arises from the transfer of the ϕ_{cb} electron of **III** into the c AO, to give the $(\phi'_{ba})^1(\phi''_{ab})^1(c)^1$ configuration. At the commencement of the reaction, $l = 0$, and $\lambda = 0$ at the conclusion of the reaction.

At each stage along the reaction coordinate, the values for the MO polarity parameters k', k'', l, κ', κ'', and λ are determined variationally. The wave function for the reacting system is given by eq 1 (cf. eq 11 of ref 5)

$$\Psi = \Psi_{RC} + \rho\Psi_{PC} \equiv \Psi_{\mathbf{II}} + \rho\Psi_{\mathbf{III}} \tag{1}$$

in which the wave functions for the reactantlike and productlike complexes are defined according to eqs 9 and 10 of ref 5, or

$$\Psi_{RC} \equiv \Psi_{\mathbf{II}} = \Phi'_{\mathbf{II}} + \mu\Phi''_{\mathbf{II}} \tag{2a}$$

$$\Psi_{PC} \equiv \Psi_{\mathbf{III}} = \Phi'_{\mathbf{III}} + \nu\Phi''_{\mathbf{III}} \tag{2b}$$

There are eight $S = M_S = {}^1/_2$ spin Lewis structures, with different AO configurations. These structures are displayed in both refs 1 and 5. We shall use the VB structural numberings[11] of Figure 1 of ref 5. The AO occupancies are indicated here in Table 1. We shall initially designate these structures as $\Phi_{\mathbf{1}}$ instead of $\Phi_{HL}(r;\mathbf{1})$ or $\Phi_{HL}(p;\mathbf{1})$ for example. The $\Phi'_{\mathbf{II}}$, $\Phi''_{\mathbf{II}}$, $\Phi'_{\mathbf{III}}$, and $\Phi''_{\mathbf{III}}$ wave functions of eqs 5−8 of ref 5 are then given by eqs 3−6 here:

$$\Phi'_{\mathbf{II}} = a\Phi_{\mathbf{1}} + 2k''\Phi_{\mathbf{2}} + 2k'\Phi_{\mathbf{3}} - l(a\Phi_{\mathbf{5}} - 2k'\Phi_{\mathbf{7}}) \tag{3}$$

$$\Phi''_{\mathbf{II}} = b(-\Phi_{\mathbf{1}} + 2\Phi_{\mathbf{4}} - 3l\Phi_{\mathbf{5}}) \tag{4}$$

$$\Phi'_{\mathbf{III}} = u\Phi_{\mathbf{4}} + 2\kappa''\Phi_{\mathbf{5}} + 2\kappa'\Phi_{\mathbf{6}} - \lambda(u\Phi_{\mathbf{2}} - 2\kappa'\Phi_{\mathbf{8}}) \tag{5}$$

$$\Phi''_{\mathbf{III}} = v(2\Phi_{\mathbf{1}} - 3\lambda\Phi_{\mathbf{2}} - \Phi_{\mathbf{4}}) \tag{6}$$

in which $a = 1 + k'k''$, $b = 1 - k'k''$, $u = 1 + \kappa'\kappa''$, and $v = 1 - \kappa'\kappa''$.

The $\Psi_{\mathbf{II}}$ and $\Psi_{\mathbf{III}}$ of eq 1 and the Ψ of eq 2 can then be expressed according to eqs 7−11, in which CT = charge transfer, $C_{CT}(r) = -l$, and $C_{CT}(p) = -\lambda$:

$$\Psi_{\mathbf{II}} = \{(a - \mu b)\Phi_{\mathbf{1}} + 2k''\Phi_{\mathbf{2}} + 2k'\Phi_{\mathbf{3}}\} + 2\mu b\Phi_{\mathbf{4}} - l(a + 3\mu b)\Phi_{\mathbf{5}} + 2lk'\Phi_{\mathbf{7}} \tag{7}$$

$$= \Phi'_L(r) + 2\mu b\Phi_{\mathbf{4}} + C_{CT}(r)\Psi\{X^+(RY)^-\}$$

$$\Psi_{\mathbf{II}} = \Psi'_{\mathbf{I}}(r) + 2\mu b\Phi_{\mathbf{4}} + C_{CT}(r)\Psi_{\mathbf{V}} \tag{8}$$

$$\Psi_{\mathbf{III}} = \{(u - \nu v)\Phi_{\mathbf{4}} + 2\kappa''\Phi_{\mathbf{5}} + 2\kappa'\Phi_{\mathbf{6}}\} + 2\nu v\Phi_{\mathbf{1}} - \lambda(u + 3\nu v)\Phi_{\mathbf{2}} + 2\lambda\kappa'\Phi_{\mathbf{8}} \tag{9}$$

$$= \Phi'_L(p) + 2\nu v\Phi_{\mathbf{1}} + C_{CT}(p)\Psi\{(XR)^-Y^+\}$$

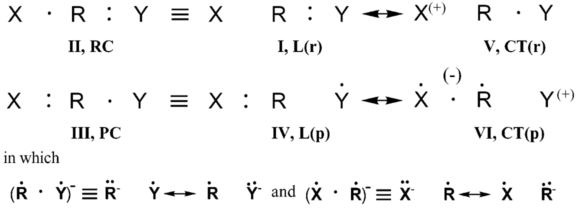
$$\Psi_{\mathbf{III}} = \Psi'_{\mathbf{IV}}(p) + 2\nu v\Phi_{\mathbf{1}} + C_{CT}(p)\Psi_{\mathbf{VI}} \tag{10}$$

$$\Psi = (a - \mu b + 2\rho\nu v)\Phi_{\mathbf{1}} + \{2k'' - \rho\lambda(u + 3\nu v)\}\Phi_{\mathbf{2}} + 2k'\Phi_{\mathbf{3}} + \{2\mu b + \rho(u - \nu v)\}\Phi_{\mathbf{4}} + \{-l(a + 3\mu b) + 2\rho\kappa''\}\Phi_{\mathbf{5}} + 2\rho\kappa'\Phi_{\mathbf{6}} + 2lk'\Phi_{\mathbf{7}} + 2\rho\lambda\kappa'\Phi_{\mathbf{8}} \tag{11}$$

$$\Psi \equiv \sum d_i\,\Phi_i \qquad i = \mathbf{1}-\mathbf{8} \tag{12}$$

The variationally best values for the d_i coefficients of eq 12 can be used to determine the values of the six polarity parameters and ρ when two further equations for μ and ν are included; see below. It is to be noted that when the variationally best d_i coefficients are used to determine the coefficients of Φ_i in eqs 7 and 9, the latter coefficients will not correspond to the variationally best values for $\Psi_{\mathbf{II}}$ and $\Psi_{\mathbf{III}}$. Conversely, the variationally best values for the Φ_i coefficients in eqs 7 and 9 do not correspond to the variationally best values for the d_i coefficients.

In eqs 8 and 10, $\Psi'_{\mathbf{I}}(r) \equiv \Phi'_L(r)$ and $\Psi'_{\mathbf{IV}}(p) \equiv \Phi'_L(p)$, in which the subscript L refers to the Lewis-type designation of ref 1. When $\mu = 0$ in eqs 7 and 8, and $\nu = 0$ in eqs 9 and 10, the resulting VB structures that correspond to the identities of eqs 8 and 10 are displayed below.



With nonzero values for μ and ν, structures **4** and **1** need also to be included in the resonance schemes, as indicated by eqs 8 and 10.

Transition-State Wave Function

At the transition state for a symmetrical system, the parameters λ, κ', κ'', ν, and ρ are equal to l, k', k'', μ, and -1, respectively.[2] With these equalities, eq 13 is obtained from eq 11:

$$\Psi_{\mathrm{TS}} = [(a - 3\mu b)\Phi_{\mathbf{1}} + \{2k'' - l(a + 3\mu b)\}\Phi_{\mathbf{2}} + 2k'\Phi_{\mathbf{3}}\,] - [(a - 3\mu b)\Phi_{\mathbf{4}} + \{2k'' - l(a + 3\mu b)\}\Phi_{\mathbf{5}} + 2k'\Phi_{\mathbf{6}}] + 2lk'(\Phi_{\mathbf{7}} - \Phi_{\mathbf{8}}) \quad (13)$$

$$\Psi_{\mathrm{TS}} = \Phi_{\mathrm{L}}(\mathrm{r}) - \Phi_{\mathrm{L}}(\mathrm{p}) + 2lk'(\Phi_{\mathbf{7}} - \Phi_{\mathbf{8}}) \quad (14)$$

The Lewis-type wave functions $\Phi_{\mathrm{L}}(\mathrm{r})$ and $\Phi_{\mathrm{L}}(\mathrm{p})$ of eq 14 correspond to $\Psi_{\mathbf{I}}$- and $\Psi_{\mathbf{IV}}$-type wave functions for the reactants and products.

The Ψ_{TS} of eq 14 is proportional to the Shaik et al. expression of eq 15 (i.e., eq 9 of ref 1) for Ψ_{TS}.

$$\Psi_{\mathrm{TS}} = c_{\mathrm{L}}N\{\Phi_{\mathrm{L}}(\mathrm{r}) - \Phi_{\mathrm{L}}(\mathrm{p})\} + c_{\mathrm{F}}(\Phi_{\mathbf{7}} - \Phi_{\mathbf{8}}) \quad (15)$$

Therefore the two treatments of the transition state are equivalent. A modified result is obtained when $\Phi_{\mathbf{1}}$, $\Phi_{\mathbf{2}}$, $\Phi_{\mathbf{4}}$, and $\Phi_{\mathbf{5}}$ in the $\Psi_{\mathbf{II}}$ of eq 7 are replaced by $\Phi_{\mathbf{1}}(\mathrm{r})$, $\Phi_{\mathbf{2}}(\mathrm{r})$, $\Phi_{\mathbf{4}}(\mathrm{r})$, and $\Phi_{\mathbf{5}}(\mathrm{r})$, and the same wave functions in the $\Psi_{\mathbf{III}}$ of eq 9 are replaced by $\Phi_{\mathbf{1}}(\mathrm{p})$, $\Phi_{\mathbf{2}}(\mathrm{p})$, $\Phi_{\mathbf{4}}(\mathrm{p})$, and $\Phi_{\mathbf{5}}(\mathrm{p})$. The corresponding designations for $\Phi_{\mathbf{3}}$, $\Phi_{\mathbf{6}}$, $\Phi_{\mathbf{7}}$, and $\Phi_{\mathbf{8}}$ are $\Phi_{\mathbf{3}}(\mathrm{r})$, $\Phi_{\mathbf{6}}(\mathrm{p})$, $\Phi_{\mathbf{7}}(\mathrm{r})$, and $\Phi_{\mathbf{8}}(\mathrm{p})$. The resulting expression for Ψ_{TS} is then given by

$$\Psi_{\mathrm{TS}} = \{(a - \mu b)\Phi_{\mathbf{1}}(\mathrm{r}) + 2k''\Phi_{\mathbf{2}}(\mathrm{r}) + 2k'\Phi_{\mathbf{3}}(\mathrm{r})\} - \{(a - \mu b)\Phi_{\mathbf{4}}(\mathrm{p}) + 2k''\Phi_{\mathbf{5}}(\mathrm{p}) + 2k'\Phi_{\mathbf{6}}(\mathrm{p})\} + \{2\mu b\Phi_{\mathbf{4}}(\mathrm{r}) - l(a + 3\mu b)\Phi_{\mathbf{5}}(\mathrm{r})\} - \{2\mu b\Phi_{\mathbf{1}}(\mathrm{p}) - l(a + 3\mu b)\Phi_{\mathbf{2}}(\mathrm{p})\} + 2lk'\{\Phi_{\mathbf{7}}(\mathrm{r}) - \Phi_{\mathbf{8}}(\mathrm{p})\} \quad (16)$$

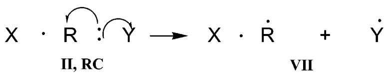
$$\Psi_{\mathrm{TS}} = \Phi_{\mathrm{L}}(\mathrm{r}) - \Phi_{\mathrm{L}}(\mathrm{p}) + \{2\mu b\Phi_{\mathbf{4}}(\mathrm{r}) - l(a + 3\mu b)\Phi_{\mathbf{5}}(\mathrm{r})\} - \{2\mu b\Phi_{\mathbf{1}}(\mathrm{p}) - l(a + 3\mu b)\Phi_{\mathbf{2}}(\mathrm{p})\} + 2lk''\{\Phi_{\mathbf{7}}(\mathrm{r}) - \Phi_{\mathbf{8}}(\mathrm{p})\} \quad (17)$$

in which the $\Phi_{\mathrm{L}}(\mathrm{r})$ and $\Phi_{\mathrm{L}}(\mathrm{p})$ are now defined in terms of the $\Phi_i(\mathrm{r})$ and $\Phi_i(\mathrm{p})$ structures, respectively.

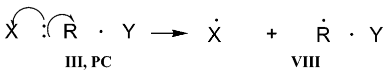
The Promotion Gap, *G*

Assuming that the $\Phi_i(\mathrm{r})$ and $\Phi_i(\mathrm{p})$ are identical, i.e., the same AOs are used to construct them to give $\Phi_i(\mathrm{r}) = \Phi_i(\mathrm{p}) \equiv \Phi_i$, in this section and the next, we shall demonstrate that the definitions of the promotion gap, *G*, and the resonance energy of the transition state, *B*, differ in the refs 1- and 5-type treatments of them. The theory for H_3 will be used to illustrate the differences.

In refs 5 and 6, it is shown that one VB representation for the dissociation of the R−Y bond of the reactant complex **II** generates the XR + Y products of **VII**.



Similarly, one VB representation for the dissociation of the X−R bond of the product complex **III** generates the X + RY reactants of **VIII**.



When $\Psi_{\mathbf{II}} = \Phi'_{\mathbf{II}}$ and $\Psi_{\mathbf{III}} = \Phi'_{\mathbf{III}}$, the polarity parameters *l* and λ for **VII** and **VIII** have nonzero values when they are determined variationally.[5] But the resultant wave functions for **VII** and **VIII** are then not orthogonal to the ground-state wave functions for the separated products or reactants,[5] and therefore they do not correspond to spectroscopic (excited) states.

When nonzero values for the parameters μ and ν are included in eq 2, their values can be chosen so that the orthogonality requirements of eq 18

$$\langle\Psi_{\mathbf{II}}(R_{\mathrm{BC}}{=}\infty)|\Psi_{\mathbf{IV}}(R_{\mathrm{BC}}{=}\infty)\rangle = \langle\Psi_{\mathbf{III}}(R_{\mathrm{AB}}{=}\infty)|\Psi_{\mathbf{I}}(R_{\mathrm{AB}}{=}\infty)\rangle = 0 \quad (18)$$

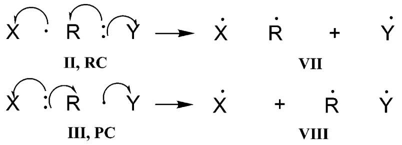
together with variationally determined energies, can be obtained.[5] We reconsider $\langle\Psi_{\mathbf{II}}(R_{\mathrm{BC}}{=}\infty)|\Psi_{\mathbf{IV}}(R_{\mathrm{BC}}{=}\infty)\rangle = 0$ here. When $R_{\mathrm{BC}} = \infty$, k' and k'' have values of zero, and eq 6 then generates eq 19 (cf. eq 20 of ref 5):

$$\Psi_{\mathbf{II}}(R_{\mathrm{BC}}{=}\infty) = (1 - \mu)\Phi_{\mathbf{1}} + 2\mu\Phi_{\mathbf{4}} - l(1 + 3\mu)\Phi_{\mathbf{5}} \quad (19)$$

In the Appendix, and in ref 5, it is demonstrated that $\mu = 0.2$, and therefore $l = 0$ (cf. eq 22 of ref 5), generating eq 20 (cf. eq 26 of ref 5) for $\Psi_{\mathbf{II}}(R_{\mathrm{BC}}{=}\infty)$:

$$\Psi_{\mathbf{II}}(R_{\mathrm{BC}}{=}\infty) = \Psi\{\mathrm{H_A}{-}\mathrm{H_B}(S{=}1)\} + \mathrm{H_C}(S{=}{}^1/_2) \quad (20)$$

Equation 20 involves spectroscopic spin states for H_2 and the H atom. With $l = 0$, the VB representations for **II** → **VII** and **III** → **VIII** can then be modified as follows, in order that spectroscopic excited states are generated for the relevant bond dissociations.



The resulting promotion gap *G* corresponds to the $G' = \Delta E_{\mathrm{ST}}$ of eq 15 of ref 1 and represents the energy difference between the singlet-spin ground state and the triplet-spin excited state for H_2. As was done in ref 1, *G* can be related to the bond energy for the R−Y bond.

Resonance Energy *B* at the Avoided Crossing

The results of the H_3 VB calculations[12] reported in Table 4 of ref 5 show that *G* is approximately related to $E(\Psi^*_{\mathrm{cross}}) - E(\Psi_{\mathrm{cross}})$ according to

$$G = E\{\Psi_{\mathbf{II}}(R_{\mathrm{BC}}{=}\infty)\} - E\{\Psi_{\mathbf{IV}}(R_{\mathrm{BC}}{=}\infty)\} \approx 2\{E(\Psi^*_{\mathrm{cross}}) - E(\Psi_{\mathrm{cross}})\} \quad (21)$$

in which $E(\Psi_{\mathrm{cross}}) \equiv E(\Psi_{\mathrm{TS}})$.

With normalized $\Psi_{\mathbf{II}}$ and $\Psi_{\mathbf{III}}$, we have $\langle\Psi_{\mathbf{II}}|H|\Psi_{\mathbf{II}}\rangle = \langle\Psi_{\mathbf{III}}|H|\Psi_{\mathbf{III}}\rangle = Q$ at the crossing point, $K = \langle\Psi_{\mathbf{II}}|H|\Psi_{\mathbf{III}}\rangle \equiv \langle\Psi_{\mathbf{III}}|H|\Psi_{\mathbf{II}}\rangle$, and $S_{\mathbf{II,III}} = \langle\Psi_{\mathbf{II}}|\Psi_{\mathbf{III}}\rangle$. When the approximation of eq 21 is invoked, eqs 22 and 23 are obtained for $E(\Psi^*_{\mathrm{cross}}) - E(\Psi_{\mathrm{cross}})$ and *B*:

$$E(\Psi^*_{\mathrm{cross}}) - E(\Psi_{\mathrm{cross}}) = -2(K - S_{\mathbf{II,III}}Q)/(1 - S_{\mathbf{II,III}}{}^2) \approx G/2 \quad (22)$$

$$B = E(\Psi_{\mathrm{TS}}) - E(\Psi_{\mathbf{II},\mathrm{cross}}) = (K - S_{\mathbf{II,III}}Q)/(1 + S_{\mathbf{II,III}}) \approx -(1 - S_{\mathbf{II,III}})G/4 \quad (23)$$

In ref 1, B is defined as $B = E(\Psi_{TS}) - E(\Phi_{L,cross})$, and a value of $G'/4$ has been assigned to it from semiempirical VB theory.

Simplifications to *B* and *G*

We can simplify eqs 22 and 23 as follows. We have indicated that, at the conclusion and commencement of the reaction, the orthogonality relationships of eq 18 obtain in order that the associated wave functions represent spectroscopic states, or eigenstates, for the reactants and products. At intermediate stages along the reaction coordinate, each of $\Psi_{\mathbf{II}}$ and $\Psi_{\mathbf{III}}$ alone does not correspond to an eigenstate. But we can still require that these wave functions be orthogonal, i.e., $S_{\mathbf{II,III}} = 0$. This requirement ensures that $\Psi_{\mathbf{II}}$ and $\Psi_{\mathbf{III}}$ correlate simply with $\Psi_{\mathbf{II}}(R_{BC}{=}\infty)$ and $\Psi_{\mathbf{III}}(R_{AB}{=}\infty)$, respectively. We thereby obtain eqs 24 and 25.

$$E(\Psi^{*}_{cross}) - E(\Psi_{cross}) = -2K = G/2 \tag{24}$$

$$B = E(\Psi_{TS}) - E(\Psi_{RC,cross}) = K = -G/4 \tag{25}$$

We now deduce an *approximate* condition for orthogonality of $\Psi_{\mathbf{II}}$ and $\Psi_{\mathbf{III}}$ at the avoided crossing, for which $\kappa' = k'$, $\kappa'' = k''$, $\lambda = l$, and $\nu = \mu$ in eqs 2−6. The following approximations will initially be introduced: (a) All two-center AO overlap integrals ($S_{ab} = S_{bc}$ and S_{ac}) will be omitted from the canonical structure overlap integrals, $S_{ij} = \langle \Phi_i | \Phi_j \rangle$. As a consequence, it can be deduced that $S_{ij} = 0$ except for $S_{\mathbf{11}} = S_{\mathbf{44}} \approx 2$; $S_{\mathbf{14}} \approx -1$, and $S_{\mathbf{22}} = S_{\mathbf{55}} \approx 1$. (b) The product $k'k''$ is set equal to zero. The resulting expression for $\langle \Psi_{\mathbf{II}} | \Psi_{\mathbf{III}} \rangle = 0$ is then given by eq 26.

$$\begin{aligned}\langle \Psi_{\mathbf{II}} | \Psi_{\mathbf{III}} \rangle &= 2\mu(1-\mu)(S_{\mathbf{11}} + S_{\mathbf{44}}) + \\ &\quad 2k''l(1-3\mu)(S_{\mathbf{22}} + S_{\mathbf{55}}) + \{(1-\mu)^2 + \mu^2\}S_{\mathbf{14}} \\ &\equiv 8\mu(1-\mu) + 4k''l(1-3\mu) - \{(1-\mu)^2 + \mu^2\} \\ &= 0\end{aligned} \tag{26}$$

When the values of k'', l, and μ are assumed to be small, eq 27

$$\mu \approx 0.1(1 - 2.8k''l) \tag{27}$$

is obtained as the approximate requirement for $\Psi_{\mathbf{II}}$ and $\Psi_{\mathbf{III}}$ to be orthogonal. For illustrative purposes here, we shall approximate[13] further the value of μ to 0.1. When this value of μ is introduced into eq 13, values of $k' = 0.1_6$, $k'' = 0.3_3$, and $l = 0.71_2$ are obtained. (The approximations of neglecting $k'k''$ and μ^2 can therefore be seen to be reasonable.) Because $\Psi_{\mathbf{II}}$ and $\Psi_{\mathbf{III}}$ were not required to be orthogonal in ref 5,these values for k' and k'' differ from those reported in ref 5, namely, $k' = k'' = 0.143$. With $\mu = 0.1$ for $S_{\mathbf{II,III}} = 0$, and $\rho = +1$ in eq 11, we obtain $k' = 0.2_2$, $k'' = 0.2_3$, and $l = 0.55_5$ for Ψ^{*}_{cross}.

Triple-ζ 1s AO Basis Set

For $l \neq 0$ in eqs 3 and 4, the charge-transfer structures **5** and **7** contribute to the reactantlike complex with wave function $\Psi_{\mathbf{II}}$. Similarly for $\lambda \neq 0$ in eqs 5 and 6, the charge-transfer structures **2** and **8** contribute to the productlike complex with wave function $\Psi_{\mathbf{III}}$. The single-ζ 1s AO exponent for the (free) H^- ions of these structures is 0.6875, which differs substantially from the values of 1.0 and 1.193 for the free H-atom and (Weinbaum)[14] H_2 1s exponents, respectively. To take account of each of these exponents in the construction of wave functions for VB structures **II** and **III**, we have performed further calculations, which use the canonical Lewis structures that contribute to the following wave functions:

$$\begin{aligned}\Psi_{RC} &= C_{\mathbf{II},1}\Psi_{\mathbf{II},1}(1.0,1.193,1.193) + \\ &\quad C_{\mathbf{II},2}\Psi_{\mathbf{II},2}(1.0,0.6875,1.0) + C_{\mathbf{II},3}\Psi_{\mathbf{II},3}(1.0,1.0,0.6875)\end{aligned} \tag{28}$$

$$\begin{aligned}\Psi_{PC} &= C_{\mathbf{III},1}\Psi_{\mathbf{III},1}(1.193,1.193,1.0) + \\ &\quad C_{\mathbf{III},2}\Psi_{\mathbf{III},2}(1.0,6875,1.0) + C_{\mathbf{III},3}\Psi_{\mathbf{III},3}(0.6875,1.0,1.0)\end{aligned} \tag{29}$$

The numbers in parentheses refer to the exponents that have been used for the a, b, and c AOs. Each of the $\Psi_{\mathbf{II},i}$ and $\Psi_{\mathbf{III},i}$ is constructed according to eq 2. There are 32 H_3-type canonical Lewis structures of the types **1**−**8** of Figure 1 of ref 5, or Table 1 here, which contribute to the Ψ_{RC} and Ψ_{PC} of eqs 28 and 29. By use of these structures and Roso's ab initio VB program,[15] variational-best calculations were performed for the transition state and the H + H_2 dissociation products. The energies and bond lengths are $E = -1.618\,40$ au and $R_{ab} = R_{bc} = 1.839$ au for the transition state, and $E = -1.648\,28$ au and $R_{bc} = 1.431$ au for H + H_2. The resulting barrier height is 17.4 kcal/mol, cf. 23.6 kcal/mol,[5] 15.1 kcal/mol (double-ζ + p basis),[16a] and 9.6 kcal/mol (exact).[16b,c]

Inspection of Table 1 reveals that $\Psi_{\mathbf{II},1} - \Psi_{\mathbf{III},1}$ is the primary contributor to $\Psi_{RC} - \Psi_{PC}$. Twelve canonical Lewis structures (Table 1) contribute to it. Resonance between these structures generates a minimum energy of $-1.611\,85$ au with $R_{ab} = R_{bc} = 1.842$ au. When $R_{ab} = R_{bc} = 1.839$ au, as occurs for the 32 structure calculation, the energy is $-1.611\,84$ au, cf. $-1.618\,40$ au for the 32 structure resonance. However each of $\Psi_{\mathbf{II},2} - \Psi_{\mathbf{III},2}$ and $\Psi_{\mathbf{II},3} - \Psi_{\mathbf{III},3}$ is dissociative. For $R_{ab} = R_{bc} = 1.839$ au, their energies are $-1.543\,58$ and $-1.490\,77$ au, respectively.

When $R_{ab} = R_{bc} = 1.839$ au, the reactant-complex wave function, $\Psi_{\mathbf{II},1}$ has a minimum energy of $-1.589\,83$ au with $\Psi_{\mathbf{II},1} = 0.31654\Phi_{\mathbf{1}} + 0.15928\Phi_{\mathbf{2}} + 0.08785\Phi_{\mathbf{3}} - 0.29221\Phi_{\mathbf{4}} - 0.03676\Phi_{\mathbf{5}} + 0.07404\Phi_{\mathbf{7}}$. When l is set equal to $c_7/c_3 = 0.843$, as in eq 7 for the increased-valence configuration $(a + lb)^1(b + k'c)^1(c + k''b)^1$, this configuration has a minimum energy of $-1.543\,82$ au for $k' = 0.15$, $k'' = 0.30$, and $\mu = -0.0053$.

Additional variational parameters can be introduced by use of a linear combination of increased-valence configurations, such as

$$\begin{aligned}\Psi_{\mathbf{II},1} = &\{(a + lb)^1(b + k'c)^1(c + k''b)^1\}' + \\ &C_1\{(a + lb)^1(b + k'c)^1(c + k''b)^1\}'' + \\ &C_2\{(a + k'b)^1(b + lc)^1(c + k''b)^1\}' + \\ &C_3\{(a + k''b)^1(b + k'c)^1(c + lb)^1\}' + \\ &C_4\{(a + lb)^1(b + k'c)^1(c + k'b)^1\}' + \\ &C_5\{(a + lb)^1(b + k''c)^1(c + k''b)^1\}'\end{aligned} \tag{30}$$

for which the $\{\}'$ and $\{\}''$ groupings represent the spin-pairings of eqs 3 and 4.

With $l = 0.843$, $k' = 0.15$, and $k'' = 0.30$, it is calculated that the reactant increased-valence energy is lowered to $-1.589\,83$ au when the five $\Phi'_{\mathbf{II},1}$ configurations and *any* one of the five $\Phi''_{\mathbf{II},1}$ configurations are used to construct the $\Psi_{\mathbf{II},1}$ of eq 30. With *any* set of nonequivalent l, k', and k'' values, for example, $l = 0.4$, $k' = 0.2$, and $k'' = 0.3$, the same energy, $-1.589\,83$ au, is obtained. The variational mixing is transferred from the polarity parameters l, k', and k'' to the coefficients of the five $\Phi'_{\mathbf{II},1}$ and the $\Phi''_{\mathbf{II},1}$ increased-valence configurations (cf. complete MO−CI treatments with orthogonal MOs). Therefore, resonance between the associated increased-valence structures, each of which involves three bonding localized MOs (LMOs) is equivalent to the lowest-energy resonance between the Lewis structures that contribute to the increased-valence structures. If the $\Phi''_{\mathbf{II},1}$ configuration is omitted, the resulting $\Psi_{\mathbf{II},1}$ with the five $\Phi'_{\mathbf{II},1}$ configurations gives an energy of −1.562 21 au, which is equivalent to the best linear combination of the $\Phi_{\mathbf{1}}$, $\Phi_{\mathbf{2}}$, $\Phi_{\mathbf{3}}$, $\Phi_{\mathbf{5}}$, and $\Phi_{\mathbf{7}}$ Lewis AO configurations that contribute to the $\Phi'_{\mathbf{II},1}$ of eq 3.

The same type of result is obtained for $\Psi_{\mathbf{II},1} - \Psi_{\mathbf{III},1}$, with $\Psi_{\mathbf{III},1}$ given by eq 31 and $\Psi_{\mathbf{II},1} - \Psi_{\mathbf{III},1}$ calculated as either eq 32 or 33 in which the numerical coefficients are now those for normalized AO or LMO configuration wave functions.

$$\begin{aligned}\Psi_{\mathbf{III},1} = {} & \{(\mathrm{c} + l\mathrm{b})^1(\mathrm{b} + k'\mathrm{a})^1(\mathrm{a} + k''\mathrm{b})^1\}' + \\ & C_1\{(\mathrm{c} + l\mathrm{b})^1(\mathrm{b} + k'\mathrm{a})^1(\mathrm{a} + k''\mathrm{b})^1\}'' + \\ & C_2\{(\mathrm{c} + k'\mathrm{b})^1(\mathrm{b} + l\mathrm{a})^1(\mathrm{a} + k''\mathrm{b})^1\}' + \\ & C_3\{(\mathrm{c} + k''\mathrm{b})^1(\mathrm{b} + k'\mathrm{a})^1(\mathrm{a} + l\mathrm{b})^1\}' + \\ & C_4\{(\mathrm{c} + l\mathrm{b})^1(\mathrm{b} + k'\mathrm{a})^1(\mathrm{a} + k'\mathrm{b})^1\} + \\ & C_5\{(\mathrm{c} + l\mathrm{b})^1(\mathrm{b} + k''\mathrm{a})^1(\mathrm{a} + k''\mathrm{b})^1\}\end{aligned} \tag{31}$$

$$\begin{aligned}\Psi_{\mathbf{II},1} - \Psi_{\mathbf{III},1} = {} & 0.22072\{\Phi_{\mathbf{1},1}(\mathrm{r}) - \Phi_{\mathbf{4},1}(\mathrm{p})\} + 0.39834\{\Phi_{\mathbf{2},1}(\mathrm{r}) - \Phi_{\mathbf{5},1}(\mathrm{p})\} + 0.08219\{\Phi_{\mathbf{3},1}(\mathrm{r}) - \\ & \Phi_{\mathbf{6},1}(\mathrm{p})\} - 0.19428\{\Phi_{\mathbf{4},1}(\mathrm{r}) - \Phi_{\mathbf{1},1}(\mathrm{p})\} + \\ & 0.31570\{\Phi_{\mathbf{5},1}(\mathrm{r}) - \Phi_{\mathbf{2},1}(\mathrm{p})\} + 0.05987\{\Phi_{\mathbf{7},1}(\mathrm{r}) - \Phi_{\mathbf{8},1}(\mathrm{p})\}\end{aligned} \tag{32}$$

$$\begin{aligned}\Psi_{\mathbf{II},1} - \Psi_{\mathbf{III},1} = {} & \{(\mathrm{a} + l\mathrm{b})^1(\mathrm{b} + k'\mathrm{c})^1(\mathrm{c} + k''\mathrm{b})^1 - \\ & (\mathrm{c} + l\mathrm{b})^1(\mathrm{b} + k'\mathrm{a})^1(\mathrm{a} + k''\mathrm{b})^1\}' - 0.03100\{(\mathrm{a} + l\mathrm{b})^1 \times \\ & (\mathrm{b} + k'\mathrm{c})^1(\mathrm{c} + k''\mathrm{b})^1 - (\mathrm{c} + l\mathrm{b})^1(\mathrm{b} + k'\mathrm{a})^1(\mathrm{a} + k''\mathrm{b})^1\}'' + \\ & 0.03961\{(\mathrm{c} + k'\mathrm{b})^1(\mathrm{b} + l\mathrm{a})^1(\mathrm{a} + k''\mathrm{b})^1 - (\mathrm{a} + k'\mathrm{b})^1 \times \\ & (\mathrm{b} + l\mathrm{c})^1(\mathrm{c} + k''\mathrm{b})^1\}' - 0.23949\{(\mathrm{a} + k''\mathrm{b})^1(\mathrm{b} + k'\mathrm{c})^1 \times \\ & (\mathrm{c} + l\mathrm{b})^1 - (\mathrm{c} + k''\mathrm{b})^1(\mathrm{b} + k'\mathrm{a})^1(\mathrm{a} + l\mathrm{b})^1\}' - 0.72122\{(\mathrm{a} + \\ & l\mathrm{b})^1(\mathrm{b} + k'\mathrm{c})^1(\mathrm{c} + k'\mathrm{b})^1 - (\mathrm{c} + l\mathrm{b})^1(\mathrm{b} + k'\mathrm{a})^1(\mathrm{a} + k'\mathrm{b})^1\}' - \\ & 0.12443\{(\mathrm{a} + l\mathrm{b})^1(\mathrm{b} + k''\mathrm{c})^1(\mathrm{c} + k''\mathrm{b})^1 - (\mathrm{c} + l\mathrm{b})^1(\mathrm{b} + \\ & k''\mathrm{a})^1(\mathrm{a} + k''\mathrm{b})^1\}'\end{aligned} \tag{33}$$

For both cases, the calculated energy is −1.611 84 au.

Eighteen increased-valence configurations with 27 distinct LMOs contribute to the Ψ_{RC} of eq 28. With $l = 0.843$, $k' = 0.15$, and $k'' = 0.30$ as previously, the resulting energy, −1.608 17 au, is the same as that calculated for the best linear combination of the 18 component AO configurations (cf. Table 1).

Inclusion of 2p AOs as Polarization Functions

There are two (nonequivalent) ways to include polarization functions such as 2p AOs in the above treatment:

(a) To formulate the a, b, and c AOs as hybrid AOs, such as $\mathrm{a} = 1\mathrm{s}_\mathrm{a} + k_\mathrm{a}2\mathrm{p}\sigma_\mathrm{a}$, $\mathrm{b} = 1\mathrm{s}_\mathrm{b} + k_\mathrm{b}2\mathrm{p}\sigma_\mathrm{b}$, and $\mathrm{c} = 1\mathrm{s}_\mathrm{c} + k_\mathrm{c}2\mathrm{p}\sigma_\mathrm{c}$, with the hybridization parameters k_a, k_b, and k_c determined variationally at each stage along the reaction coordinate.[17] The theory is then identical to that which has already been described.

To provide a simple example, we have assumed that, for the reactant complex wave function $\Psi_{\mathbf{II},1}$, $k_\mathrm{a} = 0$, $\zeta(1\mathrm{s}_\mathrm{a}) = 1.0$ and that the 1s and 2p AO exponents for the b and c AOs are each equal to 1.193 (cf. the Rosen calculation for H_2).[18] Variationally best estimates of −0.08 and −0.01 are obtained for k_b and k_c at $R_\mathrm{ab} = R_\mathrm{bc} = 1.839$ au, to give the linear combination

$$\Psi_{\mathbf{II},1} = 0.30335\Phi_{\mathbf{1}} + 0.15291\Phi_{\mathbf{2}} + 0.11969\Phi_{\mathbf{3}} - 0.03849\Phi_{\mathbf{4}} - 0.07615\Phi_{\mathbf{5}} + 0.29911\Phi_{\mathbf{7}} \tag{34}$$

for $\Psi_{\mathbf{II},1}$ with an energy of −1.581 89 au. With $\mathrm{a} = 1\mathrm{s}_\mathrm{a}$, $\mathrm{b} = 1\mathrm{s}_\mathrm{b} - 0.08(2\mathrm{p}\sigma_\mathrm{b})$, $\mathrm{c} = 1\mathrm{s}_\mathrm{c} - 0.01(2\mathrm{p}\sigma_\mathrm{c})$, $l = 0.843$, $k' = 0.15$, and $k'' = 0.30$ as previously (for which the 2pσ AOs were omitted), the $\Psi_{\mathbf{II},1}$ of eq 35 is also calculated to give an energy of −1.581 89 au:

$$\begin{aligned}\Psi_{\mathbf{II},1} = {} & \{(\mathrm{a} + l\mathrm{b})^1(\mathrm{b} + k'\mathrm{c})^1(\mathrm{c} + k''\mathrm{b})^1\}' - \\ & 0.71459\{(\mathrm{a} + l\mathrm{b})^1(\mathrm{b} + k'\mathrm{c})^1(\mathrm{c} + k''\mathrm{b})^1\}'' + \\ & 0.02437\{(\mathrm{a} + k'\mathrm{b})^1(\mathrm{b} + l\mathrm{c})^1(\mathrm{c} + k''\mathrm{b})^1\}' - \\ & 0.19747\{(\mathrm{a} + k''\mathrm{b})^1(\mathrm{b} + k'\mathrm{c})^1(\mathrm{c} + l\mathrm{b})^1\}' - \\ & 0.02188\{(\mathrm{a} + l\mathrm{b})^1(\mathrm{b} + k'\mathrm{c})^1(\mathrm{c} + k'\mathrm{b})^1\}' - \\ & 0.11879\{(\mathrm{a} + l\mathrm{b})^1(\mathrm{b} + k''\mathrm{c})^1(\mathrm{c} + k''\mathrm{b})^1\}'\end{aligned} \tag{35}$$

(b) To formulate wave functions according to

$$\begin{aligned}\Psi_{\mathrm{RC}} = {} & C_{\mathbf{II},1}\Psi_{\mathbf{II},1}(1\mathrm{s}_\mathrm{a},1\mathrm{s}_\mathrm{b},1\mathrm{s}_\mathrm{c})_{\mathrm{RC}} + \\ & C_{\mathbf{II},2}\Psi_{\mathbf{II},2}(1\mathrm{s}_\mathrm{a},2\mathrm{p}\sigma_\mathrm{b},1\mathrm{s}_\mathrm{c})_{\mathrm{RC}} + C_{\mathbf{II},3}\Psi_{\mathbf{II},3}(1\mathrm{s}_\mathrm{a},1\mathrm{s}_\mathrm{b},2\mathrm{p}\sigma_\mathrm{c})_{\mathrm{RC}} + \\ & C_{\mathbf{II},4}\Psi_{\mathbf{II},4}(1\mathrm{s}_\mathrm{a},2\mathrm{p}\sigma_\mathrm{b},2\mathrm{p}\sigma_\mathrm{c})_{\mathrm{RC}}\end{aligned} \tag{36}$$

$$\begin{aligned}\Psi_{\mathrm{PC}} = {} & C_{\mathbf{III},1}\Psi_{\mathbf{III},1}(1\mathrm{s}_\mathrm{a},1\mathrm{s}_\mathrm{b},1\mathrm{s}_\mathrm{c})_{\mathrm{PC}} + \\ & C_{\mathbf{III},2}\Psi_{\mathbf{III},2}(1\mathrm{s}_\mathrm{a},2\mathrm{p}\sigma_\mathrm{b},1\mathrm{s}_\mathrm{c})_{\mathrm{PC}} + C_{\mathbf{III},3}\Psi_{\mathbf{III},3}(2\mathrm{p}\sigma_\mathrm{a},1\mathrm{s}_\mathrm{b},1\mathrm{s}_\mathrm{c})_{\mathrm{PC}} + \\ & C_{\mathbf{III},4}\Psi_{\mathbf{III},4}(2\mathrm{p}\sigma_\mathrm{a},2\mathrm{p}\sigma_\mathrm{b},1\mathrm{s}_\mathrm{c})_{\mathrm{PC}}\end{aligned} \tag{37}$$

which are analogous to eqs 28 and 29. The $(1\mathrm{s}_\mathrm{a}, 1\mathrm{s}_\mathrm{b}, 1\mathrm{s}_\mathrm{c})_{\mathrm{RC}}$ and $(1\mathrm{s}_\mathrm{a}, 1\mathrm{s}_\mathrm{b}, 1\mathrm{s}_\mathrm{c})_{\mathrm{PC}}$ sets of exponents are (1.0, 1.193, 1.193) and (1.193, 1.193, 1.0), respectively. Each 2pσ AO exponent is equal to 1.193. However, three-electron configurations, which include $(1\mathrm{s}_\mathrm{c}, 2\mathrm{p}\sigma_\mathrm{c})$ for Ψ_{RC}, $(1\mathrm{s}_\mathrm{a}, 2\mathrm{p}\sigma_\mathrm{a})$ for Ψ_{PC}, and $(1\mathrm{s}_\mathrm{b}, 2\mathrm{p}\sigma_\mathrm{b})$, $(1\mathrm{s}_\mathrm{b}, 1\mathrm{s}_\mathrm{b}, 2\mathrm{p}\sigma_\mathrm{b})$, and $(1\mathrm{s}_\mathrm{b}, 2\mathrm{p}\sigma_\mathrm{b}, 2\mathrm{p}\sigma_\mathrm{b})$ for each of Ψ_{RC} and Ψ_{PC}, need to be added to eqs 36 and 37. For the Ψ_{RC} and Ψ_{PC} increased-valence configurations, the AOs are $\mathrm{a} = 1\mathrm{s}_\mathrm{a}$, $\mathrm{b} = 1\mathrm{s}_\mathrm{b}$ or $2\mathrm{p}\sigma_\mathrm{b}$, $\mathrm{c} = 1\mathrm{s}_\mathrm{c}$ or $2\mathrm{p}\sigma_\mathrm{c}$, and $\mathrm{a} = 1\mathrm{s}_\mathrm{a}$ or $2\mathrm{p}\sigma_\mathrm{a}$, $\mathrm{b} = 1\mathrm{s}_\mathrm{b}$ or $2\mathrm{p}\sigma_\mathrm{b}$, $\mathrm{c} = 1\mathrm{s}_\mathrm{c}$, respectively.

Conclusions

For any AO basis set, the VB formulation presented in ref 5 for radical transfer reactions and in earlier publications[6,7] (as in **I** → [**II** ↔ **III**] → **IV** here) can generate diabatic potential energy curves via those for the reactantlike and productlike complexes (cf. Figure 2 of ref 5). The formulation provides a compact VB representation that indicates succinctly how electronic reorganization could occur as the reaction proceeds. It also allows for the possibility of using orthogonal forms of the wave functions for the reactantlike and productlike complexes to provide a simple definition of the resonance energy at the crossing point. Other developments are possible,[19] but that presented here should be sufficient to show how extended AO basis sets can be incorporated into the **I** → [**II** ↔ **III**] → **IV** VB formulation, and to make some comparison between the theory of refs 1 and 5.

It is noted that the reactantlike complex **II** involves some productlike character, via the inclusion of the product Lewis structures **4** and **5** in the equivalent Lewis structure resonance scheme. Similarly, the productlike complex **III** involves some reactantlike character via its inclusion of the reactant Lewis structures **1** and **2**.

VB modeling of barriers in the nonidentity hydrogen abstraction reactions has been described recently in ref 20. The compact

VB representation[5−7] of **I** → [**II** ↔ **III**] → **IV** is also relevant for these types of reactions. However, at the transition state, for which the energies for nonequivalent **II** and **III** are equal, the variational parameters for the reactant complex **II** must differ from those for the product complex **III**.

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Appendix

Although eq 20 for $\Psi_{\mathbf{II}}(R_{BC}{=}\infty)$ represents an overall (S, M_S) spin state with $S = M_S = 0.5$, it involves mixed spin states for the $H_A{-}H_B$ product of $H_A{-}H_B + H_C$. To obtain a spectroscopic state (with a definite total spin quantum number, S), the $S = M_S = 0.5$ wave functions for $\Phi_{\mathbf{1}}$, $\Phi_{\mathbf{4}}$, and $\Phi_{\mathbf{5}}$ (cf. ref 2) are expressed in terms of the spin states of their $H_A{-}H_B$ components. The $\Psi_{\mathbf{II}}(R_{BC}{=}\infty)$ is then given by eq A1.

$$\Psi_{\mathbf{II}}(R_{BC}{=}\infty) = (1-\mu)\{\Phi_{\mathbf{1}}(1,1) - 0.5\Phi_{\mathbf{4}}(1,0)\} + 0.5(5\mu-1)\Phi_{\mathbf{4}}(0,0) - l(1+3\mu)\Phi_{\mathbf{5}}(0,0) \quad \text{(A1)}$$

When $\mu = 0.2$, orthogonality of $\Psi_{\mathbf{II}}(R_{BC}{=}\infty)$ with $\Psi_{\mathbf{IV}}(R_{BC}{=}\infty)$ gives $l = 0.0$ via eq 22 of ref 2. Therefore eq A1 reduces to eq A2,

$$\Psi_{\mathbf{II}}(R_{BC}{=}\infty) = (1-\mu)\{\Phi_{\mathbf{1}}(1,1) - 0.5\Phi_{\mathbf{5}}(1,0)\} \quad \text{(A2)}$$

which corresponds to eq 20 for $H_A{-}H_B(S{=}1) + H_C$, or eq 26 of ref 2.

When $\mu = 1.0$, the $H_A{-}H_B(S{=}0)$ wave function of eq A3 is obtained from eq A2:

$$\Psi_{\mathbf{II}}(R_{BC}{=}\infty) = 2\{\Phi_{\mathbf{4}}(0,0) - 2l\Phi_{\mathbf{5}}(0,0)\} \quad \text{(A3)}$$

Although l in eq A3 can be chosen so that $\Psi_{\mathbf{II}}(R_{BC}{=}\infty)$ is orthogonal to $\Psi_{\mathbf{IV}}(R_{BC}{=}\infty)$, eq A3 excludes $\Phi_{\mathbf{6}}(0,0)$, which interacts with each of $\Phi_{\mathbf{4}}(0,0)$ and $\Phi_{\mathbf{5}}(0,0)$. Therefore $\Psi_{\mathbf{II}}(R_{BC}{=}\infty)$ represents a nonspectroscopic $S = 0$ valence state.

Note Added in Proof

For a symmetrical transition state with a = 1s, b = 2pσ, and c = 1s, the parameters κ', κ'', and λ are equal to the parameters $-k'$, $-k''$, and $-l$, respectively.

References and Notes

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(7) Harcourt, R. D. *Eur. J. Inorg. Chem.* **2000**, 1901.

(8) Harcourt, R. D. *J. Mol. Struct. THEOCHEM* **2002**, *617*, 179. (In eq A8, replace $2kl$ with $2k$.) Explicit reasons for designating the three-electron three-center bonding VB structures **II** and **III**, as "increased-valence" structures are deduced in this reference. However the definitions of AO valence that were used in this treatment, and in refs 2−4 therein, have now been revised (Harcourt, R. D. *J. Mol. Struct. THEOCHEM* **2003**, *634*, 265). In the latter reference, it is deduced that, whereas the maximum R-atom valence in structures **I** or **IV** is unity, the maximum R-atom valence in each of the VB structures **II** or **III** is 1.073 when their (fractional) electron-pair bond is formulated as a doubly occupied MO rather than as two singly occupied Coulson−Fischer MOs.

(9) Goddard, W. A.; Ladner, R. C. *J. Am. Chem. Soc.* **1971**, *93*, 6750. The GVB orbitals for the transition state of Figure 7 of this reference can be expressed as $\phi_1 = a + k_1b + c$, $\phi_2 = a + k_2b + c$, and $\phi_3 = a - c$. The GVB wave function $|\phi_1^{\alpha}\phi_2^{\beta}\phi_3^{\alpha}| + |\phi_2^{\alpha}\phi_1^{\beta}\phi_3^{\alpha}|$ is then equivalent to $(k_1 + k_2)(\Phi_{\mathbf{1}} - \Phi_{\mathbf{4}} + \Phi_{\mathbf{7}} - \Phi_{\mathbf{8}}) + 2k_1k_2(\Phi_{\mathbf{2}} - \Phi_{\mathbf{5}}) + 4(\Phi_{\mathbf{3}} - \Phi_{\mathbf{6}})$. With two variational parameters (k_1 and k_2), it does not correspond to the variational best wave function of eq 13 of the present study. Configuration interaction—for example, by interaction of $|\phi_1^{\alpha}\phi_1^{\beta}\phi_3^{\alpha}|$ and $|\phi_2^{\alpha}\phi_2^{\beta}\phi_3^{\alpha}|$ with the GVB wave function—is needed to obtain the equivalence.

(10) Coulson, C. A.; Fischer, I. *Philos. Mag.* **1949**, *40*, 386.

(11) VB structures **1**−**8** of Scheme 1 of ref 1 correspond to structures **1**, **4**, **3**, **2**, **6**, **5**, **7**, and **8** of Figure 1 of ref 5. When (r) and (p) are used as designations, they refer to reactants and products, respectively. One distinction between $\Phi_{\boldsymbol{i}}(r)$ and $\Phi_{\boldsymbol{i}}(p)$ would arise if the AO exponents for these wave functions were determined variationally for $\Psi_{RC} \equiv \Psi_{\mathbf{II}}$ and $\Psi_{PC} \equiv \Psi_{\mathbf{III}}$, respectively.

(12) The calculations for the transition state have been revised to give $R_{AC} = 3.73$ au, $E(\Psi_{cross}) = -1.609\,97$ au, $E(\Psi^*_{cross}) = -1.337\,13$ au, and $E(\Psi^*_{cross}) - E(\Psi_{cross}) = 0.2728$ au. $G/2 = [E\{\Psi_{\mathbf{II}}(R_{BC}{=}\infty)\} - E\{\Psi_{\mathbf{IV}}(R_{BC}{=}\infty)\}]/2 \approx 0.2818$.

(13) When $\rho \neq -1$, μ is not equal to ν, and $\mu + \nu = 0.2$ replaces $\mu = 0.1$ as the approximate requirement that $\langle\Psi_{\mathbf{II}}|\Psi_{\mathbf{III}}\rangle = 0$ at intermediate stages along the reaction coordinate. Because there are nine parameters, (l, k', k'', λ, κ', κ'', ρ, μ, and ν), and seven independent coefficients in eq 11, as well as $\mu + \nu = 0.2$, an additional equation is needed in order to determine numerical values for these parameters. Simple equations that could be used are $\mu = 0.2 + 0.1/\rho$ for $R_{AC}/2 \leq R_{BC} \leq \infty$, and $\nu = 0.2 + 0.1\rho$ for $R_{AC}/2 \leq R_{AB} \leq \infty$.

(14) Weinbaum, S. *J. Chem. Phys.* **1933**, *1*, 593, for the H−H ↔ H^-H^+ ↔ H^+H^-covalent−ionic resonance with the same AO exponents for the H and H^-.

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(17) The 2pπ_x and 2pπ_y AOs can similarly be included—for example, with $a = 1s_a + k_a 2p\sigma_a$, $b = 1s_b + k_b 2p\sigma_b$, $b' = 2p\pi_b$, and $c' = 2p\pi_c$, in which both 2pπ AOs are either 2pπ_x or 2pπ_y. The $(\phi_{ab})^1(\phi'_{bc})^1(\phi''_{cb})^1$ configuration is then given by $(a + Kb)^1(b' + K'c')^1(c' + K''b')^1$.

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(19) For example, the use of the open-shell atomic configurations $(a')^1(a'')^1$, $(b')^1(b'')^1$, and $(c')^1(c'')^1$ instead of $(a)^2$, $(b)^2$, and $(c)^2$ in the VB structures that have $(a)^1(b)^2$, $(a)^1(c)^2$, $(b)^1(c)^2$, $(a)^2(b)^1$, $(a)^2(c)^1$, and $(b)^2(c)^1$ configurations with a, b, and c AOs. (The latter AOs can also be hybrid AOs, with double-ζ or triple-ζ AOs, or s-p-d hybridized AOs as particular cases.)

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