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Some Comments on Valence Bond Representations for the Radical Exchange Reaction $X^{\bullet} + R{:}Y \rightarrow X{:}R + Y^{\bullet}$

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Qualitative valence bond formulations by Hiberty and co-workers (Hiberty, P. C.; Megret, C.; Song, L.; Wu, W.; Shaik, S. *J. Am. Chem. Soc*. **2006**, *128*, 2836) of mechanisms for the radical exchange reactions $H^{\bullet} + F{:}H \rightarrow H{:}F + H^{\bullet}$ and $F^{\bullet} + H{:}F \rightarrow F{:}H + F^{\bullet}$ are compared to a previously published formulation of the generalized radical exchange reaction $X^{\bullet} + R{:}Y \rightarrow X{:}R + Y^{\bullet}$. The former formulation uses covalent−ionic VB complexes, and the latter formulation, which is more general, involves the formation of reactant-like and product-like complexes at intermediate stages along the reaction coordinate.

Introduction

In refs 1 and 2, the radical transfer/exchange reaction $X^{\bullet} + R{:}Y \rightarrow X{:}R + Y^{\bullet}$ has been formulated according to Scheme A in which **I** and **IV** are the reactants and products, and **II** and **III** are reactant-like (RC) and product-like (PC) complexes, respectively. As the $X^{\bullet}$ radical approaches the substrate R:Y and the X and R atomic orbitals (AOs) x and r overlap,[3] the $X^{\bullet}$ odd electron delocalizes into an X−R bonding molecular orbital (MO), $\phi_{xr} = x + lr$, to form the reactant-like complex **II**. Electronic reorganization proceeds via a one-electron transfer from an R−Y bonding MO into an X−R bonding MO, as displayed in **II** to give the product-like complex **III**. The products of **IV** are generated via the transfer of the electron from the singly occupied R−Y bonding MO, $\phi_{yr} = y + \lambda r$, of **III** into the Y AO y. At intermediate stages along the reaction coordinate, the VB structures **II** and **III** participate in resonance.

In this paper, we provide further consideration to the structure of a symmetrical transition state (i.e., when X and Y are equivalent atoms and x and y are equivalent AOs) and compare it with those provided recently by Hiberty and co-workers (HMSWS[4]) for F + H−F → F−H + F and H + F−H → H−F + H. The results of STO-6G VB calculations are used to illustrate aspects of the theory.

Wave Functions for Reactant-Like and Product-Like Complexes and the Symmetrical Transition State

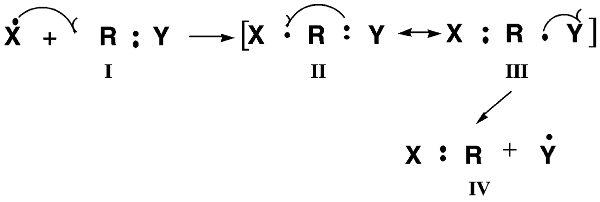
To provide the basis for further development of theory, in this section, we redescribe the theory presented in refs 1 and 2.

For a symmetrical transition state (with $\lambda = l$ in $\phi_{yr} = y + \lambda r$), the electrons occupy the bonding MOs of eqs 1 and 2

$$\phi_{xr} = x + lr \quad \phi'_{ry} = r + k'y \quad \phi''_{yr} = y + k''r \tag{1}$$

$$\phi_{yr} = y + lr \quad \phi'_{rx} = r + k'x \quad \phi''_{xr} = x + k''r \tag{2}$$

SCHEME A



(A)

The $S = M_S = 1/2$ spin wave functions for the reactant-like and product-like complexes **II** and **III** can be expressed according to eq 3

$$\Phi_{RC} = \Phi'_{\mathbf{II}} + \mu\Phi''_{\mathbf{II}} \quad \Phi_{PC} = \Phi'_{\mathbf{III}} + \mu\Phi''_{\mathbf{III}} \tag{3}$$

in which

$$\begin{aligned}\Phi'_{\mathbf{II}} &= |\phi_{xr}{}^{\alpha}\phi'_{ry}{}^{\alpha}\phi''_{yr}{}^{\beta}| + |\phi_{xr}{}^{\alpha}\phi''_{yr}{}^{\alpha}\phi'_{ry}{}^{\beta}| \\ &= (1 + k'k'')\Phi_{\mathbf{1}} + 2k''\Phi_{\mathbf{2}} + 2k'\Phi_{\mathbf{3}} - l(1 + k'k'')\Phi_{\mathbf{5}} + 2lk'\Phi_{\mathbf{7}}\end{aligned} \tag{4}$$

$$\begin{aligned}\Phi''_{\mathbf{II}} &= 2|\phi_{xr}{}^{\beta}\phi'_{ry}{}^{\alpha}\phi''_{yr}{}^{\alpha}| - |\phi_{xr}{}^{\alpha}\phi'_{ry}{}^{\beta}\phi''_{yr}{}^{\alpha}| - |\phi_{xr}{}^{\alpha}\phi'_{ry}{}^{\alpha}\phi''_{yr}{}^{\beta}| \\ &= (1 - k'k'')(-\Phi_{\mathbf{1}} + 2\Phi_{\mathbf{4}} - 3l\Phi_{\mathbf{5}})\end{aligned} \tag{5}$$

$$\begin{aligned}\Phi'_{\mathbf{III}} &= |\phi_{yr}{}^{\alpha}\phi'_{rx}{}^{\alpha}\phi''_{xr}{}^{\beta}| + |\phi_{yr}{}^{\alpha}\phi''_{xr}{}^{\alpha}\phi'_{rx}{}^{\beta}| \\ &= (1 + k'k'')\Phi_{\mathbf{4}} + 2k''\Phi_{\mathbf{5}} + 2k'\Phi_{\mathbf{6}} - l(1 + k'k'')\Phi_{\mathbf{2}} + 2lk'\Phi_{\mathbf{8}}\end{aligned} \tag{6}$$

$$\begin{aligned}\Phi''_{\mathbf{III}} &= 2|\phi_{yr}{}^{\beta}\phi'_{rx}{}^{\alpha}\phi''_{xr}{}^{\alpha}| - |\phi_{yr}{}^{\alpha}\phi'_{rx}{}^{\beta}\phi''_{xr}{}^{\alpha}| - |\phi_{yr}{}^{\alpha}\phi'_{rx}{}^{\alpha}\phi''_{xr}{}^{\beta}| \\ &= (1 - k'k'')(-\Phi_{\mathbf{4}} + 2\Phi_{\mathbf{1}} - 3l\Phi_{\mathbf{2}})\end{aligned} \tag{7}$$

The $\Phi_{\mathbf{1}}-\Phi_{\mathbf{8}}$ wave functions and their associated canonical VB structures **1**−**8** are provided in Table 1.

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The resulting expressions for Φ_{RC}, Φ_{PC}, and $\Psi_{TS} = \Phi_{RC} - \Phi_{PC}$ are then given by eqs 8−13

$$\Phi_{RC} = \{1 + k'k'' - \mu(1 - k'k'')\}\Phi_1 + 2k''\Phi_2 + 2k'\Phi_3 + 2\mu(1 - k'k'')\Phi_4 - l\{(1 + k'k'') + 3\mu(1 - k'k'')\}\Phi_5 + 2k'l\Phi_7 \quad (8)$$

$$\approx (1 - \mu)\Phi_1 + 2k''\Phi_2 + 2k'\Phi_3 + 2\mu\Phi_4 - l(1 + 3\mu)\Phi_5 + 2k'l\Phi_7 \quad (9)$$

$$\Phi_{PC} = \{1 + k'k'' - \mu(1 - k'k'')\}\Phi_4 + 2k''\Phi_5 + 2k'\Phi_6 + 2\mu(1 - k'k'')\Phi_1 - l\{(1 + k'k'') + 3\mu(1 - k'k'')\}\Phi_2 + 2k'l\Phi_8 \quad (10)$$

$$\approx (1 - \mu)\Phi_4 + 2k''\Phi_5 + 2k'\Phi_6 + 2\mu\Phi_1 - l(1 + 3\mu)\Phi_2 + 2k'l\Phi_8 \quad (11)$$

$$\Psi_{TS} = \{1 + k'k'' - 3\mu(1 - k'k'')\}(\Phi_1 - \Phi_4) + \{2k'' + l(1 + k'k'') + 3\mu l(1 - k'k'')\}(\Phi_2 - \Phi_5) + 2k'(\Phi_3 - \Phi_6) + 2k'l(\Phi_7 - \Phi_8) \quad (12)$$

$$\approx (1 - 3\mu)(\Phi_1 - \Phi_4) + \{2k'' + l(1 + 3\mu)\}(\Phi_2 - \Phi_5) + 2k'(\Phi_3 - \Phi_6) + 2k'l(\Phi_7 - \Phi_8) \quad (13)$$

Equations 9, 11, and 13 arise when $k'k''$ is small and ignored. The Ψ_{TS} of eqs 12 and 13 can be expressed according to eq 14, with Φ'_{TS} and Φ''_{TS} given by eqs 15−18

$$\Psi_{TS} = \Phi'_{TS} + \mu\Phi''_{TS} \quad (14)$$

$$\Phi'_{TS} = (1 + k'k'')(\Phi_1 - \Phi_4) + \{2k'' + l(1 + k'k'')\}(\Phi_2 - \Phi_5) + 2k'(\Phi_3 - \Phi_6) + 2k'l(\Phi_7 - \Phi_8) \quad (15)$$

$$\approx \Phi_1 - \Phi_4 + (2k'' + l)(\Phi_2 - \Phi_5) + 2k'(\Phi_3 - \Phi_6) + 2k'l(\Phi_7 - \Phi_8) \quad (16)$$

$$\Phi''_{TS} = -3(1 - k'k'')(\Phi_1 - \Phi_4) - 3l(1 - k'k'')(\Phi_2 - \Phi_5) \quad (17)$$

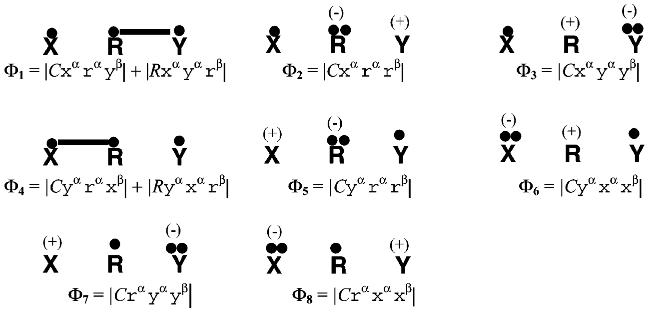
$$\approx -3\{\Phi_1 - \Phi_4 + l(\Phi_2 - \Phi_5)\} \quad (18)$$

In eqs 12 or 13, for $\Psi_{TS} = C_1(\Phi_1 - \Phi_4) + C_2(\Phi_2 - \Phi_5) + C_3(\Phi_3 - \Phi_6) + C_7(\Phi_7 - \Phi_8)$, only three independent variational parameters are needed to determine the lowest-energy linear combination. However, eqs 12 and 13 contain four variational parameters, namely, l, k', k'', and μ. The requirement that Φ_{RC} and Φ_{PC} be orthogonal provides an additional equation so that each of l, k', k'', and μ can be assigned a numerical value. Here, we shall use the approximate expressions of eqs 9 and 11 for Φ_{RC} and Φ_{PC} and take the primary terms of the resulting expression for $<\Phi_{RC}|\Phi_{PC}> = 0$ in order to determine an approximate value for μ for the symmetric transition state. With $S_{11} = S_{44}$ and $S_{ij} \equiv <\Phi_i|\Phi_j>$, this approach gives eq 19

$$<\Phi_{RC}|\Phi_{PC}> = 0 \approx S_{14} + (4S_{11} - 2S_{14})\mu \quad (19)$$

for small μ, which will be used for the STO-6G calculations reported below.

TABLE 1: Eight Canonical XRY Lewis Structures with $S = M_S = 1/2$ Spin Wave Functions for Three Active-Space AOs x, r, and y; See Refs 1−3[a]



$\Phi_1 = |Cx^\alpha r^\alpha y^\beta| + |Rx^\alpha y^\alpha r^\beta|$

$\Phi_2 = |Cx^\alpha r^\alpha r^\beta|$

$\Phi_3 = |Cx^\alpha y^\alpha y^\beta|$

$\Phi_4 = |Cy^\alpha r^\alpha x^\beta| + |Ry^\alpha x^\alpha r^\beta|$

$\Phi_5 = |Cy^\alpha r^\alpha r^\beta|$

$\Phi_6 = |Cy^\alpha x^\alpha x^\beta|$

$\Phi_7 = |Cr^\alpha y^\alpha y^\beta|$

$\Phi_8 = |Cr^\alpha x^\alpha x^\beta|$

[a] C = doubly occupied AOs for the core electrons.

Wave Functions for the Reactant-Like Complex at the Conclusion and the Product-Like Complex at the Commencement of the Reaction

At the conclusion (with distance $r(XR\cdots Y) = \infty$) and commencement (with distance $r(X\cdots RY) = \infty$) of the reactions, it has been deduced[2,5] that $\mu = 0.2$ and $l = k' = k'' = 0$, to give eqs 20 and 21

$$\Phi_{RC}\{r(XR\cdots Y) = \infty\} = 0.8\Phi_1 + 0.4\Phi_4 = 0.8|Rx^\alpha r^\alpha y^\beta| - 0.4|Rx^\alpha r^\beta y^\alpha| - 0.4|Rx^\beta r^\alpha y^\alpha| = 0.8\{XR(S = M_S = 1) + Y(S = 1/2)\} + 0.4\{XR(S = 1, M_S = 0) + Y(S = 1/2)\} \quad (20)$$

$$\Phi_{PC}\{r(X\cdots RY) = \infty\} = 0.4\Phi_1 + 0.8\Phi_4 = 0.8|Rx^\beta r^\alpha y^\alpha| - 0.4|Rx^\alpha r^\beta y^\alpha| - 0.4|Rx^\alpha r^\alpha y^\beta| = 0.8\{X(S = 1/2) + RY(S = M_S = 1)\} + 0.4\{X(S = 1/2) + RY(S = 1, M_S = 0)\} \quad (21)$$

when these values for μ, l, k', and k'' are substituted into eqs 8 and 10.

The resulting wave functions for the H + FH and F + HF reactions are then those of eqs 22 and 23 at the conclusion and the commencement of the reaction, respectively

$$\Phi_{RC}\{r(XR\cdots Y) = \infty\} = HF(S = 1) + H(S = 1/2) \qquad FH(S = 1) + F(S = 1/2) \quad (22)$$

$$\Phi_{PC}\{r(X\cdots RY) = \infty\} = H(S = 1/2) + FH(S = 1) \qquad F(S = 1/2) + HF(S = 1) \quad (23)$$

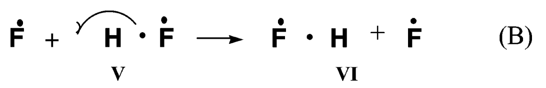
Each of these equations involves the same ($S = 1$ spin) spectroscopic excited state for HF. Therefore, the energy gap (E_G) of eqs 24 and 25

$$E_G = E\{X(S = 1/2) + RY(S = 1)\} - E\{X(S = 1/2) + RY(S = 0)\} \quad (24)$$

$$= E\{XR(S = 1) + Y(S = 1/2)\} - E\{XR(S = 0) + Y(S = 1/2)\} \quad (25)$$

at the commencement and conclusion of the reaction is the same for the H + FH and F + HF reactions.

SCHEME B



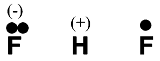
Simplifications for Scheme A

(a) HMSWS[4] have used structures **1**, **3**, **4**, and **6** of Table 1 (or explicitly structures **9**−**12** for X = F) and structures **1**, **2**, **4**, and **5** of Table 1 (or explicitly structures **13**−**16** for X = F) to construct state correlation diagrams (SCD) for X + H−X → X−H + X and H + X−H → H−X + H. Earlier, Balint-Kurti et al.[6] also used VB structures **1**, **3**, **4**, and **6** to provide a VB study for F + H−F → F−H + F. HMSWS[4] have derived expressions for the energy gap and the activation energies for these reactions.

9

10

11



12

13

14

15

16

In ref 2, it was shown that the VB structures **V** and **VI** of Scheme B are equivalent to the **9** ↔ **10** and **11** ↔ **12** resonances, respectively, and that the electronic reorganization as one proceeds from reactants to products can be represented according to Scheme B, with the one-electron transfer from the R−Y bonding MO $\phi_{yr} = y + \lambda r$ into the X−R bonding MO $\phi_{xr} = x + ly$.

This VB formulation provides an approximation to Scheme A and involves setting $l = k'' = 0$ to give eq 26 for the symmetrical transition state

$$\Psi_{TS} = (1 - 3\mu)(\Phi_1 - \Phi_4) + 2k'(\Phi_3 - \Phi_6) \tag{26}$$

For the transition state, **V** ≡ **9** ↔ **10** and **VI** ≡ **11** ↔ **12** are equivalent VB structures. There is one independent variational parameter when one AO per atomic center is used to construct the wave functions for these VB structures at the transition state, and this parameter is equal to $2k'/(1-3\mu)$.

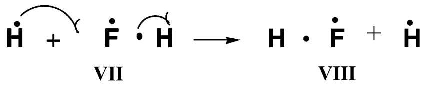
(b) For the H + F−H → H−F + H reaction, use of Lewis structures **13**−**16** requires that $k' = 0$, to give eq 27 for the symmetrical transition state

$$\Psi_{TS} = (1 - 3\mu)(\Phi_1 - \Phi_4) + \{2k'' + l(1 + 3\mu)\}(\Phi_2 - \Phi_5) \tag{27}$$

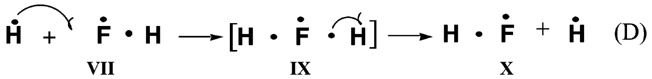
For this equation, only one of the parameters, k'' and l, is needed to obtain the "best" linear combination of $(\Phi_1 - \Phi_4)$ with $(\Phi_2 - \Phi_5)$. Because of symmetry, $l = k''$, to give eq 28

$$\Psi_{TS} = (1 - 3\mu)(\Phi_1 - \Phi_4) + 3k''(1 + \mu)(\Phi_2 - \Phi_5) \tag{28}$$

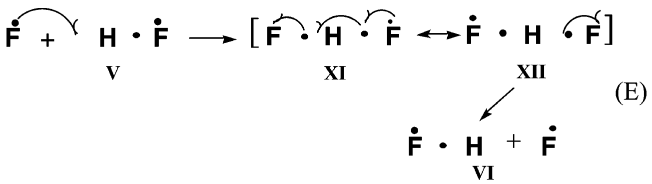
SCHEME C



SCHEME D



SCHEME E



Two VB representations can be developed to give eq 28 for the transition state, namely, those of Schemes C and D. For Scheme C, the transition state involves equal weights for VB structures **VII** and **VIII** for the **VII** ↔ **VIII** resonance. For Scheme D, the reactant-like complex is identical to the product-like complex at the transition state, as is discussed further below.

The four structure models require that

$$\Phi_{RC} = (1 - \mu)\Phi_1 + 2k'\Phi_3 + 2\mu\Phi_4 \tag{29}$$

$$\Phi_{PC} = (1 - \mu)\Phi_4 + 2k'\Phi_6 + 2\mu\Phi_1 \tag{30}$$

for F + HF → FH + F, and

$$\Phi_{RC} = (1 - \mu)\Phi_1 + 2k''\Phi_2 + 2\mu\Phi_4 - l(1 + 3\mu)\Phi_5 \tag{31}$$

$$\Phi_{PC} = (1 - \mu)\Phi_4 + 2k''\Phi_5 + 2\mu\Phi_1 - l(1 + 3\mu)\Phi_2 \tag{32}$$

for H + FH → HF + H, in order that each of the Φ_{RC} and Φ_{PC} generates an $S = 1$ spin excited state for HF at the conclusion and commencement of the reactions, respectively. The mechanism of Scheme D requires that $k'' = l$ at the transition state for eqs 31 and 32.

(c) If the first step in the VB mechanism for F + HF → FH + F is formulated as is done in Scheme C for H + FH → HF + H (cf. ref 2 for H + H_2 → H_2 + H), that is, with $l \neq 0$, we obtain eq 33

$$\Psi_{TS} = (1 - 3\mu)(\Phi_1 - \Phi_4) + l(1 + 3\mu)(\Phi_2 - \Phi_5) + 2k'(\Phi_3 - \Phi_6) + 2k'l(\Phi_7 - \Phi_8) \tag{33}$$

for the transition state and the VB formulation of Scheme E. Because μ is chosen so that $\langle\Phi_{RC}|\Phi_{PC}\rangle = 0$, eq 33 involves two ($k'$ and l) rather than three (k', k'', and l) independent variational parameters, Scheme E does not correspond to the lowest-energy VB formulation of the reaction mechanism.

Illustrative STO-6G Calculations

To illustrate aspects of the above theory, we have used Roso's ab initio VB program[6] to perform STO-6G VB calculations for the H + FH and F + HF reactants and the symmetrical linear HFH and FHF transition states, with best-atom exponents for the fluorine atoms, and the hydrogen atom exponent and internuclear separations energy-optimized. Relevant results are reported in Tables 2 and 3 when the eight Lewis structures of Table 1 are used to construct the reaction profiles. Although only a minimal basis set is used, the same types of general features (larger activation energy and longer HF bonds for the HFH transition state, compared with those for the FHF transition state) are calculated to occur as have been obtained from the

TABLE 2: STO-6G VB Energies for H + FH → HF + H and F + HF → FH + F[a]; in All Tables, Energies Are in au, unless Stated Otherwise

	reactants H + F−H	products H−F + H	transition state HFH		reactants F + H−F	products F−H + F	transition state FHF
r(HF)/Å	∞	1.005 (0.926)[4]	1.296 (1.1759)[4]	r(FH)/Å	∞	1.005 (0.926)[4]	1.175 (1.1105)[4]
r(FH)/Å	1.005 (0.926)[4]	∞	1.296 (1.1759)[4]	r(HF)/Å	1.005 (0.926)[4]	∞	1.175 (1.1105)[4]
ζ_H	1.23	1.23	1.04	ζ_H	1.23	1.23	1.21
E	−100.02140	−100.02140	−99.97474	E/au	−198.43262	−198.43262	−198.40127
E_{RC}		−99.57025	−99.72678	E_{RC}/au		−197.98148	−198.26965
E_{act} (kcal mol^{-1})			29.3 (46.6)[4]	E_{act} (kcal mol^{-1})			19.9 (22.4)[4]
E_G (kcal mol^{-1})	283.0	283.0		E_G (kcal mol^{-1})	283.0	283.0	
$E_{RC} - E_{TS}$ (kcal mol^{-1})			155.5	$E_{RC} - E_{TS}$ (kcal mol^{-1})			82.6

[a] E_{RC} for r(HF···H) or r(FH···F)= ∞ is equal to E_{PC} for r(H···FH) or r(F···HF) = ∞. $\Phi_{RC}\{r(\text{HF}\cdots\text{H}) = \infty\} = \text{HF}(S = 1) + \text{H}(S = 1/2)$ and $\Phi_{PC}\{r(\text{H}\cdots\text{FH}) = \infty\} = \text{H}(S = 1/2) + \text{FH}(S = 1)$. $\Phi_{RC}\{r(\text{FH}\cdots\text{F}) = \infty\} = \text{FH}(S = 1) + \text{F}(S = 1/2)$ and $\Phi_{PC}\{r(\text{F}\cdots\text{HF}) = \infty\} = \text{F}(S = 1/2) + \text{HF}(S = 1)$.

TABLE 3: STO-6G Coefficients and Parameters for H + FH → HF + H and F + HF → FH + F

	reactants H + F−H	products H−F + H	transition state HFH		reactants F + H−F	products F−H + F	transition state FHF
C_1	0.54976		0.34141	C_1	0.54976		0.33321
C_4		0.54976	−0.34141	C_4		0.54976	−0.33321
C_2	0.37605		0.19210	C_2	0.18681		0.16672
C_5		0.37605	−0.19210	C_5		0.18681	−0.16672
C_3	0.18681		0.18996	C_3	0.37605		0.26879
C_6		0.18681	−0.18966	C_6		0.37605	−0.26879
C_7			0.10420	C_7			0.07990
C_8			−0.10420	C_8			−0.07990
μ	0.2	0.2	0.10559	μ	0.2	0.2	0.10874
l	0.0	0.0	0.54853	l	0.0	0.0	0.29725
k'	0.18112	0.18112	0.19008	k'	0.36460	0.36460	0.27176
k''	0.36460	0.36460	−0.16983	k''	0.18112	0.18112	−0.02855
k_0''			0.00707	k_0''			0.10155

better-quality calculations of HMSWS[4]. The Ψ_{TS} and Φ_{RC} are eqs 12 and 8 with no approximations for Tables 2 and 3. The results of STO-6G calculations that use some of the approximations for Ψ_{TS} and Φ_{RC} are reported in the Supporting Information. In accordance with the findings of HMSWS[4], the results of all calculations show that the F + HF reaction has a smaller activation energy than has the H + FH reaction.

The value of l is determined from $C_7/C_3 = l$. Approximate estimates for k' and k'' are obtained from $2k'/(1 - 3\mu) = C_3/C_1$ and $\{2k'' + l(1 + 3\mu)\}/(1 - 3\mu) = C_2/C_1$, respectively.

It is noted that the resulting values for k'' are negative. However we can write $k'' = k_0'' + d$, with $d = -(3/2)\mu(l + C_2/C_1)$, for which k_0'' pertains for $\Phi'_{\mathbf{II}}$ or $\Phi'_{\mathbf{III}}$ at the transition state, that is, when $\mu = 0$. For both HFH and FHF, the k_0'' is positive in sign. The resulting approximate expression for Ψ_{TS} can then be expressed as

$$\Psi_{TS} \approx (\Phi_1 - \Phi_4) + (2k_0'' + l)(\Phi_2 - \Phi_5) + 2k'(\Phi_3 - \Phi_6) + 2k'l(\Phi_7 - \Phi_8) - 3\mu\{\Phi_1 - \Phi_4 + (2k_0'' + l)(\Phi_2 - \Phi_5)\} \quad (34)$$

The $\Phi_1 - \Phi_4 + (2k_0'' + l)(\Phi_2 - \Phi_5)$ of eq 34 involves the same Lewis-type VB structures as those used by HMSWS[4] to provide an approximate VB formulation for the HFH transition state.

For each of Φ_{RC}, Φ_{PC}, and Ψ_{TS}, the magnitude of l (0.29725) for the F + HF → FH + F reaction is substantially smaller than it is (0.54853) for the H + FH → HF + H reaction. Obviously, this result is due to the larger electronegativity of fluorine relative to hydrogen. As a consequence, the hydrogen → fluorine electron attraction for HFH is greater than the fluorine → hydrogen electron attraction for FHF.

Although this section and the Supporting Information do include the results of STO-6G VB calculations, the primary purpose of this paper is to demonstrate how the qualitative VB theory of ref 4 can be related to the more generalized formulations that had been presented in refs 1 and 2.

Acknowledgment. We are indebted to and thank Dr. W. Roso for his ab initio VB program, Mr. P. P. Wolynec and Drs. F. L. Skrezenek and H. M. Quiney for program installations, and Dr. Jonathan White for the provision of a workstation. K.S. thanks Professor T. M. Klapötke, LMU Munich, for supervision in Munich, and M.L.C. acknowledges the Australian Research Council for financial support under their Centres of Excellence program.

Note Added in Proof. VB structures **II** and **III** are examples of increased-valence structures.[1,2] A revised expression for the valence of the central atom has been deduced (Harcourt, R.D., submitted for publication).

Supporting Information Available: Additional tables of Ψ_{TS} and Φ_{RC} and results of STO-6G calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Harcourt, R. D. *J. Mol. Struct.:THEOCHEM* **1991**, *229*, 39 (see also Harcourt, R. D. *J. Mol. Struct.:THEOCHEM* **1992**, *253*, 363 for a

similar approach to nucleophilic substitution reactions and corrections for the 1991 paper.) (b) Harcourt, R. D. *Eur. J. Inorg. Chem.* **2000**, 1901. (c) Harcourt, R. D. *J. Phys. Chem. A* **2003**, *107*, 10324.

(2) Harcourt, R. D.; Ng, R. *J. Phys. Chem.* **1993**, *97*, 12210; Corrections: Harcourt, R. D.; Ng, R. *J. Phys. Chem.* **1994**, *98*, 3226.

(3) It is assumed that the primary active space AOs x, r, and y are oriented so that the AO overlap integrals S_{xr} and S_{ry} are each greater than zero for finite r(XR) and r(RY) distances. The AOs are assumed to be normalized. With a double zeta basis set for each atom (x′,x″,r′, r″, y′, and y″), with both closed-shell and open-shell two-electron AO configurations, there are 76 structures of types **1**−**8** of Table 1, 12 of which have one of the (x′,x″), (r′,r″), and (y′,y″) configurations. Each of Φ_{RC} and Φ_{PC} can be formulated to accommodate up to five of the AO basis functions.

(4) Hiberty, P. C.; Megret, C.; Song, L.; Wu, W.; Shaik, S. *J. Am. Chem. Soc.* **2006**, *128*, 2836.

(5) In ref 2, the deduction was made for $H + H_2 \rightarrow H_2 + H$, for which $\psi(H_2) = \psi(H{-}H) + \gamma\{\psi(H^- H^+) + \psi(H^+ H^-)\}$. For each of $F + HF \rightarrow FH + F$ and $H + FH \rightarrow HF + H$, we have calculated (cf. Tables 2 and 3) that the same result occurs when $\psi(HF) = \psi(H{-}F) + \gamma_1\psi(H^- F^+) + \gamma_2\psi(H^+ F^-)$ is used for the three active-space electrons.

(6) Benneyworth, P. R.; Balint-Kurti, G. G.; Davis, M. J.; Williams, I. H. *J. Phys. Chem.* **1992**, *96*, 4347.

(7) (a) Harcourt, R. D.; Roso, W. *Can. J. Chem.* **1978**, *56*, 1093. (b) For a recent application to H_2, see: Harcourt, R. D.; Klapötke, T. M.; Li, J. *Inorg. Chim. Acta*, **2005**, *358*, 4049; addendum: **2006**, *359*, 2328.