# ADDITIONS AND CORRECTIONS

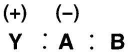
## 1999, Volume 103A

**Richard D. Harcourt:** Four-Electron Three-Center Bonding: One-Electron and Concerted Two-Electron Delocalizations into Bonding and Antibonding Molecular Orbitals

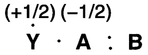
Page 4293. The entries for $T_{\mathrm{II,III}}$ and $A_{\mathrm{I,III}}$ in Table 2 should be +0.089 699 and 2.780 373 au, respectively. As in ref 1, $\rho = 0.495\,318$. Use of these corrected values affects only slightly the values for the $\mu$ and $\Delta E_{\mathbf{4}}$ which depend on them.

Valence bond structures **4** and **6** of ref 1 were obtained when

**1**



**4**



**6**

two electrons and one electron were respectively delocalized from the doubly occupied Y-atom AO of VB structure **1** of ref 1 into the Y−A bonding MO $\psi_{ya} = y + la$. For small $\mu$, the resulting stabilization energies for structures **4** and **6** relative to structure **1**, $\Delta E_{\mathbf{4}}$ and $\Delta E_{\mathbf{6}}$, were given by eqs 17 and 18 of ref 1.

The results of calculations[1] for the F:H−F component of the HF dimer $(HF)_2$, with both the inclusion and omission of the small matrix element $T_{\mathrm{I,III}}$ in eq 17 of ref 1, gave $\Delta E_{\mathbf{6}} - \Delta E_{\mathbf{4}} < 0$, or $E_{\mathbf{6}} < E_{\mathbf{4}}$; i.e., the delocalization of one of the Y-atom lone-pair electrons of structure **1** into the Y−A bonding MO is preferred energetically to the concerted two-electron delocalizations into this MO. Here we retain $T_{\mathrm{I,III}}$ in eq 17 and derive the condition for $E_{\mathbf{6}}$ to lie below $E_{\mathbf{4}}$ for small $\mu$ and $\nu$. Each $\mu$ and $\nu$ is greater than zero for Y−A bonding.

The $\nu$ of eq 18 of ref 1 approximates to $-T_{\mathrm{I,II}}/A_{\mathrm{I,II}}$. From eq 17 of ref 1, we obtain

$$\Delta E_{\mathbf{4}} = \Delta E_{\mathbf{6}} + 2\rho\nu\mu(T_{\mathrm{I,III}} + \nu T_{\mathrm{II,III}} + 0.5\rho\nu\mu A_{\mathrm{I,III}}) \quad (1)$$

as the approximate expression for $\Delta E_{\mathbf{4}}$. The corresponding approximate expression for $\mu$ is given by

$$\mu = \nu - \rho\mu(T_{\mathrm{I,III}} + 2\nu T_{\mathrm{II,III}} + \rho\nu\mu A_{\mathrm{I,III}})/A_{\mathrm{I,II}} \quad (2)$$

From eq 1, we obtain

$$T_{\mathrm{I,III}} + \nu T_{\mathrm{II,III}} + 0.5\rho\nu\mu A_{\mathrm{I,III}} > 0 \quad (3)$$

as the approximate requirement for $E_{\mathbf{6}}$ to be less than $E_{\mathbf{4}}$. For the $(HF)_2$ calculations,[1] eq 3 is equal to +0.010 64 au, and $T_{\mathrm{I,III}}$ is the only negative term. Its value (−0.009 54 au) is almost canceled by $0.5\rho\nu\mu A_{\mathrm{I,III}}$ (+0.009 52 au). The $\nu T_{\mathrm{II,III}}$ term is then primarily responsible for the energetic preference of a one-electron delocalization over concerted two-electron delocalizations. It remains to be determined whether these types of results are also appropriate for other systems.

**Note Added in Proof.** For revised definitions for the A-atom valence in each of the valence bond structures **4** and **6** see: Harcourt, R. D. *J. Mol. Struct. THEOCHEM* **2003**, *634*, 265.

**Note Added after ASAP Posting.** This addition/correction was posted ASAP on 11/13/2003. A correction was made to the displayed valence bond structure **4**. The corrected version was posted on 11/21/2003.

### References and Notes

(1) Harcourt, R. D. *J. Phys. Chem A* **1999**, *103*, 4293.

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