Aust. J. Chem., 1978, **31**, 199–201

Hückel Theory with Overlap for the Three-Electron Bond

Richard D. Harcourt

Department of Chemistry, University of Melbourne, Parkville, Vic. 3052.

Abstract

For a three-electron bond between two equivalent atoms, Hückel molecular orbital theory with overlap generates a resonance stabilization energy which is formally identical to that obtained from molecular orbital theory when electronic repulsions are included and the Mulliken approximation ($ab \approx \frac{1}{2}S(aa+bb)$) is invoked. The latter energy is the constructive interference energy.

Hückel molecular orbital theory with atomic orbital overlap integrals (S) included has been used[1] to predict that the three-electron bond* $\mathbf{A}\cdots\mathbf{B}$ between a pair of equivalent atoms generates destabilizing interactions when $S > 1/3$. Specifically, if **A** and **B** are equivalent atoms with (normalized) overlapping atomic orbitals a and b, then the bonding and antibonding molecular orbitals

$$\psi_+ = (a+b)/(2+2S)^{1/2} \quad \text{and} \quad \psi_- = (a-b)/(2-2S)^{1/2}$$

have Hückel molecular orbital energies

$$\varepsilon_+ = (\alpha+\beta)/(1+S) \quad \text{and} \quad \varepsilon_- = (\alpha-\beta)/(1-S)$$

for which α and β are the Coulomb and resonance integrals of Hückel theory. The total Hückel electronic energy for the three-electron bond configuration $(\psi_+)^2(\psi_-)^1$ is then given by equation (1), which gives $E > 3\alpha$ when $S > 1/3$. The energy 3α is the energy for $\mathbf{A}\colon\cdot\mathbf{B}$ or $\mathbf{A}\cdot\ \colon\mathbf{B}$ when a and b do not overlap. For π (but not σ) orbitals, zero overlap may be obtained by rotation of a relative to b around the **AB** bond

* Here, we follow the usual practice to represent the three-electron bond as $\mathbf{A}\cdots\mathbf{B}$. However, the Green and Linnett[2] representation $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$ is more appropriate, because there is effectively only one bonding electron; the antisymmetrized product wavefunction $|\psi_+\overline{\psi}_+\psi_-|$, with the normalized molecular orbitals defined above, is equivalent[2,3] to $-|a\overline{\psi}_+b|$ with one bonding and two non-bonding electrons. It may be noted here that if the odd electron of ψ_- can overlap with a singly occupied orbital located on a third atom **Y**, then these electrons may be spin-paired to generate[4] an 'increased-valence' structure $\mathbf{Y}\text{–}\mathbf{A}\cdot\dot{\mathbf{B}}$, for which three electrons participate in bonding. (The latter electrons occupy the spin-orbitals y, $\overline{\psi}_-$ and ψ_+, or $\bar{y}$, ψ_- and $\overline{\psi}_+$.)

[1] Baird, N. C., *J. Chem. Educ.*, 1977, **54**, 291.
[2] Green, M., and Linnett, J. W., *J. Chem. Soc.*, 1960, 4945.
[3] Linnett, J. W., *Sci. Prog. (London)*, 1972, **60**, 1.
[4] Harcourt, R. D., *J. Mol. Struct.*, 1972, **11**, 1; 1973, **18**, 515; *Biopolymers*, 1972, **11**, 1551; *J. Phys. B*, 1974, **7**, L41; see also Harcourt, R. D., and Scollary, G. R., *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 821, for three-electron bond theory and transition-metal complexes.

axis. Of course, for each non-zero and finite internuclear separation, the variation theorem requires that $\mathbf{A}\cdots\mathbf{B}$ must be stabilized by resonance relative to either $\mathbf{A}:\cdot\mathbf{B}$ or $\mathbf{A}\cdot:\mathbf{B}$ when the same internuclear separation and orbital overlap occur in each structure. Here, we shall demonstrate that Hückel theory with overlap generates an expression for the resonance stabilization energy which is formally identical to that obtained from molecular orbital theory when electronic repulsions are included and the Mulliken approximation[5] for atomic orbital products is invoked.

$$E(\mathbf{A}\cdots\mathbf{B}) \equiv 2\varepsilon_+ + \varepsilon_- = \{(3-S)\alpha+(1-3S)\beta\}/(1-S^2) \tag{1}$$

The wavefunctions for $\mathbf{A}:\cdot\mathbf{B}$ and $\mathbf{A}\cdot:\mathbf{B}$ are constructed* from the atomic orbital configurations $(a)^2(b)^1$ and $(a)^1(b)^2$. Because these structures are degenerate when **A** and **B** are equivalent atoms (and a and b are equivalent orbitals), we need only give consideration to one of them, $(a)^2(b)^1$ for example. In order that the atomic orbital overlap be included in the Hückel energy for any internuclear separation, it is necessary to use the Slater determinantal wavefunction of equation (2) to evaluate the energy. (For this wavefunction, the presence or absence of a bar over the atomic orbital designates an s_z spin quantum number of $-\frac{1}{2}$ or $+\frac{1}{2}$; N is the normalization constant $1/\{6(1-S^2)\}^{1/2}$.)

$$\begin{aligned}|\,a\bar{a}b\,| = N\{&a(1)\bar{a}(2)b(3)-a(1)b(2)\bar{a}(3)+b(1)a(2)\bar{a}(3)-b(1)\bar{a}(2)a(3)\\&+\bar{a}(1)b(2)a(3)-\bar{a}(1)a(2)b(3)\}\end{aligned} \tag{2}$$

The Hückel electronic energy of equation (3) for $\mathbf{A}:\cdot\mathbf{B}$ is calculated from

$$\langle|\,a\bar{a}b\,||\hat{H}(1)+\hat{H}(2)+\hat{H}(3)||\,a\bar{a}b\,|\rangle$$

where the $\hat{H}(i)$ terms are the one-electron effective Hamiltonian operators of Hückel theory.

$$E(\mathbf{A}:\cdot\mathbf{B}) = \{(3-S^2)\alpha-2S\beta\}/(1-S^2) \tag{3}$$

The Hückel resonance stabilization energy for the three-electron bond is then given by equation (4), which is identical in form to that obtained from Hückel theory for the ground state of H_2^+, namely

$$E(\psi_+)-E(a) \equiv (\alpha+\beta)/(1+S)-\alpha = (\beta-S\alpha)/(1+S)$$

This resonance stabilization energy corresponds to the constructive interference energy[7,8] (E_I), which gives the bulk of the binding energy for H_2^+ when the α and β are evaluated as core Coulomb and resonance integrals.[7,8] For H_2^+, E_I is negative[7,8] for all internuclear separations >0, and the same must be true for the three-electron bond (see also below).

$$E(\text{resonance}) \equiv E(\mathbf{A}\cdots\mathbf{B})-E(\mathbf{A}:\cdot\mathbf{B}) = (\beta-S\alpha)/(1+S) \tag{4}$$

* We have used the same types of atomic orbitals for **A** and **B** in $\mathbf{A}:\cdot\mathbf{B}$ and $\mathbf{A}\cdot:\mathbf{B}$ in order that the molecular orbital and valence-bond descriptions for the three-electron bond are equivalent. Valence-bond calculations for He_2^+ that relax this requirement have been reported by a number of workers.[6]

[5] Mulliken, R. S., *J. Chim. Phys. Phys.-Chim. Biol.*, 1949, **46**, 497, 675.
[6] Murrell, J. N., and Ralston, B. J., *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 1393, and references therein.
[7] Feinberg, M. J., and Ruedenberg, K., *J. Chem. Phys.*, 1971, **54**, 1495.
[8] Driessler, F., and Kutzelnigg, W., *Theor. Chim. Acta*, 1976, **43**, 1.

Hückel theory does not explicitly treat the electron–electron interactions. If these are included in the three-electron Hamiltonian operator, then both the molecular orbital and valence-bond wavefunctions (namely $|\psi_+\bar{\psi}_+\psi_-|$ and $(|a\bar{a}b|+|a\bar{b}b|)/(2+2S)^{1/2}$) generate the electronic energy of equation (5) for the three-electron bond. In equation (5), the α° and β° are core Coulomb and resonance integrals, and

$$(aa\,|\,bb) \equiv \langle a(1)b(2)\,|\,1/r_{12}\,|\,a(1)b(2)\rangle$$

etc. The electronic energy for either $\mathbf{A}\colon\cdot\mathbf{B}$ or $\mathbf{A}\cdot\,:\mathbf{B}$, and the resonance energy for a given internuclear separation are then given by equations (6) and (7). If we introduce the Mulliken approximation[5] for the *ab* orbital product ($ab \approx \frac{1}{2}S(aa+bb)$) into each of $(aa\,|\,ab)$ and $(ab\,|\,ba)$ in equation (7), then E(resonance) reduces to

$$E_I = (\beta^\circ - S\alpha^\circ)/(1+S)$$

which is formally identical to equation (4) for the Hückel theory.

$$E(\mathbf{A}\cdots\mathbf{B}) = \frac{(3-S)\alpha^\circ+(1-3S)\beta^\circ}{1-S^2} + \frac{(aa\,|\,aa)+(2+S)(aa\,|\,bb)+2(1-S)(aa\,|\,ab)-(1+3S)(ab\,|\,ba)}{(1+S)(1-S^2)} \quad (5)$$

$$E(\mathbf{A}\colon\cdot\mathbf{B}) = \frac{(3-S^2)\alpha^\circ-2S\beta^\circ}{1-S^2}+\frac{(aa\,|\,aa)+2(aa\,|\,bb)-2S(aa\,|\,ab)-(ab\,|\,ba)}{1-S^2} \quad (6)$$

$$E(\text{resonance}) \equiv E(\mathbf{A}\cdots\mathbf{B})-E(\mathbf{A}\colon\cdot\mathbf{B}) = \frac{\beta^\circ-S\alpha^\circ}{1+S}+\frac{2(1+S^2)(aa\,|\,ab)-S\{(aa\,|\,aa)+(aa\,|\,bb)+2(ab\,|\,ba)\}}{(1+S)(1-S^2)} \quad (7)$$

For each of the ground-state molecular orbital configurations of H_2^+, H_2, He_2^+ and He_2, the Hückel resonance stabilization energy* may be expressed as $n(\beta-S\alpha)/(1+S)$, with n defined as half the difference between the number of bonding electrons and the number of antibonding electrons. The Hückel electronic and resonance energies for the Heitler–London wavefunction of H_2 are equal to $2(\alpha+S\beta)/(1+S^2)$ and $2S(\beta-S\alpha)/(1+S^2)$. Hückel theory predicts that the Heitler–London function $(|a\bar{b}|+|b\bar{a}|)/(2+2S^2)^{1/2}$ should be degenerate with the ionic wavefunction $(|a\bar{a}|+|b\bar{b}|)/(2+2S^2)^{1/2}$; this result of course does not pertain when electron–electron interactions are taken account of.

Acknowledgments

I thank Drs N. C. Baird, J. Burdett and P. Mehrotra for useful discussion, and Professor R. Hoffmann for the use of the facilities of his department at Cornell University.

Manuscript received 2 August 1977

* Each of the Slater determinants $|a\bar{b}|$ and $|b\bar{a}|$ for H_2 has a Hückel energy of 2α when overlap is included. For He_2, the molecular orbital and atomic orbital configurations $|\psi_+\bar{\psi}_+\psi_-\bar{\psi}_-|$ and $|a\bar{a}b\bar{b}|$ are equivalent, and therefore no resonance stabilization is possible.