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## The Isoelectronic Principle and the Accuracy of Binding Energies in the Hückel Method

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of the parameters determining the potential field, which governs the motion of the particles is assumed to be dependent on the initial energy of the hot atom X. Doing this we reproduced what the hot particle "sees" from the true surface while possessing its high initial energy. This assumption has fully justified itself, because in contrast to the kinematic model, the present model yields a good fit with the curve for the reaction  $D_2 + T \rightarrow DT + D$  computed by Karplus, *et al.*, and also the right isotopic effect for the reactions  $HD + T \rightarrow H(D)T + D(H)$ . For the respective isotopic ratio  $R_{HT}/R_{DT}$  we derived the value of 0.89, the experimental value is  $0.62 \pm 0.06$ , and Suplinskas' value is 1.6.

The good fit obtained with the theoretical calculations of Karplus, Porter, and Sharma and with the different experiments indicates that the main repulsive interaction during the reaction process is between the hot atom and the atom to be replaced, *viz.*, atom Y. The nature of this repulsion is not of a pure billiard-

ball type; however, it is not of too soft a nature either, since, in contrast to the hard-sphere approximation, the energy-dependent hard-sphere approximation yields the correct results.

The two main features of this model consist (1) in its being easily handled since the calculations involved are short (about 5 to 10 min for each curve) and (2) in its applicability to a large variety of reactions, since the potential field assumed is constructed using the experimental value of the threshold energy for the reactions and other parameters derived from the Morse potential of the molecule ZY.

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## The Isoelectronic Principle and the Accuracy of Binding Energies in the Hückel Method

Jerry Goodisman<sup>1</sup>

*Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois. Received June 2, 1969*

**Abstract:** In the Hückel and other methods, binding energies are calculated by subtracting the sum of orbital electronic energies for the molecule from the sum of orbital electronic energies for the separated atoms, and not considering the internuclear repulsion. Since this last may be several orders of magnitude greater than the binding energy, reasonable results could not be obtained without an approximate cancellation with another neglected term. It is shown that such a cancellation is a consequence of the isoelectronic principle (invariance of binding energy to change in atomic number of constituent atom). Numerical examples are given.

In a number of *a priori* and semiempirical methods, of which the extended Hückel method<sup>2</sup> is the best known, one calculates molecular binding energies by subtracting the electronic energy (sum of orbital contributions) of the molecule from the sum of the electronic energies of the atoms, without considering the internuclear repulsion. If we accept the argument that the parameterization in the method effectively simulates a Hartree-Fock calculation, the "electronic energies" are really sums of orbital energies. To get the true electronic energies of atom or molecule, one must subtract off in each case the interelectronic repulsion, which is being counted twice. Thus the above recipe will be valid if

$$V_{NN} \approx V_{ee}^m - \sum_A V_{ee}^A \equiv \Delta V_{ee} \quad (1)$$

where  $V_{ee}^m$  and  $V_{ee}^A$  are the interelectronic repulsions (expectation values) for the molecule and for atom A, and  $V_{NN}$  is the internuclear repulsion.<sup>3</sup> The binding

energy may be orders of magnitude smaller than  $V_{NN}$ . Thus the error in eq 1 must be small (*i.e.*, of the size of the binding energy itself) if reasonable binding energies are to be obtained from a wave function which is reasonable in other respects. Below, we show<sup>4</sup> that this is in fact true in general, being a consequence of the isoelectronic principle.

The proof is closely related to the derivation of a formula<sup>5</sup> for calculating diamagnetic shieldings in molecules, also starting from the isoelectronic principle. According to this principle, two isoelectronic species have the same binding energies if they differ only by a change by unity in a nuclear charge. The example of CO *vs.* N<sub>2</sub><sup>6</sup> is perhaps the best known; one can easily find others.<sup>7</sup> Writing  $Z_B$  for the charge of nucleus B, we express this as

(3) Note that it is the *change* in  $V_{ee}$  from atoms to molecule which must be approximately equal to  $V_{NN}$ , not  $V_{ee}$  itself as has been sometimes stated.

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(7) J. Berkowitz, *J. Chem. Phys.*, **30**, 858 (1959); also *cf.* ref 5.

(1) Research supported by the National Science Foundation under Grant No. GP-5861; correspondence should be addressed to Chemistry Department, Syracuse University, Syracuse, N. Y.

(2) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3179 (1962); R. Hoffmann, *ibid.*, **39**, 1397 (1963).

$$\frac{\partial}{\partial Z_B} (\text{BE}) \approx 0 \quad (2)$$

We define the binding energy (a positive quantity) as

$$\text{BE} = -(E_e^m + V_{\text{NN}}) + \sum_A E_e^A \quad (3)$$

where  $E_e^m$  is the molecular electronic energy

$$E_e^m = T^m + V_{ee}^m + \sum_A V_{Ae}^m \quad (4)$$

$E_e^A$  the electronic energy of atom A

$$E_e^A = T^A + V_{ee}^A + V_{Ae}^A \quad (5)$$

and  $V_{\text{NN}}$  the internuclear repulsion

$$V_{\text{NN}} = \frac{1}{2} \sum_{A,B}^{(A \neq B)} Z_A Z_B / R_{AB} \quad (6)$$

Here,  $T^m$  and  $T^A$  are the kinetic energies (expectation values) for the molecule and for atom A,  $V_{ee}^m$  and  $V_{ee}^A$  the interelectronic repulsion energies for the molecule and for atom A, and  $V_{Ae}^m$  and  $V_{Ae}^A$  the expectation values of

$$V_{Ae} = \sum_i -Z_A e^2 / r_{Ai} \quad (7)$$

for the molecule and for atom A.

Substitute eq 3 into eq 2, and note that obviously  $\partial E_e^A / \partial Z_B = 0$  for  $A \neq B$  and that the Hellmann-Feynman theorem<sup>8</sup> gives

$$\frac{\partial E_e}{\partial Z_B} = \frac{\partial \langle H_e \rangle}{\partial Z_B} = \left\langle \frac{\partial H_e}{\partial Z_B} \right\rangle = \left\langle \frac{\partial V_{Be}}{\partial Z_B} \right\rangle \quad (8)$$

the last step because  $V_{Be}$  is the only operator depending on  $Z_B$ . The brackets refer to expectation values over the atomic or molecular wave function, as the case may be. Further, eq 7 shows that

$$\left\langle \frac{\partial V_{Be}}{\partial Z_B} \right\rangle = \left\langle \frac{V_{Be}}{Z_B} \right\rangle = Z_B^{-1} V_{Be} \quad (9)$$

Therefore, eq 2 becomes

$$-Z_B^{-1} V_{Be}^m - \sum_A^{A \neq B} Z_A / R_{AB} + Z_B^{-1} V_{Be}^B \approx 0$$

Multiplying by  $Z_B$  and summing over B

$$-\sum_B V_{Be}^m - 2V_{\text{NN}} + \sum_B V_{Be}^B \approx 0 \quad (10)$$

The virial theorem<sup>9</sup> tells us that  $V_{Be}^B + V_{ee}^B = 2E_e^B$  for each atom B and

$$\sum_B V_{Be}^m + V_{ee}^m + V_{\text{NN}} = 2(E_e^m + V_{\text{NN}})$$

so we have from eq 10

$$\Delta V_{ee} - V_{\text{NN}} \approx -2(\text{BE}) \quad (11)$$

This accounts for the possibility of obtaining reasonable binding energies by putting  $V_{\text{NN}} \approx \Delta V_{ee}$ . The binding energy will actually be increased by  $2(\text{BE}) - \sum_B Z_B \partial(\text{BE}) / \partial Z_B$ , and the second term is small by the isoelectronic principle. There is a relation to Wilson's charging process.<sup>10</sup> Write  $Z_B = \eta \bar{Z}_B$ , where  $\eta = 1$  corresponds to the actual molecule. Then it appears

that

$$2(\text{BE}) - \sum_B Z_B [\partial(\text{BE}) / \partial Z_B] = - \left[ \frac{d}{d\eta} \left( \frac{\text{BE}}{\eta^2} \right) \right]_{\eta=1}$$

which is zero if the binding energy is proportional to  $\eta^2$ . This, in turn, may be related to an expansion similar to the atomic  $1/Z$  expansion.<sup>8,11</sup> For a molecule with nuclear charges  $\{Z_B\}$  and in a configuration given by the internuclear distances  $\{R\}$  (this includes the separated atoms), the energy  $E(Z_B, R)$  is calculable<sup>11</sup> by perturbation theory to give

$$E(Z_B, R) = \eta^2 E_0(\bar{Z}_B, \eta R) + \eta E_1(\bar{Z}_B, \eta R) + E_2(\bar{Z}_B, \eta R) + \dots \quad (12)$$

Here, the interelectronic repulsion is the perturbation, and scaled coordinates are introduced. Keeping only the leading term in eq 12 makes any energy difference, such as (BE), proportional to  $\eta^2$ .

The accuracy of the approximation, eq 1, may be checked using the results from some recent SCF calculations.  $\Delta V_{ee}$  is obtained as the difference of orbital energy sums for molecule and atoms minus the difference of total electronic energies. The results are given in Table I.

Table I. Approximate Equality of  $V_{\text{NN}}$  and  $\Delta V_{ee}$

Molecule	Ref <sup>a</sup>	$V_{\text{NN}}$ , au	$\Delta V_{ee}$ , au	$(V_{\text{NN}} - \Delta V_{ee}) / V_{\text{NN}}$
N <sub>2</sub>	b	23.902	22.832	0.045
HF	c	5.193	5.490	-0.057
NH <sub>3</sub>	d	11.986	12.139	-0.012
C <sub>2</sub> H <sub>2</sub>	e	24.805	24.420	0.015
C <sub>2</sub> H <sub>4</sub>	e	33.472	33.160	0.009
H <sub>2</sub> O	f	9.238	9.421	-0.020
CH <sub>2</sub> O	g	31.114	30.413	0.022

<sup>a</sup> These are for the molecular wave functions. The atomic wave functions used were from E. Clementi, "Tables of Atomic Functions," Supplement to *IBM J. Res. Develop.*, **9**, 2 (1965). <sup>b</sup> P. E. Cade and K. D. Sales, *J. Chem. Phys.*, **44**, 1973 (1966). <sup>c</sup> P. E. Cade and W. M. Huo, *ibid.*, **47**, 614 (1967). <sup>d</sup> J. Smith, *Z. Naturforsch.*, **A**, **20**, 1557 (1967). <sup>e</sup> R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *J. Chem. Phys.*, **46**, 2029 (1967). <sup>f</sup> D. Neumann and J. W. Moskowitz, *ibid.*, **49**, 2056 (1968). <sup>g</sup> N. W. Winter, T. H. Dunning, Jr., and J. H. Letcher, *ibid.*, **49**, 1871 (1968).

Boer, Newton, and Lipscomb<sup>12</sup> have argued that the validity of summing orbital energies and neglecting  $V_{\text{NN}}$  to get (BE) is due to the approximate cancellation of  $V_{\text{NN}}$  with half the difference between molecular and atomic core energies (kinetic plus nuclear attraction energies). They define

$$\Delta = V_{\text{NN}} + \frac{1}{2} \left[ T^m + \sum_A V_{Ae}^m - \sum_A T^A - \sum_A V_{Ae}^A \right] \quad (13)$$

and find  $\Delta$  to be 10% of  $V_{\text{NN}}$  for certain diatomics, and a per cent or so for some small polyatomics (amounting to a few tenths of an atomic unit). As seen in Table I, the equality of  $V_{\text{NN}}$  and  $\Delta V_{ee}$  is of the same order of approximation. In the present work, we have shown that this approximate equality is equivalent to the isoelec-

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tronic principle, familiar to chemists. We have made no separation of core and valence electrons, but it may be argued that  $\Delta V_{ee}$  is largely due to the valence electrons.

Note that if  $\partial(\text{BE})/\partial Z_B$  were exactly zero, the binding energy calculated by assuming eq 1 to be valid would be too high by a factor of 3. As  $\partial(\text{BE})/\partial Z_B$  is probably positive, the binding energy will be somewhat less, and

in fact Boer, *et al.*,<sup>12</sup> suggest correcting the calculated binding energy by dividing by 2. In concluding, we must agree with Boer, *et al.*, that, since the cancellation of  $V_{NN}$  and  $\Delta V_{ee}$  is good only to a few tenths of an atomic unit, a true SCF calculation cannot be expected to yield correct binding energies by this procedure, but that trends within a series of related molecules may be predicted.

## Selection Rules for Singlet-Oxygen Reactions. Concerted Addition Reactions

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**Abstract:** In this paper we have used molecular orbital and state correlation diagrams to predict the reactions of molecular oxygen with monoolefins and conjugated dienes. From this analysis the following selection rules are obtained. (1) The concerted addition of ground-state ( $^3\Sigma$ ) oxygen to olefins and dienes is forbidden unless the  $\pi$ -ionization potential of the acceptor is unusually low. (2) The reaction of excited singlet oxygen in its  $^1\Delta$  state with *cis*-dienes is predicted to be allowed. The addition of  $^1\Delta$  oxygen to olefins may be forbidden unless the olefin has a low  $\pi$ -ionization potential. (3)  $^1\Sigma$  oxygen is expected to be unreactive toward olefins and dienes in concerted addition reactions. The thermochemical and photochemical properties of the diene and olefin oxygenation products have been examined, and selection rules for their thermal and photodecomposition have also been derived. The selection rules for the oxygen reactions are compared with those for the corresponding reactions of ethylene and their relation to the Woodward-Hoffmann selection rules is discussed.

During the past 4-5 years a large body of data has been collected which indicates that electronically excited singlet-state oxygen molecules (presumably  $^1\Delta$ ) are the reactive intermediates in numerous photooxygenation reactions.<sup>1-11</sup> With the recent spectroscopic detection of the photosensitized formation of singlet ( $^1\Delta$ ) oxygen,<sup>12-14</sup> and the demonstration that the quantum yield for this process is high (perhaps 100%),<sup>12</sup> the evidence for the involvement of singlet oxygen in many photooxygenation reactions is now virtually unassailable.

In previous papers we presented a relatively simple theoretical procedure for predicting the relative reactivity of ground-state and electronically excited oxygen molecules toward various organic acceptors.<sup>15,16</sup>

In the present paper this approach is further refined and used to investigate the various factors which control the reactivity of oxygen toward different types of acceptors. Since the 1,4 addition of oxygen to dienes appears to be one of the simpler reactions which singlet oxygen undergoes,<sup>7,8,11</sup> this reaction is considered first. The addition of oxygen to isolated olefins and polyenes is also examined and useful conclusions regarding the reactivity of oxygen with these acceptors are drawn.

Inasmuch as the products of some of the singlet-oxygen reactions appear to have unusual chemical and photochemical properties, as in chemiluminescent systems,<sup>17-19</sup> the properties of some of the oxygenation products are also examined theoretically.

Finally, since there are interesting parallels between the reactions of oxygen and olefins with conjugated dienes,<sup>1,9,11,20</sup> we have carried out a comparison of these two types of reactions. This comparison also allows us to investigate the extent to which the Woodward-Hoffmann selection rules for concerted cycloaddition reactions are applicable to cycloaddition reactions of singlet oxygen.<sup>21-23</sup>

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