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Bonding Criteria for Diatomic Molecular Orbitals and Inter-Relations among Them*

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Bonding criteria for molecular orbitals in diatomic molecules are discussed. An orbital force criterion is shown to have several conceptual and practical advantages, providing a basis for the investigation of inter-relations among many of the commonly employed criteria.

It is found that interconsistency among those criteria is guaranteed, within the framework of Koopmans' Theorem, if the orbital energies are monotonic in the range (R_e, ∞).

The application of the orbital force criterion to the second row homonuclear diatomics exhibits reasonable chemical trends concerning the valence-shell orbitals, as well as indications of a slightly antibonding nature of the inner orbitals.

Key words: Diatomic molecules, bonding criteria for ~ – Orbital energies

1. Introduction

The qualitative ideas concerning the nature of the chemical bond date back to the early days of quantum chemistry. They include concepts such as bonding, nonbonding and antibonding orbitals, as well as dogmas such as the statement that an antibonding orbital is more antibonding than the corresponding bonding orbital is bonding. These concepts and ideas enabled a rationalization of the basic chemical observations concerning the stability of simple molecules in their ground states.

Progress in synthetic inorganic chemistry and in spectroscopy, and, to an even greater extent, the availability of large-scale computational facilities, have pointed

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out several aspects in which the most naive theoretical concepts have to be revised. Consequently, several attempts to formulate improved concepts and bonding criteria were put forward, based for the most part on accurate HF calculations.

In the present work we try to reveal the interrelations among the existing criteria and establish some of the conditions for their interconsistency. After a brief review of the most common bonding criteria, we discuss a criterion of the orbital force type and examine its effectiveness in interpreting chemical facts and its relation to the other criteria reviewed.

2. Bonding Criteria Based on Physical Observables

The most obvious characteristics of a chemical bond are its length, vibrational frequency and dissociation energy. The changes in these properties, brought about by ionization, were suggested by Mulliken [1] as criteria for the bonding characteristics of the ionized electron. Denoting the bond length of the molecule by R_e, and that of the ion by R_e^+, the difference $\Delta R_e \equiv R_e^+ - R_e$ will be positive for an ionization out of a bonding orbital, and negative for an ionization out of an antibonding orbital [2]. The applicability of this criterion was enhanced by the advent of photoelectron spectroscopy, which enables the study of the changes in bond lengths associated with the ionization of any electron in the molecule [3]. Similarly, the change of dissociation energy upon ionization, $\Delta D_e \equiv D_e^+ - D_e$, should be positive for an antibonding electron and negative for a bonding electron. The agreement between this criterion, which examines a global property of the chemical bond, and the bond length criterion, which stresses the local properties of the bond at equilibrium, has been reviewed by Mulliken, who pointed out the discrepancy in the case of the alkali diatomic molecules. The naive expectation of a behaviour similar to that in H_2, for which $\Delta R_e > 0$ and $\Delta D_e < 0$, in agreement with the simple idea about two bonding electrons being about twice as bonding as one, is not borne out by the experimentally and theoretically evaluated $\Delta D_e > 0$ for the alkali diatomics!

3. Bonding Criteria Depending on Theoretical Constructs

The criteria belonging to the present category depend on quantities which are not directly observable, but which can be extracted out of the molecular wavefunction in a well defined way. Ruedenberg's [4] analysis of the chemical bond is a genuine and penetrating approach, which demonstrates that such criteria, when wisely used, can be of much benefit. However, since the full power of this approach, within the context of many-electron molecules, has not yet been elucidated, we shall concentrate on simpler, yet useful, schemes.

3.1. Criteria Associated with Nodal Properties of Molecular Orbitals

The most naive characterization of bonding vs. antibonding orbitals is based on the absence or existence of a nodal surface bisecting the internuclear axis. Within the simplest LCAO-MO framework, maximum overlap [5] and other orbital-shape criteria are often used to quantify this notion. These ideas are reflected in the dependence of the orbital energies on the internuclear separation and thus can be qualitatively understood on the basis of the united-atom separated-atoms correlation diagram. The following formulation was suggested by Eyring *et al.*: [6] "If an orbital maintains the same principal quantum number as the transition is made from the separated atoms to the united atom it is said to be a 'bonding orbital'. If the principal quantum number increases it is said to be an 'antibonding orbital'."

The relevance of the united atom can be interpreted in relation to the existence of a nodal plane in the antibonding orbitals, which is closely related to the increase in the principal quantum number. From an energetic point of view, Eyring's criterion implies that for a bonding orbital the united atom orbital is lower than that in the separated atoms. This is relevant to the binding properties provided that monotonicity of $\varepsilon(R)$ is assumed, from which we immediately obtain that for a bonding orbital $\varepsilon(R_e) < \varepsilon(\infty)$. However, a non-monotonic behaviour of $\varepsilon(R)$ in the range $0 < R < R_e$ is frequently observed [7].

In the following section a more restricted, and therefore more generally valid, monotonicity assumption is shown to be relevant to the characterization of molecular orbitals with respect to their bonding properties.

3.2. *Criteria Based on Molecular Forces*

3.2.1. Additive Orbital Forces

Berlin [8] suggested a partitioning of space into regions in which an electron exerts a binding force on the nuclei, and others in which it exerts a force in a direction which opposes binding. An orbital is designated binding if it is mostly localized in the binding region, and vice versa.

These ideas were developed by Bader *et al.* [9] for many-electron systems. They pointed out that since the force on the nucleus A in the diatomic molecule AB is, according to the Hellmann–Feynman theorem, the expectation value of

$$\partial\hat{H}/\partial R = \partial[Z_A Z_B/R - \sum_{i=1}^{n} Z_A/r_{Ai}]/\partial R \tag{1}$$

it is appropriate to define additive orbital forces as

$$\eta_j \equiv Z_A \cdot \langle \phi_j(i) | \cos\theta_{Ai}/r_{Ai}^2 | \phi_j(i) \rangle \tag{2}$$

They further introduced the quantity

$$f_j \equiv \frac{n_j R^2}{Z_A} \cdot \eta_j \tag{3}$$

where n_j is the occupation number of the orbital ϕ_j.

From the Hellmann–Feynman theorem it follows that at equilibrium

$$\sum_i f_i(R_e) = Z_B \tag{4}$$

and furthermore,

$$\lim_{R\to\infty} f_i(R)=1 \tag{5}$$

Thus, an orbital is defined as binding if $f_i>1$ and antibinding if $f_i<1$.

The computed values of f_i, in Ref. [9], are in reasonable agreement with the traditionally accepted notions for the valence electrons, except that $3\sigma_g$ appears as antibinding. However, the behaviour of the inner $1\sigma_g$ and $1\sigma_u$ orbitals is more difficult to accommodate within the conventional conceptual framework.

3.2.2. Criterion of Orbital Forces

The total energy in the unrestricted Hartree–Fock approximation is

$$E=\sum_k n_k h_k+\frac{1}{2}\sum_{k\neq l} n_k n_l g_{kl} \tag{6}$$

h_k and g_{kl} are the one-electron and two-electron integrals. n_k is the occupation number of spin-orbital k, ranging between 0 and 1. The partial derivative with respect to n_i, keeping the orbitals, as well as all other occupation numbers constant, is

$$\partial E/\partial n_i=h_i+\sum_{j(\neq i)} n_j\cdot g_{ij}\equiv\varepsilon_i \tag{7}$$

Hence, Eq. (7) expresses the orbital energy as the differential contribution of an electron in orbital i to the total energy. This relation is motivated by the treatment of Slater *et al.* [10], but differs in (significant) details.

The differential contribution of an electron in orbital i to the total force on a nucleus, $F\equiv-\partial E/\partial R$, can be defined in an analogous manner,

$$-\partial F/\partial n_i=\partial^2 E/\partial n_i\,\partial R=\partial\varepsilon_i/\partial R\equiv\varepsilon_i' \tag{8}$$

The ionization energy and the change in the force acting on a nucleus due to (vertical) ionization can, in principle, be expressed as $-\int_0^1 \varepsilon_i(n_i)\,dn_i$ and $-\int_0^1 \varepsilon_i'(n_i)\,dn_i$, respectively.

By neglecting the dependence of ε_i on n_i, which is due to the change in the form of the orbitals, one obtains Koopmans' theorem, $\varepsilon_i\simeq E-E_i^+$. Introducing a similar approximation with respect to ε_i', one obtains

$$\varepsilon_i'=\partial E/\partial R-\partial E_i^+/\partial R\equiv F_i^+-F \tag{9}$$

which can be interpreted as Koopmans' approximation for the change in the force acting on a nucleus due to the ionization of an electron out of orbital i. Hence, $\varepsilon_i'(R_e)$ can be used as a binding criterion. An orbital is binding if it exerts a force on the nucleus in the direction of the other nucleus, i.e. $\varepsilon_i'>0$, and antibinding if $\varepsilon_i'<0$. Although relaxation of the orbitals on ionization, as well as correlation effects, can modify the magnitude of the orbital force, they are less likely to upset its sign.

This criterion was recently discussed by Goscinski [11] with respect to the bond length shrinkage on ionization of core electrons in diatomics, which is examined in the following section.

The orbital forces presented in Table 1 exhibit, for the most part, expected trends. The most remarkable observation is that the orbital forces in the $1\sigma_g$ as well as in the $1\sigma_u$ orbital for second row molecules are (slightly) antibinding! The different behaviour in He_2 indicates that this feature is a consequence of the interaction with the valence-shell electrons, which deform the $1\sigma_g$ orbital so as to push it away from the bonding region. Rather than a pair of virtually non-bonding orbitals of opposite nature, the $1\sigma_g$ and $1\sigma_u$ orbitals both exert antibinding forces. It is noted that only towards the end of the second row the $1\sigma_g$ and $1\sigma_u$ orbitals become virtually non-bonding core orbitals.

Table 1. Comparison of additive and Koopmans' orbital forces for homonuclear diatomics[a]

		H_2	He_2[d]	Li_2	Be_2[d]	B_2	C_2	N_2	O_2	F_2
$1\sigma_g$	ε_i'[b]	0.164	0.0043	−0.0031	—	−0.034	−0.147	−0.131	−0.090	—
	η_i[c]	—	—	0.0415	0.172	0.271	0.527	0.949	0.946	0.779
$1\sigma_u$	ε_i'[b]	—	−0.0044	−0.0041	—	−0.037	−0.156	−0.149		—
	η_i[c]	—	—	0.0387	0.168	0.269	0.519	0.888		0.704
$2\sigma_g$	ε_i'[b]	—	—	0.0094	—	0.100	0.185	0.423	0.513	—
	η_i[c]	—	—	0.0935	0.327	0.638	1.224	2.195	2.254	1.533
$2\sigma_u$	ε_i'[b]	—	—	—	—	−0.071	−0.141	−0.145	−0.199	—
	η_i[c]	—	—	—	−0.065	−0.136	−0.237	−0.379	−0.398	−0.105
$1\pi_u$	ε_i'[b]	—	—	—	—	0.077	0.126	0.264	0.223	—
	η_i[c]	—	—	—	—	0.329	0.612	0.995	1.000	0.772
$3\sigma_g$	ε_i'[b]	—	—	—	—	—	—	0.0857	0.137	—
	η_i[c]	—	—	—	—	—	—	0.123	0.134	0.323
$1\pi_g$	ε_i'[b]	—	—	—	—	—	—	—	−0.195	—
	η_i[c]	—	—	—	—	—	—	—	0.327	0.411

[a] All values in atomic units.

[b] Values of ε_i' were computed using the HF results of the following references:
H_2 Ref. [12], He_2 Ref. [13], C_2 Ref. [14], N_2 Ref. [15], Li_2, B_2 and O_2 present work.

[c] Values of η_i were computed by Eq. (3) using values of Ref. [9].

[d] Values for He_2 and Be_2 which have repulsive ground state potential curves were computed at $R=5.3$ [13] and $R=3.5$ [9] a.u. respectively.

4. Inter-Relations Among the Bonding Criteria

In the present section we apply the orbital force criterion in order to formulate conditions for the interconsistency of some of the bonding criteria discussed.

4.1. Relation between the f_i and ε_i' Criteria

The Hartree–Fock approximation satisfies the Hellmann–Feynman theorem in two different ways

1) From the Fock eigenvalue equation

$$\hat{F}\phi_i = \varepsilon_i \phi_i, \quad \text{where } \hat{F} = \hat{h} + \hat{G}$$

it follows that

$$\varepsilon_i' = \langle \phi_i | d\hat{F}/dR | \phi_i \rangle = \eta_i + \langle \phi_i | d\hat{G}/dR | \phi_i \rangle \tag{10}$$

which is the Hellmann–Feynman theorem with respect to the orbital energy.

2) The N-electron Hartree–Fock wavefunction satisfies the Hellmann–Feynman theorem with respect to the total energy and the exact Hamiltonian

$$dE_{\mathrm{HF}}/dR = \langle \psi_{\mathrm{HF}} | d\hat{H}/dR | \psi_{\mathrm{HF}} \rangle = \sum_i n_i \cdot \eta_i = (Z_{\mathrm{A}}/R^2) \cdot \sum_i f_i \tag{11}$$

The orbital force in the sense of Eq. (10) differs from the ith term of the total force in Eq. (11) by the interelectronic repulsion terms. Equation (11), which forms the basis for Bader's treatment [9], has the advantage of partitioning the total binding force into additive one-electron contributions. However, the orbital force in the sense of Eq. (10) is more closely related to Mulliken's criteria, stressing the effect of a single electron ionization on the binding characteristics. The difference between these binding criteria is an obvious consequence of the fact that $E_{\mathrm{HF}} \neq \sum n_i \varepsilon_i$. This difference was pointed out by Goscinski [11]. The values of n_i and ε_i' presented in Table 1 indicate that the two electron term is of major significance. Specifically, the values of f_i presented in Ref. [9] correspond to the orbitals $1\sigma_g$ and $1\sigma_u$ both turning from antibinding in the lower half of the second row diatomics (Li_2, B_2, C_2) into binding for N_2, O_2, F_2.

On the other hand, ε_i' characterizes both $1\sigma_g$ and $1\sigma_u$ as antibinding for all these molecules. The decrease in the antibinding nature of these orbitals beyond N_2 is an expected consequence of their contraction. A further interesting feature is that $2\sigma_g$ is more binding than $2\sigma_u$ is antibinding, and $1\pi_u$ is more binding than $1\pi_g$ is antibinding. This is also a consequence of the two electron term, as the comparison to the f_i values indicates. $3\sigma_g$ is binding on the basis of ε_i' and antibinding on the basis of f_i.

4.2. Relation between the ε_i' and ΔR_e Criteria

Denoting by $U(R)$ the potential curve of the diatomic molecule AB, and by $U_i(R)$ that of the molecular ion AB^+ with an electron missing in orbital i we have in Koopmans' approximation

$$U_i(R) = U(R) - \varepsilon_i(R); \qquad R_e^+ \equiv R_e + \Delta R_e$$

Expanding $U_i(R)$ about R_e we get

$$\begin{aligned} U_i(R_e + \Delta R) &= U(R_e + \Delta R) - \varepsilon_i(R_e + \Delta R) \\ &\simeq \{U(R_e) - \varepsilon_i(R_e)\} - \Delta R \cdot \varepsilon_i'(R_e) + (\Delta R)^2 \cdot \{U''(R_e) - \varepsilon_i''(R_e)\}/2 \end{aligned} \tag{12}$$

Hence, from $\partial U_i(R_e + \Delta R)/\partial \Delta R|_{\Delta R_e} = 0$ we get

$$\Delta R_e \simeq \varepsilon_i'(R_e)/\{U''(R_e) - \varepsilon_i''(R_e)\} \tag{13}$$

At least if ΔR_e is not too large, the positive curvature of $U_i(R)$ at R_e guarantees that ΔR_e and $\varepsilon_i'(R_e)$ have the same sign, so that the force and equilibrium distance criteria coincide. This is, perhaps, not surprising because they both reflect local properties of the chemical bond.

A comparison between values of ΔR_e computed from Eq. (13) and ΔSCF or experimental results is carried out in Table 2, indicating the validity of this relation even with respect to the characterization of $1\sigma_g$ as antibonding, in second row diatomics.

Table 2. Comparison of Koopmans' ΔR_e with accurate values

		ΔR_e (Koopmans')	ΔR_e
$1\sigma_g$	H_2	0.32	0.60[b]
	N_2	−0.07	−0.05[a]
$2\sigma_g$	Li_2	0.71	1.14[a]
$2\sigma_u$	N_2	−0.08	−0.04[b]
$1\pi_u$	N_2	0.12	0.15[b]
$3\sigma_g$	N_2	0.04	0.04[b]
$1\pi_g$	O_2	−0.27	−0.16[b]

[a] ΔSCF [Refs. 16, 17].

[b] Experimental [Refs. 18, 19].

4.3. *Relation between the ΔR_e and ΔD_e Criteria*

We shall show that the monotonicity of $\varepsilon(R)$ between $R = \min(R_e, R_e^+)$ and $R = \infty$ is a sufficient condition for the agreement between the ΔD_e and ΔR_e criteria.

In addition to notation already introduced we shall define

$$D_e \equiv U(\infty) - U(R_e)$$

and

$$D_e^+ \equiv U_i(\infty) - U_i(R_e^+)$$

Hence

$$\Delta D_e = D_e^+ - D_e = [U_i(\infty) - U(\infty)] - [U_i(R_e^+) - U(R_e)] = \\ -\varepsilon_i(\infty) - [U_i(R_e^+) - U(R_e)].$$

We now consider the two possibilities:

1) $\Delta R_e < 0$

By the result of the previous section $\varepsilon'(R_e) < 0$ so that from the monotonicity requirement it follows that

$$\varepsilon_i(\infty) - \varepsilon_i(R_e) < 0.$$

Furthermore,

$$U_i(R_e^+) - U(R_e) = [U_i(R_e) - U(R_e)] - [U_i(R_e) - U_i(R_e^+)] = -\varepsilon_i(R_e) - \Delta U_i$$

and, obviously, $\Delta U_i > 0$.

Hence,

$$\Delta D_e = -[\varepsilon_i(\infty) - \varepsilon_i(R_e)] + \Delta U_i,$$

which is certainly positive.

2) $\Delta R_e > 0$

In this case we shall write

$$U_i(R_e^+) - U(R_e) = [U(R_e^+) - \varepsilon_i(R_e^+)] - U(R_e) = \Delta U - \varepsilon_i(R_e^+)$$

Hence

$$\Delta D_e = [\varepsilon_i(R_e^+) - \varepsilon_i(\infty)] - \Delta U$$

Again, $\Delta U > 0$ and $\varepsilon_i'(R_e) > 0$ which, assuming $\varepsilon_i(R)$ to be a monotonic function of R implies $\varepsilon_i(R_e^+) - \varepsilon_i(\infty) < 0$. It follows that $\Delta D_e < 0$.

In conclusion, the only way that the thermochemical and the geometrical criteria can contradict one another is by a non-monotonicity in $\varepsilon_i(R)$.

A further complication can take place if the Hartree–Fock approximation does not approach the correct dissociation limit. In this case the local criteria such as ε_i' or ΔR_e are still valid and applicable within that approximation. However, the thermochemical criterion does not necessarily reflect the same type of behaviour simply because the argument of the present section becomes irrelevant.

5. Conclusions

Any attempt to partition the chemical bond into orbital contributions is an approximation and necessarily leads to difficulties of one kind or another. However, an important class of binding criteria has been shown to be interconsistent with respect to their interpretations of chemical behaviour. One or another of these criteria may be easiest to apply in a particular context; Spectroscopic studies provide ΔR_e values, Hartree–Fock computations provide orbital energies, and thermochemistry provides ΔD_e values. One would certainly like to know whether interpretations made on the basis of one of these criteria are commensurable with the others. These internal consistencies, important and useful as they may be, do not necessarily imply a fundamental superiority of this class of criteria.

The extension of the results presently discussed to polyatomic molecules requires consideration of some formal aspects, but seems largely feasible. In particular, the orbital force criterion is extended by replacing the orbital energy derivative with the appropriate gradient.

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