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MAGIC FORMULA, STRUCTURE OF BOND ENERGIES,

AND ISOVALENT HYBRIDIZATION[1,2]

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ABSTRACT

In order to give approximate quantitative form to the Slater-Pauling "criterion of maximum overlapping" of bond orbitals as a measure of bond strength, a "magic formula" is presented. It gives the energy of atomization D_0 of any molecule as a sum of terms of which the principal ones are functions of overlap integrals (available in tables based on theoretical computations), of atomic ionization potentials (obtainable from experimental data), and also of degree of hybridization in cases where the latter can occur without change of valence (isovalent hybridization). For satisfactory results, self-consistent-field-orbital overlap integrals appear to be needed.

A preliminary fitting to three molecules whose D_0 values are sufficiently well known yields a magic formula, containing three coefficients determined empirically by the fitting, which is suitable for molecules containing first-row atoms and hydrogen, and which fits the molecules CH, N_2, O_2, F_2, CH_4, C_2H_6, C_2H_4, C_2H_2, H_2^+, He_2^+,

within about ± 0.3 ev per bond (counting double and triple bonds as two and three bonds). The formula fitted to CH, whose D_0 value is reliably known, gives good agreement for CH_4 if the <u>highest</u> of the currently disputed values of the heat of sublimation of graphite is used. However, since the magic formula, both as to precise form and as to coefficients, is still in a somewhat preliminary stage, this agreement cannot be considered entirely conclusive.

In using the magic formula for molecules where there may be isovalent hybridization, a tentative D_0 is first computed and plotted as a function of degree of hybridization; the maximum of this curve is taken as giving the actual D_0. The actual degree of hybridization is obtained as a by-product. The results are similar to those indicated recently by several other methods; they point to very considerable amounts of isovalent hybridization in such molecules as CH, OH, H_2O, HCl, O_2, and N_2.

Especially interesting also is what the magic formula says about the <u>structure</u> of bond energies; that is, about the way in which a large number of theoretical terms, some bonding, some repulsive, add and subtract to give D_0. The general structure of the magic formula is adapted from VB (valence-bond) theory, but with functions of overlap integrals substituted for the bonded and most of the non-bonded electron-pair exchange terms of VB theory. The choice of the forms of these functions has been guided largely by LCAO molecular orbital theory, which thus is here grafted into the framework of VB theory. In the special case of two rare gas atoms, the magic formula reduces to a form suitable to represent the repulsions between them ($D_0 < 0$) as a function of their distance apart; it gives encouraging results for the case of two helium atoms. In general, it includes terms which should be able to represent the effect on D_0, as

a function of distances between nonbonded atoms, of steric repulsions between such atoms; but it is not yet quantitatively adapted to represent the variation of D_0 with the distances between bonded atoms; with respect to the latter, it is at present applicable only when they are at their equilibrium distances apart.

As compared with earlier, somewhat similar, VB theory analyses by Van Vleck, Penney, and others, the magic formula indicates much larger bonding and repulsive exchange terms, including strikingly large exchange repulsions by inner shells (here in agreement with earlier conclusions of James and of Pitzer). Some of the discrepancy may perhaps be removed by future improvement of the formula to include Coulomb terms explicitly, and possibly such a revised formula will give a better fit for such molecules as H_2 and Li_2, whose D_0 values are now poorly fitted. The magic formula shows that the π bonding terms in multiple bonds are much larger than is generally believed. For example, it appears that in the nitrogen molecule the net effect of all the σ electrons is strongly antibonding, but that the π bonding terms more than overcome this handicap and give the molecule its high stability. Another striking conclusion is that isovalent hybridization is often very important for molecular stability, operating by increasing bonding terms and simultaneously cutting down nonbonded repulsions. This conclusion is in harmony with recent work of Moffitt on CH, NH, and OH, and of Kotani and collaborators on H_2O, using conventional VB formulas and parameters. For N_2, the magic formula gives $D_0 = -0.04$ ev if one assumes no isovalent hybridization (i.e., pure p valence, s^2p^3), as compared with 8.32 ev for 21% s,p hybridization (i.e., 21% of sp^4 character).

With usually only a little arbitrariness, the terms in the magic formula for D_0 can be collected into groups, one for each bond

corresponding to the usual concept of <u>bond energies</u>. (Serber once did something similar using conventional VB theory and parameters.) In the case of multiple bonds, a division of their bond energies into σ and π parts can be made, but only with considerable arbitrariness. Gross and net bond energies (the concepts of which were introduced earlier by Van Vleck in terms of VB theory) are tabulated for several molecules. Gross bond energies (referred to atoms promoted to their appropriate valence states) are truer measures of intrinsic bond character; net bond energies are of more direct practical importance. Gross (or "intrinsic") bond energies should tend to be the more closely correlated with bond properties such as force constants and especially bond distances.

I. INTRODUCTION

Quantum mechanics gives a satisfactory qualitative explanation of the major facts of chemical valence, and is capable "in principle" of predicting all energy relations quantitatively. But because of mathematical difficulties, no such quantitative accounting has yet been attained. Slater and Pauling, in 1931, proposed as a rough measure of the strength of any covalent bond, formed by two electrons on adjacent atoms, the quantum-mechanical criterion of maximum overlapping of the orbitals (one-electron wave functions) occupied by these electrons. With the idea of implementing this criterion somewhat quantitatively, Mrs. C. A. Rieke and the writer before the war sought semi-empirical relations between overlap integrals and bond energies.[3] Recently the writer proposed a preliminary

[3] Some of the material in Sections II and III below was presented at a symposium in 1942, but only an Abstract was published: R. S. Mulliken and C. A. Rieke, Rev. Mod. Phys., 14, 159 (1942).

equation for this purpose.[4] An improved although still preliminary

[4] R. S. Mulliken, J. Am. Chem. Soc., 72, 4493 (1950), in particular Eqs. (8) and (9), footnote 14a, and Table X.

"magic formula"[5] is described below.

[5] J. Chem. Phys., 19, 900 (1951), Note added in proof.

In the history of valence theory, two main quantum-mechanical methods for describing molecular electronic structures have proved useful, namely the VB (valence-bond) method, and the MO (molecular orbital) method in its LCAO form. The magic formula has been

built in a general pattern indicated by the VB method, and in this respect is by no means entirely novel, but the specific forms of its details have been suggested largely by LCAO MO theory. The structure of the formula and the numerical values of the terms which appear in it are such, it is believed, as to afford increased insights into the nature of chemical binding or at least to provide helpful suggestions for further work. ¶ It should be emphasized that the magic formula in its present form and with the present values of its coefficients is still preliminary. And further, as compared with the hoped-for future development of really quantitative calculations of chemical binding energies, the attempt to construct a magic formula should probably be looked on as a stop-gap effort.

II. LCAO MO BACKGROUND OF MAGIC FORMULA

It is instructive to begin with a survey of LCAO MO energy expressions for the simple molecules H_2^+, H_2, He_2^+, He_2, for states involving occupation of the lowest-energy MO's $1\sigma_g$ and $1\sigma_u$; in LCAO approximation

$$1\sigma_g \approx (1s_a + 1s_b)/(2 + 2S)^{\frac{1}{2}} \; ; \; 1\sigma_u \approx (1s_a - 1s_b)/(2 - 2S)^{\frac{1}{2}}.$$

Here $1s_a$ and $1s_b$ are 1s AO's (atomic orbitals) on the two atoms a and b, and S is their overlap integral:

$$S \equiv \int 1s_a \, 1s_b \, dv.$$

For H_2^+, the energies of the ground state (one electron in $1\sigma_g$) and the first excited state (one electron in $1\sigma_u$) can be respectively expressed in the forms

$$E = E_H - (C^+ + E') \pm \beta/(1 \pm S). \tag{1}$$

Here E_H is the energy of a normal hydrogen atom,

$$c^+ = -e^2/R - \omega,$$

$$\beta = \uparrow - S\omega,$$

$$\omega = \int u_b \, 1s_a^2 \, dv \; ; \quad \uparrow = \int u_b \, 1s_a \, 1s_b \, dv.$$

(2)

R is the internuclear distance, and u_b is the potential due to nucleus b. It should be noted that ω, $\uparrow$, and β are all negative quantities. $-E'$ (which is included merely for bookkeeping purposes) is whatever energy is needed to correct the error of the LCAO approximation so as to make Eq. (1) exact. Resonance energy expressions of the type β are of central importance in ordinary LCAO theory.[6]

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[6] Combinations of the form of β of Eq. (2a) were introduced with the symbol Y by Mulliken, J. Chem. Phys., 3, 573 (1935), Eq. (15), and identified with Hückel's semi-empirical LCAO quantity β by Mulliken and Rieke, J. Am. Chem. Soc., 63, 44 and 1770 (1941).

Eq. (1) is obtained as follows.[7] As is well known,

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[7] For further details, see R. S. Mulliken, J. chimie physique, 46, 497 (1949). For H_2^+, see Eqs. (38)-(40) for $\uparrow$, ω, and β; Eq. (43) and Table II for dissociation energy equation and data. For H_2, see Eqs. (65) and (69) for ω and β (β is slightly different for H_2 than for H_2^+, but this is neglected in Eq. (5)); Eq. (77) and Table III for dissociation energy equation and data. For similar material on C_2H_2 and C_2H_4, see Tables V and VI.

$$E = e^2/R - E' + (\alpha \pm \chi)/(1 \pm S),$$

where

$$\alpha \equiv \int 1s_a \, h \, 1s_a \, dv \, , \qquad \gamma \equiv \int 1s_b \, h \, 1s_a \, dv,$$

h being the electronic Hamiltonian. On substituting

$$\beta \equiv \gamma - S\alpha \qquad (2a)$$

and

$$h = h_a + u_b,$$

h_a being the Hamiltonian for atom a alone, one readily obtains $\alpha = E_H + \omega$, $\beta = \gamma - S\omega$, and Eq. (1).

For the ground state of H_2^+, Eq. (1) gives for the dissociation energy D_e, equal to $E_H - E$,

$$D_e = (C^+ + E') - \beta/(1 + S). \qquad (3)$$

How it would be very pleasant if $C^+ + E'$ in Eq. (3) could be neglected and D_e put equal to the dominant resonance term $-\beta/(1 + S)$ alone. Actually, this procedure gives rather good results ($D_e = 2.79$ ev, $-\beta/(1 + S) = 2.22$ ev, by direct theoretical computation).[8,9]

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[8] The D_e value given is the experimental value corrected to no zero-point energy. Later in the paper, uncorrected D values (D_0 values) will be used. For H_2, $D_0 = 4.48$ ev.

[9] The theoretical C^+ is -0.74 ev, requiring $E' = 1.31$ ev. It is seen that a much better result is obtained by ignoring the Coulomb term C^+ of LCAO theory than by including it.

Similarly for H_2, where[7]

$$D_e = (C + E') - 2\beta/(1 + S), \qquad (4)$$

the theoretically computed resonance term $-2\beta/(1 + S)$ agrees rather well (4.07 ev) with the observed $\underline{D}_e$ (4.76 ev).[8,10] The results on

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[10] In Eq. (4),

$$\underline{c} = -e^2/R - 2\omega - \tfrac{1}{2}(J_{aa} + J_{ab}),$$

where $\underline{J}_{aa}$ and $\underline{J}_{ab}$ are as in Eq. (18). Here, just as for H_2^+, inclusion of $\underline{C}$ (computed value -1.55 ev) would only have worsened the agreement ($\underline{E}' = 2.24$ ev).

H_2 and H_2^+, reinforced by similar (though less reliable) evidence on π bonds in C_2H_2 and C_2H_4,[7] suggest that the resonance terms of LCAO theory may be used as a basis for a semi-empirical systematics of bond energies. One might now try to use $\underline{D}$ expressions of the form $A\beta/(1 + S)$, computing β theoretically for each type of bond. However, a different path will be followed here, on which the next step is to replace β by a function of $\underline{S}$.

The simplest reasonable choice is to put

$$-2\beta = ASI, \tag{5}$$

where $\underline{I}$ is the ionization energy for the appropriate valence AO. $\underline{A}$ is then a factor to be determined empirically so as to satisfy equations like (3) and (4), omitting terms like $\underline{C} + \underline{E}'$, as well as may be possible for a number of molecules simultaneously. This procedure gives for a one-electron bond and an electron-pair bond respectively.

$$D = \tfrac{1}{2}AIS/(1 + S) \; ; \tag{6}$$

$$D = AIS/(1 + S). \tag{7}$$

Rough proportionality of β to $\underline{S}$ is seen to be plausible if

one studies the forms of Υ, ω, and β in Eqs. (2). Among other things, the rough relation

$$\Upsilon \approx \tfrac{1}{2}S(\omega + \int u_a \, 1s_a^2 \, dv)$$

is involved. Also by direct computation in two instances, β has been found approximately proportional to $\underline{S}$. Namely, for 1s—1s binding i: H_2^+ or H_2, in ev, $-\beta \approx 7\underline{S}$ for $\underline{R} > 1\text{Å}$ (but at the equilibrium distance for H_2, $-\beta \approx 4.7\underline{S}$); and for $2p\pi$—$2p\pi$ binding as in C_2H_2 or C_2H_4, $-\beta$ $\approx 10\underline{S}$ (this is valid over a range of $\underline{R}$ extending to both sides of the equilibrium distances for these molecules).[11] These results suggest

[11] For further details, see R. S. Mulliken, J. chimie physique, 46, 675 (1949), Section 28.

the following conclusions, confirmed later in this paper: (1) $-\beta$ may usually be taken proportional to $\underline{S}$, but with a larger proportionality constant for π than for σ bonds; (2) but if $\underline{R}$ is unusually small (relative to AO size), $-\beta$ may become smaller (cf. Ref. 56 below).

Another instructive approach to Eqs. (6) and (7) is the following. Consider the charge density ρ for an electron in the MO $1\sigma_g$ in H_2^+. In LCAO approximation (cf. Eq. (1)), this is (in units of $-\underline{e}$)

$$\rho = (1\sigma_g)^2 \approx \tfrac{1}{2}(1s_a^2 + 1s_b^2)/(1 + S) + (1s_a \, 1s_b)/(1 + S).$$

As compared with the charge distribution $\tfrac{1}{2}(1s_a^2 + 1s_b)^2$, which would exist if the electron were distributed with equal probability between 1s AO's on the two nuclei, the above distribution represents a shift of a fraction $\int 1s_a \, 1s_b \, dv \,/(1 + S) = S/(1 + S)$ of the charge into the region of overlap between the two nuclei. Since, aside from the Coulomb term, which would correspond to the unshifted distribution

$1s_a^2 + 1s_b^2$), it is precisely this partial shift into the increased field in the overlap region which is primarily responsible for the stability of H_2^+, it is to be expected that $\underline{D}_e$ for the latter should be approximately proportional to $S/(1 + S)$.

The assumption of approximate proportionality of $-\beta$ to $\underline{I}$ is made plausible by the following reasoning. Molecule-formation viewed according to the VB method is a phenomenon which causes perturbations in the energies of the valence electrons of the participating atoms. Bond energy is then a measure of the extent of these perturbations. Other things being equal, the perturbation energy should be more or less proportional to (perhaps a nearly constant fraction of) the original energy of the valence electrons, for any one of which its binding energy $-\underline{I}$ is a measure. (See also Ref. 39 below.)

In the ground states of He_2^+ and He_2, there are two $1\sigma_g$, and respectively one or two $1\sigma_u$ electrons. The resonance contributions to $\underline{D}$ are $-\beta/(1 + S)$ for each $1\sigma_g$ and $+\beta/(1 - S)$ for each $1\sigma_u$ electron ($\underline{cf}$. Eqs. (1), (4), (5)). Putting $-2\beta = ASI$, one obtains for He_2^+ and He_2 respectively,

$$D = -\beta\left(\frac{2}{1+S} - \frac{1}{1-S}\right) = AI\left(\frac{S}{1+S} - \frac{\frac{1}{2}S}{1-S}\right) = \frac{1}{2}AIS(1 - 3S) ; \qquad (8)$$

$$D = -2\beta\left(\frac{1}{1+S} - \frac{1}{1-S}\right) = AI\left(\frac{S}{1+S} - \frac{S}{1-S}\right) = -2AIS^2/(1 - S^2) . \qquad (9)$$

Eq. (9) predicts $\underline{repulsion}$ for two He atoms, in agreement with VB theory. Eq. (8) for the three-electron bond indicates weaker bonding than for the one-electron bond.

In the process of generalizing Eqs. (7)-(9) to obtain a magic formula, as described later in this paper, it

was found necessary empirically to introduce a correction factor ν (of Eq. (23)) to temper somewhat repulsions like those of Eq. (9). Because of the largely empirical character of the final formulas, Eq. (9) may as well also be simplified by dropping the factor $1/(1 - S^2)$, which usually is not far from 1.[12] The result is:

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[12] At first, a different empirical modification of Eq. (9) was tried consisting in replacing the terms $S/(1 + S)$ and $S/(1 - S)$ by $S/(1 + aS)$ and $S/(1 - \beta S)$ respectively, and trying to determine a and b to give as good fits as possible to observed D values for H_2^+, H_2, He_2^+, He_2. A number of trial values of a and b were tested, mostly with $a > b > 0$, but finally it was concluded that the use of a form like Eq. (10) has better possibilities for fitting observed D's, besides being simpler.

$$He_2: \qquad D = AI\left(\frac{S}{1 + S} - \frac{\mu S}{1 - S}\right) = -2\nu AIS^2 , \qquad (10)$$

with ν near 0.7 (see later in this paper). Introduction of the factor μ into the antibonding term in the first form of Eq. (10) makes the two forms of Eq. (10) agree if

$$\left.\begin{aligned}
\mu &= \left[(1 - S)/(1 + S)\right] + 2\nu S(1 - S) \\
&= 1 - 2S(1 - S)(1 - \nu) + \ldots.
\end{aligned}\right\} \qquad (11)$$

If this factor μ is empirically needed in (10), use of the same factor in the antibonding term in (8) is indicated. Eq. (8) then becomes

$$He_2^+: \qquad \underline{D} = AI\left(\frac{S}{1 + S} - \frac{\frac{1}{2}\mu S}{1 - S}\right) = \frac{1}{2}AIS\left[(2 - \mu) - (2 + \mu)S\right] . \qquad (12)$$

This predicts a somewhat stronger three-electron bond than Eq. (8)

does.

Although Eqs. (6)-(9) above have been obtained by LCAO MO theory, it is well known that VB theory gives identically the same wave functions as LCAO theory for H_2^+, He_2^+, and He_2 in their ground states, the two theories differing only for H_2.[13] Hence, Eq. (6),

[13] This is readily verified by setting up the complete antisymmetrized VB and LCAO wave functions for each case in detail, including spins, and comparing. The statement is true, of course, only if $1s$ hydrogenic AO's with a single Z value are used in each case.

Eq. (8) or (12), and Eq. (9) or (10), may be considered to be based on either the VB or the LCAO approximation, only (7) being LCAO only. Since VB theory is tolerable for all values of R, all the equations but (7) should likewise be acceptable for all R values. Although the LCAO formula (7) will be used below as a basis for dealing with bonded attractions by the magic formula, it must be recognized that Eq. (7) cannot be valid outside a limited range of smaller R values near equilibrium. For larger R values, the corresponding VB formula must be given preference.

As has been shown previously,[4] Eq. (9) with $A = 0.65$ fits the curve of repulsion between two He atoms over a broad range of R. Eq. (10) with $\nu = 0.7$ and an increased A also gives a good fit.

In using Eqs. (6)-(12), the necessary S values can be looked up in existing tables.[14]

[14(a)] Mulliken, Rieke, Orloff, and Orloff, J. Chem. Phys., 17, 1248 (1949);

[(b)] R. S. Mulliken, ibid., 19, 900 (1951). The symbolism and nota- of Ref. 14b has been used in the present paper.

III. VALENCE-BOND THEORY BACKGROUND OF MAGIC FORMULA

In the VB method, each electron is first assigned to an AO on one atom. Electrons with unpaired opposite spins on adjacent atoms may then form electron-pair bonds. In the simplest example, H_2, the approximate energy of the $^1\Sigma_g^+$ ground state according to VB theory[15] is usually given in the form

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[15] See for example L. Pauling and E. Bright Wilson, Jr., Introduction to Quantum Mechanics, McGraw Hill, 1935, Section 42a.

$$E \approx \left(H_{11} + H_{12}\right)/(1 + S^2) \ . \tag{13}$$

In Eq. (13), H_{11} and H_{12} can be written in the form

$$H_{ij} = H_{ji} = \int \psi_j \left(H_{a1} + H_{b2} + H_{int}\right) \psi_i \ dv_1 \ dv_2 \ ,$$

where

$$\psi_1 \equiv 1s_a(1) \ 1s_b(2) \ ; \quad \psi_2 \equiv 1s_b(1) \ 1s_a(2) \ ,$$

$$H_{a1} = -\tfrac{1}{2}\hbar^2 \nabla_1^2/m - e^2/r_{a1} \ ; \quad H_{b2} = -\tfrac{1}{2}\hbar^2 \nabla_2^2/m - e^2/r_{b2} \ ,$$

and the interaction operator H_{int} is

$$H_{int} \equiv e^2/R + e^2/r_{12} - e^2/r_{b1} - e^2/r_{a2} \ .$$

Eq. (13) can be recast[16,17] to

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[16] The definition of η_i is constructed in analogy to that of the LCAO MO parameter β (cf. footnote 6). The quantity here called η (earlier--see footnote 3--called α) has also been used recently by van Dranen and Ketelaar: J. Chem. Phys., 18, 1125L (1950)-- their α'.

[17] The energy of the $^3\Sigma_u^+$ repulsive state is also given by Eqs. (13) and (14) if the plus signs are changed to minus signs.

$$E \simeq H_{11} + \eta/(1 + S^2) \, , \qquad \text{where } \eta \equiv H_{12} - S^2 H_{11} \, . \tag{14}$$

If a bookkeeping term $-E'$ is now added to the right of the first Eq. (14), such as to convert it from an approximate to an exact equality, and if then E is subtracted from $2E_H$, one obtains for the dissociation or bond energy

$$D_e = (C + E') - \eta/(1 + S^2) \, , \qquad \text{where } C \equiv 2E_H - H_{11} = -\int \psi_1 H_{int} \psi_1 \, dv \tag{15}$$

is the relatively small[15] "Coulomb" term.[18] The "exchange" term X,[18]

[18] In the customary terminology of atomic structure theory, intra-atomic repulsion integrals analogous in form to the interatomic (two-center) integrals J_{ab} and K_{ab} of Eq. (18) are called Coulomb and exchange integrals respectively, and it seems appropriate to use the same terminology for J_{ab} and K_{ab}. In VB theory, on the other hand, integrals $\int \psi_i H_{int} \psi_i \, dv$ and $\int \psi_1 H_{int} \psi_j \, dv$ are commonly called Coulomb and exchange integrals. In the following, expressions of the type $\eta/(1 + S^2)$ will be called "exchange terms" to signalize the fact that their dominant components are "exchange integrals" in the VB sense.

$$X \equiv -\eta/(1 + S^2) \, , \tag{1}$$

is the main term responsible for bonding.

The detailed structure[15] of $\underline{X}$ can be written in the form

$$X = -\left[2S\beta + (K_{ab} - S^2 J_{ab})\right] / (1 + S^2) . \tag{17}$$

Here β is the familiar resonance energy quantity of LCAO theory (cf Eqs. (2), (2a)), and[18] $\underline{K}_{ab}$ and $\underline{J}_{ab}$ are

$$
\left.
\begin{aligned}
K_{ab} &\equiv \iint 1s_a^{(1)} 1s_b^{(1)} \, e^2/r_{12} \, 1s_a^{(2)} 1s_b^{(2)} \, dv_1 \, dv_2 , \\
J_{ab} &\equiv \iint 1s_a^{(1)} 1s_a^{(1)} \, e^2/r_{12} \, 1s_b^{(2)} 1s_b^{(2)} \, dv_1 \, dv_2 .
\end{aligned}
\right\} \tag{18}
$$

The convenient and rather accurate approximation[19]

[19] R. S. Mulliken, Ref. 7, Eqs. (63).

$$K_{ab} \approx \tfrac{1}{2} S^2 (J_{aa} + J_{ab}) ,$$

where $\underline{J}_{aa}$ is an intratomic Coulomb integral defined analogously to $\underline{J}_{ab}$ in Eqs. (18), may now be introduced into Eq. (17). One then has

$$\underline{D}_e = (C + E') + X ; \quad \underline{X} \sim -\left[2S\beta + \tfrac{1}{2}S^2(J_{aa} - J_{ab})\right] / (1 + S^2) . \tag{19}$$

Usually[20] $\underline{X} > 0$, as a result of strong predominance of the positive

[20] Heisenberg's theory of ferromagnetism assumes $\underline{X} < 0$ for 3d—3d bonds between iron or similar atoms at metallic $\underline{R}$ values. Eq. (19) shows how $\underline{X} < 0$ might be possible in special cases.

term $-2S\beta$ (cf. Section II) over the negative term $-\tfrac{1}{2}S^2(J_{aa} - J_{ab})$. (Note that $\underline{J}_{aa} > \underline{J}_{ab}$ for $\underline{R} > 0$.)

It is now instructive to compare the VB expression (19) for $\underline{D}_e$ of H_2 with the corresponding LCAO expression of Eq. (4). Quantitative theoretical computations have of course been made[15] by both equations, with the result that (omitting the bookkeeping terms $\underline{E}'$)

the VB expression gives a somewhat better computed $\underline{D}_e$ than does the LCAO expression. However, if the primary bonding terms alone are used, that is, $-2\beta/(1 + S)$ of Eq. (4) and $\underline{X}$ of Eq. (19), Eq. (4) gives a surprisingly good $\underline{D}$ value, but Eq. (19) a poor $\underline{D}$ value.[21]

[21] This happens because of the terms $\underline{C}$, which have opposite effects in the two cases, making the computed $\underline{D}_e$ somewhat better in Eqs. (19), but much worse (cf. footnote 10) in Eq. (4). See sentence containing Eq. (4) for actual values of $\underline{D}_e$ and $-2\beta/(1 + S)$.

This points toward adoption of the procedure proposed in Section II, of approximating $\underline{D}$ semi-empirically by $-2\beta/(1 + S)$ with -2β replaced by $\underline{ASI}$ (cf. Eqs. (5), (7)).

Before continuing, it is of interest to compare further the primary bonding terms of Eqs. (4) and (19). It is seen that these both take the form of a <u>resonance energy expression</u>[22] -2β, modified

[22] By this is here meant (although the terminology is not very satisfactory) a term such as occurs for H_2^+, where removal of (electron-)exchange degeneracy is not involved. The fact that the "exchange energy" of VB theory owes its negative sign to a predominant term of "resonance" character was pointed out by the writer some time ago (<u>Chem</u>. <u>Rev</u>., <u>9</u>, 354 (1931)), but probably is not generally realized.

by a <u>factor</u> which is somewhat different in the two cases—and plus an added term in the case of Eq . (19). In Eq. (4), the factor is $1/(1 + S)$; in Eq. (19) it is $S/(1 + S^2)$. For a strong bond as in H_2, the difference is not great (for H_2, $1/(1 + S) = 0.57$, $S/(1 + S^2) = 0.48$), but for bonds with smaller $\underline{S}$ the VB factor leads to the prediction of much weaker bonding than does the LCAO factor; in the VB

case, the added term $\frac{1}{2}S^2(J_{aa} - J_{ab})$ acts to cut down the predicted $\underline{D}$ somewhat further. All in all, the slower variation of $\underline{D}$ with $\underline{S}$ indicated by LCAO theory seems to be in much better general agreement with observed bond energies than the more rapid variation suggested by VB theory.[23]

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[23] By reasoning similar to that used in Section II, the VB equation (19) with -2β put equal to $\underline{cSI}$ suggests the use of a semi-empirical form $AS^2I/(1 + S^2)$ for bond energies. Indeed, this fits the observed $\underline{D}$ values on the series H_2, Li_2, Na_2,...better than the form $ASI/(1 + S)$--but not very well. In other cases, the fit is not good. For example, it appears impossible with this form to escape from a computed $\underline{D} < 0$ for F_2, after necessary antibonding terms are included as described below (Eqs. (20) et seq.).

In view of the strongly empirical character of the search for a magic formula, a definite decision in favor of expressions of the form $ASI/(1 + S)$ for the energies of the bonding electrons of electron-pair bonds, rather than of any expression suggested by VB theory, seems now to be justified for the case of molecules with the distances between bonded atoms near their equilibrium values.

The preceding discussion must now be generalized to the many-electron, polyatomic, case. Here no exact general VB theory expression is available, but for molecules with all electrons paired at least in rough approximation,[24] conventional VB theory yields

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[24] Cf., e.g., Ref. 15, p. 376, recast in terms of quantities η and $\underline{X}$ instead of H_{12}. In Eq. (20), multiple exchange integrals and certain other complications have been ignored. It is here assumed that their effects can be taken care of sufficiently well.

along with those of the terms $\underline{C} + \underline{E}'$, by empirical adjustment of the coefficients in Eq. (21).

$$\underline{D} = (C + E') + \sum_{\text{bonds}} X_{ij} - \frac{1}{2}\sum_{\substack{\text{nonbonded} \\ \text{pairs}}} X_{kl} - P + RE . \tag{20}$$

In Eq. (20), each exchange term $\underline{X}$ is defined as in Eq. (16), $\underline{P}$ denotes promotion energy (see below), and $\underline{RE}$ refers to resonance energy if present. $\underline{D}$ is now the total energy required to dissociate the molecule (devoid of thermal energy, as at $0^\circ K$.) completely into atoms in their ground states (energy of atomization).

Eq. (20) contains one term of the type $\underline{X}_{ij}$ for each electron-pair bond in the predominant VB structure, and one term $-\frac{1}{2}\underline{X}_{kl}$ for every pair of electrons not on the same atom and not bonded to each other. For $\underline{X}_{ij}$'s, generalizing from the case of H_2, expressions of the form $ASI/(1 + S)$ will be adopted for the magic formula. The $\underline{X}_{kl}$'s may be classified in various ways. For present purposes, they may first be divided into the following two types: (1) homogeneous: those involving (as do also the $\underline{X}_{ij}$'s) two AO's of the same kind (both σ, or both π); (2) heterogeneous: those involving orbitals of different kinds (one σ, one π; or one π^+, one π^-, or one π_x, one π_y).[25] For type (2) $\underline{X}_{kl}$'s, $\underline{S} = 0$, and Eq. (17) shows that these

[25] Among σ orbitals are $\underline{ns}$, $\underline{np\sigma}$, $\underline{nd\sigma}$, and hybrids of these. The most usual π orbitals, and the only ones considered in the present paper, are $\underline{np\pi}$.

reduce to the relatively simple exchange integrals $\underline{K}_{kl}$ (cf. Eqs. (18)); the notation $\underline{K}_{kl}$ will therefore be used hereafter for the type (2) $\underline{X}_{kl}$'s. The type (1) $\underline{X}_{kl}$'s, on the other hand, should according

to VB theory be of the same structure as the X_{ij}'s (cf. Eq. (17))! However, LCAO MO theory indicates a different structure for the X_{ij}'s and X_{kl}'s, as can be seen by considering the cases of H_2 and He_2 as special cases of Eq. (21), and comparing with Eqs. (4) and (9), respectively:

$$H_2(VB): D = (C + E') + X_{1s,1s} \; ; \quad (LCAO): D = (C + E') - 2\beta/(1 + S) \; .$$

$$He_2(VB): D = (C + E') - 2X_{1s,1s} \; ; \quad (LCAO): D = (C + E') + 4\beta S \; .$$

In the one case, X corresponds to $-2\beta/(1 + S)$, in the other to $-2\beta S$ a difference of a factor $S(1 + S)$. Since it has already been decided to follow the lead of LCAO theory for the X_{ij}'s, it will make for clarity to adopt at this point a distinctive notation for the two kinds of X's. Accordingly, the X_{ij}'s will still be called X_{ij}'s but the X_{kl}'s will hereafter be called Y_{kl}'s.

Eq. (20) is now ready to be recast to form a basis for the magic formula. For this purpose, (a) the term $(C + E')$ will be considered as absorbed into the other terms (primarily into the X_{ij}'s); (b) the homogeneous X_{kl}'s will be called Y_{kl}'s; (c) the heterogeneous X_{kl}'s, times -1, will be called K_{mn}'s; (d) for D, the value D_0 uncorrected for zero-point vibrational energy will be used, since this will be more convenient than a corrected value D_e, and in view of the rough and largely empirical character of the magic formula;[26] (e) the

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[26] Fitted to D_0 values, Eq. (21) can of course reproduce D_0 for only one isotope of a molecule, but the variations of D_0 between isotopes are always less than the uncertainty involved in the roughness of the formula as at present constituted.

X's and Y's will from here on be considered as semi-empirical

quantities, to be so adjusted as to reproduce as nearly as possible the exact $\underline{D}_0$ values of actual molecules. Eq. (20) now takes the form

$$D_0 = \sum_{\text{bonds}} X_{ij} - \tfrac{1}{2}\sum Y_{kl} + \tfrac{1}{2}\sum K_{mn} - P + RE \, . \qquad (21)$$
$$\text{bonds} \qquad \text{nonbonded pairs}$$

The quantities on the right of Eq. (21) have been so defined that every letter symbol now stands for an intrinsically positive quantity, with possible rare exceptions for the $\underline{X}$'s.[20]

IV. MAGIC FORMULA

For molecules in their ground states with all electrons paired, Eq. (21), taken together with semi-empirical "magic" expressions for the $\underline{X}$ and $\underline{Y}$ terms as functions of corresponding $\underline{S}$'s, now constitutes the magic formula. For the $\underline{X}_{ij}$'s, as already decided above, LCAO-based expressions

$$X_{ij} = A_i \, S_{ij} \, \bar{I}_{ij} \, /(1 + S_{ij}) \, , \qquad (22)$$

of the form of Eq. (7), are to be used. Here the $\underline{A}$'s are coefficients to be adjusted empirically, and the $\bar{I}$'s are suitable mean ionization energies (see below). For the most useful formula, the number of different $\underline{A}$'s should be kept to a minimum. By trial and error, it was found in the cases tested (see below) that a single $\underline{A}$, which may be called $\underline{A}_\sigma$, will serve for nearly all σ electron pairs, and another, $\underline{A}_\pi$, for all π pairs. The $\underline{S}_{ij}$'s are to be computed theoretically.

Before deciding on a magic form for the $\underline{Y}_{kl}$'s, it may be noted that they are of three kinds: (a) lone-pair:lone-pair $\underline{Y}_{kl}$'s; (b) lone-pair:bonded-electron $\underline{Y}_{kl}$'s; (c) $\underline{Y}_{kl}$'s between electrons in different bonds.[27] For the first of these kinds, at least for like

[27] It may be noted in passing that the K_{mn}'s can be classified in
the same way into three kinds.

lono pairs in the homopolar case,[28] LCAO and VB theory coincide (cf.

[28] With reference to heteropolar lone-pair:lone-pair repulsions in
LCAO theory, if one sets up an LCAO wave function for the arti-
ficial case of the interaction of a $1s)^2$ shell on one atom with
a $2s)^2$ shell on another, one finds an expression for the inter-
action energy which is roughly proportional to S^2, just as (cf.
Eq. (19)) by VB theory.

Section II), and the LCAO Eq. (9) may reasonably be adopted as proto-
type for a suitable magic form. It will now be assumed, this time
following VB theory, that the same type of expression is equally
valid for all kinds of Y_{kl}'s.[29]

[29] In general, nonbonded repulsions appear in a very different guise
in LCAO theory from that in VB theory: see R. S. Mullikon, _J.
Chem. Phys._, _19_, 912 (1951), where it is pointed out that direct
antibonding effects and "forced hybridization" effects in LCAO
theory apparently constitute the respective analogues of the
lono-pair:lone-pair and the other kinds of nonbonded repulsions
of VB theory.

However, trial and error studies suggest one modification
(already discussed in connection with Eqs. (9)-(12) in Section II),
leading to the magic form

$$Y_{kl} = \nu A_k S_{kl}^{\,2} \bar{I}_{kl} \, .$$

(23)

This form will be adopted and used from here on.[12] The effect of the factor y, for which values somewhat less than 1 were found to give the best fit to observed D_0's, is to diminish somewhat the importance of the nonbonded repulsions.[30]

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[30] This seems not unreasonable. The flexibility introduced by the adjustable A's takes care roughly of the various errors involved in the use of the simple approximation (22) for the bonding terms; in particular, the effect of the bonding parts of the omitted terms $C + E'$ of Eq. (20). The factor y then gives in the simplest way some further flexibility in representing the nonbonded repulsions. Earlier workers (cf., e.g., H. M. James, J. Chem. Phys., 2, 794 (1934)) have also felt that VB theory predicts somewhat too large nonbonded repulsions as well as too small bonded attractions.

Further explanation is now needed as to how to obtain values for certain quantities appearing in Eqs. (21)-(23). The K's (cf. Eq. (18)) of Eq. (21) are to be obtained theoretically. Fortunately, they are relatively small, so that rough estimates are adequate for the present discussion.[31]

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[31] Formulas for computing the K's involving $1s$, $2s$, and $2p$ Slater-type AO's are given in a paper by K. Rüdenberg, J. Chem. Phys., 19, 000 (1951). For the present paper, a rough procedure was used, whereby SCF-AO K's for N_2, O_2, F_2, and CH were estimated from related Slater-AO K's given for $C\!=\!O$ bonds in CO_2 by J. F. Mulligan, J. Chem. Phys., 19, 347 (1951). Taking $K_{\pi_0 s_C}$ and $K_{\pi_C s_O}$ as an example, their average (0.37 ev) may be taken as characteristic for $C\!=\!O$ and used as a basis to estimate $K_{\pi's}$ for N_2, O_2.

and F_2. In a similar way, values for $K_{\pi\sigma}$ (0.56 ev) and $K_{\pi'\pi'}$ (0.041 ev) for $C = O$ were obtained, whereas $K_{\pi,1s}$ was found negligible. To estimate $\underline{K}$ values for N_2, O_2, and F_2, it was assumed that they differ from those for $C = O$ in the ratios of the squares of the overlap integrals S_{ss}, $S_{s\sigma}$, and $S_{\pi\pi}$ for $K_{\pi s}$, $K_{\pi\sigma}$, and $K_{\pi'\pi'}$, respectively. The integral $K_{s\pi,\sigma\pi}$ was treated similarly. Since in the present paper, $\underline{X}$'s, $\underline{Y}$'s, and $\underline{K}$'s corresponding to SCF AO's are desired, the squares of ratios of estimated (cf. footnote 42) SCF-AO $\underline{S}$'s for N_2, O_2, and F_2 to Slater-AO $\underline{S}$'s for $C = O$ were used. The same sort of procedure was used also for $C\!-\!C$, $C\!=\!C$, and $C\equiv C$ bonds. To estimate the CH integral $K_{\pi h}$ (between $2p\pi_C$ and $1s_H$), the Mulligan $K_{\pi s}$ for $C = O$ (0.37 ev) was multiplied by the square of the ratio of $\underline{S}^{SCF}_{(2s_C, 1s_H)}$ to $\underline{S}^{Slater}_{(2s_C, 2s_O)}$, giving 0.68 ev.

The promotion energy $\underline{P}$ in Eq. (21) occurs because without it Eq. (21) would in general be valid only for dissociation into certain hypothetical atomic states, with the valence-electron spins completely unpaired, called "valence states".[32] Since valence states in

[32] See footnote 14 of reference given in footnote 4.

general have higher energies than atomic ground states, the quantity $\underline{P}$, equal to the sum $\sum \underline{P}_n$ of the valence-state promotional energies taken over all the atoms involved, must be subtracted in Eq. (21) in order to give the desired $\underline{D}_0$, which has been defined to correspond to dissociation into atoms in their ground states. For the special case of $\underline{s}$-univalent atoms (H, Li, etc.), ground and valence states are identical ($\underline{P}_n = 0$).

Often $\underline{P}_n$ may involve no __configurational__ excitation. For

example, to obtain trivalent nitrogen, one must "promote" the atom from its s^2p^3, ^4S_u ground state, where the spins of the three p electrons are all parallel, to a trivalent valence state V_3 of the same s^2p^3 configuration. There is required a promotion energy of 1.70 ev. This kind of promotion might be called advalent promotion, that is, intraconfigurational promotion from ground state to a valence state.

Trivalent nitrogen gives stronger bonding, however, if there is partial further promotion toward the trivalent valence state of the configuration sp^4; that is, s^2p^3, $^4S_u \rightarrow s^2p^3$, $V_3 \rightarrow$ (partially) sp^4, V_3. This second kind of promotion, extraconfigurational but without change of valence, and only partial, corresponds to a kind of s,p hybridization which Moffitt[33] has called second-order hybridiza-

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[33] W. Moffitt, Proc. Roy. Soc., 202A, 534 (1950); and further reference to Moffitt in Appendix II below.

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tion. These effects might more descriptively be called isovalent promotion and isovalent hybridization.

Other cases occur in which extraconfigurational and complete promotion is accompanied by increase in valence: say, pluvalent promotion and pluvalent hybridization. Thus for carbon, only advalent promotion (s^2p^2, ^3P_g to s^2p^2, V_2) is required for bivalency, but for tetravalent carbon, pluvalent promotion to sp^3, V_4 or to a related hybrid V_4 state is required (these tetravalent valence states, incidentally, are very considerably higher in energy than the lowest state, ^5S_u, of sp^3). Similarly for bivalent beryllium, pluvalent promotion is required from nullvalent s^2, V_0 (same as s^2, ^1S_g) to sp, V_2 (lying between sp, ^3P_u and sp, ^1P_u).

Valence-state promotion energies are obtainable from spectroscopic data on atoms.[34] Table VIII in Appendix I contains

[34] R. S. Mulliken, *J. Chem. Phys.*, 2, 782 (1934).

illustrative values for several first-row atoms in valence states suitable for use in linear molecules.[35] Table IX in Appendix I con-

[35] See also footnote 33.

tains additional valence-state promotion energies, suitable for tetra-valent carbon in molecules of several types of symmetry. Use will be made of Tables VIII and IX later in this paper.

The resonance energy $\underline{RE}$ in Eq. (21) refers first of all to resonance energy in the usual sense, as for example in benzene.[36]

[36] If the term "resonance energy" is used in a strict sense, some resonance energy is present for nearly all molecules, since in general numerous "excited" and "ionic" VB structures mix to some extent into the usual single predominant ground-state structure. However, the corresponding numerous small "normal" resonance terms are covered (as part of the $\underline{C} + \underline{E}'$ term in Eq. (20)) in the empirical adjustment of the $\underline{A}$'s and perhaps especially ν in Eqs. (22) and (23). Hence, $\underline{RE}$ in Eq. (21) corresponds only to "excess" resonance energy above normal, which is really what is usually meant by the term "resonance energy".

But it may sometimes include further terms. In particular, when one uses Eq. (21) for carbon compounds in which tetravalent carbon is as-sumed, with $\underline{P}_n$ values from Table IX, one underestimates $\underline{D}$. As Voge has shown,[37] methane is about 1.3 ev more stable because the carbon

[37] H. H. Voge, *J. Chem. Phys.*, 4, 581 (1936); 16, 984 (1948).

is very considerably more in the s^2p^2 condition than if it were purely tetravalent with tetrahedral AO's. This difference may be regarded in connection with Eq. (21) as _demotional_ resonance energy, to be added as part of the RE term after the bond energy has been obtained for pure tetrahedral valence.

For any molecule with polar bonds, a _polar_ RE term must be included in Eq. (21). These polar RE values would presumably be of the same orders of magnitude as the observed deviations from additivity of bond energies for heteropolar bonds, used by Pauling in setting up his electronegativity scale.[38]

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[38] See, _e.g._, L. Pauling, The Nature of the Chemical Bond (Cornell University Press: Ithaca, 1940).

A procedure is now needed for obtaining the mean I values in Eqs. (22) and (23). On the basis of rough theoretical considerations[39,40] and of simplicity and empirical acceptability, each $\bar{I}$ is

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[39] Referring to Eqs. (2) for the case of homopolar bonding, it is seen that insofar as T is its major term, the quantity β is the potential energy of a charge of magnitude S, located in the overlap region, in a field of potential u_b. If then -2β is put equal to $AS\bar{I}$ (Eq. (5)), the $\bar{I}$ used should be so chosen as to be a measure of the magnitude of u_b in the overlap region. But since u_b in this region depends on _all_ the electrons in the outer shell, an $\bar{I}$ averaged over the latter is suitable (Rule (1) for $\bar{I}$). A similar analysis for the heteropolar case (_cf._ Ref. 7, Section 15-16), leads again to Rule (1), _plus_ Rule (2). The foregoing arguments are directly applicable to the bonding terms X_{ij} in Eq. (21) and to Y_{kl} repulsions between like lone pairs (_cf._ Eqs. (8), (9)). It is here _assumed_ that the same kind of argument based

on tho form of β in Eq. (2) can be extended to <u>all Y_{kl}</u> terms.

40 The application of Rule (<u>2</u>) to AO pairs differing greatly in $\underline{I}$ deserves further discussion. Consider for example $\underline{Y}_{1s,2s}$ between the <u>1s</u> lone pair of carbon and the <u>2s</u> lone pair of fluorine in CF_4. The overlap integral is small but not negligible. Most of tho overlap occurs in tho region where <u>1s</u> of carbon is strong. The potential in which the overlap charge finds itself is then nearly the same as for a <u>1s</u> carbon AO, suggesting that $\underline{I}$ for <u>1s</u> carbon should be used. Rule (<u>2</u>), which calls for the arithmetic mean of this and $\underline{I}$ of tho outer shell of fluorine, is a compro- mise between this and the use of a smaller $\overline{\underline{I}}$ such as for example a geometric mean. Considerable support for Rule (<u>2</u>) for inner- shell:outer-shell $\underline{Y}_{kl}$'s is afforded by tho magnitudes of $\underline{K}_{mn}$'s as estimated theoretically (<u>cf</u>. J. F. Mulligan, <u>J. Chem. Phys.</u>, <u>19</u>, 347 (1951)). That inner-shell:outer-shell repulsions are very large is shown also by the work of H. M. James, <u>J. Chem. Phys.</u>, <u>2</u>, 794 (1934), on Li_2. Also, a direct estimate by the writer of $\underline{Y}_{1s,2s}$ for Li_2 gives a result in close agreement with the magic formula expression Eqs. (23) with $\underline{A} = 1.16$, $\nu = 0.7$.

to be obtained by averaging (<u>1</u>) intratomically, for each AO, over (<u>valence-state</u>) $\underline{I}$ values, obtained from spectroscopic data,[34] for all electrons in the same valence shell as tho given AO; (<u>2</u>) then interatomically.[40,41]

41 What is meant by Rule (<u>1</u>) should be clear from footnotes <u>d</u> of Table VIII and <u>b</u> of Table IX. As an example of Rule (<u>2</u>), $\overline{\underline{I}}_{1s_a 2s_b}$ would be $\frac{1}{2}(I_{1s_a} + \overline{I}_{(n\,=\,2)b})$.

Tho $\underline{S}$'s in Eqs. (22)-(23) may be taken from theoretically-

computed tables.[14] Extensive trials were made first using $\underline{S}$'s based
on Slater AO's, and then on SCF AO's. The latter should of course
be more accurate, and after numerous trials it was tentatively con-
cluded that they must be used, and they have been used below,[42] al-

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[42] Actually, SCF $\underline{S}$'s have been published only for C—C and C—H
bonds (cf. footnote 14b). In the work below, they were estimated
in the following way for N≡N, O=O, and F—F bonds. From the
Slater μ value for N, O, or F, together with the equilibrium $\underline{R}$
value, a Slater ρ value (cf. Ref. 14a, Table I and Eq. (12)) was
determined. The $\underline{S}$ value corresponding to this ρ was then looked
up in a table of SCF $\underline{S}$'s for carbon-carbon bonds. This was done
for $\underline{S}(1\underline{s},2\underline{p}\sigma)$ using Table IX of Ref. 14b, and for $\underline{S}(2\underline{s},2\underline{p}\sigma)$,
$\underline{S}(2\underline{p}\sigma,2\underline{p}\sigma)$, and $\underline{S}(2\underline{p}\pi,2\underline{p}\pi)$ using Table VI of Ref. 14b. Hybrid
$\underline{S}$'s, $S(1\underline{s},\beta)$, $\underline{S}(\beta,\beta)$, and $\underline{S}(\beta,O\beta)$ were then computed using Eqs.
(2), (4), (6) of Ref. 14b. [Accurate analytical expressions for
1$\underline{s}$, 2$\underline{s}$, and 2$\underline{p}$ SCF AO's of C, N, O, and (by extrapolation) F have
recently been determined by Dr. P.-O. Löwdin, and will soon be
published. Direct computation of $\underline{S}$'s for N_2 and O_2 using these
expressions, by Mr. C. W. Scherr in this Laboratory, gives values
in satisfactory agreement with those obtained in the manner de-
scribed above. Details will be published later.]

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though it had been hoped at first that the much simpler Slater $\underline{S}$'s
would give acceptable results.

Since most of the terms in Eq. (21), likewise the $\underline{S}$'s in
Eqs. (22)-(23), depend on $\underline{R}$ values, it needs to be emphasized that
Eqs. (21)-(23) are intended here to be used primarily for molecules
with their bonds at equilibrium lengths; and the $\underline{S}$ values are to be
computed, and the $\underline{A}$ values and ν determined, to fit this situation.

However, the possibility that Eqs. (21)-(23) can be extended or adapted to reproduce interatomic potential curves over considerable ranges of bond distances may well deserve exploration.[43,44] Moreover,

[43] Note that in general Eqs. (21)-(23) are capable of giving a minimum of energy (maximum D_0) as a function of the bond distances, though only if important Y_{kl} terms are present--not, for example, for H_2. To make the single term $ASI/(1 + S)$ give a maximum D for H_2, one would have to make A a suitable function of distance.

[44] In fact, calculations with a preliminary form of the magic formula, as applied to $N \equiv N$, $N = N$, $N - N$, etc., show that it gives maximum values for D, calculated and plotted as a function of R, at R values very roughly equal to the observed equilibrium values.

it is to be noted that the nonbonded repulsion (Eq. (23)) and attraction terms, the Y's and K's, are not limited in their validity to any particular range of R values. Thus they should be capable as they stand of representing closed-shell interactions and the repulsion potentials of steric hindrance for varying configurations of nonbonded atoms (here see last paragraphs of Section II and Ref. 4).[45]

[45] Computations on the variations of exchange energies with bond angle, and their effect on bending vibration frequencies, have been made by various authors using VB theory: e.g., J. H. Van Vleck and P. C. Cross, J. Chem. Phys., 1, 357 (1934); footnote 55 of the present paper; and other more recent articles.

V. MAGIC FORMULA FOR SPECIAL CASES

The magic formula Eqs. (21)-(23) is applicable for molecules in their ground states with all electrons paired. It can, however, easily be modified to include several other cases.

Odd-electron molecules involving what Pauling calls one-electron or three-electron bonds are easily included by using Eq. (6) for the former and Eqs. (11)-(12) for the latter instead of Eq. (22), just as in the prototype cases of H_2^+ and He_2^+ for which these equations were developed. Various molecule-ions (e.g., N_2^+, O_2^+) fall under this case.

For radicals containing unused valence electrons, e.g., CH or NH, Eqs. (21)-(23) can be used directly, although some care may be needed in determining what valence states and P values are required.

The case of O_2 is somewhat special, but is most easily treated by computing D_0 for the first excited $(^1\Delta_g)$ state, to which Eqs. (21)-(23) are directly applicable, then correcting to the $^3\Sigma_g^-$ ground state.

For excited states, LCAO theory (Section II) may often be used as a guide in setting up a magic formula.

VI. DETERMINATION OF A'S AND ν IN MAGIC FORMULA; AND OF DEGREES OF HYBRIDIZATION

In order to give empirical reality to the magic formula, Eqs. (21)-(23), values of A and ν must first be determined so as to make it fit a few molecules whose D_0 values are reliably known. Predicted D_0 values obtained from the resulting formula can then be checked against empirical D_0 values for additional molecules.

After considerable preliminary exploration, the following plan was adopted for the first step in this procedure. First it was decided to try to get along with only three empirical parameters: A_σ (for all σ bonds and σ-σ nonbonded repulsions), A_π (for all π bonds and π-π nonbonded repulsions), and ν. This plan required a fitting to at least three representative molecules whose D_0 values

are reliably known. For this purpose, the molecules CH, O_2, N_2, and F_2 were selected, the first two to be fitted exactly, the last two as well as possible.

For the CH radical, the value D_0 = 3.47 ev is known with a high degree of probability, although there may be a very slight possibility that it is 0.1-0.3 ev higher (not more).[46] For O_2, the

[46] The value 3.47 ev for the $^2\Pi$ ground state of CH (and 3.52 ev for CD) was determined from predissociation in the v = 0 and 1 levels of the $^2\Sigma$ excited state by T. Shidei, Jap. J. Phys., 11, 23 (1936), and confirmed by others. This value is accepted by Herzberg (cf. footnote 47) and by Gaydon. On the other hand, by a Birge-Sponer extrapolation of the vibrational levels of the $^2\Sigma$ state, one obtains 3.70 ev as a probable upper limit to D_0. (That the $^2\Pi$ is the ground state is shown by the occurrence of absorption from it in interstellar space.)

value D_0 = 5.08 ev (within about 0.01 ev) is certain.[47]

[47] Cf. G. Herzberg, Spectra of Diatomic Molecules, Second Edition, D. Van Nostrand, Inc., 1950.

For F_2, there has been some uncertainty about D_0, but there is scarcely any doubt that it is in or close to the range 1.6 ± 0.3 ev.[48] For N_2, there is perhaps some doubt as to whether D_0 is 7.37

[48] R. N. Doescher, J. Chem. Phys., 19, 1070 (1951), and references given there. Evans, Warhurst, and Whittle, J. Chem. Soc., 1524 (1950). H. J. Schumacher, Chem. Abstracts, 45, 2300[b] (1951).

ev or 9.76 ev, but the evidence is decidedly in favor of the second of these values, and all other values seem to be definitely excluded.

[49] Cf. G. B. Kistiakowsky, _J. Am. Chem. Soc._, 73, 2972 (1951); A. E. Douglas and G. Herzberg, _Can. J. Phys._, 29, 294 (1951). The latter work definitely eliminates all values but 7.38 ev and 9.76 ev; the former work seems to be incompatible with the smaller value. Considerations on the nature of active nitrogen advanced by G. Cario and L. H. Reinecke, _Abh. Braunschw. Wiss. Gesell._, 1, 8-13 (1949), also strongly favor 9.76 ev. But in favor of 7.38 ev, see H. D. Hagstrum, _Rev. Mod. Phys._, 23, 185 (1951).

The magic formula for CH involves only $\underline{A}_\sigma$ and ν; for the other three molecules, it also involves $\underline{A}_\pi$. It is convenient then to begin with CH, determining $\underline{A}_\sigma$ for each of several assumed ν values; that is, $\underline{A}_\sigma$ as a function of ν. Then assuming the same $\underline{A}_\sigma(\nu)$ for O_2, $\underline{A}_\pi(\nu)$ is determined. Using $\underline{A}_\sigma(\nu)$ and $\underline{A}_\pi(\nu)$, $\underline{D}_0$ is computed as a function of ν for N_2 and for F_2,[23] and compared with the empirical $\underline{D}_0$ values to obtain a best-compromise ν.

A very interesting by-product of the process of determining $\underline{A}_\sigma$, $\underline{A}_\pi$, and ν is that at the same time the degree of $\underline{s},\underline{p}\sigma$ hybridization α^2 in each of the molecules used must and (to the extent that the magic formula is correct in structure) can be determined (see Sections VII-IX, in particular, Fig. I for CH, and its caption).

VII. THE FITTING FOR THE CH RADICAL

The VB electron configuration for CH may be written[14b]

$$k)^2 \; h_{\sigma\beta})^2 \; h_\beta \cdot h) \; \pi) \;,$$

where all the AO's but $\underline{h}$ are carbon atom AO's; $\underline{h}_\beta$ and $\underline{h}_{\sigma\beta}$ are mutually orthogonal $2\underline{s},2\underline{p}\sigma$ hybrids of the forms

$$h_\beta = \alpha s + \beta p\sigma ; \quad h_{o\beta} = \beta s - \alpha p\sigma , \tag{24}$$

where $\alpha > 0$, $\beta > 0$ (thus making $\underset{\beta}{h}$ overlap $\underline{h}$ more strongly than if $\beta = 0$), with $\alpha^2 + \beta^2 = 1$. The magic formula Eq. (21) becomes:

$$D_0 = X_{\beta h} - Y_{kh} - Y_{o\beta,h} + \tfrac{1}{2}K_{hh} - P \tag{25}$$

if $\underline{RE}$ is assumed negligible.[50] In each subscript, the first symbol

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[50] If the C—H bond were strongly polar, there would be an appreciable $\underline{RE}$. To estimate the polarity, one needs the relative electronegativity of C and H for an $\underset{\beta}{h}$—$1\underline{s}$ bond. As was pointed out some time ago (cf. footnote 34), the electronegativity of carbon depends strongly on the degree of $\underline{s},\underline{p}$ hybridization α^2 in the carbon bond orbital. As it happens, α^2 as deduced below for $\underset{\beta}{h}$ in CH (cf. Table I) is such that carbon $\underset{\beta}{h}$ and hydrogen $1\underline{s}$ are almost equally electronegative. Thus the assumption $\underline{RE} = 0$ is justified.

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refers to the carbon AO, the second to $1\underline{s}_H$. It can be shown (see Appendix II) that $\underline{P}$ is given by $P_0 + \alpha^2\Delta P$, and $\underline{P}_0$ and ΔP have the meaning and numerical values given in Table VIII. Next making use of Eqs (22)-(23), Eq. (25) becomes

$$3.47 = D_0 = A_\sigma\left\{ 14.24\, S_{\beta h}/(1 + S_{\beta h}) - 151\nu S^2_{kh} - 14.24\nu\, S^2_{o\beta,h} \right\}$$
$$-\alpha^2\Delta P + (\tfrac{1}{2}K_{hh} - P_0) . \tag{26}$$

The numbers 14.24 and 151 are average $\underline{I}$ values as required, being respectively $\tfrac{1}{2}(\overline{I}_L + \underline{I}_H)$ and $\tfrac{1}{2}(\underline{I}_K + \underline{I}_H)$, where $\overline{I}_L$ and $\underline{I}_K$ refer to carbon and are taken from Table VIII, and $\underline{I}_H = 13.60$ ev.

Since ν cannot yet be determined, trials were made for each of the four assumed ν values 1.0, 0.85, 0.70, and 0.55. The right

side of Eq. (26) is a sum of three groups of terms: first, $\underline{A}_\sigma\left\{\cdots\right\}$, which, with ν assumed fixed, depends on two adjustable quantities, namely $\underline{A}_\sigma$ and α^2; second, $-\alpha^2\underline{\Delta P}$, which is a constant times α^2; third, $(\frac{1}{2}\underline{K}_{Nh} - \underline{P}_0)$, a constant. For each assumed value of ν, values of $\underline{A}_\sigma$ and α satisfying Eq. (26) were simultaneously determined by a graphical procedure described in the caption of Figure I. The necessary $\underline{S}$ values, for any α value, were first looked up in published tables.[51]

51 $\underline{L.c.}$, Ref. 14b, Table XI (SCF values) for $\underline{S}_{\beta h}$ and $\underline{S}_{o\beta,h}$ (positive hybrids for $\underline{S}_{\beta h}$, negative hybrids for $\underline{S}_{o\beta,h}$); Ref. 14a, Table IV, for $\underline{S}_{kh}$ values.

$\underline{P}_0$ and $\underline{\Delta P}$ were taken from Table VII, and $\underline{K}_{Nh}$ was taken as 0.8 ev.[52]

52 J. R. Stehn, $\underline{J}$. $\underline{Chem}$. $\underline{Phys}$., $\underline{5}$, 186 (1937), and G. W. King, $\underline{ibid}$., $\underline{6}$, 378 (1938), applied VB theory in instructive studies of CH, NH, OH, and FH. Using atomic and molecular spectroscopic data, they obtained empirical values for various exchange and Coulomb energies. However, they made assumptions (including neglect of inner-shell nonbonded repulsions, and no hybridization), which in the light of the present work render very questionable the meanings of the numerical values they obtained. However, their value of 0.8 ev for $\underline{K}_{Nh}$ ($\underline{J}_{\sigma\sigma}$ in their notation) appears free from serious objection. It agrees well with the value 0.68 ev estimated semi-theoretically at the end of footnote 31 above.

The graphical eigenvalue procedure used in Figure I needs justification. First of all, it should be noted that it is not necessary that the procedure be valid except near the correct value of ν (which, moreover, need not at first be known), and the following reasoning is to be understood as applying only to that value of ν.

Suppose, then, that one is working with a magic formula, including
correct values of ν and $\underline{A_0}$, such that when the degree of hybridiza-
tion existing in the true molecular wave function is assumed, the
formula will correctly reproduce the true bond energy. Under these
circumstances, an <u>exact</u> formula for the energy of the true wave func-
tion and of others differing from it only in degree of hybridization
would show a maximum $\underline{D}_0$ (minimum total energy) for the true degree
of hybridization. If the structure of the magic formula represents
approximately correctly the various elements which combine to give
the final $\underline{D}_0$, it should show essentially the same property. If the
magic formula were really bad, it might give no maximum at all for $\underline{D}_0$
as function of α, and the fact that it actually gives well-defined
maxima (<u>cf.</u> Figure I) is reassuring. The writer feels that if coeffi-
cients for the magic formula can be obtained by the procedure de-
scribed, such that observed $\underline{D}_0$ values for a reasonably large and var-
ied group of molecules can subsequently be reproduced, then both the
formula <u>and</u> the procedure are probably valid to a reasonable degree
of approximation.

The results obtained for CH are summarized in Table I. In
Table II, details of the individual terms in Eqs. (25) and (26) for
$\underline{D}_0$ of CH are given, for the parameter values ($\nu = 0.7$, $A_0 = 1.16$)
later adjudged to be about correct. This tabulation gives a vivid
picture of how the various bonding, repulsive, and promotion terms
combine to give the final resultant $\underline{D}_0$.

A comparison, for $\nu = 0.7$, between the results computed
for the case of no hybridization ($\alpha = 0$) and for the probable actual
hybridization ($\alpha^2 = 0.155$) likewise shows vividly the importance of
the relatively small amount of isovalent hybridization in stabilizing
the molecule (see Figure I and Table II). Moffitt,[33] using VB theory

CAPTION FOR FIGURE I

<u>Figure I</u>. $\underline{D}_0$ for CH computed using the right side of Eq.
(26), and plotted as function of degree of hybridization α^2 in the
carbon bonding AO $\underline{h}_\beta$ (cf. Eqs. 24)), for each of two assumed values
of ν (0.7 and 1.0). For each graph, the ordinate scale has been ad-
justed (by adjusting the value of $\underline{A}_\sigma$) until the maximum ordinate of
the graph is equal to the empirical $\underline{D}_0$ of 3.47 ev (left side of Eq,
(26)). In this way, for any assumed value of ν, a simultaneous de-
termination is made of those values of $\underline{A}_\sigma$ and α^2 which can reproduce
the empirical $\underline{D}_0$. In this procedure, the final α^2 has the character
of an eigenvalue. For the <u>correct</u> value of ν, the α^2 value so deter-
mined should be the actual degree of hybridization, if the magic for-
mula is essentially correct in form.

(To make the curves have their maxima exactly at 3.47 ev,
$\underline{A}_\sigma$ should be slightly increased for $\nu = 0.7$, slightly decreased for
$\nu = 1.0$; but there is no point in determining $\underline{A}_\sigma$ to more than two
decimals.)

$\nu=0.7$, $A_\sigma=1.16$

$\nu=1.0$, $A_\sigma=1.33$

$D_0(ev)$

$\alpha^2 \longrightarrow$
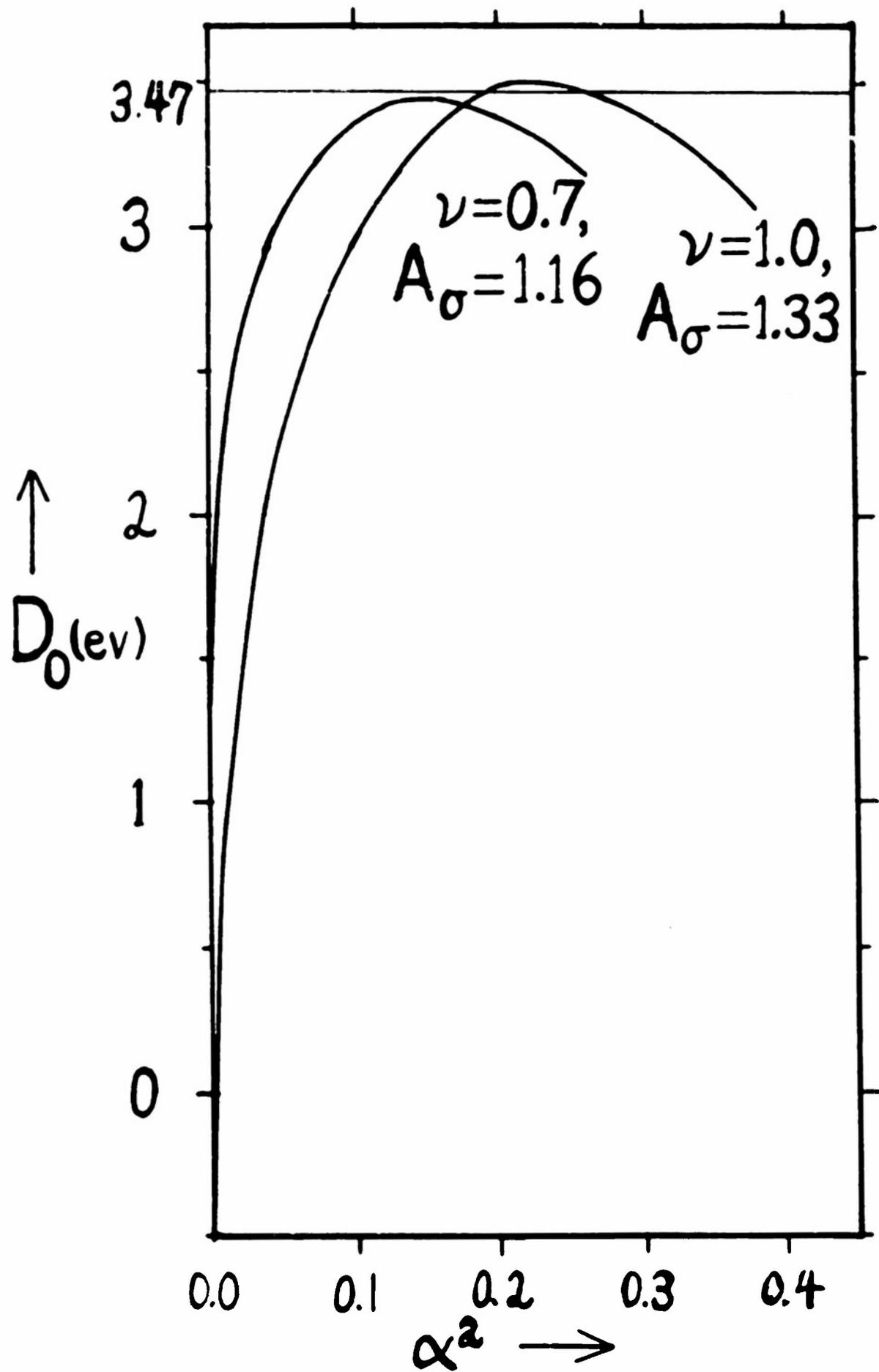
TABLE I

VALUES OF $\underline{A}_\sigma$ AND α^2 FOR CH AS FUNCTION OF ASSUMED VALUE OF ν

ν	1.0	0.85	0.70	0.55
A_σ	1.33	1.25	1.16	1.07
α^2	0.22	0.20	0.155	0.10

TABLE II

STRUCTURE OF $\underline{D}_0$ FOR CH IF $\nu = 0.7$, $\underline{A}_\sigma = 1.16^{\underline{a}}$

	$\alpha = 0$	$\alpha^2 = 0.155$
$S_{\beta h}$	0.509	0.686
S_{kh}	0.071	0.071
$S_{o\beta,h}$	0.553	0.308
$X_{\beta h}$ (ev)	5.57	6.73
$-Y_{kh}$	-0.62	-0.62
$-Y_{o\beta,h}$	-3.54	-1.09
$-\alpha^2 \Delta P$	0.00	-1.46
$\frac{1}{2}K_{\Pi h}$	0.40	0.40
$-P_0$	-0.49	-0.49
D_0	1.32	3.47

$\underline{a}$ See Table VIII for $\underline{P}_0$ and $\triangle P$, Ref. 51 for $\underline{S}$ valuos, Ref. 52 for $\underline{K}_{\Pi h}$, Eqs. (25)-(26) for magic formula.

with semi-empirical values of the necessary exchange integrals (instead of Eqs. (22) and (23)), and maximizing the bond energy with respect to degree of hybridization in essentially the same way as here, has obtained similar results (α^2 about 0.1 for CH; he has also discussed NH and OH). Noteworthy in Table II is the fact that hybridization is effective in two ways, namely by <u>increasing</u> the size of bonding term $X_{\beta h}$ and by <u>decreasing</u> the magnitude of the nonbonded repulsion term $-Y_{o\beta,h}$.

VIII. THE FITTING FOR O_2

Since the $^3\Sigma_g^-$ ground state of O_2 is a somewhat special case in terms of VB theory, it will be more convenient to make a fitting to the first excited, $^1\Delta_g$, electronic state, whose VB electron configuration[14b] is

$$k)^2 \; \iota)^2 \; h_{o\beta})^2 \; h_{o\beta})^2 \; h_\beta \cdot h_\beta) \; \pi \cdot \pi) \; \pi')^2 \; \pi')^2 \; , \qquad (27)$$

with one h_β—h_β bond and one π—π bond;[53] h_β and $h_{o\beta}$ are as defined

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[53] One has either $\pi^+ \cdot \pi^+) \; \pi^-)^2 \; \pi^-)^2$ or $\pi^- \cdot \pi^-) \; \pi^+)^2 \; \pi^+)^2$, the two cases corresponding to the $M_L = -2$ and $+2$ sub-states of the doubly degenerate electronic state $^1\Delta_g$.

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in Eqs. (24). For the $^1\Delta_g$ state, D_0 is less by its known excitation-energy (0.98 ev)[47] than D_0 (5.08 ev) of the $^3\Sigma_g^-$ state. Eq. (21) now takes the form:

$$\left. \begin{aligned} 4.10 = D_0 = (X_{\beta\beta} + X_{\pi\pi}) - (2Y_{\beta,o\beta} + 2Y_{o\beta,o\beta} + 2Y_{k,\beta} + 4Y_{k,o\beta} + 2Y_{\pi\pi'}) \\ + (3K_{\beta\pi} + 6K_{o\beta,\pi} + 6K_{k\pi} + 2K_{\pi\pi'}) - 2(P_0 + \alpha^2 \Delta P) \; , \end{aligned} \right\} (28)$$

with P_0 and ΔP as given for the V_2 valence states of the oxygen atom listed in Table VIII.[54]

For $\alpha = 0$, $\beta = 1$ in Eqs. (24), the state of each oxygen atom would be $\underline{s}^2\sigma\pi\pi'^2$, $\underline{V}_2$; for $\alpha = 1$, $\beta = 0$, it would be $\underline{s}\sigma^2\pi\pi'^2$, $\underline{V}_2$. The proof that $\underline{P}$ for each oxygen atom is $\underline{P}_0 + \alpha^2\underline{\Delta P}$ is indicated in Appendix II. A factor two is then required since both oxygen atoms are promoted.

In Eq. (27), $\underline{K}_{k\pi}$ is negligible and can be dropped. Further, it is convenient to rewrite some of the other terms as follows (the relations stated are easily proved):

$$2(Y_{k\beta} + Y_{k,\sigma\beta}) = 2(Y_{ks} + Y_{k\sigma}) \; ; \quad 3(K_{\beta\pi} + K_{\sigma\beta,\pi}) = 3(K_{s\pi} + K_{\sigma\pi}) \; . \quad (29)$$

The terms in Eq. (27) can then be usefully regrouped as follows:

$$4.10 = D_0 = C + E(\nu) + F(\alpha) + G(\alpha,\nu) + H(A_{\pi},\nu) \; , \quad (30)$$

where

$$\underline{C} = -2P_0 + (3K_{s\pi} + 3K_{\sigma\pi} + 2K_{\pi\pi}) \; ;$$

$$E(\nu) = -2(Y_{ks} + Y_{k\sigma}) \; ;$$

$$F(\alpha) = -2\alpha^2\Delta P + X_{\beta\beta} + 3K_{\sigma\beta,\pi} \; ;$$

$$= -2\alpha^2\Delta P + X_{\beta\beta} + \alpha^2 K_{\sigma\pi} + \beta^2 K_{s\pi} - 2\alpha\beta K_{s\pi,\sigma\pi} \;$$

$$G(\alpha,\nu) = -2(Y_{\beta,\sigma\beta} + Y_{\sigma\beta,\sigma\beta} + Y_{k,\sigma\beta}) \; ;$$

$$H(A_\pi,\nu) = X_{\pi\pi} - 2Y_{\pi\pi} = A_\pi I_K \left[S_\pi/(1 + S_\pi) - 2\nu S_\pi^2 \right] \; . \quad (31)$$

Using Eq. (23) for the $\underline{Y}$'s and the method of Ref. 31 for the $\underline{K}$'s, $\underline{C}$ becomes a known constant and $\underline{E}(\nu)$ a known function of ν. Similarly, $\underline{F}(\alpha)$ becomes a known function of α. $\underline{G}$ is an expression which (using Eqs. (22) and (23)) is seen to be proportional to $\underline{A}_\sigma$ and also to

depend on α and ν, but after inserting the value of $\underline{A}_\sigma$ (as determined in Section VIII for CH) corresponding to any one of the ν values 1.0, 0.85, 0.7, 0.55, $\underline{G}$ becomes a quantity which depends only on α and ν. To obtain the hybrid SCF $\underline{S}$'s required in computing the $\underline{Y}$'s by Eq. (23), in $\underline{C}$ and $\underline{G}$, the method of Refs. 42 and 51 was used. Finally $\underline{H}$, after inserting $\underline{I}_K$ for the oxygen atom from Table VIII, depends only on ν and on the as yet undetermined $\underline{A}_\pi$.

For any assumed value of ν, the complete expression on the right of Eq. (30) now depends (aside from known constants) only on $\underline{A}_\pi$ and α. It is then possible, for any particular assumed ν value, to determine simultaneously $\underline{A}_\pi$ and α^2 by the method that was used to determine $\underline{A}_\sigma$ and α^2 for CH. The results are included in Table IV below.

IX. DEFINITE DETERMINATION OF EMPIRICAL PARAMETERS
FOR THE MAGIC FORMULA.
DETERMINATION OF DEGREES OF HYBRIDIZATION.

For the final determination of $\underline{A}_\sigma$, $\underline{A}_\pi$, and ν, it is convenient next to compute $\underline{D}_0$ for several molecules by the magic formula, for each of the ν values 1.0, 0.85, 0.70, 0.55, using the corresponding appropriate values of $\underline{A}_\sigma$ and $\underline{A}_\pi$ as determined in Sections VII and VIII. By comparing these computed $\underline{D}_0(\mu)$ values with empirical $\underline{D}_0$ values, one can determine what ν value gives the best average fit. With ν thus fixed, the values of $\underline{A}_\sigma$, $\underline{A}_\pi$, and of α^2 for the molecules considered are determined.

Selecting first the ground states of N_2 and F_2, it may be noted that their electron configurations are formally identical with (27) for the $^1\Delta_g$ state of O_2, except for the π electrons. The respective π partial configurations are

$$N_2 : \quad \pi\cdot\pi)\ \pi'\cdot\pi')$$

$$O_2 : \quad \pi\cdot\pi)\ \pi')^2\ \pi')^2 \qquad\qquad\qquad (32)$$

$$F_2 : \quad \pi)^2\ \pi)^2\ \pi')^2\ \pi')^2 \ .$$

Equations for N_2 and F_2 corresponding to Eqs. (28)-(31) are easily written; values of $\underline{P}_0$, $\triangle P$, $\underline{I}_K$, and $\underline{\bar{I}}_L$ for use in connection with these equations are found in Table VIII, and the necessary $\underline{S}$'s and $\underline{K}$'s are obtained in the manner described for O_2 following Eqs. (31). Regarding $\underline{A}_\sigma$ and $\underline{A}_\pi$ now as known (for any given ν), and $\underline{D}_0$ as a quantity to be computed as a function of ν, the analogue of Eq. (30) is

$$D_0(\alpha,\nu) = \underline{C} + \underline{F}(\alpha) + \underline{G}(\alpha,\nu) + \underline{H}(\nu) \ , \qquad\qquad (33)$$

with

$$\underline{C} = (2 \text{ or } 0)X_{\pi\pi} - 2P_0 + (2 \text{ or } 4)(K_{s\pi} + K_{\sigma\pi}) + (1 \text{ or } 4)K_{\pi\pi'} ;$$

$$\underline{E}(\nu) = -2(Y_{ks} + Y_{k\sigma}) + (0 \text{ or } -4)Y_{\pi\pi'} ;$$

$$\underline{F}(\alpha) = -2\alpha^2\triangle P + X_{\beta\beta} + (2 \text{ or } 4)K_{\sigma\beta,\pi} ; \text{ for reduction of } \underline{K}_{\sigma\beta,\pi},$$

see Eqs. (31);

$$\underline{G}(\alpha,\nu) = -2(Y_{\beta,\sigma\beta} + Y_{\sigma\beta,\sigma\beta} + Y_{k,\sigma\beta}) \ .$$

$$\left.\vphantom{\begin{array}{c}1\\1\\1\\1\\1\end{array}}\right\}(34)$$

Where a choice is given in Eqs. (34), the first alternative refers to N_2, the second to F_2. The next step, for either N_2 or F_2, for each assumed ν value, is to plot the computed $\underline{D}_0$ against α^2, as in Figure I. The maximum of each such curve then gives the desired value of $\underline{D}_0$ (also of α^2) for the given ν value.

If the electron configuration of CH_4 is written using tetrahedral carbon orbitals,[14b,55]

55 For some discussions of hydrocarbons using VB methods, see for example J. H. Van Vleck and A. Sherman, Rev. Mod. Phys., 7, 167 (1935) and references there cited; R. Serber, J. Chem. Phys., 17, 1022 (1935); W. G. Penney, Trans. Faraday Soc., 31, 734 (1935).

$$k)^2 \; te_a \cdot h_a) \; te_b \cdot h_b) \; te_c \cdot h_c) \; te_d \cdot h_d) \;,$$

the magic formula becomes

$$D_0 = 4X_{te,h} - 4Y_{kh} - 2Y_{ote,h} + 4K_{\aleph h} - 3Y_{hh} - P(te_4, V_4) + \underline{V} \;. \qquad (35)$$

The terms $- 2\underline{Y}_{ote,h} - 4\underline{K}_{\aleph h}$ come from transformation of a term $- 6\underline{Y}_{te'h}$ corresponding to the 12 nonbonded exchange terms between H atoms and the $\underline{te}$ AO's to which they are not bonded; $\underline{K}_{\aleph h}$ is taken as in Ref. 52, except for a slight correction for the smaller C—H distance. $\underline{P}$ is Voge's value for case $\underline{D}$ of Table IX, and $\underline{V}$ is Voge's demotional RE correction[37] (see Section IV). A polar RE term, though probably appreciable, has been neglected in Eq. (35). In computing $\underline{X}$ and the $\underline{Y}$'s using Eqs. (22)-(23), the $\underline{S}$ values are obtained as for CH,[51] the $\underline{I}$ values are $I_H = 13.60$ ev, $I_K = 288$ (Table VIII), and $\bar{I}_L = 13.68$ (Table IX).

For C_2H_n ($\underline{n} = 2$, 4, or 6), the nonbonded exchange terms are very numerous, and the $\underline{D}_0$ formulas are best presented in tabular form (Table III).[55] The electron configurations[14b] are

$$C_2H_6 : \; k)^2 \; k)^2 \; te_a \cdot h_a) \; te_b \cdot h_b) \; te_c \cdot h_c) \; te_d \cdot te_d^*) \; te_c^* \cdot h_c^*) \; te_b^* \cdot h_b^*)$$

$$te_a^* \cdot h_a^*) \;,$$

$$C_2H_4 : \; k)^2 \; k)^2 \; tr_a \cdot h_a) \; tr_b \cdot h_b) \; tr_c \cdot tr_c^*) \; tr_b^* \cdot h_b^*) \; tr_a^* \cdot h_a^*) \; \aleph_x \cdot \aleph_x^*) \;, \qquad (36)$$

$$C_2H_2 : \; k)^2 \; k)^2 \; di' \cdot h) \; di \cdot di^*) \; di'^* \cdot h^*) \; \aleph \cdot \aleph^*) \; \aleph' \cdot \aleph'^*) \;.$$
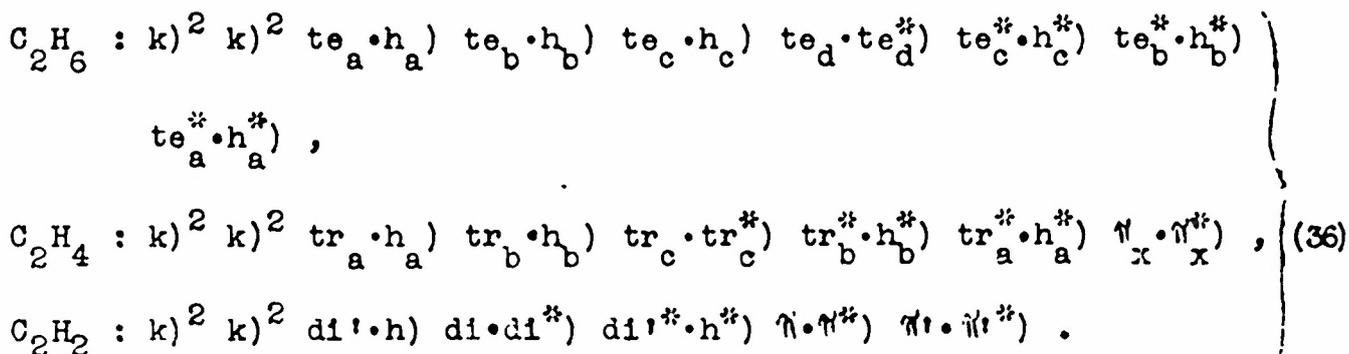
Many of the nonbonded exchange integrals involving hybrid AO's occur in groups which (by using relations similar to Eqs. (29) above) can conveniently and rigorously be transformed into $\underline{Y}$'s and $\underline{K}$'s which are largely non-hybrid, and this transformation has been done in Table III.

For H_2 and He_2, Eqs. (31)—(23) reduce to Eqs. (7) and (10) respectively. For H_2^+ and He_2^+, Eqs. (6) and (11)-(12) are respectively applicable.

The results of computations on all the molecules mentioned above, carried out in accordance with the first paragraph of this Section, are presented in Table IV. As will be seen from this Table, the computed $\underline{D}_0$ varies rapidly, and in opposite ways for N_2 and F_2, with ν, so that the best ν is rather sharply determined. On the whole, agreement of observed and computed $\underline{D}_0$ values is best for about $\nu = 0.7$, with $\underline{A}_\sigma = 1.16$, $\underline{A}_\pi = 1.53$. The fact that a compromise ν can be determined at all to fit (even though roughly) such different molecules as N_2 and F_2 gives important support to the validity of the general structure of the magic formula.

Excluding H_2 and Li_2 as exceptional,[56] the average

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[56] The figures on H_2 and Li_2 suggest that a distinct coefficient A_s, with value about 0.7, may be needed for pure $\underline{s}$—$\underline{s}$ bonds, as was proposed in Ref. 4. Or possibly $\underline{A}_\sigma$ is anomalous for molecules which have unusually small ξ values, as is true of H_2 and Li_2 (cf second column in Table IV); the fact that proportionality of the theoretically computed LCAO quantity $-\beta$ to $\underline{S}$ fails when ξ gets small (see Section II: sentence with Ref. 11) suggests this possibility. The discrepancy for F_2 might then possibly be attributed to its exceptionally large ξ value. For other possible ways of dealing with H_2, Li_2, and F_2, see also footnote 23 and Section XIII.

TABLE III

COEFFICIENTS OF TERMS IN D_0 FORMULAS (EQ. (21)) FOR C_2H_n [a]

	$X_{\beta h}$	$X_{\beta\beta}$	$X_{\pi\pi}$	$-Y_{ss}$	$-Y_{s\sigma}$	$-Y_{\sigma\sigma}$	$+Y_{\beta\beta}$	$-Y_{\pi\pi}$	$-Y_{ks}$	$-Y_{k\sigma}$
n = 2	2	1	2	$\tfrac{1}{2}$	1	$\tfrac{1}{2}$	$\tfrac{1}{2}$	0	2	2
n = 4	4	1	1	$\tfrac{1}{2}$	1	$\tfrac{1}{2}$	$\tfrac{1}{2}$	$\tfrac{1}{2}$	2	2
n = 6	6	1	0	$\tfrac{1}{2}$	1	$\tfrac{1}{2}$	$\tfrac{1}{2}$	1	2	2

	$+Y_{\sigma\beta,h}$	$-Y'_{sh}$	$-Y'_{\sigma h}$	$-Y_{kh}$	$-Y'_{kh}$	$-Y_{hh}$	$-Y'_{hh}$	$-Y''_{hh}$
n = 2	1	1	1	2	2	0	0	$\tfrac{1}{2}$
n = 4	2	2	2	4	4	1	1	1
n = 6	3	3	3	6	6	3	3/2	3

	$-P_t$ [b]	V [c]	$K_{s\pi}$	$K_{\sigma\pi}$	$K_{\pi\pi'}$	$K_{k\pi}$ [d]	K_{hh}	$K'_{\pi h}$
n = 2	2	2	2	2	1	4	2	2
n = 4	2	2	2	2	1	4	4	4
n = 6	2	2	2	2	1	4	6	6

---

[a] Unprimed exchange terms refer to AO pairs on nearest, singly primed to those on more distant, and doubly primed to pairs on most distant neighbor atoms. The subscripts β refer to di, tr, te for $n = 2, 4, 6$ respectively, $\sigma\beta$ to the corresponding orthohybrids (cf. footnote 14b). For C_2H_6, the coefficients given above were worked out on the basis of the opposed form (symmetry D_{3h}).

[b] See Table IX for the P_t values (cases B', C, D for $n = 2, 4, 6$ respectively).

[c] For the computations of Table IV, it is assumed that the RE correction analogous to the Voge demotional RE correction (cf. footnote 37) for CH_4 ($V = 1.28$ ev) is the same per carbon atom in C_2H_n. This must be considered a guesstimate. Polar RE corrections for the C—H bonds have been neglected.

[d] Negligible.

TABLE IV

COMPUTED D_0 VALUES FROM MAGIC FORMULA

Molecule	ξ [d]	Computed D_0 Values (ev)[a,b,c]				Observed D_0 (ev)[a]
		ν 1.0 A_∞ 1.33 A_H 3.36	0.85 1.25 2.28	0.70 1.16 1.53	0.55 1.07 0.975	
CH	0.9	3.47 (α^2=0.22)	3.47 (α^2=0.20)	3.47 (α^2=0.155)	3.47 (α^2=0.10)	3.47
O_2 [f]	1.3	4.10 (α^2=0.14)	4.10 (α^2=0.12)	4.10 (α^2=0.09)	4.10 (α^2=0.06)	4.10
H_2	1.0	27.27 (α^2=0.31)	13.70 (α^2=0.26)	8.32 (α^2=0.21)	4.91 (α^2=0.15)	9.76 or 7.37
F_2	1.8	-0.46 (α^2=0.031)	1.97 (α^2=0.024)	3.12 (α^2=0.018)	3.82 (α^2=0.014)	+0.2 -1.6
H_2^+	1.0	3.32	3.12	2.89	2.66	2.65
H_2	0.7	7.79	7.32	6.78	6.24	4.48
He_2^+	1.7			1.46		(3.1)
He_2 [g]	1.7	-4.30	-3.66	-3.01	-2.37	(-2.38)[h]
Li_2	0.8			2.06		1.03
CH_4	0.9	17.31	17.64	17.61	17.36	15.02 or 17.30
C_2H_6	1.2	22.05	25.03	26.72	27.62	24.90 or 29.46
C_2H_4	1.0	25.86	24.23	22.79	21.47	19.11 or 23.67
C_2H_2	0.9	31.81	23.83	18.36	14.15	12.90 or 17.46

FOOTNOTES FOR TABLE IV

a See text of this Section for methods of computation.

b The α^2 values given were determined by maximizing the computed D_0 in the manner illustrated in Figure I.

c For the hydrocarbons, α^2 values were _assumed_ corresponding to the electron configurations in (36), but demotional RE corrections were then included in the computed D_0's to allow for deviations from the assumed states of hybridization. This correction was 1.28 ev for CH_4, 2.56 ev for all C_2H_n (_cf._ Table III, note _c_). Polar RE corrections have been neglected.

d For definition of ξ, see Eq. (3) of Ref. 4.

e For CH, Ref. 46; for F_2 and N_2, Refs. 48, 49; for He_2, Ref. 4, Table X; for the other diatomic molecules, Ref. 47. The values for CH_4 and C_2H_n are based on heats of formation ΔH_f^0 for $0°K$ taken from the American Petroleum Institute Project No. 47 Tables (15.99 kcal per mole for CH_4, 16.52 for C_2H_6, -14.52 for C_2H_4, and -54.33 for C_2H_2), combined with $D_0 = 4.478$ ev = 103.2 kcal for H_2 and, for the heat of sublimation L of graphite, either (_a_) 124 kcal or (_b_) 175 kcal (see footnote 58). 1 ev = 23.06 kcal/mole is assumed throughout.

f $^1\Delta_g$ state.

g At 1.06 Å.

h Theoretical.

difference per electron-pair bond between observed and computed D_0
values for $\nu = 0.7$ is about ± 0.3 ev.[57] In view of the presence of

[57] If the hydrocarbons, for which both the observed D_0 values and
the assumed resonance energies (Table III, footnote c) are rather
uncertain, were omitted, a somewhat improved fit for the remain-
ing molecules could be obtained with (say) $\nu = 0.75$ (or perhaps
0.85, if A_π is made somewhat smaller than for $\nu = 0.85$ in Table
IV, and exact agreement for O_2 is sacrificed).

only three adjustable parameters in the magic formula, the agreement
found is all that one could reasonably hope for, and much too good to
be reasonably attributable to accident. As a corollary, this argu-
ment indicates that the hybridization coefficients in the $\nu = 0.7$
column in Table IV are probably fairly near the truth.

The following further point is worth emphasizing. Although
the specific values for the coefficients in the magic formula were
obtained by procedures which some readers may question, the formula
with these coefficients now stands on its own merits, independent of
these procedures. Its degree of quantitative validity should be
judged by its empirical success in representing observed bond energies.
One should also bear in mind that the present magic formula is a first
edition, in need of further test by application to more molecules,
and undoubtedly capable of further improvement in various ways (see
Section XIII).

X. VALIDITY AND USES OF THE MAGIC FORMULA PROCEDURE

The magic formula has now been implemented with specific
values for its coefficients. One may ask: How good is it? What can
it be used for? The first question is discussed at the end of Sec-
tion IX and in Section XIII.

In answer to the second question! the magic formula, used in connection with the maximizing procedure described above, may be expected to be valuable principally in three ways. They are: (1) as a tool for the approximate computation or estimation of bond energies; (2) as an expression which depicts the theoretical structure of bond energies, that is, which shows roughly quantitatively how the total energy of atomization results from the addition and subtraction of significant individual terms; (3) in determining approximate degrees of isovalent hybridization. The first of these applications will be considered now, the second in Section XI, and the third in Section XII.

As can be seen from Table IV, the magic formula is not as yet reliable enough to yield conclusive decisions between controversial alternative observed D_0 values, such as occur in several cases (see last column of Table IV). However, it is striking that, no matter what value-pairs A_σ, ν that fit CH are taken, the magic formula always predicts for CH_4 a value of D_0 which agrees closely with the highest   of   the   "observed" D_0 values corresponding to the several competing values[58] for the heat of sublimation of

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[58] The extreme values are 124 kcal and 175 kcal. For recent reviews, see H. D. Springall, Research, 3, 260 (1950); H. D. Hagstrum, Rev. Mod. Phys., 23, 185 (1951).

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graphite. (Note that A_π is not involved for either CH or CH_4.) In view of the nature of the similarities and differences in the structure of the C—H bond in CH and CH_4 (cf. Eq. (25) and Table II; Eq. (35) and Tables III, VI), and in view of the fact that the only possibly needed further corrections to the computed D_0 of CH_4 would probably be polar RE corrections which would increase D_0, the definite

indioation given by the magic formula in favor of the high heat of sublimation of carbon may have real significance.

The magic formula should be applicable to radicals, and so, by the use of differences between heats of atomization for molecules and radicals, should permit the calculation of energies of dissociation *into* radicals.

The magic formula may be helpful also in the prediction of bond energies for excited and ionized molecules.

The formula, either in its present form or after improvement, may also be particularly useful in dealing with nonbonded repulsions (see the last paragraph of Section IV).

XI. THE THEORETICAL STRUCTURE OF CHEMICAL BOND ENERGIES

Any system of dividing the total energy of atomization of a molecule into a sum of individual terms is more or less arbitrary unless these terms correspond to realizable physical processes--as, for example, if D_0 is expressed as the sum of energies required to remove the atoms one by one in a specified order.[59] Even then, there

[59] For a recent analysis of these problems, see M. Szwarc and M. G. Evans, J. Chem. Phys., 18, 618 (1950).

is no *unique* way of analyzing D_0 into a sum of terms. Even in a purely theoretical approach, any attempt to break D_0 down into a sum of terms must ultimately be regarded as merely a matter of convenience for computation or understanding. In spite of all these considerations, everyone recognizes the usefulness of writing D_0 as a sum of terms of more or less theoretical character. Most often, D_0 is calculated as a sum of standard contributions ("bond energies") one for each chemical bond--plus corrections if necessary for "resonance". The standard bond energies are determined empirically to fit observed

thermal data.[38]

The present magic formula likewise is a sum of terms, including corrections for "resonance",[36] and contains coefficients adjusted to make it fit observed thermal data. However, it has (like the VB theory formulas[55] from which it is adapted) a much richer structure than the ordinary additive bond energy formula, and, if soundly based, should afford a much deeper and more detailed theoretical insight into the various factors which determine the total energies of chemical binding, and greater possibilities of prediction. The possibilities of the magic formula for steric hindrance effects have already been mentioned.

Finally, whereas the use of a table of bond energies involves a different empirical bond energy for each kind of bond, the magic formula has a more universal character in that, for all molecules built from first-row atoms, or first-row atoms and hydrogen, it contains only three empirical coefficients. (More will of course probably be needed to cover the whole periodic system.) To be sure, the magic formula involves also certain other quantities which must be determined: the overlap integrals $\underline{S}$, theoretically; the ionization and promotion energies, best from empirical spectroscopic data on atoms.

The way in which the magic formula gives insight into the structure of chemical bond energies can best be appreciated in terms of examples. For this purpose, reference may be made to Table II and Figure I above, for the CH radical, to Table V below, for the N_2 molecule, and to Table VI. Table VB indicates, contrary to the usual idea, that π bonds are weak, that the π contribution to the bonding is very large, the sum of the σ contributions actually being strongly negative.[60] Comparing the calculated results for $\sigma^2 = 0$ and $\sigma^2 = 0.21$.

[60] This can be understood as follows. As two nitrogen atoms approach each other, σ bonding first sets in, with little hybridization and only moderate nonbonded repulsions; π bonding is weak because the π overlap integral is small. At closer approach, both hybridization and nonbonded σ repulsions increase. Meantime the π bonding increases so rapidly with increasing π overlap that equilibrium is not established until long after the σ interaction sum has turned negative.

it further indicates that without isovalent hybridization (which is equivalent--see Table VIII--to partial promotion from $\underline{s}^2\underline{p}^3$ to $\underline{s}\underline{p}^4$ without change of the formal valence three), the bond strength would be very small.

A notable feature of Tables V and VI is the large size of the nonbonded repulsion terms $\underline{Y}_{ks}$, $\underline{Y}_{k\sigma}$, $\underline{Y}_{k,o\beta}$, etc., involving the inner-shell (1$\underline{s}$) electrons.[40] The valence-shell repulsion terms $\underline{Y}_{\beta,o\beta}$ and $\underline{Y}_{o\beta,\beta}$ would be large if there were no hybridization ($\omega^2 = 0$), but are made much smaller by hybridization. Another point of interest is the very considerable positive contributions made by the nonbonded attractions ($\underline{K}$ terms).

The break-downs of the total energies of atomization into individual terms in Tables II, V, and VI are similar to those presented by Van Vleck, Penney, and others some years ago,[61] guided by

[61] See J. H. Van Vleck and A. Sherman, Rev. Mod. Phys., 7, 167 (1935), for a review; also Refs. 37, 52, 55. Reference should also be made to the important work of M. Kotani and collaborators in Japanese journals.

theoretical computations and by spectroscopic and other empirical data,

TABLE V

TERMS IN COMPUTED N_2 BOND ENERGY[a] USING THE MAGIC FORMULA[b]

A1. CONSTANT TERMS (TOTAL $\underline{C}$)

$$2X_{\pi\pi} - 2Y_{ks} - 2Y_{k\sigma} - 2P_0 + 2K_{s\pi} + 2K_{\sigma\pi} + K_{\pi\pi_1} = \underline{C}$$
$$14.97 - 1.04 - 3.24 - 3.40 + 0.89 + 1.68 + 0.10 = 9.96$$

A2. TERMS INCLUDING THOSE DEPENDING ON HYBRIDIZATION

	$\underline{C}$	$-2\alpha^2\Delta P$	$+2K_{\sigma\beta,\pi}$	$+X_{\beta\beta}$	$-2Y_{\beta,\sigma\beta}$	$-2Y_{\sigma\beta,\sigma\beta}$	$-2Y_{k,\sigma\beta}$	$= \underline{D}_0$
$\alpha^2 = 0$	$+9.96$	$+0.00$	$+0.89$	$+3.26$	-7.15	-5.96	-1.04	$= -0.04$
$\alpha^2 = 0.21$	$+9.96$	-5.44	$+0.03$	$+8.22$	-4.38	-0.05	-0.02	$= +8.32$

B. DISTRIBUTION OF TERMS BETWEEN σ AND π BONDS[c]

	$\alpha^2 = 0$	$\alpha^2 = 0.21$
σ bond: $X_{\beta\beta} + \frac{1}{2}\sum K_{\sigma\pi} - 2P_0/3 - 2\alpha^2\Delta P - \sum Y$	-14.57	-5.78
π bonds: $2X_{\pi\pi} + K_{\pi\pi_1} + \frac{1}{2}\sum K_{\sigma\pi} - 4P_0/3$	$+14.53$	$+14.10$
Total $(\underline{D}_0)$	-0.04	$+8.32$

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[a] Cf. Eqs. (33)-(34).

[b] Eqs. (21)-(23) with $A_\sigma = 1.16$, $A_\pi = 1.53$, $\nu = 0.7$ (cf. Section IX)

[c] For certain terms where the distribution between the σ and π bonds is of necessity rather arbitrary, it has been effected as follows: Of the promotion energy, the amount $2P_0$ is necessary for the trivalent valence state, and it is here assigned one-third to the one σ and two-thirds to the two π bonds. The additional promotion energy $2\alpha^2\Delta P$ is assigned exclusively to the σ bond, since hybridization affects almost exclusively this bond. The mixed terms $\underline{K}_{\sigma\pi}$ are divided equally between the σ and π bonds.

TABLE VI. STRUCTURE OF ATOMIZATION ENERGIES[a]

A. HOMOPOLAR DIATOMIC MOLECULES

Terms in Atomization Energy (ev)[b]

		σ,σ Terms		σ,π Terms	π,π and π,π' Terms			Bond Energies (ev)[c]	
	−P[d]	X	(ΣY_k)[e]	ΣY	ΣK	X	ΣY	ΣK	Gross	Net
F_2	−0.80	6.25	(−0.25)	−1.91	0.83	----	−1.29	0.04	3.92	3.12
O_2	−4.31	7.95	(−1.60)	−5.50	2.21	6.29	−2.62	0.08	9.39[f]	5.08[f]
N_2	−8.84	8.22	(−4.30)	−8.73	2.60	14.97	----	0.10	17.16	8.32

B. HYDROCARBON MOLECULES[g]

1. CH_m Intragroup Terms (ev per C—H Bond)

	σ,h Terms			h,h	π,h
	X	(ΣY_k)[e]	ΣY	ΣY	ΣK
CH	6.73	(−0.62)	−1.71	----	0.40
CH_4	6.66	(−0.70)	−1.00	−0.65	0.82
C_2H_6	6.63	(−0.68)	−0.97	−0.44	0.83
C_2H_4	6.77	(−0.74)	−0.90	−0.18	0.86
C_2H_2	6.91	(−0.79)	−0.80	----	0.89

2. Intergroup Terms (ev per Molecule)

	H—H and C—H Terms				C—C Terms						
	h,h	σ,h		π,h	σ,σ Terms				σ,π	π,π and π,π'	
	ΣY	(ΣY_k)[e]	ΣY	ΣK	X	(ΣY_k)[e]	ΣY	ΣK	X	ΣY	ΣK
C_2H_6	−0.56	(−0.07)	−2.86	0.36	6.20	(−1.38)	−2.16	1.86	----	−1.20	0.06
C_2H_4	−0.21	(−0.07)	−2.26	0.30	6.72	(−2.54)	−3.43	2.48	5.56	−0.96	0.09
C_2H_2	−0.01	(−0.02)	−0.67	0.09	7.22	(−4.23)	−4.80	2.96	12.45	----	0.13

TABLE VI. STRUCTURE OF ATOMIZATION ENERGIES[a] (continued)

C. HYDROCARBON BOND ENERGIES (ev)[h]

	$-P + RE$[k]	C—H Bonds		C—C, C=C, or C≡C	
		Gross	Net	Gross	Not
CH	-1.95	5.42	3.47		
CH_4	-1.42	5.82	4.40		
C_2H_6	$\begin{cases} -1.42 \\ -2.845 \end{cases}$	5.75	4.33	3.51	0.67
C_2H_4	$\begin{cases} -1.465 \\ -5.86 \end{cases}$	6.25	4.79	9.48	3.62
C_2H_2	$\begin{cases} -1.63 \\ -9.765 \end{cases}$	6.85	5.22	17.67	7.91

[a] Computed by magic formula with coefficients as in $\nu = 0.7$ column of Table IV. The terms are grouped by type ($\underline{X}$, $\underline{Y}$, $\underline{K}$, $\underline{P}$) and by category (σ,σ; σ,π; etc.), in a way which will be made clear by comparison with the detailed table of terms for N_2 (Table V, with $\alpha^2 = 0.21$.

[b] The nature of the terms in detail can be seen in Eqs. (28)-(31) for O_2, Eqs. (33)-(34) for N_2 and F_2 (also Table V for N_2).

[c] The net bond energy is the sum of all the terms listed (except the $\underline{Y}_k$'s (cf. footnote e), which are included in the $\sum\underline{Y}$'s). The gross bond energy is the sum obtained excluding $-\underline{P}$ and so corres ponds to the energy of formation from the promoted valence stat..

[d] $\underline{P}$ is $2\underline{P}_0 + 2\alpha^2\Delta\underline{P}$ with $\underline{P}_0$ and $\Delta\underline{P}$ from Table VIII and α^2 from Table IV ($\nu = 0.7$ column).

[e] These sums represent those portions of the immediately-following $\sum\underline{Y}$'s which result from nonbonded repulsions between the inner shell ($\underline{K}$ shell, $1\underline{s}^2$ or $\underline{k}^2$) electrons of one atom and the valence electrons of its neighbor. They are separately listed to show

their frequently large magnitude.

f Here for the $^3\Sigma_g^-$ ground state of O_2, an additional term $+0.98$ ev (determined empirically from the molecular spectrum) has been included, equal to the extra bond energy of the $^3\Sigma_g^-$ state as compared with the $^1\Delta_g$ state for which the magic formula computation was made.

g In CH_4, and within each CH_m group in C_2H_n ($\underline{m} = \underline{n}/2$), there are C—H terms (intragroup $\sigma,\underline{h}$ and $\pi,\underline{h}$ in Table VIB) and H—H terms (intragroup $\underline{h},\underline{h}$ in Table VIB). In addition, there are in C_2H_n also intergroup terms of three kinds: H—H terms, between one H_m group and the other; C—H terms ($\sigma,\underline{h}$ and $\pi,\underline{h}$) between H_m in one group and carbon atom electrons of the other; and carbon-carbon terms of various categories. (See Eq. (25) and Table II for CH, Eq. (35) for CH_4, and Table III for C_2H_n, for a complete listing of all these terms; cf. also footnote 55.)

h Each C—H bond energy is taken (cf. footnote 55) as one $\underline{m}^{th}$ of the sum of the following terms: (a) all intragroup C—H and H—H terms in CH_m; (b) all intergroup H—H terms; (c) one-half the sum of the intergroup C—H terms. Each C—C or C=C or C≡C bond energy is taken (cf. also footnote 55) as the sum of (a) one-half the sum of the intergroup C—H terms; (b) the total of all C—C terms. For each net bond energy, a term (cf. footnote k below) $-\underline{P} + \underline{RE}$ from the second column is included; for the gross bond energies, these promotion terms are omitted.

k The values in this column are all per bond (C—H or C—C or C=C or C≡C). For CH, $\underline{RE} = 0$ and $-\underline{P} = -\underline{P}_0 - \alpha^2 \Delta\underline{P}$, with $\underline{P}_0$ and $\Delta\underline{P}$ as in Table VIII, and $\alpha^2 = 0.155$ (cf. Table I). For CH_4, $-\underline{P} + \underline{RE}$ is one-fourth of $(-6.97 + 1.28)$, where 6.97 ev is the tetrahedral promotion energy $\underline{P}_t$ of carbon (Table IX, case $\underline{D}$), and 1.28 ev is the

Voge resonance energy ($\underline{RE}$) correction $\underline{V}$ (see Section IV and Ref. 37). Similarly for C_2H_n (somewhat arbitrarily), the amount $-(\underline{P}_t - \underline{V})/4$ is assigned to each individual <u>electron-pair-bond</u> <u>terminus</u> ending on carbon; hence $-(\underline{P}_t - \underline{V})/4$ to each C—H bond and $-(\underline{a}/2)(\underline{P}_t - \underline{V})$ to the carbon-carbon bond, with $\underline{a} = 1, 2, 3$ for C_2H_6, C_2H_4, and C_2H_2 respectively; note that $\underline{P}_t$ differs somewhat in the three molecules (see Table III, especially footnotes $\underline{b}$, $\underline{c}$); <u>cf</u>. also footnote 55.

However, the individual terms are now in many cases much larger.
There are two main reasons for this difference: (1) the terms corres-
ponding to inner-shell:outer-shell repulsions earlier were almost al-
ways neglected, whereas actually they are probably fairly large;[40]
(2) the possibility of hybridization was usually neglected earlier
except for CH_4 and C_2H_n, and except for CH, NH, and OH in a recent
paper by Moffitt.[52] When these two effects are considered, one ar-
rives at much larger bonding terms than when they are ignored.

By making suitable combinations of individual terms in the
magic formula, theoretical expressions or numerical values can be ob-
tained which are counterparts of the ordinary "bond energies". In
the case of diatomic molecules, the bond energy is the same as the
atomization energy, hence is the sum of all terms in the magic formula.
For polyatomic molecules, as illustrated by the hydrocarbons C_2H_n in
Table VIC, there is some arbitrariness (especially for the promotion
energy corrections) in dividing the total atomization energy among
the carbon-hydrogen and carbon-carbon bonds.[62]

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[62] For earlier VB theory discussions of the division of D_0 among
bond energies, see Ref. 55, especially the paper by Serber.

The ordinary assumptions[38] of approximate constancy and
additivity of standard bond energies have been criticized by Serber[62]
and others.[59] It will be noted that the magic formula yields defi-
nite bond energies which are not necessarily constant or additive;
but in particular cases where they actually are so—as for example in
a series of molecules such as the normal paraffins—it should be able
to show the reasons why; and in cases where they are not, it should
make clear the reasons why not. Here the magic formula (preferably
in a future improved edition, including if possible a systematic

formulation of the RE term) should give interesting insights. As an example, using the present magic formula--and probably significant in spite of the latter's limitations--Table VIC shows approximate equality of C—H bond strengths for CH_4 and C_2H_6--a relation which presumably would extend also to the higher paraffins--but somewhat varying C—H bond strengths for other types of hydrocarbons.

As Van Vleck clearly pointed out in the case of hybrid carbon bonds,[63] it is useful to distinguish between gross bond energies,

[63] Cf. Ref. 61, p. 195; also Ref. 37.

referred to atoms in suitable valence states, and net bond energies, representing what is left after promotion energy deductions have been made.[62] Gross bond energies are truer measures of real or intrinsic bond strengths, and it is with these rather than with net bond energies that equilibrium distances and force constants should tend to be correlated. (This idea should, however, be applied with caution, since degrees of hybridization or promotion may often vary appreciably with interatomic distances even near equilibrium; for sufficiently large distances, of course, they must change.)

Table VI lists both gross and net bond energies for a number of bonds, as computed using the magic formula based on the $\nu = 0.7$ column of Table IV. Interesting, and probably significant in spite of the preliminary character of the present magic formula, is the slowly increasing C—H bond strength from CH to CH_4, C_2H_6, C_2H_4, and C_2H_2, in spite of a nearly constant primary bonding term $X_{h\beta}$.[64] For the

[64] For an earlier VB calculation, based on similar consideration of varying hybrid character in the carbon bonding AO in the C—H bond, and in the bond energy of the latter, see T. Förster, Zeits. f. Physik. Chemie, 43B, 58 (1939), in particular the Figure. In a

recent semi-empirical analysis relating bond energies to bond distances, G. Glockler (J. Chem. Phys., 16, 842 (1948)) also obtains similar results.

carbon-carbon bonds,[62] the computed variation from $C-C$ to $C=C$ to $C\equiv C$ in Table VIC seems to be too rapid, and this impression is confirmed by reference to Table IV, where the computed atomization energy (for $\nu = 0.7$) is relatively too small for C_2H_6 and too large for C_2H_2, as compared with the observed values.[65]

[65] Possibly hyperconjugation (R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc., 63, 41 (1941)) is partly responsible. However, the authors mentioned estimated the hyperconjugation energy per mole as 2.5 kcal for C_2H_6, and 5.5 kcal for C_2H_4, not nearly large enough to account for the discrepancies under discussion. It seems just barely possible that a revision of the calculations (cf. footnote 30 of Ref. 74) might give considerably larger computed hyperconjugation energies.

An interesting problem is the possible resolution of the (net or gross) bond energy of a double or triple bond into a σ bond energy plus a π bond energy or bond energies. Unfortunately there is no uniquely justifiable logical basis for doing so. Nevertheless, it can be done in one or another way if one is willing to accept a considerable degree of arbitrariness (particularly so for net bond energies) in making fractional assignments of some of the terms in $\underline{D}_0$ partly to the σ and partly to the π bonds. The terms in question include the promotion energy, the σ,π $\underline{K}$ terms, and in C_2H_n the $H-H$ and $C-H$ intergroup terms of Table VIB.[62] One way of making such a division is illustrated by Table VB for the nitrogen molecule. This makes the σ net bond energy negative in the

TABLE VII

σ AND π BOND ENERGIES

ASSUMING CONSTANCY OF C—H AND C—C σ BOND ENERGIES[a]

Bond	Type	Bond Energies $\underline{B}$ (ev)	
		Net[b]	Gross[c]
H—H in H_2	σ	4.48	4.48
C—H in CH_4	σ	3.78 or 4.35	5.20 or 5.77
C—C in C_2H_6	σ	2.41 or 3.55	5.26 or 6.40
C=C in C_2H_4	σ π	$[2.41 \text{ or } 3.55]^d$ 1.69 or 2.83	4.62 or 5.76
C≡C in C_2H_2	σ π	$[2.41 \text{ or } 3.55]^d$ 1.48 or 2.62	4.74 or 5.88

[a] This material was first presented at a meeting in 1942 (footnote 3), and was later published in part in Ref. 7 (see footnotes ** to Tables V and VII there). See also footnote 62.

[b] Obtained as follows (and see Table IV, footnote o):

$$\underline{B}(C_mH_n) = \Delta H_f^O(C_mH_n) + m\underline{L} + \tfrac{1}{2}n\underline{D}_0(H_2) \; ;$$
$$\underline{B}(C—H) = \tfrac{1}{4}\underline{D}_0(CH_4) \; ; \quad \underline{B}(C—C) = \underline{D}_0(C_2H_6) - 6\underline{B}(C—H) \; ;$$
$$\underline{B}_\pi(C=C) = \underline{D}_0(C_2H_4) - 4\underline{B}(C—H) - \underline{B}(C—C) \; ;$$
$$\underline{B}_\pi(C≡C) = \tfrac{1}{2}\left[\underline{D}_0(C_2H_2) - 2\underline{B}(C—H) - \underline{B}(C—C)\right] \; .$$

[c] $\underline{B}$(gross) = $\underline{B}$(net) + $\tfrac{1}{4}m(\underline{P}_t - \underline{V})$, with $m = 1$ for CH_4, 2 for C_2H_n, and $\underline{V} \equiv 1.28$ ev (cf. Table VI, footnote k), with $\underline{P}_t$ values from Table IX.

[d] Assumed.

N_2 triple bond, and the π net bond energy very large and positive.[60] Applying the same method also to other molecules listed in Table VI, one would obtain as a general result that σ net bond energies are positive for single bonds, near zero in double bonds, negative in triple bonds. The σ gross bond energies appear to be always positive.

A very arbitrary but simple way to obtain separate σ and π bond energies is to use the assumption of constancy of bond energies, including equality of energies of σ bonds in single and multiple bonds. Although this procedure cannot be logically justified, and is seriously at variance with the results of the magic formula approach, a few results obtained by it may be of interest for comparative purposes (see Table VII; the assumption of constancy of σ bond energies is embodied in footnote b of the Table).

XII. DEGREES OF HYBRIDIZATION AND BOND PROPERTIES

Recently evidence has appeared from a number of sources indicating the essential importance of isovalent hybridization (i.e., partial hybridization without increase of formal valence---see Section IV) for the energy and other properties of many molecules. One of the most interesting aspects of the magic formula, taken in connection with the procedure for maximizing $\underline{D}_0$ as a function of degree of isovalent hybridization, is its ability to yield information about the latter quantity (see Table IV, $\nu = 0.7$ column, for results on CH, N_2, O_2, and F_2). Moffitt[33] has already applied a similar procedure to CH, NH, and OH, using a conventional VB formula with smaller values than here for the $\underline{X}$'s and $\underline{Y}$'s, and neglecting the $\underline{Y}_k$'s;[61] he obtained calculated degrees of isovalent hybridization somewhat smaller than here.

The interpretation of information on the following properties of molecules has also yielded rough values for degrees of

isovalent hybridization: molecular dipole moments,[66,67] atomic elec-

[66] D. Z. Robinson, _J. Chem. Phys._, 17, 1022 (1949), theoretical cal-
culations on HCl.

[67] Ref. 7, p. 541.

tronegativities,[67,68] molecular quadrupole moments,[69] coupling con-

[68] The effect of isovalent hybridization on the electronegativities
of N and O was discussed in Ref. 34 (p. 787 and Table I), and it
was pointed out there that the observed (Pauling) electronega-
tivities of N and O could be explained (aside from an improbable
explanation using "second-stage electronegativities") only by as-
suming fairly large amounts of isovalent _s,p_ hybridization. For
the trivalent N atom, the result was 44%, which, however, now
seems rather too large to be credible. In the same discussion,
Pauling's electronegativity for the carbon atom was found to agree
fairly well with that calculated by the writer for a tetrahedral
hybrid carbon AO.

[69] C. Greenhow and W. V. Smith, _J. Chem. Phys._, 19, 1298 (1951),
explanation of molecular quadrupole moments deduced from micro-
wave line-broadening. Theoretical computations indicated that
20% _s,p_ hybridization in the σ bond of N_2, and 5-10% in that of
O_2, could explain the magnitudes of these quadrupole moments.

stants of molecular force-fields with nuclear quadrupole moments,[70]

[70] C. H. Townes and B. P. Dailey, _J. Chem. Phys._, 17, 782 (1949):
"Hybridization of the normal covalent bonds of N, Cl, and As with
at least 15% _s_ character is clearly shown."

absolute intensities of molecular electronic spectra.[71] The degrees

71 H. Shull: intensities in O_2 and N_2^+ spectra (to be published soon).

of isovalent hybridization indicated by all these methods agree roughly with those by the present method.

A brief discussion will be given here only of the effect of isovalent hybridization on dipole moments and on electronegativities. Robinson[66] has shown that if HCl were covalent, it would have. according to a VB theory calculation, a considerable dipole moment of polarity H^-Cl^+ if there were no s,p hybridization, while about 12% s,p hybridization in the chlorine bonding AO would give a dipole moment of the observed magnitude and with sign H^+Cl^-. Actually, there is no reasonable doubt that HCl has primary heteropolar character of polarity H^+Cl^-, so that less than 12% hybridization would be sufficient to account for the observed moment. However, the VB calculation is not reliable enough to permit quantitative conclusions. The main point to be emphasized here is that dipole moments are extremely sensitive to small amounts of isovalent hybridization.

In a rough LCAO calculation,[67] the writer concluded that as much as 20% s,p hybridization in the bonding AO of Cl in HCl would be needed to explain: (a) the observed dipole moment; (b) a sufficient electronegativity of the chlorine atom to account for the latter. The second point is quite distinct from the first, and is also of interest for itself. Some time ago,[34] in setting up a semi-theoretical scale of electronegativities, the writer pointed out that the electronegativity of an atom should vary greatly with the type of bonding AO it was using, and in the case of a hybrid AO should depend strongly on the degree of hybridization. As applied to the chlorine atom, the writer's conclusion[67] was that, for it to have the degree of

electronegativity necessary to account for a strong enough H^+Cl^- heteropolarity in the H—Cl bond to reproduce the observed HCl dipole moment, there must be a considerable amount of s,p hybridization in the bonding AO. Regardless of the quantitative soundness of the conclusion in this particular case, it is clear that isovalent hybridization must be of essential importance in determining the actual electronegativities of atoms like N, O, and Cl.[68]

The effect, on electronegativities, bond strengths, bond lengths, and dipole moments, of varying degrees of hybridization of σ bonds formed by carbon atoms—in particular, of C—H bonds in CH_4 and C_2H_6, C_2H_4, C_2H_2—has been discussed by various authors.[72]

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[72] Ref. 64; Ref 4 (Fig. 2 and p. 4500, and references in footnote 24 there); A. Maccoll, Trans. Faraday Soc., 46, 359 (1950); and see Table VI above.

XIII. CRITICISMS AND POSSIBLE IMPROVEMENTS
ON THE MAGIC FORMULA

As has been emphasized above, the present magic formula (cf. Section IV, in particular Ref. 30), both as to its precise form and as to the choice of numerical values of its coefficients, is still preliminary. In this Section some criticisms of its possible shortcomings and some possible leads for its future improvement will be sketched.

First of all, it may be an oversimplification to lump the "Coulomb" terms C of VB theory into the other terms (compare Eq. (21) with Eqs. (19), (20)). This procedure was adopted because in the VB theory for H_2, the theoretically computed Coulomb term C is relatively small, especially at the equilibrium R; also because in LCAO MO theory for H_2—which was used as a basis for the adopted form of the X's

(Eq. (22)) in the magic formula—it was found empirically that the sum of Coulomb plus error terms ($\underline{C} + \underline{E}'$ in Eq. (4)) is small. However, theoretically computed Coulomb energies indicate[37,55] that in C—H bonds (and in general whenever $p\sigma$ and hybrid σ bonds are present) the Coulomb terms of VB theory are much larger than in H_2.[73] If so,

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[73] Also in Li_2, the Coulomb energy seems to be relatively larger than in H_2 (cf. H. M. James, J. Chem. Phys., 2, 794 (1934)).

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the fact that the magic formula, using Eq. (22) for the primary bonding terms $\underline{X}$ of VB theory, works as well as it does may be a result of the likely possibility that in general the Coulomb terms, if actually important, may be more or less proportional to the overlap integral $\underline{S}$. The fact that the value of A_σ, determined by fitting CH and other molecules involving $p\sigma$ and hybrid-AO bonds, is too large to fit H_2 and Li_2 might then be explainable as a result of the presence of much larger Coulomb terms in the former. However, all this is as yet hypothetical.

Another rather uncertain feature in the magic formula lies in the method of calculating the nonbonded repulsions between inner (here $1\underline{s}$) and outer electrons. As computed using Eq. (23) with $\underline{I}$ values taken as averages of $1\underline{s}$ and outer-electron $\underline{I}$ values, these particular nonbonded repulsions are often rather large (cf. $\sum_k Y_k$ columns in Table VI). Although there are rather good reasons[39] for giving credence to those large values, a more thorough study—theoretical or empirical—would be desirable. (It seems possible even that such a study might point to somewhat larger rather than smaller values.)

When a study of the effect of Coulomb terms is made, possible effects corresponding to the "multiple exchange integrals" of

VB theory[24] should also be looked into.

With explicit inclusion of Coulomb terms in the magic formula (and possibly smaller Y_k terms), leading to smaller A_σ and revised A_π and ν values, the resulting revised Table IV might perhaps show improved agreements between computed and observed D_0 values, in particular for H_2, Li_2, and F_2,[56] and for the molecules C_2H_n. (For CH_4 and C_2H_n, polar RE corrections for the CH bonds, neglected in Table IV, should be included.). With smaller A_σ values, the X's and Y's would become smaller, and thereby closer to the much smaller effective exchange integrals indicated by the earlier work of Van Vleck and others.[61]

The magic formula should of course be tested and adjusted by fitting to more molecules, including molecules containing atoms higher in the periodic system. For this purpose, it will be necessary to obtain self-consistent-field S values for overlaps between such atoms. The hybridization situation will also be more complicated.

The usefulness of the present magic formula is to some degree limited by the fact that corrections under the general heading of resonance energy are often needed (cf. Section IV); these corrections, although usually of moderate size, must be obtained by outside considerations. They are needed in the following situations: (1) where strongly polar bonds are present; (2) where there is unusual stabilization by conjugation or aromatic resonance;[74] (3) where

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[74] For a theoretical analysis and some theoretical computations of conjugation and resonance energies, see R. S. Mulliken and R. G. Parr, J. Chem. Phys., 19, 1271 (1951). Serber (cf. footnote 55) has also discussed the problem. Mulliken and Parr also give some analysis of hyperconjugation energies.

atoms are present in a partially demoted valence state.

With regard to polar bonds, reference may be made to Section V above. In extreme _ionic_ bonds, the procedure indicated there fails, but the magic formula should now be valid with the molecular structural units taken as ions instead of atoms, and an ionic attraction term added.

In addition to RE terms like those used in VB theory for aromatic or conjugated molecules, a small second-order hyperconjugation RE term[65,74] is probably needed in the magic formula for C_2H_4, C_2H_6, and higher olefines and paraffins.

The magic formula is particularly good in cases where there is only _isovalent_ hybridization (_cf._ Section IV). Here the use of hybrid-AO S values, together with a subtractive correction for the corresponding excess promotion energy, completely takes care of the effect of hybridization on D_0. But when, as in CH_4 and C_2H_n (_cf._ Section IV), _pluvalent_ hybridization is modified by partial demotion, no simple way is apparent for taking care of the demotion energy except by an RE correction like the Vogo correction in Tables III and VI. Like other RE terms, this one must be computed or estimated by special methods.

Finally, it may be recalled that the use of the magic formula is at present limited to molecules with bond lengths at their equilibrium values, except with respect to nonbonded interactions (see last paragraph of Section IV). It seems possible that, when perfected, the magic formula may be capable of reproducing D as a function of all the interatomic coordinates for large ranges of these. In relation to this possibility, the magic formula, taken in connection with the standard procedure adopted above of always maximizing the computed D_0 with respect to degree of hybridization, has the very

good property that it permits needed adjustment of hybridization with varying $\underline{R}$ without extra complications.

APPENDIX I. VALENCE-STATE ENERGY DATA

TABLE VIII

SOME VALENCE-STATE ENERGY DATA

APPLICABLE TO FIRST-ROW ATOMS WHEN IN LINEAR MOLECULES[a]

Atom	Ground State	Promotion Energies[b]				Ionization Energies (ev)	
		State[c]	P_0 (ev)	State[b]	ΔP(ev)	I_K[d]	$\bar{I}_L$[e]
Li	$s,\ {}^2S$	$s,\ V_1$	0.00	---	---	(66)	5.39
C	$s^2p^2,\ {}^3P_0$	$s^2\sigma\pi,\ V_2$	0.49	$s\sigma^2\pi,\ V_2$	9.45	288	14.88
N	$s^2p^3,\ {}^4S$	$s^2\sigma\pi\pi',\ V_3$	1.70	$s\sigma^2\pi\pi',\ V_3$	(12.60)	(398)	18.11
O	$s^2p^4,\ {}^3P_2$	$s^2\sigma\pi\pi'^2,\ V_2$	0.67	$s\sigma^2\pi\pi'^2,\ V_2$	16.49	530	21.22
F	$s^2p^5,\ {}^2P_{3/2}$	$s^2\sigma\pi^2\pi'^2,\ V_1$	0.02	$s\sigma^2\pi^2\pi'^2,\ V_1$	[20.92]	686	[24.88]

a   All energies are in ev, assuming 13.60 ev as the ionization energy of the H atom.

b P_0 denotes energy above the ground state, ΔP the _additional_ promotion energy to reach the state listed. The P_0 values are from Re. 34, and the ΔP values (estimated uncertainties a few tenths ev) are from data in Ref. 34, except the value for fluorine which is extrapolated. (The values for carbon are slightly inconsistent with Voge's G_1, G_2, and P_t values in Table IX, but since the present values had already been used in the later computations, it did not seem worth while to readjust them. Voge's parameters would lead to $P_0 = 0.32$ and $P_0 + \Delta P = 10.04$ ev.)

c   The detailed configurations given correspond to quantization in a force-field of cylindric symmetry, as in diatomic or other linear molecules; the symbols s, σ, π, π', respectively mean $2s$, $2p\sigma$,

$2p\pi^+$, and $2p\pi^-$.

__d__ The I_K values are ls I's of Holweck quoted by Dauvillier, J. de phys. et le radium [6], 8, 1 (1927)(see also J. Thibaud, ibid., 8, 447 (1927)), corrected slightly to agree with footnote a; (Actually, slightly higher estimated values--291, 401, 542, 696, for C, N, O, F--were used in the calculations in this paper.)

__e__ The $\bar{I}_L$ values are L shell valence-state values from footnote 34 or from data given there, obtained by averaging over the $3 + m$ electrons in the $s^2\sigma\pi^m$ valence states above. For example, $\bar{I}_L$ for nitrogen is one-fifth of

$$2I_s(s^2\sigma\pi\pi\pi,V_3 \rightarrow s\sigma\pi\pi\pi,V_4) + I_\sigma(s^2\sigma\pi\pi\pi,V_3 \rightarrow s^2\pi\pi\pi,V_2)$$
$$+ 2I_\pi(s^2\sigma\pi\pi\pi,V_3 \rightarrow s^2\sigma\pi,V_2) .$$

APPENDIX I. VALENCE-STATE ENERGY DATA (continued)

TABLE IX

VALENCE-STATE ENERGY DATA FOR TETRAVALENT CARBON[a]

Case	State	P_t (ov)	$\overline{I}_L$ (ov)[b]
A	$s\sigma\pi_x\pi_y$, V_4	8.47	13.68
A'	$s\sigma\pi\pi'$, V_4	8.78	
B'	$didi'\pi\pi'$, V_4	7.79	
C	$trtr'tr''\sigma$, V_4	7.14	
D	$teteto'te''te'''$, V_4	6.97	

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[a] The AO symbols are in part as in Table VII, note c; in addition, di, tr, te refer to digonal, trigonal, and tetrahedral $2s,2p$ hybrids respectively. P_t denotes promotion energy to a tetravalent valence state. The value 6.97 ev for Case D is from H. H. Voge, J. Chem. Phys., 4, 581 (1936); 16, 984 (1948). The values for the other unprimed cases are obtained from this by using Voge's 1948 values of G_2 (0.21 ev) and G_1 (2.24 ev) and a formula of J. H. Van Vleck, J. Chem. Phys., 2, 20 (1934), Eq. (7), noting that Cases D, C, B ($didi'\pi_x\pi_y$), A, correspond to $\mu = \frac{1}{4}$, 1/3, $\frac{1}{2}$, and 1, respectively in Van Vleck's formula. The cases A', B', are obtained from A and B respectively by adding $1\frac{1}{2}G_2$ ($cf.$ Tables in Ref. 34).

[b] One-fourth of $2s$ plus three-fourths of $2p$ ionization energy for State A. Since the whole magic formula procedure is rough, this I for State A can serve for all tetravalent states.

APPENDIX II

ENERGIES OF ISOVALENT HYBRID VALENCE STATES

For the carbon atom in the state $k)^2 h_{o\beta})^2 h_\beta) \pi)$, V_2, first consider the antisymmetrized wave function written in determinant form, $(6!)^{-\frac{1}{2}}$ Det $k(1)$ $k'(2)$ $h_{o\beta}(3)$ $h_{o\beta}'(4)$ $h_\beta(5)$ $\pi(6)$, where the unprimed symbols refer to AO's with positive spin $(\underline{m}_s = +\frac{1}{2})$, the primed ones to AO's with negative spin $(\underline{m}_s = -\frac{1}{2})$. Writing out $\underline{h}_{o\beta}$ and $\underline{h}_\beta$ as per Eqs. (24), the determinant may be expanded (cf., e.g., Margenau and Murphy, The Mathematics of Physics and Chemistry, D. Van Nostrand: 1943, p. 289) into a linear combination of eight determinants of which four vanish, and the remaining four combine (using $\alpha^2 + \beta^2 = 1$) to give the result

$$\psi(k^2 \, h_{o\beta}^2 \, h_\beta \, \pi) = \alpha\psi(k^2 \, s \, p\sigma^2 \, \pi) + \beta\psi(k^2 \, s^2 \, p\sigma \, \pi) \, . \tag{37}$$

This derivation is for the case of a carbon atom with $\underline{m}_s = +\frac{1}{2}$ for the spins of $\underline{h}_\beta$ and π. An analogous derivation evidently holds for each of the other three possible combinations of $\underline{m}_s$ values for these two AO's, hence also for the $k^2 \, h_{o\beta}^2 \, h_\beta \pi$, V_2 valence state, since each V_2 valence state wave function is a linear combination, of like form in all cases, of wave functions for the four different $\underline{m}_s$ combinations mentioned.

W. Moffitt,[75] in a similar discussion of hybrid valence

[75] Proc. Roy. Soc., 96A, 524 (1948), top of p. 527.

states, arrives at a relation the same as Eq. (37) except that, apparently erroneously, he gives α^2 and β^2 as coefficients instead of α and β. In a later paper,[33] he makes computations whose results, when graphed (his Fig. 1), are in agreement with Eq. (38) and Table VIII of the present paper.

By computing $\underline{E} = \int \psi^* H \psi \, dv$ with ψ taken as a V_2 valence-state function given by an equation corresponding to Eq. (37), one obtains, after noting that the two terms on the right of Eq. (37) are mutually orthogonal if orthogonal AO's are used or in general if true exact ψ's are used,

$$
\begin{aligned}
E(k^2 \, h_{\alpha\beta}^2 \, h_\beta \, \mathcal{N}, \, V_2) &= \beta^2 E(k^2 \, s^2 \, p\sigma \, \mathcal{N}, \, V_2) + \alpha^2 E(k^2 \, s \, p\sigma^2 \, \mathcal{N}, \, V_2) \\
&= E(k^2 \, s^2 \, p^2, \, {}^3P) + P_0 + \alpha^2 \Delta P,
\end{aligned}
\tag{38}
$$

where P_0 and ΔP have the meanings and the numerical values given in the carbon atom entry in Table VIII. (The derivation of Eq. (38) based on determinant wave functions, though strictly not exactly valid for true exact wave functions, should be very nearly so, and entirely satisfactory for present purposes. The values of P_0 and ΔP listed in Table VIII, being based on spectroscopic data, correspond to accurate wave functions.)

For hybrid valence states of other atoms, like that of carbon in having the configuration $k)^2 \, h_{\alpha\beta})^2 \, h_\beta)\ldots$, but containing additional $\mathcal{N}$ electrons, equations analogous to (37) and (38) can be proved by the same kind of procedure.