TABLE B. SCF input information.

Molecule	State	Electron configuration[a]			Internuclear distance R_e[b]	
		s	$+p$	$-p$	A	a.u.
Li_2	$^1\Sigma_g^+$	3	0	0	2.672_5	5.051
Be_2	$[^1\Sigma_g^+]$	4	0	0	2.0	(3.780)
C_2	$^1\Sigma_g^+$	4	1	1	1.2422	2.3475
N_2	$^1\Sigma_g^+$	5	1	1	1.094	2.068
F_2	$^1\Sigma_g^+$	5	2	2	1.418	2.680
LiH	$^1\Sigma^+$	2	0	0	1.5953_5	3.015
BH	$^1\Sigma^+$	3	0	0	1.2325	2.329
NH*	$^1\Sigma^+$	2	1	1	$[1.045_5]$	1.976
HF	$^1\Sigma^+$	3	1	1	0.9171	1.733
CO	$^1\Sigma^+$	5	1	1	1.1281_9	2.132
BF	$^1\Sigma^+$	5	1	1	1.262	2.385
LiF	$^1\Sigma^+$	4	1	1	1.51	2.85

[a] s, $+p$, and $-p$ refer to MO's of l value 0, +1, and −1, respectively.
[b] 1 a.u.=0.5291 A.

TABLE C. One-center overlap integrals.

Molecule	Overlap integral	Slater LCAO-MO	Best atom LCAO-MO	Best limited LCAO-MO
LiH	S_{12}	0.1662 6484	0.1620 4403	0.1930 7013
BH	S_{12}	0.2099 1853	0.2216 0079	0.2101 5522
NH	S_{12}	0.2279 2130	0.2248 6784	0.2284 5502
FH	S_{12}	0.2377 1090	0.2346 3500	0.2332 2147
Li_2	$S_{12}=S_{45}$	0.1662 6484	0.1620 4403	0.1601 1469
Be_2	$S_{12}=S_{45}$	0.1937 9309	0.1888 9342	0.1894 0733
C_2	$S_{12}=S_{45}$	0.2204 7827	0.2185 0310	0.2239 2555
N_2	$S_{12}=S_{45}$	0.2279 2130	0.2248 6784	0.2235 0663
F_2	$S_{12}=S_{45}$	0.2377 1090	0.2346 3500	0.2366 1054
CO	S_{12}	0.2204 7827	0.2185 0310	
	S_{45}	0.2334 4716	0.2307 4713	
BF	S_{12}	0.2099 1853	0.2216 0079	
	S_{45}	0.2377 1090	0.2346 3500	
LiF	S_{12}	0.1662 6484	0.1620 4403	
	S_{45}	0.2377 1090	0.2346 3500	

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Role of Coulomb Energy in the Valence-Bond Theory[*,†]

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I. INTRODUCTION

IN VB (valence-bond) theory calculations using covalent structures only, the binding energy is regarded as the sum of two terms, namely, a Coulomb term and an exchange term.[1,2] For the hydrogen molecule the computed energy at the r value at which it is a maximum (about 1.0 A) is about 12% of the experimental binding energy at that r value. (At the equilibrium internuclear distance in H_2, however, the contribution of the Coulomb energy to the binding energy is only about 1%.) It has very often been assumed that the ratio of Coulomb to total binding energy is about 12% in any chemical bond.

There are relatively few accurate calculations on this subject. Rosen and Ikehara[3] computed the Coulomb and exchange binding energies for the interaction between a pair of identical neutral atoms, each having one ns electron, for $n=1, 2, 3, 4, 5$. The results showed that both energies decrease with increasing n, but that the proportion of Coulomb energy in the total binding energy increases with increasing n. On extrapolating beyond $n=5$ they found greater values for the Coulomb than for the exchange binding energy. It has been shown also that for p electron bonds the Coulomb binding energy can have larger values than for s electron bonds.[4] The same is true for bonds formed by $2s-2p$ hybrid orbitals; the calculations of Woods[5] on CH_4 showed a Coulomb binding energy greater than 50% of the total binding energy.[6] A few unpublished calculations made some time ago in this Laboratory by C.W. Scherr also indicated large Coulomb energies. Fischer[7] too has made some calculations of Coulomb energies, but in a modified way directed toward the evaluation of hybridizations.

These few calculations raise the serious question

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[‡] Supported by a fellowship from the Fundacion Juan March, Madrid, Spain.

[1] Cf. J. H. Van Vleck and A. Sherman, Revs. Modern Phys. **7**, 167 (1935); L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935); H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York); C. A. Coulson, *Valence* (Clarendon Press, Oxford, England, 1957).

[2] R. S. Mulliken, J. Phys. Chem. **56**, 295 (1952).

[3] N. Rosen and S. Ikehara, Phys. Rev. **43**, 5 (1953).

[4] J. H. Bartlett, Phys. Rev. **37**, 507 (1931).

[5] H. J. Woods, Trans. Faraday Soc. **28**, 877 (1932).

[6] For more references on the subject cf. reference 2, Sec. XIII.

[7] I. Fischer-Hjalmars, Arkiv Fysik **5**, 349 (1952); **7**, 165 (1953).

whether, in general, the VB theory terms involving the exchange integrals are really predominant as they are in H_2, or whether, instead, the Coulomb terms may not often or even usually be of predominant importance. In any event, we thought it would be interesting to compute the Coulomb energy for several simple cases.

II. VALENCE-BOND THEORY BACKGROUND

In the Heitler-London theory of H_2, the normalized wave functions for the ${}^1\Sigma_g{}^+$ and ${}^3\Sigma_u{}^+$ states derived from two normal atoms are given by

$$[2(1\mp\Delta)]^{-\frac{1}{2}}(\psi_{\mathrm{I}}\mp\psi_{\mathrm{II}});\ \psi_{\mathrm{I}}\equiv 2^{-\frac{1}{2}}\,|a(1)\bar{b}(2)\,|,$$

$$\psi_{\mathrm{II}}\equiv 2^{-\frac{1}{2}}\,|\,\bar{a}(1)\bar{b}(2)\,|;\quad \Delta\equiv\int\psi_{\mathrm{I}}\psi_{\mathrm{II}}dv=-S^2,\tag{1}$$

where S is the overlap integral

$$\int a(1)b(1)dv_1.$$

Thus they are linear combinations of two Slater determinants (a and b refer to $1s$ atomic functions with α spin, $\bar{a}$ and $\bar{b}$ with β spin, on atoms A and B). The corresponding total molecular energies E are given by

$$(1-S^2)E=\int a(1)b(2)Ha(1)b(2)dv_1dv_2$$

$$\pm\int a(1)b(2)Ha(2)b(1)dv_1dv_2$$

$$\equiv(H_{11}\pm H_{12}).\tag{2}$$

Equation (2) can be rewritten[2] as

$$E=H_{11}\pm\eta/(1\pm S^2),\tag{3}$$

where

$$\eta\equiv H_{12}-S^2H_{11},\tag{4}$$

$\pm\eta/(1\pm S^2)$ being the exchange energy. (H_{12} is the usual exchange integral and η is the effective exchange integral or bond integral.[8])

Then the interaction energy U is

$$U\equiv E-E(\infty)=C\pm\eta/(1\pm S^2),\tag{5}$$

where

$$C\equiv H_{11}-E(\infty)\tag{6}$$

is the Coulomb energy. In Eqs. (2)–(5), E, U, H_{11}, C, H_{12}, η, and S are all functions of the internuclear distance r. The binding energy is the value of $-U$ at the equilibrium value r_e of r.

From Eqs. (2)–(5), after putting

$$H=H_0+H'$$

with

$$H_0=H_{a1}+H_{b2},$$

and

$$H'=-1/r_{b1}-1/r_{a2}+1/r_{12}+1/r\tag{7}$$

(in atomic units, a_H and e^2/a_H), one finds that C contains potential energy terms only:

$$C=J_{ab}-2I_{ab}+1/r,\tag{8}$$

where J_{ab} is an electrostatic repulsion integral

$$J_{ab}=\int a(1)b(2)(1/r_{12})a(1)b(2)dv_1dv_2,\tag{9}$$

and I_{ab} a nuclear attraction integral

$$I_{ab}=\int a(1)(1/r_b)a(1)dv_1.\tag{10}$$

Thus C is the same as if we had computed it as $E-E(\infty)$ using

$$E=\int\psi_{ab}{}^*H'\psi_{ab}dv_1dv_2$$

with ψ_{ab} equal to the simple orbital-product function $a(1)b(2)$. In short, C is here simply the change of electrostatic energy which would result classically if the charge clouds $a^2(1)$ and $b^2(2)$ of the two atoms could interpenetrate without any deformation.

One wonders whether molecular interaction energies in general, when approximated by VB theory, may not usefully be expressed by the equation

$$U=C+X(\eta_i,\ S\text{'s})+(P_0+\alpha^2\Delta P)+R,\tag{11}$$

that is, as a sum of C plus a function X of the overlap and effective exchange integrals, plus the *promotion energy* $P_0+\alpha^2\Delta P$ (see the following) required to reach the appropriate (in general, hybrid) atomic valence states corresponding to the actual molecular structure, plus R, the resonance energy arising when ionic structures, the existence of more than one independent VB structure, and/or other refinements, are taken into account. The function X would if possible be approximated as a sum of individual exchange energy terms. The effects of valence-shell hybridization, here taken into account in C, X, and $\alpha^2\Delta P$, as is convenient and customary in VB theory following Slater and Pauling, might somewhat more *logically* have been included in R. Note that $P_0+\alpha^2\Delta P$ is always positive; stable binding is produced when $C+X$ (assisted to some extent by R, which is always negative) is sufficiently strongly negative. U is a function of r, $-U(r_e)$ being the binding energy.

In most VB theory discussions, the terms in S have simply been neglected. It has been recognized that this is bad, and some attempts have been made to correct it, but, so far as we know, no really very serious efforts have been made. In most discussions, authors have thought in terms of dropping the S terms corresponding to S^2 *in Eq. (2)*. However, it is obviously very much less harmful[8] to neglect them only in Eqs. (3) or (5) instead of in Eq. (2), and our viewpoint is based on Eq. (5) and its generalization in Eq. (11). In many of the

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[8] Cf. reference 2, Eqs. (13)–(19); also J. van Dränen and J. A. A. Ketelaar, J. Chem. Phys. **18**, 1125 (1950), and W. T. Simpson, J. Chem. Phys. **25**, 1124 (1956).

earlier discussions, empirically obtained effective exchange integrals have been used. It can be seen that these really correspond to quantities more or less like $\eta/(1\pm S^2)$ of Eq. (3).

In general, for an N-electron diatomic molecule,

$$C\equiv\int\psi_a{}^{(1\cdots m)}\psi_b{}^{(m+1\cdots N)} \times H'\psi_a{}^{(1\cdots m)}\psi_b{}^{(m+1\cdots N)}dv_1dv_2\cdots dv_N, \quad (12)$$

where $\psi_a{}^{(1\cdots m)}\psi_b{}^{(m+1\cdots N)}$ is a simple product of two atomic functions, and

$$H'=-Z_b\sum_{i=1}^{m}(1/r_{bi})-Z_a\sum_{j=m+1}^{N}(1/r_{aj})+\sum_i\sum_j(1/r_{ij}) +Z_aZ_b/r \quad (13)$$

is the corresponding interaction Hamiltonian. Each atomic function may be approximated as a Slater determinant or a linear combination of these, each built using a set of AO's (atomic orbitals) so chosen as to minimize the energy. However, it is sufficiently exact for our purposes in computing C to treat each atomic wave function as a simple product of mutually orthogonal occupied AO's χ of the familiar Slater (or orthogonalized-Slater) type, e.g., $\psi_a=\chi_{a1}(1)\chi_{a2}(2)\cdots\chi_{am}(m)$. Electron spins are taken into account in assigning electrons to AO's but thereafter can be omitted. Equation (12) yields

$$C=\sum_i\sum_j[\chi_{ai}(1)\chi_{ai}(1)\,|\,1/r_{ij}\,|\,\chi_{bj}(2)\chi_{bj}(2)] +Z_aZ_b/r-Z_b\sum_i(\chi_{ai}\,|\,1/r_b\,|\,\chi_{ai}) -Z_a\sum_j(\chi_{bj}\,|\,1/r_a\,|\,\chi_{bj}. \quad (14)$$

We proceed shortly to the matter of computing C for several diatomic molecules selected as illustrative examples. But first some further explanation of the promotion energy terms in Eq. (11), and of the use of hybrid AO's, is needed.

Confining our discussion to diatomic molecules, we note first that in the case that an atom forms more than one bond, ordinary VB theory requires that the atom be placed in a state called a valence state in which the spins of the valence electrons are uncorrelated. Valence states are not atomic stationary states, but their wave functions can be written as linear combinations of those of stationary states; for example, that of the trivalent (V_3) valence state of the N atom with detailed electron configuration $1s^2\,2s^2\,2p\sigma\,2p\pi\,2p\bar{\pi}$ is a linear combination of suitable ${}^4S$, ${}^2D$, and ${}^2P$ stationary state wave functions of the $1s^2\,2s^2\,2p^3$ ground *configuration*. The energy of a valence state is therefore in general greater than that of the ground *state* (${}^4S$ for the N atom) by a promotion energy, here designated as P_0.

One also can consider valence states of excited electron configurations. For the N atom, the V_3 valence state of detailed configuration $1s^2\,2s\,2p\sigma^2\,2p\pi\,2p\bar{\pi}$ is of special interest; its wave function can be constructed as a linear combination of those of the ${}^4P$ and other stationary states of the $1s^2\,2s\,2p^4$ configuration. It is well known that it is often necessary in the VB method to use *hybrid* AO's to form valence bonds of sufficient strength to approach reality. The appropriate trivalent valence state configuration for the N atom may be described using hybrid AO's as $1s^2\,hy'^2\,hy\,2p\pi\,2p\bar{\pi}$.

Here hy and hy' are *two mutually orthogonal hybrids* of $2s$ and $2p$ AO's. In general, any $2s-2p$ hybrid is of the form

$$hy=\alpha\chi_{2s}+(1-\alpha^2)^{\frac{1}{2}}\chi_{2p\sigma} \quad (15a)$$

with α positive for a positive hybrid and α negative [or equally well, α positive but $(1-\alpha^2)^{\frac{1}{2}}$ replaced by $-(1-\alpha^2)^{\frac{1}{2}}$] for a negative hybrid.[9] Positive hybrids on an atom give large, negative hybrids small, overlap with σ AO's of the partner atom in a diatomic molecule provided, as is to be understood here, $\chi_{2p\sigma}$ is so defined that its positive lobe for either atom is directed toward the other atom. If hy is written as in Eq. (15a), the hybrid hy' *orthogonal to it* must be written as

$$hy'=(1-\alpha^2)^{\frac{1}{2}}\chi_{2s}-\alpha\chi_{2p\sigma}; \quad (15b)$$

hy' is a negative hybrid if α is positive, and vice versa. In the appropriate N atom hybrid V_3 valence state for stable compounds, mentioned previously, α is positive, but we later also contemplate an unsuitable but formally possible V_3 valence state where it is negative.

The several atoms B, C, N, O, and F all have among their valence states one with electron configuration of the type $1s^2\,hy'\,{}^2hy\cdots$, where $\cdots$ stands for a set of π electrons (0, 1, 2, 3, 4, π electrons for B, C, N, O, F, respectively). It is these V_n valence states ($n=1, 2, 3, 2, 1$ for B, C, N, O, and F) which are utilized in the ground states of those compounds of these atoms (BH, CH, NH, FH, N_2) for which Coulomb energy calculations are reported herein. It can be shown[10] that the hybrid V_n wave function of any electron configuration $k^2{\cdot}hy'\,{}^2hy\cdots$ (k stands for $1s$) is identical with a simple linear combination of the ground state V_n function of configuration $k^2\,2s^2\,2p\sigma\cdots$ (briefly, $k^2s^2\sigma\cdots$ and the excited V_n function $k^2s\sigma^2\cdots$, namely,

$$\psi(k^2\,hy'^2\,hy\cdots)=(1-\alpha^2)^{\frac{1}{2}}\psi_1(k^2s^2\sigma\cdots) +\alpha\psi_2(k^2s\sigma^2\cdots). \quad (16)$$

As mentioned in the preceding paragraph, α can be either positive (the actual case in ground states) or negative.

The functions ψ, ψ_1, and ψ_2 could be written out in detail as linear combinations of Slater determinants, but for our purposes in computing C, this is not necessary. Although the use of valence-state ψ's is essential

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[9] R. S. Mulliken, J. Chem. Phys. **19**, 900 (1951).

[10] Cf. reference 2, Appendix II.

in correctly computing *exchange energies*, the Coulomb energy C depends only on the electron configuration and can be computed using simple product wave functions with one electron assigned to each valence AO of the configuration and two to each nonvalence (closed shell) AO. However, the value of C does depend on the *specific* valence AO's used; for example, C is different for the configuration $2p\sigma^2 2p\pi$ (or even for $2p\sigma\, 2p\pi^2$) than for the trivalent configuration $2p\sigma\, 2p\pi\, 2p\bar{\pi}$ in which we are most interested.

Further, for a correct evaluation of the relative importance of Coulomb and exchange terms, we must keep in mind that the binding energy computed by the VB method is relative not to the ground state energy of the two atoms, but to hypothetical hybrid valence states of the atoms as exemplified in Eqs. (16). The net binding energy $-U$, relative to ground state atoms, is obtained after adding $P_0+\alpha^2\Delta P$ in Eq. (11). ΔP is the additional configurational promotion energy which would be required to go from the ground-configuration to the appropriate excited-configuration valence state; for example, ΔP corresponding to Eq. (16) is the difference in energy between ψ_1 and ψ_2.[10] $P_0+\alpha^2\Delta P$ is then the total promotion energy from the ground state to a hybrid valence state. Values of P_0 and ΔP are available in the literature,[2,11] and although the values for α in actual cases are somewhat uncertain, approximate values can be computed[12] from available theoretically determined LCAO MO wave functions.

In addition to Eq. (16), which covers cases with three σ electrons in the valence shell, we need a similar equation for atoms like lithium which have only one such σ electron. For these it is readily seen that

$$\psi(k^2hy)=(1-\alpha^2)^{\frac{1}{2}}\psi_1(k^2s)+\alpha\psi_2(k^2\sigma), \qquad (17)$$

with hy as in Eq. (15a) and with α either positive (actual ground state) or negative.

In the actual computations of C, each hybrid AO is expanded as in Eq. (15a). In order to obtain full orientation as to the possible effects of hybridization in actual molecules, a variety of hypothetical cases with various values of α have been calculated. Then to obtain a realistic appraisal of the effects of hybridization in actual molecules, calculations have been made for values of α believed to be approximately correct for these molecules. In addition, extensive calculations have been made for the case of two H atoms with one or both excited to a 2-quantum AO for hybrid and nonhybrid forms of the latter.

III. DETAILS OF THE CALCULATIONS

The AO's used here are normalized Slater AO's, namely,

TABLE I. Coulomb energy for H_2.[a]

	Internuclear distance									
Configuration[b]	1.4	1.6	2.4	3.2	4.4	4.8	5.6	6.4	8.0	9.6
$(1s_a)(1s_b)$	−0.00227	−0.01535	−0.01414	−0.00527	−0.00086	−0.00045	−0.00012	−0.00003	−0.0	0.0
$(2s_a)(2s_b)$	(0.399)	0.32488 (0.312)	(0.120)	0.06229 (0.041)	(−0.002)	−0.00142 (−0.006)	(−0.010)	−0.01037 (−0.009)	−0.00710 (−0.005)	−0.00353 (−0.003)
$(2s_a)(2p\sigma_b)$	(0.378)	0.29357 (0.287)	(0.083)	0.01010 (−0.0003)	(−0.037)	−0.03853 (−0.039)	(−0.036)	−0.03103 (−0.029)	−0.01703 (−0.015)	−0.00782 (−0.007)
$(2s_a)(2di_b)$	(0.343)	0.28911 (0.249)	(0.042)	−0.01101 (−0.039)	(−0.066)	−0.06145 (−0.064)	(−0.054)	−0.04623 (−0.042)	−0.02497 (−0.021)	−0.01139 (−0.009)
$(2p\sigma_a)(2p\sigma_b)$	0.36776	0.27203	0.05240	−0.03840	−0.07322	−0.07195	−0.06151	−0.04736	−0.02282	−0.00874
$(2p\sigma_a)(2di_b)$	(0.320)	0.25987 (0.221)	(−0.002)	−0.06619 (−0.087)	(−0.108)	−0.09855 (−0.102)	(−0.082)	−0.06261 (−0.060)	−0.02863 (−0.026)	−0.00955 (−0.008)
$(2di_a)(2di_b)$	(0.247)	0.22631 (0.148)	(−0.070)	−0.10476 (−0.144)	(−0.142)	−0.12745 (−0.129)	(−0.097)	−0.07496 (−0.066)	−0.09215 (−0.022)	−0.00467 (−0.0005)
$(2di_a')(2di_b')$	(0.446)	0.31238 (0.366)	(0.189)	0.09375 (0.110)	(0.057)	0.04212 (0.047)	(0.033)	0.02295 (0.024)	0.01407 (0.014)	0.00931 (0.009)
$(2p\pi_a)(2p\pi_b)$		0.33978		0.08200		0.02623		0.00999	0.00435	0.00209
$(2px_a)(2px_b)$		0.34933		0.08922		0.03100		0.01285	0.00598	0.00300

[a] Energies and internuclear distances in atomic units. Values in parentheses were computed using $2s^n$, all others using orthonormal AO's.

[b] $(2di)\equiv2^{-\frac{1}{2}}\{(2s)+(2p\sigma)\}$; $(2di')\equiv2^{-\frac{1}{2}}\{(2s)-(2p\sigma)\}$; positive end of $2p\sigma_a$ taken as directed toward b and vice versa.

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[11] R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934); W. Moffitt, Proc. Roy. Soc. (London) **A96**, 524 (1948); H. O. Pritchard and H. A. Skinner, J. Chem. Phys. **22**, 1936 (1954).

[12] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).

TABLE II. Coulomb energies for H_2: configurations $(1s_a)(2hy_b)$ and $(1s_a)(2p\pi_b)$.[a]

Configuration		Internuclear distance					
	α_b	1.6	3.2	4.8	6.4	8.0	9.6
$(1s_a)(2hy_b)$	$-(2)^{-\frac{1}{2}}$	0.05000 (0.064)	−0.00133 (−0.0006)	−0.00084 (−0.0008)	−0.00028 (−0.00004)	−0.00008 (−0.0001)	−0.00002 (−0.00004)
	1	0.05739 (0.056)	−0.00286 (−0.006)	−0.00387 (−0.004)	−0.00178 (−0.001)	−0.00062 (−0.0005)	−0.00018 (−0.0001)
	$(15)^{\frac{1}{2}}/4$	0.05724 (0.049)	−0.00837 (−0.013)	−0.00746 (−0.007)	−0.00328 (−0.003)	−0.00113 (−0.001)	−0.00033 (−0.0003)
	$(3)^{\frac{1}{2}}/2$	0.05543 (0.042)	−0.01487 (−0.010)	−0.01126 (−0.011)	−0.00482 (−0.004)	−0.00165 (−0.001)	−0.00049 (−0.0004)
	$(2)^{-\frac{1}{2}}$	0.05255 (0.037)	−0.02003 (−0.025)	−0.01387 (−0.014)	−0.00583 (−0.005)	−0.00198 (−0.002)	−0.00059 (−0.0005)
	0	0.04516	−0.01850	−0.01085	−0.00432	−0.00144	−0.00043
$(1s_a)(2p\pi_b)$		0.06190	0.00071	−0.00031	−0.00009	−0.00001	−0.0

[a] See footnotes to Table I.

$$1s=(\zeta_1{}^3/\pi)^{\frac{1}{2}}\exp(-\zeta_1 r)$$

$$2s^n=(\zeta_2{}^5/3\pi)^{\frac{1}{2}}\, r\exp(-\zeta_2 r)$$

$$\left.\begin{matrix}2p\sigma\\ \\ 2p\pi\\ \\ 2p\bar{\pi}\end{matrix}\right\}=(\zeta_2{}^5/\pi)^{\frac{1}{2}}r\exp(-\zeta_2 r)\left\{\begin{matrix}\cos\theta\\ \\ 2^{-\frac{1}{2}}\sin\theta\exp(i\phi)\\ \\ 2^{-\frac{1}{2}}\sin\theta\exp(-i\phi).\end{matrix}\right. \qquad (18)$$

In all cases the computations have been carried out for Slater's values of ζ_1 and ζ_2. The z axis centered on each atom lies along the internuclear axis, with the positive z directions toward each other. The AO's indicated in (18) constitute an orthonormal set, with the exception of the $2s^n$ AO which is not orthogonal to the $1s$ AO. The orthogonalized $2s$ is given by

$$2s^{or}=(1-S_{12}{}^2)^{-\frac{1}{2}}[(2s^n)-S_{12}(1s)],$$

where S_{12} is the mononuclear overlap integral between the $1s$ and the $2s^n$ AO's, its values being 0.48384983, 0.22047827, 0.22792130 for H, C, and N, respectively. Since, however, the computation of C is much simplified using $2s^n$ instead of $2s^{or}$, yet the values of C are but little affected, and since the Slater AO's used even if orthogonalized are (except for H atoms) but rough approximations to best AO's, most of the following calculations have been made using $2s^n$ AO's.

The required integrals are exclusively two-center nuclear attraction and Coulomb-type interelectronic repulsion integrals.[13] These integrals have here been computed exactly at several internuclear distances for H_2, N_2, CH, but only for the equilibrium distance for all the other molecules (Li_2, F_2, LiH, BH, NH, FH). For H_2 the integrals were easily evaluated on a desk machine to six to eight significant figures.[14] For the other molecules the integrals were evaluated with the use of a Univac Scientific Model 1103 computer using a fully automatic program.[15]

As already indicated, the evaluation of the promotion energy for various states of hybridization has been done by means of the expression $P=P_0+\alpha^2\Delta P$. For N_2 and CH, C was evaluated at various internuclear distances for degrees of promotion α^2 [cf. Eq. (16)] equal to 0, 0.50, 1.0. For each of the molecules Li_2, N_2, F_2, LiH, BH, CH, NH, and FH, C was evaluated at the equilibrium distance for α^2 values 0, 0.25, 0.50, 0.75, 1.0, and for a value corresponding to the actual state of hybridization as determined[11] from LCAO–MO–SCF calculations. The promotion energy was obtained using existing tables[2,11] for P_0 and ΔP.

For each degree of promotion α^2, the calculations have been carried out for the two possible hybrid atomic configurations which correspond to a positive or a negative value of α in Eq. (15a) and in Eqs. (16) or (17). In all cases, positive α corresponds to use of a positive hybrid *for the σ valence electron* but to a negative hybrid for the two additional (lone-pair) σ valence-shell electrons in case these are present.

If we had used self-consistent field instead of Slater AO's in our calculations, the results probably would have been somewhat more realistic, especially at larger internuclear distances. However, the major features of our results would certainly not have been changed.

IV. RESULTS AND THEIR INTERPRETATION

The Coulomb energy for H_2 has been computed over a broad range of internuclear distances for various con-

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[13] C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951).

[14] The Coulomb-type interelectronic repulsion integrals were evaluated using a four-point Lagrangian interpolation in the "Tables of two-center Coulomb integrals between $1s$, $2s$ and $2p$ orbitals," by C. C. J. Roothaan, Spec. Tech. Rept., Department of Physics, University of Chicago, 1955 (available on request).

[15] C. C. J. Roothaan, J. Chem. Phys. **28**, 982 (1958).

TABLE III. Coulomb energies for H_2: configurations $(2hy_a)(2hy_b)$.[a]

α_a	α_b	1.4	1.6	2.4	3.2	4.4	4.8	5.6	6.4	8.0	9.6
		Internuclear distance									
$-(2)^{-\frac{1}{2}}$	1	(0.435)	0.32933 (0.350)	(0.162)	0.08340 (0.079)	(0.027)	0.02150 (0.019)	(0.009)	0.00483 (0.004)	0.00084 (0.0005)	0.00005 (0.0001)
$-(2)^{-\frac{1}{2}}$	0	(0.426)	0.30572 (0.338)	(0.137)	0.03790 (0.049)	(−0.003)	−0.01193 (−0.009)	(−0.015)	−0.01577 (−0.016)	−0.01122 (−0.012)	−0.00701 (−0.007)
1	$(15)^{\frac{1}{2}}/4$	(0.376)	0.31319 (0.286)	(0.089)	0.03617 (0.009)	(−0.026)	−0.02381 (−0.029)	(−0.027)	−0.02402 (−0.022)	−0.01397 (−0.011)	−0.00656 (−0.005)
1	$(3)^{\frac{1}{2}}/2$	(0.354)	0.29964 (0.262)	(0.059)	0.00836 (−0.021)	(−0.051)	−0.04661 (−0.051)	(−0.044)	−0.03765 (−0.034)	−0.02076 (−0.017)	−0.00955 (−0.007)
$(15)^{\frac{1}{2}}/4$	$(15)^{\frac{1}{2}}/4$	(0.343)	0.29511 (0.252)	(0.051)	0.00590 (−0.026)	(−0.053)	−0.04749 (−0.051)	(−0.043)	−0.03661 (−0.032)	−0.01859 (−0.014)	−0.00714 (−0.005)
$(15)^{\frac{1}{2}}/4$	0	(0.352)	0.28112 (0.258)	(0.048)	−0.01813 (−0.036)	(−0.065)	−0.06159 (−0.063)	(−0.053)	−0.04339 (−0.040)	−0.02161 (−0.019)	−0.00849 (−0.007)
$(3)^{\frac{1}{2}}/2$	$(3)^{\frac{1}{2}}/2$	(0.280)	0.25378 (0.185)	(−0.025)	−0.05983 (−0.099)	(−0.107)	−0.09617 (−0.098)	(−0.075)	−0.06078 (−0.052)	−0.02600 (−0.019)	−0.00647 (−0.003)
$(3)^{\frac{1}{2}}/2$	0	(0.329)	0.26833 (0.233)	(0.015)	−0.04710 (−0.069)	(−0.092)	−0.08440 (−0.087)	(−0.071)	−0.05539 (−0.052)	−0.02602 (−0.023)	−0.00915 (−0.008)

[a] See footnotes to Table I.

figurations in which the two electrons (one for each atom) are assigned to a variety of combinations of the atomic orbitals $1s$, $2s$, $2p\sigma$, $2p\pi$, and various hybrid orbitals. The results are listed in Tables I–IV. In all the Tables the values in parentheses have been evaluated using the $2s^n$AO. The value of α is indicated when hybrid orbitals are involved. The results are also displayed for the most interesting cases in Figs. 1 and 2. The computed Coulomb energies are in some cases astonishingly large; the largest $-C$ (3.7 ev at $r=2.2$ A) is found for the configuration $(2di_a)(2di_b)$, where $(2di)$ indicates a positive digonal hybrid AO ($\alpha = +1/2^{\frac{1}{2}}$). For most of the cases, C corresponds to an attraction. But for the configurations $(2p\pi_a)(2p\pi_b)$ and $(2di_a')(2di_b')$, where $(2di')$ indicates a negative diagonal hybrid AO ($\alpha = -1/2^{\frac{1}{2}}$), and for a few others, C corresponds to a repulsion.

Although these results are not directly applicable to actual states of the H_2 molecule nor to many-electron molecules, we believe that they are highly significant as to what may be expected in actual cases. They clearly suggest (in agreement with the early computations mentioned in the Introduction) that Coulomb energies make major contributions to binding energies when $2p\sigma$ or, especially, positive $2s-2p\sigma$ hybrid AO's are involved, even though for H_2 at r_e in its ground state $-C$ is only one percent of the Heitler-London binding energy.

[In fairness to ground state H_2, it should be noted that if $1s$, $2p\sigma$ hybrid instead of pure $1s$ AO's had been used, $-C$ would no doubt be larger for the ground state. However, we ought then for other atoms to extend the hybridization used to include higher than valence-shell quantum numbers. In the present formulation, any effects on U which would have resulted from such extension are taken up in R of Eq. (11).]

Even though the results on H_2 may at first sight seem surprising, an examination of the charge distributions involved shows that they are qualitatively entirely reasonable. Each C consists of two attraction and two repulsion terms, which tend to cancel, their respective values being roughly $-1/r$, $-1/r$, $+1/r$ (nuclear attractions and interelectronic repulsion), and $+1/r$ (nuclear repulsion, always exactly $1/r$). It is seen that the first three terms should be relatively close to the rough values $\pm 1/r$ in the $s_a s_b$ case. For the $2px_a\, 2px_b$ or $2py_a\, 2py_b$ case (using real AO's), it is seen that the attractions of nucleus b for electron a and vice versa are each less than $1/r$, while the interelectronic repulsion is greater than $1/r$, making the over-all effect a repulsion. For the $2p\sigma_a\, 2p\sigma_b$ and especially for the $2di_a\, 2di_b$ case, the two attraction terms are each considerably greater than $1/r$, and it looks plausible that this effect can outweigh (as the calculations show it must) the increase which also occurs in the interelectronic repulsion. Conversely, the two attraction terms are smaller than $1/r$ in the $2di_a'\, 2di_b'$ case, and

TABLE IV. Coulomb energies for H_2: configurations $(2hy_a)(2p\pi_b)$.[a]

	Internuclear distance					
α_a	1.6	3.2	4.8	6.4	8.0	9.6
$-(2)^{-\frac{1}{2}}$	0.32720 (0.356)	0.08541 (0.094)	0.03062 (0.033)	0.01310 (0.014)	0.00642 (0.006)	0.00351 (0.004)
1	0.33019 (0.325)	0.07178 (0.061)	0.01308 (0.010)	0.00066 (0.0003)	−0.00088 (−0.0008)	−0.00058 (−0.0005)
$(15)^{\frac{1}{2}}/4$	0.32094 (0.301)	0.04905 (0.032)	−0.00630 (−0.011)	−0.01140 (−0.012)	−0.00749 (−0.007)	−0.00407 (−0.004)
$(3)^{\frac{1}{2}}/2$	0.30879 (0.277)	0.02380 (0.003)	−0.02654 (−0.032)	−0.02365 (−0.025)	−0.01409 (−0.014)	−0.00752 (−0.007)
$(2)^{-\frac{1}{2}}$	0.29806 (0.264)	0.00518 (−0.015)	−0.04023 (−0.046)	−0.03159 (−0.032)	−0.01827 (−0.018)	−0.00965 (−0.010)
0	0.29507	0.01881	−0.02269	−0.01915	−0.01097	−0.00557

[a] See footnotes to Table I.

this effect doubtless outweighs the reduced interelectronic repulsion, so that the over-all effect is repulsion.

Computations over a broad range of internuclear distances, similar to those for H_2 but now exemplifying more typical many-electron molecules in their ground states, have been made for CH and N_2 including all electrons. The results are shown graphically in Figs. 3–5. (The detailed numerical values of C are of no great interest and so are not tabulated here.) The results obtained are in many respects striking. They are consistent with those obtained for H_2 and qualitatively understandable in a similar way.

Figures 3 and 4 show C as a function of r for CH and N_2, for carbon atom electron configurations varying

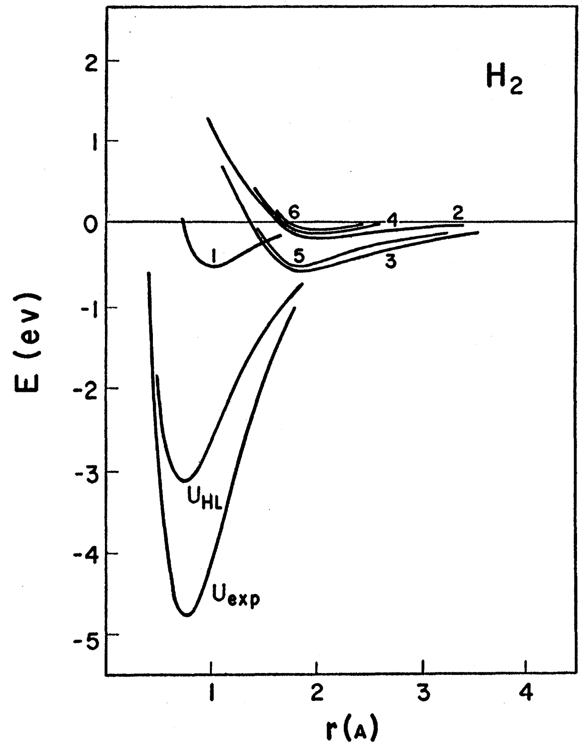

FIG. 1. Coulomb energies of two hydrogen atoms as functions of r, with the two electrons assigned to AO's as follows. Curve 1: $1s_a$, $1s_b$; curve 2: $1s_a$, $2s_b$; curve 3: $1s_a$, $2di_b$; curve 4: $1s_a$, $2di_b'$; curve 5: $1s_a$, $2p\sigma_b$; curve 6: $1s_a$, $2p\pi_b$. The $2s^{or}$ AO was used in the calculations. Curves U_{HL} and U_{exptl}. represent the interaction energy of two hydrogen atoms with the two electrons assigned to $1s$ atomic orbitals, the first one corresponding to the Heitler-London interaction energy and the latter to the experimental energy.

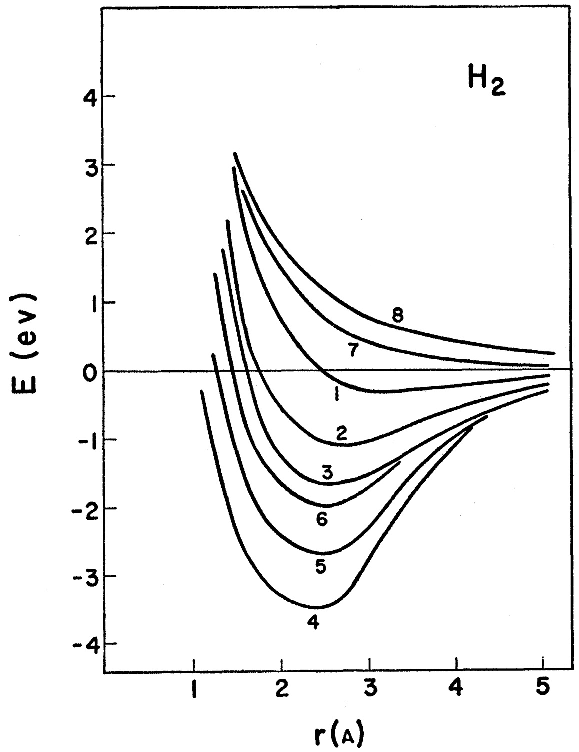

FIG. 2. Coulomb energies of two hydrogen atoms as functions of r, with the two electrons assigned to AO's as follows. Curve 1: $2s_a$, $2s_b$; curve 2: $2s_a$, $2p\sigma_b$; curve 3: $2s_a$, $2di_b$; curve 4: $2di_a$, $2di_b$; curve 5: $2p\sigma_a$, $2di_b$; curve 6: $2p\sigma_a$, $2p\sigma_b$; curve 7: $2di_a'$, $2di_b'$; curve 8: $2p\pi_a$, $2p\pi_b$. The $2s^{or}$ AO was used in the calculations.

from $1s^2\,2s^2\,2p\sigma\,2p\pi$ (a ground state configuration) to $1s^2\,2s\,2p\sigma^2\,2p\pi$, and for nitrogen atom configurations from $1s^2\,2s^2\,2p\sigma\,2p\pi\,2p\bar{\pi}$ to $1s^2\,2s\,2p\sigma^2\,2p\pi\,2p\bar{\pi}$. It is seen that $-C$ is especially large for the configurations involving $(2di)^2(2di')$ as might have been expected from the results for H_2. Notably, $-C$ is still increasing at the equilibrium values r_e of the actual molecules CH and N_2, and very strongly so for the configurations involving $(2di)^2(2di')$. C must, however, reach a minimum at some value of $r<r_e$, although in several cases our computations were not made at small enough r values to reach this. Further comment on Figs. 3 and 4 is made in the following.

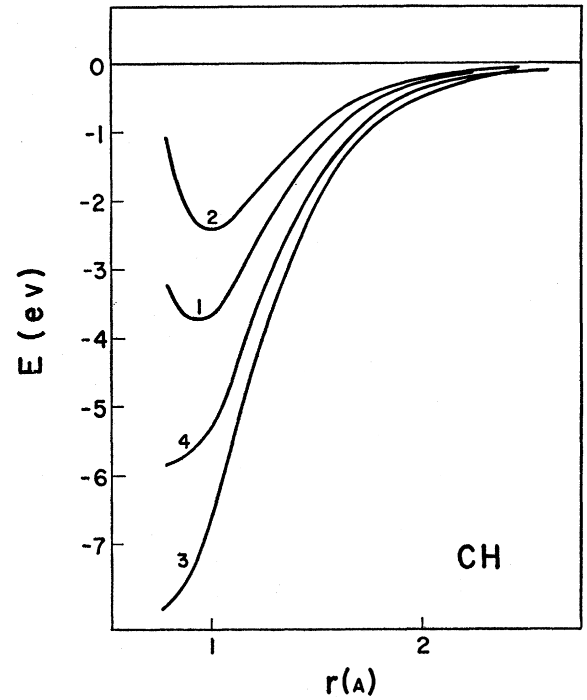

FIG. 3. Coulomb energy of CH as a function of the internuclear distance for the following atomic electron configurations.

Curve 1: $(1s_C)^2(2s_C)^2(2p\sigma_C)(2p\pi_C)$, $(1s_H)$;
Curve 2: $(1s_C)^2(2di_C')^2(2di_C)(2p\pi_C)$, $(1s_H)$;
Curve 3: $(1s_C)^2(2di_C')(2di_C)^2(2p\pi_C)$, $(1s_H)$;
Curve 4: $(1s_C)^2(2s_C)(2p\sigma_C)^2(2p\pi_C)$, $(1s_H)$.

The $2s^{or}$ AO was used in the calculations.

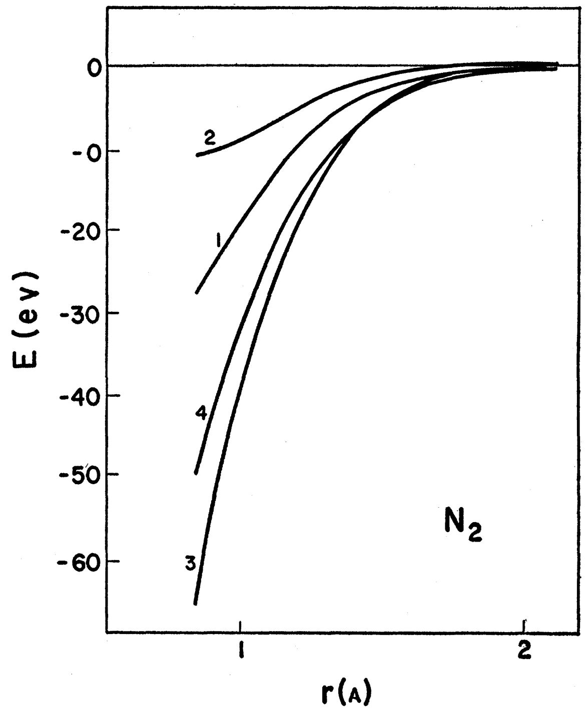

FIG. 4. Coulomb energy of N_2 as a function of the internuclear distance for the following atomic electron configurations.

Curve 1: $(1s)^2(2s)^2(2p\sigma)(2p\pi)(2p\bar{\pi})$;
Curve 2: $(1s)^2(2di')^2(2di)(2p\pi)(2p\bar{\pi})$;
Curve 3: $(1s)^2(2di')(2di)^2(2p\pi)(2p\bar{\pi})$;
Curve 4: $(1s)^2(2s)(2p\sigma)^2(2p\pi)(2p\bar{\pi})$.

The $2s^{or}$ AO was used in the calculations.

In terms of a practical application of the foregoing results to the understanding of the binding energy B of CH and N_2, it is necessary to keep in mind the following two points: (1) Except in the case of the ground state configurations, it is necessary to add a rather large promotion energy $P_0+\alpha^2\Delta P$ to C in estimating the net contribution of C to the interaction energy U of Eq. (11). (2) Although hybrid configurations of which the extreme example involves $(2di)^2(2di')$ are very favorable for large $-C$, they are very unfavorable with respect to the exchange energy, whereas hybrids of which $(2di)(2di')^2$ is the extreme example are most favorable for the latter, although relatively unfavorable for C. [The closed shell $(2di)^2$ gives maximum exchange repulsion, and $2di'$ gives very little exchange attraction, while $(2di')^2(2di)$ gives minimum exchange repulsion and maximum attraction.] Since it is convincingly known, for example, from SCF–LCAO–MO calculations,[16] that the actual states of hybridization in these molecules lie between $2s^2\,2p\sigma$ and $(2di')^2(2di)$, it is clear that the exchange terms must in CH, N_2, and other actual cases have a predominant influence.

Figure 5 shows for CH and N_2 the experimental ground state potential curves (approximated by Morse functions), together with $C+P_0+\alpha^2\Delta P$ computed for the *actual degree of hybridization* α^2 at r_e based on SCF–LCAO–MO computations. The asymptotes of the curves $C+P_0+\alpha^2\Delta P$ are $P_0+\alpha^2\Delta P$; this does not mean that there is any actual promotion at $r=\infty$, but merely that for the degree of hybridization indicated, the sum of C, the exchange energy X, and R of Eq. (11) have to overcome a handicap of $P_0+\alpha^2\Delta P$. It is of much interest that at r_e, C alone has somewhat more than overcome this handicap in the case of CH, and about $\frac{2}{3}$ overcome it in the case of N_2. This leaves the exchange energy X plus R to do the rest. R is a measure

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[16] C. W. Scherr, J. Chem. Phys. **23**, 569 (1955); M. Krauss, ibid. **28**, 1021 (1958); B. J. Ransil (unpublished).

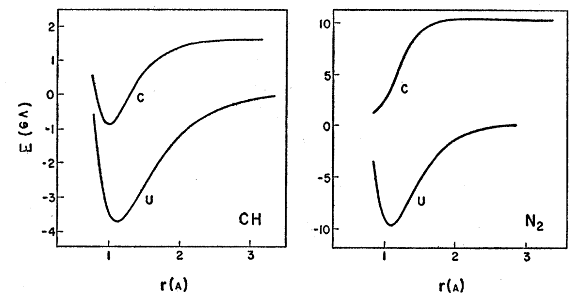

FIG. 5. Experimental interaction energy U and Coulomb energy C computed for the hybrid valence state believed to exist at r_e for CH and N_2 [12% promotion from $(1s)^2(2s)^2(2p\sigma)(2p\pi)$ toward $(1s)^2(2s)(2p\sigma)^2(2p\pi)$ for C atom in CH, 26% from $(1s)^2(2s)^2(2p\sigma)(2p\pi)(2p\bar{\pi})$ toward $(1s)^2(2s)(2p\sigma)^2(2p\pi)(2p\bar{\pi})$ for N atoms in N_2, with positive hybrid σ valence AO in each case]. The curves U are Morse curves. In computing C the $2s^{or}$ AO was used.

of the inadequacy of simple covalent VB-type wave functions to reproduce the actual binding energy; it is simply the difference between the VB computed energy and the experimental energy. It includes some alleviation of P_0 corresponding to the fact that actually the energy is minimized without full promotion from the atomic ground state (e.g., ^4S for the N atom) to the valence state of the same configuration,[17] but must be attributed primarily to what may be described as induced configuration interaction, consisting of the introduction of ionic and various excited-configuration atomic states into the wave function. (Hybridization has already brought in one type of excited-configuration state, whose effects are included in C and X.) In the case of H_2, R constitutes one third of the total binding energy.

Computations similar to those for N_2 and CH as embodied in Figs. 3–5, but for r_e only, have been carried out also for Li_2, F_2, LiH, BH, NH, and FH. The computed values of C for various degrees of promotion (also for CH and N_2) are given in Table V. Of main interest are the relative contributions of C, X, and R to the binding energy B (referred in each case to the appropriate hybrid valence state), as summarized in Table VI. From the last column of Table VI it is clear that for typical nonpolar or not very polar diatomic molecules, C makes a major contribution, although probably X is still usually the decisive factor as generally believed. However, for Li_2, C is actually very nearly as large as $B+P$, indicating that X here is of quite minor importance.

It seems fairly certain that similar conclusions will hold for molecules formed from higher-row atoms and for polyatomic molecules. For strongly polar or ionic molecules, our calculations do not do full justice to C. It seems fairly clear that for such molecules the computed C should be increased by the extra ionic attractions involved. In Eq. (11) these added contributions are represented only as a part of R. In Table VI, the relatively small computed values of C as compared with $B+P$ in the cases of LiH and HF really should have been considerably increased by adding such polar contributions to $-C$ and subtracting them from $-(X+R)$.

Although, as we have seen, the promoted states important in actual molecules formed from first-row atoms involve always the use of a *positive* hybrid *for the σ valence electron* AO, it is nevertheless of interest to extend somewhat the consideration of the behavior of C as a function of the state of hybridization which was begun in Figs. 3–5 and Table V. Figure 6 displays C as a function of degree of $s\rightarrow p\sigma$ promotion, as computed at r_e only, for LiH, Li_2, CH, and N_2, for each of two cases: (a) positive hybrid for σ valence electron, hence positive α in Eqs. (16) and (18)—full-line parts of curves; (b) negative hybrid for σ valence electron, hence negative α in Eqs. (16) and (18)—dashed parts of curves. In each case, the actual state of hybridization is marked on the curve—it falls on the full-line part. Especially to be noted is the fact that for those cases (LiH, Li_2) where there is only a single σ electron in the valence shell, C falls near the bottom of the whole curve, but where there are three (CH, N_2, and others), it falls near the top. Thus C cooperates with X in the former but fights X in the latter case; this accounts for the unusual importance of C in compounds such as Li_2.

The reason for this contrasting behavior in the two types of cases is clear. As can be seen from the discussion of the calculations on H_2 at the beginning of Sec. IV, replacement of a $p\sigma$ or especially of an s AO by a positive hybrid makes C more attractive, while replacement by a negative hybrid makes it less attractive or more repulsive. When there is only one σ electron in the valence shell, the positive hybrid, which is favorable for exchange as well as for Coulomb binding, is obviously the one which is occupied in the ground state.

But when there are *three* σ electrons in the valence shell, two must go into a lone pair while the third occupies the bonding σ orbital. In this case, either of two choices seems plausible: the lone-pair electrons might occupy a negative hybrid and the valence electron a positive hybrid orbital or vice versa. In either event, the two hybrid orbitals used have to be orthogonal to each other. The total Coulomb energy is the sum of the lone-pair and valence-electron contributions. Our calculations show that this total Coulomb energy is strongly attractive if the two lone-pair elec-

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[17] The promotion energy P_0 for each C or N atom is required for the exchange (though not for the Coulomb) forces to be maximally effective. This fact is partially alleviated, however, by a part of the contribution R corresponding to the fact that actually the energy after all is minimized without complete promotion to the valence state; for example, in N_2, the actual valence state undoubtedly corresponds more to ^4S and less to ^2D and ^2P than does the V_3 valence state of configuration $k^2s^2\sigma\pi\bar{\pi}$. [Compare H. H. Voge's discussion of the actual state of the carbon atom in methane: J. Chem. Phys. **4**, 581 (1936); **16**, 984 (1948); and see reference 2].

TABLE V. Coulomb energies for some diatomic molecules.[a]

Molecule	σ valence electron[b]	Degree of promotion α^2 (%)[c] 0	25	50	75	100	Actual value[d]
Li_2	Positive hybrid	−0.013	−0.067	−0.084	−0.091	−0.062	−0.047
	Negative hybrid	−0.013	0.032	0.029	0.006	−0.062	
N_2	Positive hybrid	−0.549	−0.250	−0.279	−0.437	−0.899	−0.247
	Negative hybrid	−0.549	−0.965	−1.091	−1.128	−0.899	
F_2	Positive hybrid	−0.017	0.029	0.029	0.007	−0.041	−0.003
	Negative hybrid	−0.017	−0.034	−0.033	−0.037	−0.041	
LiH	Positive hybrid	−0.011	−0.033	−0.041	−0.043	−0.031	−0.042
	Negative hybrid	−0.011	0.001	−0.001	−0.009	−0.031	
BH	Positive hybrid	−0.104	−0.073	−0.077	−0.094	−0.145	−0.074
	Negative hybrid	−0.104	−0.155	−0.172	−0.176	−0.145	
CH	Positive hybrid	−0.116	−0.077	−0.081	−0.100	−0.162	−0.083
	Negative hybrid	−0.116	−0.178	−0.197	−0.201	−0.162	
NH	Positive hybrid	−0.114	−0.071	−0.075	−0.096	−0.162	−0.084
	Negative hybrid	−0.114	−0.181	−0.201	−0.205	−0.162	
FH	Positive hybrid	−0.105	−0.053	−0.055	−0.078	−0.155	−0.075
	Negative hybrid	−0.105	−0.183	−0.205	−0.208	−0.155	

[a] Energies in atomic units. All values are computed for each molecule at its equilibrium internuclear distance (cf. Table VI). Values for N_2 and CH were computed using orthonormal AO's, all others using $2s^n$. The computations were made to five figures but have been rounded off to three.

[b] The designations "positive hybrid" and "negative hybrid" refer to the σ *valence electron* and, respectively, correspond to positive or negative α in Eqs. (15)–(17).

[c] Cf. Eqs. (15)–(17).

[d] See fourth column in Table VI.

TABLE VI. Contributions of the Coulomb, exchange, and resonance energies in Eq. (11) to the binding energy (in ev).[a]

	r_e(A)	B	100 α^2	P_0	ΔP	P	$B+P$	$-C$	$-(X+R)$	$-100C/(B+P)$
H_2	0.7416	4.75	0	0	0	0	4.75	0.06	4.69	1
Li_2	2.6725	1.05	9	0	1.84	0.33	1.38	1.28	0.10	93
N_2	1.0940	9.90	26	1.70	12.60	9.95	19.85	6.73	13.12	34
F_2	1.4530	2.81	2	0.02	20.92	0.88	3.69	0.09	3.60	2
LiH	1.5953	2.59	59	0	1.84	1.09	3.68	1.15	2.53	31
BH	1.2325	3.66	19	0	6.28	1.19	4.85	2.02	2.83	42
CH	1.1198	3.65	12	0.49	9.45	1.62	5.27	2.27	3.00	43
NH	1.0380	4.00	8	1.70	12.60	2.71	6.71	2.27	4.44	34
FH	0.9171	6.65	5	0.02	20.92	1.07	7.72	2.04	5.68	26

[a] All energies are in ev. The equilibrium internuclear distances r_e and binding energies B, where B is $-U(r_e)$, have been taken from G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1957). To obtain the B values, the empirical binding energies have been corrected by adding the zero-point energy in each case.

The α^2 values given are approximate actual values of the degree of promotion based on theoretical computations by the SCF-LCAO-MO method. (see reference 16.)

The C values are from the computations of the present paper (cf. Table V). The values for N_2 and CH were computed using orthonormal AO's, all others using $2s^n$.

trons occupy the positive hybrid and small or repulsive if they occupy the negative hybrid) (see Fig. 6). If *only* the Coulomb energy were involved, the lone-pair electrons would then in the ground state certainly occupy the positive hybrid, giving extremely strong binding. However, they actually are found to occupy the negative hybrid, even though the Coulomb energy contribution to the binding is then enormously reduced. This must be attributed to the fact that occupation of the positive hybrid by the lone-pair electrons would result in a very strong exchange repulsion (nonbonded repulsion) toward the other atom, together with only a weak attraction by the bonding electron in the negative hybrid, whereas for occupation of the negative hybrid by the lone-pair electrons and of the positive hybrid by the σ valence electron, the net exchange energy is very much more favorable. Evidently the minimization of the exchange energy counts more than minimization of the Coulomb energy in the three-σ-electron situation where the two cannot be simultaneously minimized.

The results listed for Li_2 in Table VI not only show a relatively large $-C$ (1.28 ev) but also a remarkably small $-(X+R)$, 0.10 ev, of which some part must be

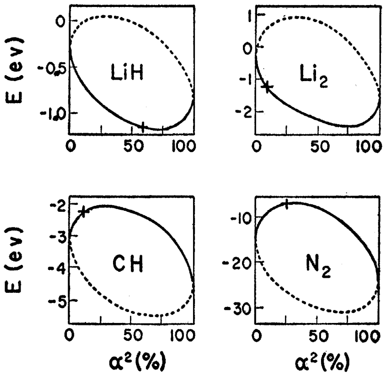

FIG. 6. Coulomb energy of LiH, Li_2, CH, N_2 at r_e as a function of the degree of promotion α^2 (full-line parts of curves: positive hybrid for σ valence electron; dashed-line parts of curves: negative hybrid for σ valence electron). In each case, what is believed to be the actual state of hybridization is marked on the curve. For LiH, Li_2, the $2s^n$ AO was used; for CH, N_2, the $2s^{\sigma r}$ AO.

attributed to $-R$. Even supposing R negligible (in fact, the literature[18] indicates that the wave function actually has very little ionic character, which would be the main contributer to R here), $-X$ is still remarkably small. Now $-X$ necessarily includes not only the exchange attraction between the valence electrons but also the exchange repulsions between each K shell ($1s^2$ lone pair) on one atom and the valence electron on the other and (but probably negligible) between the two K shells; also[18] multiple-exchange terms. We must probably conclude that in Li_2 the nonbonded repulsions have nearly canceled the exchange attraction, which one would otherwise have expected to be much larger, perhaps about 1 or 2 ev.

It is of interest here that the $1s_a{}^2-2hy_b$ nonbonded repulsions when computed by Mulliken's rough empirical magic formula[2] for a 9% positive hybrid $2hy$ amount to 1.16 ev, so that the $+0.10$ ev value found previously for the net $-X$ could be accounted for by $+1.26$ ev bonded exchange attraction minus 1.16 ev nonbonded repulsion. (The magic formula gives 2.66 ev for the bonded attraction but, as is discussed further in Sec. V, it lumps C and X together.) These rough results are in agreement with the earlier conclusions of H. M. James[18] that the binding energy in Li_2 is greatly diminished by nonbonded repulsions. James' VB calculation[19] assumed no hybridization, in which case $-C$ is small (cf. Fig. 6 or Table V) though much larger than in H_2. The assumption of 9% hybridization makes $-C$ much larger, to give the results shown in Table VI, where nearly all of B is attributable to $-C$.

In Fig. 6, however, one notes that $-C$ would be considerably larger if there were *more* hybridization. That this is not actually realized may probably be attributed to $X+\alpha^2\Delta P$: the nonbonded repulsions plus $\alpha^2\Delta P$ increasingly raise the energy as α increases, and although $-C$ and the bonded attraction also continue to increase with α, their sum may well increase less rapidly than the other terms so that energy minimization occurs at 9% hybridization.

An examination of Figs. 3–6 now throws further light on the relations of C and X in general. The fact that, for $r=r_e$, the Coulomb binding energy $-C$ for CH and especially for N_2 in Fig. 5 is still continuing to increase strongly, while the total binding energy $-U$ is decreasing, can only mean that the exchange part $-X$ of the binding energy is now decreasing strongly and must have already begun decreasing even at some r value greater than r_e.[20] How can this be explained? It should be recalled that X is a sum of a number of exchange terms, including the bonding terms but also several nonbonded repulsion terms.[21] It must probably be concluded that on the whole these exchange repulsion terms (including those involving the K shells) increase rapidly for $r<r_e$, while the bonding terms increase more slowly or (for hybrid σ bonds) finally reach a maximum and then decrease.[22] One thus sees that these exchange repulsions must play a very important part in limiting the stability of most molecules and determining their r_e values. A familiar extreme case is that of F_2, but the present calculations show that also in N_2 and even in hydrides such as CH, these nonbonded repulsions are important and increasingly so for $r<r_e$. Figure 4 shows that if interatomic exchange forces were absent, $-C$ might sometimes reach very large values at very small r_e values.

In complete contrast, C for H_2 (cf. Fig. 1) has its minimum at $r>r_e$, and one sees that the roles of X and C are now reversed; X must continue to increase for $r<r_e$, while C has become repulsive instead of attractive. In H_2, X consists only of a bonded attraction and includes no nonbonded repulsions.

V. CONCLUSIONS

The analysis in Sec. IV of the results obtained in the present calculations shows that the usual procedure in VB theory of neglecting Coulomb energies, not to mention promotion energies, nonbonded repulsions and attractions, and overlap integrals, can yield only a caricature of the true structures of bond energies. The empirical exchange integrals obtained by the neglect of most or all of these factors can seldom be expected to have much relation to the true theoretical exchange integrals or even to the effective exchange integrals η of Eq. (4). It appears that they must usually correspond to composites of Coulomb and exchange terms strongly modified by overlap corrections and the other neglected terms mentioned. It is further evident from

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[18] H. M. James, J. Chem. Phys. **2**, 794 (1934).

[19] James made also a more accurate variational calculation using elliptic coordinates, but this is not useful for present purposes.

[20] Of course $-R$ must also be changing, but experience indicates that it should, if anything, still be increasing at $r<r_e$.

[21] And some nonbonded attraction terms, but these probably are smaller and vary less rapidly with r.

[22] Like the corresponding overlap integrals: cf. R. S. Mulliken, J. Am. Chem. Soc. **72**, 4493 (1950).

Sec. IV that the true exchange integrals and even the effective exchange integrals η must often be much larger than is usually supposed.

In the past, true VB theory calculations except for H_2 have been much too discouragingly complicated, but they have now become worth considering again in view of the fact that for diatomic molecules at least, all the necessary individual one- and two-electron integrals can be obtained by machine calculations. However, in Eq. (11), computation of the term X, which one may hope to express in the form $\sum_i X_i(\eta_i\text{'s}, S\text{'s})$, in general involves so numerous and complicated integrals as to make an exact calculation still extremely difficult, though not entirely impracticable for simple molecules. Some effort toward obtaining reasonably good simplified approximations of the form $\sum X_i$ is being made in this Laboratory, although whether this will be successful is not yet apparent. Even then, one would still have to face the serious problem of practicable approximate expressions for the terms denoted by R in Eq. (11).

In an earlier paper,[2] one of the writers proposed a "magic formula" similar to Eq. (11), including simple expressions for promotion energy, bonded attraction, and nonbonded repulsion and attraction terms explicitly. Parameter values for these expressions were determined empirically from three molecules so as to make it possible to compute bond energies for other molecules. The magic formula differed from Eq. (11) in two respects: (1) it did not include a C term; (2) the bonded attractions were represented by expressions based on molecular orbital rather than VB theory. By means of item (2), part of R of Eq. (11) corresponding to ion-pair terms in VB theory was, in effect, taken into the bonded attraction terms. The need to improve the magic formula, in particular by explicitly including C instead of lumping it into the effective bonding and exchange integrals, was discussed at some length,[23] and it was suggested that an improved magic formula including C explicitly might lead to improved agreement between computed and observed binding energies. The present work supports this suggestion.

In other earlier papers,[24] it was shown that there is a nearly one-to-one correspondence between the occurrence, on the one hand, of positive (bonding) and negative (antibonding) overlap populations in LCAO–MO theory and, on the other hand, of bonded attractions and nonbonded repulsions in VB theory. However, the correlations are often somewhat rough. This may well be ascribable in part to the fact that both theories in their usual form give rather poor approximations to true molecular wave functions.[25] The present paper suggests the possibility that the correlations found might be improved if proper allowance were made in the VB theory for the Coulomb energy terms. On the other hand, it should be pointed out that in the SCF–LCAO MO calculations, the *total* energy including both resonance and Coulomb terms is minimized, so that the overlap population should be a measure (to the extent that the approximation is a good one) of the quantum mechanical response of the electron distribution to all the forces acting. Hence, perhaps after all, the overlap populations should *not* be closely correlated with pure exchange terms. The matter may be worth further study.

VI. SUMMARY

Computations of the Coulomb energy part of the binding energy in the valence-bond method, using Slater atomic orbitals, with hybridization, have been made for LiH, BH, CH, NH, HF, Li_2, N_2, and F_2, and for excited states of H_2. The Coulomb energy is much larger for $p\sigma$ and especially for s-$p\sigma$ hybrid bonds than for s bonds. Using degrees of hybridization which are believed to be actually present, it amounts to 30–40% of the gross bond energy in typical cases, as compared with 1% for H_2 at equilibrium in its ground state. For Li_2 the figure is 93%.

In hypothetical cases with more favorable hybridization, the Coulomb energy would assume very large values. For two ground-state N atoms with their 2-quantum lone-pair electrons in positive digonal hybrid orbitals, the computed gross binding energy would exceed 60 ev, at an r_e of perhaps 0.5 A, and even after subtracting about 20 ev promotion energy, the net binding energy would be as much as 50 ev. That this large binding energy for N_2 is not actually realized must be attributed to an overcompensating extremely large exchange repulsion between the lone pairs in the two atoms. Contrastingly, in the actual N_2 molecule, the lone-pair σ electrons are in negative hybrid orbitals, and the bonding σ electrons in positive hybrids, greatly weakening both the total Coulomb attraction and the nonbonded exchange repulsion but strengthening the exchange attraction. Nevertheless, the Coulomb attraction still contributes 6.7 ev to the (gross) binding energy. These and other conclusions are discussed.

The fact that in Li_2 the Coulomb energy is 93% of the gross binding energy is explained by the fact that, since there are no lone pairs in the valence shell, maximum Coulomb energy and exchange attraction energy are now mutually compatible instead of antagonistic. The smallness of the net exchange energy must be attributed to the presence of strong exchange repulsions involving the K shell of each atom and the valence electron of the other.

ACKNOWLEDGMENT

We are very much indebted to Mr. Tracy J. Kinyon for his assistance in the computations.

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[23] Reference 2, p. 309.

[24] R. S. Mulliken, J. Chem. Phys. **23**, 2343 (1955).

[25] In LCAO theory, somewhat better results might be expected if self-consistent field AO's were used. [Cf. A. M. Karo, J. Chem. Phys. **31**, 182 (1959).]