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The Low Electronic States of Simple Heteropolar Diatomic Molecules

I. General Survey

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The three lowest energy states of molecules H_2, M_2, and MH are here deemed more or less analogous and labeled *N*, *T*, *V*; these are respectively of the types $^1\Sigma^+$, $^3\Sigma^+$, $^1\Sigma^+$. States *N*, *T* and *V* must exist also in all other uni-univalent molecules, e.g., X_2, XY, HX, AgX, MX (M = alkali metal atom, X or Y = halogen atom). The characteristics of the states *N*, *T*, *V* (*polarity*, *ionicness*, etc.) are surveyed. Only in H_2 is state *T* yet known empirically; *N* is the normal state always; *V* is to be identified with a state known from band spectra in the case of most molecules of the types above named. In molecules containing one halogen atom, there should be an additional low energy group of states (types $^3\Pi$, $^1\Pi$), here labeled the *Q* group. Various points connected with the approximation of polar diatomic molecule wave functions using atomic orbitals, and using molecular orbitals, are discussed. Difficulties and arbitrariness inherent in the definition of polarity and ionicness are examined.

1. INTRODUCTION

THE primary object of the present papers is a study of the low energy electron levels of uni-univalent diatomic molecules, especially those of the types MH, HX, AgX, MX, with the object of finding how the energies and other characteristics of analogous electron states change as one goes from the homopolar to the heteropolar case (X = halogen, M = alkali metal atom). This study is based on an interpretation of empirical data in relation to theoretical considerations, and represents in part a continuation of work done previously[1] on molecules of the types X_2, XY (X, Y = halogen atoms).

At present the electronic states of strongly heteropolar diatomic molecules are less well understood than those of homopolar or slightly polar molecules. It is hoped that the present work, by helping to clarify the situation for several important special cases of simple uni-univalent molecules, will prove valuable for further work on other heteropolar types.

As an interesting by-product, it has been found possible to throw light on the theoretical background of Franck's empirical spectroscopic criterion[2] for distinguishing between diatomic "atom-molecules" and "ion-molecules."

The present paper (I) begins with an introductory survey of the characteristics of the low energy electron levels of molecules of the types H_2, M_2, MH, HX, AgX and MX. This is followed by sections containing a discussion of methods used in constructing approximate wave functions, and of the concepts of polarity and ionicness. In II there will be a detailed consideration of the two known states of MH together with brief discussion of corresponding states of M_2, H_2, CuH, AgH, BeH^+, ZnH^+. The detailed consideration of HX, AgX and MX will follow in III.

2. NATURE OF LOW ENERGY ELECTRONIC STATES

For our purposes, the diatomic molecules to be considered in the present set of papers are built from just two kinds of univalent atoms: (*a*), atoms H, Ag, M, etc. with just one *ns* electron in the outer shell; (*b*), halogen atoms with five *np* electrons in the outer shell. All electrons except the one *ns* electron in the first case and the five *np* electrons in the second case can be classified as inner electrons and neglected in the following; except that in Ag and especially Cu and Au, the electrons of the just-completed *d* shell are important for some of the low energy electron levels.

We shall first consider the electron configurations of our molecules using exclusively orbitals of the separate atoms, i.e., according to the Heitler-London-Slater-Pauling method of approach. When an X atom enters a diatomic molecule, its *np* electrons become divided into two types, $np\sigma$ and $np\pi$. Only $np\sigma$ enters into chemical valence relations, but $np\pi$, because it

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[1] R. S. Mulliken, Phys. Rev. **46**, 549 (1934), and earlier papers there cited.

[2] J. Franck, H. Kuhn and G. Rollefson, Zeits. f. Physik **43**, 155 (1927); J. Franck and H. Kuhn, Bull. Acad. Sci. Un. Prov. India **2**, 223 (1933).

does not differ greatly in energy from $np\sigma$, i.e., like the latter lies "on the surface," is also important when spectra are considered. In the case of atoms H, Ag, M, however, we have only the $ns\sigma$ electron to deal with (or perhaps also $nd\sigma$ in the case of Ag).

The catalog of low energy electronic states is simplest when we deal with combinations of two atoms of the ns type, e.g., H_2, MH, M_2, AgH. It is much more complicated when two halogen atoms are involved (X_2, XY), because of the presence of two sets of $np\pi$ electrons. An intermediate degree of complexity occurs when there is one halogen atom, which gives one set of $np\pi$ electrons (HX, AgX, MX).

In predicting low energy electron states of a molecule AB, it proves usually to be advisable, and sufficient, to consider all states which can be built from the normal states of the pairs of atoms or ions A+B, A^++B^-, and A^-+B^+. For molecules such as H_2, MH, M_2, this means considering only certain electron configurations and states which, in terms of the separated atoms or ions, may be described as

$$n_As\sigma_A\cdot n_Bs\sigma_B,\ {}^1\Sigma^+,\ {}^3\Sigma^+;\quad (n_Bs\sigma_B)^2,\ {}^1\Sigma^+;$$

$$\text{and}\qquad (n_As\sigma_A)^2,\ {}^1\Sigma^+. \tag{1}$$

In case A and B are identical atoms (as in H_2, M_2, etc.), the ${}^1\Sigma^+$ and ${}^3\Sigma^+$ from $ns\sigma_A\cdot ns\sigma_B$ are, respectively, the ${}^1\Sigma^+_g$ normal state and a ${}^3\Sigma^+_u$ repulsion state, as is well known through the work of Heitler and London on H_2. Also, when A and B are identical, there is of course degeneracy between $(ns_A)^2$ and $(ns_B)^2$ for $r=\infty$ (A^++B^- and A^-+B^+), but for $r<\infty$ this is split up giving a ${}^1\Sigma^+_u$ (lower energy) and a ${}^1\Sigma^+_g$ (higher energy). The wave function of each of these, however, corresponds to a 50,50 mixture of $ns_A{}^2$ and $ns_B{}^2$, so that for this case (1) is really not correct as it stands. If A and B are not identical, then A^++B^- is lower in energy than A^-+B^+, if A is the more easily ionized of the two atoms. In this case (cf., e.g., HM) the ${}^1\Sigma^+$ state $(ns_B)^2$ derived from A^++B^- may compete with that derived from $ns_A\cdot ns_B$ for the position of normal state.

Whether or not A and B are identical, the four electronic states just referred to (three ${}^1\Sigma^+$, one ${}^3\Sigma^+$) are important for our considerations. The *lowest* of the ${}^1\Sigma^+$ states will hereafter be referred to as N, the *next lowest* as V, the highest as Z, while the ${}^3\Sigma^+$ state will be labeled T. In practice, we need not consider the Z state, since it should always lie very high in energy, and is experimentally unknown except probably[3] in the case of H_2. In homopolar molecules, state N is of homopolar type and V usually of ionic but nonpolar type. In strongly heteropolar molecules, N should be of polar ionic type, V of nearly homopolar type. T is always homopolar in character, even when N is ionic. The molecules M_2 are exceptional in that the V state appears to be mainly of a homopolar type $ns\sigma\cdot np\sigma$, ${}^1\Sigma^+_u$ rather than of the ionic type ns^2.

Although the preceding outline of the nature of states N, T, V, Z is oversimplified and will need later to be elaborated, nevertheless it will serve for the moment as a convenient basis for our main line of thought.

Turning to molecules of the types MX, AgX, HX, X_2, XY, we can in each case expect again to find four states N, T, V, Z, plus additional states due to the presence of $np\pi$ electrons. The states N, T, V, Z are obtained when for each halogen atom the $np\pi$ electrons form a *closed shell* $(np\pi)^4$. Such a closed shell, like the inner electron shells, does not affect the resultant electronic state, and can be neglected for our purposes. For a neutral halogen atom X, there thus remains in this case just one outer electron, in the $np\sigma$ condition. The number of $np\sigma$ electrons is two for X^-, however, while it is zero for X^+. These $np\sigma$ electrons now function exactly like the $ns\sigma$ electrons of an H or M atom. Thus for HX, we have $np\sigma_X\cdot ms\sigma_H$ from H+X, $(np\sigma_X)^2$ from H^++X^-, and $(ms\sigma)^2$ from H^-+X^+. These give the states ${}^1\Sigma^+$ and ${}^3\Sigma^+$ from $p\sigma\cdot s\sigma$, ${}^1\Sigma^+$ from $(p\sigma)^2$, and ${}^1\Sigma^+$ from $(s\sigma)^2$, much as in (1). The results for AgX and MX are entirely analogous. The two first-mentioned ${}^1\Sigma^+$ states represent N and V (or V and N), the third is Z, while the ${}^3\Sigma^+$ is T. The cases of X_2 and XY are similar.[1]

Numerous additional low energy states can be obtained by departing from the cases where there is a closed shell $np\pi^4$. In the HX, AgX, MX types, the lowest energy electron levels not involving a closed $np\pi^4$ shell, and the only such levels which will concern us, are states where there are *three*

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[3] Cf. G. H. Dieke, Phys. Rev. **50**, 797 (1936).

$np\pi$ electrons. Considering HX again as a typical example, we have just the electron configuration and states

$$(np\pi_X)^3(np\sigma_X)^2\cdot ms\sigma_H,\quad {}^3\Pi_{2,1,0} \text{ and } {}^1\Pi. \tag{2}$$

Consideration of $H^+ + X^-$ gives us nothing new, since the π_X shell *has* to be completed, giving $(np\pi_X)^4$, if we are to have low energy X^-, while the $H^- + X^+$ states with incomplete π_X shell are too high in energy to be of interest. Analogous statements apply to AgX and MX. Hence, in addition to the low energy states N, V, and T of (1), we need here consider, for molecules HX, AgX, MX, only the $^3\Pi$ and $^1\Pi$ states given by (2).

This group of states will hereafter be designated Q. Of the states Q, the multiple level $^3\Pi$ consists of three substates $^3\Pi_2$, $^3\Pi_1$, $^3\Pi_0$, of which the last is again split into two sub-sub-states $^3\Pi_{0^+}$ and $^3\Pi_{0^-}$. In addition, there is the single level $^1\Pi$. Among all these states, the $^3\Pi_{0^+}$ will prove to be of special importance to us, and will therefore for convenience here be given the special designation Q_0.

The discussion of the states (2) just given, like that of (1) above, omits certain complications and qualifications which will have to be gone into later.

In the discussion so far, all electron configurations have been given in terms of *atomic orbitals* of the two separate atoms or ions from which the molecule or molecular state in question is thought of as formed. This is the Heitler-London-Slater-Pauling mode of approach.[4] A much more complete understanding of the various electron states is obtained if electron configurations are *also* given for them using *molecular orbitals* for the *shared electrons*, and if we then think of the true structure as more or less intermediate between those suggested by the two types of electron configurations, the degree of approach to the one or the other type varying with the value of r.

Making the change to molecular orbitals really never needs to affect seriously more than two of the electrons in any electron configuration, in the case of the types of molecules here considered, since at most two of the electrons are shared to an important degree. Thus ordinarily the only electrons for which we shall use molecular orbitals are those which in (1) and (2) are assigned to $ns\sigma$ or $np\sigma$ atomic orbitals (valence orbitals) of the separated atoms or ions. The *$np\pi$ orbitals* are nearly unshared (nearly nonbonding), so that the substitution of molecular orbitals for them usually involves only a slight improvement.

The molecular orbitals to be used for the shared electrons are two in number, namely a lower energy bonding orbital here called σ (or σ_g in homopolar molecules, like H_2, M_2, X_2), and a higher energy antibonding orbital here called σ^* (or σ_u in homopolar molecules). In LCAO approximation,[4] these have the following forms:

$$\begin{aligned}\sigma(\text{or } \sigma_g) &= b\sigma_B + a\sigma_A + \cdots;\\ \sigma^*(\text{or } \sigma_u) &= a'\sigma_A - b'\sigma_B + \cdots,\end{aligned} \tag{3}$$

with $b > a$, $a' > b'$ if *atom B is more electronegative than atom A*, as we shall always assume. In the ideal heteropolar case we should have $b = a' = 1$, $a = b' = 0$; in the homopolar case (σ_g, σ_u), $a = b$, $a' = b'$.[5] In (3), σ_A and σ_B refer to the valence orbital of atom A or B, i.e., $ns\sigma$ for atoms H, Ag or M, $np\sigma$ for atoms X.

In the normal electronic state N of every one of the molecules here considered, the two shared electrons are both assigned to the molecular orbital σ of (3). The changing character of the molecules as we go from homopolar to heteropolar is then well expressed in the changing nature of this orbital. In the extreme heteropolar case, it reduces automatically to σ_B, i.e., the valence atomic orbital of atom B. Thus even when we use the molecular orbital viewpoint, we here arrive at a description identical with that (A^+B^- ionic structure) obtained using atomic orbitals. A similar coincidence between the results of atomic and molecular orbital viewpoints is obtained in the extreme heteropolar case also for excited states; this will be discussed in the section on alkali halides, in III.

In some earlier papers on hydride molecules AH (H_2, MH, HX, etc.) a special kind of molecular orbitals, namely united atom orbitals, was used exclusively.[6] Each united atom orbital is

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[4] Cf. R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935), and references given there.

[5] Cf. R. S. Mulliken, J. Chem. Phys. **3**, 573 (1935).

[6] Cf. F. Hund, Zeits. f. Physik **51**, 759 (1928); R. S. Mulliken, Phys. Rev. **33**, 738 (1929); R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

TABLE I. *Electron configurations.*[1, 2]

Mole-cule	State	Using United Atom Orbitals	Using Molecular Orbitals	Using Separate Atom Atomic Orbitals[3] (ionic states A^+B^- or A^-B^+ in bold face)	Dissociation Products[3]
H$_2$	$N\,^1\Sigma^+_g$	$1s\sigma_g^2$	σ_g^2 *s.ad.* σ_u^2	$1s\cdot 1s$ *s.ad.* $\mathbf{1s}^2$	$1s+1s$ (H+H)
	$T\,^3\Sigma^+_u$	$1s\sigma_g 2p\sigma_u$	$\sigma_g\sigma_u$	$1s\cdot 1s$	$1s+1s$
	$V\,^1\Sigma^+_u$	$1s\sigma_g 2p\sigma_u$	$\sigma_g\sigma_u$	$\mathbf{1s}^2$	$1s+2\sigma$ (H+H′) or $1s^2$ ($H^+ + H^-$)
	$Z\,^1\Sigma^+_g$	$2p\sigma_u^2$	σ_u^2 *s.ad.* σ_g^2	$\mathbf{1s}^2$ *ad.*	
M$_2$	$N\,^1\Sigma^+_g$		σ_g^2 *s.ad.* σ_u^2	$ns\cdot ns$	$ns+ns$ (M+M)
	$T\,^3\Sigma^+_u$		$\sigma_g\sigma_u$ *ad.*	$ns\cdot ns$	$ns+ns$
	$V\,^1\Sigma^+_u$		$\sigma_g\sigma_u$ *ad.*	$ns\cdot np\sigma$ *s.ad.* $\mathbf{ns}^2$	$ns+np$ (M+M′)
MH	$N\,^1\Sigma^+$	$ns\sigma^2$	σ^2 *s.ad.* $\sigma\sigma^*$	*Mix.* $\mathbf{1s}_\mathbf{H}^2$, $1s_H\cdot ns_M$	$1s+ns$ (H+M)
	$T\,^3\Sigma^+$	$ns\sigma np\sigma$	$\sigma\sigma^*$	$1s_H\cdot ns_M$	$1s+ns$
	$V\,^1\Sigma^+$	$ns\sigma np\sigma$	$\sigma\sigma^*$ *s.ad.* σ^2	*Mix.* $1s_H\cdot ns_M$, $\mathbf{1s}_\mathbf{H}^2$	$1s+np$ (H+M′) or $1s^2$ ($H^- + M^+$)
HX (except HF)	$N\,^1\Sigma^+$	$np\sigma^2 np\pi^4$	$\sigma^2\pi_X^4$ *s.ad.* $\sigma\pi_X^4\sigma^*$	$\sigma_X\pi_X^4\cdot 1s_H$ *ad.* $\boldsymbol{\sigma}_X^2\boldsymbol{\pi}_X^4$ and $\boldsymbol{\pi}_X^4\cdot\mathbf{1s}_\mathbf{H}^2$	mp^5+1s (X+H)
	$T\,^3\Sigma^+$	$np\sigma np\pi^4(n+1)s\sigma$	$\sigma\pi_X^4\sigma^*$	$\sigma_X\pi_X^4\cdot 1s_H$	mp^5+1s
	$V\,^1\Sigma^+$	$np\sigma np\pi^4(n+1)s\sigma$	$\sigma\pi_X^4\sigma^*$ *s.ad.* $\sigma^2\pi_X^4$	*Mix.* $\boldsymbol{\sigma}_X^2\boldsymbol{\pi}_X^4$, $\boldsymbol{\pi}_X^4\cdot\mathbf{1s}_\mathbf{H}^2$ and $\sigma_X\pi_X^4\cdot 1s_H$	mp^6 ($X^- + H^+$)
	$Q\,^{1,\,3}\Pi$	$np\sigma^2 np\pi^3(n+1)s\sigma$	$\sigma^2\pi_X^3\sigma^*$	$\sigma_X^2\pi_X^3\cdot 1s_H$ *ad.*	mp^5+1s
HF	N, T, V, Q	Like HX	Like HX, but stronger *ads.*	Like HX, except stronger $\sigma_X^2\pi_X^4$ *ads.* and only *s.* $\boldsymbol{\pi}_X^4\cdot\mathbf{1s}_\mathbf{H}^2$ *ads.*	Like HX
AgX			Similar to HF		
MX[4, 5]	N T V Q		$\sigma^2\pi_X^4$ $\sigma\pi_X^4\sigma^*$ $\sigma\pi_X^4\sigma^*$ $\sigma^2\pi_X^3\sigma^*$ } See[4]	$\boldsymbol{\sigma}_X^2\boldsymbol{\pi}_X^4$ *s.ads.* $\sigma_X\pi_X^4\cdot ns_M$ *etc.* $\sigma_X\pi_X^4\cdot ns_M$ $\sigma_X\pi_X^4\cdot ns_M$ $\sigma_X^2\pi_X^3\cdot ns_M$ } See[5]	mp^6 ($X^- + M^+$) mp^5+ns (X+M) mp^5+ns mp^5+ns

Abbreviations: ad. =with considerable or strong admixture of (other configurations); *s.ad.* =with small or rather small admixture of; *mix.* =mixture; σ, σ^*, σ_g, σ_u, see (3) in text; $\pi_X = mp\pi_X$; $\sigma_X = mp\sigma_X$. *Notes:* [1] The fourth and fifth columns of Table] I apply to r values near r_e of state N. The third column, for H$_2$, MH and HX, is applicable for r values near $r=0$ and, in increasingly rough approximation with increasing r, for larger r values. The sixth column is applicable for very large r values and for $r=\infty$. [2] In regard to an improvement of the approximation for the larger r values by giving up the electron configuration idea, and using whole atom wave functions instead of atomic orbital electron configuration functions, see the last paragraph of Section 2. [3] In connection with the V state of H$_2$, M$_2$ and MH, see Paper II for further explanation. [4] Using molecular orbitals for MX, we have, nearly, $\sigma = mp\sigma_X$ and $\sigma^* = ns\sigma_M$, giving nearly the same results for T, V and Q as using atomic orbitals. [5] In using atomic orbitals for MX, it would be much better for states T, V and Q to write $mp_X\cdot ns_M$ for all these, with case c coupling (see Paper III).

really the limiting case of a molecular orbital, approached by the latter as r tends toward zero. Although an approximation built up from this limiting case is often of value for molecules AH (but hardly for other types), it has become evident[1] that the approximation can in general be improved markedly if we use, at least for the shared electrons, molecular orbitals of a less specialized character.

In Table I the electron configurations for the low energy electron states of the molecules considered in these papers are summarized, omitting inner electrons. For each electronic state, the best electron configuration using molecular orbitals for the shared electrons is first given, then that using exclusively atomic (i.e., separate-atom) orbitals. [In the cases H$_2$, MH and HX, however, the electron configuration is first of all given in terms of *united-atom* orbitals.] Finally, the electron configurations of the dissociation products for the given electronic state are indicated; here the subdivision of p atomic orbitals into $p\sigma$ and $p\pi$ is dropped.

In general, the descriptions using molecular or united-atom orbitals are most nearly correct for small r values, those using atomic orbitals for large r values. For dissociation ($r=\infty$), and in some cases also for large r values short of $r=\infty$, the dissociation product electron configurations and states are the most nearly correct.

In connection with Table I, it must be mentioned that in the case of some electronic states, for their actual equilibrium r values r_e (or for moderate r values in the case of unstable states), an acceptable approximation to the true wave function of a given electronic state cannot always be obtained corresponding to a "pure electron configuration," i.e., to a single definite electron configuration. Instead, the wave function in such cases must be expressed by a linear combination of forms corresponding to two or more pure electron configurations. In Table I, such admixing has been indicated in all cases where it is thought to be important near r_e. It should be especially noted that admixing is sometimes important when the electron configuration is expressed in terms of atomic orbitals but not when it is expressed in terms of molecular orbitals, or *vice versa;* or sometimes it may be necessary in both cases. It should further be noted that admixing changes with r; using molecular orbitals, it increases for, say, $r>r_e$; using atomic orbitals, it increases for, say, $r<r_e$ (cf. Table I, note 1).

In reality, every many electron wave function corresponds of course to an admixture of an infinite number of pure electron configuration wave functions. In ordinary cases, however, one of these, or at worst two or three in the case of molecules,[4] are sufficiently predominant in the admixture so that a fairly good approximation can be obtained by neglecting all the rest. It is these approximations, especially the pure ones, in terms of which we ordinarily think.

Throughout the foregoing discussion in this section, it has been tacitly assumed that an approximate molecular wave function is to be built up of one or more pure electron configuration approximate wave functions. Although it appears necessary in the present survey to adopt the point of view corresponding to this usual class of approximations, it should be borne in mind that better results can, at least in principle although with difficulty in practice, be obtained by another class of approximations in which coordinates of interelectronic distances appear explicitly and the concept of electron configurations is sacrificed. This method has been employed for H_2 and Li_2 by James and Coolidge.[7] The method as used by these authors might be called the *whole-molecule* approximation, and is analogous to the *whole-atom* approximation as carried out by Hylleraas for the He atom. The whole-molecule approximation, at least in H_2, bears to the molecular orbital electron configuration approximation the same relation as does the whole-atom approximation to the ordinary atomic orbital electron configuration approximation for atoms.

Among the useful approximations for molecular electronic wave functions, especially for the larger r values, two different types which are both extensions of the original Heitler-London idea are of importance. One is the Slater-Pauling extension, involving the use of separated atom atomic orbital electron configurations; the other (at least in principle) involves using separated-atom whole-atom wave functions (Heitler and others). The second of these, when it can be adequately carried out, may be considered as a refinement on the first, similar to the refinement involved in passing from an electron configuration approximation of an atom or molecule to a whole-atom or whole-molecule approximation. In the present work, when molecular wave functions are constructed from linear combinations of $A\cdot B$, A^+B^- and A^-B^+ functions, one should of course get better approximations by using whole-atom approximations instead of electron configuration approximations for the atoms A, B and ions A^+, B^+, A^- and B^-. We shall, however, for the most part not refer explicitly to this type of refinement in the present papers. For the sake of comprehensiveness and unity of viewpoint, we shall, generally speaking, think in terms of electron configuration approximations (cf. Table I). Nevertheless, when we refer to wave functions of $A\cdot B$, A^+B^-, A^-B^+, or the like, we shall often wish to be ambiguous, leaving somewhat open the possibility of improving the approximation by using whole-atom or whole-ion approximations in constructing these atomic or ionic wave functions. Throughout the text of I, II and III,

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[7] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933) on H_2; H. M. James, J. Chem. Phys. **2**, 794 (1934) on Li_2.

the existence of this tentative ambiguity should be tacitly understood by the reader. When, however, we refer to *energies* of $\mathrm{A^+ + B^-}$ or of $\mathrm{A^- + B^+}$ etc. relative to $\mathrm{A+B}$, the energy data we actually use (cf. e.g., Table III) will correspond always to exact whole-atom wave functions, not to simple electron configuration approximations.

3. Polarity and Ionicness

Understanding of the electronic structures in states N, T, V is clarified by classifying these states according to the two qualities of (1), polarity, (2), ionicness. Polarity is zero for all states of all strictly homopolar molecules (H_2, M_2, X_2, etc.), and is a maximum for the normal states of molecules such as the alkali halides MX.

Ionicness is a quality which is necessarily strongly present when polarity is strong (e.g., normal state of MX), but it can also be present even in strictly homopolar molecules. In an electronic state of a molecule AB, ionicness is present whenever, using atomic orbitals, the wave function contains terms corresponding to $\mathrm{A^+B^-}$ or $\mathrm{A^-B^+}$ or both.

In homopolar molecules, ionic or partially ionic states are nonpolar because $\mathrm{A^+B^-}$ and $\mathrm{A^-B^+}$ terms in the atomic-orbital approximation wave function, for reasons of symmetry, are present in equal proportions (cf., e.g., the V state of H_2). Polarity exists when, in an ionic or partially ionic state, the $\mathrm{A^+B^-}$ terms preponderate over the $\mathrm{A^-B^+}$, or *vice versa*. "Polarity" here might be defined as "net ionicness."

"Ionicness" *has meaning* only with reference to electron configurations expressed wholly in terms of atomic orbitals (fifth vertical section in Table I). Polarity has meaning in terms of atomic orbital electron configurations, in which case it is measured by preponderance of $\mathrm{A^+B^-}$ over $\mathrm{A^-B^+}$ or *vice versa*: but also it has meaning when molecular orbitals are used for "shared" electrons, in which case the polarity of the molecule is determined largely by the polarity or polarities of the molecular orbital or orbitals present (cf., e.g., (3) and accompanying discussion), and by the numbers of electrons occupying them.

Table II contains a set of rough estimates of polarity and ionicness of states N, T, V for typical examples of the molecules considered in this paper. These estimates are already at least qualitatively implicit in Table I, but it seems worth while to set them forth more accurately and explicitly as in Table II. The basis for the estimates given in Tables I and II will be discussed in later sections.

From Table II it will be seen that while the polarity of state N increases steadily from the homopolar to the heteropolar type of molecule, that of state V rises to a maximum in the intermediate type of molecules, then falls again, while the polarity of state T maintains (very nearly) the constant value zero. Ionicness behaves in a

Table II. *Ionicness and polarity.*

		Type of Molecule					
		Homopolar			Intermediate		Heteropolar
Property	State	H_2	M_2	HI	MH	HF	MX
Polarity	N	0	0	$s(\mathrm{H^+})$	$m(\mathrm{M^+})$	$m(\mathrm{H^+})$	$l(\mathrm{M^+})$
	T	0	0	0	0	0	0
	V	0	0	$vs(\mathrm{H^+})$	$m(\mathrm{M^+})$	$m(\mathrm{H^+})$	$vs(\mathrm{M^+})$
Ionicness	N	s	vs	s	m	m	l
	T	0	0	0	0	0	0
	V	l	s	l	m	m	vs

Abbreviations: s = small, m = medium, l = large, v = very. *Notes:* The estimates given refer to $r = r_e$ for N and V, to r_e of N for T. The estimate zero does not mean *precisely* zero except in the case of the polarity of H_2 and M_2. Ionicness is small in V of M_2 because $ns\cdot np\sigma$ predominates in the wave function (cf. Paper II).

TABLE III. *Energies of some atomic, ionic and molecular states, and r_c values, for molecules AB. Energies in each case are in electron volts, relative to unexcited $A+B$ taken as zero.*

Molecule AB	Molecular states[1]			Dissociated states[2]			Values of r_c[5]
	N (for $r=r_e$)	V (for $r=r_e$)	Q_0 (for $r=r_e$ of N)	$A'+B$	A^++B^-	A^-+B^+	
H_2	−4.72	+6.60		10.16	12.82		1.1, 5.4
Li_2	−1.16	0.58		1.84	(5.0)		2.9, 4.5
Na_2	−0.77	1.09		2.09	(4.8)		3.0, 5.3
K_2	−0.52	0.94		1.61	(4.1)		3.5, 5.7
LiH	−2.68	0.59		1.84	4.65	(13.2)	3.1, 5.1
NaH	−2.24	0.68		2.09	4.40	(13.2)	3.3, 6.2
KH	−2.08	0.33		1.61	3.60	(13.3)	4.0, 7.2
AgH	−2.5			3.72	6.82		2.1, 4.6
HI	−3.2	—	[2.6]	10.16	10.3	12.5	1.4
HF	−6.64	—	—	10.16	9.4	20.5	1.5
AgI	−2.1	1.8[3]		3.72	4.3		3.3
AgBr	−2.6	1.3[3]		3.72	4.0		3.6
AgCl	−3.1	0.8[3]		3.72	3.8	(15.4)	3.8
AgF				3.72	3.4		4.2
LiBr	−4.5	[0.8][4]		1.84	1.8	(14.3)	7.9
CsF	−[5.3]	[0.8][4]		1.41	−0.3	(20.9)	$>\infty$
I_2	−1.55	3.6	0.9	6.74($^4P_{5/2}$)	10.0		1.4, 2.1

Notes. [1] Energies given for states N and V of any AB are for the *bottoms* of their respective $U(r)$ curves; the energies for state Q_0, however, are for an r value equal to r_e of state N. [2] Under "$A'+B$" is given the energy of the lowest configurationally excited state of A, relative to its normal state. [3] The figure given refers to a state which is probably a mixture of Q_0, V, and another $^1\Sigma^+$ state. [4] For LiBr and CsF and other molecules of type MX (see Paper III), states V and Q_0 are replaced by two nearly 50,50 mixed states. [5] Values of r_c are obtained by setting $U(r)=0$ in Eq. (4). When just one value of r_c is given in Table III, this corresponds to the intersection of the normal state curve (unexcited $A+B$) by the A^+B^- curve, with A put equal to the value listed under A^++B^- in Table III; when two values are given, the first is as just stated, while the second corresponds to the intersection of the $A'+B$ excited state curve by the A^+B^- curve, A then being equal to the difference between the energy values in the A^++B^- and $A'+B$ columns in Table III.

similar way, except for state V, where it is often large for homopolar molecules.

4. CRITERIA FOR POLARITY

The stages of transition from the pure homopolar to the extreme heteropolar type of binding in a molecule AB have been discussed by Hund, by London, and by Pauling.[8] In the pure homopolar case, at $r=\infty$, there is degeneracy between A^++B^- and A^-+B^+, and both lie so high above $A+B$ that they make only a small contribution to the wave function of state N for $r=r_e$, although they are important for state V. With increasing polarity, A^++B^- comes down and A^-+B^+ goes up in energy (cf. Table III). For the most nearly ideal heteropolar cases, A^++B^-, helped by the long range Coulomb attraction of its oppositely charged ions, is so low as to dominate the wave function of state N. In general, the $A\cdot B$ $U(r)$ curve, that is the curve derived from $A+B$, runs nearly horizontal until r is fairly small, and the A^+B^- curve may come down and cross it, so as to become state N, if A^++B^- is not too far above $A+B$.

What has just been called "the $A\cdot B$ curve" is really in general one of several potential energy curves derived from normal atoms $A+B$. The one we are interested in is that one which has $^1\Sigma^+$ character (in regard to certain complications in MX, cf. Paper III). This leads in the less polar molecules to state N. From the ions A^++B^-, in the cases we are interested in, only one curve is derived, and this is of $^1\Sigma^+$ character.

Let us designate by r_c the value of r at which the $A\cdot B$ curve, assumed horizontal, is crossed by the A^+B^- curve, assumed given by the Coulomb law (energy in electron volts, r in A),

$$U(r)=A-14.30/r. \qquad (4)$$

The value of r_c (cf. Table III) constitutes a useful criterion for deciding whether or not a molecule in its N state may be expected to be predominantly heteropolar (cf. London[8]). Or instead of r_c, the energy interval A from $(A+B)$ to (A^++B^-) (cf. Eq. (4)) may be used as a criterion.

Of course if r_c, calculated by putting $U(r)=0$ in Eq. (4), is small, it no longer gives even approximately the crossing point of the A^+B^- and $A\cdot B$ curves, since at small r Eq. (4) is inadequate for the former, while the latter is no longer nearly horizontal. As a simple rough approximation, the A^+B^- curve may then be represented by the Born-type formula

$$U(r)=A-14.30/r+\beta/r^n, \qquad (5)$$

and the $A\cdot B$ curve perhaps by a Morse formula. Values of β and n for Eq. (5) can be taken, in the case of substances AB forming ionic crystal lattices, from the Born lattice energy formula for the substance. Using in part this method, Pauling[8] has plotted approximate A^+B^- and $A\cdot B$ curves for several molecules of types HX and MX.

Whenever r_c as calculated from Eq. (4) is so large that one can be sure that the $A\cdot B$ curve is still practically horizontal, then one can be fairly sure that state N is essentially of A^+B^- character. There is, it is true, always a tendency for the two curves to interact at and near their

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[8] F. Hund, Zeits. f. Physik **40**, 762 (1927); F. London, Zeits. f. Physik **46**, 472–5 (1928); L. Pauling, J. Am. Chem. Soc. **54**, 988 (1932); it should be mentioned that Pauling's $A\cdot B$ curves have minima which are much too deep.

crossing point (quantum-mechanical resonance), but for our purposes this may be ignored if r_c is fairly large (cf. Hund, London[8]). In effect, state N has in this case a $U(r)$ curve which is of character A^+B^- from $r=r_e$ to $r=\infty$; and the molecule in state N tends to dissociate into $A^+ + B^-$ if its energy of vibration is steadily increased. It then conforms to Franck's definition[2] of an *ion molecule.*

When r_c is smaller (perhaps even including some cases where the $A \cdot B$ curve is still nearly horizontal), the interaction near the calculated crossing point may become so strong that it cannot reasonably be ignored. Then we obtain two new curves which do not cross. This case is illustrated by Fig. 1 of Paper II, where a dotted hypothetical curve marked Li^+H^-, given by an assumed equation of the form of Eq. (5), is shown as coming down from above and crossing a dotted hypothetical curve marked $Li \cdot H$. When a suitable interaction between the two dotted curves is assumed, one finds that they are replaced by the two new (*actual*) curves N and V, such that the molecule in state N, even though predominantly ionic for small r values, goes over smoothly into neutral atoms for $r=\infty$. Such a molecule conforms to Franck's definition[2] of an *atom molecule.* State V, although predominantly of $Li \cdot H$ type for small r according to Fig. 1, becomes ionic (Li^+H^-) for large r.

From this discussion one sees that even an "atom molecule" may have a predominantly (i.e., more than 50 percent) ionic and polar wave function, for small r values. Or it is possible to have the wave function of an atom molecule predominantly ionic but not predominantly polar. Or it may be predominantly nonionic and nonpolar, the most usual case. This case always exists if the hypothetical A^+B^- curve fails to cross the hypothetical $A \cdot B$ curve at all.

It is of interest to examine the values of r_c and of A for various types of molecules (cf. Table III). For the undoubted ion molecules MX, one gets $r_c \geqq 6.7$A. For the strongly polar atom molecules MH and AgX, one gets $r_c \leqq 4.5$A. For HX, r_c is about 1.4 to 1.5A; here, except perhaps in HF, there is no real tendency toward crossing. The same is true for H_2, $r_c = 1.1$A, and for K_2, $r_c = 3.5$A; it should be noted that in both cases r_c is only moderately larger than r_e of state N. It appears that there is, roughly speaking, a critical region of r_c values near about 5A which marks the border line between atom molecules and ion molecules. In practice, known molecules at present seem to fall well to one side or the other of this line. In theory, however, the line is arbitrary, since no sharp distinction between crossing and noncrossing of $A \cdot B$ and A^+B^- curves can be made.

Turning to the A values, we find about 10 volts for HX, 13 volts for H_2 and 4 volts for K_2, about 4 volts for AgX and MH, and about 1 volt for MX. These figures suggest that the border line between ion molecules and atom molecules may be rather sharply drawn for an A value of about 3 volts.

Of course the critical values $r_c = 5$A and $A = 3$ volts just suggested should not be taken too seriously. Especially, the effect of atom or ion size should be given consideration. For large atoms and ions, the critical r_c must be larger and the critical A smaller than for small atoms or ions. Better than r_c as an index would be r_c/r_e, taking r_e for state N.

5. CRITIQUE OF ATOMIC ORBITAL DEFINITIONS OF IONICNESS AND POLARITY

The concept of degree of (gross) ionicness used in Table II and Sections 2–4 is really based on a rather arbitrary, although simple and useful, assumption.[9] This is, usually, that the molecular wave function is to be approximated (cf. Table I, column 5), by a linear combination of wave functions of the types $A \cdot B$, A^+B^-, A^-B^+ (cf. near end of Section 2), with the atoms or ions in each case taken as in their normal states, and with their orbitals undeformed, except possibly for symmetrical contractions or expansions. [It seems necessary, however, in the case of the V state of M_2 (and possibly for the V state of H_2) to admit also $A' \cdot B$ as an indispensable ingredient of the linear combination. Here $A' \cdot B$ for M_2 means $M(np, {}^2P) \cdot M(ns, {}^2S)$.]

It should of course always be borne in mind that the various components we are using here for the wave function, especially when ionic and atomic states are used simultaneously, are by no means fully independent, i.e., not mutually orthogonal.

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[9] Cf. L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

"Degree of ionicness" is definite only to the extent that we stick to a definite type of approximation. Insofar as one type of approximation may reasonably be replaced by another, "degree of ionicness" is inherently arbitrary. In judging the relative reasonableness of different approximations, a fair criterion would seem to be one of convergence. For perfect representation of the actual wave function, an infinite series would in general be needed. That type of series which gives a good approximation with a minimum number of terms may well be adjudged the best. From this point of view, it appears probable that the mode of approximation followed here is on the whole the best, and that the corresponding concept of degree of ionicness is therefore on the whole well founded. This is true, however, only for moderate and large r values. As $r \rightarrow 0$, this type of approximation, and the concept of ionicness, gradually lose all sense.

Statements similar to the above are applicable to polarity (net ionicness), if we use approximations based only on atomic orbitals. Polarity can also be defined using molecular orbitals (cf. Section 6). "Degree of ionicness," however, ceases entirely to have a meaning if we use molecular orbitals.

In view of the foregoing considerations, there is little point in trying to reduce the concept of polarity or, especially, that of ionicness, to a quantitative basis. Thus in Table II we have described the polarity and ionicness of molecular states merely as small, medium or large (s, m or l).

As an illustration of the difficulties and arbitrariness involved in defining polarity and ionicness we may consider the type MX. For state N the simplest approximation is a pure electron configuration M^+X^- wave function built of atomic orbitals, with the orbitals of M^+ and X^- undistorted, except perhaps for a symmetrical compression in X^-. This approximation has 100 percent ionicness and polarity.

Clearly, however, we ought to allow for mutual polarization of the two ions, affecting especially the X^-. In the present type of approximation this can be done by admixing $M \cdot X$ in the wave function. This reduces both polarity and ionicness considerably.

One is tempted, however, to use instead another pure M^+X^- approximation in which each ion is taken as polarized and deformed just in the right way to make the wave function exactly right for the molecule. This would be possible, and the actual molecule would then be classified as 100 percent ionic and polar. The approximation would, however, be equivalent to having used an infinite series of *undeformed* atomic orbitals (or atomic states) in order to build up the necessary *deformed* ions M^+ and X^-. A two or three-term approximation representing the first members of such a series would very likely not be as good as the combination of undeformed approximate M^+X^- and $M \cdot X$.

The same objection would apply, with greater force, to various other possible modes of approximation, e.g., approximations based on $M \cdot X$ functions alone, or still worse, on M^-X^+ functions alone. Yet it is to be noted that such approximations *could* legitimately be used,[9] and that the molecule would then, in the two cases mentioned, be respectively adjudged completely nonpolar and nonionic, or 100 percent polar and ionic with reversed sign of polarity to the usual. The criterion of convergence, however, leads to rejection of such approximations on the ground of not being sensible, even though admissible, as a basis for definition of polarity and ionicness.

Even the convergence criterion loses its definiteness if one sufficiently broadens the type of unit to be used in the approximations. In the foregoing, we have kept to pure electron configuration forms using central field atomic orbitals of the usual Hartree type. If we admit "pure electron configurations" based on *polarized* atomic orbitals, i.e., orbitals as of atoms in a suitable external field, then, as we have seen, a good approximation could be secured from a single M^+X^- function, and the molecule could be regarded as 100 percent ionic and polar. By the same procedure, however, any molecule, e.g., HCl or even H_2, could be made to appear 100 percent ionic and polar. Reacting from such possibilities, one arrives at the conclusion that if any at all definite meaning is to be attached to the concepts of ionicness and polarity, one should, *for this purpose*, stick to central field orbitals of the pure s, p, d, f, $\cdots$ types.

6. POLARITIES OF STATES N, T, V DEDUCED FROM MOLECULAR ORBITALS

If we use molecular orbitals (cf. Table I, column 4) for the two σ electrons which, at least in the less polar molecules AB, are shared between A and B, the polarity of the molecule can be expressed fairly well in terms of the polarity of these orbitals. For to the extent that our approximation, using undeformed atomic orbitals for the "nonbonding" or "unshared" electrons, holds good, only the shared electrons contribute to the polarity of the molecule.

In states N, T, V and Q, we make use of two molecular orbitals, called σ and σ^* (cf. Eq. (3)). In *LCAO* approximation, σ is more or less polarized in favor of atom B, σ^* about equally in favor of atom A. [In the homopolar case, of course, both σ and σ^* are nonpolar.] Thus, in this approximation, the configuration σ^2 which occurs in the N state makes this state polar with B negative, while configuration $\sigma\sigma^*$, which occurs in states V and T, should make these states practically nonpolar. If the *LCAO* approximations for σ and σ^* are replaced by the exact molecular orbitals, the conclusion that V and T must be nonpolar becomes less rigorous, but most probably remains nearly correct.[5]

It is instructive to compare the conclusions just reached with corresponding results based on the method of atomic orbitals. We may well consider three cases: (*a*) homopolar molecules; (*b*) molecules which (in state N) are of intermediate polarity; (*c*) molecules which (in state N) are of pure A^+B^- character. In case (*a*) the two methods (atomic orbitals, and molecular orbitals), although representing different approximations, agree in making all states nonpolar. In case (*c*), the two approximations given by the two methods automatically reduce to one (state N pure polar A^+B^-, states V and T pure nonpolar $A\cdot B$, —cf. Section 2).

In case (*b*), the state T is pure nonpolar according to both methods. Since this is true of state T also in cases (*a*) and (*c*), it appears safe to conclude that this state actually is always essentially nonpolar.

For state V in case (*b*), the two methods appear at first to give contradictory results. Using the simplest admissible approximation in each case, the results, for small or moderate r values, are as follows. Using molecular orbitals, a good one-term approximation is available, corresponding to the pure electron configuration $\sigma\sigma^*$. According to this, state V should be nonpolar. Using atomic orbitals, we cannot in general get along without at least two terms ($A\cdot B$ and A^+B^-) in the approximation. According to this, state V should be more or less strongly polar.

Reconciliation of the contradictory predictions of the two methods should be sought in a refinement of the approximations used. In the case of the molecular orbital method, state V can be made somewhat polar by admixing some σ^2 from state N. At the same time state N is made less polar than before, since it receives some admixture of $\sigma\sigma^*$, but it should always remain more polar than V. In the atomic orbital method, the approximation is refined by admixing some A^-B^+, thus reducing the polarity. In this way, the results of the two methods are brought nearer together. By further refinement they could of course be made identical.

It should be borne in mind that the foregoing relations change rapidly with r. For small r and presumably up to about r_e of state N, the molecular orbital method is the more convergent, requiring probably but a single term ($\sigma\sigma^*$) for a fairly good approximation. Hence for such r values, state V should be not very far from nonpolar. For these r values, the atomic orbital method is not so convergent, two or three terms being required for an approximation which even then may be not very good. For large r values, the molecular orbital method becomes poor, losing its convergence, while the atomic orbital method gets more convergent. For large r, state V must always go over definitely into a single pure atomic orbital configuration type, namely A^+B^- except in MX. At the same time, N goes over into $A\cdot B$, except in MX. Thus state V can be highly polar for large r values, and in such cases N is nearly nonpolar for these r values; but for small r values V must be nearly nonpolar, and certainly less polar than N.

From the foregoing discussion it seems safe to deduce the theorem: *for small and moderate r values, in nonhomopolar molecules, state V is less polar than state N.* Applications of this theorem will be made in Papers II and III.

Another relation which may be pointed out here is that between the energies of states T and V. So long as the molecular orbital configuration $\sigma\sigma^*$ gives a good approximation for both, i.e., for r values from zero up to perhaps near r_e of state N, T should normally lie below V, for the same reason that in atoms the triplet normally lies below the singlet state for a given electron configuration. For large r, however, where molecular orbitals no longer give a good approximation, this need no longer be true.

For moderate r values, the necessity of admixing of some σ^2 with $\sigma\sigma^*$ was indicated above in order to get polarity in state V. This should tend to raise the energy of V and depress that of N, although it must be partly compensated, as also the polarity, by simultaneous admixing of some σ^{*2}. The energy of state T, however, should not be raised in this way, since σ^2 and σ^{*2} admixture (both $^1\Sigma^+$) are impossible for it. Thus T should remain below V, even when this polarity difference exists between them.

In the whole preceding discussion, one important tacit assumption has been made. This is that the thing defined as polarity using molecular orbitals is essentially the same as that defined using atomic orbitals. A critical examination shows that the two definitions cannot coincide exactly, but that a sufficient degree of agreement does exist to confirm the validity of the theorem stated in a preceding paragraph, and other qualitative conclusions, e.g., the nonpolarity of state T.

It does not seem worth while here to go into details in proving the correctness of the results just stated. The following outline should suffice to show the general method of attack. Insofar as we can neglect the difference between atomic orbitals of negative ions and like-designated orbitals of neutral atoms, and insofar as we can use simple linear combinations of these atomic orbitals in constructing molecular orbitals (*LCAO* molecular orbitals), it can be shown that any linear combination of $^1\Sigma^+$ type wave functions corresponding to the pure molecular orbital configurations σ^2, $\sigma\sigma^*$, and σ^{*2} is identical with some linear combination of $^1\Sigma^+$ type wave functions corresponding to pure atomic orbital configurations of A^+B^-, $A \cdot B$, and A^-B^+; and that predominance in the former case of σ^2 (which, as we have seen above, is polarized in favor of atom B), corresponds to predominance of A^+B^- in the latter, so that the occurrence and direction of polarity as defined in the one method agree with these as defined in the other. This relation emerges into obviousness in the ideal heteropolar case, where the approximations σ^2 and A^+B^- have become identical.