# PHYSICAL AND INORGANIC CHEMISTRY

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## The Rydberg States of Molecules.[1a] Parts I–V[1b]

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The Rydberg states of atoms are reviewed, and those of molecules, especially of homopolar diatomic molecules, are discussed. For atoms, the quantum defect $\delta$ is due mainly to the effect of penetration of the Rydberg electron into inner shells, and is then always positive, but exchange forces between a nonclosed-shell core and a Rydberg electron can also make positive or negative contributions to $\delta$. The total $\delta$ after excluding such exchange contributions is a measure of a phase shift in the outer nodes and loops of the radial factors of the Rydberg orbital relative to their positions in hydrogen atom orbitals of like $n$ and $l$. It is shown that the MO's (molecular orbitals) of $H_2^+$ fall into good Rydberg series whose $\delta$ values (all zero at $R = 0$) change with $R$, and can be positive or negative depending on $l$ and $\lambda$. These $\delta$'s, resulting from splitting of the united-atom nucleus, are called core-splitting $\delta$'s ($\delta_{c.s.}$). Like the usual $\delta$'s due to penetration, they must produce phase shifts in the nodes and loops of the MO's. It is shown in sections VI and VII that the nonpenetrating Rydberg MO's of homopolar diatomic molecules, in particular their term values (ionization energies), should conform to the "demi-$H_2^+$" model." This model corresponds to the same core field as for $H_2^+$ except that the core charge ($+1$ on each nucleus for $H_2^+$) is less by a factor $\rho$, which is about $1/2$; the model requires a $\delta_{c.s.}$ contribution to $\delta$ in addition to the usual contributions (namely, mainly a contribution $\delta_{pen}$ due to core penetration), with corresponding contributions to phase shifts. Further, it is shown that the variation cf the term values with $R$ near the equilibrium distance $R_e$ can be very simply obtained from experimental vibrational and rotational data by making use of $\delta_{c.s.}$ ($R$) as predicted from the demi-$H_2^+$ model. In the case of penetrating Rydberg MO's, correction for penetration is of course required; this is discussed. Experimental data for Rydberg state term values and their $R$ variation are tabulated for $H_2$ and $He_2$ in section VII and compared with what is predicted from the demi-$H_2^+$ model. The agreement is satisfactory in view of approximations used. The validity of the model is limited to $R$ values where the s.c.f. (self-consistent-field) MO approximation is valid; as an example of what happens at larger $R$ values, the way in which typical Rydberg states of $H_2$ go over, through configuration interaction, into their Heitler–London-type asymptotic forms as $R \rightarrow$ is discussed in section VI. However, for actual discrete energy levels of observed Rydberg states, these large-$R$ effects are unimportant except perhaps for vibrational levels close to dissociation. At small $R$ values near $R = 0$, one must consider large changes which can occur in the penetrational characteristics of Rydberg MO's; even in $He_2$ the lowest-energy Rydberg MO's become valence-shell MO's as $R \rightarrow 0$. However, these effects are unimportant for actual spectroscopically observable Rydberg levels. In Rydberg states of all molecules, the atomic quantum number $l$ should be sharply defined, except often for the lowest series members, for the inner loops of penetrating MO's, and for vibrational levels close to dissociation. In analyzing diatomic band spectrum data involving Rydberg states, special coupling relations, especially between rotational and electronic angular momenta, must be taken into account: Van Vleck's case of pure precession, accidental pure precession (examples in $N_2$ and $NO$), $l$ uncoupling, and inhibition of $l$ uncoupling are discussed (section IV). The relations between Rydberg, valence-shell, and inner-shell MO's are discussed. Some MO's can be either essentially Rydberg or valence-shell MO's, or intermediate, depending on $R$ (section I, 2 where reference is made to MO's of this kind for $H_2$, $N_2$, $CH_4$, $NH_3$). Every Rydberg MO belongs to a series whose first member may itself be a Rydberg MO, an MO of intermediate type, or a core MO, *i.e.*, a valence-shell or inner-shell MO (section III). Rydberg MO's with only Rydberg precursors are nonpenetrating; those with precursors in the core are penetrating. The core and Rydberg MO's of $N_2$ and heavier molecules are briefly discussed (section VI). The two sets of criteria (1) dissociation energies, (2) $R_e$ and/or $\omega_e$ values, for the bonding characteristics of diatomic MO's are briefly discussed (section VI). For valence-shell MO's these run parallel, but (1) seems to be the more fundamental. Rydberg MO's are essentially nonbonding by criterion (1), yet in $H_2$ and $He_2$ show distinctive $R_e$ and $\omega_e$ effects which suggest bonding or antibonding but cannot properly be so interpreted; these effects are explained by the demi-$H_2^+$ model (section VII). For molecules of geometrical types other than the homopolar diatomic, an approach similar in philosophy to that used here, but differing in detail for different types, may be suitable.

## I. Introduction

Numerous Rydberg states of diatomic and polyatomic molecules are known as a result of spectroscopic studies, especially of absorption spectra. However, relatively little systematic attention has been given to identifying these states in terms of electronic quantum

numbers,[2] or to studying what governs the positions of Rydberg states of various types. The present paper reports some progress in this area, with particular reference to homopolar diatomic molecules. The analysis also involves a discussion of correlation diagrams for diatomic molecular orbitals in general. The behavior of diatomic Rydberg states is most easily elucidated by first reviewing the simpler case of atomic Rydberg states, and we now begin with that approach.

**1. Rydberg States of Atoms.**—In s.c.f. (self-consistent-field) descriptions of atomic wave functions, the electrons are assigned to AO's (atomic orbitals). States in which one electron is excited to an AO large in size compared with a usually singly-charged "core" are called Rydberg states. Rydberg states fall into series such that the term value (that is, the energy, in cm.$^{-1}$, to remove the excited electron) is expressible in the form

$$T = RyZ_c^2/n^{*2} = RyZ_c^2/(n - \delta)^2 \qquad (1)$$

where $Z_c$ is the charge on the core ($Z_c = 1$ for a neutral atom) and $Ry$ is the Rydberg constant[3a]; the *term defects* $\delta$ are positive quantities which depend on $l$, also slightly on $n$ at lower $n$ values; in each series, $\delta$ approaches a limiting value $\delta_\infty$ as $n$ increases.[3b] The occurrence of $\delta$ is attributable mainly to penetration of Rydberg orbitals into the core, but where this is small, a small $\delta$ due to polarization of the core becomes important; exchange effects also contribute.[4]

In contrast to eq. 1, it is customary to use for the ionization energies of core AO's expressions of the type

$$T = Ry(Z - S)^2/n^2 \qquad (2)$$

For a neutral atom, the field in which a Rydberg electron spends at least most of its time is approximately like that of a hydrogen atom electron, but for core electrons the effective field is that of a nucleus of charge $Z$ partially shielded by other electrons. The effective shielding constant $S$ allows for "outer" as well as "inner" shielding.[4a]

For alkali metal atoms, even the normal state, of type $C$ $ms$, and the first excited state $C$ $mp$, are Rydberg states, since the single valence-shell electron $ms$ or $mp$ moves in the field of a closed-shell core $C$ much smaller in size than the $ms$ or $mp$ AO.

(2) *Cf.* R. S. Mulliken, *Proc. Natl. Acad. Sci. U. S.*, **12**, 158 (1926); *Rev Mod. Phys.*, **4**, 1 (1932); *Phys. Rev.*, **61**, 277 (1942), mainly on diatomic molecules. On NO, K. P. Huber, *Helv. Phys. Acta*, **34**, 929 (1961); K. P. Huber and E. Miescher, *ibid.*, **36**, 257 (1963). See also R. C. Nelson and W. T. Simpson, *J. Chem. Phys.*, **23**, 1146 (1955).

(3) (a) Although the accepted abbreviation for the Rydberg constant is $R$, $Ry$ is used in the present paper in order in some equations to avoid confusion with interatomic distance $R$. (b) J. C. Slater, "Quantum Theory of Atomic Structure," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1960, section 9-8; H. G. Kuhn, "Atomic Spectra," Academic Press, Inc., New York, N. Y., 1962, p. 156, and references given there, and p. 160. For a detailed treatment, see B. Edlén in a forthcoming volume of the "Handbuch der Physik" on atomic spectra, in particular, sections 19-22. For a discussion of penetrating and nonpenetrating orbits in terms of the old quantum theory, see A. Sommerfeld, "Atombau und Spektrallinien," 4th Ed., Fr. Vieweg and Sons, Braunschweig, 1924, Chapter 7, section 4. On the Rydberg-Ritz formula in quantum mechanics, including some integral representations of the forms of Rydberg AO's, see R. Jastrow, *Phys. Rev.*, **73**, 60 (1948).

(4) Exchange effects between electron and core make small positive contributions; C. A. Coulson and J. G. Stamper, *Mol. Phys.*, **6**, 609 (1963), have discussed this for the (nearly nonpenetrating) 2p Rydberg AO of the Li atom. Larger contributions can occur for nonclosed-shell-core Rydberg AO's (*cf.* section II, 4).

(4a) J. C. Slater, ref. 3b, section 9-7.

When the valence shell contains more than one electron, several valence-shell states occur (*e.g.*, Be $2s^2,{}^1S$ and $2s2p,{}^3P$ and ${}^1P$; B $2s^22p,{}^2P$ and $2s2p^2,{}^4P$, etc.; N $2s^22p^3,{}^4S$, etc., and $2s2p^4,{}^4P$, etc.). These may best be classed as non-Rydberg states.

For such atoms, Rydberg states are obtained by exciting a valence electron to a higher shell (as, *e.g.*, in Be $2s3s,{}^3S$ and ${}^1S$, $2s3p,{}^3P$ and ${}^1P$; N $2s^22p^23p,{}^4D$, etc., or $2s2p^33s,{}^6S$, etc.). The use of eq. 1 for Rydberg states like these is complicated by the occurrence of more than one Rydberg state or even also more than one core state per electron configuration. The most logical procedure would be to use the centroid of each such group of Rydberg and/or core states for $T$ in eq. 1. However, we shall be concerned in this paper with no cases more complicated than $ms$ $ns$, ${}^3S$ and ${}^1S$ or $ms$ $np$, ${}^3P$ and ${}^1P$. The average of the $T$ values of the singlet and triplet state can then be used in obtaining $n^*$. However, it is convenient also (especially when data are incomplete) to use eq. 1 to obtain $n^*$ and $\delta$ values for the singlet and triplet states separately.

**2. Rydberg States of Molecules.**—When one describes molecular wave functions using s.c.f. MO's (molecular orbitals), all that has just been stated for atomic Rydberg states finds a parallel if one considers any one fixed nuclear configuration. In particular, eq. 1 is valid. However, the mode of variation of the MO's and their energies as one varies the nuclear configuration is a new feature of interest. A complication (see section IV) is the fact that the interaction of the molecular rotation with the $l$ vector of the Rydberg electron changes radically as $n$ increases in a Rydberg series.

For molecules, both Rydberg and non-Rydberg orbitals generally include a greater number and variety than for atoms, because of lower symmetry and the consequent subdivision of the orbital shells into more subshells. In their $T$ values, valence-shell MO's come next to Rydberg MO's. They can be defined as those MO's which can be approximately constructed as linear combinations of valence-shell AO's of atoms.

However, there are borderline cases between Rydberg and other excited MO's. A notable example is found in the $1\sigma_g 1\sigma_u,{}^3\Sigma^+_u$ and ${}^1\Sigma^+_u$ states of $H_2$. At small $R$ values, say near the equilibrium distance $R_e$ of the normal state, the $1\sigma_u$ MO is nearly of the UAO (united-atom Rydberg AO) form $2p\sigma$. At larger $R$ values, the close resemblance to the $2p\sigma$ UAO is progressively lost and the non-Rydberg antibonding LCAO form $1s_a–1s_b$ is assumed. Nevertheless the qualitative form of $1s_a–1s_b$ at moderate $R$ values is identical with that of $2p\sigma$, and the one goes over continuously into the other. (However, the limiting form of $1s_a–1s_b$ as $R \to 0$ is not $2p\sigma$ but has been described as $1p\sigma$, which is unacceptable; hence it becomes necessary to abandon $1s_a–1s_b$ as $R \to 0$.)

A rather similar case is that of the $1\pi_g$ MO, which as $R \to 0$ takes the UAO form $3d\pi$, but as $R \to \infty$ takes the antibonding LCAO form $2p\pi_a–2p\pi_b$. Qualitatively the two forms are identical at moderate $R$ values. At $R_e$ in the Rydberg states of $H_2$ and $He_2$, $1\pi_g$ is close to $3d\pi$ in form. At $R_e$ in certain excited states of $N_2$, $1\pi_g$ is only partially promoted, being more like $2p\pi_a–2p\pi_b$ but still strongly resembling the Rydberg UAO form $3d\pi$.

Another similar example is that of the $3a_1$ MO of $CH_4$. The $1a_1$ MO here is essentially $1s_C$. The $2a_1$ valence-shell MO has the bonding LCAO form $\alpha(2s_C) + {}^1/_2\beta(1s_a + 1s_b + 1s_c + 1s_d)$, where the subscripts a, b, c, d refer to the four H atoms and $\alpha > \beta$. Qualitatively, $2a_1$ has the characteristics of the UAO 2s; in particular, it has one roughly spherical nodal surface due to the radial node in $\alpha(2s_C)$. The excited MO $3a_1$ can be approximated by the antibonding LCAO form

$$\gamma(2s_C) - {}^1/_2\delta(1s_a + 1s_b + 1s_c + 1s_d)$$

This evidently has all the qualitative characteristics (in particular, two more or less nearly spherical nodal surfaces) of a 3s Rydberg MO or united-atom 3s AO. It seems likely that, just as the Rydberg UAO form $2p\sigma$ in $H_2$ represents a better approximation than $1s_a - 1s_b$ at $R$ values near or below $R_e$ of the normal state, so in $CH_4$ in its normal-state equilibrium configuration the Rydberg UAO 3s may represent a better approximation than the antibonding valence-shell LCAO form.

A similar though more imperfect relation of the 3s Rydberg MO to an antibonding LCAO–MO holds for $NH_3$, and in other similar cases. In the literature, one sometimes sees discussion as to whether the first excited MO of such molecules is 3s or is an LCAO–MO. The answer is that the two are more or less the same. A more detailed discussion of the exact forms of MO's, including such borderline MO's (e.g., $1\sigma_u$), using $H_2^+$ MO's as examples, is given in section V, 1.

In using eq. 1 for Rydberg MO's, one should ideally always work with *vertical* $T$ values; that is, one should consider the energy to remove the Rydberg MO at some fixed nuclear configuration. More generally, one would be interested in vertical $T$, $n^*$, or $\delta$ values *as functions of the nuclear configuration*. In practice, for a set or sets of Rydberg MO's all sharing a single core electron configuration and state, the directly observed $T$ values are usually very nearly vertical for (in the diatomic case) an $R$ value equal to $R_e$ of the core. This is because $R_e$ is nearly constant as $n$ increases in an MO Rydberg series, except for usually rather small deviations for the lowest $n$ values. Further, instead of correcting for zero-point vibrations, one can usually without its making more than a slight difference use $T$ values corresponding to removal of the Rydberg electron from the $v = 0$ level of the Rydberg state to the $v = 0$ level of the core ion.

However, if one has sets of Rydberg MO's associated with *different* core states each having its own $R_e$, one may expect *the same* Rydberg MO to have a *slightly different* $T$ and $n^*$ because of the different core.

## II. General Characteristics of Rydberg Orbitals

1. **The Forms of Rydberg Atomic Orbitals.**—For an atomic Rydberg state with a *closed-shell* core, the total wave function $\psi$ may be closely approximated in the form

$$\psi \approx \mathcal{A}\psi_{core}^{(1, \cdots N - 1)}\psi_{Ryd}^{(N)} \tag{3}$$

where the indices $1 \cdots N$ refer to individual electrons, and the operator $\mathcal{A}$ makes $\psi$ antisymmetric in all the electrons. In eq. 3, $\psi_{core}$ may be assumed to be an *accurate* wave function for the core in the average field of the Rydberg electron. In a series of Rydberg

states with increasing $n$, $\psi_{core}$ asymptotically approaches $\psi_{core}$ for the free ion, but differs relatively little from this even for the states of smallest $n$. For an accurate $\psi_{core}$, electron correlation within it must be taken into account, and this in turn must somewhat affect $\psi_{Ryd}$.

However, it will suffice for present purposes to think of $\psi_{core}$, and the total $\psi$, in terms of the very considerably less accurate s.c.f. approximation, in which $\psi_{core}$ can be approximated as a single Slater determinant in $N - 1$ electrons. In this approximation, any Rydberg AO is orthogonal to all core AO's. As a result of the self-consistency requirements, the core must be slightly different for different Rydberg states, most so for those of low $n$ values, with differences vanishing as $n \to \infty$. If the core were identical for all Rydberg states, the Rydberg AO's of any one series (and of course of different series) would all be orthogonal. Actually, they should be very nearly orthogonal.

Like the Rydberg orbits of Bohr theory, the Rydberg orbitals of quantum mechanics can be classified as penetrating or nonpenetrating,[3b] although in quantum mechanics the distinction is less sharp because the core has no really sharp boundary. Electrons in Rydberg orbitals spend a small fraction of their time within the core. This fraction becomes smaller and smaller as $n$ increases, but for given $n$ it is much larger for penetrating than for nonpenetrating orbitals.

The exchange integrals between the electron in the Rydberg AO $\psi_{Ryd}$ and those in the orbitals of a closed-shell core are relatively small.[4a] Hence very little error is introduced if we drop the over-all antisymmetrizer in eq. 3 and consider $\psi_{Ryd}$ as a solution of a simple one-electron Schrödinger equation for the $N$th electron in the mean electrostatic field of the core. (It is necessary, however, to keep in mind that $\psi_{Ryd}$ has to be orthogonal to all core AO's of the same species.) Aside from relatively small perturbations (due to variations or possible nonsphericity in the field of the Rydberg electron) which for present purposes can be ignored, the core is spherically symmetrical; thus its field can be expressed in the form $U(r)$.

With a $U(r)$ field, the one-electron Schrödinger equation for $\psi_{Ryd}$ yields eigenfunctions of the familiar form $R_{nl}(r)Y_{lm}(\theta,\phi)$, in which the $Y_{lm}(\theta,\phi)$ are standard expressions and only the radial factor $R_{nl}(r)$ presents a problem. A familiar type of discussion of the differential equation for $R_{nl}$ for the H atom (see standard texts), and which is seen to be valid also for $R_{nl}$ of the Rydberg orbital problem, shows that its acceptable asymptotic solutions go as $e^{-ar}$, where $a$ is proportional to $T^{1/2}$. Since we know that solutions which satisfy the boundary conditions at $R = 0$ have energies $Ry Z_c^2/n^{*2}$ (cf. eq. 1), $T^{1/2}$ has to be taken proportional to $1/n^*$. Except for the H atom, the $n^*$ values deviate from integers, and to a different extent for different $l$ values. The asymptotic form of $R_{nl}$ for any Rydberg AO is thus seen to be $e^{-br/n^*}$, exactly as for a hydrogen atom AO except that $n^*$ is nonintegral. Further, as one proceeds to smaller $r$ values, $R_{nl}$ must go through a succession of nodes and loops exactly like those which one would expect for a hydrogen atom if $n^*$ could be nonintegral. In other words, the nodes and loops are like those of a hydrogen atom except for an inward phase shift of amount $n - n^*$, *i.e.*, $\delta$. One could also say that the form of $R_{nl}$ corresponds at large $r$ to an interpolation

between the two nearest H atom solutions with integral $n$.[3b]

The phase-shifted H-atom-like form of $R_{nl}$ remains exact so long as the potential remains $-e^2/r$. Finally, however, the potential begins to depart from $-e^2/r$ because of penetration and polarization. Satisfaction of the boundary conditions at $r = 0$ then leads to departures in form for the inner part of the Rydberg AO from H-atom-like character, and to an energy as given by eq. 1. For penetrating orbitals these departures may be large; for nonpenetrating orbitals they are small.

It is useful to have analytical expressions for $R_{nl}(r)$ for both Rydberg and core AO's. For *hydrogenic* AO's, *exactly*

$$R_{nl} = \left( \sum_{k=l}^{n-1} c_k r^k \right) e^{-\zeta r/a_0}, \text{ with } \zeta = Z/n$$

where the $c_k$'s are well known standard coefficients which depend on $n$ and $l$ and decrease in magnitude with decreasing $k$, and *which alternate in sign giving* $n - l - 1$ *nodes and* $n - l$ *loops in* $R_{nl}$. The outermost loop has the largest amplitude. Similarly, s.c.f. core AO's can be *approximated*[5] (though only somewhat inaccurately)[5a] by

$$R_{nl} \approx \sum_{k=l}^{n-1} c_k r^k e^{-\zeta_k r/a_0}, \text{ with } \zeta_k = (Z - s_k)/n \quad (4)$$

where now the $|c_k|$'s fall off much faster with decreasing $k$ than in the hydrogenic case, as a result of the fact that $s_k$, for the $k$th loop, decreases with decreasing $k$, thus increasingly shrinking the inner loops. It should be noted here that the *field* shielding constant $s_n$ (for the outermost and principal loop) is considerably smaller than the *energy* shielding constant $S$ which appears in eq. 2.[4]

Rydberg AO's should be as nearly as possible hydrogenic in their outer loops but, if penetrating, should be core-AO-like in their inner loops. To meet these requirements, approximately

$$R_{nl} \approx \sum_{k=l}^{n_c-1} c_k r^k e^{-\zeta_k r/a_0} +$$

$$\left( \sum_{k=n_c}^{n-1} c_k r^{k-\delta} \right) e^{-\zeta_{Ry} r/a_0} \text{ with } \zeta_{Ry} = Z_c/(n-\delta)$$

$$(5)$$

where $n - \delta \equiv n^*$ and $n_c$ is the highest $n$ value for a core AO of the same $l$ as the Rydberg AO. For example, $n_c = 3$ for potassium $ns$ Rydberg AO's: the core contains 1s, 2s, and 3s electrons. The second summation in eq. 5 is strictly hydrogenic except for a phase shift corresponding to $\delta$ (for example, $\delta = 2.23$ for the 4s AO of potassium). For nonpenetrating AO's, *only* the second summation is present, and $\delta$ is small or very small.

The size of an AO is often of interest. For this the $r$ value at which the radial density $(rR_{nl})^2$ has its maximum—call it $a$—is a convenient measure. An approximate value of $a$ can be obtained if $R_{nl}$ is approximated by its outermost and most important loop.[6] Then for core AO's

$$a \approx na_0/\zeta_{nl} = n^2 a_0/(Z - s_{nl}) \quad (6)$$

for Rydberg AO's

$$a \approx n^* a_0/\zeta_{Ry} = n^{*2} a_0/Z_c$$

## 2. The Forms of Rydberg Molecular Orbitals.—

For a molecular Rydberg state with an MO *closed-shell* core, a discussion largely paralleling that just given for atomic Rydberg states holds good, including the validity of eq. 3, the orthogonality of Rydberg to core orbitals if the s.c.f. approximation is used, the approximate orthogonality of different MO's in any one Rydberg series, and the occurrence of penetrating and nonpenetrating orbitals. However, it is necessary to generalize the previous discussion of the forms of Rydberg orbitals. The one-electron Schrödinger equation is no longer rigorously separable in spherical coordinates as it was in the atomic case. However, it is still *asymptotically* separable as $r$ (measured from the electric centroid of the core) becomes very large. Hence, as before, the asymptotic solutions must go as $e^{-br/n^*} Y_{lm}(\theta, \phi)$ with sharply defined $l$ values.

As one proceeds toward smaller $r$, $\psi_{Ryd}$ goes through a succession of phase-shifted but otherwise precisely H-atom-like radial nodes and loops as in the atomic case, down to $r$ values where the potential begins to depart appreciably from $-e^2/r$. But as the core is approached (even before it is appreciably penetrated), the departure of its potential not merely from $-e^2/r$ but also even from spherical symmetry begins to introduce mixings of orbitals differing in $n$, $l$, and $m$. Finally, if the Rydberg MO is of the penetrating type, its innermost portions are more or less grossly distorted in shape and size as compared with AO's. In diatomic and linear molecules, however, these distortions leave unaffected the $\phi$-dependent factor $e^{\pm i\lambda\phi}$ (where $\lambda = |m|$) which is contained in $Y_{lm}$.

The preceding discussion shows that Rydberg MO's have sharply defined $l$ values in their outer parts, especially when $n^*$ is large. For any Rydberg MO taken as a whole, one can then say that in proceeding up a Rydberg term series to higher $n$ values, $l$ becomes a more and more sharply defined quantum number.

It is usually rather more difficult in the case of a penetrating Rydberg MO to assign a definite principal quantum number $n$ (or radial quantum number, $n_r$, where $n = n_r + l + 1$) than to assign an $l$ value. In the case of Rydberg AO's, $n_r$ is always precisely equal to the precisely integral number of nodal surfaces in the coordinate $r$, in spite of a shrinkage in the nodal spacings; and $n = n_r + l + 1$. But with penetrating Rydberg MO's, the distortion of the intracore parts produces not merely a shrinkage of nodal spacings,

(5) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930); see R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949), for a review.

(5a) Each term in eq. 4 is the simplest one-term approximation to what in section III, 1 is called a loop-creating function. Analytically, such a function can be rather closely approximated by replacing each single term of eq. 4 by a suitable linear combination of two or three terms having the same form as the single term, but with an *assortment* of $\zeta_k$ values (see the papers cited in ref. 5). The exact forms of the loop-creating functions are obtained by s.c.f. calculations.

(6) For core AO's the first eq. 6 is a very close approximation, because of the small amplitudes of the innermost loops. For hydrogenic AO's, $a \approx n^2 a_0/Z$ is not quite so good an approximation, because of the relatively greater importance of the inner loops, except when there is only one loop ($l = n - 1$), in which case $a = n^2 a_0/Z$ is exact. For Rydberg AO's, the second eq. 6 is a close approximation if there is only one loop outside the core, but a little less close if there is more than one such hydrogenic loop.

but also strong distortions which would correspond to a mixing of central-field AO's differing not only in $l$ but also in $n$. For nonpenetrating Rydberg MO's, however, there is no difficulty in assigning $n$ values.

**3. Spin-Orbit Coupling in Rydberg States of Atoms.**—Brief mention is desirable here of the spin-orbit coupling which occurs for atomic Rydberg states with closed-shell core when $l > 0$ for the Rydberg AO. For high $n$ values, this coupling should be very small, just as for the H atom. For low $n$ values of penetrating Rydberg orbitals in atoms where $Z$ is not small, it can be appreciable. According to a familiar approximate formula, the doublet separation $\Delta\nu$ (in cm.$^{-1}$) between the two sublevels with $j = l + \frac{1}{2}$ and $l - \frac{1}{2}$ is

$$\Delta\nu = R\alpha^2(Z_i^2 + 1)/(n^*)^3 l(l + 1) \qquad (6a)$$

$\alpha$ is the fine-structure constant and $Z_i$ is an effective $Z$ (similar to $Z - S$ in eq. 2) for the part of the orbital within the core. For nonpenetrating orbitals, $\Delta\nu$ is extremely small for all $n$, just as for H atom orbitals.

**4. Atomic Rydberg States with Nonclosed-Shell Core.**—The foregoing discussion has assumed a closed-shell core. For a more complicated core (see ref. 3b, especially Edlén), the essential features of the discussion are in most respects unchanged. With a $^2S$ core, a singlet and a triplet Rydberg state occur for each Rydberg orbital. Here eq. 3 must be generalized to

$$\Psi = 2^{-1/2}\mathcal{Q}[\Psi_{\text{c.s.}}^{(1\cdots N - 2)}(\phi_c^{(N - 1)}\chi_{\text{Ry}}^{(N)} \pm$$
$$\phi_c^{(N)}\chi_{\text{Ry}}^{(N - 1)})\Psi_{\text{spin}}^{(N - 1, N)}] \qquad (3')$$

where the $+$ and $-$ signs correspond to the singlet and the triplet state, respectively. In eq. 3', $\psi_{\text{spin}}^{(N - 1,N)}$ takes one of four familiar forms, one for the singlet state, any one of three for the triplet. In eq. 3', the AO $\chi_{\text{Ry}}$ is in general somewhat different for the singlet and triplet states, and the AO $\phi_c$ of the odd core electron is in general also slightly different for the two cases. The most extreme case known is for the $1s^2$-$2s2p$,$^3P$ and $^1P$ states of the Be atom, where according to s.c.f. calculations the maximum of $R_{nl}$ for the 2p AO is at about twice as large an $r$ in the singlet as in the triplet state; the 2s AO is a little smaller in the singlet than in the triplet state. Here, to be sure, the states cannot be called Rydberg states, but they do illustrate an effect which must be present, though to a less extreme degree, in true Rydberg states (for example, the Be states $1s^2 2snp$,$^3P$ and $^1P$ with $n > 2$). Differences in $\delta$ values between singlet and triplet states arise partly because of differences in the form of $\chi_{\text{Ry}}$ for these, and partly (probably *mainly* in most cases) because of an exchange energy contribution of $+K_{c,\text{Ry}}$ for the singlet and $-K_{c,\text{Ry}}$ for the triplet state; here $K_{c,\text{Ry}}$ must differ somewhat for the singlet and triplet states if $\chi_{\text{Ry}}$ and $\phi_c$ are somewhat different for the two.

From the foregoing, it is seen that there are two reasons why the energies, hence the $\delta$ values, differ for singlet and triplet states. In any event, the $\delta$ values for corresponding singlet and triplet Rydberg series show empirically the usual behavior that $\delta$ for each approaches a constant value as $n$ increases.

However, it should be noted that the use of $\delta$ values as measures of phase shifts of outer nodes and loops of Rydberg orbitals relative to those of H atom AO's, which is valid in the case of a Rydberg electron in the field of a closed-shell core, must be modified here. If we neglect differences in the form of $\chi_{\text{Ry}}$ for singlet and triplet states, the correct $\delta$ to correlate with phase shifts appears to be that which is obtained from the *average* of singlet and triplet energies, so that the effects of $\pm K_{c,\text{Ry}}$ on $\delta$ are removed. On the other hand, insofar as $\chi_{\text{Ry}}$ is different for the singlet and triplet states, the effects of these differences on $\delta$ should appear in the phase shifts. However, since we are nearly always ignorant as to the relative contributions of the two causes of differences in $\delta$, and since very likely the contributions due to differences in $\chi_{\text{Ry}}$ are usually small, the best practical (though approximate) assumption appears to be to use $\delta$ values corresponding to averages of observed singlet and triplet energies as suitable measures of the phase shifts.

With a $^2P$ core, as for example for neon or other rare gases, if the $^2P$ doublet separation $\Delta\nu$ is at all appreciable, one obtains separate Rydberg series for the $^2P_{1/2}$ and the $^2P_{3/2}$ cores. Further, there is a tendency toward $J,j$-like coupling, increasing rapidly with $n$ of the Rydberg orbital. For an $ns$ Rydberg orbital with a $^2P$ core, one has for small $n$ a $^3P$ and higher in energy a $^1P$ Rydberg state if $\Delta\nu$ is not large ($L,S$ coupling). As $n$ increases (and even at small $n$ if $\Delta\nu$ is large) the Rydberg levels group themselves into $J = 0$ and 1 levels with $^2P_{1/2}$ core and $J = 1$ and 2 levels with $^2P_{3/2}$ core. The two $J = 1$ levels are now of mixed $^1P$ and $^3P_1$ character, and in the limit of high $n$ and pure $J,j$ coupling, the level with $^2P_{3/2}$ core is two-thirds $^1P$ and one-third $^3P_1$ (the coefficients in the wave function are $(^2/_3)^{1/2}$ and $(^1/_3)^{1/2}$), while the proportions are reversed for the level with $^2P_{1/2}$ core.[6a] These relations are true, rather surprisingly, even if the $^2P$ is inverted, in which case it is the lower-energy $J = 1$ level that has $^2/_3$ $^1P$ character. If an absorption spectrum leading to the Rydberg levels is observed, the transition to the upper $J = 1$ level, for given $n$, should be the more intense at the lowest $n$ values unless $\Delta\nu$ is too large. But as $n$ increases, the relative intensities (more accurately, the dipole strengths) of the two transitions must approach a $2:1$ ratio, with the transition to the $J = 1$ level with $^2P_{3/2}$ core the more intense.

**5. Diatomic Rydberg States with Nonclosed-Shell Core.**—For diatomic or linear molecules with a $^2\Sigma$ instead of a closed-shell core, one has singlet and triplet Rydberg states with differing $\delta$ values. Here exactly the same considerations as for an atom with $^2S$ core (section II, 4) are applicable.

Phenomena analogous to those for an atom having a core with $L > 0$ occur for a diatomic or linear molecule having a core with $\Lambda > 0$. With a $^2\Pi$ core, one may have separate Rydberg series for the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ core, with $J,j$-like tendencies increasing rapidly with $n$. For a $\sigma$ Rydberg MO with a $^2\Pi$ core, one has for small $n$ a $^3\Pi$ and a $^1\Pi$ state. As $n$ increases (and even at small $n$ if the spin-orbit coupling is strong enough in the core), the Rydberg levels group them-

(6a) *Cf.* E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, Cambridge, England, 1959, pp. 294, 301, etc.

selves into $\Omega = 0$ and 1 levels with $^2\Pi_{1/2}$ core, and $\Omega = 1$ and 2 levels with $^2\Pi_{3/2}$ core. The two $\Omega = 1$ levels are of mixed $^1\Pi$ and $^3\Pi_1$ character, the mixing (unlike the atomic cases with $^2P$ core) becoming $50:50$ in the limiting case of pure $J,j$-like coupling. Then if Rydberg series are observed in absorption, transitions to the $\Omega = 1$ levels should approach equal intensity as $n$ increases.

A quite different sort of complication, not possible for atoms, occurs for diatomic molecules with non-closed-shell core (or often even with closed-shell core); namely, a failure of the s.c.f. approximation at large internuclear distances (see section VI).

## III. Rydberg Series Orbitals and Their Precursors

**1. Real and Virtual Precursors in Rydberg Series.—** In embryology, there is a theorem which states that "Ontology recapitulates phylogeny": a developing organism, once started, goes through a series of stages resembling successive evolutionary precursors.[6b] One finds something formally very similar for Rydberg orbitals. To illustrate, let us for simplicity consider Rydberg states of an atom. A very similar discussion applies to molecules.

In the normal state of the potassium atom, 1s, 2s, 3s, and 4s AO's are occupied, of which the first three are core AO's, and the last is essentially a Rydberg AO. Of these $n$s AO's, 1s can be called a precursor of all the rest, 2s of 3s and 4s, and 3s of 4s. As we go up the series, one new radial node and loop are added for each succeeding member.

Each loop corresponds to a function which is approximated[5a] by one of the terms $c_k r^k e^{-\zeta_k r/a_0}$ for core AO's or loops, or $c_k r^{k-\delta} e^{-\zeta_k r/a_0}$ for outer loops of Rydberg AO's (see eq. 4 and 5). However, for $n > 1$, the *loops are not identical with these loop-creating functions*, but are the result of the superposition of two or more of them, although with the $k$th function predominantly determining the form of the $k$th loop. To illustrate, 1s is approximately $ae^{-\zeta r/a_0}$, 2s is approximately $a_2 re^{-\zeta_2 r/a_0} - b_2 e^{-\zeta_1' r/a_0}$, 3s is approximately $a_3 r^2 e^{-\zeta_3 r/a_0} - b_3 re^{-\zeta_2' r/a_0} + c_3 e^{-\zeta_1'' r/a_0}$, and so on, with $a_k > b_k > c_k \ldots$, where $\zeta'' = \zeta' = \zeta_1$ very nearly, but not quite, $\zeta' = \zeta_2$ very nearly, and so on. The $k$th loop-creating function, likewise the $k$th loop, is almost identical in all $n$s AO's. Slater[3b] gives a figure which beautifully illustrates this near-identity of inner loops for the 3s and 4s Rydberg AO's of the Na atom. Thus the inner loops of the $n$th AO recapitulate the $(n - 1)$th AO, the inner loops of the latter recapitulate the $(n - 2)$th, and so on. This is true for both core AO's and Rydberg AO's.

If we go to excited $n$s Rydberg states of potassium, with $n = 5$ or larger, one further node and loop are added for each unit increase in $n$. Consider, for example, the $C$ 6s Rydberg state ($C$ = core), in s.c.f. approximation. The 6s AO now has 1s, 2s, and 3s as *real precursors* in the core. It also has 4s and 5s as precursors, but since those AO's are not actually occupied, and so are not determined by s.c.f. criteria for the $C$ 6s Rydberg state, they may be referred to as *virtual precursors*.

Similar considerations apply to potassium states of the type $C$ $n$p, of which $C$ 4p is the lowest. The Rydberg $n$p AO's all have real precursors 2p and 3p in the core, also virtual precursors if $n > 4$. Potassium states of types $C$ $n$d ($n \geq 3$), $C$ $n$f ($n \geq 4$), and so on, have no real precursors, but have virtual precursors if $n$ exceeds the minimum value.

In general, AO's which have real precursors are *penetrating* AO's, those with no real precursors are nearly *nonpenetrating*. In the case of the potassium atom AO's just discussed, $n^* = 1.77$ for 4s, hence $\delta = 2.23$; $n^* = 2.23$ for 4p, hence $\delta = 1.77$; $n^* = 2.85$ for 3d, hence $\delta = 0.15$; $n^* = 3.99$ for 4f, hence $\delta = 0.01$. Roughly the same $\delta$ values are retained for higher $n$ values in each series (*e.g.*, $\delta = 2.20$ for 6s, 1.75 for 6p, 0.24 for 6d, 0.01 for 6f), these being close to the values for $n \rightarrow \infty$.[7] Clearly $n$s and $n$p, which have core precursors, are strongly penetrating, while $n$d and $n$f, with no core precursors, are nearly nonpenetrating and H-atom-like.

The $\zeta_k$ values for core loops in eq. 4 and 5 can be estimated using Slater's well-known simple rules for $Z_{ef}$ (*i.e.*, $Z - s_k$) values.[5] For any core loop, $Z_{ef}$ is an effective nuclear charge such that $Z_{ef}e/r^2$ is the mean effective field in a region chiefly occupied by that loop.[8] For potassium, Slater's rules give $\zeta_1 = 18.7$, $\zeta_2 = 7.42$, $\zeta_3 = 2.58$, $\zeta_4 = 0.55$. More accurate forms than are given by eq. 4 and 5 are found in s.c.f. calculations,[5a] but these equations give a qualitatively and roughly quantitatively correct picture. For the H-atom-like Rydberg loops, a different type of loop-creating function (*cf.* eq. 5) is needed. Thus for the 4s potassium atom AO, although eq. 4 with $\zeta_4 = 0.55$ can still be used to give a rough fit, the form

$$cr^{4-1-\delta}e^{-\zeta_{R_3} r/a_0} = cr^{0.77}e^{-r/1.77a_0}$$

is preferable for the fourth loop-creating term.

The 5s, 6s, 7s, $\cdots$ Rydberg AO's of potassium should in their inner parts approximately recapitulate, with diminishing coefficients as $n$ increases, the form of the 4s AO, adding one more node and loop for each increase of $n$ by 1. All the outer loops should be almost identical with the outer loops of H atom orbitals with $n$ values equal to the actual $n^*$ values of the 5s, 6s, 7s, $\cdots$ AO's of potassium, namely approximately like 3s, 4s, 5s, $\cdots$ H atom AO's except for a moderate phase shift inward.

The above discussion is applicable to states where the Rydberg electron moves in the field of a closed-shell core. The case of a nonclosed-shell core, in particular the matter of the phase shifts in the outer loops, is discussed in section II, 4.

**2. Effective $n^*$ Values for Non-Rydberg Orbitals.—** A major objective of the present papers is to understand molecular $\delta$ values (*i.e.*, $n - n^*$ values; *cf.* eq. 1) and to find how to use them in understanding or identifying experimentally observed Rydberg states. The use of $n^*$ values is well justified only for Rydberg AO's or MO's. Penetrating Rydberg orbitals, however, have *non-Rydberg core precursors* whose relation to their Rydberg descendants one wishes to study, and for which some index analogous to $n^*$ would be desirable.

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(6b) Doubts are, however, now being expressed about the validity of this theorem: see E. Caspari, *Science*, **139**, 773 (1963).

(7) See H. G. Kuhn, ref. 3b, p. 160.

(8) Actually, Slater's rules were designed for the *outermost* loop-creating function of any core AO. However, they are not far wrong also for inner loops.

Equation 2 for core AO's does not furnish such an index. It proves convenient to define a quantity $[n^*]$ (effective $n^*$) for core AO's of atoms and for core MO's of molecules by setting

$$T = RyZ_c{}^2/[n^*]^2 = RyZ_c{}^2/(n - [\delta])^2 \quad (7)$$

*as if* they were Rydberg orbitals (with $Z_c = 1$ for neutral atoms or molecules). In a series of orbitals whose lowest precursors are core orbitals, it is useful to tabulate $[n^*]$ values for the core orbitals along with the $n^*$ values of the Rydberg members, keeping in mind, of course, that the $[n^*]$ values have only a formal significance.

**3. Precursor Relations for Diatomic Molecules.—** The above discussion needs only slight modification and amplification for diatomic molecules. In the latter, each Rydberg series is characterized in general by a $\lambda$ as well as by an $l$. However, $\lambda$ loses its significance in strongly uncoupled nonpenetrating MO's at high rotational quantum numbers and/or $n$ (see section IV), and extrapolations to zero rotation must be used in determining $T$ and so $n^*$ values. Further, there is much scrambling of $n$ and $l$ values in core MO's and in the intracore portions of their Rydberg descendants. This fact also implies that the precursor relations of Rydberg MO's are probably in some cases not unambiguous, but more or less scrambled. The $N_2$ molecule furnishes examples (see section VI, 4).

## IV. Coupling Relations in Diatomic Rydberg States

In most of the present paper, the theoretical discussion tacitly assumes that molecular Rydberg $n^*$ values and other electronic features can be cleanly separated from effects due to nuclear motions. However, the experimental evidence needed for comparison with theory comes from spectroscopic data in which nuclear motions, especially molecular rotations, are strongly involved. For a realistic understanding, and as a precaution against possible pitfalls, it is therefore important to survey briefly the interaction of electronic and nuclear motions in molecular Rydberg states. The present section is devoted to this theme. Also, in the course of the discussion, some interesting rather new conclusions are reached which should be useful in interpreting the structures of bands that involve diatomic Rydberg states.

**1. Rotational and Vibrational Rydberg Uncoupling.—** In most discussions of molecular wave functions, the validity of the B.O. (Born–Oppenheimer) approximation is assumed. This approximation is most nearly accurate when the frequencies of motion, which can be gauged by energy level spacings, are much larger for the electronic than for the nuclear motions. In a Rydberg state series, as $n$ increases, the frequencies for the Rydberg electron become smaller and smaller relative to those of nuclear vibration and rotation. This leads to more or less radical changes in coupling relations. For molecules of various sizes and shapes, a considerable variety of cases occurs. However, the present paper will be restricted to diatomic molecules. The present section is further restricted to cases in which the core is of closed-shell type ($^1\Sigma^+$ or $^1\Sigma_g{}^+$ state) or is in a $^2\Sigma^+$ or $^2\Sigma_g{}^+$ state.

In the B.O. approximation, leaving aside center-of-mass and nuclear spin factors, the wave function for the lowest-$n$ Rydberg states of a diatomic molecule with closed-shell core takes the form[9] (*cf.* eq. 3 for atoms)

$$\Psi \approx \Psi_{el}\Psi_{rot}\Psi_{vib} = (\mathcal{Q}\Psi_{core}\psi_{Ryd})\Psi_{rot}\Psi_{vib} \quad (8)$$

As $n$ increases and the inner loops of the Rydberg MO become less and less important relative to the outer loops, the Rydberg electron withdraws more and more from influencing the rotational and vibrational motions of the nuclei and for large $n$ the wave function takes the form[9]

$$\Psi = \mathcal{Q}[(\Psi_{core}\Psi_{rot}\Psi_{vib})\psi_{Ryd}] \quad (9)$$

Here $\psi_{Ryd}$ is no longer included within the electronic factor of the B.O. approximation; however, this approximation still holds good for the factor in parentheses. In the eq. 8 case, the potential function $U(R)$ which governs the nuclear motions is determined by the joint fields of the core, the Rydberg electron, and the internuclear repulsion. In the Rydberg-uncoupled eq. 9 case, $U(R)$ is determined by the field of the core electrons and the internuclear repulsion only. Intermediate cases occur over a range of moderately low $n$ values.

In eq. 9, the requirement of antisymmetrization between the Rydberg and core electrons is unimportant in the case of a closed-shell core, and can then just as well be dropped. But if the core contains an unpaired $\sigma$ electron ($^2\Sigma^+$ or $^2\Sigma_g{}^+$ core), the exchange coupling between this electron and the Rydberg electron,[9] which gives rise to energy differences between corresponding singlet ($S = 0$) and triplet ($S = 1$) Rydberg state series, persists at all $n$ values. Although this exchange coupling becomes rapidly smaller, being due essentially to the interaction between the odd core electron and the Rydberg electron when the latter is in the innermost loop or loops of its MO, nevertheless its effect persists at all $n$ values in the form of two somewhat different $\delta$ values, one for $S = 0$ and one for $S = 1$. Each of these is nearly constant, and approaches exact constancy as $n$ increases (*cf.* sections II, 4, and II, 5).

For vibrational quantum numbers $v$ not too close to dissociation, the vibrational wave function $\psi_{vib}$ is not much affected by the change-over from eq. 8 through intermediate cases to eq. 9. This is because, even at

low $n$, the Rydberg electron exerts at most a rather small influence on the $U(R)$ curve for $R$ values not too far from $R_e$, so that this curve when governed by $\psi_{core}$ alone as in eq. 9 is not very different from that obtained when $\psi_{Ryd}$ also participates in governing it, as in eq. 8. Hence $\psi_{vib}$ is not very different in the two cases; and since it can properly be factored out in both extreme cases ($\alpha$ of course does not affect it), it seems safe to say that it can be factored approximately also in intermediate cases, and that it may be expected to change smoothly as $n$ increases.

For vibrational quantum numbers $v$ near dissociation, the outswing of the vibration carries the nuclei to $R$ values so large that the factorization of the electronic wave function $\psi_{el}$ into $\alpha\psi_{core}\psi_{Ryd}$ in eq. 8 becomes a very poor approximation. Configuration mixing (c.m.), for example in simple cases with a second function $\alpha\Psi'_{core}\psi'_{Ryd}$, then becomes essential (see section VI, 3). Since $\psi_{Ryd}$ and $\psi'_{Ryd}$ here have different $n$ and $l$ values, the Rydberg state no longer has a well-defined $l$ or $n$ for vibrational levels close to dissociation. However, the B.O. approximation ($\Psi = \Psi_{el}\Psi_{rot}\Psi_{vib}$) still holds, and provides the $U(R)$ curve for $\Psi_{vib}$ out to dissociation; and the state may still reasonably be called a Rydberg state. Sometimes (or perhaps very often) this $U(R)$ curve has a hump (*i.e.*, goes through a maximum) at fairly large $R$ values before dissociation.[9a]

The foregoing considerations apply to the highest $v$ levels of Rydberg states of low $n$, where eq. 8 is valid. Similar considerations must also be relevant for the highest-$v$ levels of states of high $n$, where eq. 9 applies. Although $U(R)$ is now determined by the core alone for low $v$ values, this can no longer be entirely true for $R$ values comparable to or larger than the dimensions of the Rydberg MO. It appears that as dissociation is approached, and so perhaps for the highest $v$ level if it lies close enough to the dissociation asymptote, c.m. of the type described above must set in and must affect the form of the $U(R)$ curve at very large $R$. This apparently implies that something like the B.O. approximation is then restored, and that eq. 8 generalized to include c.m. may become applicable for the top $v$ level or levels.

For all values of $n$, except when c.m. becomes important at high $v$ values as just described, $\psi_{Ryd}$ has a well defined $l$ (least so at the smallest $n$ values): see section II. The $l$ vector is then coupled to the rotational angular momentum vector of $\Psi_{rot}$, in various ways according as eq. 8 or eq. 9 or an intermediate case is applicable.[9] In the eq. 8 case, the projection of $l$ on the internuclear axis gives the sharply defined axial electronic quantum number $\lambda$. We then have Hund's case a if the spin-orbit coupling is strong, or case b if it is weak. With a $^1\Sigma^+$ or $^2\Sigma^+$ core, the only appreciable spin-orbit coupling is that of the Rydberg electron's $l$ with its own spin, and this rapidly becomes weaker as $n$ increases, just as for atoms (*cf.* section II, 3). Thus Hund's case b is usual for Rydberg states with $\Sigma$ core. In case b, the energy of nuclear rotation is given by $B[N(N + 1) - \Lambda^2] + \cdots$.[10]

At higher $n$ values, $\lambda$ tends to be destroyed, $l$ being

decoupled from the nuclear axis; the phenomenon is commonly called "*l uncoupling.*" If $l$ uncoupling is essentially complete, we have Hund's case d, *a special case* of eq. 9. In this case[10] the core rotates, with energy $BR(R + 1) + \cdots$, and vibrates, independently of the Rydberg electron, which moves in the average field of the rotating vibrating core. The $l$ vector of the Rydberg electron is now weakly coupled (by the residual influence of the nonspherical field around the nuclear axis) to the $R$ vector; the quantum number $N$ of their resultant can assume values $R + l, R + l - 1, \cdots R - l$. However, as we shall see below, complete $l$ uncoupling can under some circumstances be more or less strongly inhibited. Hund's case d is then not necessarily closely approached even at high $n$.

Reference must now be made to the electron spin (quantum number $S$). For a closed-shell core, the resultant spin $S = \frac{1}{2}$ is merely that of the Rydberg electron. For a $^2\Sigma^+$ core, parallel sets of singlet ($S = 0$) and triplet ($S = 1$) Rydberg states occur, with a sharply defined $S$ at all $n$ values. In case b or d, the $S$ and $N$ vectors are coupled to give a resultant with quantum number $J$ ($J = N + S, \cdots N - S$).[11] The situation is, however, more complicated if there is any considerable spin-orbit coupling in a core with $\Lambda > 0$, as for example with a $^2\Pi$ core (see section II, 5).

**2. Second-Order Perturbation Theory of Rotational Interactions.**—The inexactness of the B.O. approximation manifests itself, among other effects, in the occurrence of interactions between B.O. wave functions of individual vibration–rotation levels which belong to electronic states differing by ±1 in $\Lambda$ value, but which are identical in all rigorously defined quantum numbers and symmetry properties. The latter include $J$, electronic parity ($g$ or $u$) in the case of homopolar molecules, and $N$ and $S$ in Hund's case b. Further, they include over-all parity (+ or −), which goes as $(-1)^N$ for $\Sigma^+$ and $-(-1)^N$ for $\Sigma^-$ states. For case b with states with $\Lambda > 0$ ($\Pi,\Delta, \cdots$ states), each $N$ value is represented by both a + and a − rotational level.[9] Thus one set of case b $\Pi$ or $\Delta$ rotational levels has $(-1)^N$ parities like those for $\Sigma^+$ states; the other has $-(-1)^N$ parities like those for $\Sigma^-$ states. It is convenient[10] to refer to the former sets of rotational levels collectively as $\Pi^+$ or $\Delta^+$ states, to the latter as $\Pi^-$ or $\Delta^-$ states. Perturbation theory then shows[12] that in principle all $\Sigma^+$ and $\Pi^+$ states mutually perturb one another, likewise all $\Sigma^-$ and $\Pi^-$, all $\Pi^+$ and $\Delta^+$, and all $\Pi^-$ and $\Delta^-$ states; but of course the great majority of such perturbations are small or negligible. Their magnitudes depend on the particularities of the $\Psi_{el}\Psi_{rot}$ linear combinations[9] and on $\Psi_{vib}$, and of course on the energy separations of the unperturbed levels. With regard to $\Psi_{vib}$, one can say that the Franck–Condon principle applies; hence for Rydberg states, where $\Psi_{vib}$ for a given $v$ is nearly the same for all, this means that only levels of equal $v$ perturb each other more than very little, except in occasional cases with low $n$ and exceptionally close approach of unperturbed levels.

Attention will be confined now to case b Rydberg

(9a) See Note in *Phys. Rev. Letters*, in press.

(10) See G. Herzberg, "Spectra of Diatomic Molecules," Vol. 1, 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1957. The symbol $N$ is now internationally accepted instead of $K$ used in Herzberg's book.

(11) For heavy atoms and not too large $n$ values, coupling between the $l$ and the spin of the Rydberg electron may, however, take priority and lead to more complicated relations.

(12) R. de L. Kronig, *Z. Physik*, **50**, 347 (1928); J. H. Van Vleck, *Phys. Rev.*, **33**, 467 (1929). For applications and a survey of data, see R. S. Mulliken and A. Christy, *ibid.*, **38**, 98 (1931).

states with a $^1\Sigma^+$ or $^2\Sigma^+$ core; then $\Lambda$ is equal to $\lambda$ of the Rydberg MO. According to Van Vleck,[12] the second-order perturbation energy between the rotational levels of any $\Sigma^+$ and $\Pi^+$ (or $\Sigma^-$ and $\Pi^-$) state is given by

$$qN(N + 1) = [8|BP_y(\Pi,\Sigma)|^2/\nu(\Pi,\Sigma)]N[N + 1]$$

(10)

the $\Pi$ rotational levels being pushed up and the $\Sigma$ levels down by an energy $qN(N + 1)$ if the unperturbed energy is higher for the $\Pi$ than for the $\Sigma$ state [positive $\nu(\Pi,\Sigma)$], and *vice versa*. Similarly for the interaction between $\Pi^+$ and $\Delta^+$, or between $\Pi^-$ and $\Delta^-$ states, the interaction energy is

$$q[N(N + 1) - 2] =$$
$$[4|BP_y(\Delta,\Pi)|^2/\nu(\Delta,\Pi)][N(N + 1) - 2] \quad (11)$$

$|BP_y|$ in eq. 10 and 11 is the magnitude of the matrix element, between wave functions (*cf.* eq. 8) of the two states, of the product of the operators $B$ and $P_y$. Here $B$ is $h/8\pi^2c\mu R^2$, $R$ being the internuclear distance, and $P_y$ represents a component of total orbital electronic angular momentum perpendicular to the internuclear axis. With $B$ and $\nu$ in cm.$^{-1}$, $q$ is in cm.$^{-1}$. For *Rydberg* states with $^1\Sigma^+$ or $^2\Sigma^+$ cores, the only part of $P_y$ which makes an appreciable contribution is $l_y$, the operator for the $y$ component of orbital angular momentum of the Rydberg electron.

**3. The Case of Pure Precession.**—If certain special conditions are fulfilled, though not in general, eq. 10 and 11 represent incipient $l$ uncoupling, the beginning of a transformation which would go over to Hund's case d if $N$ is large enough and/or $\nu$ small enough. Equations 10 and 11 must of course be replaced by the solutions of corresponding secular equations if $l$ uncoupling becomes large.[13] For present purposes, however, it will be sufficient to couch the discussion in terms of these approximate equations for incipient $l$ uncoupling.

Van Vleck's "case of pure precession" would be very closely approached for Rydberg states of equal $n$ and $l$, nearly equal $n^*$, and nearly identical core; for example, if the core is $^2\Sigma^+$, for the three states $nd\sigma,^1\Sigma^+$, $nd\pi,^1\Pi$, and $nd\delta,^1\Delta$, or the corresponding triplet states, *if* $nd\sigma$, $nd\pi$, and $nd\delta$ are all nonpenetrating. For such a group of states, $l$ uncoupling from case b to case d should develop rapidly with increasing $N$ and/or $n$. For the initial stages of such $l$ uncoupling, eq. 10 and 11 are applicable, but will yield $q \approx 0$ for all pairs of levels except for equal-$v$ and equal-$N$ levels of a pair or group of states of equal $n$ and $l$ (and $S$) involved in "pure precession." For these latter states and levels, $q$ of eq. 10 and 11 assumes the simple forms

(13) For detailed formulas covering the intermediate stages of the transition from case b to case d, see E. L. Hill and J. H. Van Vleck, *Phys. Rev.*, **32**, 250 (1928) (for $l$ = 1); G. H. Dieke, *Z. Physik*, **57**, 71 (1929), and I. Kovács and A. Budó, *Hung. Acta Phys.*, **1**, No. 4, 1 (1949) (for $l$ = 2). The formulas given for $l$ = 2 are not completely general, but assume that the energies in case b are of the form $C + A\Lambda^2$. This relation, which would be expected for nonpenetrating MO's if $R$ is small enough (*cf.* eq. 17), is only roughly obeyed for $H_2$ and $He_2$ (Tables IV–VII), and should not hold at all if some of the $l$ = 2 MO's are penetrating, as, *e.g.*, for $N_2$. Formulas for the general case will be given in a forthcoming paper from this laboratory by Dr. Y. N. Chiu.

$l = 1:\ q = 4(B_v^0)^2/\nu(\Pi,\Sigma^+);$

$l = 2:\ q_{\Pi\Sigma} = 12(B_v^0)^2/\nu(\Pi,\Sigma^+);$

$$q_{\Delta\Pi} = 4(B_v^0)^2/\nu(\Delta,\Pi) \quad (12)$$

Since the unperturbed rotational energy in case b goes as $B_v^0[N(N + 1) - \Lambda^2]$, while the perturbation terms for $l$ uncoupling go as $\pm qN(N + 1)$, their effect is essentially the same as if the $B_v^0$ values were somewhat altered, to values which we may call $B_v^{ef}$. (In addition to the changes in $B_v^{ef}$, the $\Pi$ and $\Delta$ levels for $l$ = 2 are shifted by a small additive constant amount corresponding to the $-2$ in $[N(N + 1) - 2]$ in eq. 11.) For the interaction of a $\Sigma^+$ and a $\Pi$ state with $l$ = 1, the $B_v^{ef}$ values are

$$\Sigma^+, B_v^{ef} = B_v^0 - q;\ \Pi^-, B_v^{ef} = B_v^0;$$
$$\Pi^+, B_v^{ef} = B_v^0 + q \quad (13)$$

with $q$ from the first eq. 12, and $\nu(\Pi^+,\Sigma)$ taken as positive if the $\Pi$ state is above the $\Sigma^+$ state. Similarly for the interactions of the $\Sigma^+$, $\Pi$, and $\Delta$ states for $l$ = 2

$$\Sigma^+, B_v^{ef} = B_v^0 - q_{\Pi\Sigma};\ \Pi^-, B_v^{ef} = B_v^0 - q_{\Delta\Pi}$$
$$\Pi^+, B_v^{ef} = B_v^0 + q_{\Pi\Sigma} - q_{\Delta\Pi};$$
$$\Delta^\pm, B_v^{ef} = B_v^0 + q_{\Delta\Pi} \quad (14)$$

According to eq. 12–14, the magnitudes of $l$ uncoupling must increase if the $\nu$ denominators in eq. 12 decrease. But (*cf.* eq. 1, with $\delta$ somewhat different for each of the substates $\Sigma^+$, $\Pi$, or $\Sigma^+$, $\Pi$, $\Delta$, but essentially independent of $n$) these denominators *do* decrease with increasing $n$, so that $l$ uncoupling should increase, finally leading to pure case d coupling. However, because of the initial approximate proportionality of the $l$ uncoupling energy to $(B_v^0)^2N(N + 1)$, the increase of $l$ uncoupling with $n$ should be much slower for low than for high $N$ values, and for molecules with small than for those with large $B$ values.

The pure precession case should be realized rather well for Rydberg states with nonpenetrating Rydberg MO's, since these have $n^*$ values differing little from $n$ values. Examples are found in the $H_2$ and $He_2$ Rydberg states with $l$ = 2 (see Tables IV–VII). These show strong uncoupling even for $n$ = 3, and larger effects for $n$ = 4, in each case strongly increasing with $N$.

The pure precession case usually cannot be expected for states with penetrating Rydberg MO's. MO's of equal $n$ and $l$ but different $\lambda$ then differ, often strongly, in the extent to which they are penetrating, hence in their $n^*$ values. Thus with $l$ = 1, $np\sigma$ Rydberg MO's (except for $H_2^+$) are usually penetrating, while $np\pi$ MO's are less penetrating or in light molecules (*e.g.*, $H_2$, $He_2$) almost nonpenetrating. Under these circumstances, Van Vleck's case of pure precession and a transition to a true case d with increasing $N$ or $n$ cannot in general be realized.

**4. Accidental Pure Precession.**—There is one special situation where pure precession, and true $l$ uncoupling to case d for high $N$ or $n$, *can* be fairly well realized *without* equality of $n$ values for the MO's of two interacting Rydberg states. This special situation exists if MO's of equal $l$ have equal or nearly equal $n^*$ values without equality of $n$ values, as can happen in case the $\delta$ values differ by close to an integer.

With equal $l$ and $n^*$ values, the outer H-atom-like parts of two Rydberg orbitals are nearly identical (see section II and V). A consideration of the matrix elements of $BP_y$ and so the $q$ values in eq. 10 or 11 now shows that these should nearly vanish except for pairs of states with equal $l$ and $n^*$, while for the latter they should be only slightly smaller than for pure precession.[14]

Near-equality of $n^*$ values without equality of $n$ values is a matter of accident. Thus one may speak of *accidental pure precession*. Very close approach to this case is of course very improbable, but moderately close approach is not unlikely for $l = 1$. For $l = 2$, moderately close approach to this case may occur for the pair $\lambda = 0$ and $\lambda = 1$, or for the pair $\lambda = 1$ and $\lambda = 2$, but is unlikely to occur for both simultaneously. However, the situation just suggested for $l = 2$ should perhaps be thought of as a strong perturbation effect rather than as $l$ uncoupling. In this situation, the effect involves strong mixing just of $\lambda = 0$ and 1, *or* of $\lambda = 1$ and 2 case b levels, leaving the unaffected levels ($\lambda = 2$ or 0, respectively) still essentially under case b, with eq. 8 or 9 applicable to them though not to the others. Nevertheless at sufficiently high $n$ and/or $N$ values, strong interaction involving all three $\lambda$ values may under some circumstances (namely, not too much inhibition, see section IV, 5) set in, resulting in true $l$ uncoupling and case d.

For $l = 1$, the $N_2$ molecule furnishes a very good example in the near-equality of $n^*$ values of the Rydberg MO's whose UAO's are $3p\pi$ and $4p\sigma$ (see section VI). For the NO molecule, where the homopolar diatomic theory is probably rather well applicable for the familiar Rydberg states with closed-shell ($^1\Sigma^+$) core, Huber and Miescher[15] have reported what (as they have pointed out) appears to be an excellent example of accidental pure precession between $l = 2$ states with $\lambda = 0$ and $\lambda = 1$ (H $^2\Sigma^+$ and H' $^2\Pi$ states), with the exclusion of $\lambda = 2$. The $\lambda = 0$ and 1 states involve $\sigma$ and $\pi$ MO's with $n^* = 3.02$, the same for both; these are almost certainly $4d\sigma$ and $4d\pi$ MO's[15] with $\delta = 0.98$ for both. A nearby state with $\lambda = 2$ has $n^* = 2.94$ and no doubt involves a $3d\delta$ MO with $\delta = 0.06$; but this state is not close enough to interact at all strongly with the $\lambda = 0$ and 1, $l = 2$, states. However, for sufficiently high $n$ and/or $N$ values, the analogs of these three states should tend to enter into a completely uncoupled accidental case d relationship.

**5. The General Case of Rotational Interactions.—** Except when for a given $l$ the MO's are nonpenetrating for all $\lambda$ values, chance will favor differences in $\delta$ values which are not close to integers. The opposite extreme to the case of accidental pure precession is that where the $\delta$ values of the interacting states differ by roughly half-integral amounts. Consider for example the perturbation of an $np\pi$ Rydberg state by the two nearest $p\sigma$ states, one higher and one lower in energy.

If the $np\pi$ state is just half-way in energy between the two $p\sigma$ states (for example if $\delta \approx 0$ for the $np\pi$ state and $\delta$ has an appropriate value, say roughly about 0.5, for the $p\sigma$ states, which would then be $np\sigma$ and $(n + 1)p\sigma$), reference to eq. 10 shows that if the matrix elements of $BP_y$ between the $\pi$ and $\sigma$ states were *about equal* for the two $\sigma$ states, then the energy perturbations of the $\pi$ state by the two $\sigma$ states would approximately cancel, although considerable mixing between the $\pi$ and $\sigma$ wave functions would still occur unless the $BP_y$ matrix elements were especially small. Actually, the $BP_y$ matrix elements *should* be small when $\delta$ differs by an amount rather near a half-integer for the two interacting states, because of the phase shift between the $R_{nl}$ factors of the main, hydrogen-atom-like, outer loops of the interacting MO's. It is evident on cursory examination that for certain critical values of the $\delta$ difference more or less near half-integers (probably depending somewhat on $n$), the $BP_y$ matrix elements should be zero. Thus for $\delta$ differences somewhere in the neighborhood of 0.5 or 1.5, etc., but depending somewhat on $n$, one expects at the same time small matrix elements and thus small wave function mixing, and *also* cancellation of energy perturbation effects because of $q$ values equal in magnitude but opposite in sign for perturbation of the $np\pi$ state by the two neighboring $p\sigma$ states. One must also consider other higher and lower $p\sigma$ states, but their effects (if $n$ is not too small) should also tend to cancel in pairs, and also involve decreased matrix elements, although complete cancellation is probably not expected.

The foregoing reasoning, while qualitative, suffices to show that $l$ uncoupling should be more or less strongly inhibited if the $\delta$ values of the interacting states differ by amounts which are far from integers. If $l$ uncoupling is inhibited, then for $l = 1$, case b coupling should persist up to high $n$ values. For penetrating Rydberg MO's with $l = 2$, matters are more complicated, since $\Sigma^+–\Pi$ interactions might be inhibited but $\Pi–\Delta$ interactions not, or *vice versa*.

As noted in section IV, 1, the foregoing considerations, which assume a well-defined $l$ for the Rydberg electron, can break down for $v$ values close to dissociation.

## V. The Forms and Energies of $H_2^+$ MO's

In section III it was pointed out that an understanding of the $n^*$ values of penetrating Rydberg MO's requires an understanding also of core MO's. In spite of various modifications needed when more electrons are present, the MO's of $H_2^+$ serve in several respects as useful prototypes for both Rydberg and core MO's of homopolar diatomic molecules. Theoretical computations on a number of the lower-$n$ MO's of $H_2^+$, for $R$ values covering much of the range from 0 to $\infty$, are available[16] with sufficient accuracy so that they can be accepted as the equivalent of experimental information. Some relevant aspects of what is known about $H_2^+$ will be examined here, with emphasis

(14) The slight difference has two reasons: (1) the core must be slightly different for Rydberg states with different $\delta$ values, because of differences in penetration of the Rydberg MO's; (2) even though the outer parts of the Rydberg MO's are nearly identical, the inner parts are different, leading to a smaller value of the $l_y$ matrix element; but only slightly so because the by far predominant contributions to these matrix elements (unless $n^*$ is very small) come from an integral over the outer parts of the MO's.

(15) K. P. Huber and E. Miescher, *Helv. Phys. Acta*, **36**, 257 (1963). See K. P. Huber, ref. 1, for a further survey of Rydberg states of NO. The essentially united-atom interpretation of the $l = 2$ states of NO given here differs from that of Huber and Miescher.

(16) D. R. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans. Roy. Soc.* (London), **A246**, 215 (1954), and references given there. See A. Dalgarno, B. L. Moisewitsch, and A. L. Stewart, *J. Chem. Phys.*, **26**, 965 (1957), for discussion and numerous additional references. For a general review of the $H_2^+$ problem, see pp. 54–60 of the article by Kotani, Ohno, and Kayama in "Handbuch der Physik," Vol. 37/2, Springer, Berlin, 1961, and J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1963, Chapters 1, 2.

on (1) the changing forms of the MO's as $R$ goes from 0 to $\infty$; (2) the corresponding energies; (3) $H_2^+$ MO's as prototypic Rydberg MO's.

**1. Forms of $H_2^+$ MO's.**—Because of the strict separability in the elliptical coordinates $\xi$, $\eta$, $\phi$, at all $R$ values, of the one-electron fixed-nuclei Schrödinger equation for $H_2^+$ MO's, every MO can be characterized by three quantum numbers $n_\xi$, $n_\eta$, and $\lambda$ ($\lambda = |n_\phi|$). These are respectively equal to the number of ellipsoidal nodal surfaces ($n_\xi$), the number of hyperboloidal nodes ($n_\eta$), and (if the $\phi$ factor is expressed in real form, namely as $\cos \lambda\phi$ or $\sin \lambda\phi$) the number of nodal planes through the line joining the nuclei ($\lambda$); each of them can have the value 0 or any integral positive value. As $R \rightarrow 0$, ellipsoids go into spheres and hyperboloids into cones, so that $n_\xi$, $n_\eta$, and $n_\phi$ or $\lambda$ go over into the UAO (united atom AO) quantum numbers $n_r$, $n_\theta$, and $m_1$ or $\lambda$; further, $n_\theta + \lambda = l$, and $n_r + l + 1 = n$. The usual UAO symbols (e.g., 1s, 2p$\pi$, 3d$\sigma$) can also conveniently be used for $R \neq 0$, with the understanding that $l$ now means $n_\eta + \lambda$ and that $n$ means $n_\xi + n_\eta + \lambda + 1$.

As $R \rightarrow \infty$, each $H_2^+$ MO goes asymptotically into either an additive or a subtractive LCAO form $2^{-1/2}$ ($\chi_a \pm \chi_b$), where each of the two like AO's $\chi_a$ and $\chi_b$, so chosen as to be mirror images in the midplane between the nuclei a and b, is an H atom Stark-effect AO; that is, a solution of the Schrödinger equation for an H atom in a uniform electric field.[17] This problem is separable in parabolic coordinates $\xi'$, $\eta'$, $\phi$, to which correspond integral quantum numbers $n_{\xi'}$, $n_{\eta'}$, $\lambda$ beginning with 0; here $n$ is equal to $n_{\xi'} + n_{\eta'} + \lambda + 1$. If the electron is *on* a but in the field of b, or *vice versa*, $n_{\xi'}$ and $n_{\eta'}$ are the numbers of parabolic nodes for paraboloids with vertices respectively pointing away from the other nucleus ($n_{\xi'}$) or toward it ($n_{\eta'}$).

These Stark-effect AO's can of course also be written as linear combinations of ordinary AO's, the number of different Stark AO's for any $n$ value then being equal to the number of AO's in the usual spherical coordinate description. For $n = 1$, only the one AO 1s occurs; it is describable either by $n_{\xi'} = n_{\eta'} = n_\phi = 0$ or by $n_r = n_\theta = m_1 = 0$. For $n = 2$, there are four independent AO's. The Stark AO's have $n_{\xi'}$, $n_{\eta'}$, $n_\phi$ value sets 1, 0, 0; 0, 1, 0; 0, 0, $\pm1$. The 0, 0, $\pm1$ Stark AO's are identical with 2p$\pi$ AO's; the others are obtainable as digonal hybrids 2di' and 2di of 2s and 2p$\sigma$ AO's

$$2\text{di}' \equiv (1, 0, 0) = 2^{-1/2}(2s - 2p\sigma)$$

$$2\text{di} \equiv (0, 1, 0) = 2^{-1/2}(2s + 2p\sigma) \quad (15)$$

Equation 15 assumes that the outer loop of 2s is taken positive, and that the positive end of 2p$\sigma$ on either atom is taken as directed toward the other atom.

For $n = 3$, the Stark AO's have parabolic quantum numbers (2, 0, 0), (1, 1, 0), (0, 2, 0); (1, 0, $\pm1$), (0, 1, $\pm1$); (0, 0, $\pm2$). The first three are three $\sigma$ AO's which are hybrids of 3s, 3p$\sigma$, and 3d$\sigma$ as

(17) The H atom whose AO's are being considered is in the cylindrically symmetrical field of the second H$^+$ nucleus. In the limit as $R \rightarrow \infty$, this field is uniform over the H atom.

$$(2, 0, 0) = 3^{-1/2}(3s) - 2^{-1/2}(3p\sigma) +$$
$$\left. \begin{array}{r} 6^{-1/2}(3d\sigma); \quad (1, 1, 0) = 3^{-1/2}(3s) - \\ (^2/_3)^{1/2}(3d\sigma); \quad (0, 2, 0) = 3^{-1/2}(3s) + \\ 2^{-1/2}(3p\sigma) + 6^{-1/2}(3d\sigma) \end{array} \right\} \quad (15a)$$

The next two pairs are hybrids of 3p$\pi$ and 3d$\pi$

$$(1, 0, \pm1) = 2^{-1/2}(3p\pi - 3d\pi); \quad (0, 1, \pm1) =$$
$$2^{-1/2}(3p\pi + 3d\pi) \quad (15b)$$

The last pair is just 3d$\delta$.

The nodal surfaces, hence quantum numbers, $n_\xi$, $n_\eta$, and $\lambda$, are simply related to those of the Stark AO's as

$$\left. \begin{array}{l} \text{Additive LCAO's } (\sigma_g, \pi_u, \delta_g \text{ types}): n_\xi = \\ \qquad n_{\xi'}, n_\eta = 2n_{\eta'}, \lambda = \lambda \\ \text{Subtractive LCAO's } (\sigma_u, \pi_g, \delta_u \text{ types}): n_\xi = \\ \qquad n_{\xi'}, n_\eta = 2n_{\eta'} + 1, \lambda = \lambda \end{array} \right\} \quad (16)$$

LCAO's formed from ordinary pure-$l$ AO's can be designated in the usual way as $\sigma_g$1s, $\pi_u$2p, $\delta_g$3d, etc., for additive types, $\sigma_u$1s, $\pi_g$2p, $\delta_u$3d, etc., for subtractive types. The pure-$l$ AO's involved are identical with Stark AO's having $n_{\xi'} = n_{\eta'} = 0$. When the Stark AO's differ from pure-$l$ AO's, symbols such as $\sigma_g(2_{10})$, $\sigma_g(2_{01})$, $\sigma_g(3_{20})$, $\sigma_g(3_{11})$, $\sigma_g(3_{02})$, $\pi_u(3_{10})$, $\pi_u(3_{01})$, etc., for additive LCAO's, $\sigma_u(2_{10})$, $\sigma_u(2_{01})$, $\sigma_u(3_{20})$, $\pi_g(3_{10})$, etc., for subtractive LCAO's, are convenient. The two subscripts after the $n$ value of the AO refer to its $n_{\xi'}$ and $n_{\eta'}$ values in that order. The prefixed symbol $\sigma$, $\pi$, etc., gives $\lambda$, and its subscript (g or u; *cf.* eq. 16) tells whether the LCAO is an additive or a subtractive one. (In the special case $n = 2$, the symbols $\sigma_g$2di', $\sigma_g$2di, $\sigma_u$2di', $\sigma_u$2di—*cf.* eq. 15—are also convenient.)

In view of eq. 16, the MO's of $H_2^+$ fall into four classes with respect to the relation of $n$ for the UAO at $R = 0$ to $n$ for the SAO (separated-atoms AO) used at $R = \infty$ in the LCAO. These classes are: (1) Additive LCAO MO's with $n_{\eta'} = 0$; these are unpromoted ($n_{UAO} = n_{SAO}$); they include all MO's which at $R = 0$ have $\lambda = l$, and only these. (2) Additive MO's with $n_{\eta'} > 0$; these become promoted ($n_{UAO} > n_{SAO}$) as $R$ is decreased. (3) Subtractive MO's with $n_{\eta'} = 0$; these become promoted as $R$ is decreased. (4) Subtractive MO's with $n_{\eta'} > 0$; these become strongly promoted.

The exact forms of $H_2^+$ MO's at $R$ values not near 0 or $\infty$, although they are known or can be calculated, are at best only approximately (and sometimes only roughly) of the simple UAO or LCAO form which they assume at $R = 0$ or $\infty$, respectively. One can, however, expand any $H_2^+$ MO at any $R$ (in the same way as for any MO of any diatomic molecule), as a linear combination of STO's (Slater-type orbitals: these are of the same forms as the individual terms of eq. 4, times $Y_{lm}(\theta,\phi)$, but with the values of the orbital exponents $\zeta$ flexibly chosen so as to minimize the total energy). In such an LCSTO form, the coefficients of various STO's rise and fall as $R$ goes from 0 to $\infty$; also the optimal values of $\zeta$ change with $R$.

Some examples will clarify the situation, and also introduce some useful notation. Let $\chi$ represent any AO of definite form and size, and let $\chi_a$, $\chi_b$, and $\chi_c$ represent this AO centered about nucleus a, nucleus b,

or the center c, of a homopolar diatomic molecule. We note that, if $R$ is small, the LCAO form $N(\chi_a + \chi_b)$ is almost identical with $\chi_c$; as $R \to 0$, $N \to {}^1/_2$ and the identity becomes exact since $\chi_a$ and $\chi_b$ are then both identical with the UAO $\chi_c$. We then see that for some of the class 1, unpromoted, $H_2^+$ MO's, the *same LCAO form* represents the MO exactly both as $R \to 0$ and as $R \to \infty$. However, the AO's involved differ in size at the two limits because $Z = 2$ for the AO's at $R = 0$ but $Z = 1$ for those at $R = \infty$; they differ also in the overlap integral $S(\int \chi_a \chi_b d\tau)$: $S \to 1$ as $R \to 0$ but $S \to 0$ as $R \to \infty$, leading to the normalization factors $N = {}^1/_2$ in the former and $2^{-1/2}$ in the latter case.

As a specific example, the lowest-energy MO $1\sigma_g$ of $H_2^+$ has at least roughly the form $\sigma_g 1s^{(\zeta)}$ at all $R$ values, where $\sigma_g 1s^{(\zeta)} = N(1s_a^{(\zeta)} + 1s_b^{(\zeta)})$, and $1s^{(\zeta)} \sim e^{-\zeta r/a_0}$. As $R \to 0$, $\zeta \to 2$ and $N \to {}^1/_2$, and the approximation becomes exact. As $R \to \infty$, $\zeta \to 1$ and $N \to 2^{-1/2}$, and the approximation again becomes exact. At intermediate $R$ values, additional terms must be brought in to supplement $\sigma_g 1s^{(\zeta)}$ to build up an LCSTO expression which can closely approximate the exact form of the MO.[18] The most important of these is $\sigma_g 2p^{(\zeta)}$; but a little $\sigma_g 3d^{(\zeta)}$ is also present; this approximates closely to $3d\sigma_c^{(\zeta)}$ as $R \to 0$. In a similar way for the unpromoted MO $1\pi_u$ of $H_2^+$,[18] the most important additions to the main LCSTO term $\pi_u 2p^{(\zeta)}$, which is alone present at $R = 0$ and $\infty$, are $\pi_u 3d^{(\zeta)}$ and to a lesser extent $\pi_u 4f^{(\zeta)}$ (which approximates to $4f\pi_c^{(\zeta)}$ as $R \to 0$). In these and the following example, the *best* $\zeta$ would be somewhat different for each STO.[19]

The MO $1\sigma_u$ illustrates the quite different situation which occurs for antibonding promoted MO's of class 3. For small $R$, $\sigma_u 2p^{(\zeta)}$ is predominant (going to the $He^+$ UAO $2p\sigma$ at $R = 0$), but with increasing $R$ this is increasingly replaced[18] by $\sigma_u 1s^{(\zeta)}$, while $\sigma_u 3d^{(\zeta)}$ and $\sigma_u 2s^{(\zeta)}$ are also present to some extent at intermediate $R$ values.[20] As $R \to \infty$, only $\sigma_u 1s^{(\zeta)}$ remains. In a similar way $1\pi_g$ is mainly $\pi_g 3d$ (going to $3d\pi$ as $R \to 0$), at small $R$, but goes over to pure $\pi_g 2p$ as $R \to \infty$; a little $\pi_g 4f$ is also present at intermediate $R$ values.[18]

Leaving out of consideration the rise and fall of admixtures of additional LCSTO forms at intermediate $R$ values, the major LCAO forms which approximate some of the lower-energy MO's of $H_2^+$ are summarized in Table I. If an energy curve is drawn for each MO from $R = 0$ to $\infty$, some of these curves would cross at one or another intermediate $R$ value, as can be seen from the differences in relative energy order (indicated by the numbers in parentheses in Table I) at small and large $R$ values. These crossings, especially in the region of higher $n$ values, include some for MO's of the same group-theoretical species. The first such crossing is between the MO $\sigma_g 2s \leftrightarrow \sigma_g 2_{10}$

(18) R. L. Miller and P. G. Lykos, *J. Chem. Phys.*, **35**, 1147 (1961); **37**, 993 (1962); O. Sovers and W. Kauzmann, *ibid.*, **35**, 652 (1961). See also R. J. Hauser, P. G. Lykos, and E. L. Mehler, *ibid.*, **38**, 583 (1963), and references there; also S. Boorstein and J. Goodisman, *ibid.*, **39**, 479 (1963), for one-center expansions for the $1\sigma_g$ MO.

(19) For a completely accurate LCSTO representation of any MO, more than one STO of each type (for example, more than one $n$s, more than one $np\sigma$, etc., with differing $n$'s and/or $\zeta$'s) must be included in the LCSTO expression.

(20) In contrast to the main LCSTO terms of $\sigma_g 1s^{(\zeta)}$ in $1\sigma_g$, where $\zeta$ increases as $R$ decreases, $\zeta$ in the LCSTO term $\sigma_u 1s^{(\zeta)}$ in $1\sigma_u$ decreases as $R$ decreases.

and the MO $\sigma_g 3d \leftrightarrow \sigma_g 2_{01}$. Such crossings occur in $H_2^+$ because of the exact separability in elliptical coordinates, but are avoided for related MO's in homopolar diatomic molecules with more than one electron.

TABLE I

APPROXIMATE FORMS OF $H_2^+$ MO'S AT SMALL AND LARGE R VALUES[a,b]

| Small R | | Large R | | Small R | | Large R | |
|---|---|---|---|---|---|---|---|
| $\sigma_g 3s$ | (10) | $\sigma_g(3_{20})$ | (14) | $\sigma_g 4s$ | (20) | $\sigma_g(4_{30})$ | (30) |
| $\pi_u 3p$ | (9) | $\pi_u(3_{10})$ | (13) | $\pi_u 4p$ | (19) | $\pi_u(4_{20})$ | (29) |
| $\delta_g 3d$ | (8) | $\delta_g 3d$ | (12) | $\delta_g 4d$ | (18) | $\delta_g(4_{10})$ | (28) |
| $\pi_g 3d$ | (7) | $\pi_g 2p$ | (7) | $\phi_u 4f$ | (17) | $\phi_u 4f$ | (25) |
| $\sigma_g 3d$ | (6) | $\sigma_g(2_{01})$ | (3) | $\delta_u 4f$ | (16) | $\delta_u 3d$ | (17) |
| $\sigma_u 3p$ | (5) | $\sigma_u(2_{10})$ | (6) | $\pi_u 4f$ | (15) | $\pi_u(3_{01})$ | (10) |
| $\sigma_g 2s$ | (4) | $\sigma_g(2_{10})$ | (5) | $\sigma_u 4f$ | (14) | $\sigma_u(2_{01})$ | (8) |
| $\pi_u 2p$ | (3) | $\pi_u 2p$ | (4) | $\pi_g 4d$ | (13) | $\pi_g(3_{10})$ | (16) |
| $\sigma_u 2p$ | (2) | $\sigma_u 1s$ | (2) | $\sigma_g 4d$ | (12) | $\sigma_g(3_{11})$ | (11) |
| $\sigma_g 1s$ | (1) | $\sigma_g 1s$ | (1) | $\sigma_u 4p$ | (11) | $\sigma_u(3_{20})$ | (15) |

[a] Each symbol for small $R$ represents an LCAO expression which is nearly identical with the corresponding UAO; $\sigma_g 3d$ is nearly identical with $3d\sigma$ of $He^+$. Note especially that like symbols have different meanings for small $R$ and large $R$, e.g., in $\sigma_g 1s$, the symbol 1s means a united-atom 1s ($Z = 2$) for small $R$, but a separated-atom 1s ($Z = 1$) for large $R$. Each symbol represents an additive (for $\sigma_g$, $\pi_u$, $\delta_g$, $\phi_u$) or a subtractive (for $\sigma_u$, $\pi_g$, $\delta_u$) LCAO expression $\chi_a \pm \chi_b$. At large $R$ the $\chi$'s are H atom Stark effect AO's whose $n$ is given by the first number. If two subscript numbers are used, these represent $n_{\xi'}$ and $n_{\eta'}$ in that order; for AO's with $n_{\xi'} = n_{\eta'} = 0$, the letters s, p, d, or f are used. [b] The numbers in parentheses for small $R$ represent the order of increasing energy as determined from the coefficients in the $R = 0.0$ column of Table III. Those for large $R$ again represent the energy order but are less certain, especially since for some pairs of MO's the order exchanges at fairly large $R$.

**2. Energies of $H_2^+$ MO's.**—Passage from $R = 0$ to $R > 0$ for $H_2^+$ adds to the potential energy in the electronic Schrödinger equation a correction term $2e^2/r_c - e^2/r_a - e^2/r_b$. One can see qualitatively from first-order perturbation theory that, for not too large $R$ values, this change increases the energy $E$ (and so decreases $T$ of eq. 1) in the case of MO's which at $R = 0$ have relatively large values in the median plane between a and b (e.g., $2p\pi$ and especially 2s), but decreases $E$ for MO's like $2p\sigma$ which avoid the median plane but have increasing magnitudes on both sides of it. First-order perturbation theory leads to the following expression for the changes in $E$ or $T$ (in cm.$^{-1}$, cf. eq. 1) due to splitting the core[21]

$$\Delta T = -\Delta E = KR^2 + \dots$$
$$\text{with } K = C(l^2 + l - 3\lambda^2) \text{ when } l > 0 \qquad (17)$$

In eq. 17, $-K$ if $l = 0$, or $C$ if $l > 0$, is a positive constant which depends on $n$ and $l$. From the qualitative considerations given above one can see that the $K$'s should decrease rapidly in size with increasing $n$. Formulas for $K$ are available for $l = 0$, 1, and 2.[21]

Values of $-E$ as a function of $R$ for various states of $H_2^+$ are listed in Table 1 of the paper by Bates, et al.[16] From them values of $\Delta E$ can be obtained and, from these, the range of validity of eq. 17 can be checked. However, it is of interest first to compute $n^*$ values corresponding to the $T$ values of ref. 16, using eq. 1 with $Z_c = 2.00$. Results for several selected $R$ values are listed for the $n$s and $np\sigma$ MO's in Table II. It is

(21) Kotani, et al., ref. 16; more explicitly, G. Jaffé, *Z. Physik*, **87**, 535 (1934). Earlier, F. Hund, *ibid.*, **63**, 719 (1930), gave the $K$ equation for $l > 0$. For a graphical presentation of the $H_2^+$ MO energies as functions of $R$, see Kotani or Slater, ref. 16.

TABLE II

VALUES OF $n^*$ FOR SOME $H_2^+$ STATES[a]

| MO | | | | —R, a.u.— | | | |
|---|---|---|---|---|---|---|---|
| | 0.0 | 0.2 | 0.4 | 1.0 | 2.0 | 4.0 | 9.0 |
| $1s\sigma_g$ | 1.0000 | 1.01831 | 1.05386 | 1.17372 | 1.34679 | 1.58503 | 1.80730 |
| $2s\sigma_g$ | 2.0000 | 2.0183 | 2.0539 | 2.1746 | 2.35429 | 2.63288 | 3.06847 |
| $3s\sigma_g$ | 3.0000 | 3.0184 | 3.0538 | 3.1747 | 3.3550 | 3.63949 | 4.12885 |
| $2p\sigma_u$ | 2.0000 | 1.9947 | 1.9788 | 1.88176 | 1.73092 | 1.69571 | 1.80974 |
| $3p\sigma_u$ | 3.0000 | 2.9947 | 2.9787 | 2.8909 | 2.7983 | 2.85650 | 3.11449 |
| $4p\sigma_u$ | 4.0000 | 3.9947 | 3.9791 | 3.89375 | 3.8164 | 3.90293 | 4.22266 |

[a] Values are $(4/-E)^{1/2}$ using $-E$ values from Table I of ref. 16, where $-E$ is given in units of $Ry$. $R$ is in atomic units (1 a.u. = 0.529 Å.).

TABLE III

VALUES OF $\delta/R^2$ FOR SOME $H_2^+$ STATES[a]

| MO | | | —R, a.u.— | | | |
|---|---|---|---|---|---|---|
| | $(0.0)^b$ | 0.2 | 0.4 | 1.0 | 2.0 | 9.0 |
| $1s\sigma_g$ | −0.667 | −0.458 | −0.3366 | −0.17372 | −0.08670 | −0.00997 |
| $2s\sigma_g$ | − .667 | − .458 | − .3369 | − .1746 | − .08855 | − .01319 |
| $3s\sigma_g$ | − .667 | − .459 | − .3365 | − .1747 | − .08876 | − .01394 |
| $2p\sigma_u$ | .133 | .133 | .133 | .11824 | .06727 | + .00235 |
| $3p\sigma_u$ | .133 | .134 | .133 | .10911 | .0504 | − .00141 |
| $4p\sigma_u$ | .133 | .134 | .131 | .10625 | .0459 | − .00275 |
| $2p\pi_u$ | − .067 | − .065 | − .0634 | − .05389 | − .03943 | − .01058 |
| $3d\sigma_g$ | .0190 | .019 | .0193 | .01980 | .021875 | + .00440 |
| $3d\pi_g$ | .0095 | .0105 | .0096 | .00896 | .007495 | − .00064 |
| $3d\delta_g$ | − .0190 | | | | | |
| $4f\sigma_u$ | .0063 | 0.006 | 0.0065 | 0.00638 | 0.006515 | +0.00795 |
| $4f\pi_u$ | .0048 | | | | | |
| $4f\delta_u$ | .0000 | | | | | |
| $4f\phi_u$ | − .0079 | | | | | |

[a] $\delta = n - n^*$ (cf. eq. 1), with $n^*$ values for $R > 0$ from Table II, or obtained from Table I of ref. 16 in the same way as in Table II. [b] This column lists coefficients $k$ of $R^2$ for eq. 18, obtained using $\delta = (n^3/8Ry)\Delta T$, which is accurate as $R \to 0$, with $\Delta T$ expressions or values from Kotani or Jaffé (ref. 21); from these references the exact $k$ values are $-2/3$ for $ns$, $+2/15$ for $np\sigma$, $-1/15$ for $np\pi$, $+2/105$ for $nd\sigma$, $+1/105$ for $nd\pi$, $-2/105$ for $nd\delta$. The same values can be obtained (but less accurately) by extrapolating the above $\delta/R^2$ values to $R = 0$; the value for $4f\sigma$ was obtained in this way. For $4f\pi$, $4f\sigma$, $4f\phi$ the listed values were obtained from the $4f\sigma$ value by using $k = c(l^2 + l - 3\lambda^2)$ as in eq. 18.

seen that the $n^*$ values conform well to normal Rydberg series behavior: for any given $R$ value $\delta \equiv n - n^*$ is going toward a limiting value as $n$ increases and deviates from this only moderately at small $n$ values, if $R$ is not too large.[22]

These results point toward the conclusion that *all MO's of $H_2^+$ can be considered as Rydberg MO's*. Reasoning establishing the correctness of this conclusion, and some corollaries, will be presented in section V, 3.

Increased perspective is gained here by examining what happens to $n^*$ and $\delta$ values for $H_2^+$ in the limit $R \to \infty$, using eq. 1 with $Z_c = 2$ at all $R$ values. (These $n^*$ and $\delta$ values might be called *united-atom-based* $n^*$ and $\delta$ values.) A few examples will illustrate. The MO's $1\sigma_g$ and $1\sigma_u$ ($1s\sigma_g$ and $2p\sigma_u$ at $R = 0$) become $\sigma_g1s$ and $\sigma_u1s$ with $n^* = 2$ as $R \to \infty$; this corresponds for $\delta$ to a steady decrease from 0 to $-1$ for $1\sigma_g$ as $R$ increases, but for $1\sigma_u$ $\delta$ first increases from 0 to a maximum, then decreases again toward 0, as $R$ increases (see Table II). The asymptotic equality of $n^*$ for $1\sigma_g$ and $1\sigma_u$ as $R \to \infty$ is already closely approached at $R = 9$ a.u. (see Table II); however, $n^*$ still falls below 2 because the energy of both $1\sigma_g$ and $1\sigma_u$ is very nearly that of a 1s electron attached to one H nucleus but in the additional attractive field of the second H nucleus.

(22) The range of $R$ where $\delta$ is nearly independent of $n$ rapidly extends to increasingly large values for increasing $l$ and $n$ (cf. Table III and section V, 3). At *large* enough $R$, however, it might seem desirable to approximate the $T$ values by eq. 1 with $Z_c = 1$, corresponding to the H atom AO's in the LCAO approximations which become valid as $R \to \infty$; but this proves not to be worthwhile. Even at $R = 9$ a.u. and low $n$, the Rydberg series representations are better for $Z_c = 2$ than for $Z_c = 1$.

This potential energy lowers the *electronic* energy considerably, although the *total* energy, which includes the internuclear repulsion energy, is lowered only a little (polarization energy).

The behavior of the unpromoted MO's $2s\sigma_g$, $2p\pi_u$, and $3d\delta_g$ (using $R = 0$ notation) is similar to that of $1s\sigma_g$. For 2s and $2p\pi$, $n^*$ increases from 2 to 4; hence $\delta$ decreases from 0 to $-2$, as $R$ goes from 0 to $\infty$. For 2s, $\delta$ is already $-1.07$ at $R = 9$ a.u. (see Table II). For $3d\delta$, $n^*$ increases from 3 to 6, $\delta$ goes from 0 to $-3$. For the promoted MO's which are $3d\sigma_g$ and $3d\pi_g$ at $R = 0$ but become $\sigma_g2_{01}$ and $\pi_g2p$ as $R \to \infty$, $\delta$ is at first positive (cf. Table III), but must go to $-1$ as $R \to \infty$; this tendency is already strongly apparent at 9 a.u. in Table III.

Equations analogous to eq. 17 for the dependence of $T$ on $R$ must also hold for $\delta$ as a function of $R$. From eq. 1 with $Z_c = 2$, one finds readily the relation $\delta = [n^2n^{*2}/4Ry(n + n^*)]\Delta T$ or, approximately (since $n^* = n - \delta$), $\delta = (n^{*3}/8Ry)\Delta T$ if $\delta$ is not too large. In any event it follows that

$$\delta(R) = kR^2 + \ldots, \text{ with } k =$$

$$c(l^2 + l - 3\lambda^2) \text{ when } l > 0 \quad (18)$$

and that $k$ is $(n^3/8Ry)$ times $K$ of eq. 17; $k$ like $K$ depends on $n$, $l$, and $\lambda$. Values of $\delta$ have been obtained from $n^*$ values which were computed as described for Table I, from the $T$ values of ref. 16. These $\delta$ values after division by $R^2$ are listed in Table III, for several selected $R$ values for each MO.

The limiting values of $\delta/R^2$ as $R \to 0$ are the coefficients $k$ (column headed 0.0). These are independent of $n$ but decrease rapidly with increasing $l$.[21] The former fact indicates that one can use the $R^2$ coefficients of Table III for rather accurate predictions of $\delta$, hence of $n^*$ and $T$, values at small $R$ for any desired higher $n$ values. (They have been used in this way to determine the precise energy order of different $H_2^+$ MO's in Table I at small $R$ values.) However, as is obvious from Table III, terms in higher powers of $R$ than $R^2$ must also be included in representing $\delta$ values, most especially for small $l$ values. Nevertheless it appears that $\delta$ even when no longer proportional to $R^2$ still remains rather independent of $n$, and tends toward constancy as $n$ increases (cf. Table II), especially in the case of unpromoted MO's.[23]

**3. $H_2^+$ MO's as Rydberg MO's.**—In section V, 2, the $\delta$ values for several low-$n$ MO's of $H_2^+$, although derived from the theoretical calculations of ref. 16, have been scrutinized as if they were empirical data. It has been seen that, in the limited examples available, they behave at all $R$ values like the $\delta$ values of the Rydberg series of atoms; namely, they seem to be approaching limiting constant values as $n$ increases, with the deviations from constancy largest at low $n$ values (and large $R$ values).

Justification of this inference is obtained by reasoning in terms of asymptotic behavior at large $r$ values (cf. section II). One sees in this way that for large $n$ the outer parts of any $H_2^+$ MO must be strictly H-atom-like except for a phase shift. That is, for $r$ values large enough so that the potential is very close to $-2e^2/r$, the $H_2^+$ MO's must be of the form $F_{n*l}(r) \cdot e^{-2r/a_0 n^*} Y_{lm}(\theta,\phi)$ with a radial factor which has nodes and loops like those of an He$^+$ AO except for the phase shift $\delta$ ($\delta \equiv n - n^*$).

In contrast to the case of penetrating Rydberg AO's, where the $\delta$'s are always positive so that the outer nodes and loops shrink inward as compared with those of an H atom with the same $n$ and $l$, the $\delta$'s for $H_2^+$ MO's assume negative as well as positive values. For negative $\delta$ the outer regions of the MO must expand outward as compared with the corresponding H-atom-like AO (here the He$^+$ UAO); for positive $\delta$ they must shrink inward. As can be seen from the $n^*$ values in Tables II and III, this expansion or shrinkage increases with $R$ over a wide range of $R$ values. However, at large $R$ values $\delta$ usually stops increasing and even changes its sign at still larger $R$, and the expansion or shrinkage of the outer parts of the MO must change accordingly.

Although phase-shifted but otherwise *accurately* H-atom-like nodes and loops should occur only for the outer parts of high-$n$ MO's, one may, qualitatively, expect a shrinkage or expansion also for inner nodes and loops and for small $n$ values. Some contour maps of the $ns$ and $np\sigma$ MO's of $H_2^+$ shown in ref. 16 illustrate the expected effects extremely well. Table IV shows the distances of the first and second nodal surfaces from the molecule center for the 2s and 3s and for the 3p$\sigma$ and 4p$\sigma$ MO's in each of two directions $x$ and $z$, the former perpendicular to and the latter along the line joining the nuclei. These distances

(23) This is illustrated in Table II only for $ns$, but qualitative considerations show that it should also be true for other unpromoted types ($np\pi$, $nd\delta$, $nf\phi$, etc.).

have been read off approximately from the contour maps of ref. 16. Since the nodal surfaces in question are of ellipsoidal shape (the number of such nodes being the quantum number $n_\xi$), the $z$ distances are larger than the $x$ distances, but the two must approach equality as $n$ increases, since for the outer nodal surfaces for large $n$ the ellipsoids become spheres. The $x$ and $z$ values in Table IV conform completely to the expected behavior.

TABLE IV

LOCATIONS OF ELLIPSOIDAL NODES OF $H_2^+$ MO's[a]

| | | 2s | | | 3s | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | $R = 2$ | $R = 4$ | He$^+$ | $R = 2$ | $R = 4$ | He$^+$ |
| First | $z$ | 1.9 | 2.9 | 1.0 | 1.9 | 2.9 | 0.95 |
| node | $x$ | 1.7 | 2.1 | 1.0 | 1.7 | 2.1 | 0.95 |
| Second | $z$ | ... | ... | ... | 4.9 | 6.25 | 3.55 |
| node | $x$ | ... | ... | ... | 4.85 | 6.0 | 3.55 |

| | | 3p$\sigma$ | | | 4p$\sigma$ | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | $R = 2$ | $R = 4$ | He$^+$ | $R = 2$ | $R = 4$ | He$^+$ |
| First | $z$ | 2.4 | 3.1 | 3.0 | 2.3 | 3.1 | 2.77 |
| node | $x$ | 2.3 | 2.4 | 3.0 | 2.2 | 2.3 | 2.77 |
| Second | $z$ | ... | ... | ... | 6.45 | 7.0 | 7.24 |
| node | $x$ | ... | ... | ... | 6.15 | 6.75 | 7.24 |

[a] The numbers following $x$ and $z$ in the table give in a.u. the $x$ and $z$ values at which the first and second ellipsoidal nodal surfaces of the 2s, 3s, 3p$\sigma$, and 4p$\sigma$ MO's of $H_2^+$ intersect the $x$ or $z$ axis ($x$ and $z$, respectively, being measured from the molecule center perpendicular to and along the line joining the nuclei), for each of two internuclear separations $R = 2$ and 4 a.u. (The $x$ and $z$ values given were read off roughly from the contour diagrams of ref. 16.) The corresponding nodal distances for the 2s, 3s, 3p$\sigma$, and 4p$\sigma$ He$^+$ UAO's are given for comparison.

These $x$ and $z$ values are also compared in Table IV with the theoretical values for the corresponding orbitals of He$^+$. Reference to the $n^*$ values in Table II shows that the expansion or contraction of the nodal surfaces as compared with He$^+$ parallels the $\delta$ values completely. For 2s and 3s ($\delta < 0$) the nodal surfaces are expanded relatively to He$^+$, and more so for $R = 4$ than for $R = 2$ in accordance with the larger $\delta$ values at $R = 4$. For 3p$\sigma$ and 4p$\sigma$ ($\delta > 0$) the nodal surfaces at $R = 2$ are contracted relative to He$^+$, but to a lesser extent than 2s and 3s are expanded, in agreement with the fact that the $\delta$ values are smaller in the former than the $-\delta$ values in the latter case. For 3p$\sigma$ and 4p$\sigma$ at $R = 4$ the nodal surfaces are only slightly contracted, in agreement with the fact that $\delta$ has now become considerably smaller than at $R = 2$, especially for 4p$\sigma$ (see Table II).

The demonstration that the MO's of $H_2^+$ are Rydberg MO's implies that all that was said in section III about progenitors and about recapitulation of lower-$n$ loops in higher-$n$ AO's or MO's is applicable also to the $H_2^+$ MO's. Consider for example an $ns$ MO of $H_2^+$ at $R = 4$ a.u. The innermost loop-creating function (whose coefficient in the complete MO is of course very small) must closely resemble the 1$\sigma_g$ MO, which at $R = 4$ is rather well approximated by the strongly ellipsoidal LCAO form $1s_a^{(1.03)} + 1s_b^{(1.03)}$ but not at all well by the UAO form $1s_c^{(2.00)}$. The next loop-creating function must resemble the outer loop of the 2s MO of $H_2^+$, which is perhaps not extremely different from that of a 2s UAO except (cf. Table IV) that it is greatly expanded. Successive loops farther out must become more and more nearly spherically symmetrical and more and more nearly resemble those of $ns$ UAO's except that they are all much expanded, corresponding

to a phase shift $\delta$ of about $-0.64$. If now we consider increasing $R$ values, more and more of the inner nodes must become strongly ellipsoidal; yet if $n$ is large enough, the outermost nodes must be nearly spherical even for very large $R$ values.

A comparison between the cause of the quantum defect $\delta$ for penetrating Rydberg AO's and that for $H_2^+$ MO's is of interest. In both cases, $\delta$ arises mainly from departures in the innermost loop or loops from an H-atom-like $(-Z_c e^2/r)$ potential. In the case of the Rydberg AO, its penetration into the core exposes it to a stronger field. This alone would give rise to a $\delta$, because it lowers the energy of the AO even if unchanged in form (first-order effect). However, shrinkage and radial distortion of the inner loops of the AO, especially if the penetration is deep, further increases

$\delta$. Higher members of the Rydberg series, because of orthogonality, approximately recapitulate in their innermost loops the distortions and (with a small weighting factor) the energy changes of their early progenitors, so that $\delta$ persists in the energy formula (eq. 1) and phase shifts persist in the asymptotically H-atom-like AO's.

In a similar way for any higher-$n$ $H_2^+$ MO, the departure of the potential from $-2e^2/r$, mainly in the first progenitor and in the innermost loop or loops of the MO, establishes a $\delta$ which then persists in the energy formula and in phase shifts of the outer loops. The two cases are very similar except for the extra degree of freedom in $H_2^+$ whereby $\delta$ varies with $R$ (but is always zero for $R = 0$), and except for the fact that $\delta$ in $H_2^+$ can as well be negative as positive.

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# Mechanisms of Photochemical Reactions in Solution. XXII.[1] Photochemical *cis–trans* Isomerization

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We report a detailed study of the photochemical isomerization of four pairs of *cis–trans* isomers, the stilbenes, the 1,2-diphenylpropenes, the piperylenes (1,3-pentadienes), and ethyl maleate–ethyl fumarate. Principal emphasis has been placed on isomerization in the presence of photosensitizers although the results have been correlated with those obtained by direct excitation in the case of the stilbenes and diphenylpropenes. The composition of the mixtures in the photostationary states is a complicated, but rational, function of the nature of the photosensitizers. All results can be understood if it is assumed that transfer of triplet excitation may involve excitation of acceptors to nonspectroscopic as well as spectroscopic states. We infer that the stilbene triplet exists in two interconvertible states, one transoid and one twisted. Probably the only stable triplet in the 1,2-diphenylpropene system is a twisted form. Self-quenching of stilbene triplets by ground-state *trans*-stilbene is significant. Sensitizers having low excitation energies function as true "photocatalysts," *i.e.*, in the presence of excited states of the sensitizers the composition of the photostationary mixture approaches that at thermal equilibrium.

Many studies of photochemical *cis–trans* isomerization have been reported and the mechanisms of these processes have been the subject of frequent, lively discussions.[7] Most of the work has involved irradiation with light absorbed directly by the substrate molecules or under conditions such that the primary absorption process is undefinable. Recent work[14–17]

has shown that the reaction can also be effected by irradiation in the presence of suitable photosensitizers. Since the sensitized reaction is in some ways more amenable than the direct process to study in depth, we have investigated several systems in detail. The results not only clarify the specific photochemical process but also give useful information concerning the mechanisms of triplet excitation transfer and the properties of electronically excited states of molecules.

## General Theory

We presume the *a priori* hypothesis that most photosensitized reactions involve transfer of electronic excitation from the sensitizer to an acceptor. Transfer of either triplet or singlet excitation can be realized. Triplets are generally much longer-lived than singlets. Consequently triplets are more likely than singlets to live long enough to encounter potential acceptors. All available evidence indicates that triplet transfer requires close contact of the partners in energy exchange. On the other hand, it has been shown[18] that transfer of singlet excitation in solution may occur even when molecules are separated by large distances. However, the requirements for long-range transfer of singlet energy also place stringent restrictions on

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(7) Thorough documentation of the literature is impractical because of its volume. Considerable pertinent discussion has recently been focused on the stilbenes.[8–16] Reference 9 gives a representative treatment.

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