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The Rydberg States of Molecules. VI. Potential Curves and Dissociation Behavior of (Rydberg and Other) Diatomic States[1]

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[Dedicated to Professor Masao Kotani on the occasion of his sixtieth birthday]

Abstract: The ways in which the electronic wave functions of diatomic states change in various ranges of R values from $R = 0$ to ∞ (R = internuclear distance) are first discussed in a general way (section 2, on State Correlation Diagrams), and some needed terminology is introduced; at large R values, LCAS (*linear combination* of *atomic substate*, including Heitler–London and *various other*) types of wave functions are needed. In section 3, avoided crossings and other causes for irregularly shaped potential curves are reviewed, and homogeneous perturbations are also considered. Section 4 contains a critical discussion of MO correlation diagrams, emphasizing that the ordinary more or less H_2^+-like correlations usually represent only *pseudo-correlations* in the range from large R values out to dissociation, *except* in the case of those electrons which on dissociation correspond to atomic closed shells; the forms of MO's as linear combinations of *modified* AO's (modified united-atom AO's at small R and modified separate-atom AO's at large R) are also discussed. In section 5, the course of the transformation of wave functions of the Rydberg states of H_2 and He_2 from MO-configuration forms near R_e (where they are good approximations) to LCAS forms on dissociation is examined. For the MO's themselves, from R_e to ∞, there is only a pseudo-correlation. Aside from further complications in some cases, the Rydberg states fall into two classes, of which the $1\sigma_g 2p\pi_u$ and $1\sigma_g 3d\pi_g$ (either singlet or triplet) states of H_2 (using MO descriptions which are appropriate near R_e) are typical. The $1\sigma_g 2p\pi_u$ type dissociates smoothly along a normal potential curve into a Heitler–London-like $(1s2p\pi)_u$ atom-pair LCAS, while the $1\sigma_g 3d\pi_g$ type dissociates along a potential curve with a hump, in the neighborhood of which the wave function (as shown by J. C. Browne) can be approximated in terms of LCAS's only by a mixture of $(1snp\pi)_g$ and $(1s3d\pi)_g$ atom-pair LCAS's, but as $R \rightarrow \infty$ attains a pure $(1s2p\pi)_g$ LCAS. In both cases, the use of the atom-pair LCAS's mentioned affords rather good wave functions even at R_e, although, of course, corresponding ion-pair functions must be added (though this is less important than might appear at first sight because of their very marked lack of orthogonality to corresponding atom-pair LCAS's) if one is to obtain (good approximations to) the much better MO-configuration functions.

1. Introduction

Since publication of parts I–V of this work,[2] some relevant new developments have occurred.[3–5] The present part VI deals especially (see section 5) with the dissociation behavior of diatomic Rydberg

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[2] R. S. Mulliken, *J. Am. Chem. Soc.*, **86**, 3183 (1964). A number of references to particular sections of that paper are given in the present text; for example, "V,2" means part V, section 2 of that paper.

[3] R. S. Mulliken, *Phys. Rev.*, **136**, A962 (1964).

[4] J. C. Browne (a) *J. Chem. Phys.*, **42**, 2826 (1965): 2s and $3p\sigma$ He_2 states; (b) *Phys. Rev.*, **138**, A9 (1965): $3d\pi$ states of H_2 and He_2; (c) *J. Chem. Phys.*, **41**, 1583 (1964): $3d\delta$ states of H_2 and long-range parts of $2p\pi$- and $3d\pi$-state potential curves.

[5] (a) W. M. Wright and E. R. Davidson, *ibid.*, **43**, 840 (1965): $3d\pi$ $^3\Pi_g$ state of H_2; (b) C. B. Wakefield and E. R. Davidson, *ibid.*, **43**, 834 (1965): 2s, 3s, and $3d\sigma, {}^3\Sigma_g^+ H_2$ states; also 2s, 3s, $3d\sigma, {}^1\Sigma_g^+$, and $3d\delta, {}^{1,3}\Delta_g$ states for a few R values.

states, but sections 2, 3, and 4 are devoted to a review and clarification of some related matters, including the introduction of descriptive terminology which the writer feels to be much needed as an aid to clear understanding.

2. State Correlation Diagrams

Correlation diagrams for diatomic MO's indicating how the forms and energies of MO's change with internuclear distance R from $R = 0$ ("united-atom") through R_e to large R values (separate atoms) are familiar.[6] These will be reviewed in section 4. The present section deals with the general characteristics of correlation diagrams for diatomic electronic *states* which have simple normal potential curves. These are states for which (a) the validity of the BO (Born–Oppenheimer) approximation can be assumed and (b) whose potential curves $U(R)$ either have a single fairly deep minimum (typical *attractive states*) or no minimum (*repulsive states*). States with potential curves of less regular shape are considered in section 3.

From $R = 0$ to somewhat beyond R_e (*the MO region of R values*), it is convenient to formulate the accurate electronic wave function Ψ as a linear combination of terms $\Sigma c_i \Psi_i$ each of *MO electron configuration* type. Usually Ψ contains just *one dominant term* Ψ_0 with coefficient near 1.0, of SCF-MO (self-consistent field MO) form, plus a large number of other terms Ψ_i with relatively small coefficients, representing CM (*configuration mixing*). This really means mixing of *state* wave functions *of the same species* but from *different electron configurations;* for example, $1\sigma_u^2, {}^1\Sigma_g^+$ mixes somewhat with $1\sigma_g^2, {}^1\Sigma_g^+$ in H_2; as an analogous atomic example, $1s^2 2p^6, {}^1S$ mixes somewhat with $1s^2 2s^2 2p^4, {}^1S$. The situation with one dominant term of MO type may be called the *minor MO-CM* case. When spin-orbit coupling is important, CM of course includes some terms differing in multiplicity.

At large R values (the *transition region of R values*) a major MO-CM case (two or more CM terms having relatively large coefficients) is usually[7] reached or approached if we continue to build Ψ from MO-configuration terms. At still larger R values (the *AO region of R values*, where AO means *separate-atom* AO), *major MO-CM* usually[7] is required if MO-configuration terms are used.

However, major CM can be avoided at large R values if Ψ is shifted to a *two-atom AO-configuration* basis. Ψ then takes the form of an LCAPAS molecular wave function, meaning a function which is an *antisymmetrized product* $\mathcal{A}\psi_a\psi_b$ (an AP) of *atomic substate* (AS) wave functions ψ_a and ψ_b, or usually a *linear combination* (LC) of such antisymmetrized products.[8] In general, each *atomic-state function* Ψ may usually be expressed using one dominant SCF-AO term belonging to a single AO configuration, plus minor CM; the dominant term itself, likewise each of the minor CM terms, may consist either of a single Slater determinant or a linear combination of these, depending on the AO configuration and on M_L and M_S. Each atomic *substate* function ψ used must be of strong-field type, that is, with definite M_L and M_S values. In general, there are several substate ψ's (each one in the form of a single Slater determinant) for the dominant term in each of the participating atomic-state functions Ψ_a and Ψ_b, but in general this degeneracy is partially split in the molecule and linear combinations only of suitably selected $\psi_a\psi_b$ products (each such product then made over-all antisymmetric in all the electrons) are taken; similarly for the minor CM terms.

Although less clearly self-explanatory than LCAPAS, the letters LCAS will be used hereafter for the sake of brevity. Every LCAS is associated with one single two-atom AO configuration, as for example $1s_B^2 2s_B^2 2p_B$-$1s_O^2 2s_O^2 2p_O^4$ for a molecule BO. Such a two-atom AO configuration can be thought of as similar to a single-atom AO configuration; for example, the BO two-atom just mentioned is comparable to a single-atom configuration $1s^2 2s^2 2p 3s^2 4s^2 4p^4$. In the normal case that only minor AO-CM is present in the atomic wave functions Ψ_a and Ψ_b used in constructing any LCAS molecular Ψ which is valid at large R values, one can say that there is only *minor AO-CM* in this Ψ.

Simple examples of LCAS functions suitable in the AO region include the normal and various excited-state functions of H_2^+, H_2, He_2^+, HeH, Li_2, BeH, and also H^+H^- and other ion-pair functions. Heitler–London (HL) and ion-pair functions are special cases of LCAS functions. Thus for the H_2 configuration $1s_a 1s_b$, the $M_S = +1$ substate of the ${}^3\Sigma_u^+$ state is represented by the single APAS

$$\mathcal{A}1s_a(1)\alpha(1)1s_b(2)\alpha(2)$$

while for $M_S = 0$, LCAS's are needed

$$\mathcal{A}1s_a(1)\alpha(1)1s_b(2)\beta(2) \pm \mathcal{A}1s_b(1)\beta(1)1s_b(2)\alpha(2)$$

with the + and − signs belonging to the ${}^3\Sigma_u^+$ and ${}^1\Sigma_g^+$ states, respectively. When there is only one electron, as in H_2^+, the LCAO MO function at large R values can be regarded equally well as a simplified LCAS function. For the Rydberg states of H_2 and He_2 at large R, LCAS forms are required (see section 5).

Matters are somewhat more complicated in cases where the electron configuration of either or both atoms is "wide open," that is, differs from a set of closed shells by more than ±1 electron. Such a two-atom electron configuration gives rise to more than one atomic-state pair; going asymptotically to *each* of these as $R \rightarrow \infty$, there are in general several molecular $U(R)$ curves corresponding to various LCAS's derived from the given pair of atomic states. For example, the lowest-energy AO configuration $1s^2 2s^2 2p^2$ of the C atom gives a ${}^3P$, a ${}^1D$, and a ${}^1S$ state. Two normal atoms (both ${}^3P$) give a number of C_2 molecule LCAS's each with its own $U(R)$ curve. Each of the other atomic-state pairs ${}^3P$–${}^1D$, ${}^3P$–${}^1S$, ${}^1D$–${}^3P$, ${}^1D$–${}^1D$, ${}^1D$–${}^1S$, ${}^1S$–${}^3P$, ${}^1S$–${}^1D$, and ${}^1S$–${}^1S$, belonging to the same two-atom AO configuration $1s^2 2s^2 2p^2 1s^2 2s^2 2p^2$, likewise gives rise to $U(R)$ curves.

Although at large R each molecular Ψ consists of a single LCAS, at smaller R forced *intraconfigurational state-mixing* (forced AO-SM) sets in between LCAS's *of the same diatomic species* (*e.g.*, ${}^1\Sigma_g^+$ or ${}^3\Pi_u$) associ-

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(6) *Cf.* R. S. Mulliken, *Rev. Mod. Phys.*, 4, 40 (1932).

(7) Exceptions in which only minor MO-CM is needed at all R values will be discussed in section 4.

(8) In connection with his "atoms-in-molecules" method, W. Moffitt, *Proc. Roy. Soc.* (London), A210, 245 (1951), introduced the term "composite (atomic) function" for what is called here an APAS function. However, there seems to be a need for a more explicitly descriptive symbol, especially since we usually need to deal with *linear combinations* of APAS's.

ated with other energy asymptotes corresponding to other state pairs (*e.g.*, ^{3}P–^{1}D, ^{3}P–^{1}S, etc., mentioned above) of the *same* two-atom AO configuration. Then as the transition region of R is approached at still smaller R, forced AO-CM from *extraconfigurational mixing* (from LCAS's derived from state pairs belonging to *excited* two-atom AO configurations, *e.g.*, $1s^2$-$2s^22p^21s^22s2p^3$ or $1s^22s^22p1s^22s^22p^3$ in our C_2 example) also sets in increasingly.

In the correlation of a group of electronic states from small to large R values, or *vice versa*, the course of the several potential curves depends very much on the energy patterns of MO-configuration and AO-configuration states. Thus for H_2, the $U(R)$ curves of the two dominant MO-configuration states $1\sigma_g1\sigma_u,{}^3\Sigma_u^+$ are near together at small R values but separate widely as R increases, with the $^3\Sigma_u^+$ going to the low-energy $^3\Sigma_u^+$ HL state of AO configuration $1s_a1s_b$ and the $^1\Sigma_u^+$, after approaching $1s^2$ ion-pair form, finally going to a $^1\Sigma_u^+$ LCAS state of 1s2p AO configuration. Correlating in the reverse direction, from large to small R, the low-energy AO configuration $1s_a1s_b$ gives rise to the HL attractive state $1s\cdot1s,{}^1\Sigma_g^+$ and the repulsive state $1s\times1s,{}^3\Sigma_u^+$ which at small R values belong respectively to two different MO configurations $1\sigma_g^2$ and $1\sigma_g1\sigma_u$ of widely different energy.[9] The subject of the effect of differing dissociation products on the molecular constants of different states of the same MO electron configuration is discussed further in another paper.[10]

3. Irregularly Shaped Diatomic Potential Curves

Although most $U(R)$ curves of low-energy diatomic electronic states are either smooth attraction curves with one minimum, or else smooth repulsion curves, curves of less regular form are increasingly being found. Possible causes of these irregularities are now reviewed.

Avoided Crossings and Homogeneous Perturbations. The most important cases of humps or deformation in attractive curves can be understood in terms of interaction at a crossing of two attractive potential curves associated with electronic states which are of the same group-theoretical species. It will be recalled that, in atoms, the energies of two zero-order states of the same species but of different dominant AO electron configuration usually are quite different but occasionally by accident are nearly equal, in which case major CM between them occurs if the matrix element of their interaction is large enough. In molecules, where the electronic energy varies with R, it can happen that the $U(R)$ curves of two zero-order states of the same species, but whose wave functions are orthogonal or nearly so, and each of which has only minor CM (MO-CM if small R, AO-CM if large R), can come near each other, or may cross, *in some range* of R. If they interact strongly, what may be called *accidental major CM* then results over the range of R where the two curves are sufficiently near.

In terms of the size of the interaction matrix element involved, crossings can be weak or strong. If the interaction matrix element is *small*, it is best to think in terms of strong mutual perturbations (*homogeneous perturbations*) between sets of vibronic-rotational levels belonging to the two potential curves which approach or cross. (In the case that one of two $U(R)$ curves which cross is repulsive and the other attractive, the interaction causes either an avoided crossing or very strong homogeneous *predissociation* of the energy levels of the attractive curve.) These perturbations are strongest for energy levels with electronic energy near that of the point of crossing or closest approach. They represent strong departures from the validity of the BO approximation.

The NO molecule affords many examples of this type of interaction[11] with one wave function that of a Rydberg state (MO electron configuration $\cdots5\sigma^21\pi^4$Ry, where Ry denotes a Rydberg MO) and the other that of a valence-shell state (of MO configuration, for example, $\cdots5\sigma^21\pi^32\pi^2$). Another interesting example is that of the $1\sigma_g3s,{}^3\Sigma_g^+$ and $1\sigma_g3d\sigma,{}^3\Sigma_g^+$ H_2 Rydberg-state curves,[12] which cross almost exactly at R_e of both curves and of the positive ion. The interaction matrix element is only 75 cm^{-1} and the homogeneous perturbation viewpoint is appropriate. The smallness of the matrix element is no doubt a result of the nearly UAO forms of the 3s and 3dσ Rydberg MO's, together with nearly identical $1\sigma_g$ forms, in the two zero-order functions.

If the matrix element is large enough, the interaction between two minor MO-CM (or minor AO-CM) potential curves which would cross can best be thought of as resulting in two new resultant curves which do *not* cross (*avoided crossing* case). For this case it is necessary that the *new* curves be sufficiently far apart, compared with vibrational energy level spacings, so that the Born approximation holds reasonably well for them.

Similar considerations apply in the case of avoidance *without crossing*, which occurs if two minor CM curves come close and interact strongly yet do not cross.

One example of avoided crossing is that of two minor MO-CM $^2\Sigma_u^+$ curves of N_2^+ with MO electron configurations $\cdots2\sigma_u1\pi_u^43\sigma_g^2$ and $\cdots2\sigma_u^21\pi_u^33\sigma_g1\pi_g$; here two resultant curves are found experimentally which are somewhat abnormal in shape but show no humps or extra minima.[13] Here the avoided crossing occurs at a small R value and between two valence-shell MO states, a situation which favors strong interaction.

Another striking example is that of the lowest excited $^1\Sigma_g^+$ state of H_2, with two minima and a hump between.[14] This is explainable by an avoided crossing

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(9) Symbols like $1s\cdot1s$ and $1s\times1s$ will be used in this paper for LCAS singlet and triplet states, respectively. Similarly for a single atom, symbols like $1s\cdot1s$ and $1s\times2s$ for the $1s2s,{}^1S$ and $1s2s,{}^3S$ states of the He atom will be used.

(10) R. S. Mulliken in "Quantum Theory of Atoms, Molecules, and the Solid State," P. O. Löwdin, Ed., Academic Press Inc., New York, N. Y., 1966.

(11) *Cf.* K. Dressler and E. Miescher, *Astrophys. J.*, **141**, 1266 (1965).

(12) See ref 5b. The authors (*cf.* their Figure 1) treat this case as that of an avoided crossing. From the homogeneous perturbation viewpoint, however, the 3s and 3dσ curves should be allowed to cross in their Figure 1. The 3dσ curve then goes over a hump 0.41 ev above the asymptote, toward a dissociation asymptote with one 2-quantum H atom, while the 3s curve goes, without a hump, to an asymptote with a 3-quantum atom.

(13) *Cf.* R. S. Mulliken, "The Threshold of Space," Pergamon Press, New York, N. Y., 1957, p 177, note on states 180 and 183. For another example of crossing in N_2, but belonging to the homogeneous perturbation type, see P. K. Carroll and R. S. Mulliken, *J. Chem. Phys.*, **43**, 2170 (1965).

(14) (a) *Cf.* E. R. Davidson, *ibid.*, **35**, 1189 (1961); (b) G. H. Dieke and S. P. Cunningham, *J. Mol. Spectry.*, **18**, 288 (1965). This paper tends to suggest that the homogeneous perturbation viewpoint may be more appropriate even here than the avoided crossing viewpoint.

between the minor MO-CM curve of the Rydberg state $1\sigma_g 2s, {}^1\Sigma_g^+$, rising fairly fast toward a dissociation asymptote corresponding to an LCAS wave function with one 2-quantum excited atom, and that of the doubly excited minor MO-CM $1\sigma_u^2, {}^1\Sigma_g^+$ state which because of its ion-pair character in AO approximation has a rather deep minimum at large R. At still larger R, where now the two states can best both be described as minor AO-CM states, a second avoided crossing of the same two curves must occur so as to permit the actual lowest-excited ${}^1\Sigma_g^+$ state curve to dissociate into the LCAS state mentioned above, while the ion-pair state goes toward a higher-energy asymptote.

Typical examples of avoided crossings in the AO region are found in the alkali halide molecules MX where avoided crossings occur of covalent LCAS wave functions $M \cdot X$ and ion-pair functions M^+X^-.[15]

In the foregoing examples and probably in most other cases of avoided crossings, probably the two minor CM wave functions whose curves tend to cross are strongly mixed *only in a moderate range* of R values in the neighborhood of the value R_c at which the minor CM curves would cross. (At R_c, of course, there must be a 50:50 mixing.) The breadth of the R range in which there is strong mixing should be greatest if the interaction matrix element is large, and if the zero-order potential curves intersect at a small angle.

At R values distant from an R_c, the wave functions in typical cases may be minor CM functions which are nearly as pure single-configuration functions as in cases where there is no avoided crossing. Granting this, if one follows the lower of the two curves resulting from an avoided crossing, from small R values through R_c to large R values, the character of the wave function must shift from being near that appropriate to one of the two nearly pure electron configurations to that for the other, while for the upper of the two curves the reverse change occurs.

In a *state correlation diagram* (*cf.* section 2), either of two points of view can then be adopted in cases where an avoided crossing occurs. One can follow each of the *resultant* $U(R)$ curves and say that the nature of the electron configuration (and/or state) changes radically in passing through R_c. Or one can correlate the segments of the two $U(R)$ curves below and above R_c *as if* crossing had occurred, so that segments of like configuration and state are correlated, although at the same time recognizing that near R_c there is a range of R where the actual states are strongly mixed. The second viewpoint makes sense especially in cases where the R range of strong mixing is reasonably well localized.

London Dispersion Force Effects. Small humps, minima, or other deviations from simple form in $U(R)$ curves can be produced by (a) second-order or (b) first-order London dispersion forces. The former (a) can produce shallow van der Waals minima in what otherwise would be pure repulsion curves.[16] The latter[17] (b) can produce shallow minima at large R in repulsion curves, or small maxima at large R for stable attraction states. A good example is the hump in the lowest ${}^1\Pi_u$ Rydberg state of H_2;[18] further similar examples are known in a ${}^1\Pi_u$ state of Na_2 and in other cases.[17]

Another interesting example is that of the lowest Rydberg ${}^1\Pi_g$ state of H_2 (of MO configuration $1\sigma_g 3d\pi$ at R_e), which has a stable minimum, then with increasing R a maximum due to avoided crossing of LCAS type (see section 5), and finally a first-order dispersion minimum[4c] of depth 0.015 ev at large R.

Exchange Effects. In atoms, singlet- and triplet-state energies differ approximately by the presence of an exchange energy $+K$ for the singlet and $-K$ for the triplet, with the exchange integral K always a positive quantity. In LCAS states of HL type, singlets and triplets again differ by the presence of $+K$ or $-K$, but now K is *negative* in cases like that of two normal H atoms where as a result $1s \cdot 1s, {}^1\Sigma_g^+$ is attractive and $1s \times 1s, {}^3\Sigma_u^+$ is repulsive.[9] (The negative value of K is connected with the nonzero value of the overlap integral between the 1s AO's of the two atoms.) Similarly for the BH molecule at large R values, the normal state HL function $(1s^2 2s^2 2p\sigma_B) \cdot 1s_H, {}^1\Sigma^+$ is attractive, while the $(1s^2 2s^2 2p\sigma_B) \times 1s_H, {}^3\Sigma^+$ must be repulsive.[9] However, in the ${}^1\Pi$ and ${}^3\Pi$ excited states with LCAS configuration $(1s^2 2s^2 2p\pi)_B 1s_H$, K is *positive* as in atoms, since the overlap integral and bonding between $2p\pi_B$ and $1s_H$ are *nil*. This exchange term contributes, along with another, toward making the ${}^1\Pi$ state repulsive at large R, but finally at smaller R an avoided crossing creates a minimum, leaving, however, a hump of 0.12-ev height between R_e and $R = \infty$. The other exchange effect is a nonbonded repulsion (as in HeH) between the $1s_H$ electron and the $2s^2$ closed shell on boron. Very likely the latter effect makes the larger contribution to the repulsion at moderately large R, but the presence of the other exchange effect is interesting at least in principle.[19]

4. Correlation Diagrams for Diatomic MO's

The familiar *correlation diagrams* for diatomic MO's[6] are supposed to indicate, for each MO in the MO electron configuration of any particular electronic state, something about how the MO changes from $R = 0$ through R_e to $R = \infty$. For homopolar molecules the correlation diagram for H_2^+ serves as prototype. Here for each MO its term value or binding energy T is shown as a function of R, and names or symbols indicating the asymptotic forms of the MO at $R = 0$ (UAO limit) and at $R = \infty$ (AO limit) are given. Near $R = \infty$ the MO is of LCAO form $\chi_a \pm \chi_b$, with an AO χ which in general is a hybrid of AO's differing in l; as $R \rightarrow \infty$, T of the MO approaches equality to T of this AO. At intermediate R values the MO can be given a name based on its form near $R = 0$ or near $R = \infty$, or on some other basis. For H_2^+, the UAO name is most often used. The function $T(R)$

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[15] Here the R value (R_c) at crossing is sometimes so large and the interaction matrix element so small that homogeneous perturbation instead of an avoided crossing occurs (see R. S. Berry, *J. Chem. Phys.*, 27, 1288 (1957)).

[16] As an example, very accurate calculations by W. Kolos and L. Wolniewicz, *ibid.*, 43, 2429 (1965), show a van der Waals minimum of depth 4.3 cm^{-1} at 4.15 A in the $1s \times 1s, {}^3\Sigma_u^+$ repulsion state of H_2.

[17] *Cf.* R. S. Mulliken, *Phys. Rev.*, 120, 1674 (1960); J. C. Browne, ref 4c on Π states.

[18] Accurate calculations by Kolos and Wolniewicz[16] gave a hump of height 105 cm^{-1} at R = 4.75 A. *Cf.* also ref 17 and J. C. Browne, *J. Chem. Phys.*, 40, 43 (1964).

[19] For a discussion of the nature of the ${}^1\Pi$ state of BH and the height of its hump, see A. C. Hurley, *Proc. Roy. Soc.* (London), **A261**, 237 (1961). Hurley, however, did not consider the $+K$ contribution to the repulsion at large R.

for each MO is unique and is quantitatively known or calculable. Each $T(R)$ is equal to the vertical ionization energy $I(R)$, that is, $U^+(R) - U(R)$, where $U^+(R)$ and $U(R)$ are the potential curves of H_2^{2+} (here of course U^+ is merely e^2/R) and H_2^+. Another point is that for each MO and $T(R)$ of H_2^+ there is only one electronic *state*.

In other molecules, even for ionization of an electron out of one particular MO, there is no unique $I(R)$ with which a $T(R)$ for that MO can be identified, since occupancy of this MO occurs for many different states of the molecule and its positive ion, each with its own potential curve. In practice, to be sure, one is likely to be most interested in removing the electron from a molecule in some particular state, for example, the normal state, so that the difficulty in deciding on a single or perhaps an average $I(R)$ to be identified with $T(R)$ is reduced.

But further and most especially, the identification of $I(R)$ or $T(R)$ with a particular MO has meaning only to the extent that the wave functions of the relevant molecule state or states and ion state or states can be approximated by Ψ's with minor MO-CM only. Usually this condition is satisfactorily fulfilled near R_e but fails at large R values because of increasing MO-CM For this reason the meaning of the usual correlation curves as $R \rightarrow \infty$ is in general open to very serious question. At best they have in general only *qualitative* meaning at large R values.

Before exploring this major difficulty, it is useful to summarize some of the other differences between the $T(R)$ curves of H_2^+, discussed[2] in section V,2, and those of other molecules.

(1) At $R = 0$ the hydrogenic l degeneracy which occurs in He^+ is removed, resulting in some changes in the energy order shown in Table 1 of ref 2 for H_2^+, but not in the splitting patterns (eq 17 of ref 2) for MO's of given n and l which differ in λ.

(2) At $R = \infty$ removal of the hydrogenic l degeneracy causes hybrid LCAO forms to be replaced by pure l LCAO forms, in a familiar way (*cf.* Table I). At smaller R, hybridization is partially restored.

(3) The noncrossing rule (*cf.* section 3) tends to introduce some shortcuts which do not occur in H_2^+ because of separability there in elliptical coordinates. Consider for example the MO's which at small R have the LCUAO forms $\sigma_g 3s$ and $\sigma_g 3d$, essentially the same as the UAO forms 3s and $3d\sigma$ (*cf.* Table II). Of these, 3s is lower in energy at small R, but correlates, as R increases to large values, with the $\sigma_g 3s$ LCAO form, which is *higher* in energy than the $\sigma_g 2p$ form with which $3d\sigma$ of small R correlates. Thus the correlation curves would cross at intermediate R values. For H_2 the two MO's are both Rydberg MO's, and the crossing takes place at R values where both are still so near to being UAO's that their interaction at the crossing point is weak enough that it makes good sense to ignore the noncrossing rule.[20] The same two MO's, of course, occur in all homopolar diatomic molecules. In N_2 at R_e of its normal state, one of them is a Rydberg MO of nearly 3s UAO form while the other (resembling $3d\sigma$) is a valence-shell MO of $\sigma_g 2h$ LCAO form, where h is a hybrid of mostly $3p\sigma$ with some 2s. The curves of these MO's would cross only at quite small R values such that both are of LCUAO form, and again it makes good sense to ignore the noncrossing rule. It seems likely that this situation is quite general, so that it is justifiable to assume the same crossings to occur in other homopolar diatomic molecules as in H_2^+.

Table I. Approximate Forms of Homopolar Diatomic MO's at Small and Large R Values[a]

Small R (LCUAO form)	Large R (LCAO form)	Small R (LCUAO form)	Large R (LCAO form)
$\delta_g 3d$ (10)	$\delta_g 3d$ (17)	$\phi_u 4f$ (20)	$\phi_u 4f$ (36)
$\pi_g 3d$ (9)	$\pi_g 2p$ (7)	$\delta_u 4f$ (19)	$\delta_u 3d$ (18)
$\sigma_g 3d$ (8)	$\sigma_g 2p$ (5)	$\pi_u 4f$ (18)	$\pi_u 3d$ (16)
$\pi_u 3p$ (7)	$\pi_u 3p$ (12)	$\sigma_u 4f$ (17)	$\sigma_u 2p$ (8)
$\sigma_u 3p$ (6)	$\sigma_u 2s$ (4)	$\delta_g 4d$ (16)	$\delta_g 4d$ (29)
$\sigma_g 3s$ (5)	$\sigma_g 3s$ (9)	$\pi_g 4d$ (15)	$\pi_g 3p$ (13)
$\pi_u 2p$ (4)	$\pi_u 2p$ (6)	$\sigma_g 4d$ (14)	$\sigma_g 3p$ (11)
$\sigma_u 2p$ (3)	$\sigma_u 1s$ (2)	$\pi_u 4p$ (13)	$\pi_u 4p$ (24)
$\sigma_g 2s$ (2)	$\sigma_g 2s$ (3)	$\sigma_u 4p$ (12)	$\sigma_u 3s$ (10)
$\sigma_g 1s$ (1)	$\sigma_g 1s$ (1)	$\sigma_g 4s$ (11)	$\sigma_g 4s$ (21)

[a] Table I is constructed like Table 1 in V,1 of ref 2. The numbers in parentheses represent the energy orders at small $R > 0$, and large $R < \infty$, for atoms with more than one electron. The energy order for given l but different λ *for small* R is what is expected on splitting the united atom. *For large* R the energy order for given l and λ is based on whether the overlap is positive, giving bonding (σ_g, π_u, δ_g, ϕ_u *for all* l), or negative, giving antibonding (σ_u, π_g, δ_u, for all l), while for given l and different λ it is based on the *magnitude* of the overlap (decreasing as λ increases from $\lambda = 0$). For small R the overlap within the LCUAO form is positive in every case, having suffered a reversal of sign as compared with large R in the case of those MO's (*e.g.*, $\sigma_u 2p$) which are antibonding at large R.

(4) Electrons in non-Rydberg MO's (*e.g.*, $\sigma_g 2h$ of N_2) in general move in much stronger fields than for corresponding H_2^+ MO's (which except for $1\sigma_g$ and $1\sigma_u$ must all be classed as Rydberg MO's), and so have much higher ionization energies.

Returning now to the problem of the failure of the minor MO-CM or SCF-MO approximation at large R values, we note again that in the transition region of R values ($R > 1.5R_e$ or $2R_e$ perhaps), and still more in the AO region, strong MO-CM usually is required, and then (with some exceptions to be discussed later) one cannot in general identify any actual I with the T of a particular MO. The normal, ${}^1\Sigma_g^+$, state (state N) of H_2 furnishes a simple example. At R_e of H_2 (0.74 A), according to very instructive calculations by Das and Wahl,[21] the MO configuration $1\sigma_g^2$ strongly predominates (Ψ is 98% $1\sigma_g^2$), but there is minor CM (mostly $1\sigma_u^2$, $1\pi_u^2$, and $2\sigma_g^2$). At 1.59 A, Ψ is still 90% $1\sigma_g^2$, while $1\sigma_u^2$ CM has increased to 9% and other CM has decreased. At 3.18 A, $1\sigma_g^2$ has fallen to 56% and $1\sigma_u^2$ has risen to 44%; other CM has now almost disappeared. As $R \rightarrow \infty$, Ψ becomes $2^{-1/2}(1\sigma_g^2 + 1\sigma_u^2)$, $1\sigma_g$ becomes accurately $\sigma_g 1s \equiv 2^{-1/2}(1s + 1s)$, and $1\sigma_u$ becomes accurately $\sigma_u 1s \equiv 2^{-1/2}(1s - 1s)$, where in the limit 1s is accurately free H-atom 1s. This Ψ is, of course, identical with the HL function $1s \cdot 1s, {}^1\Sigma_g^+$.

The example of state N of H_2 suggests that the usual correlation 1s(UAO)–$1\sigma_g$(MO)–$\sigma_g 1s$(LCAO) for the $1\sigma_g$ MO as R goes from 0 to ∞, with the implication

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(20) See the discussion on homogeneous perturbations near the beginning of section 3, including ref 12, and also especially the next-to-last paragraph of the first subsection of section 3. Strictly speaking, it is not the 3s and $3d\sigma$ MOs' of H_2 whose curves cross, but only the $U(R)$ curves of the $1\sigma_g 3s$ and $1\sigma_g 3d\sigma, {}^3\Sigma_g^+$ states, and (at a somewhat different R) of the corresponding ${}^1\Sigma_g^+$ states.

(21) See forthcoming paper by G. Das of this laboratory and A. C. Wahl of Argonne National Laboratory, and subsequent paper by G. Das.

that the 1s in σ_g1s at $R = \infty$ is a *free H-atom* 1s, is seriously wrong or misleading in the range of R values larger than about $2R_e$.[22] However, instead of following the actual state N Ψ from $R = 0$ to R_e to ∞, it is possible by theoretical calculations to follow the pure SCF-MO $1\sigma_g^2$ wave function from $R = 0$ to ∞. At $R = 0$, this coincides with the SCF-AO $1s^2$ wave function for the He atom. It is of interest to note that the *energy* of this Ψ is too high by 1.144 ev (the correlation energy, CE)[23] compared with that of the accurate Ψ, because it lacks the needed minor CM. At R_e, the CE for the SCF-MO $1\sigma_g^2$ Ψ is still almost the same (1.111 ev). At larger R values, the CE rises, along with the need for increasing CM, at first slowly, then faster, to 7.74 ev[21] as $R \rightarrow \infty$; this CE is the energy difference between pure SCF-MO $1\sigma_g^2$ (here the same as $\sigma_g 1s^2$) and the 50:50 mixture of $1\sigma_g^2$ and $1\sigma_u^2$ (identical with the 1s·1s HL function) which accurately represents state N of H_2 at $R = \infty$ in MO language. At $R = \infty$, I for state N of H_2 is just $I = T = 13.6$ ev for 1s of the free H atom if we use the HL function, whereas $I(1\sigma_g) = T(1\sigma_g)$ for the pure SCF-MO configuration $1\sigma_g^2$ is less than this by 7.74 ev: $T(1\sigma_g) = 13.60 - 7.74 = 5.86$ ev. For molecules other than H_2, similar but more complicated discussions and results are applicable.

One way to look at the above results for H_2 is to note that as MO-CM increases and becomes *major* MO-CM at large R, the identification of I of state N with $T(1\sigma_g)$ becomes unacceptable, and the usual correlation 1s(UAO)–$1\sigma_g$–σ_g1s is simply wrong.

An alternative viewpoint is reached on examining *why* the $1\sigma_g^2$ SCF-MO energy is so much higher than the accurate energy at $R = \infty$. Namely, each electron, in an MO of form σ_g1s, is required to move in the field of the nuclei shielded by the *other* σ_g1s electron, which means that each nucleus is shielded by $-{}^1/_2$e. The energy of $1\sigma_g^2$ is then roughly halfway between that of the HL function 1s·1s and that of the ionic LCAS function $2^{-1/2}(1s_a^2 + 1s_b^2)$, and the form of the 1s AO in σ_g1s is roughly halfway between that of 1s in H and 1s in $1s^2$ of H^-. If the latter kind of 1s is used, the correlation 1s(UAO)–$1\sigma_g$–σ_g1s(LCAO) which in the previous paragraph was found unacceptable, is now acceptable, though academic. Further, the two correlations are qualitatively, or formally, the same.

Correlations and correlation diagrams based on the use of single-configuration SCF–MO wave functions (no CM) all the way from $R = 0$ to ∞ can be designated as *ideal correlations* and correlation diagrams. At the present state of computer capability, it would be feasible, though only of academic or heuristic value, to compute $T(R)$ curves fairly accurately for ideal correlation diagrams of light molecules. However, one would still have to contend with the fact that in general one would obtain different $T(R)$ values for the same MO in different states.[24]

A more practical point of view is that MO correlation diagrams are not intended to have better than rough meaning. Then in ranges of R values where there is only minor MO-CM, the use as T values of I values averaged in some manner over different states if necessary is surely acceptable. But as soon as there is major MO-CM, a proper correlation no longer exists. An *improper* correlation such as that which for H_2 would connect $1\sigma_g$ at R_e (using I of state N for T) with σ_g1s constructed from free H-atom 1s AO's at ∞, with neutral H-atom I for T, can be called a *pseudo-correlation.*

As will be seen in another paper,[10] such pseudo-correlations are of real interest in connection with bonding powers of MO's. Aside from that, pseudo-correlation diagrams have qualitative value as rough empirical approximations to ideal correlation diagrams.

Fortunately there are some situations in which the ordinary correlations remain valid at all R values. Namely, for MO's in those MO closed shells which stand in correspondence to atomic closed shells on dissociation, the complications just discussed largely disappear. The simplest example is state N (a repulsive state) of the He_2 molecule. Here the SCF-MO wave function corresponding to the MO shell structure $1\sigma_g^2 1\sigma_u^2$ becomes identical as $R \rightarrow \infty$ with that for the SCF-AO structure $1s_a^2 1s_b^2$, while the wave functions of the two SCF-MO ionized structures $1\sigma_g^2 1\sigma_u$ and $1\sigma_g 1\sigma_u^2$, corresponding to removal of a $1\sigma_u$ or a $1\sigma_g$ electron, respectively, are rather nearly identical (see below) with those of the respective SCF-AO LCAS structures $2^{-1/2}(1s_a^2 1s_b \pm 1s_a 1s_b^2)$. Hence the correlations $1\sigma_g \rightarrow \sigma_g$1s and $1\sigma_u \rightarrow \sigma_u$1s are valid as R increases from small values to dissociation, with 1s meaning nearly just the SCF 1s of the He atom.[25]

[In the MO wave function of form $\{\mathcal{A}(1\sigma_g^2 1\sigma_u^2)$ + minor MO-CM$\}$ for He_2, where $\mathcal{A}$ is the antisymmetrizer, the MO's $1\sigma_g$ and $1\sigma_u$ must asymptotically approach the respective forms $2^{-1/2}(1s_a \pm 1s_b)$ as $R \rightarrow \infty$. By expanding and rearranging, it is then easily found that $\mathcal{A}(1\sigma_g^2 1\sigma_u^2)$ is *the same* as $\mathcal{A}(1s_a^2 1s_b^2)$, and presumably the same equality holds between the *exact* MO-type wave function and the exact APAS function $\mathcal{A}\{(1s_a^2$ + minor AO-CM$)(1s_b^2$ + minor AO-CM$)\}$.

For the two He_2^+ states as $R \rightarrow \infty$, now neglecting CM for simplicity, the SCF-MO functions are $\mathcal{A}[g_1\bar{g}_2u_3]$ and $\mathcal{A}[u_1\bar{u}_2g_3]$, while the corresponding LCAPAS functions are $2^{-1/2}[a_1a_2b_3'' \mp b_1\bar{b}_2a_3'']$, for the ${}^2\Sigma_u^+$ and ${}^2\Sigma_g^+$ states, respectively. Here a and b stand for $1s_a$ and $1s_b$ He-atom SCF AO's, a″ and b″ for $1s_a$ and $1s_b$ AO's of He^+, g and u refer to $2^{-1/2}(a' \pm b')$ where a′ and b′ are 1s AO's which are intermediate in form between He and He^+ AO's but nearer to the former, the numerical subscripts 1, 2, 3 refer to the three electrons, and the orbital symbols with or without a bar over the letter denote that the orbital is to be multiplied by a spin function α or β, respectively, in case the total M_S is $+{}^1/_2$, but β or α in case $M_S = -{}^1/_2$. Here expansion of the antisymmetrized MO functions in terms of AO's and rearrangement yields expressions $2^{-1/2}\mathcal{A}[a_1'a_2'b_3' \mp b_1'b_2'a_3']$ which are *formally* the same as the accurate LCAPAS functions but differ in having a′ and b′ throughout, instead of a, b for the neutral He atom and a″, b″ for the He^+ ion.

This difference, while somewhat like that between the SCF-MO and HL wave function for state N of H_2 as $R \rightarrow \infty$, can be seen to be a much less major one. This conclusion is decisively supported by an energy computation for which the writer is indebted to Drs. T. L. Gilbert and A. C. Wahl of Argonne National Laboratory. They find an electronic energy of −4.824275 hartrees for either of the SCF-MO functions $1\sigma_g^2 1\sigma_u$ or $1\sigma_g 1\sigma_u^2$ of He_2^+ at $R = \infty$, as compared with −4.861673 hartrees for either of the LCAS functions $2^{-1/2}[1s_a^2 1s_b'' \pm 1s_b^2 1s_a'']$ using the SCF-AO approximation for $1s^2$. Thus the SCF-MO functions are 0.0374 hartrees or 1.017

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(22) In some loosely bound molecules (*cf.* ref 21 for Li_2 and F_2) the SCF-MO approximation is less good at R_e than for H_2, and becomes worse more rapidly with increasing R.

(23) The word "correlation" is of course here being used in a different sense than in "correlation diagram."

(24) Even in H_2, where we have been considering $T(1\sigma_g)$ just for the ${}^1\Sigma_g^+$ normal state, we could also ask for $T(1\sigma_g)$ for among others the states which in MO approximation are denoted $1\sigma_g 1\sigma_u, {}^3\Sigma_u^+$ and $1\sigma_g 1\sigma_u, {}^1\Sigma_u^+$, and find somewhat different values for each of these three states, whether we use ideal correlations or ordinary I values.

(25) For He_2 at very small R, however, there is major CM near a *crossing* of $1\sigma_g^2 1\sigma_u^2$ (approximately $1s^2 2p\sigma^2$) by $1\sigma_g^2 2\sigma_g^2$ (approximately $1s^2 2s^2$).

ev higher in energy than the SCF-AO LCAS functions, or 2.161 ev higher than the *accurate* APAS functions after allowing for 1.144 ev of He atom CE in $1s^2$. In other words, the CE is 2 ev for the SCF-MO function at ∞, as compared with 1 ev for the SCF-AO APAS function. Thus although more CM is needed for the SCF-MO than for the SCF-AO function to convert it to an exact Ψ at large R values, still only *minor* CM is needed. Hence this case is very different from that of the normal state of H_2, where major MO-CM was required for the SCF-MO function.]

Typical stable molecules have both inner-shell MO's whose correlation behavior as $R \rightarrow \infty$ is like that of the $1\sigma_g$ and $1\sigma_u$ MO's in He_2, and valence-shell MO's which behave like $1\sigma_g$ in state N of H_2. For example, in N_2 the correlations $1s_{UA} \rightarrow 1\sigma_g \rightarrow \sigma_g 1s_{SA}$, $2p\sigma_{UA} \rightarrow 1\sigma_u \rightarrow \sigma_u 1s_{SA}$, $2s_{UA} \rightarrow 2\sigma_g \rightarrow \sigma_g 2s_{SA}$, and $3p\sigma_{UA} \rightarrow 2\sigma_u \rightarrow \sigma_u 2s_{SA}$ (where UA refers to the united atom, SA to the separated atoms) all involve *closed-shell* electrons of the separate atoms, and as $R \rightarrow \infty$ the MO T values to a good approximation go continuously into those of the SAO's indicated.[26] Thus these inner-shell MO's follow conventional correlation behavior at all R values. *Pseudo-correlation* at large R values as $R \rightarrow \infty$ occurs only for outer-shell LCAO-type MO's whose corresponding AO's (*i.e.*, SAO's) typically are valence AO's in the HL theory, *e.g.*, in the case of N_2, the $2p\sigma$ and $2p\pi$ AO's.

It is worth while now to give some attention to the intermediate ranges of R values, beginning with H_2^+ as prototype. The following scheme (*cf.* section V,1 of ref 2) summarizes how the form of an H_2^+ MO changes from $R = 0$ to ∞.

$$\mathrm{UAO} \equiv \mathrm{LCUAO} \longrightarrow \left\{\begin{matrix}\mathrm{mUAO\ or}\\ \mathrm{LCmUAO}\end{matrix}\right\} \longrightarrow \left\{\begin{matrix}\mathrm{MUAO\ or}\\ \mathrm{LCMUAO}\\ =\mathrm{LCMAO}\end{matrix}\right\} \longrightarrow \mathrm{LCMAO} \longrightarrow \mathrm{LCAO} \quad (1)$$

In the symbols, m or M means *modified.*[27] The form of the MO can be described at all R values as $\chi_a \pm \chi_b$ if in the middle range χ is taken as a strongly modified (M) UAO (He^+ AO) or, alternatively, as a strongly modified H-atom SAO. At small R, however, χ is best taken as a mildly modified (m) UAO, and at large R as a mildly modified separated-atom AO. Equation 1 holds not only for H_2^+ but, in ranges of R where they are valid, also for the correlation diagrams of all homopolar diatomic molecules, with UAO and AO taken as SCF AO's of united atom or separated atoms, respectively. Particularly in the middle range of R, the actual MO is an entity which sometimes is far from either a simple LCUAO or a simple LCAO form. Equation 1 is also valid for pseudo-correlation diagrams from $R = 0$ to ∞, but then, of course, has not the same meaning in regions of major MO-CM (mainly at large R values).

On the basis of eq 1, the MO region as defined in section 2 includes a UAO or LCUAO subregion. For H_2^+, this region extends to larger and larger R values with increasing l for given n (*cf.* Table III of ref 2) and with increasing n for given l.

The R-value ranges for various R regions are conveniently characterized by the *reduced internuclear distance* ξ, defined[28] by $R/2a$, where a (*cf.* eq 6 of ref 2) is the approximate radius of maximum density for a suitable AO or (see below) STO. In the UAO region (roughly $\xi < {}^1/_2$), a of the UAO is of course suitable. Rydberg MO's at Rydberg-state R_e values fall in the UAO region. At larger R values (say $\xi \geqslant 1$), one makes use of the fact that any MAO χ in a LCMAO form $\chi_a \pm \chi_b$ can be expressed by a linear combination of STO's. Each STO is characterized by an n and a ζ. A good rule for estimating a and so ξ is then to use in the formula $a = na_0/\zeta$ of eq 6 of ref 2 the n and ζ of the STO whose coefficients are largest in the MAO expression at the given R value (see section V,1 for discussion of $1\sigma_g$, $1\pi_u$, and $1\sigma_u$ of H_2^+ as examples).

In molecules with many electrons, different MO's are in different ξ regions. At R values near R_e, the inner-shell MO's are far out in the LCAO region ($\xi >> 1$), the normally occupied valence-shell MO's are in the middle region ($\xi \approx 1$), any excited valence-shell MO's are in the intermediate region with ξ perhaps somewhat less than 1, while any Rydberg MO's are in the LCUAO region with $\xi << 1$.

As already discussed, ordinary MO correlation is usually replaced for outermost-electron MO's by pseudo-correlation in R ranges where major CM is required. For Rydberg states of *even-electron* molecules the onset of major CM depends mainly not on ξ of the Rydberg MO but on ξ for the valence-shell electrons of the core. CM becomes important when ξ for these reaches perhaps about 1.5 or 2; *i.e.*, R reaches about $1.5R_e$ or $2R_e$. At these R values, ξ for Rydberg MO's, even for those of smallest n, is already small. Thus for Rydberg states, major CM normally sets in already in the UAO region of the Rydberg MO, long before its LCAO region is reached. For H_2, the beginning of major CM is estimated to occur for Rydberg states, $1\sigma_g nx$ (nx = Rydberg MO) at about 1.8 A, or ξ about 0.4 for 2s or $2p\pi$ Rydberg MO's and about 0.2 for 3s, $3p\pi$, or $3d\sigma,\pi,\delta$ MO's. The discussion in this section has been nearly entirely in terms of homopolar molecules. However, rather similar considerations apply to heteropolar molecules.

For *odd-electron* molecules with core at R_e in a closed-shell MO state, major CM at *large R* affects the valence MO's in the core, yet leaves any Rydberg electron essentially independent so that ordinary HeH^+-like correlation can occur; hence, now the Rydberg MO and its T remain significant as $R \rightarrow \infty$. For example, the lowest excited Σ state of NO is a Rydberg state of structure $(NO^+,{}^1\Sigma^+)3s,{}^2\Sigma^+$ at all R values, if we ignore the homogenous perturbations (see section 3) which must occur during the successive crossings of its potential curve by those of nine valence-shell ${}^2\Sigma^+$ states on its way out to dissociation into $N(p^3,{}^4S) + (O^+,p^3,{}^4S)$-$3s,{}^5S$. During the passage to large R values, the NO^+ *core* has to go through radical CM changes.

5. Dissociation Correlations for Rydberg States of H_2 and He_2

It might be thought that the complication of major MO-CM at large R discussed in section 2 would not

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(26) At R_e the SCF MO's $2\sigma_g$ and $2\sigma_u$ deviate greatly from the simple forms $\sigma_g 2s$ and $\sigma_u 2s$ with 2s of N atom SCF form, but as $R \rightarrow \infty$ they must approach $2^{-1/2}(2s_a \pm 2s_b)$ with 2s forms the same and T values *nearly* the same as for free-atom 2s SCF AO's (*cf.* the discussion of He_2 above).

(27) (a) See R. S. Mulliken, *J. Chem. Phys.*, **36**, 3428 (1962), section II, 1–3; *ibid.*, **43**, S39 (1965). (b) Recent calculations by S-I. Kwun in this laboratory indicate, however, that at intermediate R values the UAO or MUAO approximation remains rather good when the LCUAO or LCMUAO fails badly, while the LCMAO also is good.

(28) *Cf.* R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950), where the parameter ξ, originally introduced in ref 6 but poorly named, was renamed.

occur for Rydberg states, and that one could assume that the molecular core and the Rydberg electron could be treated as changing independently thoughout the range of R from 0 to ∞. If that were true, the T and n^* values for a Rydberg MO could properly be followed through all the way. Such a correlation would correspond to the usual practice of finding immediate significance in a direct comparison of T and n^* values for a Rydberg MO taken near R_e with the T and n^* values of the Rydberg AO of one of the atomic dissociation products of the molecular Rydberg state in question. However, as was pointed out in section 4, such a comparison represents only a pseudo-correlation in the case of even-electron molecules. Instead, one should look for relations to united-atom T and n^* values.

To illustrate, let us first consider the $1\sigma_g 1\pi_u, {}^3\Pi_u$ and ${}^1\Pi_u$ and the $1\sigma_g 1\pi_g, {}^3\Pi_g$ and ${}^1\Pi_g$ states of H_2, each of which is the lowest member of a Rydberg series of states.[29] Near R_e, which is close to that of H_2^+, the (unnormalized) forms of the SCF MO's can be described as

$$\begin{aligned} 1\sigma_g &\approx (1\mathrm{s_a} + \lambda 2\mathrm{p}\sigma_\mathrm{a})^{1.2} + (1\mathrm{s_b} + \lambda 2\mathrm{p}\sigma_\mathrm{b})^{1.2} \equiv \\ &\qquad \sigma_g 1\mathrm{s}^{1.2} + \lambda\sigma_g 2\mathrm{p}^{1.2} \\ 1\pi_u &\approx 2\mathrm{p}\pi_{\mathrm{UA}}{}^{(1/2)} \approx \pi_u 2\mathrm{p}_{\mathrm{UA}}{}^{(1/2)} \\ 1\pi_g &\approx 3\mathrm{d}\pi_{\mathrm{UA}}{}^{(1/3)} \approx \pi_g 3\mathrm{d}_{\mathrm{UA}}{}^{(1/3)} \end{aligned} \tag{2}$$

(The superscripts in parentheses refer to orbital exponents.) As is shown by their experimental n^* values, the $1\pi_u$ and $1\pi_g$ MO's undoubtedly resemble united-atom (He) Rydberg AO's, which here are nearly H-atom-like.

Antisymmetric SCF-MO approximation wave functions (unnormalized) corresponding to the above four states can be written as follows.

$$\begin{aligned} \Psi_{\mathrm{MO}}(1\sigma_g 1\pi_u, {}^1\Pi_u \text{ or } {}^3\Pi_u) &= [1\sigma_g(1)1\pi_u(2) \pm \\ &\qquad 1\sigma_g(2)\,1\pi_u(1)][\Psi_S \text{ or } \Psi_T] \\ \Psi_{\mathrm{MO}}(1\sigma_g 1\pi_g, {}^1\Pi_g \text{ or } {}^3\Pi_g) &= [1\sigma_g(1)1\pi_g(2) \pm \\ &\qquad 1\sigma_g(2)1\pi_g(1)][\Psi_S \text{ or } \Psi_T] \end{aligned} \tag{3}$$

In eq 3, 1 and 2 refer to the two electrons, and the + or − signs go with the singlet or triplet spin factors Ψ_S or Ψ_T, respectively. For R near R_e, the briefly symbolized MO's in eq 3 are described in eq 2. But as R is increased, their forms must change; they may be expected to behave very much like those of H_2^+ (*cf.* section V,1) except that the effective Z here is always near 1 instead of being 2 for $R = 0$ and changing to 1 as $R \rightarrow \infty$. Most notably, the $1\pi_g$ MO of H_2 must change from the $\pi_g 3\mathrm{d}$ LCUAO form to the $\pi_g 2\mathrm{p}$ LCAO form when R becomes sufficiently large.[27b] More specifically, $1\pi_u$ and $1\pi_g$ at intermediate R values must assume the forms

$$\begin{aligned} 1\pi_u &= a\pi_u 2\mathrm{p}^{(\zeta)} + b\pi_u 3\mathrm{d}^{(\zeta')} + \ldots \\ 1\pi_g &= a'\pi_g 3\mathrm{d}^{(\zeta'')} + b'\pi_g 2\mathrm{p}^{(\zeta''')} + \ldots \end{aligned} \tag{4}$$

Then as $R \rightarrow \infty$, the (always relatively minor) $\pi_u 3\mathrm{d}$ term in $1\pi_u$ must disappear again while in $1\pi_g$ the $\pi_g 3\mathrm{d}$ term which is predominant at smaller R must disappear leaving only $\pi_g 2\mathrm{p}$.

In addition to changes in the forms of the MO's, other changes from eq 3 must also occur as R increases. In view of the noncrossing rule (and assuming, as calculations show to be justified, that relevant nondiagonal matrix elements are substantial), we know that the lowest energy ${}^1\Pi_u$, ${}^3\Pi_u$, ${}^1\Pi_g$, and ${}^3\Pi_g$ states of H_2, which at R_e are given by eq 2 and 3, must correlate as $R \rightarrow \infty$ with the lowest-energy LCAS states of the same species, whose (unnormalized) wave functions are as follows.

$$\begin{aligned} \Psi_{\mathrm{LCAS}}({}^{1,3}\Pi_{u,g}) &= \{[1\mathrm{s_a}(1)2\mathrm{p}\pi_\mathrm{b}(2) \pm 1\mathrm{s_b}(1)2\mathrm{p}\pi_\mathrm{a}(2)] \pm \\ &\qquad [1\mathrm{s_a}(2)2\mathrm{p}\pi_\mathrm{b}(1) \pm 1\mathrm{s_b}(2)2\mathrm{p}\pi_\mathrm{a}(1)]\}[\Psi_S \text{ or } \Psi_T] \end{aligned} \tag{5}$$

Here the ± signs between the two pairs of brackets belong with Ψ_S and Ψ_T, respectively; the ± signs in the middle of each pair of brackets correspond to the Π_u and Π_g states, respectively (+ for u, − for g). For later reference to the four LCAS states of eq 5, the following brief symbols[9] will be found convenient.

$$\begin{aligned} (1\mathrm{s}\cdot 2\mathrm{p}\pi)_u &\equiv \Psi_{\mathrm{LCAS}}({}^1\Pi_u), \quad (1\mathrm{s}\cdot 2\mathrm{p}\pi)_g \equiv \Psi_{\mathrm{LCAS}}({}^1\Pi_g) \\ (1\mathrm{s}\times 2\mathrm{p}\pi)_u &\equiv \Psi_{\mathrm{LCAS}}({}^3\Pi_u), \quad (1\mathrm{s}\times 2\mathrm{p}\pi)_g \equiv \Psi_{\mathrm{LCAS}}({}^3\Pi_g) \end{aligned} \tag{6}$$

One might be inclined to call the states of eq 5 and 6 Heitler–London-type states, but this is probably inadvisable since the interactions are more complicated than for true HL states.

To bridge the gap between eq 3 and 5, it is necessary to introduce CM, which at R_e is no doubt relatively small. Let us begin with eq 3 and mix $1\sigma_u 1\pi_g, {}^3\Pi_u$ with $1\sigma_g 1\pi_u, {}^3\Pi_u$ and $1\sigma_u 1\pi_u, {}^3\Pi_g$ with $1\sigma_g 1\pi_g, {}^3\Pi_g$, and similarly for the corresponding singlet states. For the four admixed states in SCF-MO approximation, equations identical with eq 3 are valid except that g and u are exchanged for every MO. Since $1\sigma_u$ is strongly antibonding, these states must be high-energy states, although it appears that they should have stable minima at relatively large R values (*cf.* footnote 13 of ref 3). For the mixed states

$$\begin{aligned} \Psi({}^{1,3}\Pi_u) &= \{[1\sigma_g(1)1\pi_u(2) \pm 1\sigma_g(2)1\pi_u(1)] + \\ &\qquad \alpha[1\sigma_u(1)1\pi_g(2) \pm 1\sigma_u(2)1\pi_g(1)]\}[\Psi_S \text{ or } \Psi_T] \\ \Psi({}^{1,3}\Pi_g) &= \{[1\sigma_g(1)1\pi_g(2) \pm 1\sigma_g(2)1\pi_g(1)] + \\ &\qquad \beta[1\sigma_u(1)1\pi_u(2) \pm 1\sigma_u(2)1\pi_u(1)]\}[\Psi_S \text{ or } \Psi_T] \end{aligned} \tag{7}$$

with $\alpha \rightarrow 0, \beta \rightarrow 0$ as $R \rightarrow 0$.

In eq 7, the forms of the MO's $1\sigma_g$, $1\sigma_u$, $1\pi_u$, and $1\pi_g$ must, as already noted, change continuously as R goes from 0 to ∞ (*cf.* eq 4 for the π MO's; for the σ MO's, σ_g goes from the $\sigma_g 1\mathrm{s}$ LCUAO form at 0 to the $\sigma_g 1\mathrm{s}$ LCAO form at ∞ with some admixtures (*cf.* eq 3) at intermediate R values, while σ_u goes from the $\sigma_u 2\mathrm{p}$ LCUAO or $2\mathrm{p}\sigma$ UAO form at $R = 0$ to the $\sigma_u 1\mathrm{s}$ LCAO form at $R = \infty$, with some other admixtures at intermediate R values. The behavior of the MO's (especially $1\pi_g$) at intermediate R values has interesting consequences to be discussed below, but the complete picture can be presented correctly, and more lucidly, if at first we *skip* from $R = R_e$ to $R = \infty$ and introduce in eq 7 LCAO expressions for the MO's

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[29] The ${}^3\Pi_g$ state has been the subject of a recently published intensive study,[5a] yielding an accurate potential curve from $R = R_e$ to ∞. The present more qualitative discussion seems justified as providing added physical insight.

which are good approximations at large R, namely

$$\sigma_g, \sigma_u = 1s_a \pm 1s_b; \quad \pi_u, \pi_g = 2p\pi_a \pm 2p\pi_b \qquad (8)$$

On multiplying out, one readily verifies that, for $\alpha = -1$ and $\beta = 1$, eq 7 reduce to eq 5.[30] One concludes that α and β both change gradually from small negative values at R_e to -1 at $R = \infty$.

On the other hand, for $\alpha = +1$ and $\beta = +1$, one gets[30]

$$\Psi_{\text{ionic}}({}^{1,3}\Pi_{u,g}) = \{[1s_a(1)2p\pi_a(2) \pm 1s_b(1)2p\pi_b(2)] \pm [1s_a(2)2p\pi_a(1) \pm 1s_b(2)2p\pi_b(1)]\}[\Psi_S \text{ or } \Psi_T] \qquad (9)$$

The wave functions of eq 9 are recognized as corresponding to $H^+ + H^-(1s2p\pi, {}^{1,3}\Pi)$. At $R = \infty$ these are only virtual states, since excited 1s2p states of H^- can scarcely be stable,[31] but at smaller R values the stabilizing influence of H^+ on excited H^- should convert them into real states.

One can now invert the reasoning that led from eq 7 to 5 and 9. If we start from $R = \infty$ and proceed toward R_e, we have at first the LCAS group of four states, ${}^{1,3}\Pi_{g,u}$, and a higher-energy group of virtual ion-pair states of the same types. As R decreases, the wave functions of states of like species in these two groups mix more and more, both because of increasing matrix elements and because of decreasing energy separations. Thus we have, for each of the four species

$$\Psi = \Psi_{\text{LCAS}} \pm \gamma\Psi_{\text{ionic}} \qquad (10)$$

If we approximate Ψ_{LCAS} and Ψ_{ion} by eq 5 and 9, respectively, *with the AO's 1s and 2pπ assumed the same* in Ψ_{ion} as in Ψ_{LCAS}, and assume eq 8 for the MO's, then for $\gamma = +1$ we obtain the familiar $1\sigma_g 1\pi_u, {}^{1,3}\Pi_u$ and $1\sigma_g 1\pi_g, {}^{1,3}\Pi_g$ Rydberg states as in eq 3, while for $\gamma = -1$ we obtain the high-energy $1\sigma_u 1\pi_g, {}^{1,3}\Pi_u$ and $1\sigma_u 1\pi_u, {}^{1,3}\Pi_g$ predicted Rydberg states with repulsive cores (*cf.* footnote 13 of ref 3). However, although we have used eq 7 and 8 to obtain these conclusions, we must recognize that concurrently with the growth of γ the forms of the MO's must depart from those of eq 8, the most radical departure being the change of the $1\pi_g$ MO from its large R form $\pi_g 2p_{SA}$ to its small R form $3d\pi_g$ (*cf.* eq 4).[32]

At this point it becomes relevant to refer to theoretical calculations which have been made on the lowest ${}^{1,3}\Pi_u$ and ${}^{1,3}\Pi_g$ states of H_2. Already in the early days of quantum mechanics, Kemble and Zener computed potential curves corresponding to the four pure LCAS functions 5 or 6, using free-atom ($Z = 1$) 1s and 2pπ AO's. The calculation showed stable attractive ${}^3\Pi_u$ and ${}^1\Pi_u$ states but strongly repulsive ${}^3\Pi_g$ and ${}^1\Pi_g$ states.

Let us try to understand these results, beginning with the Π_u states. For them, the agreement of the simple (*i.e.*, *free-atom* 1s and 2pπ) LCAS calculation with experiment is roughly as good as for the ${}^1\Sigma_g{}^+$ normal state of H_2, where LCAS is HL. In the case of the latter state, as is well known, the $\sigma_g 1s^2$ MO structure (which is the same as a 50:50 linear combination of HL with ionic wave functions) gives nearly as good agreement as the HL when 1s AO's with $Z = 1$ are used throughout. Better agreement with experiment is obtained for a linear combination which is predominantly HL but to some extent ionic (*cf.* eq 10 with $0 < \gamma < 1$), or, alternatively (and equivalently), for a linear combination of $\sigma_g 1s^2$ with some $\sigma_u 1s^2$. These agreements with experiment are further improved if 1s AO's with $Z \neq 1$ are used. As has been pointed out by Slater,[33] the HL and ionic AO-type functions, though orthogonal at $R = \infty$, are highly nonorthogonal at R_e of state N of H_2. In fact, they are then much more nearly alike than different.[34] Actually this is not surprising when one notes that the HL and ionic, and indeed also the MO and UAO, functions become formally *identical* at $R = 0$.

Analogous relations hold for the $1s \cdot 2p\pi$ and $1s \times 2p\pi, {}^{1,3}\Pi_u$ LCAS states (see eq 5 and 9 for the LCAS and ionic functions) and make understandable the rather good agreement of the simple LCAS Ψ's (still better if increased Z is used for 1s) with experiment without inclusion of any Ψ_{ionic}. In other words, addition of Ψ_{ionic} (*cf.* eq 10), because to a rather large extent it is the *same* as Ψ_{LCAS}, does not contribute to improving Ψ_{LCAS} as much as, on the basis of the discussion preceding eq 10, one might have naively expected. Or to put it in still another way, $1s2p\pi, \Pi_u$ LCAS functions apparently are not bad approximations to the correct Ψ's for the Rydberg states whose MO configuration description is $1\sigma_g 1\pi_u$. Nevertheless, if SCF MO's are used for $1\sigma_g$ (which is nearly the same here as in $H_2{}^+$) and for $1\pi_u$ (rather nearly like a $2p\pi_{UA}$ AO with $Z = 1$), the $1\sigma_g 1\pi_u, {}^{1,3}\Pi_u$ MO-type Ψ's are undoubtedly very considerably better than the LCAS at R_e, and at R_e doubtless need only relatively little CM to make them exact. As $R \rightarrow 0$, however, the LCAS, ionic, MO, and UAO single-configuration functions all become formally identical, in the same way as for the normal state of H_2.

Turning now to the lowest-energy ${}^3\Pi_g$ and ${}^1\Pi_g$ states, we know *experimentally* that at R values near R_e of $H_2{}^+$, these are Rydberg states with stable minima (here they are well describable by the MO configuration $1\sigma_g 3d\pi$), while according to the noncrossing rule their wave functions must as $R \rightarrow \infty$ go over to the $1s2p\pi, {}^{1,3}\Pi_g$ LCAS functions. The $v = 0$ levels for these states are only 0.66 ev below the energy of the separated (1s + 2p) atoms, and a consideration of the experimental constants of the potential curves indicates that the energies rise to a maximum with increasing R before descending to their 1s + 2p asymptotes as $R \rightarrow \infty$.[35] Since the $1s2p\pi, {}^{1,3}\Pi_g$ LCAS

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[30] In the passage from eq 7 with $\alpha < 0$ and $\beta < 0$ to the limiting case of eq 5, we may assume that 1s and 2pπ of eq 8 go over to H-atom AO's as $R \rightarrow \infty$. In the passage from eq. 7 with $\alpha >> +1$ and $\beta >> +1$ (which represent the higher energy ${}^{1,3}\Pi_u$ and ${}^{1,3}\Pi_g$ states) to the limiting case of eq 9, we must in the limit assume quite different 1s and 2pπ AO's in eq. 8. However, we are actually not much interested in eq 9, since they become completely unrealistic as $R \rightarrow \infty$.

[31] C. L. Pekeris, *Phys. Rev.*, **126**, 1470 (1962), has shown that the $1s2s, {}^3S$ and ${}^1S$ states of H^- are unstable or at best barely stable.

[32] Although the $1\sigma_u$ MO must also change its form from $\sigma_u 1s_{SA}$ to $2p\sigma_{UA}$ as $R \rightarrow 0$, the change toward the UA form cannot have progressed nearly as far, at R_e of the Rydberg states (near R_e of $H_2{}^+$), as for $1\pi_g$, and we shall in the present discussion neglect this extra complication and the related complication that $\sigma_g 1s$ does not retain quite the simple $\sigma_g 1s$ form near R_e.

[33] J. C. Slater, *J. Chem. Phys.*, **19**, 220 (1951); and "Quantum Theory of Molecules and Solids," Vol. I, "Electronic Structure of Molecules," McGraw-Hill Book Co., Inc., New York, N. Y., 1963.

[34] The extent of nonorthogonality depends, of course, on whether free-atom 1s AO's or modified AO's are used.

[35] See ref 3, footnote 13. The discussion in ref 3 refers primarily to He_2, but analogous considerations apply for most of the Rydberg states of H_2 (see Table IV below for data on both).

functions give only pure repulsion curves, something more general is evidently required.

Browne[4b] computed approximate $^1\Pi_g$ and $^3\Pi_g$ potential curves using as a trial function a linear combination of $1s2p\pi$ and $1s3d\pi$ LCAS functions.

$$\begin{aligned}\Psi(^3\Pi_g) &= c\Psi(1s\times 3d\pi)_g + d\Psi(1s\times 2p\pi)_g \\ \Psi(^1\Pi_g) &= c'\Psi(1s\cdot 3d\pi)_g + d'\Psi(1s\cdot 2p\pi)_g\end{aligned} \tag{11}$$

(He also included $1s3p\pi$ functions, but their effect was relatively minor; it is nearly the same[27a] as merely adding $2p\pi$ with a modified scale factor.) At large R, $c,c' \rightarrow 0$ and $d,d' \rightarrow 1$, while at R values near R_e of H_2^+, c,c' approach 1 and d,d' become small. The computed energy goes over a maximum at R near 2 A, with a minimum at R roughly equal to the experimental R_e (1.06 A) of the $1\sigma_g3d\pi$ Rydberg states, although considerably higher in energy. The existence of a maximum in the $^3\Pi_g$ curve has also been confirmed by the accurate calculations of Wright and Davidson.[5a]

Thus with the *double* LCAS functions of eq 11, there is a closeness of agreement with experiment similar to that found for the $^{1,3}\Pi_u$ states using the $1s2p\pi$ *single* LCAS functions. The fact that moderately good agreement with experiment and with expectations for the MO wave functions $1\sigma_g3d\pi,{}^{1,3}\Pi_g$ is obtained without adding ionic terms as in eq 10 is evidently to be explained in the same way as for the $^{1,3}\Pi_u$ states. Namely, while inclusion of the corresponding ionic terms should lead to marked improvement, the strong nonorthogonality of the former to the LCAS terms enables the latter alone to go far[36] toward representing the accurate wave functions. However, while for the normal state of H_2 eq 10 with a relatively small γ minimizes the energy, it seems clear that γ values approaching $+1$ for $^{1,3}\Pi_u$ and -1 for $^{1,3}\Pi_g$ would be best for the Rydberg states, which are much more accurately representable by a single MO configuration ($1\sigma_g2p\pi$ or $1\sigma_g3d\pi$) than in the case of the normal state. It is now evident that eq 10 gives good MO wave functions for the lowest $^{1,3}\Pi_u$ and $^{1,3}\Pi_g$ Rydberg states if for Ψ_{APAS} we use $(1s2p\pi)_u$ functions for the $^{1,3}\Pi_u$ states but use the *double* LCAS functions of eq 11 for the $^{1,3}\Pi_g$ states, and if at the same time we let $\pm\gamma$ change from 0 at large R to values near ± 1 near the R_e values of the Rydberg states. (Further, the ζ values for the AO's, especially 1s, must not be left at their free-atom values, but must be readjusted to minimize the energy.) In contrast to those for the normal and the $^{1,3}\Pi_u$ states, the $^{1,3}\Pi_g$ LCAS functions which are valid as $R \rightarrow \infty$, and the corresponding ionic functions, do *not* now become formally identical with the MO and UAO functions as $R \rightarrow 0$.

Reversing the argument used above and proceeding outward from R_e to large R values, we may start again with eq 7. If now (as was clearly what we should have done) we substitute eq 4 for $1\pi_u$ and $1\pi_g$ in eq 7, we see that as α and β change from 0 toward -1, eq 7 can reduce for the $^{1,3}\Pi_g$ states approximately to the double HL form of eq 11, with d at first large and c small as R increases beyond R_e, but d decreasing and c increasing as R increases, until $d \rightarrow 0$ and $c \rightarrow 1$ as $R \rightarrow \infty$.[37] It seems likely that the R values at which $c = d$ and $c' = d'$ are near the maxima of the respective potential curves.

If the argument of the preceding paragraph using eq 7 and 4 is applied to the $^3\Pi_u$ and $^1\Pi_u$ states, one concludes that their wave functions should be better approximated at intermediate R values by the double LCAS forms

$$\left.\begin{aligned}\Psi(^3\Pi_u) &= f\Psi(1s\times 2p\pi)_u + g\Psi(1s\times 3d\pi)_u \\ \Psi(^1\Pi_u) &= f'\Psi(1s\cdot 2p\pi)_u + g'\Psi(1s\cdot 3d\pi)_u\end{aligned}\right\} \tag{12}$$

than by the simple forms with $f = f' = 1$ and $g = g' = 0$. However, the improvement here is relatively minor,[38] in contrast to the essentiality of the corresponding improvement in eq 11 for the $^{1,3}\Pi_g$ states.

The procedure just used in approximately deriving the double LCAS functions 11 and 12 from the MO + CM equations (7) by substituting double LCAO expressions as in eq 4 for the MO's can be applied equally well to all Rydberg states of H_2. For each Rydberg state of configuration $1\sigma_g m\lambda_p$ (where p is the parity (g or u) of the Rydberg MO $m\lambda_p$) and for its CM complement $1\sigma_u m\lambda_q$ (where q is the parity opposite to p), the appropriate double LCAO expressions for $m\lambda_p$ and $m\lambda_q$, taken to be formally the same as for like-labeled MO's of H_2^+ (see V,1), can be written down in the manner of eq 4 and substituted into the proper analogs to eq 7 to yield double LCAS functions analogous to eq 11 and 12.

Results of this procedure are collected in Table II for many of the lower-energy Rydberg states of H_2 and for the valence-shell states. Only those LCAS functions (in one case also the $(1s^2)_u$ ionic APAS) are listed which are believed to be necessary and sufficient to yield qualitatively correct $U(R)$ curves. Guided by the H_2^+ forms, LCAS expressions with hybrid AO's (*i.e.*, parabolic-coordinate H-atom quantization; *cf.* V,1) occur for large R in a number of cases. Alternatively, these can be viewed as double LCAS functions; for example, $1s\cdot 2di'$ is the same as $2^{-1/2}\cdot(1s\cdot 2s - 1s\cdot 2p\sigma)$. Actually in such cases the coefficients of the components of a hybrid LCAS function at large R are for one or two reasons not expected to be exactly those for the ideal hybrid. In fact at very large R, where valence forces have become negligible, hybridization is lost because first-order dispersion forces cause otherwise degenerate LCAS functions of different l to have slightly different energies;[39] thus strictly speaking each $U(R)$ curve must correspond asymptoti-

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(36) When recognizing the nonorthogonality of corresponding LCAS and ionic terms except as $R \rightarrow \infty$, it is desirable to point out that the LCAS forms $(1s2p\pi)_g$ and $(1s3d\pi)_g$ used in eq 11 *also* are nonorthogonal except as $R \rightarrow \infty$; likewise that the LCAO forms π_g3d and π_g2p (likewise π_u3d and π_u2p) in eq 4 are nonorthogonal except as $R \rightarrow \infty$; similarly $(1s2s)_g$ and $(1s2p\sigma)_g$, and $(1s2s)_u$ and $(1s2p\sigma)_u$.

(37) The accurate description is more complicated because b/a for $1\pi_u$ in eq 4 is presumably considerably smaller than b'/a' for $1\pi_g$. It should further be kept in mind that the coefficients in eq 4 vary with R, also that the function pairs π_u2p and π_u3d, likewise π_g3d and π_g2p, are nonorthogonal.[36] Moreover, the best values of these coefficients are probably rather different for the π_u or π_g used in the CM terms (following α or β) in eq 7 than for those in the main MO terms. One must also not forget that the ζ values in eq 4 are different for π_u and π_g, and for the CM and main π_u and π_g's. In spite of all these complications, the general trend of the simple reasoning in the text seems convincing as a qualitative explanation of the transition to an eq 11 type of wave function as R gets large.

(38) The extra terms in eq 12 correspond to the occurrence of $b\pi_u3d$ in $1\pi_u$ (and of $a'\pi_g3d$ in $1\pi_g$) in eq 4 when substituted in eq 7. However, since b vanishes both as $R \rightarrow 0$ and $R \rightarrow \infty$ and so can never be very large, the related coefficients g and g' (or rather, perhaps, their squares) in eq 12 should never be large.

(39) *Cf.* R. S. Mulliken, *Phys. Rev.*, **120**, 1674 (1960).

Table II. Dissociation Correlations for H_2

MO state[a,b]		Major LCAS terms: Rather large R[c]	Very large R	Remarks[d]
Unpr	$1\sigma_g{}^2, {}^1\Sigma_g{}^+$	$1s\cdot 1s$	$1s\cdot 1s$	VS state
Partly Pr	$1\sigma_g \times 1\sigma_u, {}^3\Sigma_u{}^+$	$(1s\times 2p\sigma)_u$ and esp. $(1s\times 1s)$	$1s \times 1s$	Semi-Ry state
Partly Pr	$1\sigma_g\cdot 1\sigma_u, {}^1\Sigma_u{}^+$	$(1s\cdot 2p\sigma)_u$ and $(1s^2)_u$	$(1s\cdot 2p\sigma)_u$	Semi-Ry state[e,f]
Unpr	$1\sigma_g \times 2s, {}^3\Sigma_g{}^+$	$(1s\times 2s)_g$ and $(1s\times 2di')_g$	$(1s \times 2p\sigma)_g$	*g*
Unpr	$1\sigma_g\cdot 2s, {}^1\Sigma_g{}^+$	$(1s\cdot 2s)_g$ and $(1s\cdot 2di')_g$	$(1s\cdot 2s)_g$	*g*, *h*
Pr	$1\sigma_g \times 3p\sigma, {}^3\Sigma_u{}^+$	$(1s\times 3p\sigma)_u$ and $(1s\times 2di')_u$	$(1s \times 2s)_u$	
Pr	$1\sigma_g\cdot 3p\sigma, {}^1\Sigma_u{}^+$	$(1s\cdot 3p\sigma)_u$ and $(1s\cdot 2di')_u$	$(1s\cdot 2s)_u$	*e*, *f*
Unpr	$1\sigma_g 2p\pi, {}^{1,3}\Pi_u$	$(1s2p\pi)_u$	$(1s2p\pi)_u$	*i*
Pr	$1\sigma_g \times 3d\sigma, {}^3\Sigma_g{}^+$	$(1s\times 3d\sigma)_g$ and $(1s\times 2di)_g$	$(1s \times 2s)_g$	*j*
Pr	$1\sigma_g\cdot 3d\sigma, {}^1\Sigma_g{}^+$	$(1s\cdot 3d\sigma)_g$ and $(1s\cdot 2di)_g$	$(1s\cdot 2p\sigma)_g$	*j*, *k*
Pr	$1\sigma_g 3d\pi, {}^{1,3}\Pi_g$	$(1s\ 3d\pi)_g$ and $(1s2p\pi)_g$	$(1s2p\pi)_g$	*i*
Unpr	$1\sigma_g 3d\delta\ {}^{1,3}\Delta_g$	$(1s3d\delta)_g$	$(1s3d\delta)_g$	
Pr	$1\sigma_g \times 4f\sigma, {}^3\Sigma_u{}^+$	$(1s\times 4f\sigma)_u$ and $(1s\times 2di)_u$	$(1s \times 2p\sigma)_u$	
Pr	$1\sigma_g\cdot 4f\sigma, {}^1\Sigma_u{}^+$	$(1s\cdot 4f\sigma)_u$ and $(1s\cdot 2di)_u$	$(1s\cdot 3p\sigma)_u$	*e*

[a] Pr and Unpr refer to states with a promoted or unpromoted outer MO, respectively. For a promoted MO, the principal quantum number *n* for the UAO is larger than for the AO of the pseudo-correlated LCAO expression or, what is the same, for the outer AO of its LCAS dissociation product (see V,1 for definitions and discussion of promoted and unpromoted MO's in $H_2{}^+$). [b] A UAO symbol is used for Rydberg MO's, since these at R_e are close to being UAO's. Singlet and triplet states are given separately *in those cases* where their asymptotes as $R \to \infty$ are different; *otherwise* they are given together. [c] The first of the two LCAS functions listed in this column is that which is predominant at small R; the second is that predominant at large R. For *unpromoted* states which need two LCAS terms, these are partly identical. For example, in the $1\sigma_g 2s, {}^{1,3}\Sigma_g{}^+$ states (these are actually the *only* examples given in Table III; others would include 3s, $2p\pi$, $4d\delta$, . . .), the LCAS function $(1s2di')_g$ is the same as $2^{-1/2}[(1s2s)_g - (1s2p\sigma)_g]$ and so is partly identical with the $(1s2s)_g$ term. The pair of LCAS functions is thus equivalent to the pair $(1s2s)_g$ and $(1s2p\sigma)_g$, *but* with higher weight for the former and opposite signs for the two. For SAO's with $n > 2$, increasingly complicated hybrids are needed for the large R LCAS function in this column. [d] VS means valence state. Ry means Rydberg. [e] The three ${}^1\Sigma_u{}^+$ states which at small R are $1\sigma_g\cdot 1\sigma_g$, $1\sigma_g\cdot 3p\sigma$, and $1\sigma_g\cdot 4f\sigma$ need to be considered together, since they become strongly mixed at large R values because of avoided crossings at about 10 au of the $(U)R$ curve of the H^+H^- APAS $(1s^2)_u$ function (which on the basis of the procedure outlined in the text should be the predominant component for the first-named of these three states) with the $U(R)$ curves of the $(1s\cdot 2di')_u$ and $(1s\cdot 2di)_u$ functions, which should be the predominant components of the other two of the three states (see J. T. Lewis, *Proc. Phys. Soc.* (London), **68**, 632 (1935), for relevant calculations on this mixing). *If crossing could have occurred without mixing*, the $1\sigma_g\cdot 1\sigma_u$ curve would have dissociated smoothly following $(1s^2)_u$ to H^+ plus $H^-(1s^2)$, and the other two following $(1s\cdot 2x)_u$ to H(1s) plus H(2x), where x is 2s for one and $2p\sigma$ for the other; if first-order dispersion terms (see text) had been absent, x would be 2di′ for $1\sigma_g\cdot 3p\sigma$ and 2di for $1\sigma_g\cdot 4f\sigma$, but because these terms are present and cause $(1s\cdot 2p\sigma)_u$ to be lower in energy than $(1s\cdot 2s)_u$ at very large R (see ref 54), x would have to be $2p\sigma$ for $1\sigma_g\cdot 3p\sigma$ and 2s for $1\sigma_g\cdot 4f\sigma$. But since *actually* there is avoided crossing accompanied by profound mixing (see Lewis, above), the $1\sigma_g\cdot 1\sigma_u$ $U(R)$ curve beyond the crossing point (that is, for $R > 10$ au) must go to dissociation *via* the $1\sigma_g\cdot 3p\sigma$ asymptote, namely $(1s\cdot 2di')_u$ at large R, going over to $(1s\cdot 2p\sigma)_u$ at very large R. This forces the $1\sigma_g\cdot 3p\sigma$ curve to take over the asymptotic behavior properly belonging to the $1\sigma_g\cdot 4f\sigma$ curve, namely, $(1s\cdot 2di)_u$ at large R going over to $(1s\cdot 2s)_u$ at very large R. Finally, the $1\sigma_g\cdot 4f\sigma$ curve, after coming down toward its proper asymptote, is forced to start up again, following the $(1s^2)_u$ ion-pair curve; however, further mixing with 3-quantum ${}^1\Sigma_u{}^+$ LCAS functions will permit it to dissociate at that level, probably to $(1s\cdot 3d\sigma)_u$. [f] Experimentally (T. Namioka, *J. Chem. Phys.*, **43**, 1636 (1965)), the $1\sigma_g\cdot 1\sigma_u$ $U(R)$ curve goes smoothly toward dissociation at the 2-quantum level, as would be expected from the discussion in footnote *e*, while the $1\sigma_g\cdot 3p\sigma$ curve shows a normal shape near R_e but at larger R goes abnormally slowly toward dissociation at the 3-quantum level. This somewhat peculiar behavior of the $1\sigma_g\cdot 3p\sigma$ curve is consistent with the discussion in footnote *e*. (The analogous $1\sigma_g{}^2 1\sigma_u\cdot 3p\sigma$ curve of He_2 has a maximum at moderately large R; see below). The nature of the wave function of the $1\sigma_g\cdot 1\sigma_u$ state as a function of R has been extensively discussed in the literature on the basis of approximate theoretical calculations (see C. S. Tschudi and N. V. Cohan, *ibid.*, **34**, 401 (1961); A. Batana and N. V. Cohan, *Mol. Phys.*, **7**, 97 (1963); P. Phillipson and R. S. Mulliken, *J. Chem. Phys.*, **33**, 615 (1960), and earlier references given in these papers). A very recent, not yet published, very accurate James–Coolidge type calculation of the potential curve out to 12 au by W. Kolos now permits definite conclusions. A decomposition by Kolos (private communication) of his wave function into a linear combination, $c_1(1s\cdot 2s)_u + c_2(1s\cdot 2p\sigma)_u + c_3(1s^2)_u$, of three nonorthogonal APAS functions plus an orthogonal residue Ω, where 2s and $2p\sigma$ are free H-atom AO's ($Z = 1$) while 1s in $(1s^2)_u$ is an approximate H^- ion AO ($Z \approx 0.7$), shows $(1s\cdot 2p\sigma)_u$ strongly predominant at small R values, as expected, and $(1s^2)_u$ predominant from about 3 to 6 au, again in agreement with expectations from Table III. The component $(1s\cdot 2s)_u$ is minor until large R values; its coefficient c_1 is opposite in sign to c_2 suggesting that the above linear combination be rewritten as $c_1'(1s\cdot 2di')_u + c_2'(1s\cdot 2p\sigma)_u + c_3'(1s^2)_u + \Omega$. Between 10 and 12 au, c_3' falls rapidly, while c_2' and $-c_1'$ rise. At 12 au $-c_1' > c_3' > c_2'$ (or in terms of the c's, $c_2 > -c_1 > c_3$), in agreement with the expectations of Table III and footnote *e*, namely, $(1s\cdot 2di')_u$ predominant at large R beyond the point of avoided crossing with $(1s^2)_u$ near 10 au, but finally giving way to $(1s\cdot 2p\sigma)_u$ at very large R because of the first-order dispersion effect. [g] See comments in footnote *c*. [h] See discussion in section 3 (and *cf.* ref 14) on the two avoided crossings, one at rather small R, one near 10 au, both by the H^+H^- state $1\sigma_u{}^2, {}^1\Sigma_g{}^+$ (MO description) or $(1s^2)_g$ (APAS description). At large R well beyond 10 au, these disturbances should have subsided. [i] See comments in section 3 on London dispersion effects on the shape of the ${}^1\Pi$ $U(R)$ curve at large R. [j] Crossing with $1\sigma_g 3s$ occurs close to R_e for the ${}^1\Sigma_g{}^+$ and at somewhat smaller R for the ${}^3\Sigma_g{}^+$, but interaction is weak (see section 3 and ref 12, also section 4 and ref 20). [k] Avoided-crossing interaction with $1\sigma_u{}^2$ at rather small R and again at large R (hence, indirectly also with $1\sigma_g\cdot 2s$) must cause complications similar to those in $1\sigma_g\cdot 2s$ (see footnote *h*).

cally to a single pure *l* LCAS function; such asymptotes, making use of the noncrossing rule and theoretically calculated first-order dispersion energies, are listed for "Very large R" in Table II.

For He_2, dissociation relations similar to those for H_2 exist for the Rydberg states,[3,4] except that the complications which occur for the ${}^1\Sigma_g{}^+$ and ${}^1\Sigma_u{}^+$ states of H_2 due to avoided crossings with H^+H^- $(1s^2)_g$ and $(1s^2)_u$ curves have no counterpart for He_2. A table analogous to Table II for H_2 can be constructed by the same kind of procedure used there to go over from MO functions at small R to (usually double) LCAS functions at rather large R and single LCAS functions at large R. The procedure is simpler for He_2 because first-order dispersion effects (although not absent for some states) are not needed as in H_2 to carry over hybrid AO into pure *l* functions as $R \to \infty$.

As an example, the MO states $1\sigma_g{}^2 1\sigma_u 1\pi_u, {}^{1,3}\Pi_g$ and $1\sigma_g{}^2 1\sigma_u 1\pi_g, {}^{1,3}\Pi_u$ must respectively mix, on the way to dissociation, with $1\sigma_g 1\sigma_u{}^2 1\pi_g, {}^{1,3}\Pi_g$ and $1\sigma_g$-

Table III. Dissociation Correlations for He_2

MO state	Major LCAS terms[a]: Rather large R	Major LCAS terms[a]: Large R
$1\sigma_g{}^2 1\sigma_u{}^2,{}^1\Sigma_g{}^+$	$1s^2 1s^2$	
$1\sigma_g{}^2 1\sigma_u 2s,{}^{1,3}\Sigma_u{}^+$	$(1s^2 1s2s)_u$ and $(1s^2 1s2di')_u$	$(1s^2 1s2s)_u$
$1\sigma_g{}^2 1\sigma_u 2p\pi,{}^{1,3}\pi_g$	$(1s^2 1s2p\pi)_g$	$(1s^2 1s2p\pi)_g$
$1\sigma_g{}^2 1\sigma_u 3p\sigma,{}^{1,3}\Sigma_g{}^+$	$(1s^2 1s3p\sigma)_g$ and $(1s^2 1s2di')_g$	$(1s^2 1s2s)_g$
$1\sigma_g{}^2 1\sigma_u 3d\sigma,{}^{1,3}\Sigma_u{}^+$	$(1s^2 1s3d\sigma)_u$ and $(1s^2 1s2di)_u$	$(1s^2 1s2p\sigma)_u$
$1\sigma_g{}^2 1\sigma_u 3d\pi,{}^{1,3}\Pi_u$	$(1s^2 1s3d\pi)_u$ and $(1s^2 1s2p\pi)_u$	$(1s^2 1s2p\pi)_u$
$1\sigma_g{}^2 1\sigma_u 3d\delta,{}^{1,3}\Delta_u$	$(1s^2 1s3d\delta)_u$	$(1s^2 1s3d\delta)_u$
$1\sigma_g{}^2 1\sigma_u 4f\sigma,{}^{1,3}\Sigma_g{}^+$	$(1s^2 1s4f\sigma)_g$ and $(1s^2 1s2di)_g$	$(1s^2 1s2p\sigma)_g$

[a] In those cases where an LCAS form with a hybrid AO is indicated at intermediate R, the hybrid AO is doubtless not the ideal 50:50 hybrid indicated (or with other ideal ratios for LCAS's with hybrid AO's with $n > 2$), but rather should be weighted toward the AO which is alone present as $R \rightarrow \infty$. However, earlier calculations by Browne[4a] on the Σ states are in agreement with the conclusion reached here that hybrid-AO LCAS's are needed.

Table IV. Maxima and Minima in H_2 and He_2 Rydberg-State Potential Curves

	H_2 energies, ev[a]				He_2 energies, ev[b]		
State	H	h	D_0(to)	State	H	h	D_0(to)
$3d\delta,{}^1\Delta_g$	2.50	0	2.50 ($3d\delta$)	${}^1\Delta_u$	2.18	0	2.18 ($3d\delta$)
$3d\pi,{}^1\Pi_g$	(0.96)	(0.3)[c]	0.66 ($2p\pi$)	${}^1\Pi_u$	(0.67)	(0.3)[f]	0.37 ($2p\pi$)
$3d\sigma,{}^1\Sigma_g{}^+$	(0.98)	(0.3)[c]	0.68 ($2p\sigma$)	${}^1\Sigma_u{}^+$	[0.7?]	[0.3?][g]	0.39 ($2p\sigma$)
$3p\pi,{}^1\Pi_u$	2.44	0	2.44 ($3d\pi$)	${}^1\Pi_g$	2.25	0	2.25 ($3p\pi$)
$3s,{}^1\Sigma_g{}^+$	2.43	0	2.43 (3σ)	${}^1\Sigma_u{}^+$	2.18	0	2.18 (3s)
$3p\sigma,{}^1\Sigma_u{}^+$	0.90	0[d]	0.90 (2s)	${}^1\Sigma_g{}^+$	(1.4)[h]	(0.5)[h]	0.84 (2s)
$2p\pi,{}^1\Pi_u$	2.26	0	2.26 ($2p\pi$)	${}^1\Pi_g$	2.35	0	2.35 ($2p\pi$)
$2s,{}^1\Sigma_g{}^+$	2.25	0	2.25 (2s)	${}^1\Sigma_u{}^+$	2.19	0.17[i]	2.19 (2s)
$3d\delta,{}^3\Delta_g$	2.53	0	2.53 ($3d\delta$)	${}^3\Delta_u$	2.19	0	2.19 ($3d\delta$)
$3d\pi,{}^3\Pi_g$	1.07	0.41[e]	0.66 ($2p\pi$)	${}^3\Pi_u$	(0.48)	(0.35)[f]	0.13 ($2p\pi$)
$3d\sigma,{}^3\Sigma_g{}^+$	1.10	0.41[e]	0.69 (2s)	${}^3\Sigma_u{}^+$	[0.5?]	[0.35?][g]	0.16 ($2p\sigma$)
$3p\pi,{}^3\Pi_u$	2.59	0	2.59 ($3p\pi$)	${}^3\Pi_g$	2.21	0	2.21 ($3p\pi$)
$3s,{}^3\Sigma_g{}^+$	2.58	0	2.58 ($3p\sigma$)	${}^3\Sigma_u{}^+$	2.06	0	2.06 (3s)
$3p\sigma,{}^3\Sigma_u{}^+$	1.32	0	1.32 (2s)	${}^3\Sigma_g{}^+$	(1.0)[h]	(0.6)[h]	0.34 (2s)
$2p\pi,{}^3\Pi_u$	2.79	0	2.79($2p\pi$)	${}^3\Pi_g$	2.24	0	2.24($2p\pi$)
$2s,{}^3\Sigma_g{}^+$	2.76	0	2.76 ($2p\sigma$)	${}^3\Sigma_u{}^+$	1.69	0.14[i]	1.69 (2s)

[a] The D_0 values (energies of dissociation from the $v = 0$ vibrational level) are based on the theoretically known D_0 of $H_2{}^+$ (2.648 ev), together with the known excitation energies T_0 of the $v = 0$ levels of the various states, and the assumption of dissociation in accordance with the noncrossing rule, except that crossing of $3s,{}^3\Sigma_g{}^+$ and $3d\sigma,{}^3\Sigma_g{}^+$ is assumed to occur so that the former dissociates to give one $n = 2$ and the latter to give one $n = 3$ H atom. The T_0 values are mainly those given in Herzberg's book on diatomic molecules, with some updating. The h and H values are the heights of the maxima (if any) of the potential curves above, respectively, the dissociation asymptotes and the $v = 0$ levels of the states. [b] The statements in footnote *a* also apply here, except for the value of D_0 of $He_2{}^+$. Although this is not known exactly, the value 2.20 ev has been used here. This is the best present estimate, based on the rather accurate theoretical calculations of P. A. Reagan, J. C. Browne, and F. A. Matsen, *Phys. Rev.*, **132**, 304 (1963), who find 2.24 ev as a lower limit for D_e, from which J. C. Browne (private communication) estimates that D_e is close to 2.30 ev. For $D_e = 2.30$ ev, D_0 is 2.20 ev. [c] For $3d\pi\,{}^1\Pi_g$, Browne's[4b] theoretical calculations gave $h = 0.451$ ev. Assuming this value to be too large by 0.15 ev (*cf.* footnote *e*), 0.3 ev as given above is obtained. Then assuming equality of h for $3d\sigma$ and $3d\pi$ to exist as has been shown for the *triplet* states, the estimated value of 0.3 ev for $3d\sigma,{}^1\Sigma_g{}^+$ is obtained. [d] From *experimental* determination of the potential curve; T. Namioka, *J. Chem. Phys.*, **43**, 1636 (1965). The curve has an abnormal shape, but unlike its counterpart in He_2 has no maximum. [e] From the accurate theoretical calculations of ref 5. In the case of $3d\sigma,{}^3\Sigma_g{}^+$, *crossing* of $3s\sigma$ and $3d\sigma$ is here assumed.[12] For $3d\pi,{}^3\Pi_g$, Browne, in a less accurate calculation,[4b] found $h = 0.55$ ev, 0.15 ev larger than by ref 5a. [f] From theoretical calculations of ref 4b, ${}^1\Pi_u$ has a maximum of height 0.46 ev and ${}^3\Pi_u$ of 0.60 ev. Subtracting 0.15 from each (*cf.* footnotes *c* and *e*), the estimated values given above are obtained. [g] There seems little doubt that maxima occur in these cases[3] as in all the other analogous cases where computations have been made. [h] Approximate theoretical calculations by Browne[4a] gave $h = 0.7$ ev for $3p\sigma,{}^1\Sigma_g{}^+$ and 0.8 ev for ${}^3\Sigma_g{}^+$. These are probably (*cf.* footnote *e*) too large, and an estimated allowance for this gives the values listed in the table. Vibrational levels of the $3p\sigma,{}^3\Sigma_g{}^+$ state up to 0.58 ev ($v = 4$) and for the $3p\sigma,{}^1\Sigma_g{}^+$ up to 0.86 ev ($v = 5$) have been observed experimentally by M. L. Ginter [*J. Chem. Phys.*, **42**, 561 (1965)], and the observed levels in each case extrapolate to convergence at an H value near that given in parentheses in Table I. [i] These theoretically computed maxima (R. D. Poshusta and F. A. Matsen, *Phys. Rev.*, **132**, 307 (1963) for the ${}^3\Sigma_g{}^+$ and ref 4a for the ${}^1\Sigma_g{}^+$), supported also by experimental evidence, are of an unexplained type unless perhaps the requirement that Ψ include an LCAS with di′ AO at intermediate R values, as compared with 2s at large R values (*cf.* Table III), somehow introduces repulsion at large R values.

$1\sigma_u{}^2 1\pi_u,{}^{1,3}\Pi_u$ (each $1\pi_g$ having an LCAO form which changes, as R increases, from mainly $\pi_g 3d$ to mainly $\pi_g 2p$), in order to dissociate into the corresponding ${}^{1,3}\Pi_{g,u}$ LCAS states (briefly symbolized, $1s_a{}^2 1s_b 2p\pi_b \pm 1s_b{}^2 1s_a 2p\pi_a$ with + for Π_g and − for Π_u, respectively). Or, conversely, in order to obtain the above-mentioned MO states, the LCAS states just mentioned must mix with corresponding virtual He^+He^- states (briefly symbolized, $1s_a 1s_b{}^2 2p\pi_b \pm 1s_b 1s_a{}^2 2p\pi_a$, ${}^{1,3}\Pi_{g,u}$), and in the case of the ${}^{1,3}\Pi_u$ states *also* with additional LCAS states in which $3d\pi$ is substituted for $2p\pi$. Table III summarizes the dissociation correlations which one arrives at for these II and other states of He_2.

It is of interest now to review what is known of the dissociation energies D_0, and the heights of the dissociation maxima in those cases where they occur, for the molecules H_2 and He_2. This is done in Table IV, which shows approximate theoretical values for the heights (H) of the maxima above the lowest vibrational level ($v = 0$) of each state and then (h) above the energy of the dissociated atoms; in the absence of a maximum, $H = D_0$ and $R = 0$. In a few cases the values of D_0 are notably small, thus (in view of evidence of normal $U(R)$ shape near R_e) pointing most strongly toward the existence of a maximum. For the $3p\sigma,{}^3\Sigma_g{}^+$ state of He_2, Ginter has observed actual vibrational levels up to 0.58 ev above the $v = 0$ level, hence 0.22 ev above the dissociation asymptote if the value $D_0 = 2.20$ ev for $He_2{}^+$ is correct; the observed vibrational levels, moreover, converge toward an H value of 1.0 ev in agreement with the approximate theoretical value (*cf.* footnote *h* in Table IV).

In the event of an avoided crossing (*cf.* section 3) of an attractive and a repulsive potential curve of the same electronic species, a maximum occurs in the lower of the two resultant curves. In the case of the promoted states in eq 11 and Tables II and III one can, if one wishes, attribute the potential maxima described in earlier paragraphs to avoided crossings between repulsive and attractive LCAS potential curves. For example, for H_2 one has a strongly repulsive LCAS curve for $(1s\cdot 2p\pi)_g$ of eq 11 and a corresponding presumably moderately attractive curve for $(1s\cdot 3d\pi)_g$, and similarly for the analogous triplet H_2 and the corresponding singlet and triplet He_2 curves.[40] Thus for H_2 or He_2, avoided crossings of the separate potential curves of the two LCAS states,[36] which are required for the cases which correspond at small R to promoted Rydberg MO's, can be held responsible for the potential maxima in these cases.[41] Here the ionic components which need to be admixed into the LCAS wave functions as R decreases are being ignored, but (as was pointed out above) because of a lack of orthogonality of the ionic and covalent wave functions the presence or absence of these ionic admixings does not change the qualitative characteristics of the potential curves.

The discussion in this section has shown that, for states which are Rydberg states near R_e, it is incorrect because of strong CM at large R values to think of the core and the Rydberg electron as following independent correlation curves as $R \rightarrow \infty$. However, there is no reason why these states need be thought of as ceasing to be Rydberg states at larger R values. Further, although a T and n^* value associated with a specific Rydberg MO lack meaning at large R values, an *ionization energy* can be defined at every R value. At intermediate R values, ionization involves a considerable internal rearrangement of structure which leaves the positive ion the same *as if* an electron had merely been removed from a nonbonding Rydberg MO, while as $R \rightarrow \infty$, the ionization energy becomes equal to the T for the excited atom in an LCAS function; these relations correspond to the *pseudo-correlation* of section 4.

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(40) An interesting minor point, however, is that the $(1s^2 1s2p\sigma)_u$ and probably the $(1s^2 1s3d\pi)_g$ He_2 attractive curves are at first (at large R values) repulsive (*cf.* ref 4a), and become attractive only at smaller R values. This behavior can be correlated phenomenologically with the fact that the overlap integral S changes sign as R decreases in the cases of $S(2p\sigma_a, 2p\sigma_b)$ and $S(3d\pi_a, 3d\pi_b)$; the MO's $\sigma_u 2p$ and $\pi_g 3d$ involve negative overlap and so are antibonding at large R but attain positive overlap at smaller R, with $S = 1$ at $R = 0$. It is also of interest that the overlap for $\sigma_g 3d$ has positive maxima both at large R values and ($S = 1$) at $R = 0$, but is smaller and even becomes slightly negative between, according to unpublished calculations by Dr. S.-I. Kwun in this laboratory.

(41) On the other hand, reference to Figure 1 of ref 3 for He_2 might suggest that *repulsive* LCAS's such as $(1s^2 1s2s)_g$ and $(1s^2 1s2p\pi)_u$, taken *alone*, tend to go, as R decreases, into MO states *with repulsive cores but unpromoted Rydberg MO's* ($1\sigma_g 1\sigma_u{}^2 2s$ and $1\sigma_g 1\sigma_u{}^2 3d\pi$, respectively), whereas the corresponding *attractive* LCAS's $(1s^2 1s2s)_u$ and $(1s^2 1s2p\pi)_g$ definitely correlate with MO states with *attractive cores* and the same unpromoted Rydberg MO's ($1\sigma_g{}^2 1\sigma_u 2s$ and $1\sigma_g{}^2 1\sigma_u 2p\pi$). There seems to be no theoretical reason for such correlations for the repulsive single LCAS Ψ's, and the explanation given in the text appears much more satisfactory.

Electric Moments and Internuclear Distances in Molecules Containing Both Fixed and Rotating Polar Groups

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Abstract: Equations are derived which give the components of a rotating vector in terms of the components of its axis of rotation, the angle between the axis and the rotating vector, and the angle of rotation. It is shown how these equations can be used to calculate the electric moments of molecules with rigid frameworks to which fixed and/or rotating polar groups are attached, for which the skeletal coordinates and angles are known or can be inferred, and in which either free rotation or certain conformations of a rotatable group are assumed. An expression is derived for the calculation of the distance between an atom in a rotatable group and some vicinal fixed atom. Examples of the use of the various expressions derived are given. It is concluded that dipole moment data may be helpful in providing evidence for the absence, but not for the presence, of free rotation in the types of molecules for which the relationships given are applicable.

In the investigation of reaction mechanisms, problems regarding the configurations of fairly large molecules with rigid frameworks are often encountered. Electric moment data have proved to be helpful in the solution of these problems in many instances.[1–7] For simple molecules, they are often sufficient for immediate structural assignments, but as the molecular complexity increases, it often becomes necessary to use geometrical models from which theoretical moments are calculated in order to determine which particular configurations are consistent with the experimentally determined moments.

A systematic approach to the calculation of theoretical moments from assumed models for several bicyclic

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