Rydberg States and Rydbergization

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For a comprehensive understanding of atomic and molecular electronic spectroscopy and photochemistry, spectra of Rydberg states must be included. Further, Rydberg states are stepping stones toward ionization. For atoms and molecules of high ionization energy, Rydberg spectra lie in the vacuum ultraviolet, but for those of lower ionization energy, they come in part into the nearer ultraviolet. Many of the higher energy valence-shell excited states occur at similar energies to Rydberg states, with resultant interaction and mixing of their wave functions. Predissociation often occurs with results relevant to photochemistry. Rydberg states are important for reactions in the upper atmosphere.

Rydberg States and Rydberg Series of Atoms. Ordinary atomic states can usually be fairly well described in terms of an electron configuration, telling how many electrons are to be assigned to a series of AO's (atomic orbitals), of decreasing ionization potential in the order written.[1] For example, the ground state of silicon is a $^3P_0$ state of the configuration $1s^22s^22p^63s^23p^2$. Any one (or more) of the occupied AO's can be excited. In ordinary Rydberg states, one electron is excited to a relatively large AO, e.g., ns (n = 4, 5, or 6 ...). If the ground-state configuration is called A, the Rydberg state configuration may be described as $A^+\,ns$, where A^+ denotes the *core* configuration and state. If in A^+ an electron is removed from the 3p AO, leaving a ^2P core, the Rydberg state can be $^3P_0$, $^3P_1$, $^3P_2$, or ^1P, or ^3P and ^1P if we disregard the multiplet structure in the ^3P. A series of states with successive values of n constitutes a *Rydberg series*. Each series member is characterized by a *term value* T, $T = E(A^+) - E(A^+\,ns)$, where the energies E are usually expressed in spectroscopic units (cm^{-1}). Note that T is largest for Rydberg states of low energy. If it is written in the form Ry/n^{*2}, where n^* is an *effective* n, and Ry is the Rydberg constant (109679 cm^{-1} for the H atom and a little larger for heavier atoms), T is given to a good approximation by

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

The *quantum defect*, δ, is approximately a constant. (The deviations from constancy normally decrease steadily with increasing n.)

The value of δ is relatively large and positive for Rydberg AO's which have *precursors*, i.e., occupied AO's of the same l value (in the present example 1s, 2s, 2p, 3s, and 3p) in the core; in short, for *penetrating* Rydberg AO's. Here $n^* < n$. However, the value of δ is also appreciably affected by the particular state of the Rydberg configuration, e.g., ^3P or ^1P in our example; δ is larger for the ^3P than for the ^1P state. The two contributions to δ just mentioned may be called *penetrational* and *exchange* contributions. The exchange contribution is positive for the ^3P and negative for the ^1P. For nonpenetrating Rydberg AO's, e.g., nd or nf, δ is much smaller. Here a third, relatively small, positive *polarization* contribution to δ may be decisive. In rare cases for singlet states the negative exchange contribution can make δ slightly negative. In general, there may be a number of Rydberg states of the same Rydberg configuration, e.g., for silicon $A^+\,nd$, there are ^3P, ^3D, ^3F, ^1P, ^1D, and ^1F states for a ^2P core. In such a case, one may wish to use a weighted mean energy of the several states to calculate a mean n^* and δ for the Rydberg AO.

The simplest case is that of a closed-shell core as in the ordinary excited states of the Na atom: $1s^22s^22p^6X$, where X is ns or np or nd, etc.; here the Rydberg AO determines the overall state. In Na, even the ground state is essentially a Rydberg state (X = 3s). Table I contains illustrative data on some Rydberg states of Na, Rb, and Mg.

Molecular Rydberg States. In molecules, the same general principles apply as for atoms. Usually

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(1) For further discussion, cf. R. S. Mulliken, *J. Am. Chem. Soc.*, **86**, 3183 (1964).

Table I
Some Data on Atomic Rydberg States

Atom	X	T, cm^{-1}	n^*	δ
Na	3s	41449	1.627	1.373
	4s	15710	2.643	1.357
	7s	3437	5.650	1.350
	3d	12276	2.990	0.010
	4f	6861	3.999	0.001
Rb	5s	33691	1.805	3.195
	6s	13557	2.845	3.155
Mg	4s(^{3}S)	20472	2.315	1.685
	5s(^{3}S)	9797	3.347	1.653
	4s(^{1}S)	18166	2.458	1.542
	5s(^{1}S)	9113	3.470	1.530
	4f	6993	3.961	0.039

one considers molecular Rydberg states at or near their equilibrium configurations, but for a more general perspective, one should consider them as a function of the nuclear coordinates, and this introduces immense complications. Here I shall restrict myself almost entirely to diatomic molecules, where the energy of any electronic state is a function of the one internuclear distance, R.

In diatomic molecules, besides Rydberg states there are usually many valence-shell states. Here, using MO's (molecular orbitals) to set up electron configurations, a valence-shell state is one in which none of the occupied MO's is much larger than the AO's of the atoms from which the molecule can be formed. However, there is not always a sharp line between valence-shell and Rydberg states of molecules (see below). Many MO's become Rydberg MO's if R is sufficiently decreased (Rydbergization).

The Prototype Molecule H_2^+. It will be useful first to look at the simplest molecule, H_2^+. Because there is only one electron, the electronic wave functions are MO's which can be followed all the way from the united atom to dissociation. The united atom (UA) here is He^+, like an H atom except for $Z = 2$.

There is one interesting phenomenon about which I shall comment. For each of the two H atoms in H_2^+, there is an infinite set of AO's, but in H_2^+ at large R values, this set is doubled: we have for example (ignoring normalization factors here and hereafter) 1s + 1s and 1s − 1s. Likewise for each excited H atom AO, we have an *additive* and a *subtractive* LCAO MO; in short, a double infinity of MO's as compared with the atoms.

Most of these are LCAO's of *hybrids* of the usual s,p,d AO's, but this need not concern us here. Let us look just at the first of the LCAO MO's, namely $1s_a + 1s_b$, or $1\sigma_g$, and $1s_a - 1s_b$, or $1\sigma_u$, where a and b refer to the two H nuclei. As $R \to 0$, $1\sigma_g$ goes over into the UAO 1s, while $1\sigma_u$ is *promoted* to $2p\sigma$, a Rydberg MO. This is our first example of Rydbergization. As R decreases, this MO at large R is of valence-shell type, $1s_a - 1s_b$, but at small R it becomes, let us say, first *semi-Rydberg,* then *near-Rydberg,* and finally completely Rydberg as $R \to 0$. In other molecules, we shall find many examples, but varying a great deal as to the rate at which the MO takes on Rydberg character.

At intermediate R values the $1\sigma_u$ wave function is a linear combination

$$1\sigma_u = A2p\sigma_c + B(1s_a - 1s_b)$$
$$1\sigma_g = C(1s_a + 1s_b) \qquad (2)$$

(plus smaller terms which vanish both at $R = 0$ and ∞). As $R \to 0$, the coefficient B vanishes completely, and $A \to 1$. If one looks at the limiting form of the normalized 1s − 1s function at $R = 0$, this becomes $1p\sigma$, i.e., $\cos\theta e^{-\alpha r}$, but that is unacceptable as an eigenfunction of the Schrödinger equation. In short, it then becomes redundant. When we consider all the MO's, much the same sort of thing happens to all the subtractive, promoted, MO's. Now we find that at $R = 0$ we have left just a single infinity of acceptable H-atom-like MO's 1s, $2p\sigma$, $2p\pi$, etc. The redundancy introduced by the LCAO duplication of MO's has become unacceptable and so disappeared! On considering molecules with more than one electron, e.g. H_2 with two electrons, there is a similar LCAO redundancy for each electron, which similarly disappears as $R \to 0$.

Another interesting aspect of the MO's of H_2^+ is that, at any given R, they fall into Rydberg series, with quantum defects which are zero at $R = 0$, but appear when the UA nucleus is split.[1] Consider, e.g., the $2p\sigma$ UAO. Splitting the nucleus lowers the energy and thus increases the term value (see eq 1), for, whereas the $2p\sigma$ orbital is zero at the unsplit nucleus, splitting the nucleus causes the two nuclei to penetrate into its two lobes, thus lowering the potential energy, and the total energy. Hence the quantum defect is positive; it increases at first very nearly as R^2. On the other hand, for the 2s or $2p\pi$ Rydberg UAO, on splitting the nucleus, the two parts move into regions of decreasing density of the charge cloud, thereby *raising* the potential energy and the total energy. Hence, the term value is decreased, i.e., δ is negative, again varying approximately as R^2. Higher members of Rydberg series, e.g., $3p\sigma$, $4p\sigma$ ..., 3s, 4s, ... $3p\pi$, $4p\pi$ ... retain (at given R) very nearly the same quantum defects as the just-mentioned first members, and thus we have (at given R) true Rydberg series. The quantum defects resulting from splitting the nucleus also occur in molecules with more than one electron, e.g., H_2 and He_2, and must be present, although pretty unimportant, in bigger molecules. I call these *core-splitting* quantum defects.[2] At the same time, penetrational, exchange, and polarization contributions to δ are also present just as in atoms.

Diatomic Rydberg States. Now I turn to a consideration of Rydberg states and Rydbergization in diatomic molecules with more than one electron. Typical Rydberg states have the following three characteristics. (a) There is a stable equilibrium with a potential curve which not too far from R_e is close to that of the ion obtained by removing the Rydberg electron; the state of the ion may either be its ground state or one of the states obtainable by removal of one of the inner electrons; (b) Rydbergization of the Rydberg MO is nearly but not quite complete; (c) on dissociation, these states go to dissociation products in which one atom is in a Rydberg state.

Although a simple SCF MO description is usually good near R_e, extensive electron correlation, effected by configuration mixing (CM), is usually required as

(2) R. S. Mulliken, *J. Am. Chem. Soc.*, 91, 4615 (1969). Also see the abstract of ref 1.

one proceeds to dissociation. This situation is typical if the number of electrons is even as in most molecules, e.g., H_2 or N_2. But if the number of electrons is odd, as in NO, so that there is a closed-shell core, the Rydberg electron behaves in a fairly simple way from $R = 0$ to ∞, although extensive CM is required in the ion core on dissociation.

Examples of molecules for which many Rydberg states are known include H_2, He_2, and N_2 among even-electron diatomic molecules; and NO as an odd-electron molecule. In the even-electron molecules, the ion core is usually in a doublet state, and then there are always two Rydberg series, a triplet and a singlet series. In absorption, transitions are observed in such cases to singlet states, namely to such singlet states as are allowed by usual selection rules.

Near R_e the potential curve $U(R)$ of a diatomic Rydberg state is like that of the positive ion. At smaller R, the structure of the wave function remains essentially the same, i.e., a product of an ionic function times the Rydberg MO. As $R \rightarrow 0$, the Rydberg MO changes into a UAO, usually without radical change in form, but sometimes with radical changes due to avoided crossing of MO curves at small R. On dissociation, the wave function of even-electron molecules undergoes radical CM in which simultaneous changes occur in the valence shell and Rydberg MO's; the model of a $U(R)$ of a fixed ion plus an excited Rydberg MO is no longer valid.

H_2 Molecule. AO-Dissociating and MO-Dissociating States. It will be instructive now to look at the valence-shell and Rydberg states of H_2. The ground-state N, of configuration $1\sigma_g^2$ at R_e, is certainly a valence-shell state. If we let $R \rightarrow 0$, it becomes $1s^2$, ${}^1S$ of the He atom. If we let R increase toward dissociation, extensive CM sets in, until as $R \rightarrow \infty$ the wave function is a 50:50 mixture of $1\sigma_g^2$ and $1\sigma_u^2$. As is easily shown, the mixed function is mathematically identical with the familiar AO-type $1s_a{\cdot}1s_b$ Heitler–London wave function. (At intermediate R values, additional smaller CM terms besides $1\sigma_g^2$ and $1\sigma_u^2$ are present, but these vanish as $R \rightarrow \infty$.)

Contrastingly, the next higher, T, state, with a repulsive $U(R)$ curve, has an electron configuration whose wave function can be described at *all* R values as $1\sigma_g 1\sigma_u$, with MO forms (neglecting small CM terms at intermediate R values) as given by eq 2. The T state is valence-shell at large R and becomes Rydbergized as $R \rightarrow 0$. At dissociation, the MO wave function is easily shown to be identical with the repulsive Heitler–London form $1s_a \times 1s_b$ formed from neutral H atoms.

In general, wave functions like N for which *extensive* MO configuration mixing is *essential* on dissociation may be called AO-dissociating, since as $R \rightarrow \infty$ they can be expressed relatively simply in terms of AO's in Heitler–London-like form. Typical Rydberg states are AO-dissociating. On the other hand, where a configuration in terms of MO's (though of changing MO forms as R changes) is valid all the way to dissociation, it may be called MO-dissociating. The T state is of this kind.

The so-called V state of H_2 is a ${}^1\Sigma_u^+$ state of the same electron configuration $1\sigma_g 1\sigma_u$ as the T state. Here the MO wave function is equivalent to a Heitler–London wave function of H^+H^- character, and tends to dissociate into $H^+ + H^-$. Because of its ionic character, the $U(R)$ curve has a minimum at large R values. Actually it does not dissociate to $H^+ + H^-$, but short-cuts to dissociate to a pair of H atoms with one in its lowest Rydberg state. This behavior is an example of avoided crossing of like potential curves, and is rather a special than a fundamental feature. In the somewhat analogous case of the V state of N_2, dissociation must be actually to $N^+ + N^-$.

Let us now consider some Rydberg states of configurations $1\sigma_g X$, where X may be ns, $np\pi$, $nd\sigma$, $nd\pi$, $nd\delta$, etc., using UA symbols for the Rydberg MO's. (Near R_e, all such states are almost fully Rydbergized.) Where the X MO is LCAO-additive, as in ns, $np\pi$, and $nd\delta$, the LCAO form approximates closely to the UAO forms, e.g., $ns_a + ns_b$ approximates closely to ns_c, more and more so as n increases. Where the X MO at large R is LCAO-subtractive, Rydbergization near R_e is also nearly complete, more and more so as n increases. For example, at R_e, in the $1\sigma_g 1\pi_g$, ${}^3\Pi_g$ state, where $1\pi_g \approx A3d\pi_c + B(2p\pi_a - 2p\pi_b)$, a population analysis shows a $3d\pi$ population of 0.89: Rydbergization is 89% complete.[3] At smaller R, $A \rightarrow 1$, $B \rightarrow 0$. All these states are AO-dissociating,[4] and include both singlet and triplet states.

Near R_e, the $U(R)$ curve closely resembles that of the H_2^+ core, but as R increases beyond about $1.5R_e$, the $U(R)$ curve departs increasingly from that of H_2^+, especially for those states whose X MO is of LCAO-subtractive form at large R. For example, the $1\sigma_g 1\pi_g$, ${}^1\Pi_g$ or ${}^3\Pi_g$ state must dissociate following Heitler–London-like rules to give one normal and one $2p\pi$ excited H atom. As a consequence, the $U(R)$ curve after rising with increasing R from its minimum (which is fairly high because X is nearly pure $3d\pi$) must fall again as $R \rightarrow \infty$ in order to come down to the energy of a two-quantum dissociation product. Thus there is a hump in the $U(R)$ curve,[5] due to the promotion from $2p\pi$ to $3d\pi$ during Rydbergization. Where X is ns, $np\pi$, or $nd\delta$, however, there is no promotion and no necessity of such humps.

Because of complicated changes in the wave function,[4] in general involving both Rydbergization and CM, one cannot in the usual way define a Rydberg term value $T(R)$ as a function of R for a particular MO for R values greater than perhaps about 1.5 R_e. To be sure, as $R \rightarrow \infty$, a T exists corresponding to the excited atom in the dissociation products, but this does not really belong to an MO which has been followed all the way out with increasing R.

An examination of the quantum defects of some of the Rydberg states of H_2 for R near R_e is instructive.[2] These are obtained from the term values of vibrational levels $v = 0$ of the various states. Values of δ for states with ns, np, and nd Rydberg AO's are listed in Table II, together with data on vibrational spacings $\Delta G_{1/2}$ (energy difference in cm^{-1} between $v = 0$ and $v = 1$ levels) and R_e values (in Å). The latter data are relevant to the $U(R)$ curves, in particular to

(3) R. S. Mulliken, *Chem. Phys. Lett.*, 14, 141 (1972). Although $A = 0.89$ and $B = -0.53$, nonorthogonalities (especially between $2p\pi_a$ and $2p\pi_b$) lead to a much higher $3d\pi$ population than the coefficients A and B suggest.

(4) See R. S. Mulliken, *J. Am. Chem. Soc.*, 88, 1849 (1966), for details.

(5) For similar curves of He_2 Rydberg states, see R. S. Mulliken, *Phys. Rev. A*, 136, 962 (1964).

Table II
Data on Rydberg States of H_2

		Triplet						Singlet					
UAO		ns	$np\sigma$	$np\pi$	$nd\sigma$	$nd\pi$	$nd\delta$	ns	$np\sigma$	$np\pi$	$nd\sigma$	$nd\pi$	$nd\delta$
2	δ	0.066		0.076				−0.083	0.210	−0.081			
	$\Delta G_{1/2}$	2524		2339				2330	1318	2306			
	R_e	0.989		1.038				1.012	1.293	1.031			
3	δ	0.055	0.513	0.064	0.062	0.034	0.011	−0.091	0.196	−0.080	0.052	0.022	−0.035
	$\Delta G_{1/2}$	2269	2063	2240	2088	2115	2215	2294	1852	2226	2232	2102	2215
	R_e	1.045	1.107	1.050		1.070	1.054	(1.06)	1.134	1.047		1.069	1.054
4	δ		0.473	0.062	0.054	0.023			0.187	−0.078	0.066		−0.027
	$\Delta G_{1/2}$		2144	2210	2149	2154			2059	2204			
	R_e		1.063	1.067					1.104	1.061			

Table III
Breakdown of Experimental δ Values

MO	δ_{cs}	δ_{pen}	δ_{ex}
ns	−0.17	0.16	0.07
$np\sigma$	0.15	0.20	0.16
$np\pi$	−0.05	0.04	0.07
$nd\sigma$	0.02	0.04	0.01
$nd\pi$	0.01	0.02	0.01
$nd\delta$	−0.02	0.01	0.02

their deviations from that of H_2^+.

The δ values in Table II are seen to change slowly with increasing n, tending to approach constancy. Each δ is to be interpreted as a superposition of effects due to core-splitting (see the discussion of H_2^+ above), penetration, exchange, and polarization (see the discussion of atoms, above). Estimates of the core-splitting contribution, δ_{cs}, can be made from the data relevant to $U(R)$. The exchange contributions may be approximated by assuming that they are $\pm\delta_{ex}$ for triplet and singlet states, respectively. The difference between the experimental δ's of triplet and singlet states of the same configuration is then $2\delta_{ex}$. The remaining part, δ_{pen}, of the experimental δ can then be attributed to penetration, somewhat modified by polarization (especially for nd). The observed δ values can be well reproduced by using the estimated δ_{cs} values and the experimental δ_{ex} values, together with δ_{pen} values, all as given in Table III.

From Table III it is seen that core-splitting and penetrational contributions approximately cancel each other for ns and $np\pi$. If Rydbergization were complete, the δ values for $nd\sigma$, $nd\pi$, and $nd\delta$ should be equal; the observed δ's show that Rydbergization is somewhat incomplete for the promoted MO's $nd\sigma$ and $nd\pi$, whereas $nd\delta$ does not need to be Rydbergized.

Some Examples of Rydbergization. Let us turn now to the BH molecule. The ground state is a $^1\Sigma^+$ state of MO electronic configuration $1\sigma^2 2\sigma^2 3\sigma^2$. As in H_2, extensive CM is needed when the molecule is dissociated. In the united atom that state becomes $1s^2 2s^2 2p\sigma^2$, $^1\Sigma^+$, which represents part of a ^1D state. The lowest excited state is an MO-dissociating $^3\Sigma^+$ state analogous to the T state of H_2, with configuration $1\sigma^2 2\sigma^2 3\sigma 4\sigma$. As in the T state of H_2, this MO configuration is valid all the way from $R = 0$ to $R = \infty$. At large R, 4σ has the antibonding LCAO form $2p\sigma_B - 1s_H$, and as R decreases, the energy rises in a steep repulsion curve. However, at smaller R, $U(R)$ reaches a maximum and then descends somewhat to a minimum at an R_e approximately the same as $R_e(N)$. A SCF calculation[6] (self-consistent field, without CM) shows that at this R_e the 4σ MO has been almost completely transformed from its large-R LCAO antibonding form to a 3s Rydberg MO. In short, 4σ has become Rydbergized, so rapidly that $U(R)$ shows a Rydberg minimum as in ordinary Rydberg states. Evidently Rydbergization here proceeds more rapidly with decreasing R then in the T state of H_2, where there is no Rydberg minimum and the state is only semi-Rydberg or near-Rydberg at comparable R values. It is of interest that, in the T state of CH^+ isoelectronic with that of BH, there is now no sign of a Rydberg minimum. Evidently Rydbergization proceeds at different rates in different but related molecular states.

In BH, the T state is accompanied by a $^1\Sigma^+$ state, analogous to the V state of H_2. This has a Rydberg minimum analogous to that of the T state. However, it goes on dissociation to a Rydberg state of boron, plus 1s of hydrogen.

Having these examples of varying rates of Rydbergization, I made some calculations to see what happens in some other cases.[3] First, I looked at some MO-dissociating states of CH and NH containing a 4σ MO as in the T and V states of BH. For the CH state $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma$, $^2\Sigma^+$, the 4σ MO is found to behave like that in BH, going from antibonding LCAO form at large R to 3s Rydberg form at an R value such as to give a state with a small Rydberg minimum. For several states of NH, there is no Rydberg minimum in the repulsion curve, but the curve does show a point of inflection indicating that Rydbergization is proceeding with a *tendency* to produce a Rydberg minimum, but not rapidly enough to produce an actual minimum.

Let us now look at a somewhat different case of Rydbergization.[3] In N_2 an electron may be excited from a normally occupied MO shell to an unoccupied MO which at or near R_e of the ground state has essentially an LCAO valence-shell form but as $R \to 0$ must eventually become Rydbergized. Examples are the $2\sigma_u^{-1}1\pi_g$, $^1\Pi_u$ or $^3\Pi_u$ and $3\sigma_g^{-1}1\pi_g$, $^1\Pi_g$ or $^3\Pi_g$ states of N_2. (Here the symbol $2\sigma_u^{-1}$ means that the N_2^+ core consists of a normal molecule of configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$ from which one $2\sigma_u$ electron has been removed; similarly with $3\sigma_g^{-1}$.) The form of $1\pi_g$ at ordinary R values is approximately a linear combination of the LCAO π_g2p form $2p\pi - 2p\pi$ with a small amount of the UAO form $3d\pi$, or,

(6) R. S. Mulliken, *Int. J. Quantum Chem.*, **5**, 83 (1971); confirmed in a CM calculation by P. K. Pearson, C. F. Bender, and H. F. Schaefer, III, *J. Chem. Phys.*, **55**, 5235 (1971).

what is roughly the same, the $\pi_g 3d$ form, i.e., the linear combination $3d\pi_a + 3d\pi_b$. SCF MO calculations on the $^3\Pi_g$ states show that for these states at R_e of the ground state the wave function is about 83% $\pi_g 2p$ and 17% $\pi_g 3d$, while at two-thirds of R_e it is about 50% $\pi_g 2p$ and 50% $\pi_g 3d$, and at about one-half of R_e it is 100% $\pi_g 3d$, in other words completely Rydbergized. Furthermore, at ½Re the $1\pi_g$ MO has very nearly the *term value* of an H atom three-quantum AO, that is, the quantum defect is very nearly zero, corresponding to nearly perfect Rydbergization. In these examples, the states and MO's are generally considered as valence-shell states and MO's, as they are at ordinary R values. But if R is decreased, they become good Rydberg states long before the united atom is approached.

MO's and Excited States of N_2. An examination of the MO's occupied in the ground state of N_2 is of interest, since they are the precursors of the Rydberg MO's. The two inner-shell MO's $1\sigma_g$ and $1\sigma_u$ have essentially the simple LCAO forms $1s_a + 1s_b$ and $1s_a - 1s_b$, respectively, except at the smallest R values where $1\sigma_g$ approximates to the UAO 1s and $1\sigma_u$ to $2p\sigma$ of the Si atom. Next in order of decreasing ionization energy or term value comes $2\sigma_g$, then $2\sigma_u$, $1\pi_u$, and $3\sigma_g$. At moderate R values, these have, very roughly, the respective LCAO forms $2s_a + 2s_b$, $2s_b - 2s_b$, $2p\pi_a + 2p\pi_b$, and $2p\sigma_a + 2p\sigma_b$. However, $2s_a + 2s_b$ and $2p\sigma_a + 2p\sigma_b$ are somewhat hybridized in $2\sigma_g$ and $3\sigma_g$, and in $2\sigma_u$ there is considerable hybridization with $2p\sigma_a - 2p\sigma_b$; and there are other minor changes. A comparison with the "semi-united-atom" Mg is also relevant at R values near R_e.[7] The resemblance is to an atom with *two* K shells represented by $1\sigma_g{}^2 1\sigma_u{}^2$ (which is equivalent to $1s_a{}^2 1s_b{}^2$), and a single outer valence shell. Here $2\sigma_g{}^2$ plays the role of $2s^2$, $2\sigma_u{}^2$ the role of $2p\sigma^2$ (although as $R \rightarrow 0$ it becomes promoted to $3p\sigma^2$), $1\pi_u{}^4$ plays the role of $2p\pi^4$; as $R \rightarrow 0$, $2\sigma_g \rightarrow 2s$ and $1\pi_u \rightarrow 2p\pi$ of the united atom. The electrons so far mentioned correspond to a semi-united atom of structure $1s_a{}^2 1s_b{}^2 2s^2 2p^6$. Finally, $3\sigma_g{}^2$ is an extra shell which takes the place of $3s^2$ of Mg, but has a form which corresponds rather closely to $3d\sigma^2$, although greatly shrunken in size compared with a Rydberg $3d\sigma$ orbital. The MO's $2\sigma_g$, $2\sigma_u$, $1\pi_u$, and $3\sigma_g$ are respectively the precursors of the Rydberg MO's ns ($n \geq 3$), $np\sigma$ ($n \geq 4$, or 3 at the larger R values if we neglect the incipient promotion in $2\sigma_u$), $np\pi$ ($n \geq 3$), and $nd\sigma$ ($n \geq 3$).[8]

An SCF computation for the ground state of N_2 as a function of R down to $R = 0$ shows how the various MO's and their ionization energies ("orbital energies") change.[9] A resulting diagram of the course of the orbital energies (in atomic units, 27.2 eV each) is shown in Figure 1. Especially notable is the fact that the $3\sigma_g$ MO transforms completely to 3s as R decreases, thus increasing the resemblance of N_2 to the semiunited atom Mg.

Let us now consider some excited valence-shell and

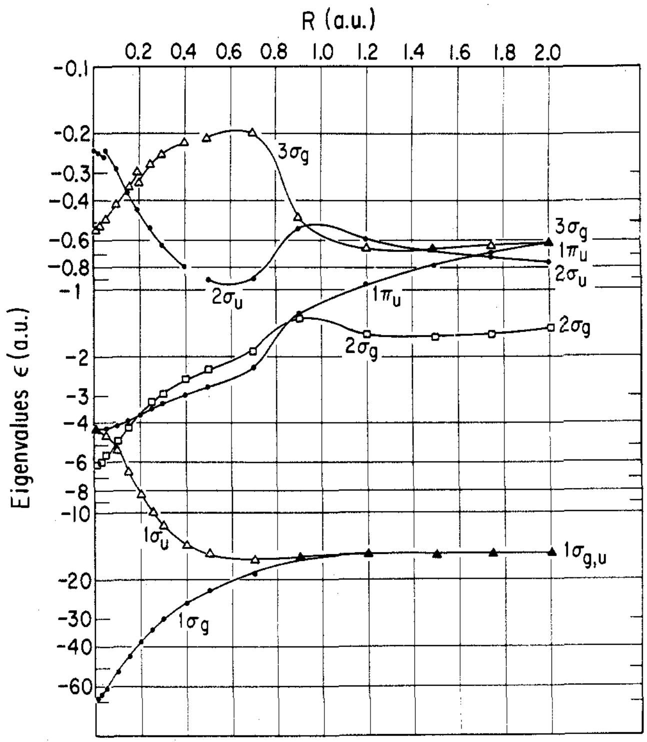

Figure 1. Orbital energies of the MO's of ground-state N_2.

then some Rydberg states of N_2. We have already seen that in the $2\sigma_u{}^{-1}1\pi_g$ and $3\sigma_g{}^{-1}1\pi_g$ states the excited MO $1\pi_g$, which must be considered as the precursor of the Rydberg MO's $nd\pi$ ($n \geq 4$), is rapidly Rydbergized to $3d\pi$ as R is decreased. The same MO appears in the several states ($^3\Sigma_u{}^+$, $^3\Delta_u$, $^3\Sigma_u{}^-$, $^1\Sigma_u{}^-$, $^1\Delta_u$, and $^1\Sigma_u{}^+$) which belong to the configuration $1\pi_u{}^{-1}1\pi_g$. At their R_e's these are valence-shell states, but $1\pi_g$ must be Rydbergized when R decreases sufficiently. A special feature of this configuration is that, when an SCF computation of its six states is made, the highest energy one, the $^1\Sigma_u{}^+$, is computed to lie a long way above the others. Also, according to the usual Wigner–Witmer correlation rules, all the other states except the $^1\Sigma_u{}^+$ on dissociation go to pairs of ground-state configuration atomic states, but the $^1\Sigma_u{}^+$ state goes to a pair of ions, $N^+ + N^-$, in their ground states. This state is classifiable as a V state, analogous to that of H_2; however, unlike the case of H_2, here there is no short-cutting to give Rydberg atomic states on dissociation, but $^1\Sigma_u{}^+$ must actually dissociate to ions. An experimentally well-known state of N_2, the b′ state, with large R_e as expected for an ion-pair state, can be identified with this predicted V state. However, there is a complication. One can predict a second V state, corresponding to the configuration $3\sigma_g{}^{-1}3\sigma_u$; let us call this a V_σ state, while $1\pi^{-1}1\pi_g$ can be called a V_π state. Further examination reveals that the observed b′ state is really a *mixed* V state, namely a mixture of perhaps 65% V_π and 35% V_σ.[10]

A number of Rydberg states of N_2 are known experimentally. These include singlet states of $3\sigma_g{}^{-1}np\sigma$, $3\sigma_g{}^{-1}np\pi$, $1\pi_u{}^{-1}ns$, $2\sigma_u{}^{-1}ns$, and perhaps $2\sigma_u{}^{-1}nd\sigma$, from absorption spectra,[11] and $^3\Sigma_u{}^+$ of

(7) Cf. R. S. Mulliken, *Int. J. Quantum Chem.*, **1**, 103 (1967), annotation 1.

(8) However, because of the interhybridization between $2\sigma_g$ and $3\sigma_g$, both of these are to some extent precursors of both the ns and $nd\sigma$ Rydberg MO's.

(9) R. S. Mulliken, *Chem. Phys. Lett.*, **14**, 137 (1972); *Int. J. Quantum Chem.*, **8**, 817 (1974).

(10) Cf. R. S. Mulliken, *Chem. Phys. Lett.*, **25**, 305 (1974).

(11) P. K. Carroll and C. P. Collins, *J. Phys. B*, **3**, L127 (1970); K. Dressler, *Can. J. Phys.*, **47**, 547 (1969).

Table IV
Quantum Defects of the Rydberg States of NO

	sσ			pσ			pπ		
n	$^2\Sigma^+$	T_0, cm^{-1}	δ	$^2\Sigma^+$	T_0, cm^{-1}	δ	$^2\Pi$	T_0, cm^{-1}	δ
3	A	44 200	1.105				C	52 372	0.785
4	E	60 863	1.188	D	53 291	1.738	K	64 290	0.759
5	S	67 135	1.201	M	64 659	1.701	Q	68 645	0.757
6	T	69 961	1.208	R	68 829	1.691	W	70 747	0.758
7	Z	71 459	1.217	Y	70 846	1.691	...	...	...
8	...	...	...	...	71 982	1.692	...	...	...

	dσπ			dδ			f		
n	$^2\Sigma^+ {}^2\Pi$	T_0, cm^{-1}	δ	$^2\Delta$	T_0, cm^{-1}	δ	...	T_0, cm^{-1}	δ
3				F	62 051	0.059			
4	H, H′	62 717	0.979	N	67 630	0.071	...	67 809	0.022
5	o, o′	67 993	0.967	U	70 210	0.078	...	70 316	0.020
6	...	...	...	...	71 585	0.102	...	71 662	0.029

$3\sigma_g^{-1}3s$, $^1\Pi_g$ of $3\sigma_g^{-1}4d\pi$, $^1\Pi_g$ of $1\pi_u^{-1}4p\sigma$, and $^1\Sigma_g^-$ from $1\pi_u^{-1}3p\pi$, from emission spectra.[12] Many of these Rydberg states are strongly perturbed by valence-shell states of the same state species.[11]

The configuration $1\pi_u^{-1}3p\pi$ must give six states, like $1\pi_u^{-1}1\pi_g$; of these only $^1\Sigma_g^-$ has been observed, the rest presumably being predissociated. One of these predicted states is a $^1\Sigma^+$ state, here $^1\Sigma_g^+$ instead of $^1\Sigma_u^+$ as in the latter case. Whereas a SCF computation places the $^1\Sigma_u^+$ far above the other states of $1\pi_u^{-1}1\pi_g$, it indicates no such unique position for $^1\Sigma_g^+$ in $1\pi_u^{-1}3p\pi$, but places it only slightly above the rest of the group.

As already noted, the 3s Rydberg MO at R_e has as its precursor $2\sigma_g$ (and $1\sigma_g$), but as $R \rightarrow 0$ it cannot go over into 3s of Si, since the ground-state MO $3\sigma_g$ has already become 3s. Instead it must transform, according to the noncrossing rule, into the lowest now unoccupied σ_g Rydberg AO of Si, namely $3d\sigma$. Thus, whereas at R_e the role of $3d\sigma$ is played by $3\sigma_g$, while 3s is a Rydberg MO (and behaves as a Rydberg 3s AO on dissociation), the $3d\sigma$ and 3s exchange their roles as $R \rightarrow 0$.

Rydberg States of NO. The Rydberg states of NO are even better known than those of N_2. As in N_2, many of these are strongly perturbed by valence-shell states. Miescher, who is responsible for much of the work, has published an instructive table,[13] which with some changes is reproduced here as Table IV. Note that in NO the Rydberg electron moves in the field of a closed-shell core. For $np\sigma$, $nd\sigma$, and $nd\pi$, Miescher assigned n values and δ values one smaller than here. The values given here are based on corresponding UAO's. In the case of $np\sigma$, Miescher's values really correspond to the semiunited atom (cf. the discussion of N_2 above). Something is to be said for this choice, since at R_e the $np\sigma$ MO's are as yet unpromoted. In fact, as one goes to heavier molecules, and to polyatomic molecules, it makes increasingly less sense to use UAO n values; in fact, they often become difficult to determine. An argument for the semiunited atom n values is that the term values of $np\sigma$ are then nearly equal for $np\sigma$ and $np\pi$.

In the case of the nd MO's, it might seem most natural to number them in such a way that the $d\sigma$ and $d\pi$ MO's whose term values are close to those of $d\delta$ are assigned the same n values. However, this choice results in negative δ values for $nd\sigma$ and $nd\pi$, unjustified by any of the contributions to δ which we have considered. The near-equality of the σ, π, and δ term values means approximate equality of size of the MO's, but the smaller δ's for $nd\sigma$ and $nd\pi$ are symptoms of incipient Rydbergization toward the UAO n values. The relatively large δ's for $nd\sigma$ and $n\sigma$ are ascribable to penetration (note the existence of precursors in the core).

In the penetrating MO's ns, $np\sigma$, and to a lesser extent $np\pi$, there is a typical small decrease in δ with increasing n. In the nonpenetrating MO's $nd\delta$ and nf, the slow *increase* of δ with increasing n is an effect which is typical when δ is due primarily to polarization.

Absence of Redundant MO's. In conclusion, I should like to say something about the lowest Rydberg states of the molecule methane and other hydrides isoelectronic with the neon atom. Let us assume tetrahedral symmetry for simplicity, although in CH_4^+ and therefore in the Rydberg states, the actual equilibrium symmetry is lower. The states are then semi-Rydberg or near-Rydberg states $1s_a{}^2 2a_1{}^2 1t_2{}^5 3a_1$, $^3T_2$ and $^1T_2$, where the Rydberg MO is of the form $C_1 3s + C_2(\lambda 2s_C - 1s_a - 1s_b - 1s_c - 1s_d)$. In the united atom neon $C_1 = 1$ and $C_2 = 0$. Some people have claimed that there exist two different states, one corresponding to a 3s MO and another with an MO of the LCAO form $C(\lambda 2s_C - 1s_a - 1s_b - 1s_c - 1s_d)$. However, just as in the case of $1s - 1s$ in the T and V states of H_2^+ or H_2, the LCAO term in the MO becomes redundant and disappears as $R \rightarrow 0$. Then by continuity we cannot claim that there are two different MO's which correspond to two different $^3T_2$ and two different $^1T_2$ excited states of CH_4. A similar argument applies to the corresponding states of NH_3, H_2O, and HF and to various other cases.

This work was supported in part by a grant from the National Science Foundation, GP-37734.

(12) P. K. Carroll and K. V. Subbaram, to be published ($^1\Pi_g$ of $3\sigma_g^{-1}4d\pi$); and cf. A. Lofthus and R. S. Mulliken, *J. Chem. Phys.*, **26**, 1010 (1957); A. Lofthus, *ibid.*, **25**, 494 (1956).

(13) E. Miescher, *J. Mol. Spectrosc.*, **20**, 130 (1966), Table VI.

Additions and Corrections

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Robert S. Mulliken: Rydberg States and Rydbergization.

Page 7. The author has communicated: "Contrary to statements in my paper, the b′ $^1\Sigma_u^+$ or V state of N_2 does *not* dissociate to a pair of ions, but to the pair of ground-state configuration atoms ^2D and ^2P."