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The Rydberg States of Molecules.[1] VII[2,3]

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Abstract: The abstract for the present contribution has already been published.[2] The model there presented is applicable to Rydberg states of H_2 and He_2 but, contrary to hopes indicated previously, is probably not useful for larger molecules.

The present publication is part VII of a paper of which parts I–V and part VI have already been published.[2,3] The abstract of the present part VII has already appeared in ref 2. That abstract refers to a "demi-H_2^+ model" which will be described here. The model is a relatively crude one which, although not useful for accurate calculations, is believed valuable in terms of the physical insight it gives in an interpretation of observed data on the Rydberg states of H_2 and He_2.

As shown by Hazi and Rice,[4] it is possible without much error to regard the Rydberg electron in a molecular Rydberg state as moving in the field of a fixed core.[5] For the case of H_2 or He_2, it will now be shown that the deviation of the core field from central symmetry, except for a scale factor of roughly $^1/_2$, is similar to that of H_2^+, so that the MO's (molecular orbitals) and their energies should tend to roughly parallel those of H_2^+. However, for MO's which penetrate the core a correction is needed.

1. The Demi-H_2^+ Model for Rydberg MO's of H and He_2. In the Rydberg states of H_2, the core (H_2^+) consists of two H nuclei plus one electron in the MO $1\sigma_g$. This MO may be approximated by the LCAO form N ($1s_a + 1s_b$), where $1s_a$ and $1s_b$ refer to 1s AO's (atomic orbitals) on the two nuclei. We consider the energy of the Rydberg electron in H_2 in the potential U due to this H_2^+ core.

As previously for H_2^+ in V,2 (*i.e.*, section 2 of part V[2]), we express U as $U_0 + V$, where U_0 is the potential for $R = 0$ (R is the internuclear distance), and $V = U - U_0$ is regarded as a perturbation potential. U_0 is U of the united-atom core, namely He^{2+} shielded by a 1s electron; in the demi-H_2^+ model, we assume complete shielding of the nucleus, so that $U_0 = -e^2/r_c$, where c denotes the center of the united atom or, later, of the H_2^+ core in H_2. In the model, we consider the perturbation energy corresponding to the perturbation potential V which results on splitting the He^+ core to make the H_2^+ core.

Splitting the core of He to make that of H_2 corresponds to replacing $U_0 = -e^2/r_c$ by $U = -e^2/r_a - e^2/r_b$ plus the potential due to the $1\sigma_g$ electron. For the latter, we consider the approximate charge distribution obtained by squaring the normalized expression $(1s_a + 1s_b)/[2(1 + S)]^{1/2}$ for the $1\sigma_g$ MO. Here S is the overlap integral $\int 1s_a 1s_b dv$, and $1s_a$ and $1s_b$ are normalized 1s AO's.[6] One obtains

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[2] Parts I–V: R. S. Mulliken, *J. Am. Chem. Soc.*, **86**, 3183 (1964). The purported proof, described in sec 2 of part II, that l values become sharply defined with increasing n in a molecular Rydberg series, now seems unconvincing.

[3] Part VI: R. S. Mulliken, *ibid.*, **88**, 1849 (1966).

[4] A. U. Hazi and S. A. Rice, *J. Chem. Phys.*, **47**, 1125 (1967); **45**, 3004 (1966).

[5] At R values somewhat larger than R_e of stable molecular states, the SCF approximation in terms of MO's usually begins seriously to break down as an adequate description of actual molecular states, and the concept of a Rydberg term value for a Rydberg electron moving in the field of a fixed core can no longer be used (see part VI[3]). We shall not deal here with such large R values.

[6] These 1s AO's correspond to an effective nuclear charge ζ greater than for a free H atom; ζ is about 1.4 at R_e of H_2^+ and of the Rydberg MO's of H_2, and $\zeta = 2.00$ at $R = 0$. Because $\zeta > 1$, the quantities S and ρ in eq 4 are smaller than they would be if $\zeta = 1$. More accurately, the 1s AO's used should be polarized, but to take account of this cor-

$$\int(1\sigma_g)^2 = 1s_a{}^2/2(1 + S) + S[1s_a1s_b/S]/(1 + S) + 1s_b{}^2/2(1 + S) \quad (1)$$

Integrating eq 1 term by term, noting that

$$\int(1\sigma_g)^2 dv = \int 1s_a{}^2 dv = \int(1s_a1s_b/S)dv = \int 1s_b{}^2 dv = 1$$

the charge distribution of $1\sigma_g$ is seen to be equal to the sum of three distributions of magnitudes $^1/_2(1 + S)$, $S/(1 + S)$, and $^1/_2(1 + S)$, respectively, centered around a, c, and b. The distributions around a and b are spherically symmetrical, while that around c is roughly so. Assuming each of the three distributions concentrated at its center,[7] the potential due to the $1\sigma_g$ electron is

$$U(1\sigma_g) = [^1/_2e^2/(1 + S)](1/r_a + 2S/r_c + 1/r_b) \quad (2)$$

It proves convenient to write $U(1\sigma_g)$ in the form

$$U(1\sigma_g) = e^2[(1 - \rho)/r_a + (2\rho - 1)/r_c + (1 - \rho)/r_b] \quad (3)$$

where

$$\rho = (1 + 2S)/2(1 + S) \quad (4)$$

Adding $-e^2/r_a - e^2/r_b$ to $U(1\sigma_g)$ to obtain U, and subtracting $U_0 = -e^2/r_c$ to obtain V, one then finds

$$V = U - U_0 = \rho e^2(-1/r_a + 2/r_c - 1/r_b) \quad (5)$$

This V differs just by a factor ρ from the corresponding perturbation potential for the electron in $H_2{}^+$ relative to the united atom (He^{2+}) potential (see section 2 of part V).[2] At R values large enough so that S of eq 1 is small,[6] $\rho \approx {}^1/_2$; at smaller R values ρ increases slowly, approaching $^3/_4$ as $R \rightarrow 0$. However, $V = 0$ at $R = 0$, since $r_a \equiv r_c \equiv r_b$ then.

Now consider the first-order perturbation energy $\Delta T_{cs}(R)$, *i.e.*, $T(R) - T(R = 0)$, due to *core splitting*, for a Rydberg state of H_2, and let us compare it with $\Delta T^+{}_{cs}$ for $H_2{}^+$. Here T is the term value for a Rydberg MO of H_2, T^+ that of the corresponding MO of $H_2{}^+$, values of which are known[2] as functions of R for many MO's. At $R = 0$ the effective nuclear charge in our model is 2e for $H_2{}^+$ and 1e for H_2, and the orbitals if nonpenetrating are identical for $H_2{}^+$ and H_2 except for a scale factor (the orbitals of $H_2{}^+$ are half as large as those of H_2). For $R > 0$, on introducing the core-splitting perturbation potential V of eq 5, it is seen that for the first-order perturbation energy

$$\Delta T_{cs}(R) = \int\psi_0 V(R)\psi_0 dv = \frac{1}{2}\rho\Delta T^+{}_{cs}\left(\frac{1}{2}R\right) \quad (6)$$

since the integral $\int\psi_0(-1/r_a + 2/r_c - 1/r_b)\psi_0 dv$ has the same scaled-down *form* for $^1/_2R$ in $H_2{}^+$ as for R in H_2, but is smaller by the factor $^1/_2$ in H_2 because the MO is twice as large.

But actually the factors $^1/_2$ in eq 6 need modification to take account of penetration effects which may modify the size of the MO in H_2. In particular, at $R = 0$, the ns Rydberg AO's of the He atom, and to a slight extent the np AO's, penetrate the core, and corresponding effects must exist in the H_2 MO's when $R > 0$. This penetration diminishes the size of the He atom AO's in the ratio $1/\gamma$ where $\gamma = (n/n^*)^2$: the effective size of any AO is proportional to the radius a of maximum radial charge density ($a = a_0n^{*2}/Z$, where Z is the core charge).[8] Hence the factors $^1/_2$ in eq 6 should be replaced by factors $\gamma/2$, giving

$$\Delta T_{cs}(R) = \frac{1}{2}\rho\gamma\Delta T^+{}_{cs}\left(\frac{1}{2}\gamma R\right) \quad (7)$$

Not only penetration, but also core splitting, affects n^* and therefore also the sizes of the MO's, in $H_2{}^+$ and in H_2. One of the most interesting conclusions of the present study is that the observed γ of approximately 1 for the ns MO's of H_2 for its Rydberg states at R_e is a result of the approximate cancellation of a considerable positive δ due to penetration by a considerable negative δ due to core splitting (recall that $n^* = n - \delta$).

Although in first-order perturbation theory here the appropriate zero-order MO's ψ_0 would be the corresponding united-atom AO's ($R = 0$), so that united-atom values of γ would be approprirate, the γ values actually used in the present calculations have been values obtained from the n^* values of actual molecular term values taken at R_e. This procedure represents a modification of first-order perturbation theory in the direction of using *better* than zero-order wave functions, although it is not clear whether or not the procedure represents an improvement. Further, in the calculations reported in Tables III and IV of section 4 using eq 7 (or rather, the related eq 9), the values of $\Delta T^+{}_{cs}$ employed will be obtained from *exact* values of $T(R)$ for $H_2{}^+$ instead of first-order perturbation theory approximate values. Our whole discussion involves using a crude model and also involves using a modified first-order perturbation theory for rather large perturbations, so that the results cannot claim to be more than very rough.

It is of interest now to look at the δ values corresponding to the core-splitting ΔT's. From $\Delta T \equiv T(H_2) - T(H)$, $T(H_2) = Ry/n^{*2} = Ry/(n - \delta)^2$, and $T(H) = Ry/n^2$, one finds $\Delta T/Ry = (n^2 - n^{*2})/n^2n^{*2} = \delta(n + n^*)/n^2n^{*2}$. So $\delta = [n^2n^{*2}/(n + n^*)]\Delta T/Ry$—for any value of R. Similarly, with $\Delta T^+ = T(H_2{}^+) - T(He^+)$, $\Delta T^+/Ry = 4\delta^+(n + n^{+*})/n^2(n^{+*})^2$. Combining these relations with eq 7, one obtains

$$\begin{aligned}\delta_{cs}(R) &= [n^2n^{*2}/(n + n^*)]\Delta T/Ry \\ &= \left[\frac{1}{2}\rho\gamma n^2n^{*2}/(n + n^*)\right]\Delta T^+\left(\frac{1}{2}\gamma R\right)\Big/ Ry \\ &= 2\rho\left[\frac{n^2}{n^{*2}}\frac{n^{*2}}{(n + n^*)}2\left(\frac{n + n^{+*}}{n + n^*}\right)\right]\delta^+{}_{cs}\left(\frac{1}{2}\gamma R\right)\end{aligned}$$

An examination of the factor in brackets shows that, at R values up to R_e of Rydberg states of H_2, its value

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rection would complicate our model unduly, and its effect is not large enough to be serious in view of the crudeness of the model.

(7) This rough assumption and the assumption of complete shielding of He^{2+} by 1s in the $H_2{}^+$ united atom to give $U_0 = -e^2/r_c$ tend to compensate each other. For *nonpenetrating* Rydberg MO's of H_2, both are well justified.

(8) The relation $\gamma = (n/n^*)^2$ is not exact, since it assumes a uniform scaling up of the whole AO from He^+ to He. Actually, in the case of a penetrating AO the scale factor $(n/n^*)^2/2$ applies only to the outer (or outermost) loop (*cf.* part III, section 1). The inner loop or loops are then relatively smaller for He than for He^+, but absolutely of about the same size as in He^+. On the other hand, $\Delta T_{cs}(R) \approx \rho\Delta T^+(R)$, which is larger than $\rho\Delta T^+(^1/_2\gamma R)$. Balancing off this larger contribution of the innermost loop against its smaller relative size in He than in He^+, a rough estimation indicates that γ may after all be approximately $(n/n^*)^2$.

Table I. Data on Rydberg States of H_2[a–c]

		Triplet						Singlet					
n		ns	npσ	npπ	ndσ	ndπ	ndδ	ns	npσ	npπ	ndσ	ndπ	ndδ
2	$n^* =$	1.934	((1.327[a]))	1.924				2.083	1.790	2.081			
	$\Delta G_{1/2} =$	2524	Unstable	2339				2330	1318	2306			
	$R_e =$	0.989		1.038				1.012	1.293	1.031			
3		2.945	2.487	2.936	2.938	2.966	2.989	3.091	2.804[f]	3.080[f]	2.948	2.978	3.035
		2269	2063	2240	2088	2115[g]	2215[g]	2294[e]	1852[f]	2226[f]	2232[e]	2102[g]	2215[g]
		1.04_5	1.107	1.050		1.070[g]	1.054[g]	(1.06)	1.134[f]	1.047		1.069[g]	1.054[g]
4			3.527[d]	3.938	3.946	3.977	(3.956)		3.813[f]	4.078[f]	3.934	(4.006)	4.027
			2144	2210	2149	2154	(2167)		2059[f]	2204[f]		2143	
			1.063	1.067					1.104[f]	1.061[f]			
5				4.939						5.079[f]			
				2196						2191[f]			
				1.057						1.045[f]			

[a] The n^* values correspond to removal of the Rydberg electron from $v = 0$ of the Rydberg state to $v = 0$ of H_2^+, except in the case of 2pσ, $^3\Sigma_u^+$ where the value is one which is *vertical* for R equal to R_e of H_2^+. [b] The $\Delta G_{1/2}$ values are in cm^{-1}, R_e values in A. The $\Delta G_{1/2}$ values are taken from G. H. Dieke, *J. Mol. Spectry.*, **2**, 494 (1958), except for those marked with superscript *f*. The R_e values are from G. Herzberg, "Spectra of Diatomic Molecules," Vol. 1, 2nd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1957, and the n^* values are based on this reference, since for the *triplet* states Dieke's absolute energy values give unreasonable n^* values. [c] For the H_2^+ ion, theoretical calculations give $\Delta G = 2187$ cm^{-1}, $R_e = 1.05_5$ Å; see D. R. Bates and G. Poots, *Proc. Phys. Soc.*, **A66**, 789 (1953). [d] Dieke (footnote *b*) identifies as 4pσ, $^3\Sigma_u^+$ a fragmentary level with $n^* = 2.941$, but this does not fit properly into the npσ series. The level here identified as 4pσ is taken from Herzberg (footnote *b*). [e] The $\Delta G_{1/2}$ values for 3s $^1\Sigma_g^+$ and especially 3dσ $^1\Sigma_g^+$ appear to be abnormally high. It seems probable that these states are strongly perturbed by the $(2\text{p}\sigma)^2$ $^1\Sigma_g^+$ state (*cf.* E. R. Davidson, *J. Chem. Phys.*, **35**, 1189 (1961)). [f] These are values of especial accuracy, from A. Monfils, *Bull. Acad. Roy. Belg.*, [5] **47**, 599, 816 (1961); **48**, 460, 482 (1962); *J. Mol. Spectry.*, **15**, 265 (1965). [g] These are values corrected for l uncoupling, from M. L. Ginter, *J. Chem. Phys.*, **46**, 3687 (1967).

does not deviate greatly from 1, so that, at least roughly

$$\delta_{cs}(R) = 2\rho\delta^+{}_{cs}\left(\frac{1}{2}\gamma R\right) \tag{8}$$

But now δ in general includes a contribution due to penetration of the Rydberg MO into the core. It appears reasonable as an approximation to assume that the two contributions to δ are additive.[9] Then

$$\delta(R) \approx \delta_{\text{pen}}(R) + 2\rho\delta^+\left(\frac{1}{2}\gamma R\right) \tag{9}$$

We shall not attempt to compute δ_{pen} values, but will obtain empirical values of δ_{pen} for H_2 by taking $\delta(R) - \delta_{cs}(R)$ using empirical values of δ and computed values of δ_{cs}. We shall find that the values of δ_{pen} obtained in this way are reasonable.

On the basis of eq 7–9, it is seen that the change in the effective core field on splitting the core must produce in H_2 the following effects which are also characteristic in H_2^+ (see part V, section 2); for penetrating MO's in H_2, however, the energy effects of penetration, which are absent in H_2^+, are superposed.

(1) For MO's with $l = \lambda$, *i.e.*, ns, npπ, ndδ, and so on, δ_{cs} is negative, ΔT is negative, and the energy change due to core splitting is positive, increasing as R increases.

(2) For MO's with $l > 0$ and $\lambda < l$, δ_{sc} is positive and the energy change due to core splitting is increasingly negative as R increases.

Both effects may be considered as due primarily to the changes in the effective field of the core which result when it is split. But also, the difference between effects 1 and 2 is related to the fact that MO's with $\lambda = l$ are *unpromoted MO's*, while those with $\lambda < l$ are *promoted MO's*, which go to LCAO forms of lower n as $R \rightarrow \infty$ in H_2^+.[10] As we shall see below, the Rydberg MO's of H_2 conform well to expectations 1 and 2 above.

Reasoning similar to that just given for H_2 shows that for the Rydberg states of He_2, with core $1\sigma_g^2 1\sigma_u$, eq 5–9 should hold to a rather similar extent to that in H_2.[11] For diatomic molecules with larger cores, the situation becomes in general more complicated.

2. Bonding Characteristics of Rydberg States of H_2 and He_2. At least for small n (*cf.* section 1 of part IV),[2] the Rydberg electron must assist in determining $U(R)$. Tables I and II, for a number of Rydberg states of H_2 and He_2, illustrate changes that occur in $\Delta G_{1/2}$ and R_e, which are especially important quantities in characterizing $U(R)$, as n increases.[12] Values of n^*, hence implicitly of δ, are also given. The variations in $\Delta G_{1/2}$ and R_e with n will be shown below to be closely related to variation of the δ values with R. Tables I and II show that, for all Rydberg series of each molecule (except for a few irregularities which can be ascribed to perturbations and/or experimental error), $\Delta G_{1/2}$ and R_e rapidly converge, as n increases, toward common limiting values which must evidently be those of the core, but differ considerably from this value at $n = 2$. The δ values likewise converge toward limiting values, as expected.

The fact that the presence of the Rydberg electron increases $\Delta G_{1/2}$ and decreases R_e for ns and npπ MO's, and the reverse for npσ MO's, suggests that the former are somewhat bonding and the latter somewhat antibonding,[13] but to a rapidly diminishing extent as n increases. It is natural to try to explain these characteristics, just as for valence-shell orbitals, by refer-

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[9] The alternative assumption that the contributions ΔT_{pen} and ΔT_{cs} are additive leads to essentially the same result as eq 9.

[10] Compare the discussion of the 3dσ, π, δ MO's of He_2 on p 963 of R. S. Mulliken, *Phys. Rev.*, **136**, A962 (1964), which applies equally to H_2 MO's.

[11] At R values near R_e, but not near $R = 0$ except for MO's with $l > 1$; near $R = 0$ there is extensive penetration of the united-atom core for orbitals with $l = 0$ and 1: see discussion in section 4.

[12] It would be preferable to present ω_e and $x_e\omega_e$ instead of $\Delta G_{1/2}$ (*i.e.*, $G_1 - G_0$) values, but in many cases these are not available or are less reliable than the directly experimental $\Delta G_{1/2}$ values, which after all are not far from ω_e values.

[13] R. S. Mulliken in "Quantum Theory of Atoms, Molecules, Solid State," Academic Press, New York, N. Y., 1966, p 231.

Table II. Data on Rydberg States of He_2[a,b]

n		Triplets ns	npσ	npπ	ndσ	ndπ	ndδ	Singlets ns	npσ	npπ	ndσ	ndπ	ndδ
	n^* =	1.788	Impossible	1.928				1.853	[0.84][e]	1.964			
2	$\Delta G_{1/2}$ =	1732		1.699				1791	Un-	1697			
	R_e =	1.045		1.063				1.040	stable	1.066			
		2.808	2.165	2.928	2.933	2.957	3.012	2.873	2.285	2.964	2.949	2.969	3.012
3		1655	1480	1651	1547	1572	1637	1675	1572	1651	1564	1590	1636
		1.071	1.096	1.075	1.091	1.086	1.079	1.069	1.092	1.076	1.089	1.085	1.079
		3.813		3.929	(3.932)	(3.957)	(4.006)	3.879		3.965			
4		1636	*d*	1638	1594	1600	1630		*d*				
		1.078		1.078		*c*		(1.079)		1.078		*c*	
		4.816		4.929	(4.938)	(4.973)	(4.989)			4.966	(4.952)	(4.980)	(5.020)
5		1632	*d*	1634					*d*				
		1.079		1.079		*c*				1.08		*c*	
		5.815		5.929		(5.939)	(5.993)			5.964			
6			*d*	1630[d]					*d*				
		1.080		1.080		*c*				1.08[f]		*c*	

[a] The n^* values correspond to removal of the Rydberg electron from the $v = 0$ level of the Rydberg state to that of He_2^+. The $\Delta G_{1/2}$ values are in cm^{-1} and the R_e values in Å, and are mostly from M. L. Ginter, *J. Chem. Phys.*, **42**, 561 (1965), **45**, 248 (1966); *J. Mol. Spectry.*, **17**, 224 (1965); **18**, 321 (1965); M. L. Ginter and D. S. Ginter, *J. Chem. Phys.*, **48**, 2284 (1968). The remaining values are from Herzberg's book (footnote *b* of Table I). [b] For the He_2^+ ion, $\Delta G_{1/2} = 1628.0$ cm^{-1}, $R_e = 1.080_6$ Å (Ginter and Ginter, footnote *a*). [c] Because of strong l uncoupling, accurate R_e values are not known, but are no doubt near 1.08 Å for the nd MO's. [d] Triplet npσ states up to $n = 12$ and npπ states up to $n = 17$ are known (Ginter and Ginter, footnote *a*). Ginter has triplet and singlet npσ data for $n = 4$, 5, and 6, but these are not yet analyzed. [e] See Table IV, footnote *h*. [f] For $n = 7$ and 8, $R_e = 1.08$ Å.

ence to LCAO expressions. The ns MO's in H_2 have an innermost loop of the same additive LCAO form (approximately $1s_a + 1s_b$) and size as the $1\sigma_g$ MO of the core. This loop should give the ns MO's a bonding effect of the same qualitative character as for $1\sigma_g$, but of much smaller magnitude, with the latter diminishing rapidly as n increases because of the diminishing relative amplitude of this loop. The fact that $\Delta G_{1/2}$ is larger and R_e smaller, in H_2 than in H_2^+, to an extent that diminishes rapidly as n increases, may be attributable in considerable or large part to this bonding effect. However, except for the innermost part of ns and perhaps npσ MO's, Rydberg MO's at R_e for Rydberg states are very much closer to united-atom AO's than to separate-atom LCAO forms, and their bonding characteristics can be sensibly explained in terms of the effects of core splitting on united-atom AO's, as is shown in sections 3 and 4.

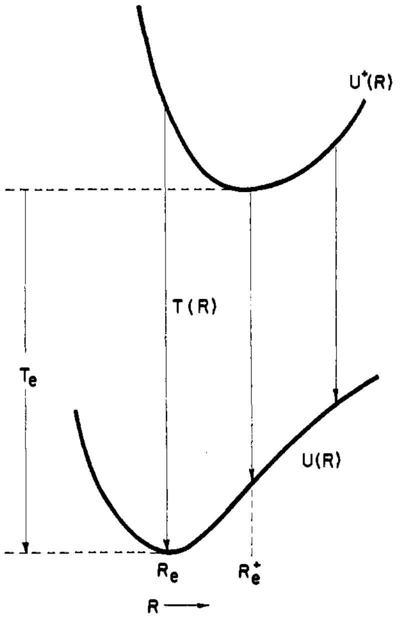

Figure 1. Rydberg and ionic states (schematic).

3. Relation of Potential Curve Data to R Variation of n^* Values. Data on ω_e (approximately equal to $\Delta G_{1/2}$)[12] and R_e give *empirical information* on how T or n^* of a Rydberg state *is changing with* R near R_e. For a molecule A_2 and its ion A_2^+, let $Q = R - R_e$ and $Q^+ = R - R_e^+$; then $U(R) = {}^1/_2kQ^2 + \ldots$, $U^+(R) = {}^1/_2k^+Q^{+2} + \ldots$ ($k = 4\pi^2c^2\mu\omega_e^2$ dynes/cm). Then at any R, if R is in centimeters, the *vertical* T (*i.e.*, T for R constant) in ergs is given approximately (see Figure 1) by

$$T(R) = T_e + \frac{1}{2}k^+Q^{+2} - \frac{1}{2}kQ^2 \qquad (10)$$

T_e is the value of T for removal of an electron from the minimum of the Rydberg state $U(R)$ curve to the minimum of the $U^+(R)$ curve. Write $Q = Q^+ + (R_e^+ - R_e)$. Then

$$T(R) = [T_e - {}^1/_2k(R_e^+ - R_e)^2] - k(R_e^+ - R_e)Q^+ + {}^1/_2(k^+ - k)(Q^+)^2 \qquad (11)$$

Now differentiating eq 11, one has

$$\mathrm{d}T/\mathrm{d}R = \mathrm{d}T/\mathrm{d}Q^+ = -k(R_e^+ - R_e) + (k^+ - k)Q^+ \qquad (12)$$

That is, T is decreasing, and n^* increasing, with increasing R if $R_e^+ > R_e$, and at an accelerating rate[14] for $R > R_e^+$ but at a decelerating rate for $R < R_e^+$; and *vice versa* if $R_e^+ < R_e$.

Now from eq 1 of ref 2, namely $T = Ry/(n - \delta)^2 \equiv Ry/n^{*2}$, one finds

$$\mathrm{d}\delta/\mathrm{d}R = (n^{*3}/2Ry)\,\mathrm{d}T/\mathrm{d}R \qquad (13)$$

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(14) Since if $R_e^+ > R_e$, then $k^+ < k$ by an application of the empirical Mecke–Birge rule (see Herzberg, footnote *b* of Table I) according to which $R_e^2\omega_e$, or R_e^4k, is approximately the same for different states of any one molecule.

Table III. Vertical δ Values of MO's for Rydberg States of H_2[a]

$R = 0$ (He)		$R = R_e$ of H_2^+					
UAO symbol	δ[a]	Obsd[a,b] δ	$(n/n^*)^2$	Calcd[c] δ_{cs}	δ_{pen} by diff[d]	Obsd[e] $d\delta/dR$	Calcd[f] $d\delta_{cs}/dR$
1s	[0.256][g]	[0.03][g]					
2pσ	0.028	0.48	1.73	+0.24	0.24	(+1.78)[h]	+0.10
2pπ	0.028	0.003	1	−0.05	0.05	−0.07	−0.05
2s	0.230	−0.003	1	−0.17	0.17	−0.25	−0.09
3pσ	0.028	0.352	1.28	+0.15	0.20	+0.24	+0.11
3pπ	0.028	−0.007	1	−0.05	0.04	−0.10	−0.05
3s	0.226	−0.011	1	−0.17	0.16	−0.15	−0.09
3dσ	0.002	0.063	1	+0.02	0.04	0.02	0.02
3dπ	0.002	0.032	1	+0.01	0.02	0.02	0.01
3dδ	0.002	−0.011	1	−0.02	0.01	0.00	−0.02

[a] The observed δ values ($\delta \equiv n - n^*$, $n^* = [109{,}707/T]^{1/2}$ with T in cm^{-1}) were computed from T values which except as otherwise indicated were *means* of singlet and triplet state values corresponding to Tables I and II. [b] The T values were first corrected to eliminate zero-point energies and were further corrected so as to be vertical values at R_e of the molecular ion. These corrections are, however, very small except for npσ (only about −0.02 even there). [c] Values of $\delta_{cs} = \delta - \delta_{pen}$ calculated using eq 9 with γ (see ref 8) taken as (n/n^*), ρ taken as 0.5, and with $\delta^+(\frac{1}{2}\gamma R)$ values [where $\delta^+(R) = n - (4Ry/T(R))^{1/2}$, *cf.* eq 1 of ref 2 with $Z_c = 2$] obtained using for $T(R)$ the energy values of Table I of D. R. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans. Roy. Soc.*, **A246**, 215 (1954) (also see Tables II and III in part V). Note that the values of Bates, *et al.*, are *exact* energy values for H_2^+, and not first-order perturbation values; for commentary see section 1, second paragraph after eq 7. [d] δ_{pen} was obtained by subtracting the calculated δ_{cs} from the observed δ values. [e] For *triplet states* (the values for the singlet states would be fairly similar), calculated from the experimental data of Table I or II using eq 14. The values are in terms of Å for R. [f] Computed using eq 15, with $d\delta^+/dR$ values obtained from $\delta^+(R)$ values obtained in the manner described in footnote *c*, and with γ values taken as $(n/n^*)^2$ and ρ taken as 0.5. As in the preceding column, R is in Å. [g] These are [δ], not δ, values (see eq 7 of ref 2), based on the *singlet* ground state, which has no triplet counterpart. [h] From the *singlet* state only, since the corresponding triplet state is unstable.

Table IV. Vertical δ Values of MO's for Rydberg States of He_2[a]

$R = 0$ (Be)		$R = R_e$ of He_2^+					
UAO symbol	δ[a]	Obsd[a,b] δ	$(n/n^*)^2$	Calcd[c] δ_{cs}	δ_{pen} by diff[d]	Obsd[e] $d\delta/dR$	Calcd[f] $d\delta_{cs}/dR$
1s	[0.675][g]	[0.32][h]					
2pσ	[0.566]	[1.16][h]					
2s	[0.865][g]	0.180	1.21	−0.22	0.40	−0.17	−0.12
2pπ	[0.566]	0.054	1.06	−0.06	0.11	−0.10	−0.06
3pσ	0.414	0.770	1.81	+0.19	0.58	+0.11	+0.05
3s	0.821	0.158	1.11	−0.20	0.36	−0.16	−0.10
3pπ	0.414	0.054	1.04	−0.06	0.11	−0.14	−0.06
3dσ	0.110	0.057	1.04	+0.02	0.04	+0.05	0.02
3dπ	0.110	0.035	1.03	+0.01	0.02	+0.04	0.01
3dδ	0.110	−0.014	1	−0.02	0.01	−0.00	−0.02

[a–g] See corresponding footnotes to Table III. [h] From approximate theoretical SCF–MO calculations (P. Phillipson, *Phys. Rev.*, **125**, 1981 (1962)) on the *singlet* normal state of He_2, at R_e of He_2^+.

Combining eq 13 (where T is in cm^{-1} if Ry is in cm^{-1}) with eq 12 (where dT/dR is in ergs/cm), one has for the empirical $d\delta/dR$

$$d\delta/dR = F(n^{*3}/2Ry)[k(R_e - R_e^+) - (k - k^+)Q^+] \quad (14)$$

where with R in cm and Ry in cm^{-1}, F converts from ergs to cm^{-1}.

In section 4 (Tables III and IV), values of $d\delta/dR$ obtained from empirical R_e, R_e^+, and k, k^+ data using eq 14 will be compared with computed values based on the demi-H_2^+ model using eq 9. Equation 9 contains several quantities (δ_{pen}, ρ, γ) which, although they must vary slowly with R, one may probably for R values near R_e treat as constant to a sufficient approximation for the purpose of making a significant though crude theoretical estimate of $d\delta/dR$. With this assumption, differentiation of eq 9 yields

$$(d\delta/dR)_R \approx \rho\gamma(d\delta^+/dR)_{1/2\gamma R} \quad (15)$$

where to obtain $d\delta/dR$ at R, $d\delta^+/dR$ must be taken at $\frac{1}{2}\gamma R$.

The fact that the effects of the Rydberg electron on $\Delta G^1/_2$ and R_e are relatively larger and more persistent in H_2 than in He_2 (see Tables I and II) can be accounted for. Namely, from eq 14 with $Q^+ = 0$, $(R_e - R_e^+)$ must be proportional to $d\delta/dR$ divided by k; and since the k values are only about half as large for H_2 as for He_2, $R_e - R_e^+$, and therefore also $\Delta G_{1/2}^+ - \Delta G_{1/2}$ in view of the Mecke–Birge rules[14] relating R_e to ω_e, are more strongly affected by core splitting for H_2 than for He_2. By the same reasoning, it is understandable that for molecules with still larger force constants (*e.g.*, N_2, NO) the apparent bonding effects of even the lowest energy Rydberg MO's are found to be very small: ΔG and R_e for N_2 and NO are very close to their values for the free ions.

4. Analysis of Rydberg Term Values. We now seek to interpret observed term defect (*i.e.*, δ) data for Rydberg states of H_2 and He_2 corresponding to the n^* data for Tables I and II. Evidence on the variation of δ values with R can also be obtained by using two further sets of data, namely united-atom δ values to represent $R = 0$, and $d\delta/dR$ values computed from the $\Delta G_{1/2}$ and R_e data of Tables I and II using eq 14. Tables III and IV summarize all such information for n values up to 3. The molecular δ values given in these tables have been computed from mean T values of corresponding singlet and triplet Rydberg states which have been corrected so as to represent *mean vertical* vibration-free T values at an R equal to R_e *of the positive ion.* (In most cases, the corrections to δ for zero-point vibration and verticality are very small.) The $d\delta/dR$ values are also for R of the positive ion, but are for triplet states only, since the time required to obtain singlet–triplet averages seemed hardly justified, also because several of the singlet states are subject to distorting perturbations.

In accordance with eq 9, the observed term defects δ of the H_2 and He_2 Rydberg MO's can be attributed to the superposition of a penetrational contribution δ_{pen} which should be more or less related to the observed δ for the united-atom orbital at $R = 0$,[15] and a core-splitting contribution δ_{cs}. The core-splitting defects as computed from the demi-H_2^+ model (fifth column of Tables III and IV) are negative for the unpromoted MO's ns, npπ, and ndδ, but positive for the promoted MO's npσ, ndσ, and ndπ. The slightly negative *observed* defects for ns, npπ, and 3dδ for H_2 (also of 3dδ for He_2) and the positive δ's for npσ, ndσ, and ndπ, can be taken as a confirmation of this prediction from the model.

The smallness of the *magnitudes* of the observed negative defects for ns and npπ of H_2 (much smaller than those of the computed δ_{cs} values) are understandable if we make the reasonable supposition that there is an approximate cancellation of the negative δ_{cs} by a positive δ_{pen}. The differences between the observed δ's and the calculated δ_{cs} values as listed in the sixth column of Tables III and IV should then represent δ_{pen}. It is seen that these listed values are very reasonable; they are roughly the same, for ns and npπ, as the observed values for the united atom (second column in Table III).

For the $^3\Sigma^+{}_g$ state of H_2 with the 3s MO, the actual values of T as a function of R, based on an accurate theoretical computation, can be seen in Figure 2 of a paper by Wakefield and Davidson.[16] T, hence also δ, decreases steadily with increasing R. At $R = 0$, δ is δ_{pen} of He, equal to $+0.31$. The decreasing value of δ as R increases is attributable to superposition of a δ_{cs} contribution which, starting from zero at $R = 0$, becomes increasingly negative as R increases.

In the case of He_2, the values of δ_{pen} obtained by subtracting computed δ_{cs} from observed δ values are larger than for H_2, and all δ's are positive except for 3dδ. But unlike the case of H_2, all the δ_{pen} values are much smaller than the δ (or [δ]) values of the united atom. The reasons for this relation are as follows. In H_2, the Rydberg MO's go smoothly into Rydberg AO's of the united atom He. Equation 9 should then be valid all the way to $R = 0$ if we recognize that δ_{pen} should change somewhat with R (it is of course small except for the ns MO's). In He_2, the changes as $R \rightarrow 0$ are much more drastic. Since the 2s and 2pπ Rydberg MO's become valence-shell MO's of the united atom Be, the demi-H_2^+ model must fail for these near $R = 0$, although it should definitely be valid for a wide range near R_e. Further, δ_{pen} for the ns and npπ MO's with $n > 2$ should increase greatly as $R \rightarrow 0$, since ns and np AO's of Be are of penetrating type. Except, however, for this rapid change of δ_{pen} as $R \rightarrow 0$, and its effects on γ and perhaps ρ, the demi-H_2 model should remain valid for these MO's all the way to $R = 0$.

Evidently δ_{pen} for He_2 must decrease rapidly as R increases from zero during the early stages of core splitting, but this decrease apparently is more or less complete well before R_e of He_2^+ (approximately the same as R_e for the Rydberg states) is reached. This conclusion is indicated by the only moderately large values of δ_{pen} obtained from $\delta_{obsd} - \delta_{cs}$ calculated (that these are somewhat larger than for H_2 is understandable in view of the now three-electron core), but is also very strongly supported by the observed values of $d\delta/dR$, whose signs and approximate magnitudes in all cases agree with the values predicted from the demi-H_2^+ model. The agreements between observed and calculated $d\delta/dR$ values for both H_2 and He_2 are amazingly good in view of the gross approximations made in obtaining the equation used to obtain the calculated values. Note expecially that the *sign* of the computed $d\delta/dR$ is practically always in agreement with the experimental sign.

The behavior of the δ's for the npσ MO's now deserves special attention. In H_2, at R equal to R_e of H_2^+, the 2pσ MO is still an incompletely promoted valence-shell MO (see next to last paragraph of section 1), but rapidly approaches Rydberg MO status as R decreases toward $R = 0$. The singlet and triplet states at R_e of H_2^+ differ very greatly in their individual vertical δ values (0.673 for $1\sigma_g1\sigma_u$, $^3\Sigma_u^+$ and 0.188 for $1\sigma_g1\sigma_u$, $^1\Sigma_u^+$), a fact which is understandable in view of their valence-shell character and different modes of dissociation. (At smaller R values, they draw rapidly together.) Nevertheless, their average vertical δ is qualitatively understandable in terms of the core-splitting demi-H_2^+ Rydberg state model (see Table III).[17]

The 3pσ MO in H_2 is definitely a Rydberg MO which, however, still shows a large δ because of the large δ of its 2pσ precursor (on precursors, see part III, section 1). But as is typical in Rydberg series with large δ's, the δ for 3pσ is smaller than for 2pσ; and, as one sees from the n^* values in Table I, the δ values for 4pσ and 5pσ have decreased still further, tending in the usual way toward limiting values as n increases. These δ's are good examples of δ's attributable to a strong core-splitting effect of a type associated with incomplete promotion; the MO's are pure npσ in character as $R \rightarrow 0$ but tend toward $\sigma_u[(n-1)s]$ as $R \rightarrow \infty$; at R_e the *outer parts* of the npσ MO's are nearly pure npσ in character for $n > 2$.

In He_2 the 2pσ MO is definitely a valence-shell MO, represented only in the closed-shell normal state $1\sigma_g{}^2 1\sigma_u{}^2$, $^1\Sigma_g{}^+$. This MO at R_e of He_2^+ is much closer to the LCAO form σ_u1s than to the united-atom form 2pσ, as is shown by its large [δ] value of 1.16 based on $n = 2$ (see Table IV). For 3pσ, the very incomplete promotion and very large [δ] for its precursor 2pσ serve to account for the exceptionally large δ.

The larger δ value of 3pσ for He_2 than for H_2 (0.832 as compared with 0.503 for the respective 3pσ triplet

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[15] Polarization also contributes to some extent to the δ's of Rydberg AO's, and is dominant when these are nearly nonpenetrating, but it may be difficult to identify separately for Rydberg MO's.

[16] C. B. Wakefield and E. R. Davidson, *J. Chem. Phys.*, 43, 834 (1965). Near R_e, crossing of the $1\sigma_g3s$, $^3\Sigma_g{}^+$ and $1\sigma_g3d\sigma$, $^3\Sigma_g{}^+$ curves complicates the experimental data, but the effects of this crossing can be disregarded here.

[17] The much larger observed than calculated $d\delta/dR$, which moreover is for the *singlet* state only, can be attributed to the special dissociation behavior of this state.

states) is clearly related to the lesser degree of promotion (at R_e of the ion) of the precursor MO $2p\sigma$, but is also attributable in part to greater penetration, although probably not as much as the calculated δ_{pen} of Table IV indicates.

Of considerable interest are the $nd\sigma$, $nd\pi$, and $nd\delta$ states of H_2 and He_2. The MO's are nonpenetrating and without core precursors, but small δ's do occur, decreasing in the order from $nd\sigma$ to $nd\pi$ just as predicted by the demi-H_2^+ core-splitting model and in accordance with the fact that $nd\sigma$ and $nd\pi$ are promoted MO's but $nd\delta$ is unpromoted. The smallness of the δ's for $nd\sigma$ and $nd\pi$ at R_e of the positive ion shows that, in sharp contrast to the $np\sigma$ cases, promotion is nearly but definitely not quite complete; this is understandable in terms of considerations advanced in section 5 of part VI.[3] The small negative δ's for $nd\delta$ are just as expected from the core-splitting model for an unpromoted nonpenetrating MO. The appearance of a small δ_{pen} for the $3d\sigma$ and $3d\pi$ MO's deserves comment. It is probably a reflection of the crudeness of the model together with the lack of complete promotion in those MO's, rather than of any real penetration effect.

The calculated δ_{cs} values, hence the derived δ_{pen} values, in Tables III and IV were based on an *assumed* value of 0.5 for the factor ρ of eq 9 and 15, which measures the extent to which the core-splitting perturbation potential (eq 5) is weaker than in H_2^+. Although slightly larger values might have been anticipated, the assumed value of 0.5 gives a distinctly more reasonable set of values for δ_{pen} than a larger value, such as, for example, 0.6.

The agreements between observed δ and $d\delta/dR$ values and those expected from the demi-H_2^+ model for H_2 and for He_2 are so good as to lead to the conclusion that this model probably represents the actual situation rather well for the Rydberg MO's of those molecules near the R_e values of their Rydberg states.

Some Hydrogen-Bond Relations between Homoconjugates and Heteroconjugates of Phenols and Phenolates in Acetonitrile[1]

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Abstract: With the exception of *ortho*-substituted phenols, the hydrogen-bond donating capacity with reference to chloride ion of substituted phenols (HA) as indicated by the heteroconjugation constant $K^f_{\mathrm{HA\cdot Cl^-}} = [\mathrm{HA\cdot Cl^-}]/[\mathrm{HA}][\mathrm{Cl^-}]$ increases with increasing acid strength of HA. The hydrogen-bond accepting capacity of A^-, as indicated by $K^f_{\mathrm{HR\cdot A^-}}$, HR being *p*-bromophenol, increases with increasing basic strength of A^-. This is also true for *ortho*-substituted phenolate ions. A plot of log $K^f_{\mathrm{HA\cdot Cl^-}}$ *vs.* the Hammett substituent constants σ yields a straight line with slope of 1.0 except for *ortho*-substituted phenols, while the plot of log $K^f_{\mathrm{HR\cdot A^-}}$ *vs.* σ is linear for all phenols tested and has a slope of -1.28. A value of $\sigma = 1.10$ for the *o*-nitro group was used. The equilibrium constant of the reaction $\mathrm{HA_2^-} + \mathrm{HR\cdot Cl^-} \rightleftharpoons \mathrm{HA\cdot Cl^-} + \mathrm{HR\cdot A^-}$ was expected and found to be equal to 1, except for 2,6-dinitro-4-chlorophenol. *ortho*-Substituted phenols form only a monoconjugate $\mathrm{HA\cdot Cl^-}$, whereas *meta*- and *para*-substituted phenols also form a diconjugate $\mathrm{(HA)_2Cl^-}$. A plot of $\mathrm{p}K^d_{\mathrm{HA}}$ *vs.* α yields a straight line, but the plot of $(\mathrm{p}K^d_{\mathrm{HA}})_{\mathrm{AN}}$ *vs.* $(\mathrm{p}K^d_{\mathrm{HA}})_{\mathrm{water}}$ exhibits considerable scatter.

In an aprotic protophobic solvent like acetonitrile (AN), anions with a localized charge have a large medium activity coefficient with reference to that in water. Such anions can be stabilized in AN either by homoconjugation

$$\mathrm{A^-} + \mathrm{HA} \rightleftharpoons \mathrm{AH\cdots A^-}$$

$$K^f_{\mathrm{HA_2^-}} = \frac{[\mathrm{HA_2^-}]f_{\mathrm{HA_2^-}}}{[\mathrm{HA}][\mathrm{A^-}]f_{\mathrm{A^-}}} \tag{1}$$

$$f_{\mathrm{HA_2^-}} = f_{\mathrm{A^-}}$$

or by heteroconjugation

$$\mathrm{A^-} + \mathrm{HR} \rightleftharpoons \mathrm{RH\cdots A^-}$$

$$K^f_{\mathrm{HR\cdot A^-}} = \frac{[\mathrm{HR\cdot A^-}]f_{\mathrm{HR\cdot A^-}}}{[\mathrm{HR}][\mathrm{A^-}]} \tag{2}$$

$$f_{\mathrm{HR\cdot A^-}} = f_{\mathrm{A^-}}$$

in which HR is a reference hydrogen bonder which is such a weak acid that it does not undergo proton exchange with A^-. In the present work we have used *p*-bromophenol as HR. The value of $K^f_{\mathrm{HA_2^-}}$ depends on the hydrogen-bond donating capacity of HA and the hydrogen-bond accepting capacity of A^-.[2] Thus the ratio $K^f_{\mathrm{HA_2^-}}/K^f_{\mathrm{HR\cdot A^-}}$ gives the ratio of the hydrogen-bond donating capacities of HA and HR relative to the anion A^-. The relative hydrogen-bonding capacity of a series of phenols, denoted by HA, with reference to a given hydrogen-bond accepting anion, for which we have used the chloride ion, is given by

$$\mathrm{Cl^-} + \mathrm{HA} \rightleftharpoons \mathrm{AH\cdots Cl^-}$$

$$K^f_{\mathrm{HA\cdot Cl^-}} = \frac{[\mathrm{HA\cdot Cl^-}]f_{\mathrm{HA\cdot Cl^-}}}{[\mathrm{HA}][\mathrm{Cl^-}]f_{\mathrm{Cl^-}}} \tag{3}$$

$$f_{\mathrm{HA\cdot Cl^-}} = f_{\mathrm{Cl^-}}$$

We have also determined the hydrogen-bond donating

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(2) See also J. Gordon, *J. Org. Chem.*, **26**, 738 (1961).