

THE ORIGIN OF RYDBERG ORBITALS

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

The concept of hybridization and the principle of maximum overlap are invoked to explain the origin of the Rydberg character of the lowest excited MO of LiH. It is found that the nodal surface of this antibonding MO is not bisecting the bond. The origin of the Rydberg character of the lowest singlet and triplet MO's of the H₂ molecule is studied by means of an energy partitioning. The repulsion of electrons is found to be responsible for the diffuse character of the excited so-called antibonding MO's. The singlet-triplet separation is controlled to a large extent by one-electron contributions.

The occurrence of Rydberg molecular orbitals (RMO) can be understood most simply by the use of MO correlation diagrams. A diatomic molecule is considered to be an intermediate system between the corresponding united atom and the separated atoms. If the MO's of an excited state correlate with AO's which are unoccupied in the ground states of the united atom and/or the separated atoms, then we have to expect RMO's which are characterized by extremely large orbital radii. It should be noted that a molecule in its equilibrium geometry reflects much more the situation of the separated atoms rather than that of the united atom. The consideration of AO's, in particular their principal quantum numbers, of the separated atoms is sometimes not sufficient for the prediction of RMO's. In the case of ion pairs instead of neutral separated atoms the large ionic radii of anions are then responsible for the presence of RMO's.

The use of only MO correlation diagrams for the discussion of RMO's can sometimes be misleading. On the one hand it is the topological character of the correlation diagram which does not include specific properties of RMO's; on the other hand the repulsion of electrons, which likely has an important influence on the MO's, is not involved in MO correlation diagrams. Therefore, we should use state correlation diagrams in addition. Two examples should warn of too much simplified considerations.

RESULTS AND DISCUSSION

The LiH Molecule

The HOMO with its bonding nature is represented by a simple LCAO expansion of the form

$$\psi(2\sigma) = a 2s(\text{Li}) + b 1s(\text{H}) \quad a, b > 0 \quad (1)$$

so that the LUMO is immediately fixed by the condition of orthogonality; it is an antibonding MO of the form

$$\psi(3\sigma) = b 2s(\text{Li}) - a 1s(\text{H}) \quad (2)$$

(in order to achieve a simple notation the overlap between the contributing AO's is neglected in the normalization factor). The HOMO (1) correlates with the 2s AO and the LUMO (2) correlates with the 3s AO of the Be atom when the LiH molecule is compared with the united atom. But which property of the 3σ MO reflects the Rydberg character? This misleading situation arises because we took care, in the sense of the energy variation principle, only for the 2σ MO but not for the 3σ MO. In an excited state 2σ as well as 3σ are occupied and there is no reason to consider 3σ only as an accidental by-product of the calculation of the 2σ MO. The 2σ MO in its simple representation (1) is qualitatively well described, however, for the 3σ MO, in the representation (2), the fundamental principle of maximum overlap is ignored which is the basis of all kinds of MO computational procedures. According to Fig. 1 an essential stabilization of the 3σ MO can be achieved by the increase of the overlap of the contributing AO's. Consequently the 2s(Li) AO should be promoted to a hybrid of the form

$$\psi_{\text{hyb}}(\text{Li}) = c 2s(\text{Li}) + d 3s(\text{Li}) . \quad (3)$$

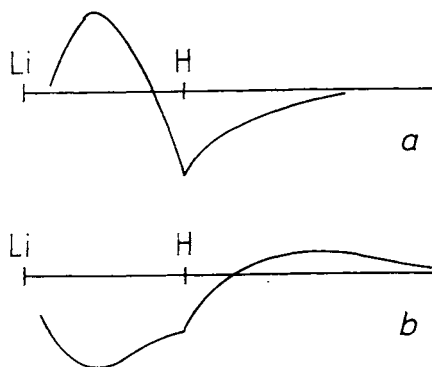


FIG. 1

The LUMO of the LiH molecule: *a* the 2s(Li)-1s(H) representation (the valence nodal surface is intersecting the bond); *b* the same orbital when the admixture of 3s(Li) is allowed (the valence nodal surface is outside the bond)

The orthogonality condition requires (3) to be included also in the 2σ MO, but in contrast to 3σ no essential changes in the bonding MO 2σ can be expected.

At the point a critical remark is necessary to be emphasized concerning one of some well known maxims for the construction of LCAO-MO's: the energies of AO's in their respective atoms should be of comparable magnitude. This recipe works only if the resulting MO energy is far from the energy of any further AO, and this is generally true for bonding orbitals. However, the energies of antibonding orbitals are shifted upwards to the dense ladder of AO's with higher principal quantum numbers so that the above maxim must be extended: AO's should be added to an LCAO-MO if their energies are comparable with the MO energy. The use of Eq. (3) in Eq. (2) causes a shift of the nodal surface out of the bond so that some bonding character converts the former antibonding MO to a nonbonding MO with an increased radius which is caused by the admixture of $3s(\text{Li})$.

The procedure for the stabilization of an "antibonding" MO just described is by far no unimportant improvement of numerical data. In general the stabilization energy has an amount of several eV! and shifts the MO energy from the ionization continuum below the ionization limit^{1,2}.

The H₂ Molecule

The Rydberg character of MO's of a homopolar molecule cannot be explained by the arguments just applied to polar bonds. The promotion energy which is to pay for the admixture of AO's with higher quantum numbers cannot be paid back for reasons of symmetry. The nodal surface remains in the center of the bond. The "antibonding" MO has to choose another way for its stabilization: without changing its topological structure the orbital simply increases its size. For the discussion of the Rydberg character of MO's of polar bonds simple pictorial models were successful, in contrast to MO's in homopolar molecules where the Rydberg character cannot be rationalized in such a simple manner. In order to achieve also more or less primitive patterns of understanding for the origin of RMO's the energetically lowest excited states of the H₂ molecule will be considered.

The ground state of H₂ described by a simple LCAO-MO wave function (appropriate spin functions are omitted)

$$\begin{aligned} \Psi({}^1\Sigma_g^+) &= \sigma_g(1) \sigma_g(2) \\ \sigma_g &= [2(1 + S)]^{-1/2} \{1s_a + 1s_b\} \end{aligned} \quad (4)$$

correlates with the ground states of the neutral separated atoms. The lowest excited singlet state

$$\begin{aligned} \Psi({}^1\Sigma_u^+) &= 2^{-1/2} \{ \sigma_g(1) \sigma_u(2) + \sigma_u(1) \sigma_g(2) \} \\ \sigma_u &= [2(1 - S)]^{-1/2} \{1s_a - 1s_b\} \end{aligned} \quad (5)$$

correlates with the ion pair $H^+ + H^-$; the latter exhibits a pronounced diffuse character in its ground state wave function by which the MO wave function is influenced. The lowest triplet state

$$\Psi(^3\Sigma_u^+) = 2^{-1/2} \{ \sigma_g(1) \sigma_u(2) - \sigma_u(1) \sigma_g(2) \} \quad (6)$$

correlates in the same manner as the ground state. Therefore, the triplet state should have less Rydberg character than the singlet state of the "same" configuration. As a direct consequence the MO's σ_g and σ_u in Eqs (4), (5), and (6) can no longer be seen to be the same. The commonly accepted formulation "multiplets with the same configuration" should be used carefully.

In order to study the different MO's in different states a comparison between the systems H_2^+ and H_2 should also be performed. In the ground states of both systems a common σ_g MO can be used. This situation causes the possibility to eliminate (but not to neglect) the electron repulsion in primitive MO theories. However, in the excited states of the systems H_2^+ and H_2 the σ_u orbitals are expected to be essentially different so that the electron repulsion will be the central quantity in our discussion.

The MO's $1\sigma_g$ and $1\sigma_u$ in H_2^+ . For the discussion of the effect of electron repulsion on the shape of the MO's in H_2 we have to examine first the system H_2^+ which is free of electron interaction. In a second step changes can be observed when going from H_2^+ to H_2 .

A simple LCAO-MO wave function is used and the variation principle is applied

$$\begin{aligned} \sigma_{g,u} &= [2(1 \pm S)]^{-1/2} \{ 1s_a \pm 1s_b \} \\ 1s_a &= (k^3/\pi)^{1/2} \exp(-kr_a) \\ E_{g,u} &= (H_{aa} \pm H_{ab}) / (1 \pm S) = \alpha + V_{aa}^b \pm (H_{ab} - SH_{aa}) / (1 \pm S). \end{aligned} \quad (7)$$

The scaling factor k is estimated separately for both orbitals. All electronic contributions to the total energy are seen as functions of k . These are the energy of the free H atom α ; the quasi-classical interatomic Coulomb interaction between H and H^+ V_{aa}^b ; $H_{aa} = \alpha + V_{aa}^b$; the "resonance" integral (better is bond integral) H_{ab} . The overlap integral between $1s_a$ and $1s_b$ is called S .

The results are presented in Table I. As is well known the quasi-classical interaction in H_{aa} cannot explain the bond, but it is interesting to note that the function $H_{aa}(k)$ is minimal at a reasonable value of $k = 1.06$. The function $E_g(k)$ has a minimum at $k = 1.25$ and yields a binding energy of 2.3 eV. It is often believed that the resonance integral indicates the binding energy. However, with $k = 0.85$ a zero binding energy*

* The SI expressions of atomic units hartree and bohr, referred hereafter in this paper as to 1 h and 1 b, respectively, are $E_h = 2.6255 \cdot 10^6 \text{ J mol}^{-1}$ and $a_0 = 0.52917706 \cdot 10^{-10} \text{ m}$.

is obtained ($E_g = -0.5$ h) although the resonance integral in its reduced form $E_g - H_{aa}$ is lowered only by a factor two with respect to $k = 1.25$. The surprising answer to this obvious dilemma is given by the quasi-classical interaction which solely cannot explain the bond but it shows a drastic increase for lower k values. The minimum of $E_u(k)$ occurs at $k = 0.90$. The vertical transition energy $\sigma_g \rightarrow \sigma_u$ of 11.4 eV is in good agreement with the exact value of 11.6 eV (see ref.³). The use of a common k value of the separated atoms ($k = 1$) for both orbitals increases the ground state energy by 0.84 eV and the excited state energy by only 0.08 eV. The use of a common k value of the ground state ($k = 1.25$) for both orbitals increases the excited state energy by 1.5 eV. The antibonding orbital can hardly be seen as RMO although the $1s$ AO's in σ_u are larger in their size by 0.3 b than those in σ_g . The size of the $1s$ AO's in σ_u has the same magnitude than that of the free H atom. An extensive description of the MO's of H_2^+ with respect to their Rydberg character is given by Mulliken⁴.

The MO's $1\sigma_g$ and $1\sigma_u$ in H_2 . The wave functions which can be constructed by the MO's $1\sigma_g$ and $1\sigma_u$ are those for the ground state (4) as well as for the lowest singlet and triplet states (5) and (6), respectively. The one-electron contributions to the total energy can be taken from H_2^+ in the previous section (7). The internuclear distance of 2 b is held fixed in order to study the effect of scaling and to have a distance near the equilibrium of the excited singlet state.

TABLE I

The energies of the ground E_g and the first excited states E_u as functions of the scaling factor k for H_2^+ . (The unit of k is a_0^{-1} ; $a_0 = 53.9$ pm. All energies are measured in hartree; 1 hartree = = 27.2 eV. All quantities which are functions of the internuclear distance are calculated at the experimental equilibrium distance of H_2^+ ($2a_0$). For S , α , H_{aa} see Eq. (7))

k	S	α	H_{aa}	E_g	E_u
0.5	0.858	-0.375	-0.240	-0.253	-0.071
0.6	0.807	-0.420	-0.320	-0.343	-0.113
0.7	0.753	-0.455	-0.382	-0.416	-0.143
0.8	0.697	-0.480	-0.427	-0.475	-0.160
0.9	0.641	-0.495	-0.457	-0.521	-0.164
1.0	0.586	-0.500	-0.473	-0.554	-0.161
1.1	0.533	-0.495	-0.475	-0.575	-0.147
1.2	0.483	-0.480	-0.466	-0.585	-0.124
1.3	0.435	-0.455	-0.445	-0.584	-0.091

The electron repulsion in the ground state is given by the Coulomb integral $(\sigma_g\sigma_g, \sigma_g\sigma_g)$ which is expressed in atomic orbitals a and b . The application of the Mulliken approximation yields:

$$(\sigma_g\sigma_g, \sigma_g\sigma_g) \simeq 1/2\{(aa, aa) + (aa, bb)\}. \quad (8)$$

The numerical values of these integrals together with their k dependence yield the electron repulsion in the simple form

$$E_{e1} = 0.526k. \quad (9)$$

The total energy is

$$E(k) = 2E_g(k) + E_{e1}(k) - E_{nuc} \quad (10)$$

(the nuclear repulsion E_{nuc} must be subtracted because it is counted twice in $2E_g$). The new term E_{e1} tries to lower the k value against the trend of E_g . A compromise is achieved at $k = 1.05$ with the corresponding energy of $E = -1.082$ h. (At the equilibrium distance of 1.40 b the values $k = 1.18$ and $E = -1.120$ h are well known⁵.)

In both the excited states $^1\Sigma_u^+$ and $^3\Sigma_u^+$ the respective electron repulsion energies are

$$E_{e1}^S = (\sigma_g^S\sigma_g^S, \sigma_u^S\sigma_u^S) + (\sigma_g^S\sigma_u^S, \sigma_g^S\sigma_u^S) \quad (11a)$$

$$E_{e1}^T = (\sigma_g^T\sigma_g^T, \sigma_u^T\sigma_u^T) - (\sigma_g^T\sigma_u^T, \sigma_g^T\sigma_u^T). \quad (11b)$$

The evaluation of these integrals must be performed with different AO's in different MO's. The Mulliken approximation together with a further simplifying approximation

$$(a(k_g) a(k_g), a(k_u) a(k_u)) \simeq (a(k_g) a(k_u), a(k_g) a(k_u)) \quad (12)$$

yield

$$E_{e1}^S = (a(k_g^S) a(k_g^S), a(k_u^S) a(k_u^S)) \quad (13a)$$

$$E_{e1}^T = (a(k_g^T) a(k_g^T), b(k_u^T) b(k_u^T)). \quad (13b)$$

The reasonable form

$$E_{e1}^S = (a(1) a(1), a(1) a(1)) (k_g^S k_u^S)^{1/2}, \quad (14)$$

which holds at least for not very different values of k_g and k_u , is obtained for the dependence of the electron repulsion on the scaling factors; a corresponding form is used for E_{e1}^T . Similar to Eq. (9) the final results are

$$E_{e1}^S = 0.625(k_g^S k_u^S)^{1/2} \quad (15a)$$

$$E_{e1}^T = 0.427(k_g^T k_u^T)^{1/2}. \quad (15b)$$

Instead of Eq. (10) the total energies of the excited states are

$$E(S) = E_g(k_g^S) + E_u(k_u^S) + E_{e1}^S + E_{nuc} \quad (16a)$$

$$E(T) = E_g(k_g^T) + E_u(k_u^T) + E_{e1}^T + E_{nuc} \quad (16b)$$

(E_g and E_u are now pure electronic energies without E_{nuc}).

The variation principle applied to Eqs (16) gives the results (a) in Table II. Both the orbitals σ_g and σ_u in (a) are increased in their size due to the electron repulsion, the singlet orbitals more than the triplet orbitals. This behaviour is a direct consequence of Eqs (15). The results of unscaled AO's ($k = 1$) are presented in (b). The energy of the singlet state is 2.7 eV higher than that in (a). Even worse are the results when the scaling factor of the ground state is used in excited states. The energy of the singlet state (c) is then 3.3 eV higher than that of the correct scaling in (a). The results of the H_2^+ scaling are presented in (d). If the quantities of (d) and (a) are compared it can be seen that both the one-electron energies E_g and E_u are increased, but it is E_u which mainly has to pay for the reduction of electron repulsion.

The singlet-triplet separation in (a) is 4.3 eV in good agreement with 4.1 eV of accurate calculations⁶. The corresponding value without scaling is 5.4 eV (b) and this value is increased to 5.7 eV in (c). The origin of the singlet-triplet separation can also be explained. Although the presence of electron repulsion is responsible for a singlet-triplet separation at all, this does not mean that the electron repulsion

TABLE II

The total energies E of the lowest excited singlet (S) and triplet (T) states of H_2 and their partitioning for different scaling factors k_g and k_u ; cf. Eqs (16): (a) the use of the variation principle for each state; (b) no scaling; (c) the scaling factors of the ground state; (d) the scaling factors of H_2^+

Calc. type	Multiplicity	k_g	k_u	$E_g(k_g)$	$E_u(k_u)$	E_{e1}	E
(a)	S	1.06	0.55	-1.065	-0.591	0.475	-0.683
	T	1.09	0.65	-1.073	-0.628	0.359	-0.843
(b)	S	1.00	1.00	-1.054	-0.661	0.625	-0.590
	T	1.00	1.00	-1.054	-0.661	0.427	-0.788
(c)	S	1.05	1.05	-1.065	-0.654	0.656	-0.563
	T	1.05	1.05	-1.065	-0.654	0.448	-0.771
(d)	S	1.25	0.90	-1.086	-0.664	0.703	-0.547
	T	1.25	0.90	-1.086	-0.664	0.480	-0.770

alone reflects the separation of the total energies; the one-electron contribution is also responsible to a large extent to fulfil Hund's rule.

The energies of the excited MO's can also be discussed in Table II. The excited singlet orbital energy according to $\epsilon_u^S = E_u^S + E_{e1}^S$ is positive in the case of the ground state scaling (c) which corresponds to an unbound electron. With the neglect of scaling (b) the singlest state is stable against the loss of an electron by only 1 eV. The correct scaling in (a) shifts ϵ_u^S below the ionization limit to -3.2 eV. If a common k_g value in ground and excited states is used the excited orbital energy $\epsilon_u^S = -3.2$ eV indicates the position of the excited state energy with respect to the ionization limit in the sense of the Koopmans approximation⁸; the corresponding value obtained by the total energies difference of accurate calculations of the systems H_2 and H_2^+ is -4.0 eV (ref.⁶).

CONCLUSION

The aim of this paper was not the presentation of new numerical data of small diatomic molecules. These are certainly already published^{5,7} although the behaviour of the scaling factor as a function of the internuclear distance was sometimes doubtful⁹.

The aim of this paper was the discussion of various contributions to the total energies of ground and excited states as functions of a scaling factor of the atomic orbitals which contribute to the respective wave functions. The strategy of an energy partitioning was successfully applied to excited states. Many results on Rydberg orbitals can be found in the literature but not the least explanation is found in the textbooks of theoretical chemistry or spectroscopy. For instance the theoretical foundation of Hund's rule, at least for atoms, is still erroneous in the corresponding textbooks¹⁰. The question why excited orbitals are often blown up is not yet answered, at least not in the sense of commonly accepted and widely used terms. A distinction between three categories of excited orbitals is suggested by Sandorfy¹¹.

A last comment is concerned with computational methods for excited states. In practice a common basis set is used throughout the calculation of ground and excited states so that a prohibitive large basis set can quickly be obtained. If the basis set is not sufficient for a suitable description of the states it is expected that additional computational work (for instance configuration interaction), which initially is seen to be necessary to overcome the correlation error, can also avoid the lack of the basis set to a large extent. In general, Gaussians are used in the basis set, but it should be noted that these functions are unsuitable not only for the description of the cusp but also for the description of the wave function at larger distances from the center. This situation makes us believe that excited states calculations are the domain of huge numerical work, but obviously this is caused by the worst tool we have chosen.

REFERENCES

1. Janoschek R., Sax A., Halevi E. A.: *Isr. J. Chem.* **23**, 58 (1983).
2. Halevi E. A., Winkelhofer G., Meisl M., Janoschek R.: *J. Organomet. Chem.* **294**, 151 (1985).
3. Slater J. C.: *Quantum Theory of Molecules and Solids*, Vol. 1. McGraw-Hill, New York 1963.
4. Mulliken R. S.: *J. Am. Chem. Soc.* **86**, 3183 (1964).
5. Phillipson P. E., Mulliken R. S.: *J. Chem. Phys.* **28**, 1248 (1959).
6. Kolos W., Wolniewicz L.: *J. Chem. Phys.* **43**, 2429 (1965); **45**, 509 (1966); **50**, 3228 (1969).
7. Mulliken R. S., Emmler W. C.: *Diatomic Molecules*. Academic Press, New York 1977.
8. Janoschek R. in: *Excited States in Organic Chemistry and Biochemistry* (B. Pullman and N. Goldblum, Eds). Reidel, Dordrecht 1977.
9. Hurley A. C.: *J. Chem. Phys.* **32**, 301 (1960).
10. Katriel J., Pauncz R.: *Adv. Quantum Chem.* **10**, 143 (1977).
11. Sandorfy C.: *Int. J. Quantum Chem.* **19**, 1147 (1981).