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Valence Bond Study of the $B\,^1\Sigma_u^+$ State of the Hydrogen Molecule

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A $1s$, $2p\sigma$ valence bond wave function for the $B\,^1\Sigma_u^+$ state of the hydrogen molecule is variationally optimized with respect to the two atomic orbital exponents for internuclear separations in the vicinity of the equilibrium value. The optimization is tested by use of the molecular virial theorem, and the resulting binding energy compares favourably with other calculations based on limited sets of atomic orbitals. The nature of the electron distribution in the state is analyzed by use of a particular kind of two electron correlation diagram. This analysis indicates that the actual electron distribution is largely ionic in the vicinity of the equilibrium separation in contrast to the formal covalency of the wave function.

Eine $1s$, $2p\sigma$ Valenzstruktur-Wellenfunktion für den $B^1\Sigma_u^+$-Zustand des Wasserstoffmoleküls wird nach der Variationsmethode bezüglich der beiden Atomorbital-Exponenten optimiert. Als Kernabstände werden Werte in der Nähe des Gleichgewichtsabstandes gewählt. Die Optimierung wird mit dem Virialtheorem getestet; weiterhin hat die Bindungsenergie einen vergleichbaren Wert mit entsprechenden Ergebnissen, die mit beschränkten Sätzen von Atomorbitalen erreicht wurden. Die Elektronenverteilung für diesen Zustand wird mit Hilfe eines speziellen Zwei-Elektronen-Korrelationsdiagrammes untersucht. Dabei ergibt sich, daß die tatsächliche Elektronenverteilung stark ionisch für Kernabstände nahe dem Gleichgewichtsabstand ist, im Gegensatz zur formal kovalenten Wellenfunktion.

Une fonction d'onde de liaisons de valence $1s$, $2p\sigma$ pour l'état $B^1\Sigma_u^+$ de la molècule d'hydrogène est optimisée par variation par rapport aux exposants des orbitals atomiques pour des distances internucléaires voisines de la distance d'équilibre. L'optimisation est testée par l'emploi du théorème du viriel moléculaire, et l'énergie de liaison correspondante est comparable à celle obtenue par d'autres calculs dans des bases limitées d'orbitales atomiques. La nature de la distribution électronique dans l'état est analysée en utilisant une espèce particulière de diagramme de corrélation biélectronique. Cette analyse indique que la véritable distribution électronique est largement ionique au voisinage de la distance d'équilibre en contraste avec l'aspect de covalence formelle de la fonction d'onde.

1. Introduction

The $B\,^1\Sigma_u^+$ state of the hydrogen molecule is a well-esteemed prototype of a low excited molecular state, and the study of this state has been pursued throughout the history of quantum chemistry. However, only quite recently has a really high accuracy wave function been reported by Kolos and Wolniewicz [1]. The availability of a high-accuracy wave function does not, on the other hand, make treatments based on simpler functions superfluous, especially since the Kolos-Wolniewicz function is so complex that extensions to larger molecules are not presently feasible.

The purpose of the present note is twofold. We first report a variational calculation on the B state, using a $1s$, $2p\sigma$ valence bond wave function. The variational parameters are the orbital exponents of the atomic orbitals, and we shall investigate the dependence of these parameters on the internuclear separation in the vicinity of the equilibrium. This wave function is subsequently employed together with other types of functions in an analysis of the nature of the state which is intended to supplement the discussion given by Kolos and Wolniewicz [1]. The present discussion differs from the Kolos-Wolniewicz analysis by using a graphical approach to illustrate the difference between the wave functions with a view specifically towards their so-called ionic and/or covalent nature.

2. Wave Function and Energies

The wave function for the lowest ${}^1\Sigma_u^+$ state of hydrogen is in the present approach a valence bond combination of 1*s* and 2*pσ* atomic orbitals:

$$\Psi = N[s_a(1)\,p_b(2) + p_b(1)\,s_a(2) - s_b(1)\,p_a(2) - p_a(1)\,s_b(2)] \tag{1}$$

where N is a normalization factor and:

$$s_a(1) = \pi^{-1/2}\zeta_s^{3/2}\exp(-\zeta_s r_{a1})$$
$$p_a(1) = \pi^{-1/2}\zeta_p^{5/2} r_{a1}\cos\vartheta_{a1}\exp(-\zeta_p r_{a1})$$

with analogous expressions for the orbitals on atom b. The phases in Eq. (1) correspond to local coordinate systems with z-axes pointing towards each other. For simplicity we have omitted the two-electron spin function for the singlet state.

A wave function of this form was used by Mulliken and Rieke [2] and Shull [3] in discussion of electron transition probabilities. In neither case was any optimization of the function attempted. Tschudi and Cohan [4] performed a partial optimization in which they determined the 1*s*-orbital exponent variationally while keeping the 2*pσ*-orbital exponent fixed at its limiting value for infinite separation. We shall here optimize the wave function fully by treating both orbital exponents as variational parameters. The wave function is in this way automatically scaled such that the molecular virial theorem is fulfilled [5, 6] *(vide infra).*

The Hamiltonian for the two electrons in the hydrogen molecule is (in atomic units):

$$\mathscr{H} = \sum_{i=1}^{2}\left[-\frac{1}{2}\nabla_i^2 - \frac{1}{r_{ai}} - \frac{1}{r_{bi}}\right] + \frac{1}{r_{12}} + \frac{1}{R} \tag{2}$$

where the nuclear-nuclear repulsion $(1/R)$ is included since we wish to calculate the total binding energy. The optimal values of the orbital exponents are now found by minimizing the energy:

$$E = \langle\Psi|\mathscr{H}|\Psi\rangle \tag{3}$$

numerically with respect to these two non-linear parameters for the internuclear separations listed in Table 1. For each value of R the two parameters ζ_s and ζ_p were varied systematically, first in rather coarse grids and subsequently in finer intervals in order to close in on the optimal values. All the necessary integrals were calculated exactly with the Diatom molecular integral program [7] and the resulting minimized energies are shown in Table 1 together with the corresponding values of ζ_s and ζ_p. Also included in the table are the results of some other non-empirical calculations.

Table 1. *Calculated energies for the $B\,^1\Sigma_u^+$ state of the hydrogen molecule*

R (a.u.)	This work			Other calculations of the energy (eV)				
	ζ_s	ζ_p	E (eV)[a]	A	B	C	D	E
1.40	1.39	0.520	−1.46			−1.29	−1.92	−2.17[b]
1.60	1.33	0.548	−2.08	−2.07				
2.44	1.16	0.613	−2.70	−2.54	−2.64	−2.33	−3.21	−3.58
2.80	1.12	0.608	−2.59	−2.41	−2.59			
4.00	1.04	0.554	−1.85	−1.71	−2.18	−1.27[b]	−2.38	−3.00

[a] The energies are given relative to the sum of the energies of a 1*s* and a 2*s* state of the separated atoms.

[b] Interpolated values.

A Tschudi and Cohan (Ref. [4]) using Eq. (1) with $\zeta_p = 0.50$.

B Tschudi and Cohan (Ref. [4]) using Eqs. (1) and (4) with $\zeta_p = 0.50$.

C Phillipson and Mulliken (Ref. [10]).

D Taylor (Ref. [13]).

E Kolos and Wolniewicz (Ref. [1]).

Before turning to a discussion of the results we shall consider the connection to the molecular virial theorem, according to which the kinetic energy and the potential energy of a diatomic molecule are related to the total energy, as follows [8]

$$E_{\text{kin}} = -E - R(dE/dR)\,, \tag{4a}$$

$$E_{\text{pot}} = 2E + R(dE/dR)\,. \tag{4b}$$

It was pointed out above that the wave function is automatically scaled to fulfill these relations in the present approach. This is shown explicitly in Table 2 for the experimental equilibrium separation. In this table the energies calculated from Eqs. (4) are compared to the kinetic and potential energies calculated directly from the optimized wave function by the relations.

Table 2. *Kinetic and potential energy at the equilibrium separation (all energies in eV)*

E	E_{kin}	$\langle T\rangle$	$E_{\text{kin}}/\langle T\rangle$	E_{pot}	$\langle V\rangle$	$E_{\text{pot}}/\langle V\rangle$
−19.701	19.190	19.378	0.990	−38.891	−39.078	0.995

$$\langle T\rangle = \langle \Psi|\hat{T}|\Psi\rangle \tag{5a}$$

$$\langle V\rangle = \langle \Psi|\hat{V}|\Psi\rangle \tag{5b}$$

where $\hat{T}$ and $\hat{V}$ are respectively the kinetic energy part and the potential energy part of the Hamiltonian Eq. (2). The value of the first derivative of the energy with respect to R, which is required in Eqs. (4), is found by fitting a polynomium to the five computed energies in Table 1. This gives $dE/dR = 0.209$ (eV/a_0) for $R = 2.44$ a.u. which shows that the equilibrium separation predicted by the present wave function is somewhat shorter than the experimental. From the ratios given in the table it follows that the virial theorem is in fact fulfilled within the accuracy of the computations (considering the uncertainty in the estimate of the first derivative of the energy).

3. Discussion

The most conspicuous feature of Table 1 is perhaps the distance variation of the $2p\sigma$ orbital exponent which goes through a miximum in the vicinity of the equilibrium separation. This indicates, in some loose sense, a shift in the balance between nuclear and electronic screening [9], however, we do not want to go too deeply into such arguments since the concept of screening is actually rather ill-defined [9] for an electronic pair wave function like the present. On the other hand, the magnitude of ζ_p, which is close to the hydrogenic value, leaves little doubt about a non-trivial Rydberg-character to this state [2]. This interpretation is supported by the fact that the $1s$ orbital exponents are close [9, 10] to the values in H_2^+.

Turning now to the energies listed in Table 1, it is observed that the simultaneous optimization of ζ_s and ζ_p leads to some improvement over the Tschudi and Cohan calculation [4] (column *A*) in which ζ_p was fixed at 0.50. Our results are also slightly better than the results obtained by Tschudi and Cohan in a second calculation (column *B*) in which they included interaction with the ionic function:

$$\Psi_i = N_i[s'_a(1)\, s'_a(2) - s'_b(1)\, s'_b(2)] \tag{6}$$

with optimized orbital exponent ζ'_s. The Phillipson-Mulliken treatment [10] quoted in column *C* is a molecular orbital calculation, based on linear combinations of $1s$ atomic orbitals, where the orbital exponent in the bonding and antibonding orbitals were optimized independently. The over-all agreement between our results and the results quoted in columns *A*, *B* and *C* presumably indicates that we are close to the limit of what can be obtained with only two non-linear variational parameters.

The error in the binding energy is about 0.9 eV (compare column *E*) which incidentally is close to the absolute error in the best Hartree-Fock calculation on the ground state [11, 12]. Part of this error is undoubtedly associated with the neglect of angular correlation [12] in the electronic motion. The magnitude of this can be estimated from a configuration interaction calculation by Taylor [13] and seems to be of the order of 0.2 eV, which is again close to the corresponding value for the ground state [12]. To correct for the remaining error of about 0.7 eV it is necessary to include more linear and/or non-linear parameters. In the full calculation by Kolos and Wolniewicz [1] a total of 60 linear and 4 non-linear parameters was employed; Taylor [13] obtained a good compromise (column *D* in Table 1) using 8 non-linear parameters.

4. Analysis of the Wave Functions

The $B\,^1\Sigma_u^+$ state of the hydrogen molecule is in the lowest approximation described by the wave function (6) which arises from simple molecular orbital theory and from simple Heitler-London theory as well. This kind of wave function ascribes an ionic character to the state, and early discussions of molecular electronic transition probabilities were founded on this notion (see Ref. [2] and references therein). The improvements which Phillipson and Mulliken [10] obtained by use of different exponents in respectively the bonding and antibonding molecular orbitals can be viewed as the result of allowing some covalent character in the state. This is seen by observing that the expansion of their wave function contains terms of the form $s_a(1)\, s'_b(2) - s'_a(1)\, s_b(2)$. In the lowest approximation such terms vanish ($s'_a = s_a$) giving the function (6) back. Following this line of thought the valence bond wave function Eq. (1), apparently represents the antipode to the ionic function Eq. (6) since it consists of "covalent products" only.

The conclusion of Tschudi and Cohan [4] and of the present work is then that the 1*s*, 2*pσ* valence bond wave function is a better approximation than the predominantly ionic simple molecular orbital functions (in the vicinity of the equilibrium separation). Kolos and Wolniewicz [1] reached the same conclusion by considering the overlap integrals between their very accurate wave function and the wave functions (1) and (6), using orbital exponents for the separate-atom limit in the latter cases. The Phillipson-Mulliken function was not considered. At the equilibrium separation they found that the overlap with the valence bond function (1) is 0.7 compared to an overlap with the ionic function (6) of only 0.3. On the other hand, for somewhat longer separations ($3 < R < 7$ a.u.) they found that the ionic function had a larger overlap with the accurate function than the valence bond function. This seems to indicate a change in the nature of the state such that it becomes predominantly ionic in this intermediate region.

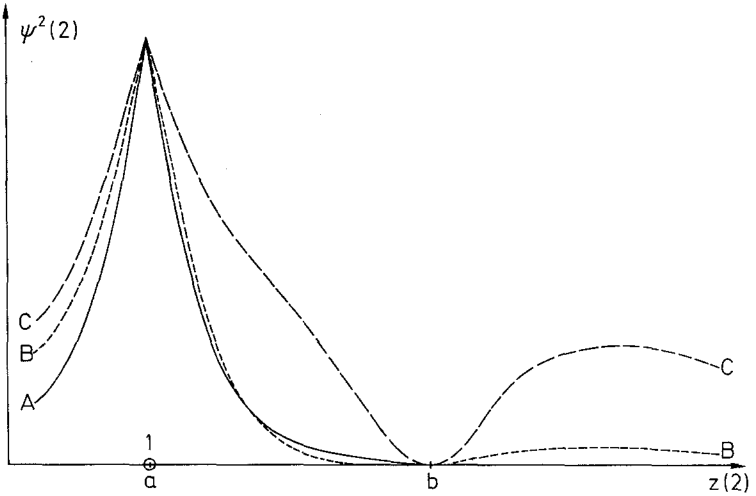

Fig. 1. Probability densities for the *B* state as function of the position of electron 2 along the internuclear axis assuming electron 1 at nucleus *a*

The designation ionic and covalent have in the preceding paragraphs been based on the formal appearance of the wave functions. However, a more realistic picture of the electron distributions can be gained from a type of diagram which was used by McLean, Weiss and Yoshimine [12] in their study of the correlation effects in the ground state. In this diagram the square of the wave function is plotted as function of the position of electron 2 along the internuclear axis assuming that electron 1 is fixed at nucleus *a*. Curve *A* of Fig. 1 shows the resulting graph for the simple ionic function (6); the Phillipson-Mulliken function [10] is shown as curve *B* and the valence bond function (1) as curve *C*. The Kolos and Wolniewicz function [1] is not reported in sufficient detail for such a representation. The wave functions are all cases taken with optimal orbital exponents for the equilibrium distance, and the scales are chosen to yield identical peak heights.

We note in passing that the density of electron 2 is zero at nucleus *b* in all the the graphs. This follows from the fact that the spatial part of the wave function for a $^1\Sigma_u^+$ state is symmetric in the electrons and antisymmetric in the nuclei. When electron 1 is fixed at nucleus *a* these two requirements can be met only if the density of 2 is strictly zero at nucleus *b*. This feature must therefore persist in any approximation which represents the symmetry of the state correctly.

The two first curves in Fig. 1 are in good agreement with the qualitative expectations. In the ionic function the density of electron 2 is centered at the nucleus where electron 1 is already located and the density vanishes beyond nucleus *b*. In the Phillipson-Mulliken case some of the density of electron 2 is shifted out on the far side of nucleus *b*, thereby introducing some covalent character. This shift in the density of electron 2 is further enhanced in the valence bond function, however, the bulk of the density is still found at the nucleus where electron 1 is. Therefore, in spite of its formally covalent construction the $1s$, $2p\sigma$ function, Eq. (1), actually represents an electron distribution which is largely ionic. This is of course intimately connected to the small numerical value of ζ_p, since such a $2p\sigma$ atomic orbital centered on atom *b* will have its radial maximum in the region around center *a*.

The different wave functions depicted in Fig. 1 therefore all agree on assigning a large amount of ionic character to the *B* state in the region around the equilibrium separation. There are on the other hand rather severe differences between the details in the electron distribution predicted by the functions. These differences are (part of) the physical basis for the spread in the calculated values for the intensity of the transition from the ground state to the *B* state [2, 3].

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