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$1s1p$, $1s2p$, and $1s3p$ Hybrids in the H_2^+ Molecule

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The search of approximate wave functions being at the same time sufficiently accurate and reasonably simple is a basic problem in theoretical chemistry. A widely applied method to build up molecular wave functions involves a finite, linear expansion in terms of atomic orbitals, centered at the nuclei of the molecular framework (LCAO approximation). The most used basis is that involving Slater functions $\chi_{n,l,m}(r, \vartheta, \varphi)$, defined as follows:

$$\chi_{n,l,m}(r, \vartheta, \varphi) = N_n\, r^{n-1}\, e^{-\zeta r}\, S_{l,m}(\vartheta, \varphi)\ . \tag{1}$$

Here N_n is the normalization factor, $S_{l,m}(\vartheta, \varphi)$ a real spherical harmonic of the indicated argument and indices, while ζ is the "orbital exponent".

The problem to be solved is then to obtain, by variational technique, the coefficients of the expansion above mentioned. About which and how many Slater orbitals should be included into a finite basis set, one is largely faced by a problem of physical feeling and the exigence that the calculations should be as simple as possible. For many-electron systems, however, the actual task is really formidable, even though we have at our disposal high-speed computers.

Thus, it does not seem useless to investigate about possible advantages arising from the inclusion of less common functions into the atomic basis. Some attempts in this direction (e.g. the use of ns orbitals, with n not-integer [*4*], $0s$ orbitals for the helium atom ground state wave function [*7*, *9*]) have already been reported in the literature. A fairly general way to proceed could be to relax in (1) the constraint that n is an integer so restricted that $n \geq l + 1$. In this note we propose to examine the effectiveness of the use of $1p$ orbitals for the simplest molecular system H_2^+ .

In principle, one could hope that the inclusion into the basis set of functions associated at the same time with directional character and high values of the probability density around the nucleus should be a valuable choice. $1p_z$ orbitals are so defined:

$$1p_z \equiv \chi_{1,1,0}(r, \vartheta, \varphi) = 2\,\zeta^{3/2}\, e^{-\zeta r} \left(\frac{3}{4\pi}\right)^{1/2} \cos\vartheta\ . \tag{2}$$

From a quantum mechanical point of view, of course, a basis function like (2) is not acceptable. This is due to its lack of single-valuedness at $r = 0$, and to the fact that the resulting wave function cannot satisfy the cusp condition at the nuclei [*8*].

As far as the single-valuedness is concerned, however, the use of $1p$ orbitals may be justified by regarding each of them as the limit:

$$1p_z = \lim_{n \to 1} (N_n\, r^{n-1}\, e^{-\xi r}) \left(\frac{3}{4\pi}\right)^{1/2} \cos\vartheta\ . \tag{3}$$

In other words, we assume that a chosen basis set $\{\chi\}$ include a subset of "*np*" orbitals; best *n*'s of these orbitals are to be determined. Since the resulting variational problem does not involve only linear parameters, one can approach it by fixing a set of *n*'s, solving the linear variational problem, varying the set of *n*'s, and so on: in this paper the limit case $n = 1$ is considered.

The failure to fulfill the cusp condition appears unescapable, but it should not be too serious for the observables we are concerned with [7].

We have therefore assumed as trial wave function the following one:

$$\Psi(\vec{r}_A, \vec{r}_B) = C_s[\chi_{1,0,0}(r_A) + \chi_{1,0,0}(r_B)] + \\ + C_p[\chi_{1,1,0}(r_A, \vartheta_A, \varphi_A) + \chi_{1,1,0}(r_B, \vartheta_B, \varphi_B)] \,. \tag{4}$$

Table 1

Ref.	Wave Function	Equilib. Dist. R_{AB} (a.u.)	Total Energy $\langle\mathscr{H}\rangle$ (a.u.)	$-\frac{2\langle T\rangle}{\langle V\rangle}$	LCAO Coeff.	Orbital Exponents
This Paper	$1s(\zeta_s) + 1p(\zeta_p)$	2.006	−0.594126	1.00007	$C_s = 0.56885$ $C_p = 0.0434523$	$\zeta_s = 1.2445$ $\zeta_p = 0.870$
This Paper and Ref. [3]	$1s(\zeta_s) + 2p(\zeta_p)$	2.001	−0.600362	0.99999	$C_s = 0.554055$ $C_p = 0.0764962$	$\zeta_s = 1.2458$ $\zeta_p = 1.4830$
This Paper	$1s(\zeta_s) + 3p(\zeta_p)$	2.006	−0.600208	1.00000	$C_s = 0.558181$ $C_p = 0.0698144$	$\zeta_s = 1.2406$ $\zeta_p = 2.2640$
Ref. [5]	$1s(\zeta) + 2p(\zeta)$	2.005	−0.599802	—	$C_s/C_p = 0.1605$	$\zeta = 1.254$
Ref. [5]	$1s(\zeta) + 3p(\zeta)$	2.028	−0.592696	—	$C_s/C_p = 0.1616$	$\zeta = 1.2653$
Ref. [1]	Exact	2.00	−0.6026	—	—	—

Table 2

Wave Function	$\langle x^2\rangle$ (a.u.)	$\langle z^2\rangle$[a] (a.u.)	ω_e (cm^{-1})
$1s(\zeta_s) + 1p(\zeta_p)$	0.7054	1.2637	2208
$1s(\zeta_s) + 2p(\zeta_p)$	0.6967	1.1183	2261
$1s(\zeta_s) + 3p(\zeta_p)$	0.6931	1.1422	2361
$1s(\zeta) + 2p(\zeta)$	0.7031	1.0963	—
$1s(\zeta) + 3p(\zeta)$	0.7251	1.2082	—
Exact	0.6416[b]	1.1110[b]	2297[c] 2332[d]

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[a] z coordinate measured from the midpoint between the nuclei.

[b] See Ref. [*2*].

[c] See Ref. [*6*].

[d] See Ref. [*10*].

The minimization of the functional $E = \langle\Psi \mid \mathscr{H} \mid \Psi\rangle / \langle\Psi \mid \Psi\rangle$ where $\mathscr{H} = -\frac{1}{2}\Delta^2 - 1/r_A - 1/r_B + 1/R_{AB}$, has been carried out with respect to each parameter contained in E.

In the actual calculations, for any given pair of values of the orbitals exponents ζ_s, ζ_p, the functional E has been made stationary with respect to variations of the linear coefficients C_s, C_p. The lattice of ζ_s, ζ_p values to be spanned was progressively thickened, as the minimum zone got sharper and sharper. Such a procedure has been performed for several values of the internuclear distance R_{AB}, till obtained the absolute minimum value of E, afterwards indicated $\langle\mathscr{H}\rangle$

The results we have found are collected in Tab. 1, and are indicated in correspondance of the abridged writing $1s(\zeta_s) + 1p(\zeta_p)$; the same table shows other reference data.

As far as the hybrid $1s(\zeta_s) + 2p(\zeta_p)$ is concerned, we have only repeated the old calculation by Dickinson [*3*]. We have also performed a calculation by employing a trial function as:

$$\Psi(\vec{r}_A, \vec{r}_B) = C_s[\chi_{1,0,0}(r_A) + \chi_{1,0,0}(r_B)] + \\ + C_p[\chi_{3,1,0}(r_A, \vartheta_A, \varphi_A) + \chi_{3,1,0}(r_B, \vartheta_B, \varphi_B)], \quad (5)$$

containing different ζ's for different orbitals. A similar calculation, using a hybrid $1s - 3p$, but involving only one orbital exponent, has been already reported in Ref. [*5*], together with the analogous $1s - 2p$ in the same simplified version: we shall refer to these as $1s(\zeta) + 3p(\zeta)$ and $1s(\zeta) + 2p(\zeta)$ respectively.

The high accuracy of the performed minimization is well tested by the values of the ratio $2\langle T\rangle / \langle V\rangle$ (virial theorem), also shown in Tab. 1.

From the inspection of the data one can immediately conclude that no advantage resulted in using $1p$ orbitals. The comparison of the results is unfavorable to $1s - 1p$ hybrid with respect to the hybrid (5) too; the energy calculated by the hybrid $1s - 1p$ is better than that obtainable with $1s(\zeta) + 3p(\zeta)$, which, however, involves only one orbital exponent.

To the end of completeness, we have reported in Tab. 2 the quadrupole moments $\langle x^2\rangle$, $\langle z^2\rangle$ of the charge distribution, together with the vibrational frequencies ω_e. These latter have been obtained by a simple parabolic fitting.

Once more, the comparison is quite favorable to Dickinson's $1s(\zeta_s) + 2p(\zeta_p)$ hybrid, even though fairly good results are obtained by means of $1s(\zeta_s) + 3p(\zeta_p)$.

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