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An Application of the 0s-Function to Molecular Systems of H_2^+ and H_2

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Recently, several authors[1-8] have pointed out the usefulness of 0s- and other so-called Hulthén functions for atoms. The Hulthén function often gives a better approximation to the Hartree-Fock wavefunction than the conventional Slater-type function. This has been shown not only by the numerical results, but also by analytical approaches.[9-13] Among these investigations, the work by McWeeny[10] is particularly instructive, because his results suggest the applicability of the 0s-function to molecular systems. However, as far as we know, there has been no numerical application of the 0s-function to molecular systems. Furthermore, since the 0s-function is the lowest eigenfunction of an s-electron in a kind of screened Coulomb potential (Hulthén potential) which has Jacobi polynomials as its eigenfunctions,[14] it seems that it would be interesting to investigate the usefulness of 0s- or other subsequent functions for molecular systems:

$$V_{\mathrm{Hu}}(r) = -[(\beta^2-\alpha^2)/2]\mathrm{e}^{-(\beta-\alpha)r}/(1-\mathrm{e}^{-(\beta-\alpha)r}), \tag{1}$$

$$\left.\begin{aligned}\psi_1(r) &= 0\mathrm{s}_{\alpha\beta}(r) = N(\mathrm{e}^{-\alpha r}-\mathrm{e}^{-\beta r})/r,\\ N^2 &= \alpha\beta(\alpha+\beta)/2\pi(\alpha-\beta)^2 \quad (\alpha<\beta)\end{aligned}\right\} \tag{2}$$

$$E_1 = -\alpha^2/2. \tag{3}$$

We calculate here the energies of the hydrogen molecule ion and the hydrogen molecule variationally, using the 0s-function.

TABLE 1. THE ENERGY OF HYDROGEN MOLECULE ION (in a.u.)

R	1s+1s[a] (ζ=1.0)	1s+1s[a] (ζ=1.228)	0s+0s	Hylleraas[a]
1.0			−0.441004	−0.45230
2.0	−0.565050	−0.582691	−0.586380	−0.60263
3.0			−0.564483	−0.57755
4.0			−0.537356	−0.54608
5.0			−0.519217	−0.52442

a) Ref. 15, p. 336.

TABLE 2. THE VALUES OF THE PARAMETERS, α AND β, AT EACH R

R (a.u.)	1.0	2.0	3.0	4.0	5.0
α	1.453	1.162	1.079	1.016	0.992
β	1.643	1.351	1.112	1.041	1.012

a) As a matter of course, α and β which give the optimal energy are not equal (though not so different) to the values used by McWeeny (Ref. 10), namely 1.228 and 1.485, respectively.

In Table 1, the energies of the hydrogen molecule ion at several R values (the internuclear distances) are listed alone with other results, while Table 2 shows the values of the parameters, α and β, at each R. The present calculation gives energies improved by the amounts of 0.021 and 0.004 in a.u. at the equilibrium internuclear distance of 2.0 a.u. when compared with those of the 1s-function with the exponents (ζ) of 1.0 and 1.228 respectively. The behavior of α and β shows that, when the internuclear distance increases, the 0s-function approaches the 1s-function.

TABLE 3. THE ENERGY OF HYDROGEN MOLECULE AT THE EQUILIBRIUM DISTANCE R (in a.u.)

	VB(1s)[a] (ζ=1.0)	VB(1s)[b] (ζ=1.166)	VB(0s) (α=1.13, β=1.20)	Exact[c]
Energy	−1.115	−1.1390691	−1.1390878	−1.17445
R	1.4	1.406	1.416	1.400

a) Ref. 15, p. 349.
b) The energy value was recalculated in our laboratory.
c) Ref. 16.

In Table 3, the results for the hydrogen molecule obtained by the use of the valence bond method are listed. In the calculation, the exchange integral $<0\mathrm{s}_{\alpha\beta}(r_{\mathrm{a}1})0\mathrm{s}_{\alpha\beta}(r_{\mathrm{b}2})|1/r_{12}|0\mathrm{s}_{\alpha\beta}(r_{\mathrm{a}2})0\mathrm{s}_{\alpha\beta}(r_{\mathrm{b}1})>$, was easily obtained by the use of the formula given by Kotani *et al.*,[17] but a part of the Coulomb integral, $<0\mathrm{s}_{\alpha\beta}(r_{\mathrm{a}1})0\mathrm{s}_{\alpha\beta}(r_{\mathrm{b}2})|1/r_{12}|0\mathrm{s}_{\alpha\beta}(r_{\mathrm{a}1})0\mathrm{s}_{\alpha\beta}(r_{\mathrm{b}2})>$, was not so easily obtained ($r_{\mathrm{a}1}$ is the distance between the nucleus, a, and the electron, 1, and so forth). Therefore, after some modification, we expanded the part in the form of an infinite series and got a value with the required accuracy. The error of the energy given by the 0s-function is 2.05% smaller than that of the 1s-function with an exponent of 1.0, and the improvement over

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the Wang's result is small but definite.

In comparing the two cases where a proton or a hydrogen approaches a hydrogen atom, it is clear that the perturbation in the former should be greater than in the latter.[18] Therefore, the deviation from the 1s-function should be more significant in the hydrogen molecule ion; this is reflected in the difference between α and β and in the improvement of the energies in the two cases.

Thus, taking the examples of the hydrogen molecule ion and the hydrogen molecule, we have numerically shown that the 0s-function is more effective not only in the atomic system, but also in the molecular one, than the conventional 1s-function. Of course, further improvement in the energy could be achieved by using wavefunctions with angular dependencies.

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18) α and β for the hydrogen molecule ion in the treatment by McWeeny (Ref. 10) correspond to the momenta of an electron in the hydrogen isolated and that perturbed by a proton, respectively.