

On the use of Gaussian bond-functions in *ab initio* calculations of the proton potential curves in hydrogen-bonded systems

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Received 11 December 1975

Accepted for publication 3 March 1976

The effect of extending the minimum contracted Gaussian basis by simple Gaussian functions localized on hydrogen bond (bond-functions) upon potential curves of the H-bonded hydrogen in $\text{H}_2\text{O}-\text{OH}^-$ has been investigated. The potential curves have been calculated for the $\text{O}_{(1)}-\text{O}_{(2)}$ distances equal to 4.5 and 4.75 a.u. As follows from the results, the extension of the basis by bond-functions is a simple way to obtain more realistic potential curves in comparison with those obtained by the use of the minimum basis.

В работе было рассмотрено влияние расширения минимального сгруппированного гауссовского базиса с помощью простых гауссовых функций, помещенных на водородной связи (связевых функций), на кривые потенциала Н-связывающего водорода в $\text{H}_2\text{O}-\text{OH}^-$. Были вычислены потенциальные кривые для расстояний $\text{O}_{(1)}-\text{O}_{(2)}$ 4,5 и 4,75 ат.ед. Из результатов вытекает, что расширение базиса на связевые функции является простым средством получения более реалистических потенциальных кривых по сравнению с расчетом в минимальном базисе.

In the *ab initio* SCF MO LCAO calculations of many chemically interesting systems we are frequently obliged to use small or even minimum bases. When interpreting the results obtained by the use of minimum bases, we must be careful because there are known a few cases from the literature that the use of these bases led to incorrect results. One of the possibilities how to improve the reliability of the results obtained with small bases is the use of the so-called bond-functions, *i.e.* the functions localized on chemical bonds or on "lone pair" orbitals which are added to usual atom-centred functions [1—6]. The idea to use the functions localized outside the atoms was put forward by *Preuss* [7] and *Whitten* [8] and afterwards modified in different ways by other authors [9—11]. The addition of bond-functions to the usual nucleus-centred basis is a particular way of using the outside-nucleus functions. The aim of this procedure is to improve the description of electron density in the region of chemical bonds. These functions, in some respect,

substitute for the polarization functions [1, 2, 5]. A systematic study of bond-functions in the Gaussian basis as well as the optimization of their exponents and localization was performed in the Theoretical Chemistry Laboratory at Vienna University [3, 4]. One of the most important results consists in the statement that the exponent and position of Gaussian bond-function are not to much dependent on a particular molecule but are rather characteristic of a given bond. The usefulness of bond-functions was tested by the calculations of various physical properties of molecules [2, 3, 12, 13]. The success in using them to the calculations of force constants [2, 3, 13] suggested the idea of using bond-functions for the calculations of the potential curves of the H-bonded hydrogen. It is well known that the potential curves of the H-bonded hydrogen obtained by using small bases are usually non-realistic as compared with the results obtained with larger bases [14]. The main shortcoming consists in that the potential curve found with a small basis exhibits double-minimum at a larger distance between proton—donor and proton—acceptor molecule than that obtained with a larger basis. If two minima appear on the curve, their distance and the height of the barrier between them are usually distorted.

The problem how the addition of bond-functions to the minimum basis influences the shape of the curve of H-bonded hydrogen will be solved in this study for the $\text{H}_2\text{O—OH}^-$ system.

Method

The calculations were carried out by the SCF MO LCAO method [15] with Gaussian basis, namely ($7s3p$) for oxygen [16] and ($3s$) for hydrogen [17] which was contracted to minimum basis [$2s1p/1s$]. The scaling parameters of exponents of the Gaussian functions for the $2s$, p_x , p_y , p_z oxygen functions and the s hydrogen function (0.901, 0.983, 2.058) were optimized for a water molecule. By using this basis which represents the initial nuclei-centred basis, we obtained the optimum geometry of water with the bond length of 1.814 a.u., bond angle of 109° , total energy of -75.80426 a.u., and dipole moment of 8.60×10^{-30} Cm [18]. The primitive Gaussian s function was added to this initial basis for both OH bonds of a water molecule in optimum geometry. The optimization of the exponent and position of this function for water molecule is the first suitable step in the determination of parameters of bond-function for the OH bond in the systems the component of which is a water molecule.

Results and discussion

In the calculations of proton potential curves of the H-bonded hydrogen for the system $\text{H}_2\text{O—OH}^-$ we started to work with bond-functions the parameters of which had been used earlier for water dimer [19]. The position and exponent of

bond-functions were determined in this case from the condition that the dipole moment of the water molecule obtained by their addition to the initial basis showed the value which was possibly the closest to that obtained experimentally. This method of optimization was chosen instead of the usual minimization of total energy because of the fact that the dipole moment of water molecule in the initial atom-centred basis was considerably greater than that found experimentally (8.60×10^{-30} Cm and 6.13×10^{-30} Cm, respectively). That is one of the reasons why a too high dimerization energy of water molecule is obtained with this basis [18]. The optimum bond-function in the above-mentioned sense was a function with the centre on OH bonds in the distance of 0.604718 a.u. from oxygen (*i.e.* in 1/3 of OH bond) and with exponent 2.0. By optimizing the geometry of H₂O with a basis extended by these functions we found the following data: bond length 1.786 a.u., HOH angle 109°, total energy -75.82368 a.u., and dipole moment 8.01×10^{-30} Cm. The bond-functions thus obtained, of course, are not optimum for H₃O₂⁻. However, it may be supposed that they are satisfactory as a first estimate.

The influence of the addition of bond-functions on the potential curves of the H-bonded hydrogen was appreciated by two ways

— by comparing with the calculations carried out with equal initial basis but without bond-functions,

— by comparing with the calculations carried out with a larger basis comprising polarization functions. For this comparison we used the results obtained by *Kraemer and Diercksen* [20]. We calculated the symmetric complex H₃O₂⁻ and the complex in which the H-bonded hydrogen was shifted by Δr from the symmetric position (Fig. 1). We have chosen equal geometry of H₃O₂⁻ as described in [20]. This geometry corresponds to the experimental geometry of water (length of O—H bonds 1.809 a.u. and HOH angle 104° 52'). We calculated the potential curves of H-bonded hydrogen H₍₂₎ for the O₍₁₎—O₍₂₎ distances equal to 4.75 and 4.5 a.u. The smaller of these distances approaches that distance in which the potential with two minima is still to be found in the SCF approximation [21]. The positions of bond-functions f_1 — f_4 localized on all OH bonds, including hydrogen bond are marked in Fig. 1. Preliminary calculations have shown that the functions f_3 and f_4 have nearly no influence on the potential curves of the H-bonded hydrogen. Therefore, other calculations with bond-functions have been performed merely with the functions f_1 and f_2 . The results for the distance O₍₁₎—O₍₂₎ equal to 4.75 a.u.

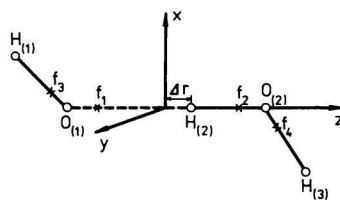


Fig. 1. Geometry of the H₂O—OH⁻ complex.

are presented in Fig. 2. It is obvious that two minima appeared on the curve after adding bond-functions to the fundamental basis. However, the height of the barrier (0.00035 a.u.) is considerably different from the height of the barrier with large basis (0.00424 a.u.) [20] as well as the distance of both minima (0.41 or 0.75 a.u.). These parameters could be improved by optimizing bond-functions directly for the H_3O_2^- system.

For the $\text{O}_{(1)}-\text{O}_{(2)}$ internuclear distance of 4.5 a.u., two minima did not appear on the curve of the H-bonded hydrogen even if the basis was extended by bond-functions which optimized the dipole moment of water. Only the curve exhibited considerable flattening (Fig. 3). Therefore, we optimized the position and exponent of bond-functions directly for the H_3O_2^- system at this distance. In the optimization, we did not use, in this case either, the minimum of the total H_3O_2^- energy as a criterion. Our aim was to find such functions which could give a double-minimum potential for the $\text{O}_{(1)}-\text{O}_{(2)}$ distance of 4.5 a.u. In order to save the computer time, we did not calculate the whole potential curves of H-bonded hydrogen, but we compared the energies of H_3O_2^- at the position of $\text{H}_{(2)}$ in the middle of the $\text{O}_{(1)}-\text{O}_{(2)}$ bond ($\Delta r = 0$) and at the deflection of $\text{H}_{(2)}$ by 0.147 a.u. from the centre of this bond (on the curves in Fig. 3, it is the calculated point which is situated nearest to the centre of the $\text{O}_{(1)}-\text{O}_{(2)}$ bond). The results are presented in Table 1. The function localized at the distance of 0.704 a.u. from oxygen with the exponent

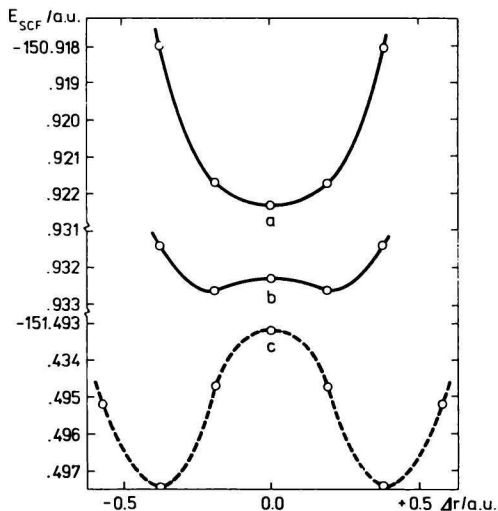


Fig. 2. Proton potential curves in H_3O_2^- for the $\text{O}_{(1)}-\text{O}_{(2)}$ distance equal to 4.75 a.u.

a) Minimum basis; b) basis with bond-functions f_1, f_2 optimized for H_2O ; c) basis $[5s\ 4p\ 1d/3s\ 1p]$; Ref. [20].

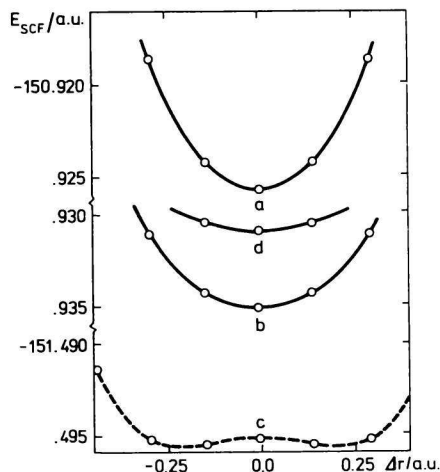


Fig. 3. Proton potential curves in H_3O_2^- for the $\text{O}_{(1)}-\text{O}_{(2)}$ distance equal to 4.5 a.u.

a) Minimum basis; b) basis with bond-functions f_1, f_2 optimized for H_2O ; c) basis $[5s\ 4p\ 1d/3s\ 1p]$; Ref. [20]; d) basis with bond-functions f_1, f_2 optimized for H_3O_2^- .

Table 1

Optimization of the position and exponent of bond-functions for H₂O—OH⁻

$d(\text{O}-f)$ a.u. ^{a, c}	Exponent	$\Delta r/\text{a.u.}^a$		$E_{\text{SCF}}/\text{a.u.}^b$	$\Delta E_{\text{SCF}}/\text{a.u.}^b$
		0.000	0.147		
0.604718	2.0	-150.93508	-150.93430		0.00078
0.654718	2.0	-150.93237	-150.93167		0.00070
0.704718	2.0	-150.93070	-150.93005		0.00065
0.804718	2.0	-150.92986	-150.92919		0.00067
0.704718	1.8	-150.93064	-150.93008		0.00056
0.704718	1.6	-150.93066	-150.93017		0.00049
0.704718	1.4	-150.93101	-150.93057		0.00044
0.704718	1.2	-150.93230	-150.93182		0.00048

a) 1 a.u. = 0.529172×10^{-10} m.b) 1 a.u. = 2625.29 kJ mol⁻¹.c) $d(\text{O}-f)$ is the distance of bond-functions f_1, f_2 from oxygen O₍₁₎ and O₍₂₎, respectively.

1.4 is optimum function. We did not find a double-minimum potential function in this case either, but the curve flattened again. Finally, let us mention that by using the standard minimization of the total energy of H₂O, we obtained the optimum bond-functions at the distance of 0.9 a.u. from oxygen and with the exponent 1.2.

Furthermore, we had to verify whether the double-minimum potential could be obtained with the p_x, p_y, p_z functions localized on H₍₂₎ hydrogen [22]. By comparing the energies for $\Delta r = 0.0$ and $\Delta r = 0.147$ a.u., we revealed that these three functions were less effective in the correction of the potential curve than two bond-functions. We did not find any double-minimum potential, the curve was less flattened and the calculations necessitated more computer time.

Our results may be summarized in the following items:

— The addition of primitive s bond-functions to the minimum contracted Gaussian basis is a simple way to obtain more realistic potential curves of the H-bonded hydrogen. Using a basis extended by these functions, we obtained potential curves which differed from the curves obtained with a large basis less than the curves obtained with the initial basis. Naturally, a quantitative agreement with the results obtained with a large basis is not, in general, to be expected in whatever way we improve the minimum basis. In the calculations with larger bases, it is also important to take into consideration the influence of correlation energy on the potential curves of the H-bonded hydrogen. The correlation energy reduces the barrier between both minima [23]. It may be that the errors due to the use of

smaller basis and the neglect of correlation effects, to a certain extent, compensate each other.

— The potential curve of the H-bonded hydrogen in H_3O_2^- is not too much susceptible to the position and exponent of bond-function (Table 1). The optimization with respect to the total energy of H_2O is the first good step to obtain the parameters of bond-functions for the $\text{H}_2\text{O}-\text{OH}^-$ system.

— The bond-functions are more effective in the correction of proton potential curves than the p_x , p_y , p_z functions localized on the H-bonded hydrogen. Moreover, the computer time is shorter for bond-functions.

The calculations for other systems as well as the calculations in which bond-functions would be added to a larger basis (e.g. double zeta) would be useful for definitive conclusions.

Acknowledgements. The authors wish to express their gratitude to Professor P. Schuster for sending them the unpublished results. They are indebted to Dr J. Kollár for his aid in adapting the programme to Siemens 4004 computer as well as to the Computing Centre of Komenský University, Bratislava, for providing the computer time.

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Translated by R. Domanský