

ABOUT NON-EXISTENCE OF THE MOLECULAR ION  $H_3^{++}$ Héctor MEDEL-COBAXIN<sup>a1,\*</sup>, Alexander ALIJAH<sup>b</sup> and Alexander V. TURBINER<sup>a2</sup><sup>a</sup> Instituto de Ciencias Nucleares, UNAM, Apartado Postal 70-543, 04510 México;e-mail: <sup>1</sup> medel@nucleares.unam.mx, <sup>2</sup> turbiner@nucleares.unam.mx<sup>b</sup> Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal;

e-mail: alijah@ci.uc.pt

Received May 12, 2008

Accepted May 19, 2008

Published online November 27, 2008

*Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday.*

It is shown that the molecular ion  $H_3^{++}$  does not exist in a form of the equilateral triangle. To this end, a compact variational method is presented which is based on a linear superposition of six specially tailored, Coulomb-type trial functions containing non-linear parameters. Careful optimization of a total of fifteen parameters gives consistently lower variational results for the electronic energy than can be obtained with standard methods of quantum chemistry even with huge basis sets as large as mcc-pV7Z. Taking the proton (electron) charge as a continuous parameter the critical charges are found where the ion  $H_3^{++}$  becomes (meta)-stable.

**Keywords:** Hydrogen; Trihydrogen dication; Coulomb-type trial functions; Schrödinger equation; Born-Oppenheimer approximation; ab initio calculations.

The trihydrogen dication,  $H_3^{++}$ , which consists of three protons and one electron, is among the simplest Coulomb systems. Its stability has been studied intensely in the sixties and early seventies. In a series of articles, Conroy<sup>1-3</sup> investigated the potential energy surfaces of the electronic ground state and the lowest excited states at linear and isosceles triangular configurations. He employed a variational approach in which the electronic trial wavefunction is expanded around the center of the nuclear charges. Analyzing the contour plots Conroy concluded that  $H_3^{++}$  is not stable. Schwartz and Schaad<sup>4</sup>, and Somorjai and Yue<sup>5</sup>, who reported single-point calculations of the system (*pppe*) at the supposed equilibrium equilateral triangular configuration of  $H_3^{++}$ , did not address the stability problem. The existence of  $H_3^{++}$ , with a lifetime of at least 2  $\mu$ s, was suggested by Papp and Kervin<sup>6</sup>, studying the hydrogenic mass spectrum, to account for some of its features. In an erratum<sup>7</sup>, a different explanation for one of the signals was

then given and the evidence for the identification of  $H_3^{++}$  considered "tenuous". Berkowitz and Stocker<sup>8</sup> searched for this ion through charge stripping experiments on  $H_3^{++}$  to assess Conroy's results, not however referencing the experiment by Papp and Kerwin. They could not find evidence of stable  $H_3^{++}$ . Later, the issue was reconsidered also from the theoretical side, by Shoucri and Darling<sup>9</sup>, who examined equilateral configurations with the variational linear combination of atomic orbitals (LCAO) method, and by Hernández and Carbó<sup>10</sup>, who studied two particular configurations with a more compact variational approach and obtained total energy values below those published before. No bound state has been determined in these calculations. Johnson and Poshusta<sup>11</sup> reported another single-point calculation in the context of Gaussian basis set optimization for some one-electron systems. About twenty years later Ackermann et al.<sup>12</sup> revisited the question about the existence of  $H_3^{++}$  using the finite element method which provided much higher accuracy than previously achieved. The problem of the stability of  $H_3^{++}$  was treated keeping the nuclear charge as a continuous parameter. Critical values of the charges for the existence of metastable or possibly stable (towards dissociation to  $H + 2p$ , see a discussion in Results) equilateral triangular configurations were obtained as  $Z_c^+ = 0.95$  and  $0.82$ , respectively. The authors excluded the possibility of stable  $H_3^{++}$  in the electronic ground state. However, the explicit electronic energy data are reported only for one particular equilateral triangular configuration at the triangle size  $R = 1.68$  a.u. Summarizing we state that the accurate *ab initio* results on the basis of which the non-existence of  $H_3^{++}$  can be demonstrated are scarce and not that convincing. This question is thus addressed once again in the present study. It is worth mentioning that one of the motivations of our study is related to a fact that  $H_3^{++}$  in equilateral triangular configuration may exist as metastable state in a magnetic field  $B \geq 10^8$  G (as it was predicted by Lopez Vieyra in ref.<sup>13</sup> for a discussion see review paper<sup>26</sup>).

## METHODS

We study a Coulomb system of one electron and three protons (*pppe*) which form an equilateral triangle of size  $R$ . The protons are assumed to be infinitely massive according to the Born-Oppenheimer approximation at zero order. The Schrödinger equation for the system is written as

$$\left[ \mathbf{p}^2 + \frac{6Z^2}{R} - \frac{2ZZ}{r_1} - \frac{2ZZ}{r_2} - \frac{2ZZ}{r_3} \right] \Psi(\mathbf{r}) = E(Z^2, zZ) \Psi(\mathbf{r}) \quad (1)$$

where  $\mathbf{p} = -i\nabla$  is the electron momentum,  $Z = 1$  is the proton charge and  $z = 1$  is the electron charge (measured in unit  $(-1)$ ),  $r_1$ ,  $r_2$  and  $r_3$  are the distances from each proton to the electron and  $R$  is the interproton distance (Fig. 1). Atomic units are used throughout ( $\hbar = m_e = e = 1$ ).

Our goal is to study the stability of the molecular ion  $\text{H}_3^{++}$ . If such an ion exists, it implies the existence of the ground state of the system (*pppe*). Based on symmetry arguments it seems evident that the optimal geometry of (*pppe*) in the case of existence of a bound state is the equilateral triangle.

Two methods are used to explore the system: (i) variational with physically relevant trial functions (see e.g.<sup>13</sup>) which we will call *specialized* and (ii) *standard* variational based on using standard Gaussian trial functions as implemented in *ab initio* quantum chemistry packages such as MOLPRO<sup>14</sup>. Both methods lead to highly accurate quantitative results for total energy versus the size of the triangle.

In the first variational approach, a trial function is taken in a form of linear superposition of six basis functions

$$\Psi_{\text{trial}} = \sum_{j=1}^6 A_j \psi^{(j)} \quad (2)$$

where  $A_j$  are linear parameters. Each function  $\psi^{(j)}$  is chosen in such a way as to describe different physical characteristics of the system. In general,  $\psi^{(j)}$  has the form of a symmetrized product of three 1s-Coulomb orbitals (Slater functions)

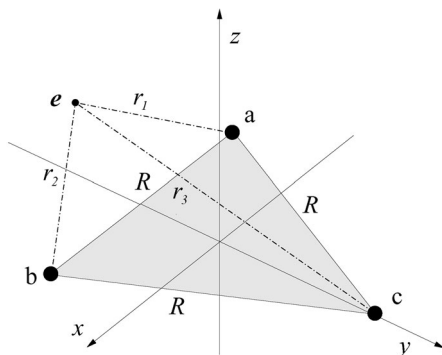


FIG. 1

Molecular ion  $\text{H}_3^{++}$  in equilateral triangular configuration. Protons are fixed on the vertexes (on the  $x$ - $y$  plane). Point  $e$  represents the electron position

$$\psi_C = e^{-\alpha_1 r_1 - \alpha_2 r_2 - \alpha_3 r_3}. \quad (3)$$

Let us give a brief description of each of them:

$\psi^{(1)}$ : All  $\alpha$ 's are chosen to be equal to  $\alpha_1$ ,

$$\psi^{(1)} = e^{-\alpha_1 (r_1 + r_2 + r_3)}. \quad (4)$$

It is a Heitler–London<sup>15</sup> type function. This corresponds to *coherent* interaction between the electron and all protons. Supposedly, it describes the system at small interproton distances and, probably, the equilibrium configuration. It might be verified a posteriori.

$\psi^{(2)}$ : Two  $\alpha$ 's are equal to zero and the remaining one is set to be equal to  $\alpha_2$ ,

$$\psi^{(2)} = e^{-\alpha_2 r_1} + e^{-\alpha_2 r_2} + e^{-\alpha_2 r_3}. \quad (5)$$

It is a Hund–Mulliken<sup>16,17</sup> type function. This function possibly describes the system at large distances, where essentially the electron interacts with only one proton at a time thus realizing *incoherent* interaction.

$\psi^{(3)}$ : One  $\alpha$  is equal to zero, two others are different from zero but equal to each other and to  $\alpha_3$ ,

$$\psi^{(3)} = e^{-\alpha_3 (r_1 + r_2)} + e^{-\alpha_3 (r_1 + r_3)} + e^{-\alpha_3 (r_2 + r_3)}. \quad (6)$$

It is assumed that this function describes the system  $H_2^+$  plus proton when a triangle is of a sufficiently small size. In fact, it is the Heitler–London function of  $H_2^+$  symmetrized over protons.

$\psi^{(4)}$ : One  $\alpha$  is equal to zero and two others are different from each other being equal to  $\alpha_{4,5}$ , respectively,

$$\begin{aligned} \psi^{(4)} = & e^{-\alpha_4 r_1 - \alpha_5 r_2} + e^{-\alpha_4 r_2 - \alpha_5 r_1} + e^{-\alpha_4 r_1 - \alpha_5 r_3} + \\ & + e^{-\alpha_4 r_3 - \alpha_5 r_1} + e^{-\alpha_4 r_2 - \alpha_5 r_3} + e^{-\alpha_4 r_3 - \alpha_5 r_2}. \end{aligned} \quad (7)$$

It is assumed that this function describes the system  $\text{H}_2^+$  plus one proton. In fact, it is the Guillemin–Zener<sup>18</sup> function of  $\text{H}_2^+$  symmetrized over protons. If  $\alpha_4 = \alpha_5$ , the function  $\psi^{(4)}$  is reduced to  $\psi^{(3)}$ . If  $\alpha_4 = 0$ , the function  $\psi^{(4)}$  is reduced to  $\psi^{(2)}$ . Hence  $\psi^{(4)}$  is a non-linear interpolation between  $\psi^{(2)}$  and  $\psi^{(3)}$ . It has to describe intermediate interproton distances.

$\psi^{(5)}$ : Two  $\alpha$ 's are equal but the third one is different,

$$\begin{aligned} \psi^{(5)} = & e^{-\alpha_6 r_1 - \alpha_6 r_2 - \alpha_7 r_3} + e^{-\alpha_6 r_1 - \alpha_6 r_3 - \alpha_7 r_2} + \\ & + e^{-\alpha_6 r_2 - \alpha_6 r_1 - \alpha_7 r_3} + e^{-\alpha_6 r_2 - \alpha_6 r_3 - \alpha_7 r_1} + \\ & + e^{-\alpha_6 r_3 - \alpha_6 r_1 - \alpha_7 r_2} + e^{-\alpha_6 r_3 - \alpha_6 r_2 - \alpha_7 r_1}. \end{aligned} \quad (8)$$

It describes a “mixed” state of three hydrogen atoms. If  $\alpha_6 = \alpha_7$ , the function  $\psi^{(5)}$  is reduced to  $\psi^{(1)}$ . If  $\alpha_6 = 0$ , the function  $\psi^{(5)}$  is reduced to  $\psi^{(2)}$ . If  $\alpha_7 = 0$ , the function  $\psi^{(5)}$  is reduced to  $\psi^{(3)}$ . Hence  $\psi^{(5)}$  is a non-linear interpolation between  $\psi^{(1)}$ ,  $\psi^{(2)}$  and  $\psi^{(3)}$ . As function (7) this is a type of Guillemin–Zener function and should describe intermediate interproton distances.

$\psi^{(6)}$ : All  $\alpha$ 's are different,

$$\begin{aligned} \psi^{(6)} = & e^{-\alpha_8 r_1 - \alpha_9 r_2 - \alpha_{10} r_3} + e^{-\alpha_8 r_1 - \alpha_9 r_3 - \alpha_{10} r_2} + \\ & + e^{-\alpha_8 r_2 - \alpha_9 r_1 - \alpha_{10} r_3} + e^{-\alpha_8 r_2 - \alpha_9 r_3 - \alpha_{10} r_1} + \\ & + e^{-\alpha_8 r_3 - \alpha_9 r_1 - \alpha_{10} r_2} + e^{-\alpha_8 r_3 - \alpha_9 r_2 - \alpha_{10} r_1}. \end{aligned} \quad (9)$$

This is a general non-linear interpolation of all functions  $\psi^{(1-5)}$ .

The total number of parameters of the function (2) is equal to 15, where five are linear ones. Note that without a loss of generality the parameter  $A_6$  in (2) can be fixed putting  $A_6 = 1$ .

In standard *ab initio* calculations,  $\Psi_{\text{trial}}$  is most commonly expanded in terms of Gaussian basis functions  $\psi_{I,i}$  centered at protons  $I = 1, 2, 3$  (see Fig. 1),

$$\Psi_{\text{trial}} = \sum_{I=1}^3 \sum_{i=1}^n \psi_{I,i}(\mathbf{r}_I) c_{Ii} \quad (10)$$

whose coefficients  $c_{Ii}$  are then determined variationally<sup>19</sup>. The basis functions  $\psi_{Ii}$  themselves are built up by primitive Gaussians<sup>20</sup>

$$\Psi_{I,i=\{n,l,m\}}(\mathbf{r}_I) = \sum_{\kappa} NY_{lm}(\theta, \phi) r^{2n-2-l} e^{-\alpha_{\kappa} r^2} d_{\kappa} \quad (11)$$

with contraction coefficients  $d_{\kappa}$  held fixed.

Our calculations were performed using the Hartree–Fock code implemented in the MOLPRO suite of programs<sup>14</sup> with the correlation consistent cc-pV6Z and modified mcc-pV7Z basis sets<sup>21,22</sup>. The cc-pV6Z basis set contains 91 contracted Gaussians per proton, with  $l$  quantum numbers up to  $\ell = 5$ , i.e. [6s5p4d3f2g1h], yielding a total of 273 basis functions. The mcc-pV7Z basis includes  $\ell = 6$  functions, leading to 140 contracted Gaussians per proton, [7s6p5d4f3g2h1i], or 420 basis functions in total. Calculations were carried out for a range of equilateral triangular configurations using  $C_s$  symmetry. In this point group, the lowest electronic state is  ${}^2A'$ . The total number of contracted Gaussians of this symmetry is 168 for the cc-pV6Z basis set and 255 for the mcc-pV7Z basis set, respectively. The cc-pV6Z results, which are not reported here explicitly, have been generated to assess the accuracy of this type of calculations. Based on such a comparison, we estimate the accuracy of the mcc-pV7Z data to about  $10^{-5}$  a.u. over a large range of distances, deteriorating somewhat at short distances where the basis functions tend to become linearly dependent.

## RESULTS

In framework of the specialized variational method (i) some numerical computations were made. The minimization routine MINUIT<sup>23</sup> from the CERN-LIB library was used as well as D01FCF routine from the NAG-LIB<sup>24</sup> for three-dimensional numerical integration. Numerical values of the total energy  $E_T$  of the system (*pppe*) for different values of the interproton distance  $R$  were obtained (Table I). The results from the MOLPRO calculation with a huge standard-type basis set (mcc-pV7Z) are given for comparison. A problem of the standard approach is its slow convergence with respect to the angular momentum quantum number  $\ell$ , requiring the use of large basis sets. The method based on the specially tailored trial function, Eq. (2), leads to systematically lower variational energy values with considerably less terms. It should be noted that this method relies on a careful optimization of non-linear parameters.

Different studies have been done for  $R = 1.68$  a.u. This distance corresponds to an early estimate of the equilibrium distance ( $R_e$ ) for the molecu-

lar ion  $H_3^{++}$  in triangular equilateral configuration<sup>2</sup>. It provides a natural explanation why this was considered. Nowadays it is known with high accuracy that the equilibrium distance for  $H_3^{++}$  is  $R = 1.65$  (ref.<sup>25</sup>). In Table II, we present a comparison of the results obtained at  $R = 1.68$  by the standard method of quantum chemistry, LCAO, which uses optimized Gauss-type (GTO) or Slater-type (STO) atomic orbitals, the finite element method, the

TABLE I

Variational results obtained with the specialized method (2) and with a standard quantum chemistry method employing MOLPRO for the total energy  $E_T$  as a function of the internuclear distance  $R$  for the system *pppe* in the equilateral triangular geometry. (For  $R = 3.50$ , in<sup>10</sup>  $E_T = -0.339$ )

Size $R$ (a.u.)	Total Energy $E_T$ (Hartree)	
	Variational, specialized	Variational, standard
0.10	25.6302842	25.6304634
0.20	10.8826122	10.8827815
0.30	6.1530169	6.1531021
0.40	3.9079404	3.9079929
0.50	2.6385500	2.6385840
0.60	1.8443338	1.8443583
0.70	1.3131266	1.3131450
0.80	0.9405366	0.9405502
0.90	0.6697137	0.6697241
1.00	0.4673239	0.4673307
1.10	0.3126804	0.3126852
1.20	0.1923582	0.1923640
1.30	0.0973269	0.0973322
1.40	0.0213184	0.0213227
1.50	-0.0401268	-0.0401253
1.65	-0.1118605	-0.1118558
2.00	-0.2177957	-0.2177932
2.50	-0.2913521	-0.2810368
3.00	-0.3243024	-0.3242965
3.50	-0.3396630	-0.3396535

MOLPRO calculation with the massive aug-mcc-pV7Z basis set<sup>22</sup> consisting of 567 basis functions, 336 of which have symmetry  $A'$ , and the variational approach, Eq. (2).

Plotting the data results in a smooth monotonous curve of the total energy  $E_T$  as a function of the internuclear distance (Fig. 2).

From a physical point of view it seems evident that if the proton charge  $Z$  is assumed as a continuous parameter and  $z = 1$  (see the Hamiltonian (1)) there exist charges  $Z < 1$  for which the system ( $ZpZpZpe$ ) becomes bound.

TABLE II  
Comparison of different results for  $E_T$  at  $R = 1.68$  a.u.

Author	Method	Energy (Hartree)
Conroy <sup>1</sup>	STO	-0.1215587
Johnson and Poshusta <sup>11</sup>	GTO	-0.12374, est. exact -0.124
Schwartz and Schaad <sup>4</sup>	Variational	-0.12373
Somorjai and Yue <sup>5</sup>	Variational	-0.11708
Ackerman et al. <sup>12</sup>	F.E.	-0.1238567
Present work	MOLPRO, aug-mcc-pV7Z	-0.1238532
Present work	Variational (2)	-0.1238566

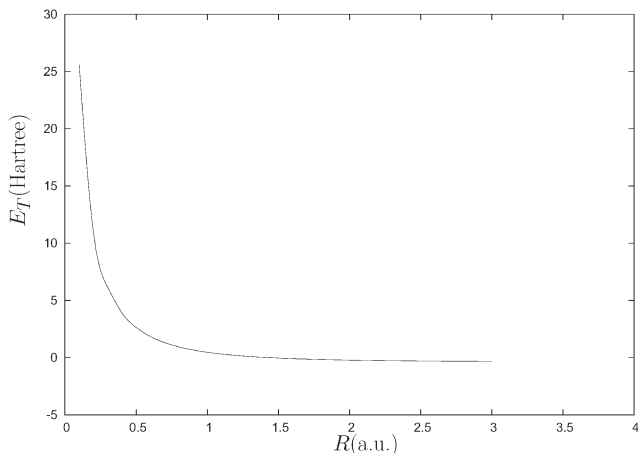


FIG. 2  
 $E_T$  as function of the internuclear distance  $R$ . Asymptotically, for  $R \rightarrow \infty$ , the energy approaches that of a hydrogen atom plus two protons, i.e.  $E_T = -0.5$



Using the variational method with the trial function (2) we found a critical charge  $Z_{cr} = 0.9535$  (cf.  $Z_{cr} = 0.95$  in<sup>12</sup>) such that for  $Z < Z_{cr}$  the total energy curve displays a minimum. In general, the emerged bound state is metastable: the system can dissociate either to  $Z$ -charged hydrogen ( $Zpe$ ) and two  $Z$ -charged protons, or to  $(ZpZpe)$ , the  $Z$ -analogue of  $H_2^+$ , and  $Z$ -charged proton. It is worth noting that  $Z_{cr}$  is very close to the proton charge. With further decrease of  $Z$  a minimum in total energy curve, which occurs at some  $R = R_{eq}$ , deepens and  $R_{eq}$  decreases. At some  $Z_{cr}^{(H)} = 0.8269$  (cf.  $Z_{cr}^{(H)} = 0.82$  in<sup>12</sup>) the system becomes stable towards a dissociation to  $(Zpe)$ -hydrogen and two  $Z$ -charged protons but still remains unstable towards a dissociation to  $(ZpZpe)$ . Eventually, for  $Z < Z_{cr}^{(H_2^+)}$ , where  $Z_{cr}^{(H_2^+)} = 0.5811$ , the system becomes stable. It remains stable until  $Z = 0$ .

The above-mentioned problem of three  $Z$ -charged protons and the electron of unit charge is related with the problem when the proton charge  $Z = 1$  and the electron charge  $z$  is assumed as a continuous parameter. In particular, there exists a relation

$$\frac{1}{Z^2} E(Z^2, zZ) = E(1, \frac{z}{Z}) \quad (12)$$

where  $E(Z^2, zZ)$  is the energy in the first problem and  $E(1, z)$  is the energy in the second problem (see the Hamiltonian (1)). Correspondingly, if the electron charge is small,  $z \leq z_{cr} = 1.0488$  the system ( $pppze$ ) is unbound. If  $z_{cr} < z \leq z_{cr}^{(H)} = 1.2093$ , the system is metastable dissociating to  $z$ -hydrogen atom ( $pze$ ) and two protons. At  $z_{cr}^{(H)} < z \leq z_{cr}^{(H_2^+)} = 1.7209$ , the system remains metastable dissociating to  $z$ -hydrogen ion ( $ppze$ ) and proton. However, for  $z > z_{cr}^{(H_2^+)}$  the system ( $pppze$ ) is stable.

## CONCLUSION

We have studied the trihydrogen dication,  $H_3^{++}$ , at various equilateral triangular configurations of side length  $R$  to assess its stability. Two different variational procedures have been employed, the first being based on specially tailored, physically motivated trial functions and the second on Gaussian functions as commonly used in quantum chemistry calculations. As a conclusion we have to state that the total energy  $E_T$  as a function of the internuclear distance  $R$  does not indicate either to a minimum or even slight non-adiabatic irregularities for finite  $R$ . Thus, the molecular ion  $H_3^{++}$  does not exist in equilateral triangular configuration in the Born-Oppenheimer approximation.

*H. Medel-Cobaxin expresses his deep gratitude to J. C. López Vieyra for the valuable comments and for their interest in the present work, A. V. Turbiner thanks Universite Libre de Bruxelles for the hospitality extended to him where this work was completed. This work was supported in part by FENOMECE as well as CONACyT 58942-F and PAPIIT IN121106 grants (Mexico).*

## REFERENCES

1. Conroy H.: *J. Chem. Phys.* **1964**, *41*, 1327.
2. Conroy H.: *J. Chem. Phys.* **1964**, *41*, 1341.
3. Conroy H.: *J. Chem. Phys.* **1969**, *51*, 3979.
4. Schwartz M. E., Schaad L. J.: *J. Chem. Phys.* **1967**, *47*, 5325.
5. Somorjai R. L., Yue C. P.: *J. Chem. Phys.* **1970**, *53*, 1657.
6. Papp N., Kervin L.: *Phys. Rev. Lett.* **1969**, *22*, 1343.
7. Papp N., Kervin L.: *Phys. Rev. Lett.* **1969**, *23*, 1473.
8. Berkowitz E. H., Stocker H.: *J. Chem. Phys.* **1971**, *55*, 4606.
9. Shoucri R. M., Darling B. T.: *J. Chem. Phys.* **1972**, *56*, 1789.
10. Hernández J. A., Carbó R.: *J. Chem. Phys.* **1975**, *62*, 2637.
11. Johnson J. W., Poshusta R. D.: *Int. J. Quantum Chem.* **1977**, *11*, 885.
12. Ackermann J., Erdmann B., Roitzsch R.: *J. Chem. Phys.* **1994**, *101*, 7643.
13. Turbiner A. V., Lopez Vieyra J. C.: *Phys. Rev. A* **2002**, *66*, 023409.
14. Werner H.-J., Knowles P. J., Lindh R., Manby F. R., Schütz M., Celani P., Korona T., Rauhut G., Amos R. D., Bernhardsson A., Berning A., Cooper D. L., Deegan M. J. O., Dobbyn A. J., Eckert F., Hampel C., Hetzer G., Lloyd A. W., McNicholas S. J., Meyer W., Mura M. E., Nicklass A., Palmieri P., Pitzer R., Schumann U., Stoll H., Stone A. J., Tarroni R., Thorsteinsson T.: *MOLPRO, A Package of ab initio Programs*, version 2006.1 (2006), see <http://www.molpro.net>.
15. Heitler W., London F.: *Z. Phys.* **1927**, *44*, 455.
16. Hund F.: *Z. Phys.* **1927**, *40*, 742.
17. Mulliken R. S.: *Phys. Rev.* **1927**, *29*, 637.
18. Guillemin V., Zener C.: *Proc. Natl. Acad. Sci. U.S.A.* **1929**, *15*, 314.
19. Boys S. F.: *Proc. R. Soc. London, Ser. A* **1950**, *200*, 542.
20. Huzinaga S.: *J. Chem. Phys.* **1965**, *42*, 1293.
21. Dunning T. H., Jr.: *J. Chem. Phys.* **1989**, *90*, 1007.
22. Mielke S. T., Garrett B. C., Peterson K. A.: *J. Chem. Phys.* **2002**, *116*, 4142.
23. CERN Program Library Long Writeup D506: *MINUIT. Function Minimization and Error Analysis Reference Manual*, version 94.1. James F., CERN Geneva, Switzerland (1994–1998).
24. NAG Fortran Library Mark 19.
25. Meyer W., Botschwina P., Burton P.: *J. Chem. Phys.* **1986**, *84*, 891.