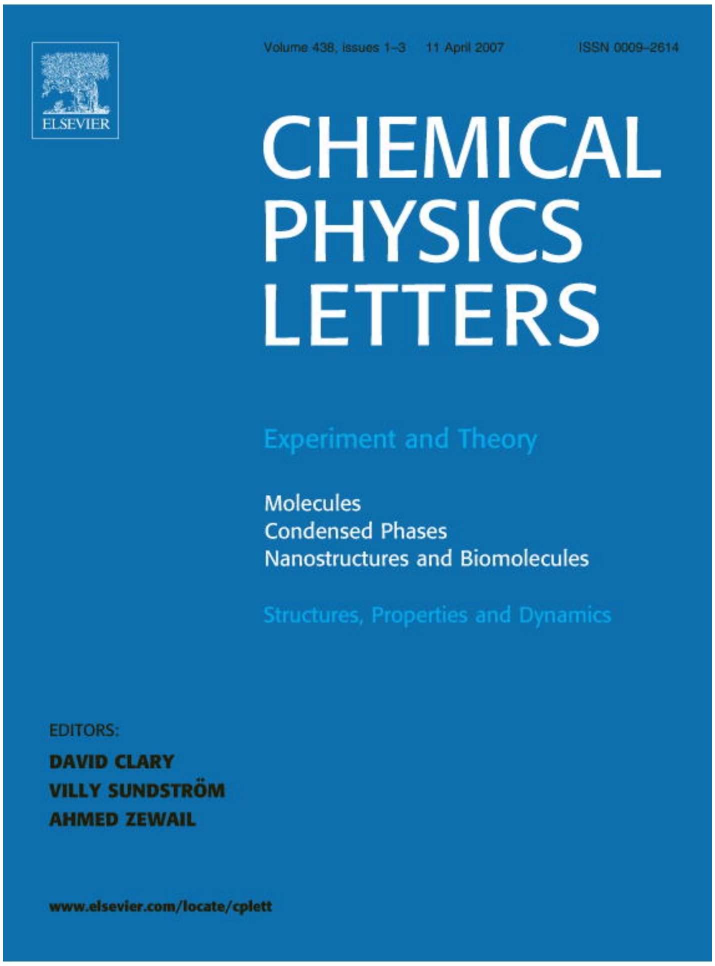
Volume 438, issues 1–3 11 April 2007 ISSN 0009-2614
ELSEVIER
CHEMICAL PHYSICS LETTERS
Experiment and Theory
Molecules
Condensed Phases
Nanostructures and Biomolecules
Structures, Properties and Dynamics
EDITORS:
DAVID CLARY
VILLY SUNDSTRÖM
AHMED ZEWAIL
www.elsevier.com/locate/cplett

Available online at www.sciencedirect.com
ScienceDirect
Chemical Physics Letters 438 (2007) 139–143
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Hartree–Fock-limit energies and structures with a few dozen distributed Gaussians

Gyula Tasi [a,*], Attila G. Császár [b]

[a] Department of Applied and Environmental Chemistry, University of Szeged, Rerrich B. tér 1, H-6720 Szeged, Hungary
[b] Laboratory of Molecular Spectroscopy, Institute of Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest 112, Hungary

Received 20 December 2006; in final form 17 February 2007
Available online 27 February 2007

Abstract

Fully variational energies and structures are obtained for the few-electron prototypical atomic and molecular systems H_2^+, H_2, HHe^+, H_3^+, Be, and LiH at the Hartree–Fock basis-set limit (HFL). The HFL computations are made possible by a global optimization technique employing analytic derivatives of the energy with respect to nuclear centers as well as to positions and exponents of Gaussian-type basis functions (GTF). The efficiency of the procedure presented means that the HFL structure and energy of few-electron systems can be obtained even with a few-dozen distributed s-type GTFs.

1. Introduction

The Hartree–Fock–Roothaan–Hall (HF) self-consistent-field theory is still the focal point of wave-function-based electronic structure theory [1]. It results in molecular orbitals (MOs) and orbital energies, upon which a substantial part of the language of chemistry is built. Furthermore, especially near the equilibrium structures of quantum systems, HF theory generally provides a good starting point for sophisticated techniques of electron correlation treatments and it often results in molecular properties that have at least semiquantitative accuracy [1].

It is fair to say that the ingenious introduction of atom-centered (AC) Gaussian-type basis functions (GTF) by Boys [2] determined most of the development of wave-function-based *ab initio* quantum chemistry techniques, including energy and derivative computations. GTFs provided a breakthrough in the evaluation of electron repulsion integrals, the most time-consuming step in a HF energy computation. To compensate for the wrong functional behavior of AC-GTFs both near and far from the nuclei, it is typical to use a substantial number of them in accurate electronic structure computations [3–8]. To allow a better distribution of Gaussians, efforts were made to augment the atom-centered basis sets with bond-centered (BC) GTFs [4,9,10]. It has been demonstrated [9,10] that bond-centered GTFs can be effectively used to replace polarization (higher angular momentum) and diffuse (low-exponent) GTFs, important elements of energy-optimized atom-centered basis sets [1,11].

As the numerical algorithms and the computer hardware employed improved, it became customary to perform large-basis HF calculations with GTFs of higher and higher angular momentum to approach the Hartree–Fock limit (HFL). Since in actual calculations for larger systems it is not possible to use even a nearly complete atom-centered GTF basis, it also became customary to estimate the HFL energy by extrapolation of results obtained with increasingly more complex basis sets [12–15].

As an alternative, for atoms and diatomic molecules the HFL energy can be obtained numerically [16–18], providing reference data for finite basis set computations. The published molecular numerical HF (NHF) data generally

---

[*] Corresponding author.
E-mail addresses: tasi@chem.u-szeged.hu (G. Tasi), csaszar@chem.elte.hu (A.G. Császár).

0009-2614/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2007.02.056

refer to a few fixed molecular geometries and they can be routinely performed with existing codes [16,17].

Instead of using more and more AC(BC)-GTFs of increasing complexity in the basis set, there is another possibility to improve the wrong functional behavior of Gaussians and make the basis set truly flexible for the particular quantum system. The GTFs can be allowed to fully relax during the electronic structure computation, both with respect to their distribution and exponents. This means that not only the optimum expansion coefficients of the MOs are determined variationally, but also the centers and the exponents of the GTFs are treated as variational parameters. In this sense one can talk about floating-centered (FC) and floating-exponent (FE) GTFs, or in the language customary in variational nuclear motion calculations, distributed Gaussian basis (DGB) functions.

In Jensen's recent studies to reach the HFL [7,8], AC-GTFs were used with their exponents optimized (ACFE-GTF HF computations). The partial derivatives of the electronic energy with respect to the exponents of the basis functions were obtained numerically by finite central differences.

There have been attempts [19–27] to perform fully variational DGB-HF electronic structure calculations on molecules. However, as emphasized also by Jensen [7,8], there has been apparently no functional code with analytic gradient capability for carrying out such calculations and the HF total energies, optimum structures, as well as simple properties presented [20,25,27] can be relatively far from their HFL values.

The procedures developed during the course of this work allow one to perform HF calculations using arbitrary angular momentum atom-centered, bond-centered, floating-center, and floating-exponent GTFs. Therefore, the possible calculations extend from standard atom-centered GTF HF to fully variational DGB-HFL, with the distinguishing feature that we employ a global optimization scheme based on analytic gradients to avoid spurious local minima and linear dependencies in the basis.

2. The DGB-HF method

In what follows details about the DGB-HF method are presented. It is built upon the Hellmann–Feynman theorem (HFT) [28,29], standard algebraic procedures, as well as standard [30] and new recursion formulae.

Let $\varphi_{\mathrm{A}}(\mathbf{r};\alpha_{\mathrm{A}},\mathbf{a},\mathbf{A})$ and $\phi_{\mathrm{A}}\left(\mathbf{r};\{d_{\mathrm{A}k},\alpha_{\mathrm{A}k}\}_{k=1}^{K},\mathbf{a},\mathbf{A}\right)$ denote the properly normalized one-electron Cartesian primitive and contracted GTFs, respectively, on center A, where the electron coordinates, angular momentum vector with nonnegative integers, and origin of the functions are denoted by three-dimensional vectors $\mathbf{r}$, $\mathbf{a}$, and $\mathbf{A}$, respectively, $\alpha_{\mathrm{A}k}$ are the orbital exponents, $d_{\mathrm{A}k}$ are the contraction coefficients, and the degree of contraction in ϕ_{A} is K.

The electronic energy E_{elec} of a closed-shell system in the atomic orbital (AO) basis within the restricted HF approximation is customarily written as

$$\begin{aligned}E_{\mathrm{elec}}(\mathbf{P}) &= \mathrm{Tr}[\mathbf{hP}]+\frac{1}{2}\mathrm{Tr}[\mathbf{PG}(\mathbf{P})]\\ &= \sum_{\mu\nu}P_{\mu\nu}h_{\mu\nu}+\frac{1}{2}\sum_{\mu\nu\sigma\lambda}P_{\mu\nu}P_{\sigma\lambda}[(\mu\nu|\sigma\lambda)\\ &\quad -\frac{1}{2}(\mu\sigma|\nu\lambda)],\end{aligned}\tag{1}$$

where $\mathbf{h}$ and $\mathbf{G}(\mathbf{P})$ are the one- and two-electron parts of the Fock matrix, respectively, and $\mathbf{P}$ is the one-electron density matrix. The molecular integrals in Eq. (1) can be efficiently evaluated via recursion formulae [30].

Generation of the gradient vector of the total energy, the sum of the electronic and nuclear repulsion energies, with respect to the variational parameters follows the HFT [28,29]. It is most advantageous if partial derivatives with respect to the nuclear coordinates are calculated first, followed by those of the origins and, finally, by the scaling factors of the exponents of the GTFs. The latter choice makes it possible to use both contracted and primitive GTFs in actual computations. Evaluation of all partial derivatives, except those with respect to the exponents [9,23,31], is straightforward and relatively simple [30], and thus are not treated here. As to the evaluation of the partial derivatives of the molecular integrals with respect to the exponents of the GTFs, we have devised new recursion formulae.

The partial derivative of the electronic energy E_{elec} in the AO basis with respect to the scaling factor Z_{A} of the exponents of ϕ_{A} can be calculated as

$$\begin{aligned}\frac{\partial E_{\mathrm{elec}}}{\partial Z_{\mathrm{A}}} &= \sum_{\mu\nu}P_{\mu\nu}\frac{\partial h_{\mu\nu}}{\partial Z_{\mathrm{A}}}\\ &\quad +\frac{1}{2}\sum_{\mu\nu\sigma\lambda}\left(P_{\mu\nu}P_{\sigma\lambda}-\frac{1}{2}P_{\mu\sigma}P_{\nu\lambda}\right)\frac{\partial(\mu\nu|\sigma\lambda)}{\partial Z_{\mathrm{A}}}\\ &\quad -\sum_{\mu\nu}Q_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial Z_{\mathrm{A}}},\end{aligned}\tag{2}$$

where $\mathbf{S}$ and $\mathbf{Q}$ are the overlap integral and the energy-weighted density matrices, respectively.

As the simplest case, let us consider the overlap between the contracted ϕ_{A} and $\phi_{\mathrm{B}}\left(\mathbf{r};\{d_{\mathrm{B}m},\alpha_{\mathrm{B}m}\}_{m=1}^{M},\mathbf{b},\mathbf{B}\right)$ GTFs:

$$\langle\phi_{\mathrm{A}}|\phi_{\mathrm{B}}\rangle=\sum_{k}\sum_{m}d_{\mathrm{A}k}d_{\mathrm{B}m}\langle\varphi_{\mathrm{A}k}|\varphi_{\mathrm{B}m}\rangle.\tag{3}$$

Its derivative with respect to Z_{A} is

$$\begin{aligned}\frac{\partial\langle\phi_{\mathrm{A}}|\phi_{\mathrm{B}}\rangle}{\partial Z_{\mathrm{A}}} &= \sum_{k}\sum_{m}\frac{2\lambda_a+3}{2Z_{\mathrm{A}}}d_{Ak}d_{\mathrm{B}m}\langle\varphi_{\mathrm{A}k}|\varphi_{\mathrm{B}m}\rangle\\ &\quad +2\sum_{k}\sum_{m}d_{\mathrm{A}k}d_{\mathrm{B}m}\frac{\alpha_{\mathrm{A}k}}{Z_{\mathrm{A}}}\frac{\partial\langle\varphi_{\mathrm{A}k}|\varphi_{\mathrm{B}m}\rangle}{\partial\alpha_{\mathrm{A}k}},\end{aligned}\tag{4}$$

where λ_a, the angular momentum index, is the sum of the components of vector $\mathbf{a}$. The primitive overlap integrals and their derivatives with respect to the exponents of the GTFs on the right-hand side of Eq. (4) can be evaluated via recursion formulae. Using a well-known simplified notation [30], the following recursion equation can be written for the primitive overlap integrals in Eq. (4):

$$\langle \mathbf{a}+\mathbf{1}_i|\mathbf{b}\rangle = (P_i - A_i)\langle \mathbf{a}|\mathbf{b}\rangle + \frac{1}{2\alpha_P}N_i(\mathbf{a})\langle \mathbf{a}-\mathbf{1}_i|\mathbf{b}\rangle + \frac{1}{2\alpha_P}N_i(\mathbf{b})\langle \mathbf{a}|\mathbf{b}-\mathbf{1}_i\rangle, \tag{5}$$

where

$$P_i = \frac{\alpha_{\mathrm{A}k}A_i + \alpha_{\mathrm{B}m}B_i}{\alpha_{\mathrm{A}k} + \alpha_{\mathrm{B}m}} = \frac{\alpha_{\mathrm{A}k}A_i + \alpha_{\mathrm{B}m}B_i}{\alpha_P}, \tag{6}$$

and $N_i(\mathbf{a})$ takes the ith component of the angular momentum vector $\mathbf{a}$. Let us differentiate both sides of Eq. (5) with respect to $\alpha_{\mathrm{A}k}$:

$$\begin{aligned}\frac{\partial\langle \mathbf{a}+\mathbf{1}_i|\mathbf{b}\rangle}{\partial\alpha_{\mathrm{A}k}} &= (P_i - A_i)\frac{\partial\langle \mathbf{a}|\mathbf{b}\rangle}{\partial\alpha_{\mathrm{A}k}} + \frac{\alpha_{\mathrm{B}m}}{\alpha_P^2}(A_i - B_i)\langle \mathbf{a}|\mathbf{b}\rangle \\ &\quad + \frac{1}{2\alpha_P}N_i(\mathbf{a})\frac{\partial\langle \mathbf{a}-\mathbf{1}_i|\mathbf{b}\rangle}{\partial\alpha_{\mathrm{A}k}} \\ &\quad - \frac{1}{2\alpha_P^2}N_i(\mathbf{a})\langle \mathbf{a}-\mathbf{1}_i|\mathbf{b}\rangle + \frac{1}{2\alpha_P}N_i(\mathbf{b})\frac{\partial\langle \mathbf{a}|\mathbf{b}-\mathbf{1}_i\rangle}{\partial\alpha_{\mathrm{A}k}} \\ &\quad - \frac{1}{2\alpha_P^2}N_i(\mathbf{b})\langle \mathbf{a}|\mathbf{b}-\mathbf{1}_i\rangle.\end{aligned} \tag{7}$$

With the help of Eq. (7), the partial derivatives of the primitive overlap integrals with respect to the exponents of the GTFs can be evaluated recursively. Similarly, the partial derivatives of the one- and two-electron integrals with respect to the scaling factor Z_{A} in Eq. (2) can be deduced and computed via recursion formulae.

Now that all the partial derivatives are available, the components of the gradient vector of the total energy can be easily generated considering optional symmetry and other constraints. Due to the nonlinear nature of the parameter estimation problem, the optimization procedure should be selected with care. The scheme adopted [32] was designed to find the global minimum in the parameter space. The BFGS quasi-Newton algorithm is used with deterministic (inexact or exact) or stochastic (Monte Carlo) line search [32,33]. At every nth iteration the program also performs, besides the deterministic one, a stochastic line search at a random direction. The direction of the deterministic line search in the next iteration may depend on the success of the previous stochastic one. The occasional linear dependency problem of the basis can be solved via Löwdin's canonical orthogonalization. To start the fully variational computation, for instance, the s, sp, ... subsets of standard AC basis sets [1,11] and their unions can be used with or without contraction, all centered on the appropriate atoms.

3. Results and discussion

Using a computer program based on the above procedure, fully variational DGB-HF computations have been performed, resulting in fully variational energies and structures, for the few-electron prototypical atomic and molecular systems H_2, HHe^+, H_3^+, Be, and LiH, used frequently for benchmark studies [3,5–8,34].

The fixed reference structures chosen (distances r in bohr) are those used frequently for benchmark studies: H_2, $r_{\mathrm{HH}} = 1.4$; HHe^+, $r_{\mathrm{HHe}} = 1.455$; H_3^+, $r_{\mathrm{HH}} = 1.65$ (with D_{3h} point-group symmetry); and LiH, $r_{\mathrm{LiH}} = 3.015$. The lowest-energy values (in E_{h}) computed are as follows: H_2, −1.133629566 ($n_{\mathrm{s}} = 50$); HHe^+, −2.933103266 ($n_{\mathrm{s}} = 64$); H_3^+, −1.300372103 ($n_{\mathrm{s}} = 84$); Be, −14.573023162 ($n_{\mathrm{s}} = 26$); and LiH, −7.987352106 ($n_{\mathrm{s}} = 62$), where n_{s} is the number of the primitive s-type GTFs used in the DGB-HF computation. Fig. 1 exemplifies, in the case of H_3^+, the facile convergence of the total energies as a function of n_{s}.

Statistical analyses of the data obtained by direct computations reveal that the total energy decreases exponentially with n_{s}. The following formula can be used to obtain very precise HFL energies via fitting the data obtained from direct computations:

$$E_{\mathrm{HF}}(n_{\mathrm{s}}; E_{\mathrm{HFL}}, a, b) = E_{\mathrm{HFL}} + a\exp(-bn_{\mathrm{s}}). \tag{8}$$

Fitting data with Eq. (8) supplies the following HFL energies (in E_{h}) for the systems under consideration at the reference structures chosen: $E(H_2) = -1.13362958 \pm 1\times10^{-8}$; $E(HHe^+) = -2.933103279 \pm 2\times10^{-9}$; $E(H_3^+) = -1.300372127 \pm 2\times10^{-9}$; $E(\mathrm{Be}) = -14.573023166 \pm 2\times10^{-9}$, and $E(\mathrm{LiH}) = -7.98735222 \pm 8\times10^{-8}$. The HFL energies are just slightly lower than the best energies obtained from the direct DGB-HF computations.

Standard AC(BC)-GTF HF computations, even with an enormous number of GTFs of high angular momentum, do not produce such high-quality results [3,5,6]. Recently, Jensen [7,8] obtained HFL energies within $1nE_{\mathrm{h}}$ for H_2 and H_3^+ at the above reference structures via ACFE-GTF HF computations. His results (in E_{h}) with n GTFs are as follows: H_2, −1.1336295710 ($n = 338$, spdfgh limit) and H_3^+, −1.300372125 ($n = 501$, spdfgh limit). These are in excellent accord with the present HFL estimates. On the other

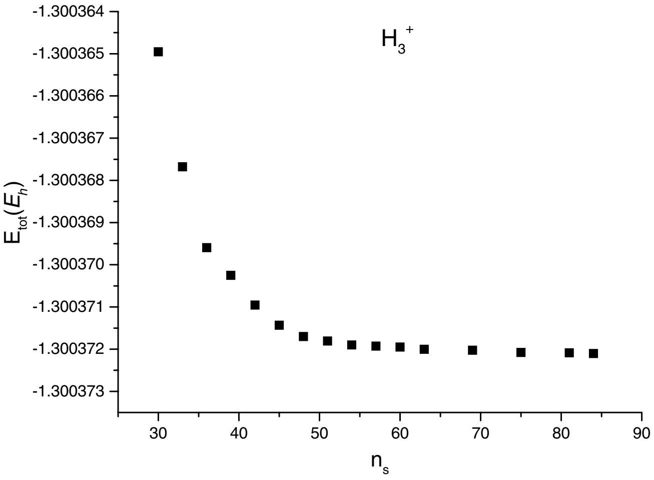

Fig. 1. The DGB-HF total energy, E_{tot}, of H_3^+ at a fixed reference structure ($r_{\mathrm{HH}} = 1.65$ bohrs with D_{3h} point-group symmetry) as a function of the number of the primitive s-type GTFs, n_{s}.

hand, published NHF energies [17] for HHe^+ and LiH, $E(HHe^+) = -2.93310325$ and $E(LiH) = -7.9873524$, are a bit higher and lower than the correct HFL values, respectively. For the beryllium atom, our result perfectly matches a published NHF value [34], $-14.57302317\ E_h$. It is worth noting that to describe the ^1S ground electronic state of the beryllium atom there is no need for polarization functions; therefore, the above high-precision energy can also be obtained from ACFE-GTF HF computation using s-type GTFs only.

By relaxing the structural parameters, it is straightforward to determine optimal HFL structures for molecules in fully variational DGB-HF computations. For the molecules studied, this adds only one more parameter to the parameter set to be optimized. The optimum energies (in E_h) computed at the optimal distances (in bohrs) are as follows: $E(H_2) = -1.133666956$ ($n_s = 50$) at $r_{HH} = 1.386232$; $E(HHe^+) = -2.933103310$ ($n_s = 64$) at $r_{HHe} = 1.455592$; $E(H_3^+) = -1.300400682$ ($n_s = 81$) at $r_{HH} = 1.638912$; and $E(LiH) = -7.987364452$ ($n_s = 58$) at $r_{LiH} = 3.033910$. Statistical analyses of the data computed directly reveal also in this case that the total energy decreases exponentially with n_s. Fitting data with Eq. (8) results in the following HFL energies at the HFL molecular geometries: $E(H_2) = -1.13366697 \pm 1 \times 10^{-8}$; $E(HHe^+) = -2.93310332 \pm 2 \times 10^{-8}$; $E(H_3^+) = -1.30040070 \pm 1 \times 10^{-8}$; and $E(LiH) = -7.98736463 \pm 8 \times 10^{-8}$. These energies are also very close to the best energies obtained from direct DGB-HF computations.

As to the distributions of the centers and exponents of the GTFs, they show similar patterns for all cases investigated. Figs. 2 and 3 show the distributions in question as statistical plots for LiH. Most of the GTFs are located close, within 0.1 bohr, to the nuclei and the exponents are mostly populated around zero considering $\log(\alpha)$. Furthermore, the larger the exponent of the GTF, the closer its origin is to one of the nuclei, and the GTFs with the largest exponents stick tightly to the nuclei.

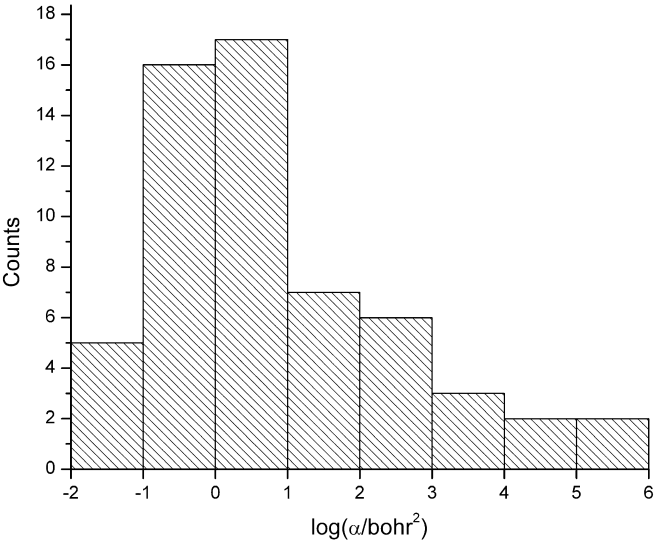

Fig. 3. Distribution of the exponents of the primitive s-type GTFs for LiH in a DGB-HF computation with relaxed centers, exponents, and structure ($n_s = 58$, $E_{tot} = -7.987364452\ E_h$, $r_{LiH} = 3.033910$ bohrs).

Note that as tests of the convergence of the DGB-HFL energies and structures, all the molecular calculations have been performed with our program using not only s- but also p-type GTFs in the basis. The converged results agree perfectly with those reported above. For instance, Fig. 4 shows the facile convergence of the total energy of H_3^+ with relaxed centers, exponents, and structure as a function of the cardinal number X (=2–6) of the standard cc-pVXZ basis sets of Dunning [11] using the s and p basis functions, *i.e.*, the sp subsets.

The availability of DGB-HFL results along a potential energy curve (PEC), in the present case that of H_2^+, allows the investigation of the relative accuracy of traditional

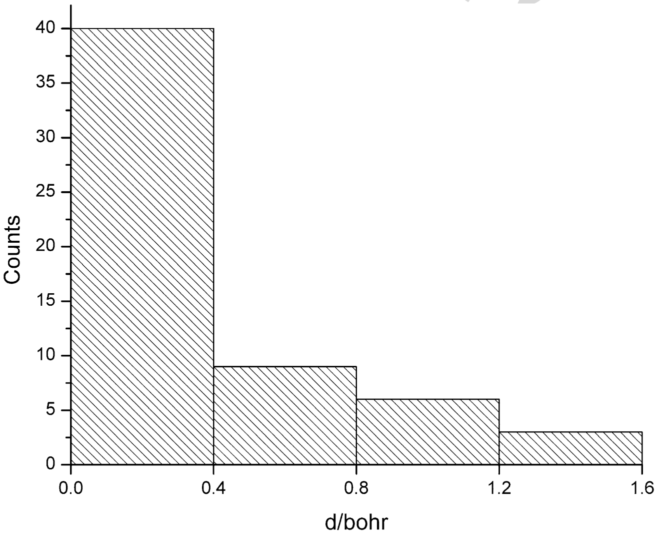

Fig. 2. Distribution of the centers of the primitive s-type GTFs for LiH in a DGB-HF computation with relaxed centers, exponents, and structure ($n_s = 58$, $E_{tot} = -7.987364452\ E_h$, $r_{LiH} = 3.033910$ bohrs).

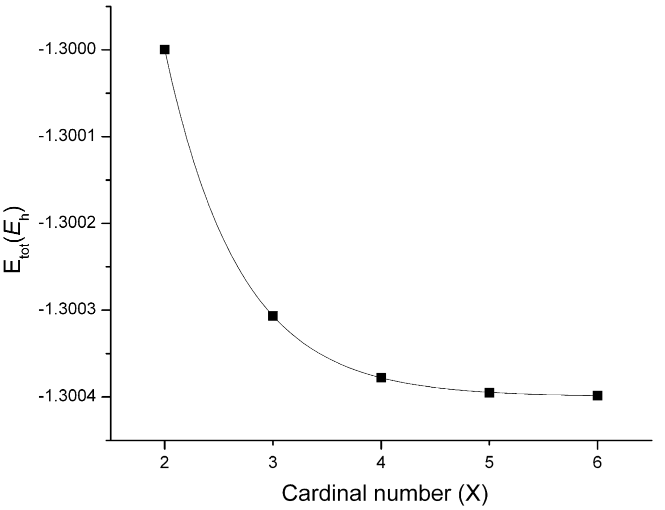

Fig. 4. The DGB-HF total energy, E_{tot}, of H_3^+ with relaxed centers, exponents, and structure as a function of cardinal number X (= 2–6) using the s and p basis functions of the cc-pVXZ basis sets.

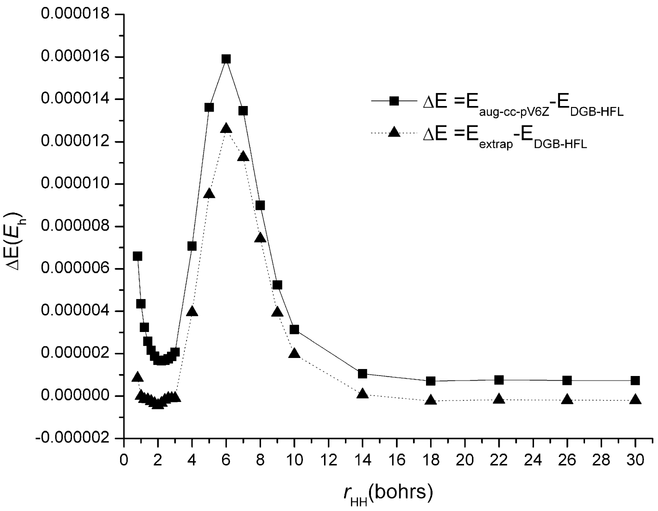

Fig. 5. Relative accuracy of traditional aug-cc-pV6Z, $E_{\text{aug-cc-pV6Z}}$, and extrapolated, E_{extrap}, HF energies, as compared to accurate DGB-HFL values, $E_{\text{DGB-HFL}}$, along the potential energy curve of H_2^+. The extrapolated curve was obtained from aug-cc-pV5Z and aug-cc-pV6Z HF energies through the use of Eq. (9). The use of the uncontracted versions of the aug-cc-pV5Z and aug-cc-pV6Z basis sets results in curves indistinguishable from those presented here.

HF computations utilizing correlation-consistent basis sets and extrapolation procedures along the PEC. As seen in Fig. 5, the relative accuracy of the traditional HF computations, with or without extrapolation, and with or without contraction of the basis, has a characteristic dependence on the internuclear separation. The direct energies are very accurate and the extrapolated energies are nearly exact close to the equilibrium structure (about 2 bohrs) and close to complete separation of the atoms (for distances larger than 14 bohrs), but at moderate and short distances the accuracy drops substantially and systematically. This behavior of the popular correlation-consistent bases should be kept in mind when traditional HF computations are used as energy components to obtain global potential energy surfaces.

4. Conclusions

A method and a computer code are presented which allow efficient computation of HFL structures and energies.

The availability of high-accuracy HFL structures and energies allow their comparison with results from traditional finite basis and extrapolated fixed-center and fixed-exponent GTF HF computations. The results obtained show that among the many possible extrapolation formulae, the form [14,15,35]

$$E_{\mathrm{HF},X} = E_{\mathrm{extrap}} + a(X+1)\exp(-9\sqrt{X}), \qquad (9)$$

works best both for energies and structures. Using the aug-cc-pV*XZ* family of basis sets of Dunning [11], with cardinal numbers $X = 5$ and 6, approaching completeness in a systematic way, results in energies and structures different from the DGB-HFL ones by less than 2 μE_h and 0.00001 bohr, respectively.

As to the expense of the DGB-HF computations presented, even in the largest computations an energy evaluation needs a couple of seconds, while a gradient vector generation takes a few times more on a common PC. One run in the global optimization process usually consists of 30–50 optimization cycles.

DGB-HFL computations on larger molecules with at least four and five atoms and/or much more than four electrons are in progress and will be reported in due time.

Acknowledgements

This work has been supported in part by the Scientific Research Fund of Hungary (OTKA) through Grants T042825 and T047185.

References

[1] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, John Wiley & Sons, New York, 1986.
[2] S.F. Boys, Proc. Roy. Soc. A 200 (1950) 542.
[3] B.H. Wells, S. Wilson, J. Phys. B: At. Mol. Opt. Phys. 22 (1989) 1285.
[4] D. Moncrieff, S. Wilson, J. Phys. B: At. Mol. Opt. Phys. 27 (1994) 1.
[5] H.F.M. Da Costa, A.B.F. Da Silva, J.R. Mohallem, A.M. Simas, M. Trsic, Chem. Phys. 154 (1991) 379.
[6] F.E. Jorge, R. Centoducatte, E.V.R. De Castro, Theor. Chem. Acc. 103 (2000) 477.
[7] F. Jensen, J. Chem. Phys. 110 (1999) 6601.
[8] F. Jensen, Theor. Chem. Acc. 104 (2000) 484.
[9] J. Bruun, T. Helgaker, F. Jensen, Mol. Phys. 102 (2004) 2559.
[10] E. Matito, J. Kobus, J. Styszynski, Chem. Phys. 321 (2006) 277.
[11] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
[12] D. Feller, J. Chem. Phys. 96 (1992) 6104.
[13] A.G. Császár, W.D. Allen, H.F. Schaefer III., J. Chem. Phys. 108 (1998) 9751.
[14] F. Jensen, Theor. Chem. Acc. 113 (2005) 267.
[15] A. Karton, J.M.L. Martin, Theor. Chem. Acc. 115 (2005) 330.
[16] C. Froese-Fischer, Comput. Phys. Rep. 3 (1986) 273.
[17] L. Laaksonen, P. Pyykkö, D. Sundholm, Comput. Phys. Rep. 4 (1986) 313.
[18] F. Jensen, Theor. Chem. Acc. 113 (2005) 187.
[19] H. Preuß, Z. Naturfosch. 11a (1956) 823.
[20] J.L. Whitten, J. Chem. Phys. 44 (1966) 359.
[21] M.E. Schwartz, L.J. Schaad, J. Chem. Phys. 46 (1967) 4112.
[22] A.A. Frost, J. Chem. Phys. 47 (1967) 3707.
[23] G. Tonachini, H.B. Schlegel, J. Chem. Phys. 87 (1987) 514.
[24] T. Helgaker, J. Almlöf, J. Chem. Phys. 89 (1988) 4889.
[25] K. Hashimoto, Y. Osamura, Chem. Phys. Lett. 164 (1989) 353.
[26] W. Cencek, J. Rychlewski, J. Chem. Phys. 98 (1993) 1252.
[27] M. Tachikawa, K. Taneda, K. Mori, Int. J. Quantum Chem. 75 (1999) 497.
[28] H. Hellmann, Einführung in die Quantenchemie, Franz Deuticke, Leipzig and Vienna, 1937.
[29] R.P. Feynman, Phys. Rev. 56 (1939) 340.
[30] S. Obara, A. Saika, J. Chem. Phys. 84 (1986) 3963.
[31] A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 97 (1992) 2571.
[32] T. Csendes, Acta Cybernet. 8 (1988) 361.
[33] L.E. Scales, Introduction to Non-linear Optimization, Macmillan Publishers, London, 1985.
[34] T. Koga, S. Watanabe, K. Kanayama, R. Yasuda, J. Chem. Phys. 103 (1995) 3000.
[35] W. Klopper, W. Kutzelnigg, J. Molec. Struct. (Theochem) 135 (1986) 339.