

PERTURBATION CALCULATION OF MOLECULAR
CORRELATION ENERGY USING GAUSSIAN-TYPE GEMINALS.
SECOND-ORDER PAIR ENERGIES OF THE FIRST-ROW
DIATOMIC HYDRIDES FROM MINIMAL GAUSSIAN GEMINAL
BASIS SETS*

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The variation-perturbation scheme due to Sinanoglu was applied for the calculation of the second-order pair energies in LiH, BH and FH using the minimal Gaussian geminal basis set approximation for the first-order pair functions. According to the proposed approach the first-order pair function for each orbital pair was represented by a single Gaussian geminal, whose all non-linear parameters were carefully optimized. The second-order pair energy calculations have been performed in two steps. First, the non-linear parameters for each Gaussian geminal were optimized using modified second-order pair energy functionals and rather crude SCF reference functions. In the second step the Gaussian geminals are treated as already fixed and the final values of the second-order pair energies are computed with quite accurate SCF reference functions. In this final step only a single linear variation parameter is optimized. The most attractive feature of the minimal Gaussian geminal bases is their conceptually simple analytic form which allows for a qualitative analysis of the intra-pair correlation effects. This is also followed by quite reasonable accuracy of the computed second-order pair energies. For LiH and BH the minimal Gaussian geminal basis set approximation is shown to recover ca. 75 per cent of the most accurate second-order correlation energies. The SCF wave function employed for the FH molecule was much poorer than those for LiH and BH. Also some of the Gaussian geminals have not been fully optimized. In spite of this, the present approach gives nearly 60 per cent of the second-order correlation energy calculated using the many-body perturbation methods. The present results unambiguously indicate a very high efficiency of the Gaussian geminal bases in molecular correlation energy calculations.

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1. Introduction

The restricted Hartree-Fock (HF) model [1] is known to account for the major portion of the total electronic energy of the closed-shell atoms and molecules. The remaining part of the non-relativistic electronic energy is attributed to the electron correlation effects [2]. In spite of its relative smallness the electronic correlation energy frequently plays a decisive role in the prediction of a variety of physical and chemical phenomena [2-5]. The understanding and calculation of the electron correlation effects represents one of the primary goals of the present-day quantum chemistry.

Going beyond the HF level, though formally simple, represents a formidable task [1, 5]. As far as the instantaneous correlation of the electronic motions can be considered as a small perturbation to the HF model, the use of the perturbation theoretic approaches is recommended, provided they recover a substantial portion of the correlation energy in the lowest orders. According to several recent calculations [6-10] the ordinary Rayleigh-Schrodinger perturbation theory built upon the HF approximation provides as much as ca. 80 per cent of the total correlation energy already in the second order. There are also some indications that this second-order correlation energy is nearly constant for a wide series of many-electron systems [6, 9]. However, in order to obtain the limiting values of the second-order correlation energies one needs fairly flexible first-order wave functions.

In the standard approaches the first-order perturbed wave functions are expanded into a set of doubly substituted Slater determinants (with respect to the HF determinant) and the flexibility of this expansion is severely limited by the number of available HF orbitals, i.e., the dimension of the original basis set employed in the restricted SCF HF calculations. Recent many-body perturbation calculations of the second-order correlation energy by Bartlett and Silver [9] clearly demonstrate that the convergence of this expansion is quite slow. On the other hand, it is known that the second-order perturbed energy problem can be given a variation formulation [11]. Therefore, the first-order perturbed wave function can be chosen in a far more general way. Moreover, the variation-perturbation technique provides separate equations for the perturbation corrections to each spin-coupled HF pair of electrons [12]. The resulting first-order perturbed pair equations are most efficiently solved by expanding the first-order perturbed pair functions into a set of basis functions with explicit dependence on the interelectronic distance r_{12} [6, 13, 14].

Recently a considerable attention has been given to the so-called Gaussian geminals (GG), i.e., two-electron functions with explicit dependence on r_{12} in the form of the Gaussian-type correlation factor, $\exp(-\beta r_{12}^2)$. The atomic and molecular integrals involving GG's are tractable [15] and much easier than the integrals with other explicitly correlated functions [13, 16]. Moreover, as shown by King [17], the Gaussian pair functions form a complete set. The efficiency of the GG expansion for the first-order perturbed pair functions was demonstrated in atomic [6] and molecular [10] calculations. It was shown [6, 10] that fairly accurate first-order pair functions and second-order pair energies can be obtained using relatively short GG expansions. However, a rather extensive optimization of all non-linear parameters entering the GG's was found necessary.

The present paper is concerned with the problem of efficiency of the shortest possible GG expansion for the first-order pair functions, i.e., the expansion involving a single GG for each pair. Such a basis, hereafter called the *minimal GG set*, if properly optimized, should still provide a considerable portion of the second-order correlation energy. This feature of the minimal GG bases was already confirmed by Pan and King [6] in the case of atoms and the aim of the present paper is to study the usefulness of the minimal GG sets in molecular calculations.

It is worth attention that the idea of the minimal GG set to some extent resembles the concept of the minimal atomic bases in the SCF HF calculations. These bases contributed a lot to our understanding of the orbital model and its accuracy, though the corresponding SCF energies were usually rather poor. Some similar features can be expected for the minimal GG bases as regards the intra-pair correlation effects.

A brief description of the theory behind the calculations reported in this paper is given in the next Section. The method of optimization of the GG non-linear parameters, which takes advantage of relatively poor SCF reference functions according to the computational scheme described elsewhere [18], is reviewed in Section 3. The final results for LiH, BH and FH are discussed in the subsequent Section. All the SCF orbitals used in the present calculations were obtained by expanding them into a set of completely optimized floating spherical Gaussian orbitals (FSGO). Since these orbitals can be used for a number of other purposes, the corresponding optimized FSGO basis sets were separately presented in the Appendix.

2. Second-order correlation energy functional and the first-order pair equations

Let us assume for the moment that the Hartree-Fock solution for a given $2n$ -electron system is available. Then, the set of n lowest energy orbitals $\{v_1, \dots, v_n\}$ is used to build the HF Slater determinant Φ^0 . Since the orbitals v_i are the eigenfunctions of the one-electron HF operator h^{HF} ,

$$h^{\text{HF}}(k)v_i(k) = e_i^{\text{HF}}v_i(k), \quad (1)$$

where e_i^{HF} denotes the HF orbital energy, the determinant Φ^0 represents the eigensolution for the so-called many-electron HF Hamiltonian H^{HF} ,

$$H^{\text{HF}}\Phi^0 = E^0\Phi^0 \quad (2)$$

and the HF energy E^{HF} is defined by

$$E^{\text{HF}} = \langle \Phi^0 | H | \Phi^0 \rangle = E^0 + E^1, \quad (3)$$

where H is the total non-relativistic Hamiltonian of a given system,

$$H^{\text{HF}} = \sum_{k=1}^{2n} h^{\text{HF}}(k), \quad (4)$$

and

$$E^0 = 2 \sum_{i=1}^n e_i^{\text{HF}}. \quad (5)$$

This standard material is repeated here for establishing the notation used throughout this paper and more details can be found for instance in Ref. [19].

Given the HF Φ^0 and the corresponding HF Hamiltonian one can set up the following perturbation problem

$$H = H^0 + H^1, \quad (6)$$

where H^0 is the HF Hamiltonian H^{HF} and the perturbation H^1 representing the correlation effects [19] is given by

$$H^1 = H - H^{\text{HF}} = H - H^0. \quad (7)$$

The Rayleigh-Schrodinger perturbation theory as used by Sinanoglu [4] results in the first-order perturbation equation

$$(H^0 - E^0)\Phi^1 = -(H^1 - E^1)\Phi^0, \quad (8)$$

where the first-order perturbed wave function Φ^1 can be written [20] as a sum of antisymmetrized products of strongly orthogonal pair functions \bar{v}_{ij} (spin-geminals) and the remaining occupied HF spin-orbitals \bar{v}_k . In this way Eq. (8) can be split into a finite set of two-electron equations [6, 19]

$$(\bar{h}^{\text{HF}}(1) + \bar{h}^{\text{HF}}(2) - e_i^{\text{HF}} - e_j^{\text{HF}})\bar{v}_{ij}(1, 2) = -\frac{1}{\sqrt{2}} Q(1 - P_{12})r_{12}^{-1}\bar{v}_i(1)\bar{v}_j(2) \quad (9)$$

for each pair function corresponding to a given pair of occupied HF spin-orbitals. Q denotes the so-called strong orthogonality projector

$$Q = q(1)q(2), \quad (10)$$

where

$$q(k) = 1 - \sum_{i=1}^n v_i(k), \quad (11)$$

and P_{12} is the permutation operator for particles 1 and 2. The strong orthogonality condition imposed by the presence of Q takes into account that only the double substitutions with respect to Φ^0 can contribute to Φ^1 . As far as Φ^0 is the exact HF solution the presence of Q in Eq. (9) does not represent any additional approximation.

Eq. (9) is the Euler equation for the second-order pair energy functional $J_{\text{HF}}[\bar{v}_{ij}]$ [6]

$$J_{\text{HF}}[\bar{v}_{ij}] = \langle \bar{v}_{ij}(1, 2) | \bar{h}^{\text{HF}}(1) + \bar{h}^{\text{HF}}(2) - e_i^{\text{HF}} - e_j^{\text{HF}} | Q \bar{v}_{ij}(1, 2) \rangle \\ + \sqrt{2} \text{Re} \langle \bar{v}_{ij}(1, 2) | Q(1 - P_{12})r_{12}^{-1} | \bar{v}_i(1)\bar{v}_j(2) \rangle, \quad (12)$$

where the subscript HF at the functional symbol indicates that $J_{\text{HF}}[\bar{v}_{ij}]$ is defined with respect to the exact HF solution of the zeroth-order problem. The minimum value of this functional corresponds to the second-order pair energy e_{ij}^{HF} with respect to the HF zeroth-order approximation

$$e_{ij}^{\text{HF}} \leq J_{\text{HF}}[\bar{v}_{ij}]. \quad (13)$$

The separate pair energies sum up to the total second-order correlation energy E_{HF}^2

$$E_{\text{HF}}^2 = \sum_{i < j} e_{ij}^{\text{HF}}, \quad (14)$$

which generally represents the main portion of the total correlation energy in closed-shell systems.

The variational formulation of the second-order energy problem permits a wide class of functions which can be used as variational approximations to \bar{v}_{ij} . Physically, the first-order pair functions should effectively create a Coulomb hole for each HF pair $\bar{v}_i(1)\bar{v}_j(2)$ and therefore, introducing an explicit r_{12} -dependence into $\bar{v}_{ij}(1, 2)$ appears to be highly desirable. A customary procedure is to expand the first-order pair functions into a set of explicitly correlated functions, say $\{g_k(1, 2; \alpha_k)\}$ with some intrinsic variation parameters comprising a vector α_k . Thus, one can write for each component of definite multiplicity

$$\bar{v}_{ij}(1, 2) = v_{ij}(1, 2)\Theta(1, 2), \quad (15)$$

and

$$v_{ij}(1, 2) = \sum_{k=1}^M A_{ij,k} g_k(1, 2; \alpha_k), \quad (16)$$

where $\Theta(1, 2)$ is the appropriate spin function and $v_{ij}(1, 2)$ represents the space part of a given first-order correction $\bar{v}_{ij}(1, 2)$. $A_{ij,k}$ are the linear variation parameters and M denotes the dimension of the set $\{g_k\}$. Provided the intrinsic variation parameters α_k are completely optimized, the second-order energies for a chosen set $\{g_1, \dots, g_M\}$ will depend only on its size, i.e.,

$$e_{ij}^{\text{HF}} = e_{ij}^{\text{HF}}(M). \quad (17)$$

If the set $\{g_k\}$ is composed of the so-called Gaussian geminals (GG), i.e., products of orbital functions multiplied by the Gaussian correlation factor, then usually a relatively small number of terms in (16) is sufficient for quite high accuracy of the computed second-order pair energies [6, 10]. It is also worth attention that the number of different first-order pair functions can be significantly reduced due to spin and space symmetry of a given many-electron system.

The formulation of the variation-perturbation scheme outlined in this Section is completely valid as far as (i) the HF Φ^0 built of $2n$ lowest energy spinorbitals corresponds to the lowest total energy in this approximation, and (ii) the HF equation (1) is exactly solved for the orbitals used in Φ^0 . Usually the first condition is satisfied even for approximate HF orbitals [21]. However, the second condition is merely an assumption. The orbitals available in practice by no means satisfy Eq. (1), since they correspond to some finite basis set SCF approximations to the exact HF solutions. The study of Pan and King shows, however, that the so-called near-HF orbitals, i.e., the SCF solutions obtained with large basis sets, can be safely used in place of the HF orbitals [6]. The errors introduced by this replacement do not seem to be very important for the second-order pair energies.

However, the calculations with near-HF orbitals and the GG expansions, accompanied by a full optimization of the parameters entering the GG set, are tremendously time consuming. Most of the computer time is apparently spent on the optimization of the non-linear parameters of a given GG set. The final determination of the linear variation parameters $A_{ij,k}$ for the optimized GG set is relatively fast and can be performed even for very accurate near-HF functions involving large orbital bases. It was therefore proposed that the GG basis set optimization is carried out with rather crude SCF wave functions [18] and only the final step leading to the second-order pair energies is repeated with near-HF orbitals. However, using crude SCF reference functions for the GG basis set optimization requires a reconsideration of the whole procedure defined for the HF Φ^0 .

3. Optimization of the GG bases with crude SCF reference orbitals

3.1. A summary of the method

The canonical SCF orbitals $\{u_1, \dots, u_n\}$ represented by the expansion into a finite set of N selected one-electron functions χ_i and used to build the approximate HF SCF Slater determinant Ψ^0 will not satisfy Eq. (1). Thus, in order to develop a perturbation treatment of the correlation effects one has to define some appropriate zeroth-order unperturbed Hamiltonian \bar{H}^{SCF} which has Ψ^0 as its eigenfunction. The Hamiltonian satisfying this condition, i.e.,

$$\bar{H}^{\text{SCF}}\Psi^0 = \bar{E}^0\Psi^0 \quad (18)$$

is conveniently represented by a sum of one-electron SCF Hamiltonians \bar{h}^{SCF}

$$\bar{H}^{\text{SCF}} = \sum_{k=1}^{2n} \bar{h}^{\text{SCF}}(k), \quad (19)$$

which in turn should have the SCF orbitals as their exact eigenfunctions

$$\bar{h}^{\text{SCF}}(k)u_i(k) = e_i^{\text{SCF}}u_i(k). \quad (20)$$

For a given ordinary SCF Hamiltonian h^{SCF}

$$h^{\text{SCF}}(1) = h_0(1) + \sum_{i=1}^n \int u_i^*(2) (2 - P_{12}) r_{12}^{-1} u_i(2) dv_2, \quad (21)$$

where $h_0(1)$ denotes the so-called bare-nucleus Hamiltonian, there is an infinite number of Hamiltonians \bar{h}^{SCF} defined by the requirement that Eq. (20) is valid in the whole Hilbert space [22, 23]. The choice of \bar{h}^{SCF} in the so-called projected form of h^{SCF}

$$\bar{h}^{\text{SCF}}(k) = p^{\text{SCF}}(k)h^{\text{SCF}}(k)p^{\text{SCF}}(k) + q^{\text{SCF}}(k)h^{\text{SCF}}(k)q^{\text{SCF}}(k), \quad (22)$$

where

$$p^{\text{SCF}}(k) = \sum_{i=1}^n |u_i(k)\rangle \langle u_i(k)|, \quad (23)$$

and

$$q^{\text{SCF}}(k) = 1 - p^{\text{SCF}}(k) \quad (24)$$

was recommended in several recent papers [9, 22–24]. With \bar{h}^{SCF} as given by Eq. (22) the eigenvalue problem (20) becomes an identity. Moreover, the projected form of the SCF Hamiltonian (20) in the limit of the HF solution becomes the spectral resolution of h^{HF} .

According to these definitions the eigenvalue \bar{E}^0 is exactly equal to the sum of the SCF orbital energies

$$\bar{E}^0 = 2 \sum_{i=1}^n e_i^{\text{SCF}}, \quad (25)$$

and Eq. (19) defines the following partition

$$H = \bar{H}^0 + \bar{H}^1 \quad (26)$$

of the total Hamiltonian H into the unperturbed part $\bar{H}^0 = \bar{H}^{\text{SCF}}$ and the perturbation \bar{H}^1 . In comparison with Eqs. (6) and (7) \bar{H}^1 is responsible for both the true correlation effects and the effects of the inaccuracy of the SCF solution [24] with respect to the HF result. Since we are interested rather in pure correlation effects than in the improvement of the SCF orbitals, the separation of the corresponding contributions to the perturbed energies is desirable. There is no problem with the first-order perturbed energy \bar{E}^1 , which is given by

$$\bar{E}^1 = \langle \Psi^0 | \bar{H}^1 | \Psi^0 \rangle \quad (27)$$

and contributes to the SCF energy E^{SCF}

$$E^{\text{SCF}} = \bar{E}^0 + \bar{E}^1. \quad (28)$$

For the second-order energies the separation of the correlation effects can be done to some extent by the appropriate selection of the first-order pair functions $u_{ij}(1, 2)$. If these are made strongly orthogonal to the occupied orbitals, i.e., if

$$p^{\text{SCF}}(1)p^{\text{SCF}}(2)u_{ij}(1, 2) = 0, \quad (29)$$

then the first-order perturbed wave function Ψ^1 will involve only double substitutions with respect to Ψ^0 .

The partition (26) allows for the legitimate use of the variation-perturbation approach, since the zeroth-order problem for \bar{H}^{SCF} is already solved. Thus, the second-order energy variation principle leads to the Hylleraas-type functional [25]

$$J_{\text{SCF}}[\Psi^1] = \langle \Psi^1 | \bar{H}^0 - \bar{E}^0 | \Psi^1 \rangle + 2 \text{Re} \langle \Psi^1 | \bar{H}^1 - \bar{E}^1 | \Psi^0 \rangle \quad (30)$$

and its minimum corresponds to the second-order energy \bar{E}_{SCF}^2 with respect to a given SCF reference function Ψ^0 . Introducing strongly orthogonal spin-geminals $\bar{u}_{ij}(1, 2)$ in the same way as for the HF approach one can show that the functional (30) is split into a finite set of independent pair functionals

$$\begin{aligned} J_{\text{SCF}}[\bar{u}_{ij}] = & \langle \bar{u}_{ij}(1, 2) | \bar{h}^{\text{SCF}}(1) + \bar{h}^{\text{SCF}}(2) - e_i^{\text{SCF}} - e_j^{\text{SCF}} | q^{\text{SCF}}(1)q^{\text{SCF}}(2) \bar{u}_{ij}(1, 2) \rangle \\ & + \sqrt{2} \text{Re} \langle \bar{u}_{ij}(1, 2) | q^{\text{SCF}}(1)q^{\text{SCF}}(2) (1 - P_{12}) r_{12}^{-1} | \bar{u}_i(1)\bar{u}_j(2) \rangle \end{aligned} \quad (31)$$

with the second-order pair energies e_{ij}^{SCF} corresponding to their minimum values. These pair energies will depend on both the size N of the basis set of one-electron functions used in the SCF calculations and the accuracy of the minimization of the functionals (31). If the pair functions are expanded in terms of some finite M -dimensional set of geminals, then

$$e_{ij}^{\text{SCF}} = e_{ij}^{\text{SCF}}(N, M), \quad (32)$$

and $e_{ij}^{\text{SCF}}(N, M)$ will approach $e_{ij}^{\text{HF}}(M)$ for sufficiently large values of N . In comparison with the ordinary approaches replacing \bar{h}^{SCF} in the functional (31) by h^{SCF} , the present formulation does not rely on a rather questionable assumption that the validity of the ordinary SCF equation

$$h^{\text{SCF}}(k)u_i(k) = e_i^{\text{SCF}}u_i(k) \quad (33)$$

can be continued beyond the selected subspace of N one-electron basis functions.

For poor SCF reference functions, i.e., for small values of N , e_{ij}^{SCF} will represent obviously a poor approximation to e_{ij}^{HF} . However, for relatively well optimized SCF wave functions the HF potential entering \bar{h}^{SCF} should properly reflect the most important features of the exact one. It was therefore proposed to use the functionals (31) built with rather poor SCF functions for the purpose of optimization of a given geminal basis set [18].

The optimization of non-linear parameters entering the geminals is obviously the most time-consuming process and its timing heavily depends on the size of the set of one-electron functions used for the calculation of the SCF orbitals. The method based on the functionals (31) was shown to provide quite reliable optimized GG bases in atomic and molecular calculations [10, 18]. According to the proposed procedure [18] the optimization of the GG bases represents the first step in the calculation of $e_{ij}^{\text{HF}}(M)$.

3.2. The SCF wave functions for the GG basis set optimization for LiH, BH and FH

As already pointed out the SCF reference orbitals used to construct the functionals (31) should satisfy the following conditions: (i) they should lead to one-particle density matrices relatively close to those corresponding to the near-HF functions, (ii) the number of one-electron basis functions used for their representation should be kept as small as possible. It is therefore convenient to use such one-electron bases which involve several easy to optimize non-linear parameters. Moreover, since the correlation effects will be accounted for by the Gaussian-type geminals, it is also convenient to use the Gaussian-type functions in the one-electron basis sets. All the above conditions are perhaps at best satisfied by the so-called floating spherical Gaussian orbitals (FSGO) [26] of the form

$$\chi_i = \exp(-\mu_i|r - R_i|^2), \quad (34)$$

with both the orbital exponent μ_i and the origin position R_i optimized with respect to the total energy of a given system. For a general molecular system each FSGO introduces 4 independent variational parameters. Therefore, the expansion

$$u_k = \sum_{i=1}^N c_{ki}\chi_i \quad (35)$$

is expected to give rather reliable molecular orbitals for a small number of optimized FSGO's. It is also worth attention that using the FSGO's results in much simpler many-electron integrals than in the case of the so-called cartesian Gaussians [27]. However, some difficulties occur when one tries to represent the atomic p -type functions using solely the FSGO's. As shown by Whitten [28], in order to generate the orbital of e.g. p_x symmetry, it is enough to take the following combination

$$(1 - P_x) \exp(-\mu_i |r - R_i|^2), \quad (36)$$

where P_x changes the sign of the x -component in the origin position vector R_i . However, for this orbital to have the properties of the p_x function the distance between X_i and $-X_i$ should be infinitesimally small [28]. This condition may affect the numerical stability of the SCF energy optimization with respect to the origin positions of the FSGO's contributing to π -type orbitals.

The initial step in the present study was to determine suitable optimized FSGO bases for the representation of the SCF functions used during the GG optimization with the functionals (31). For the LiH molecule the optimized FSGO set containing 5 functions was found to give the SCF energy $E^{\text{SCF}} = -7.852243$ a.u.¹ In the case of the BH molecule two bases containing 5 and 6 FSGO's were selected for the SCF energy optimization. The corresponding completely optimized FSGO's led to the energy values of -24.281764 a.u. and -24.822968 a.u., respectively. Since a rather small enlargement of the basis set size provides a considerable gain in the SCF energy, only the 6 FSGO set was utilized in the GG optimization process.

For the FH molecule different optimized FSGO bases were used for the optimization of $\sigma\sigma$ -type geminals and for those representing the correlation effects in $\sigma\pi$ - and $\pi\pi$ -type pairs. In the first case the optimized FSGO set comprising altogether 9 FSGO's (5 of σ -type symmetry and 4 leading to π -type molecular orbitals) was used and led to $E^{\text{SCF}} = -95.008089$ a.u. A poorer representation of σ -type molecular orbitals was allowed in the case of the GG optimization for σ - and π -pairs. For these pairs a separately optimized 7 FSGO basis set was employed (3 FSGO's of σ -type symmetry and 4 FSGO's contributing to π -type molecular orbitals) with the SCF energy $E^{\text{SCF}} = -84.656850$ a.u. All the FSGO bases employed at the SCF level of our calculations for both the GG optimization step and for the final calculation of the second-order pair energies are given a more detailed description in the Appendix.

As can be seen from the reported E^{SCF} values the FSGO bases utilized for the determination of optimized GG's according to the method described in Section 3.1, are energetically quite far from the estimated HF limits (-7.9873 a.u. for LiH, -25.1314 a.u. for BH, and -100.0703 a.u. for FH [29]). Thus, one may wonder if they are suitable even for such purposes as the GG basis set optimization. It follows from our previous calculations [10, 18] that the optimization process can be successfully accomplished using the SCF functions of low energetic quality, provided the appropriate formulation of the variation scheme [18].

¹ All molecular energies reported in this paper represent the sum of the total electronic energy, as given by Eqs. (3) and (28), and the nuclear repulsion contribution calculated for the pertinent experimental equilibrium distances ($R_{\text{LiH}} = 3.015$ a.u., $R_{\text{BH}} = 2.336$ a.u., $R_{\text{FH}} = 1.7238$ a.u.).

is employed. Moreover, the whole method anticipates a rather rough, inexpensive optimization of GG's followed by the variation calculation of the pair energies with much better SCF functions and already fixed GG basis set.

3.3. Optimization of the minimal GG basis sets for LiH, BH and FH

As discussed by Pan and King [6] the number of independent second-order pair energy functionals of the form (31) can be considerably reduced if the spin-symmetry of spin-geminals \bar{u}_{ij} is taken into account. Let us denote by $\Theta_{S,M}$ a normalized spin function for two electrons. Then for a pair of spinorbitals \bar{u}_i, \bar{u}_j given by

$$\bar{u}_i = u_i\alpha \quad \text{and} \quad \bar{u}_j = u_j\alpha, \quad (37)$$

where α denotes the one-electron spin function, the spin-geminal \bar{u}_{ij} can be written as

$$\bar{u}_{ij} = {}^3u_{ij}\Theta_{1,1} \quad (38)$$

leading to the triplet-type spinless geminal ${}^3u_{ij}$ and the corresponding second-order pair energy functional. In a similar way one obtains

$$\bar{u}_{ij} = {}^1u_{ij}\Theta_{0,0} \quad (39)$$

for

$$\bar{u}_i = u_i\alpha \quad \text{and} \quad \bar{u}_j = u_j\beta \quad (40)$$

and

$$\bar{u}_{ij} = \frac{1}{\sqrt{2}}({}^1u_{ij}\Theta_{0,0} + {}^3u_{ij}\Theta_{1,0}) \quad (41)$$

if both the space and the spin part of a given pair of spinorbitals is different. The space part of spin-geminals will be therefore either symmetric with respect to the permutation operator P_{12} (singlet-type spinless geminals) or antisymmetric (triplet-type spinless geminals). It means that the basis set $\{g_k\}$ has to be appropriately projected before it is used for the expansion of spinless geminals ${}^1u_{ij}$ and ${}^3u_{ij}$.

A further reduction of the number of different spinless geminals can be achieved due to a possible space symmetry of two-electron functions. This in turn is determined by the space symmetry of the product of spinless one-electron functions entering the r.h.s. of the corresponding pair equation. If the fundamental set of Gaussian geminals is assumed to have the form

$$w_k(1, 2) = \exp(-a_{1k}r_{1A_k}^2 - a_{2k}r_{2B_k}^2 - a_{3k}r_{12}^2), \quad (42)$$

where

$$r_{1A_k}^2 = |\mathbf{r}_1 - \mathbf{A}_k|^2, \quad r_{2B_k}^2 = |\mathbf{r}_2 - \mathbf{B}_k|^2 \quad (43)$$

the spin and space symmetry adapted functions g_k can be generated by using the appropriate projectors O , i.e.,

$$g_k(1, 2) = O w_k(1, 2). \quad (44)$$

When constructing the projection operator O for a given pair it is convenient to interpret (42) as the product of the pertinent orbital functions and the Gaussian correlation factor

$$w_k(1, 2) = f_{1k}(1)f_{2k}(2) \exp(-a_{3k}r_{12}^2). \quad (45)$$

It follows, therefore, that for (45) to contribute to the correlation correction for a pair $u_i(1)u_j(2)$, the product of orbital factors in (45) must have the symmetry properties as $u_i(1)u_j(2)$. The analysis of the partial wave contributions to the first-order pair functions for the sp and pp pairs in Ne [30, 31] leads to the conclusion that one can safely assume that the orbital factors in (44) are of the same symmetry as the initial SCF orbitals. Accord-

TABLE I

Projection operators O used to generate the permutation and space symmetry adapted strongly orthogonal geminals according to Eq. (44) and constraints imposed on the GG non-linear parameters

Orbital pair	Projection operator ^a O	Constrained parameters ^b
$^1(\sigma\sigma)$	$Q(1+P_{12})$	} $A_x = A_y = B_x = B_y = 0$
$^1(\sigma\sigma')$	$Q(1+P_{12})$	
$^3(\sigma\sigma')$	$Q(1-P_{12})$	
$^1(\sigma\pi)^c$	$Q(1+P_{12})(1-P_{xB})$	} $A_x = A_y = B_y = 0$
$^3(\sigma\pi)^c$	$Q(1-P_{12})(1-P_{xB})$	
$^1(\pi\pi)^d$	$Q(1+P_{12})(1-P_{xA})(1-P_{xB})$	$A_y = B_y = 0$
$^1(\pi\pi')$	$Q(1+P_{12})(1-P_{xA})(1-P_{yB})$	} $A_y = B_x = 0$
$^3(\pi\pi')$	$Q(1-P_{12})(1-P_{xA})(1-P_{yB})$	

^a Q denotes the strong orthogonality projector for a given SCF reference function, P_{12} permutes electrons 1 and 2, $P_{\mu C}$ changes the sign of the μ -th component of the vector C .

^b For definitions of symbols see Eqs. (42) and (43). The subscript k in these equations was dropped as immaterial for a single GG.

^c The Q operator and constraints defined for π_x orbital. The appropriate entries for $\sigma\pi_y$ pairs follow from symmetry considerations.

^d Defined for $\pi_x\pi_x$ pair. For $\pi_y\pi_y$ pair x should be replaced everywhere by y and vice versa.

^e For $\pi\pi'$ pairs only the correlation exponent a_3 was optimized. See Text for details.

ing to this argument the appropriate projection operators for $\sigma\sigma$, $\sigma\pi$, $\pi\pi$, and $\pi\pi'$ pairs were constructed and they are listed in Table I.

Each function of the form (42) in a general case will introduce as many as 9 variable parameters, i.e., two orbital-like exponents a_{1k} and a_{2k} , the correlation exponent a_{3k} , and the components of $A_k = (A_{xk}, A_{yk}, A_{zk})$ and $B_k = (B_{xk}, B_{yk}, B_{zk})$. The symmetry of linear molecules considered in this paper introduces some constraints as regards the components of A_k and B_k . The constrained parameters are listed in the last column of Table I. A comment on additional constraints imposed on the geminal parameters for the $^1(\pi\pi')$ and $^3(\pi\pi')$ pairs is necessary. In fact for these two pairs only the correlation

exponent was varied. The orbital factors were assumed to be represented by the same FSGO's as those leading to 1π and $1\pi'$ SCF orbitals of the FH molecule within the minimal FSGO basis set approximation (see Appendix). This additional assumption as regards the flexibility of the corresponding geminals was introduced for purely computational reasons. It can be justified by the fact that the product of pertinent SCF orbitals multiplied by a function explicitly dependent on r_{12} provides a reasonable approximation for the corresponding first-order pair function [13].

Since within the minimal GG basis set assumption each pair function is represented by a single GG we can actually drop the subscript k at g_k and w_k . Each GG will be therefore solely defined by the orbital pair whose second-order correlation energy is computed. The unconstrained parameters of each GG were optimized by minimizing the appropriate functionals for spinless pair functions. The minimization was performed using a modified Powell conjugate direction search technique due to Pan and King [6]. All the second-order energy functionals were set up using poor SCF functions described in Section 3.2 and the projected one-electron SCF operators of Eq. (22). Though the individual many-electron integrals contributing to the second-order energy functionals within the present approach are fairly simple [15] their number would make the GG basis set optimization impossible with the SCF functions expanded in larger atomic bases. Thus, at this step the primary goal was to obtain the minimal GG sets whose non-linear parameters reflect the main features of the electron density distribution in a given molecule. As indicated in our previous papers [10, 18] the GG parameters determined in this way are rather close to the parameters obtained with the SCF functions of much higher accuracy.

Among the computational aspects of the present calculations one should notice that computing the value of the second-order pair energy functional involves a variety of one-, two-, three-, and four-electron integrals. All of them can be reduced to a set of fundamental integrals by using the properties of Gaussian functions [15]. A convenient graphical scheme for the appropriate reductions has recently been proposed [32] and was extensively employed in the present paper.

When optimizing the non-linear GG parameters one faces all the problems characteristic for the non-linear optimization theories. As usually, also in the present case there is no way to prove that the final GG parameters correspond to the absolute minima of the second-order pair energy functionals. Since the functional value, though it refers to a rather poor SCF wave function, should be relatively close to the corresponding second-order pair energy, the false minima can be easily recognized. Also the choice of the initial values of the optimized parameters can be guided to some extent by the physical interpretation of the correlation effects introduced by a single GG for a given pair. The orbital factors in $w(1, 2)$ should resemble the shape of the SCF orbitals comprising a given pair and this allows for some preselection of a_1 , a_2 and the components of A and B . The initial value of the parameter a_3 can be guessed by discussing its rôle in the creation of the Coulomb hole for a given pair. This parameter will be large for singlet-type pairs since it must account for the interelectronic Coulomb repulsion at short distances. On the other hand, for triplet-type pairs the short range repulsion is already partly taken into account by the Pauli principle and a relatively small value of a_3 will account for the long range effects.

The optimized values of unconstrained GG parameters for LiH, BH and FH are shown in Table II, Table III, and Table IV, respectively. In all cases the z -axis of the coordinate system was assumed to coincide with the molecule axis and the results refer to the experimental equilibrium bond distances. As shown by the data of these Tables, the optimized parameters closely follow the general rules described above. However, these rules anticipated that the SCF orbitals are fairly well localized. This assumption is usually satisfied for diatomic hydrides studied in this paper, though the canonical SCF orbitals are used.

TABLE II

Minimal GG basis set for the LiH molecule ($R_{\text{LiH}} = 3.015$ a.u.) optimized with the 5 FSGO SCF reference function. All entries in a.u.

Orbital pair	Optimized GG non-linear parameters ^a					$e_{ij}^{\text{SCF}}(5, 1)^b$
	a_1	a_2	a_3	A_z	B_z	
$^1(1\sigma 1\sigma)$	3.55208	1.76234	3.15663	-0.00633	0.00840	-0.02706
$^1(1\sigma 2\sigma)$	6.42548	3.45426	2.40611	-0.00964	-0.01887	-0.00066
$^3(1\sigma 2\sigma)$	1.10743	0.09553	0.45956	0.03711	3.01203	-0.00025
$^1(2\sigma 2\sigma)$	0.15485	0.31485	0.29614	2.70740	2.88076	-1.02178
					Total ^c	-0.05025

^a The molecule lies on the z axis with the heavy atom at the origin. Parameters defined according to Eqs. (42) and (43) and Table I.

^b The calculated minimum value of the functional (31). See also Eq. (32).

^c The total second-order energy calculated according to Eqs. (46)-(48) using the $e_{ij}^{\text{SCF}}(5, 1)$ values.

TABLE III

Minimal GG basis set for the BH molecule ($R_{\text{BH}} = 2.336$ a.u.) optimized with the 6 FSGO SCF reference function. All entries in a.u.

Orbital pair	Optimized GG non-linear parameters ^a					$e_{ij}^{\text{SCF}}(6, 1)^b$
	a_1	a_2	a_3	A_z	B_z	
$^1(1\sigma 1\sigma)$	10.05464	4.71934	9.70687	0.00075	0.00009	-0.02847
$^1(1\sigma 2\sigma)$	10.99560	19.34778	7.69913	-0.00163	-0.00266	-0.00116
$^3(1\sigma 2\sigma)$	3.63329	0.03721	1.36506	0.00997	3.45940	-0.00040
$^1(1\sigma 3\sigma)$	18.95253	11.24894	7.79798	0.02664	-0.00878	-0.00045
$^3(1\sigma 3\sigma)$	3.63436	0.30517	1.34854	-0.01109	-1.34189	-0.00023
$^1(2\sigma 2\sigma)$	0.30446	0.11117	0.40709	1.15489	0.70767	-0.01960
$^1(2\sigma 3\sigma)$	0.62251	0.21234	0.53066	2.11942	2.07252	-0.00966
$^3(2\sigma 3\sigma)$	0.15483	0.24199	0.25400	-1.44955	2.11775	-0.00212
$^1(3\sigma 3\sigma)$	0.27240	0.11531	0.24791	-0.63789	-1.18789	-0.01833
					Total ^c	-0.08592
$^1(1\sigma 3\sigma)^d$	1.96974	0.43584	0.11055	-0.08473	1.40067	-0.00003
$^3(1\sigma 3\sigma)^d$	3.58312	0.43862	0.30000	0.19318	3.15353	-0.00002
$^1(3\sigma 3\sigma)^d$	0.70580	0.34147	0.25375	2.16246	2.43882	-0.00472

^a, ^b, ^c See Footnotes to Table II.

^d Local minimum. See Text.

TABLE IV

Minimal GG basis set for the FH molecule ($R_{FH} = 1.728$ a.u.) optimized with the 9 FSGO SCF reference function for $\sigma\sigma$, $\sigma\pi$ and $\pi\pi$ pairs and with the 7 FSGO SCF reference function for $\pi\pi'$ pairs. All entries in a.u.

Orbital pair	Optimized GG non-linear parameters							$e_{ij}^{SCF}(N, 1)^b$
	a_1	a_2	a_3	A_z	B_z	A_x	B_x	
$\sigma\sigma$ pairs ^a								
$^1(1\sigma1\sigma)$	18.82442	26.64445	30.63007	-0.00007	0.00012			-0.02961
$^1(1\sigma2\sigma)$	34.35274	73.43227	29.11560	-0.00280	0.00067			-0.00234
$^3(1\sigma2\sigma)$	12.64800	0.01294	6.27679	0.00454	-0.00753			-0.00051
$^1(1\sigma3\sigma)$	11.74582	5.45864	12.24369	0.06403	0.57518			-0.00017
$^3(1\sigma3\sigma)$	16.83572	2.05161	4.81014	-0.01209	-0.87625			-0.00012
$^1(2\sigma2\sigma)$	0.98280	0.50945	1.78649	0.24907	-0.26280			-0.01088
$^1(2\sigma3\sigma)$	0.42219	1.26245	1.53638	0.62690	1.12813			-0.00580
$^3(2\sigma3\sigma)$	0.77819	0.84054	0.88214	-0.47999	0.83570			-0.00138
$^1(3\sigma3\sigma)$	0.76140	0.42362	0.59640	1.02048	1.04291			-0.01624
								-0.07106
								Total $\sigma\sigma^c$
$\sigma\pi$ pairs ^d								
$^1(1\sigma1\pi)$	13.89737	1.31368	5.43210	0.00139	0.15489		B_z	-0.00051
$^3(1\sigma1\pi)$	19.37036	0.21368	5.19608	-0.00134	0.21089		0.04732	-0.00035
$^1(2\sigma1\pi)$	0.61708	1.15672	1.75158	0.06664	-0.00070		0.05270	-0.01472
$^3(2\sigma1\pi)$	0.72571	1.00839	0.77059	0.12333	0.18695		0.02997	-0.00165
$^1(3\sigma1\pi)$	1.04310	0.97568	0.76939	-0.64281	0.46577		-0.12425	-0.00600
$^3(3\sigma1\pi)$	0.72130	0.99129	0.46718	-0.80260	0.44384		0.20639	-0.00410
								-0.07906
								Total $\sigma\pi^c$
$\pi\pi$ pairs ^e								
$^1(1\pi1\pi)$	0.95031	0.86469	1.06065	A_x	A_z		B_x B_z	-0.02906
				0.21946	0.01842		0.35262 0.02370	-0.04192
								Total $\pi\pi^c$

$\pi\pi'$ pairs ^f	a_3								
$^1(1\pi1\pi')$	1.25500								-0.01262
$^3(1\pi1\pi')$	0.48754								-0.00703
									-0.03371
									-0.22576
								Total $\pi\pi'$ ^e	
								Total ^e	

^a See Footnote a to Table II.

^b See Footnote b to Table II. For $\sigma\sigma$, $\sigma\pi$ and $\pi\pi$ pairs $N = 9$, for $\pi\pi'$ pairs $N = 7$.

^c See Footnote c to Table II. The total second-order energy was subdivided into contributions due to different types of pairs.

^d The parameters in the Table correspond to $\sigma\pi_x$ pairs. Those for $\sigma\pi_y$ pairs can be obtained replacing B_x by B_y . See also Table I for the parameter constraints.

^e The parameters in the Table correspond to $\pi_x\pi_x$ pair. Those for $\pi_y\pi_y$ pair can be generated by the following replacement $A_x \rightarrow A_y$, $B_x \rightarrow B_y$. See also Table I.

^f Only the correlation exponent was optimized. The remaining GG parameters are the same as for 1π and $1\pi'$ orbitals determined for the 7 FSGO basis set. See Appendix.

The only substantial exception is provided by 3σ orbital of BH. In this case the canonical SCF orbital is mainly localized in two distinct parts of the molecule — one representing the lone pair and the other contributing to the B-H σ bond. This delocalization of 3σ SCF orbital has led to two distinct local minima of the second-order pair energy functionals for pairs involving 3σ orbital. The GG's for these pairs shown in Table III always correspond to a deeper minimum and mostly represent the correlation effects involving the lone pair region.

The relation between the localized character of the correlation effects accounted for by a single GG and the form of the SCF orbitals leads to the conclusion that for larger molecules one should use the localized orbitals rather than the canonical ones. Since the degree of delocalization of 3σ SCF orbital in BH is not too high using the GG's which mainly correlate the lone pair region does not seriously affect the computed second-order pair energies. The other minimum of the second-order pair energy functional with the GG correlating the B-H bond region is much higher than that for the GG contributing to the lone pair correlation effects, e.g., -0.00472 a.u. and -0.01833 a.u. for $(3\sigma)^2$ pair.

In Tables II–IV also the calculated minimum values of the corresponding second-order pair energy functionals are shown. They can be interpreted as the second-order pair energies computed with reference to poor SCF wave functions, i.e., $e_{ij}^{\text{SCF}}(N, 1)$ of Eq. (32) with relatively small values of N . In spite of the crudeness of the SCF reference functions used for the optimization of the GG's, the second order energies $e_{ij}^{\text{SCF}}(N, 1)$ are quite reasonable, though they may considerably differ from $e_{ij}^{\text{HF}}(1)$ of Eq. (17).

Once the optimization of the minimal GG bases is completed one can proceed to the final step of the computational procedure proposed in Ref. [18], i.e., the calculation of the second-order pair energies with fixed non-linear parameters of the GG basis set but employing more accurate, near-HF one-electron SCF functions.

4. Second-order pair energies of LiH, BH and FH. Results and discussion

4.1. The SCF wave functions

The SCF orbitals employed for the calculation of the final values of the second-order pair energies differ from those described in Section 3.2 only by the dimension N of the corresponding FSGO basis set. The optimized FSGO parameters are shown in the Appendix.

For the LiH molecule the 13 FSGO set of Karunakaran and Christoffersen [33] was further optimized leading finally to the total molecular SCF energy of -7.9853 a.u. which is fairly close to the best SCF result (-7.9873 a.u. [29]). Only a slightly worse set composed of 15 FSGO's was used for the BH molecule. A complete optimization of all parameters lead to the total molecular SCF energy of -25.1132 a.u., again quite close to the accurate SCF value of -25.1314 a.u. [29]. However, in the case of the FH molecule reaching the same level of accuracy of the SCF energy was found impossible with the FSGO bases of a reasonable size. Because of the computer time limitations the final values of the second-order pair energies for FH were computed using much

shorter than necessary FSGO expansions of the SCF orbitals. The optimized basis set was composed of 22 FSGO's (14 FSGO's for σ orbitals and 8 FSGO's for π orbitals). The calculated total molecular SCF energy (-99.3538 a.u.) was in this case considerably higher than the accurate value (-100.0703 a.u. [29]). This rather large energy difference is mainly due to relatively poor representation of the 1σ orbital of FH in the region close to the fluorine nucleus. However, this deficiency appears to be of lesser importance for the calculated pair energies. Because of a full optimization of all FSGO's the higher occupied orbitals seem to be given a much better representation. As can be seen from the data presented in the Appendix the FSGO's with relatively low exponents predominate in the 22 FSGO set.

4.2. Second-order pair energies. A comparison with the MBPT results

Using the minimal GG basis sets determined in Section 3.3 the final values of the second-order pair energies have been computed. At this step the SCF functions were assumed to be sufficiently close to the HF ones and the non-projected functional (12) or its counterparts for spinless pair functions were employed. The assumption that the SCF wave functions described in Section 4.1 are sufficiently close to the HF ones seems to be fairly well justified in the case of LiH and BH. For these two molecules one can rather safely use Eq. (33) as an equivalent of the exact Eq. (20). However, for the FH molecule replacing Eq. (20) by Eq. (33) is obviously questionable and to obtain the SCF wave function of the appropriate accuracy would require much larger than 22 FSGO basis set. Thus, in comparison with LiH and BH our results for the second-order pair energies of FH are definitely of poorer accuracy. In spite of this they seem to provide an interesting material concerning the efficiency of the GG bases for the description of the correlation effects in $\pi\sigma$, $\pi\pi$, and $\pi\pi'$ pairs.

Since the non-linear parameters of the GG's for each pair are already fixed by the calculations of Section 3.3 the minimization of the appropriate second-order energy functionals leading to the final values for the second-order pair energies is performed with respect to a single linear parameter $A_{ij,k} = A_{ij}$ (cf. Eq. (16)). Though formally trivial this final step appears to be quite time-consuming since one needs a number of many-electron integrals. The number of these integrals increases like N^4 with the FSGO basis set dimension N . The N^4 -dependence clearly shows why one should avoid the GG basis set optimization with reference to rather accurate SCF functions.

The computed second-order pair energies for singlet $^1(ii)$, $^1(ij)$ and triplet $^3(ij)$ pairs, where i and j denote molecular orbitals, are shown in Tables V-VII. In the case of $i \neq j$ the total second-order pair energy is given by

$$e_{ij} = e_{1(ij)} + 3e_{3(ij)}, \quad (46)$$

while for $i = j$

$$e_{ii} = e_{1(ii)}. \quad (47)$$

These total second-order pair energies e_{ii} , e_{ij} sum up to the total second-order energy E^2 ,

$$E^2 = \sum_i \sum_{j \leq i} e_{ij}, \quad (48)$$

TABLE V

Second-order perturbation calculations for the LiH molecule ($R_{\text{LiH}} = 3.015$ a.u.). All energies in a.u.

Orbital pair (<i>ij</i>)	Second-order pair energies				First-order pair function ^a	
	This work ^a	Reference MBPT results ^b			A_{ij} ^c	$\langle u_{ij} u_{ij}\rangle$
		I	II	III		
¹ (1σ1σ)	-0.02674	-0.01893	-0.03338	-0.03563	-0.174392	0.001578
¹ (1σ2σ)	-0.00054	-0.00064	-0.00085	-0.00118	-0.053166	0.000025
³ (1σ2σ)	-0.00025	-0.00018	-0.00021	-0.00038	0.006969	0.000032
¹ (2σ2σ)	-0.02093	-0.01508	-0.02403	-0.02745	-0.012009	0.008057
Total ^d	-0.04896	-0.03518	-0.05888	-0.06539		

^a Calculated using the minimal GG basis set of Table II and the 13 FSGO SCF reference function.

^b MBPT results of Bartlett and Silver [9] obtained with 15 STO (I), 25 STO (II) and 46 STO (III) basis set.

^c A_{ij} is the linear variation parameter of Eq. (16) for a single GG representation of the spinless pair function u_{ij} .

^d Calculated according to Eqs. (46)–(48).

TABLE VI

Second-order perturbation calculations for the BH molecule ($R_{\text{BH}} = 2.336$ a.u.). All energies in a.u.

Orbital pair (<i>ij</i>)	Second-order pair energies				First-order pair function ^a	
	This work ^a	Reference MBPT results ^b			A_{ij} ^c	$\langle u_{ij} u_{ij}\rangle$
		I	II	III		
¹ (1σ1σ)	-0.02809	-0.01778	-0.03201	-0.03327	-0.507581	0.000438
¹ (1σ2σ)	-0.00103	-0.00096	-0.00167	-0.00185	0.231906	0.000016
³ (1σ2σ)	-0.00035	-0.00016	-0.00039	-0.00047	-0.019393	0.000017
¹ (1σ3σ)	-0.00060	-0.00072	-0.00134	-0.00172	-0.176200	0.000009
³ (1σ3σ)	-0.00035	-0.00032	-0.00052	-0.00068	0.023363	0.000017
¹ (2σ2σ)	-0.02000	-0.00951	-0.01810	-0.02328	-0.011528	0.006974
¹ (2σ3σ)	-0.00707	-0.00599	-0.01285	-0.01586	-0.012872	0.001780
³ (2σ3σ)	-0.00169	-0.00111	-0.00153	-0.00240	-0.014062	0.000637
¹ (3σ3σ)	-0.01881	-0.01003	-0.01648	-0.02437	-0.011575	0.009941
Total ^d	-0.08277	-0.04978	-0.08978	-0.11103		

^a Calculated using the minimal GG basis set of Table III and the 15 FSGO SCF reference function.

^b MBPT results of Bartlett and Silver [9] obtained with 15 STO (I), 22 STO (II) and 46 STO (III) basis set.

^{c, d} See the corresponding Footnotes to Table V.

where the summation extends over all different pairs of molecular orbitals of a given molecule.

Recently the same series of molecules, i.e., LiH, BH and FH, was extensively studied within the many-body perturbation theory (MBPT) approach by Bartlett and Silver [9]

TABLE VII

Second-order perturbation calculations for the FH molecule ($R_{\text{FH}} = 1.728$ a.u.). All energies in a.u.

Orbital pair (<i>ij</i>)	Second-order pair energies				First-order pair function	
	This work ^a	Reference MBPT results ^b			A_{ij} ^c	$\langle u_{ij} u_{ij}\rangle$ ^a
		I	II	III		
$^1(1\sigma1\sigma)$	-0.02854	-0.00190	-0.02911	-0.02938	-1.614282	0.000142
$^1(1\sigma2\sigma)$	-0.00212	-0.00052	-0.00246	-0.00260	1.185540	0.000010
$^3(1\sigma2\sigma)$	-0.00042	-0.00002	-0.00038	-0.00040	-0.060028	0.000005
$^1(1\sigma3\sigma)$	-0.00039	-0.00021	-0.00049	-0.00098	-0.131786	0.000005
$^3(1\sigma3\sigma)$	-0.00029	-0.00021	-0.00065	-0.00088	0.245752	0.000004
$^1(2\sigma2\sigma)$	-0.01040	-0.00706	-0.00753	-0.00999	-0.044582	0.000850
$^1(2\sigma3\sigma)$	-0.00578	-0.00947	-0.01212	-0.01376	-0.026420	0.000538
$^3(2\sigma3\sigma)$	-0.00132	-0.00225	-0.00246	-0.00262	-0.051087	0.000140
$^1(3\sigma3\sigma)$	-0.01010	-0.02093	-0.02312	-0.02512	-0.029522	0.001682
Total $\sigma\sigma$ ^d	-0.06342	-0.04753	-0.08530	-0.09353		
$^1(1\sigma1\pi)$	-0.00087	-0.00009	-0.00015	-0.00108	0.476503	0.000013
$^3(1\sigma1\pi)$	-0.00059	-0.00023	-0.00067	-0.00112	1.614978	0.000008
$^1(2\sigma1\pi)$	-0.01377	-0.00866	-0.00898	-0.01239	-39.730760	0.001057
$^3(2\sigma1\pi)$	-0.00143	-0.00210	-0.00224	-0.00265	0.109661	0.000143
$^1(3\sigma1\pi)$	-0.00351	-0.00830	-0.00862	-0.01296	-0.062193	0.000383
$^3(3\sigma1\pi)$	-0.00216	-0.00676	-0.00682	-0.00884	-0.056450	0.000282
Total $\sigma\pi$ ^d	-0.06138	-0.08864	-0.09388	-0.12852		
$^1(1\pi1\pi)$	-0.01402	-0.01296	-0.01343	-0.02146	-0.184345	0.001441
$^1(1\pi1\pi')$	-0.00797	-0.00907	-0.00922	-0.01383	-7.200286	0.000730
$^3(1\pi1\pi')$	-0.00422	-0.00517	-0.00524	-0.00893	-5.073330	0.000512
Total $\pi\pi$ ^d	-0.04867	-0.05050	-0.05180	-0.08356		
Total ^{d, e}	-0.17347	-0.18667	-0.23098	-0.30561		

^a Calculated using the minimal GG basis set of Table IV and the 22 FSGO SCF reference function.

^b MBPT results of Bartlett and Silver [9] obtained with 19 STO (I), 29 STO (II) and 46 STO (III) basis set.

^{c, d} See the corresponding Footnotes to Table V. The total $\pi\pi$ contribution comprises both the $\pi\pi$ and $\pi\pi'$ pairs.

^e The total second-order correlation energies obtained via the direct summation of the pertinent pair energies. The MBPT values differ insignificantly from those reported by Bartlett and Silver, possibly due to round off errors.

and Wilson and Silver [34]. The second-order pair correlation energies reported in these papers have been computed using for each molecule three different SCF wave functions expanded in terms of the Slater-type orbitals (STO). The MBPT second-order pair energies calculated without the denominator shift are exactly the same quantities as those considered in the present paper. Both they contribute to the lowest-order correlation energy diagram representing E_{HF}^2 . The MBPT data of Silver et al. offer a convenient set of reference

values for the present results. However, when comparing the results of Silver et al. with the present ones, one should mention some significant differences between the finite basis set MBPT approach and the variation technique employed in this paper.

In the MBPT approach the first-order perturbed wave function is represented solely in terms of Slater determinants, which are doubly substituted with respect to the zeroth-order HF (or SCF) determinant. Thus the flexibility of the first-order function is severely limited by the number of available virtual orbitals and one has to use much larger bases than those required for near-HF accuracy of the zeroth-order energy. In the present approach one should obviously account for sufficiently accurate representation of the zeroth-order SCF wave function. However, the virtual orbitals resulting as a by-product of the SCF calculations are of no importance for the computed second-order pair energies. The use of the GG bases with explicit r_{12} -dependence is expected to be far more efficient than the expansion of the first-order pair functions in terms of products of available virtual orbitals.

In Table V the second-order pair energies calculated using the minimal GG set are compared with the results of Bartlett and Silver [9] obtained for 15, 25, and 46 STO basis sets. It is worth attention that from the point of view of the total molecular SCF energy of the LiH molecule even the smallest STO basis set used by these authors is better than our optimized 13 FSGO set. On the other hand the second-order correlation energy computed using the minimal GG basis set is considerably lower than the MBPT result for 15 STO basis set and represents almost 75 per cent of the best value of Bartlett and Silver.

A similar conclusion can be drawn from a comparison of the second-order energy data for the BH molecule given in Table VI. The present value of E^2 is almost two times lower than that computed by Bartlett and Silver using 15 STO basis set. At the same time their SCF energy $E^{\text{SCF}} = -25.1313$ a.u. [9] provides near-HF accuracy. It is also interesting to notice that once again the minimal GG basis set represents ca. 75 per cent of the best E^2 value obtained with 46 STO set [9].

For quite obvious reasons one can hardly expect the same level of accuracy for the second-order correlation energy calculated for the FH molecule. First of all, the SCF functions used for the calculation of the final values of the second-order pair energies are much poorer than those employed in the case of LiH and BH. Secondly, as already, indicated in Section 3.3, the GG's for $^1(1\pi1\pi')$ and $^3(1\pi1\pi')$ pairs have not been fully optimized, since in this case only the correlation exponent a_3 was varied. Moreover, the optimization of the GG non-linear parameters was carried out with very crude SCF reference functions. In spite of these additional approximations, the results shown in Table VII are still of reasonable accuracy.

In comparison with the calculations by Bartlett and Silver [9] our E^2 value for the FH molecule is only slightly worse than their 19 STO MBPT result. On the other hand the total molecular SCF energy corresponding to 19 STO basis set, $E^{\text{SCF}} = -99.9911$ a.u., is definitely much lower than our value for the 22 FSGO set. The inaccuracy of the present SCF orbitals of the FH molecule appears to be mostly responsible for relatively higher E^2 value, which accounts only for ca. 57 per cent of the second-order correlation energy obtained by Bartlett and Silver with 46 STO basis functions [9].

If the total second-order correlation energy is split into $\sigma\sigma$, $\sigma\pi$, and $\pi\pi$ contributions, then according to the data of Table VII, the minimal GG basis set leads to $E^2(\sigma\sigma) = -0.06342$ a.u., $E^2(\sigma\pi) = -0.06138$ a.u., and $E^2(\pi\pi) = -0.04867$ a.u. The second-order correlation energy contributions following from the 46 STO MBPT calculations by Bartlett and Silver amount to -0.09353 a.u., -0.12852 a.u., and -0.08356 a.u., respectively. Thus, one can conclude that the minimal GG basis set calculations for $\sigma\sigma$ -type pairs in FH are of a similar quality as for LiH and BH.

Finally, one should compare the minimal GG basis set results with the total correlation energies. The estimated total correlation energy E_{corr} for LiH, BH and FH amounts to -0.083 a.u., -0.155 a.u., and -0.381 a.u., respectively [35]. Thus, the second-order minimal GG basis set calculations are able to recover almost 60 per cent of E_{corr} for LiH and BH. Even in the case of the FH molecule the present second-order result is not much worse.

The second-order energy data of Tables V–VII are supplemented by the calculated values of the norm of the computed first-order pair functions $\langle u_{ij}|u_{ij}\rangle$, which can be used for the estimation of the unlinked cluster contributions to the third-order correlation energy [10].

5. Summary and conclusions

The method proposed for the optimization of the GG bases [18] in variation-perturbation calculations of molecular correlation energy was utilized for the determination of the second-order correlation energy in LiH, BH and FH. The concept of the minimal GG basis set similar to the idea of the minimal atomic orbital bases in the one-electron approximation, was introduced. It was shown that the minimal GG set, if properly optimized, can account for a substantial portion of the second-order correlation energy. If the molecular SCF orbitals are represented in terms of FSGO's, the many-electron integrals encountered during the determination of the first-order perturbed pair functions can be computed utilizing rather standard methods [15, 32, 36].

Obviously, as already indicated by the other authors [6] and also in our recent papers [10, 18, 37] the calculation of very accurate second-order molecular pair energies would require larger than minimal GG bases. However, the minimal bases lead to compact and conceptually simple form of the first-order perturbed pair functions. The correlation effects within a given pair can be easily analysed in terms of the corresponding GG parameters. According to the discussion in Section 3.3, the range of the correlation effects in a given pair is in principle determined by the optimized value of the correlation exponent a_3 .

In spite of its crudeness the minimal GG basis set approximation recovers a considerable portion of the second-order correlation energy. It follows from the data of Section 4.3 that the degree of the second-order pair correlation effects accounted for by a single GG depends on the localization of the SCF orbitals. Thus, using the minimal GG bases should lead to even better results if the whole perturbation scheme is used within the localized molecular orbital picture. It is also worth attention that the present method does not

need, in contrast to the configuration interaction schemes, very large computers. Since each pair is treated separately the core requirements are substantially reduced. The manipulation with very large bases, necessary for an efficient configuration interaction calculation is replaced by a careful optimization of relatively small number of non-linear parameters entering a given GG. It is also important that a rather time-consuming optimization process can be performed with reference to much cruder SCF wave functions than those employed in the final calculation of the pair energies. In this context one should notice that the minimum values of the projected functional (31), as shown in Tables II–IV give also a reasonable approximation to the corresponding pair energies. Moreover, the total second-order energies computed from (31) are lower than the final E^2 values (Tables V–VII) and therefore closer to the accurate results. Unfortunately, there is no way to prove that this interesting regularity observed in our calculations is valid in a general case.

At least within the minimal GG basis set approximation the study of the correlation effects appears to be possible for quite sizable molecules. The calculated first-order pair functions, owing to their simple and compact form can be used for a number of other purposes, e.g., for the calculation of the correlation contribution to molecular properties [38]. Also the calculation of the third-order correlation corrections to the total energy [10] appears to be relatively easy.

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APPENDIX

The FSGO bases proved to be very convenient in molecular calculations. However, the efficiency of small sets of FSGO's crucially depends on the degree of optimization of all non-linear parameters. According to Eq. (34) each FSGO introduces in general four non-linear parameters — the orbital exponent μ_i and three components X_i , Y_i , and Z_i of the origin position vector R_i . This provides quite high flexibility of molecular orbitals (35).

A very extensive optimization of several small FSGO bases was necessary for the present study and the determined optimized basis sets seem to be convenient also for other molecular calculations. Moreover, the optimization of the FSGO non-linear parameters is a rather expensive process. For these reasons we felt it worthwhile to present the whole set of the FSGO bases utilized in this paper.

In all calculations the XH ($X = \text{Li, B, F}$) molecule is assumed to lie on the z axis of the coordinate system with the X atom at the origin. The optimization of the FSGO parameters was carried out for the corresponding experimental equilibrium $X-H$ distances R_{XH} . Because of symmetry the FSGO's contributing to σ -type molecular orbitals have $X_i = Y_i = 0$. The FSGO's contributing to π -type molecular orbitals in FH have been generated according to Eq. (36) and its counterpart for π_y orbitals. Except for the 13 FSGO basis set for the LiH molecule, the initial values for the pertinent non-linear parameters were taken from the atomic calculations of Duijneveldt [39]. In the case of the 13 FSGO

TABLE AI

Optimized FSGO bases for the LiH molecule ($R_{\text{LiH}} = 3.015$ a.u.). All entries in a.u.^a

<i>i</i>	5 FSGO basis set		13 FSGO basis set	
	μ_i	Z_i	μ_i	Z_i
1	16.42732	-0.00297	959.6846	-0.00003
2	3.63202	0.00290	140.3080	0.00010
3	0.94487	-0.01854	30.8390	-0.00058
4	0.68482	2.95350	27.9462	3.01466
5	0.10571	2.45125	8.6188	0.00077
6			4.0767	3.00295
7			2.8180	-0.00477
8			1.0291	-0.00881
9			0.8819	3.01526
10			0.4227	-0.22703
11			0.3920	0.36467
12			0.2163	2.69490
13			0.0627	2.38063
$E^{\text{SCF b}}$		-7.852243		-7.985269

^a See Text for the definition of symbols. The FSGO's are defined by Eq. (34).

^b Total molecular SCF energy including the nuclear repulsion contribution.

TABLE AII

Optimized FSGO bases for the BH molecule ($R_{\text{BH}} = 2.336$ a.u.). All entries in a.u.^a

<i>i</i>	5 FSGO basis set		6 FSGO basis set		15 FSGO basis set	
	μ_i	Z_i	μ_i	Z_i	μ_i	Z_i
1	31.3096	0.00002	110.3867	0.00004	3540.99	0.00001
2	4.4977	0.00140	16.2114	-0.00002	565.2579	-0.00007
3	2.6129	2.32008	3.4069	0.00259	130.0441	-0.00033
4	0.27147	1.55643	2.2823	2.31601	49.8653	2.33617
5	0.19890	-0.37884	0.2645	1.54502	36.9590	0.00235
6			0.2000	-0.40500	11.5149	-0.00389
7					7.4403	2.32193
8					3.9539	0.01636
9					1.7889	-0.12401
10					1.3347	2.30958
11					1.2625	0.24634
12					0.4039	-0.38935
13					0.3429	1.45868
14					0.1205	1.81307
15					0.1060	-0.39584
$E^{\text{SCF b}}$		-24.281764		-24.822968		-25.113196

^{a, b} See Footnotes to Table AI

TABLE AIII

Optimized FSGO parameters for the FH molecule ($R_{FH} = 1.728$ a.u.). All entries in a.u.

<i>i</i>	7 FSGO basis set			9 FSGO basis set			22 FSGO basis set		
	μ_i	$X_i(Y_i)$	Z_i	μ_i	$X_i(Y_i)$	Z_i	μ_i	$X_i(Y_i)$	Z_i
FSGO's contributing to σ -type molecular orbitals ^a									
1	22.3837	0.0	0.00044	117.5192	0.0	0.00039	7213.3129	0.0	-0.00001
2	0.7484	0.0	-0.19989	18.1960	0.0	-0.00375	1080.5591	0.0	-0.00006
3	0.7045	0.0	0.67592	4.0479	0.0	0.21857	246.6377	0.0	0.00019
4				0.8440	0.0	-0.24966	68.8467	0.0	0.00053
5				0.6382	0.0	0.84213	33.8650	0.0	1.73280
6							22.0206	0.0	0.00029
7							7.5286	0.0	-0.00339
8							5.2199	0.0	0.09696
9							2.5079	0.0	-0.11382
10							1.7321	0.0	1.67782
11							1.2489	0.0	0.18097
12							0.5431	0.0	-0.08551
13							0.5064	0.0	0.47882
14							0.2569	0.0	1.68233
FSGO's contributing to π -type molecular orbitals ^b									
1	0.9462	0.04829	0.01662	0.9883	0.04118	0.01784	3.1446	0.03004	0.00474
2							0.5567	0.03016	0.06216
$E^{\text{SCF c}}$	-84.656850			-95.008089			-99.354810		

^a For σ -type molecular orbitals the FSGO origin vectors are $R_i = (0, 0, Z_i)$. The FSGO's are defined by Eq. (34).

^b For π -type molecular orbitals each FSGO with the origin vector $R_i = (a_i, 0, Z_i)$ generates three other FSGO's with the origin positions defined by $(-a_i, 0, Z_i)$, $(0, a_i, Z_i)$, $(0, -a_i, Z_i)$ and the same orbital exponent μ_i .

^c Total molecular SCF energy including the nuclear repulsion contribution.

set for LiH the initial parameters due to Karunakaran and Christoffersen [33] were further optimized in this paper.

The parameters for 5 and 13 FSGO set for the LiH molecule are shown in Table AI. The 5 FSGO set was employed for the GG optimization while the other was used for the final calculation of the second-order pair energies. Three different FSGO bases were optimized for the BH molecule and are presented in Table AII. Since the addition of one FSGO leads to a considerable improvement of the total SCF molecular energy in comparison with the 5 FSGO set, the GG optimization was finally performed with the 6 FSGO expansion of the SCF molecular orbitals. The 15 FSGO set was utilized in the calculation of the final values of the second-order pair energies.

In the case of the FH molecule (Table AIII) the 9 FSGO set was used to represent the SCF orbitals for the optimization of GG's for $\sigma\sigma$ -, $\sigma\pi$ -, and $\pi\pi$ -pairs. The GG's for

$\pi\pi'$ -pairs have been optimized with the SCF orbitals expanded in terms of 7 FSGO's. The final second-order pair energies have been recalculated using the largest, 22 FSGO set. It should be pointed out that each FSGO contributing to π -type molecular orbitals in FH, though represented in Table AIII by a single entry, corresponds in fact to four FSGO's with the same exponent and the appropriate values of X_i and Y_i .

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