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Combining explicitly correlated R12 and Gaussian geminal electronic structure theories

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Explicitly correlated R12 methods using a single short-range correlation factor (also known as F12 methods) have dramatically smaller basis set errors compared to the standard wave function counterparts, even when used with small basis sets. Correlations on several length scales, however, may not be described efficiently with one correlation factor. Here the authors explore a more general MP2-R12 method in which each electron pair uses a set of (contracted) Gaussian-type geminals (GTGs) with fixed exponents, whose coefficients are optimized linearly. The following features distinguish the current method from related explicitly correlated approaches published in the literature: (1) only two-electron integrals are needed, (2) the only approximations are the resolution of the identity and the generalized Brillouin condition, (3) only linear parameters are optimized, and (4) an arbitrary number of (non-)contracted GTGs can appear. The present method using only three GTGs and a double-zeta quality basis computed valence correlation energies for a set of 20 small molecules only 2.2% removed from the basis set limit. The average basis set error reduces to 1.2% using a near-complete set of seven GTGs with the double-zeta basis set. The conventional MP2 energies computed with much larger quadruple, quintuple, and sextuple basis sets all had larger average errors: 4.6%, 2.4%, and 1.5%, respectively. The new method compares well to the published MP2-R12 method using a single Slater-type geminal (STG) correlation factor. For example, the average basis set error in the absolute MP2-R12 energy obtained with the $\exp(-r_{12})$ correlation factor is 1.7%. Correlation contribution to atomization energies evaluated with the present method and with the STG-based method only required a double-zeta basis set to exceed the precision of the conventional sextuple-zeta result. The new method is shown to always be numerically stable if linear dependencies are removed from the two-particle basis and the zeroth-order Hamiltonian matrix is made positive definite. © 2006 American Institute of Physics. [DOI: 10.1063/1.2403852]

I. INTRODUCTION

Standard wave functions based on Slater determinants cannot be affordably computed to a precision necessary for computational studies of thermochemistry, kinetics, or spectroscopy. For example, Bak *et al.* found that first-principles computation of atomization energies accurate to 1 kcal/mol require a basis set of sextuple-zeta quality.¹ Such extended basis sets are practical only for the smallest molecules. The large and slowly decaying basis set error of conventional wave functions is due to their failure in the regions where electrons approach each other closely.² Explicitly correlated wave functions are more appropriate to model such short-range electron correlations because of their appropriate explicit dependence on the interelectronic distances.

The explicitly correlated wave function methods can be roughly divided into two groups. The first group of methods, traditional explicitly correlated approaches, expands the wave function in terms of N -electron basis functions, of which the vast majority depend on at least one interelectronic distance. Examples are the Hylleraas,^{3,4} James-Coolidge,⁵ Hylleraas-configuration interaction (CI),⁶ Gaussian-type geminals methods,⁷⁻¹¹ etc. The second group of methods

uses an N -electron basis set which consists primarily of Slater determinants augmented by a few explicitly correlated basis functions. The only examples of such methods are the R12 methods of Kutzelnigg and co-workers¹²⁻¹⁸ as well as the explicitly correlated MP2 method of Taylor and co-workers.^{19,20} Considering, for simplicity, the MP2-R12 method, the first-order pair function is expanded in terms of conventional orbital products and terms which include the correlation factor, $f_{12} \equiv f(r_{12})$,

$$|\tilde{\psi}_{ij}^{(1)}\rangle = \sum_{a<b} T_{ij}^{ab}|ab\rangle + \sum_{k<l} C_{ij}^{kl}\hat{Q}_{12}f_{12}|kl\rangle, \quad (1)$$

where I used the standard tensor notation (e.g., see Refs. 18 and 21). The number of the standard terms then is $\mathcal{O}(o^2v^2)$, whereas the explicitly correlated terms number only $\mathcal{O}(o^4)$. The explicitly correlated terms are strongly orthogonal to the conventional terms,

$$\langle ab|\hat{Q}_{12}f_{12}|kl\rangle = 0, \quad (2)$$

which can be ensured by choosing \hat{Q}_{12} appropriately.

Success of R12 and related methods hinges on the fact that standard Slater determinant expansions are precise, except at small interelectronic distances, where they cannot compensate for the singularity of the Coulomb potential. The behavior at small r_{12} is naturally corrected by terms linear in

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r_{12} which exactly represent the wave function cusp^{22,23} at $r_{12}=0$, i.e., setting f_{12} to r_{12} in Eq. (1). Addition of one such term to a conventional CI expansion for the ground state of He atom speeds up the convergence of the basis set error from $\mathcal{O}(L^{-3})$ to $\mathcal{O}(L^{-7})$,¹² where L is the maximum angular momentum of the basis set. The key technical features of the R12 methods are the resolution of the identity^{12,24–26} and the standard approximation^{12,13,27} due to which only two-electron integrals are needed. R12 methods enhanced with local correlation techniques,²⁸ density fitting,^{29,30} and parallel algorithms³¹ are efficient enough to handle molecules with tens of atoms.^{32,33} Such robustness is without precedent among explicitly correlated methods.

For small basis sets, however, a linear r_{12} factor is not ideal. Although in principle even a double-zeta basis set is sufficient to compute correlation energies in error by less than 1%,³⁴ practice showed that MP2-R12 energies computed with an aug-cc-pVXZ basis were only as precise as the standard MP2/aug-cc-pV(X+1)Z energy.^{17,35} Ten-no was first to demonstrate that a Slater-type geminal³⁶ (STG) was much more effective in combination with small-basis Slater determinant expansions and thus removed the primary source of the basis set error in linear R12 calculations.²⁷ For valence correlation energies, the basis set error in the MP2-R12/aug-cc-pVDZ energy computed with a single STG is roughly equivalent to the error in the standard MP2/aug-cc-pVQZ energy. Other exponential factors³⁵ perform comparably to the STG.

Despite the impressive performance of R12 methods with short-range correlation factors, several areas of concern exist. First, the optimal nonlinear parameter which determines the effective range of the correlation factor depends on the molecular system. Tew and Klopper found that for large basis sets it is less of a concern than for small basis sets.³⁵ When smaller basis sets were used, especially the double-zeta basis, they found that the energy was sensitive to the exponent. Second, using the same correlation factor for every pair of electrons may not guarantee consistent precision, as the core electrons are likely to need a shorter-range correlation factor than valence electrons. Thus it is clear that whether the correlation range is optimized or not, a single correlation factor may not offer consistent performance across the Periodic Table and for all chemical changes. Last, the description of electrons alongside other quantum particles (positrons and protons) will likely require more than one correlation range as well.

Here I propose to examine an R12 approach in which every pair of electrons utilizes several correlation factors of varying correlation range. In this work these correlation factors are of Gaussian form, although other factors can be chosen. A decade ago Persson and Taylor pioneered a similar approach called Gaussian-type geminal (GTG)-MP2,¹⁹ and recently Polly *et al.* reinvestigated²⁰ their approach in the context of local correlation. The method of Polly *et al.* has the following two features which distinguish it from the present method: (1) the weak orthogonality functional (WOF) approximation³⁷ is invoked to avoid computation of four-electron integrals, and (2) many-electron integrals are evaluated analytically. Taylor and co-workers reported high

precision of their method (3% basis set error using the aug-cc-pVDZ basis set and six GTGs) but also note the impractical computational cost due to the three-electron integrals.

The present method will retain the framework of R12 theory, i.e., (1) no approximations, other than the reliable generalized Brillouin condition,^{13,27} will be invoked [the impact of the generalized Brillouin condition is minimal for a linear r_{12} factor²⁷ and for short-range correlation factors (see an upcoming Ref. 38)] and (2) three- and four-electron integrals will be evaluated via the resolution of the identity (RI). Therefore it should be possible to apply this method to systems as large as those accessible with the original MP2-R12 method. Because many-electron integrals are avoided completely and WOF is not assumed, the new method should be more practical and reliable than the approach of Taylor and co-workers.

This objective of this study is to test the precision of the new MP2-R12 method for valence and all-electron second-order correlation energies of second-row atoms, and valence energies of a set of small molecules. The present method will be benchmarked against the standard MP2 method and its explicitly correlated variants using both r_{12} and STG correlation factors.

II. METHODOLOGY

A. Formalism

Following Eq. (1), the first-order pair function is expanded as

$$|\tilde{\psi}_{ij}^{(1)}\rangle = \sum_{a<b} T_{ij}^{ab}|ab\rangle + \sum_{\lambda} \sum_{k<l} C_{ij}^{kl(\lambda)} \hat{Q}_{12} f_{12}^{(\lambda)}|kl\rangle. \quad (3)$$

There are N_{CF} correlation factors, $f_{12}^{(\lambda)}$, each of which is a linear combination of n_{λ} Gaussian geminals,

$$f_{12}^{(\lambda)} = \sum_{\alpha}^{n_{\lambda}} U_{\alpha}^{\lambda} \exp(-\zeta_{\alpha} r_{12}^2). \quad (4)$$

Exponents ζ_{α} and coefficients U_{α}^{λ} are fixed at predetermined values. Any square-integrable nonsingular function of r_{12} can be represented accurately via Eq. (4) given a sufficiently complete set of GTGs. One can therefore easily use this ansatz to approximate results obtained with other correlation factors, such as r_{12} and $\exp(-\zeta r_{12})$.^{27,35} In this sense, the ansatz defined by Eqs. (3) and (4) is universal.

Equation (3) specifies a straightforward generalization of the standard MP2-R12 approach. For a complete discussion of modern R12 methodology one should consult several reviews.^{16–18,39,40} For the sake of brevity I will outline only essential technical details of the current method.

Projector \hat{Q}_{12} ensures the strong orthogonality of the explicitly correlated terms to the conventional double substitutions

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2, \quad (5)$$

where \hat{O} and \hat{V} are projectors on the occupied and virtual orbital spaces, respectively. This form of \hat{Q}_{12} has been advocated by Wind *et al.*,⁴¹ Valeev,²⁵ and, most recently, Klopper

et al. in the context of explicitly correlated coupled cluster method.¹⁷ In the complete basis set limit projector [Eq. (5)] is equivalent to that of ansatz 2 of Klopper and Samson,²⁴ although their technical expressions for matrix elements differ substantially.

To compute first-order wave function and second-order energy, matrix elements of the zeroth- and first-order Hamiltonians and overlap operator are needed. They are expressed in terms of the following intermediates:

$$V_{\mathbf{kl}(\lambda)}^{ij} = \langle kl | f_{12}^{(\lambda)} \hat{Q}_{12} \frac{1}{r_{12}} | ij \rangle, \quad (6)$$

$$X_{\mathbf{kl}(\lambda)}^{\mathbf{ij}(\kappa)} = \langle kl | f_{12}^{(\lambda)} \hat{Q}_{12} f_{12}^{(\kappa)} | ij \rangle, \quad (7)$$

$$B_{\mathbf{kl}(\lambda)}^{\mathbf{ij}(\kappa)} = \langle kl | f_{12}^{(\lambda)} \hat{Q}_{12} (\hat{F}_1 + \hat{F}_2) \hat{Q}_{12} f_{12}^{(\kappa)} | ij \rangle, \quad (8)$$

$$A_{\mathbf{kl}(\lambda)}^{ab} = \langle kl | f_{12}^{(\lambda)} \hat{Q}_{12} (\hat{F}_1 + \hat{F}_2) | ab \rangle. \quad (9)$$

Note that these intermediates are analogous to the standard intermediates of the linear R12 theory but their column and/or row dimensions are N_{CF} times larger. The many-electron integrals which appear in the intermediates in Eqs. (6)–(9) were approximated using the complementary auxiliary basis set (CABS) approach of Valeev.²⁵ The generalized (but not the extended) Brillouin condition¹³ was assumed in the evaluation of matrix \mathbf{B} . No other approximations were involved, i.e., the current method can be described as MP2-R12/B. The final expression for the first-order wave function and the second-order energy are identical to the original MP2-R12 method,

$$C_{\mathbf{kl}(\lambda)}^{ij} = - \sum_{\kappa} \sum_{m < n} (\tilde{\mathbf{B}}^{(ij)})_{\mathbf{kl}(\lambda)}^{\mathbf{mn}(\kappa)} \tilde{v}_{\mathbf{mn}(\kappa)}^{ij}, \quad (10)$$

$$E^{(2)} = \sum_{i < j} e_{ij}^{\text{MP2}} + \sum_{i < j} e_{ij}^{\text{R12}}, \quad (11)$$

$$e_{ij}^{\text{R12}} = - (\tilde{\mathbf{V}}^\dagger (\tilde{\mathbf{B}}^{(ij)})^{-1} \tilde{\mathbf{V}})_{ij}^{ij}, \quad (12)$$

where

$$\tilde{\mathbf{V}} = \mathbf{V} + \mathbf{C}\mathbf{T} \quad (13)$$

$$\tilde{\mathbf{B}}^{(ij)} = \mathbf{B} - \mathbf{X}(\epsilon_i + \epsilon_j) - \mathbf{A}^\dagger (\Delta^{(ij)})^{-1} \mathbf{A}, \quad (14)$$

$$T_{ab}^{ij} = - \frac{\langle ab | 1/r_{12} | ij \rangle}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}, \quad (15)$$

$$(\Delta^{(ij)})_{ab}^{cd} = (\delta_a^c \delta_b^d - \delta_a^d \delta_b^c) (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j). \quad (16)$$

Canonical Hartree-Fock orbitals were assumed in the derivation of Eq. (10) and in the expressions for the intermediates.

B. Computational cost

The computational expense of the energy evaluation formally scales as $\mathcal{O}(o^8 N_{\text{CF}}^3)$ due to the need to invert matrix $\tilde{\mathbf{B}}^{(ij)}$. The prefactor for this step, however, is very small. For

atoms and small molecules considered in this study the total cost of the energy computation is dominated by the integrals evaluation and the AO→MO transformation. The worst scaling integrals include a correlation factor in the bra and the ket, i.e., integrals of operators $\exp(-\zeta_\alpha r_{12}^2) \exp(-\zeta_\beta r_{12}^2)$ and $[\exp(-\zeta_\alpha r_{12}^2), [\hat{T}_1, \exp(-\zeta_\beta r_{12}^2)]]$. Such expressions do not appear in the MP2-R12 method that uses one correlation factor. These integrals, however, factorize into products of two-dimensional integrals and should be relatively inexpensive to evaluate. [The current version of the integrals engine does not yet exploit the factorizability of the integrals but will (hopefully) do so in the future.] The observed scaling of the cost of computing and transforming integrals is therefore closer to linear than quadratic and the impact of using several correlation factors is somewhat limited. Furthermore, in the context of explicitly correlated CC methods, the cost of the integrals is small compared to the cost of solving the conventional amplitude equations and the scaling of the total cost of the calculation with N_{CF} will be effectively sublinear.

C. Numerical issues

When a large set of Gaussian geminals is used, computations may become numerically meaningless. Specifically, the overlap matrix and/or matrix $\tilde{\mathbf{B}}$ may become (near)singular or even indefinite. Although both may originate in the large RI error or the loss of precision in the integral evaluation, the overlap matrix becomes singular naturally when the set of explicitly correlated two-particle basis functions $\hat{Q}_{12} f_{12}^{(\lambda)} | kl \rangle$ approaches linear dependence. This phenomenon is completely analogous to the onset of linear dependence in conventional electronic structure computations using a very large one-electron basis set.

Computations with correlated core electrons are most susceptible to the linear dependency problem. This can be understood easily. Subvalence electron pairs tend to be more compact than the valence pairs; therefore the effective integration range over the interelectronic distance will be much smaller than for valence pairs. But at small r_{12} all Gaussian geminals with sufficiently small exponents are quadratic,

$$\exp(-\alpha r_{12}^2) = 1 - \alpha r_{12}^2 + \mathcal{O}(r_{12}^4). \quad (17)$$

Thus to correlate subvalence electron pairs and avoid the linear dependency problem one must include a set of high-exponent Gaussian geminals *only*. In this work I chose to use the same set of Gaussian geminals for all pairs, valence and otherwise, and deal with the linear dependence problem using a standard orthogonalization procedure. Canonical orthogonalization,⁴² for example, can be applied straightforwardly.

- (1) A linearly independent orthonormal set of basis vectors \mathbf{U} is constructed from the two-electron overlap matrix \mathbf{X} such that

$$\mathbf{U}^\dagger \mathbf{X} \mathbf{U} = \mathbf{I}. \quad (18)$$

In canonical orthogonalization procedure, \mathbf{U} is obtained from the eigenvalues \mathbf{x} and eigenvectors \mathbf{V} of matrix \mathbf{X} as

$$\mathbf{U} = \mathbf{x}_\epsilon^{1/2} \mathbf{V}_\epsilon. \quad (19)$$

Subscript ϵ in Eq. (19) denotes discarding eigenvalues smaller than the maximum eigenvalue times some small threshold, ϵ . In this work I used $\epsilon = 10^{-8}$.

- (2) The pair energy correction in Eq. (12) is replaced with

$$e_{ij}^{\text{R12}} = -(\tilde{\mathbf{V}}^\dagger (\tilde{\mathbf{B}}^{(ij)})^{-1} \tilde{\mathbf{V}})_{ij}, \quad (20)$$

obtained by transforming matrices $\tilde{\mathbf{V}}$ and $\tilde{\mathbf{B}}^{(ij)}$ to the orthonormal basis,

$$\bar{\mathbf{V}} = \mathbf{U}^\dagger \tilde{\mathbf{V}}, \quad (21)$$

$$\bar{\mathbf{B}}^{(ij)} = \mathbf{U}^\dagger \tilde{\mathbf{B}}^{(ij)} \mathbf{U}. \quad (22)$$

The number of linearly dependent vectors discarded in step 1 depends on the threshold, ϵ , and the particular system under study. For example, the number of linearly dependent vectors in the B–Ne series increased from two to six when nine GTGs and the aug-cc-pCVDZ basis set were utilized. Heavier elements unsurprisingly have more linear dependencies because the orbitals become more compact as the nuclear charge increases. Linear dependencies in the two-electron basis were also observed in molecular computations of valence correlation energies with seven Gaussian geminals, especially for molecules with heavier elements (N, O, F), e.g., N_2H_2 , O_2H_2 , CO_2 , etc. The onset of linear dependence can be delayed by using non-even-tempered sets of GTGs. Further examination of these issues is under way.

Erratic convergence or even divergence with respect to the number Gaussian geminals was also observed when negative eigenvalues appeared in the spectrum of matrix $\bar{\mathbf{B}}^{(ij)}$ (the geminal-geminal block of the zeroth-order Hamiltonian). In the worst case, the negative eigenvalues can lead to positive pair energies, which is clearly unphysical. Because the origin of the negative eigenvalues is loss of numerical precision in computation of matrix elements, it makes sense to simply eliminate the negative part of the eigenspectrum as follows. First, matrix $\bar{\mathbf{B}}^{(ij)}$ is diagonalized,

$$\bar{\mathbf{B}}^{(ij)} = \mathbf{U} \mathbf{b} \mathbf{U}^\dagger, \quad (23)$$

and the negative eigenvalues are eliminated to yield \mathbf{b}_+ and \mathbf{U}_+ . Back transformation then produces the positive-definite zeroth-order Hamiltonian,

$$\bar{\mathbf{B}}_+^{(ij)} = \mathbf{U}_+^\dagger \mathbf{b}_+ \mathbf{U}_+. \quad (24)$$

Elimination of linear dependencies in the two-electron basis and negative eigenspectrum of zeroth-order Hamiltonian do not change the asymptotic scaling of the cost of the calculations described here. These procedures do increase the total computational cost, but the absolute increase of the cost was negligible for the systems under consideration.

I should also note that these issues are related to the convergence problems encountered in the CC-R12 methods due to the numerical issues with the zeroth-order Hamiltonian. The idea of extremal electron pairs was introduced by Klopper and co-workers^{18,43} to overcome such problems. Extremal electron pairs are defined as two-particle functions

which diagonalize some operator, e.g., r_{12}^2 . The motivation behind the extremal pairs was to handle a singular or indefinite zeroth-order Hamiltonian by taking only its diagonal in the basis of extremal pairs. The extremal pair concept may potentially be useful in the context of the present method as well, especially when applied in the coupled-cluster framework. However, even in the MP2-R12 framework the use of the diagonal ansatz can be beneficial. Preliminary tests for atoms obtained with a diagonal ansatz, without the extremal pairs, indicate that the numerical issues disappear (see Sec. III A).

D. Technical details

All computations were performed with the developmental version of the MPQC package.⁴⁴ Spin-unrestricted formulations of the second-order methods were utilized. Standard correlation consistent basis sets of Dunning⁴⁵ and Kendall *et al.*⁴⁶ were obtained from the EMSL Gaussian basis set database.⁴⁷ The RI basis sets were taken from Ref. 48 and truncated at angular momentum (3,2) for (B–Ne,H). The RI basis sets are thus composed of the primitive $15s9p7d5f$ and $9s7p5d$ spherical harmonic Gaussian sets for the heavy elements and hydrogen, respectively. The angular momentum truncation was due to technical limitation of the LIBINT2 integrals library at the time. The error due to the finite RI basis set was estimated from linear R12 calculations with a much more complete RI basis set composed of the primitive $19s14p8d6f4g3h2i$ and $9s6p4d3f2g$ sets for B–Ne and H, respectively. The RI error was confirmed negligible ($<0.1\%$ for all cases).

Even-tempered sets of three, five, seven, and nine GTGs were used in this study. The set of nine GTGs included the following geminal exponents: 0.1, 0.3333, 1.0, 3.333, 10.0, 33.33, 100.0, 333.3, and 1000.0. The 3GTG, 5GTG, and 7GTG sets were based on the same exponents but restricted to intervals [1.0,10.0], [0.3333,33.33], and [0.1,100.0], respectively. In STG computations, the Slater-type geminal was expanded in terms of six Gaussian-type geminals with fitting coefficients given in Ref. 35.

The set of small molecules from Ref. 49, used to benchmark performance, was referred to as HJO20. The experimental geometries were used in all computations, as given in Tables 15.7 and 15.9 of Ref. 49.

Complete basis set limit for valence correlation energies of the atoms was estimated by the $(X+1/2)^{-3}$ extrapolation⁵⁰ from atomic UMP2/aug-cc-pV5Z and UMP2/aug-cc-pV6Z energies. The complete basis set (CBS) all-electron atomic energies were also estimated by an extrapolation from UMP2/aug-cc-pCVQZ and UMP2/aug-cc-pCV5Z energies. The CBS limits for molecular valence energies were estimated in Ref. 34 using a triple-basis MP2-R12 approach. For the sake of brevity, these molecular MP2 CBS energies as well as absolute energies for all computations are freely available in electronic form from the EPAPS repository at epaps.aip.org.⁵¹

III. RESULTS

Present study is focused mainly on absolute correlation energies. Because the error in absolute electronic energy scales linearly with the size of the system, the basis set incompleteness in a broad selection of systems can only be analyzed in terms of the *relative* error

$$\epsilon = \frac{E_{\text{CBS}} - E}{E_{\text{CBS}}}, \quad (25)$$

where E and E_{CBS} are the correlation energies computed with the given and complete basis set, respectively (E_{CBS} can only be estimated by explicitly correlated computations or basis set extrapolation). The relative error in Eq. (25) is defined to be positive/negative when the correlation energy is underestimated/overestimated.

The ultimate goal of this work is precise computation of relative energies, i.e., chemical energy differences. Chemical energy differences of interest to thermochemistry and kinetics cannot be meaningfully evaluated at the MP2 level. Such studies will require an R12 version of a highly correlated method, such as multireference CI or coupled cluster. In the absence of a CC-R12 implementation using the new ansatz, the potential precision of the new explicitly correlated ansatz must be judged indirectly. One approach is to compare relative basis set errors in the absolute second-order energies. From the available literature data¹ one can estimate that the augmented quadruple- and sextuple-zeta basis sets are necessary to attain the “chemical” accuracy of 1 kcal/mol for reaction enthalpies and atomization energies, respectively. It is thus reasonable to gauge the basis set error of a method against the errors in conventional MP2/aug-cc-pVQZ and MP2/aug-cc-pV6Z absolute energies. If, for example, the basis set error in a given explicitly correlated computation is the same as the error in the standard MP2/aug-cc-pVQZ energy, one can reasonably assume this level of theory to compute reaction enthalpies to chemical accuracy. Precision of the new MP2-R12 methods was also benchmarked against the standard MP2 approach for the second-order correlation contribution to the atomization energies. A more thorough application of the new method to reaction enthalpies and atomization energies will be published in the future.

A. Atoms

Valence second-order correlation energies for the second-row atoms are presented in Figs. 1 and 2.

Clearly, it is exceedingly difficult to reduce basis set error in the standard MP2 energy by a brute-force extension of the basis set. For example, the conventional MP2 energies computed with the augmented quadruple- and sextuple-zeta basis sets are in error by 5%–7% and 1.5%–2.5%, respectively. This reduction of the basis set error by a factor of 3 comes at the expense of an ~2.4-fold increase in basis set size and a roughly 30-fold cost increase.

By comparison, explicitly correlated energies have much higher precision. It takes only an aug-cc-pVTZ basis in conjunction with the r_{12} correlation factor to match or exceed precision of the standard aug-cc-pVQZ computation (Fig. 2). These results fit earlier observations^{24,35} that the basis set

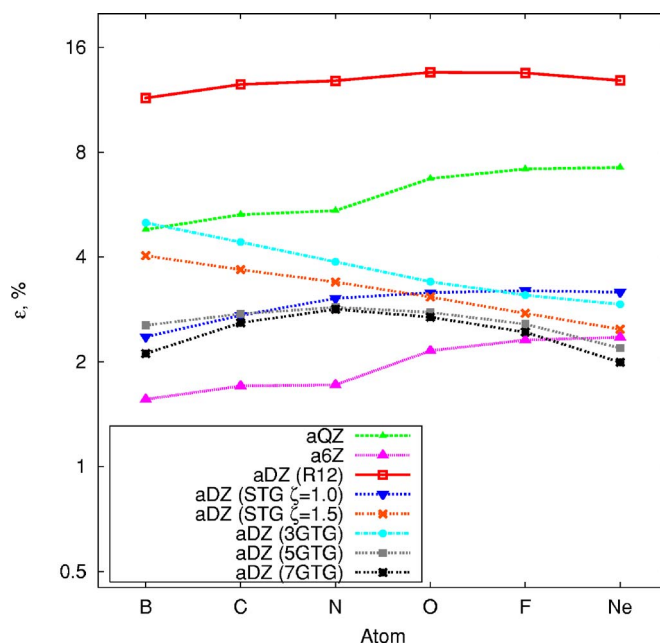


FIG. 1. Valence Møller-Plesset second-order energies for second-row atoms computed with conventional and explicitly correlated wave functions. The notation and complete details of all computations are explained in Sec. II D.

error in the MP2-R12/aug-cc-pV(X-1)Z energy is roughly equivalent to that in the standard MP2/aug-cc-pVXZ energy.

r_{12} is the least efficient correlation factor. Either a single Slater geminal or a set of three Gaussian-type geminals is sufficient to exceed the precision of the MP2/aug-cc-pVQZ energy using only an aug-cc-pVDZ basis set. Furthermore, the analogous energies obtained with the aug-cc-pVTZ basis set exceed the precision of the MP2/aug-cc-pV6Z energy. These results are even more impressive considering that the correlation-consistent basis sets were developed for the use with the standard correlation methods, not the explicitly correlated variety.

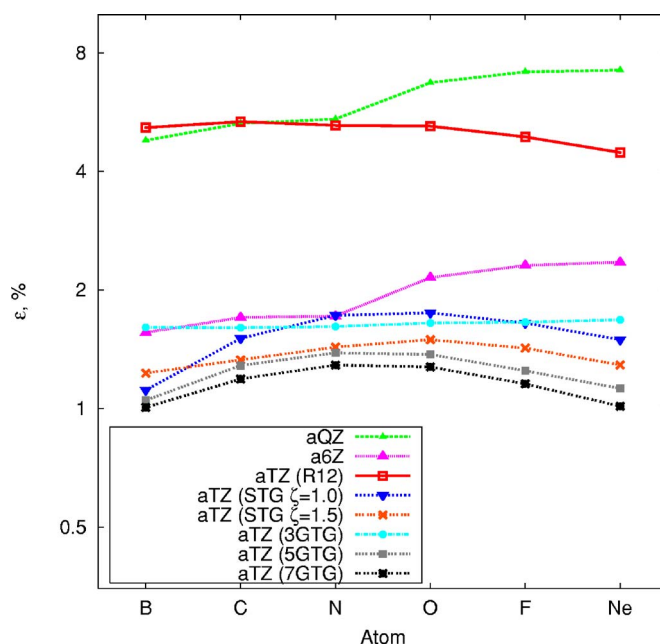


FIG. 2. Valence Møller-Plesset second-order energies for second-row atoms computed with conventional and explicitly correlated wave functions. The notation and complete details of all computations are explained in Sec. II D.

The most precise energies with either aug-cc-pVDZ or aug-cc-pVTZ sets are obtained with a set of seven primitive GTGs: the average errors are 1.99% and 1.01%, respectively. Notably, the aug-cc-pVDZ 7GTG energies for F and Ne atoms are as precise as the standard aug-cc-pV6Z energies, although the precision for lighter atoms is not as high. The aug-cc-pVTZ 7GTG valence energies are the most precise atomic valence energies obtained in this study.

The basis set error as a function of the number of GTGs decreases monotonously. This is not surprising because the MP2-R12/B energy usually approaches the CBS limit from above. Therefore as the number of GTGs in a telescoping series (i.e., the 3GTG set is included in the 5GTG set) is increased, the energy decreases and the basis set error reduces. Convergence with respect to the number of geminals is quick. For example, the 7GTG-5GTG difference is very small ($<0.4\%$ for all atoms under consideration). Thus the 7GTG energies can be considered converged.

If the set of Gaussian geminal correlation factors in Eq. (4) is extended to completeness in a regular manner, the second-order energy is shown to converge to some limiting value near the CBS limit. Such regular convergence is not possible with only one correlation factor, e.g., a Slater-type geminal. Therefore the choice of exponent in the Slater geminal becomes important. When larger basis sets (aug-cc-pVTZ and aug-cc-pVQZ) are used, the energy depends only weakly on the STG exponent.³⁵ This dependence is much more pronounced, however, with the aug-cc-pVDZ basis. The two exponents I chose, 1.0 and 1.5, result in monotonically increasing and decreasing MP2-R12/aug-cc-pVDZ errors along the B–Ne series. These exponents therefore bracket the “optimal” exponent which would produce maximally flat error profile.

The MP2-R12 method which uses GTGs as the correlation factors compares favorably to the MP2-R12 method using a single Slater-type geminal. The 5GTG set is already sufficient to exceed the performance of either STG correlation factor, regardless of the basis set. The 7GTG set yields even lower basis set errors.

The basis set error has a weak but pronounced variation across the atomic series. For the conventional MP2 method, the heavier atoms correspond to greater errors. The trend for the explicitly correlated method depends strongly on the correlation factor. For the linear r_{12} correlation factor the basis set error is relatively flat. As discussed above, the row variation of the MP2-R12 STG energies depends on the geminal exponent. MP2-R12 n GTG energies generally have largest errors for the middle atoms in the series (N and O).

All-electron correlation energies for second-row atoms are presented in Figs. 3 and 4. Generally speaking, most conclusions drawn from the valence-only results apply to the all-electron data as well. A linear r_{12} correlation factor is outperformed by both Slater and Gaussian geminals. Sets of Gaussian-type geminals produce significantly lower basis set errors than a single Slater-type geminal. The convergence with respect to the number of Gaussian-type geminals is slower than in the valence case: the error decreases significantly from 7GTG to 9GTG.

The numerical problems described in Sec. II C were ob-

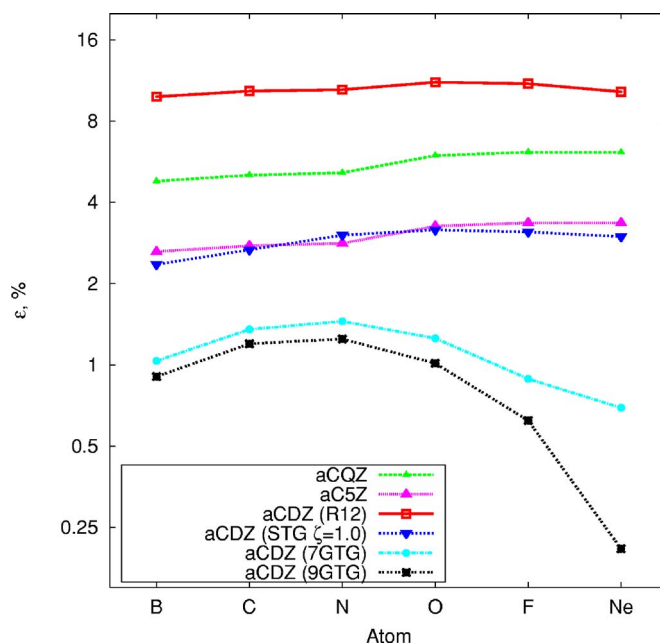


FIG. 3. All-electron Møller-Plesset second-order energies for second-row atoms computed with conventional and explicitly correlated wave functions. The notation and complete details of all computations are explained in Sec. II D.

served in all-electron computations. For example, the MP2-R12(9GTG)/aug-cc-pVDZ computation on a neon atom revealed six linearly dependent functions in the alpha-beta geminal space and up to two negative eigenvalues in the spectrum of $\tilde{\mathbf{B}}^{(ij)}$. Nonphysical pair energies were obtained unless linear dependencies were eliminated and the positive-definite spectrum of the zeroth-order Hamiltonian was enforced. All energies computed with the use of these

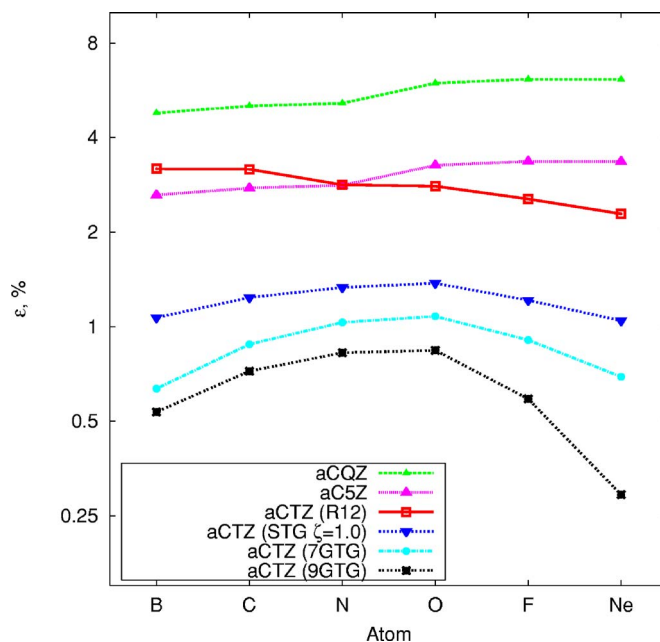


FIG. 4. All-electron Møller-Plesset second-order energies for second-row atoms computed with conventional and explicitly correlated wave functions. The notation and complete details of all computations are explained in Sec. II D.

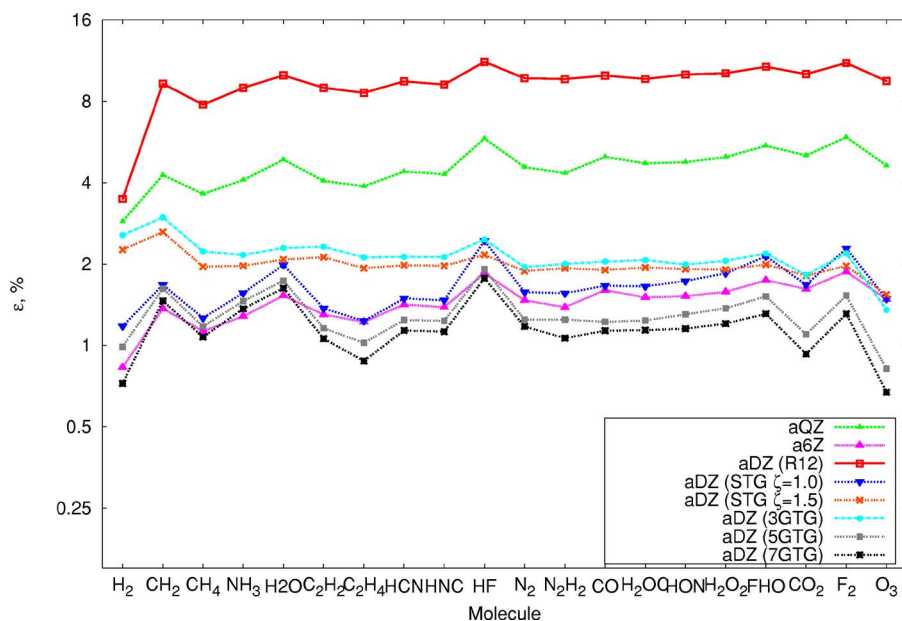


FIG. 5. Valence Møller-Plesset second-order energies for molecules in the HJO20 set computed with conventional and explicitly correlated wave functions. The notation and complete details of all computations are explained in Sec. II D.

techniques were physically reasonable.

It is hard to resist the urge to speculate about the potential manifestations of the two numerical problems in future explicitly correlated computations. Clearly, all-electron computations on heavier elements are likely to encounter these problems, perhaps even when only one correlation factor is used. It is also likely that iterative explicitly correlated methods, such as coupled cluster, will be more sensitive to the presence of linear dependencies and nonphysical spectrum of the zeroth-order Hamiltonian. Two solutions seem tenable. One could use different sets of correlation factors for each electron pair. Intracore electron pairs only need very short-range correlation factors, whereas valence pairs need also longer-range correlation factors. Second approach is to use the analog of the original “diagonal” ansatz of linear R12 theory,

$$|\tilde{\psi}_{ij}^{(1)}\rangle = \sum_{a<b} T_{ij}^{ab}|ab\rangle + \sum_{\lambda} C_{ij}^{j(\lambda)} \hat{Q}_{12} f_{12}^{(\lambda)}|ij\rangle. \quad (26)$$

This ansatz is less susceptible to the linear dependence problems because dimension of the geminal space for each pair is N_{CF} , not $N_{CF}\mathcal{O}(o^2)$. For example, initial all-electron computations for B–Ne series revealed no numerical problems when the diagonal ansatz was used. Note that both approaches will unfortunately break the invariance of the energy with respect to orthogonal transformations of the occupied and unoccupied orbitals.

B. Molecules

The qualitative behavior of basis set errors in molecular valence correlation energies (Figs. 5 and 6) is similar to that in atoms. The basis set errors in molecular aug-cc-pVQZ and

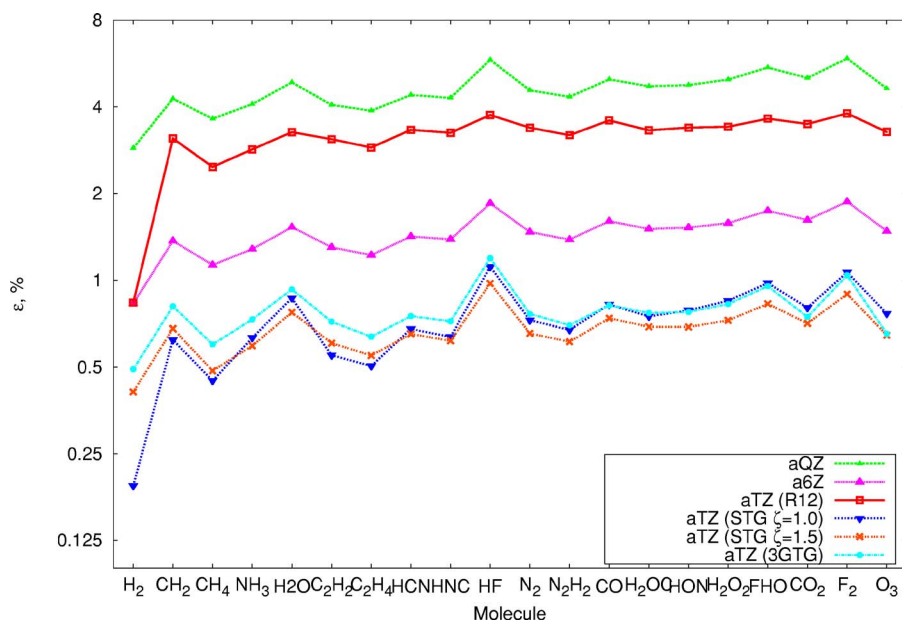


FIG. 6. Valence Møller-Plesset second-order energies for molecules in the HJO20 set computed with conventional and explicitly correlated wave functions. The notation and complete details of all computations are explained in Sec. II D.

TABLE I. Statistical analysis of the basis set errors in the second-order Møller-Plesset atomization energies for the HJO20 set of molecules computed with MP2 and MP2-R12 methods. The basis set error is defined as $\epsilon = (E_{\text{CBS}}^{(2)} - E^{(2)})/E_{\text{CBS}}^{(2)}$, where $E^{(2)}$ and $E_{\text{CBS}}^{(2)}$ are the second-order correlation contributions to the atomization energy computed with a given method and the CBS limit estimate, respectively. The notation and complete details of all computations are explained in Sec II D. $\bar{\Delta}$, Δ_{max} , $\bar{\Delta}_{\text{abs}}$, Δ_{rms} , and σ denote the mean error, the maximum absolute error, the mean absolute error, the rms error, and the standard deviation, respectively.

| Basis set | Correlation factor | $\bar{\Delta}$ | Δ_{max} | $\bar{\Delta}_{\text{abs}}$ | Δ_{rms} | σ |
|-------------|--------------------|----------------|-----------------------|-----------------------------|-----------------------|----------|
| aug-cc-pVDZ | R12 | 5.20 | 6.75 | 5.20 | 5.32 | 1.17 |
| aug-cc-pVDZ | 3GTG | 0.24 | 2.56 | 0.71 | 0.94 | 0.94 |
| aug-cc-pVDZ | 5GTG | -0.46 | 2.33 | 0.73 | 0.94 | 0.84 |
| aug-cc-pVDZ | 7GTG | -0.66 | 2.88 | 0.85 | 1.11 | 0.92 |
| aug-cc-pVDZ | STG($\zeta=1.0$) | 0.04 | 1.18 | 0.39 | 0.51 | 0.53 |
| aug-cc-pVDZ | STG($\zeta=1.5$) | 0.44 | 2.26 | 0.66 | 0.84 | 0.73 |
| aug-cc-pVTZ | 3GTG | -0.25 | 1.26 | 0.32 | 0.45 | 0.38 |
| aug-cc-pVTZ | STG($\zeta=1.0$) | -0.38 | 1.11 | 0.40 | 0.46 | 0.27 |
| aug-cc-pV5Z | ^a | 1.44 | 1.96 | 1.44 | 1.48 | 0.36 |
| aug-cc-pV6Z | ^a | 0.85 | 1.19 | 0.85 | 0.88 | 0.24 |

^aThe standard MP2 method.

aug-cc-pV6Z MP2 energies are approximately the same as those in atoms, 2.9%–5.9% and 0.8%–1.9%, respectively. r_{12} is by far the worst among the correlation factors: it takes an aug-cc-pVTZ basis to reduce the basis set error below the MP2/aug-cc-pVQZ level. Three GTGs are sufficient, however, to best the precision of the conventional MP2/aug-cc-pVQZ energy. The method with a single Slater-type geminal with $\zeta=1.0$ can approach the precision of the standard MP2/aug-cc-pV6Z energy, but not quite match it. The precision of the best standard MP2 calculation is matched or exceeded when five or seven Gaussian-type geminals are used along an only aug-cc-pVDZ basis. Note that for the molecules with only one nonhydrogen atom (H_2 , CH_2 , CH_4 , NH_3 , H_2O , and HF) the precisions of the MP2/aug-cc-pV6Z energy and the MP2-R12(7GTG)/aug-cc-pVDZ 7GTG energies are comparable, but for the “heavier” molecules the explicitly correlated method is superior.

The MP2-R12/aug-cc-pVTZ energies computed with either one STG or three GTGs are much more precise than the MP2/aug-cc-pV6Z energies. Because even three Gaussian-type geminals were superior to the conventional MP2 computations, the larger, 5GTG and 7GTG, sets were not used with the triple-zeta basis.

The basis set error varies slightly and nontrivially across the molecular set for all employed methods. It is notable that the variation pattern is the same for all methods and therefore is characteristic of the set of molecules and perhaps the correlation consistent basis sets.

Valence molecular MP2-R12 computations using sets of five and seven Gaussian-type geminals exhibit the same numerical issues that were observed in all-electron atomic computations. Their effect on the energy is particularly pronounced for molecules with heavier elements (O and F). For the MP2-R12 5GTG and 7GTG energies the variation of the basis set error across the set had a distinctly different pattern from all other methods. When the energies were recomputed using techniques described in Sec. II C, all nonphysical results disappeared and the variation pattern became “normal.”

I also briefly analyzed basis set errors in the second-order correlation contributions to atomization energies (Table

I). When Slater- or Gaussian-type correlation factors are used, the mean MP2-R12/aug-cc-pVDZ basis set errors are smaller than that of the best conventional approach, MP2/aug-cc-pV6Z. The Slater-type geminal with $\zeta=1$ seems to be the best choice for MP2-R12/aug-cc-pVDZ computations: it offers the lowest maximum absolute error and the smallest standard deviation. However, the errors increase significantly when ζ is raised to 1.5. Thus the exponent of the Slater-type geminal must be chosen carefully for computations with small basis sets. Nevertheless, these results again underscore the near-optimal character of the Slater-type geminal for R12 methods. Although mean errors in GTG-based MP2-R12/aug-cc-pVDZ method are comparable to that of STG counterparts, the standard deviation and maximum absolute errors are larger in the former. It is likely that an optimized, non-even-tempered set of GTG will decrease the maximum error and the standard deviation.

It is important to note that the largest absolute errors in STG- and GTG-based energies correspond to molecules containing O and F atoms (e.g., O_3 and F_2). It is clear that even with the explicitly correlated methods the basis set error varies significantly as the nuclear charges changes. Computations on heavier elements may pose a formidable challenge to the R12 methodology.

IV. CONCLUSIONS

Explicitly correlated methods using short-range correlation factors are spectacularly capable to yield highly precise valence correlation energies using only small basis sets, something that a linear r_{12} factor could not do. There is a strong possibility that more complex situations, e.g., electronic structure of systems with d and f electrons and correlation between electrons and nuclei, among many, will require more flexible correlation factors. Here I examined an explicitly correlated MP2 method which can be considered a marriage of the Gaussian geminal-based methods to the linear R12 methodology of Klopper and co-workers. The current method is similar to the earlier efforts of Taylor and co-workers in that a fixed set of (linear combinations of)

Gaussian-type geminals generates the geminal subspace that augments the standard orbital products. However, in this work the matrix elements are computed using the robust standard approximations of the R12 theory (the resolution of the identity and the generalized Brillouin condition). The resulting approach avoids the need for nonlinear optimization (although the exponents of the set of Gaussian geminals must be chosen with care) and needs only two-electron integrals. Systematic expansion of the set of GTGs to completeness converges the energy from above to a correlation-factor-independent limit. Such limit can in general lie below the CBS limit due to the error introduced by the finite Hartree-Fock basis;³⁴ however, it is found here to lie slightly above the basis set limit.

The most important conclusion is that for the broad sample of atomic and molecular cases considered here the new MP2-R12 method can exceed the precision of standard aug-cc-pVQZ and aug-cc-pV6Z MP2 energies using respective sets of three and seven primitive (i.e., noncontracted) Gaussian-type geminals in conjunction with only an aug-cc-pVDZ basis set. This suggests that chemical-accuracy-type precision for standard reaction enthalpies and atomization energies may be approached using the new approach with an aug-cc-pVDZ basis only. That such high precision can be attained with very small basis set bodes well for a locally correlated version of the present method.

Performance of the new method compares favorably to that of the MP2-R12 method using a single Slater-type geminal for absolute energies. For the vast majority of cases, 5GTG and 7GTG energies were more precise than the STG results. The 7GTG energies were almost converged in valence energy computations. It must be stressed (again) that a single Slater-type geminal can approach the valence basis set limit very closely. Present results strongly underscore the near-optimal character of the Slater-type geminal for MP2-R12 computations of electron correlation energies.

Correlation contribution to the atomization energies computed with the STG- and GTG-based MP2-R12/aug-cc-pVDZ methods were also more precise than the conventional aug-cc-pV6Z/MP2 results. The STG-based method seems to be the best choice for such computations. The present GTG-based MP2-R12 method can be improved in the future, for example, by using a non-even-tempered set of GTG exponents.

Scaling of the computational cost with the number of correlation factors is formally cubic, although the dominant step is quadratic. The relative cost of these steps is, however, expected to be small in highly correlated computations, such as coupled cluster. Besides, the necessary number of correlation factors will also depend on the particulars of the problem under consideration, e.g., a sufficient precision for the chemically accurate reaction energies can likely be reached with a single correlation factor. For more demanding situations, preoptimization of the correlation factor set can be used to maximize the precision while keeping the computation cost minimal.

Atomic all-electron and molecular valence calculations using large sets of Gaussian-type geminals suffer from numerical problems due to the linear dependencies in the two-

electron basis and a non-positive-definite zeroth-order Hamiltonian. When linear dependencies are removed and the zeroth-order Hamiltonian matrix is made positive definite, computed energies seem to be numerically stable even when large sets of Gaussian geminals are used. This issue clearly needs further study. The concept of extremal electron pairs in combination with the “diagonal” ansatz may provide the solution to this problem.

Studies of the last four years^{24–27,29,35,36} have completed a critical mass of evidence that explicitly correlated linear R12-type methods are a dramatic yet practical improvement for standard electronic (and molecular) structure computations. The current study provides background for future development of explicitly correlated methodology for light- and heavy-element electronic structure and non-Born-Oppenheimer computations.⁵² Work along these lines is under way.

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