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# Accurate quantum-chemical calculations: The use of Gaussian-type geminal functions in the treatment of electron correlation

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We investigate augmenting conventional Gaussian-type one-electron orbital basis sets with two-electron functions that have a Gaussian dependence on the interelectronic distance. We observe substantial improvements in calculated correlation energies for helium and neon atoms and for the water molecule. A feature of our approach is that there is no nonlinear optimization of the two-electron basis function parameters at all. © 1996 American Institute of Physics. [S0021-9606(96)02937-6]

## I. INTRODUCTION

Almost all quantum-chemical calculations performed today use an expansion in one-electron functions. The convergence of calculated energies and properties with the size of this one-electron basis is a critical issue. At the Hartree–Fock self-consistent field (SCF) level, the convergence of the total energy as the basis set is expanded is reasonably rapid, and so are properties directly related to the energy, such as the equilibrium geometry or harmonic vibrational frequencies. Comparison studies such as those performed in a recent review<sup>1</sup> show that a basis set of double-zeta quality (for the valence shell at least) augmented with a single set of polarization functions yield structures and frequencies close to the ‘‘Hartree–Fock limit’’ (complete basis) results. Properties such as the dipole moment or polarizability require somewhat larger sets, but the convergence behavior is well understood and is still reasonable. And the same arguments apply to methods such as multiconfigurational SCF, in which the aim is to account for nondynamical correlation effects such as near degeneracies.

Unfortunately, the convergence of calculations designed to recover dynamical correlation—the effects that arise from the detailed correlation in the electronic motion from the Coulomb repulsion term in the electronic Hamiltonian—is much less satisfactory. This is a basis set phenomenon quite independent of whether the dynamical correlation is treated by perturbation theory, coupled-cluster methods, or configuration interaction. Indeed, the slow convergence of computed correlation energies with the size of the orbital basis is one of the most frustrating aspects of quantum-chemical calculations. A simple quantitative example is provided by the neon atom, using the correlation-consistent basis sets developed by Dunning and co-workers<sup>2–4</sup> (these are basis sets optimized for treating dynamical correlation). The error in the SCF and MP2 valence-shell correlation energy for Ne for the sequence of basis sets denoted<sup>2</sup> cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z is listed in Table I. The slow convergence of the correlation energy is obvious. For example, since the MP2 valence-shell limit correlation energy is 320

$mE_h$  (see, e.g., Ref. 5), even the largest basis set here yields only about 95% of the correlation energy, despite containing functions of  $h$  type ( $l=5$ )! We should stress that the errors in the SCF energy are much easier to correct than in the correlation energy. An atomic natural orbital basis<sup>6</sup> contracted from a large primitive basis would show errors of less than 1  $mE_h$  in the SCF energy for any size of contracted basis, but the correlation energy errors would be similar to those of the correlation-consistent basis sets. As we have said, the situation is the same for other correlation treatments: this is a basis set problem, not a limitation of the many-body treatment. The consequence is that even neglecting correlation of the core electrons it is rarely possible to calculate total energies to an accuracy of tens of mhartree, and errors of a hundred or more would not be uncommon. What makes quantum chemistry at the level of accuracy of a few kcal/mol possible is that most phenomena of interest involve energy differences, and there are large cancellations of error that improve the accuracy of the energy differences by an order of magnitude or more over the accuracy in the total energies.

By relying on cancellations of error, therefore, it is possible to predict thermochemical quantities to an accuracy of perhaps 2–5 kcal/mol in binding energies or heats of formation by *ab initio* calculation alone. Such accuracy requires basis sets with up to  $g$  type functions on nonhydrogen atoms and  $f$  functions on hydrogen.<sup>7,8</sup> To obtain ‘‘thermochemical accuracy’’ of 1 kcal/mol requires either even larger basis sets, or the inclusion of some type of correction,<sup>7,9–15</sup> possibly empirically derived. Such corrections are valuable, but there is always concern about the range of validity of any correction treatment. The ability to calculate the energy and properties more accurately from first principles would be highly desirable.

The reason for the slow convergence of correlation energy with basis set is the behavior of the wave function as two electrons approach one another. In a helium atom, for example, the known behavior of the exact wave function as the interelectronic distance  $r_{12}$  tends to zero is  $1 + \frac{1}{2}r_{12}$ , as may be shown from the cusp analysis by Kato.<sup>16</sup> This linear behavior in  $r_{ij}$  corresponds to a two-electron cusp that is

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TABLE I. Ne atom energies using correlation-consistent basis sets ( $mE_h$ ).

	$\Delta$ SCF	$\Delta$ corr	%corr
cc-pVDZ	58	136	58%
cc-pVTZ	15	56	83%
cc-pVQZ	3.5	26	92%
cc-pV5Z	0.2	14	96%
Total	$-128.54709 E_h$	$-320.2$	

poorly represented by products of one-electron functions. The correlation contribution of high angular momentum functions can be shown by partial-wave expansion studies to go as  $(l + \frac{1}{2})^{-4}$  for functions of angular momentum  $l$ , for example. The contribution from a given higher  $l$  value is almost exhausted once about six basis functions of that  $l$  are included,<sup>17</sup> but the convergence with  $l$  itself is evidently slow. Hence attempts to obtain (for example) mhartree accuracy in correlation energies using one-electron basis sets do not look promising, and other avenues must be explored. We should perhaps also note here that the nature of the one-electron orbitals does not strongly affect calculations of the correlation energy: Slater-type orbitals do not offer any significant advantage over Gaussian-type orbitals, for example, especially when the latter have been optimized with correlation in mind.

Various alternatives have been suggested instead of using one-electron orbitals. We will not attempt a complete discussion, and we will exclude treatments applicable only to atoms. The most obvious extension to orbital-based methods is to include functions that depend on the coordinates of two electrons rather than just one. Hylleraas's work on the helium atom<sup>18</sup> is one of the best-known early explorations of this type. Hylleraas used a variational trial function that included terms linear and quadratic in the interelectronic distance  $r_{12}$ , thus allowing for a proper description of the two-electron cusp behavior. He obtained extraordinarily good results for He, as we discuss at greater length in Sec. II. It would thus seem obvious that one should base a strategy for describing correlation on the inclusion of interelectronic coordinates  $r_{ij}$  in the wave function, and in particular one should include linear terms of this type. Unfortunately, the use of linear  $r_{ij}$  basis function in many-electron calculations, especially for molecules, leads to insuperable difficulties with various two-electron and even three-electron or higher integrals. Thus linear  $r_{ij}$  terms have been used mainly in benchmark calculations for two-, three-, and four-electron systems.

Recently, however, Klopper, Kutzelnigg and co-workers<sup>19–22</sup> have introduced a remarkably ingenious approximate method for incorporating linear  $r_{ij}$  terms into electronic structure calculations, leading to a hybrid approach that employs both one-electron orbitals and  $r_{ij}$  terms to describe correlation. The basic ansatz used in their so-called MP2-R12 calculations, for example, is to write the pair-correlation function for a pair of occupied molecular orbitals (MOs)  $\phi_i$  and  $\phi_j$  as

$$w_{ij}(1,2) = \sum_{a>b} \phi_a(1)\phi_b(2)c_{ij}^{ab} + c_{ij}Qr_{12}\phi_i(1)\phi_j(2). \quad (1)$$

Here  $\phi_a$ , etc., are virtual MOs;  $Q$  is a strong orthogonality projector on the occupied orbital space. The trial function  $w_{ij}$  is used to construct an  $N$ -electron wave function

$$\Psi_{ij} = \Psi_0 + \mathcal{A} \left( w_{ij} \prod_{k \neq i,j}^N \phi_k \right), \quad (2)$$

where the antisymmetrizer  $\mathcal{A}$  produces an  $N$ -electron function that is antisymmetric to exchanging any two particles. In practice spin-coupled pairs are used but this need not concern us here. The first term in Eq. (1) is the conventional orbital contribution to the first-order wave function. The second term is intended to describe the behavior of the wave function in the region of the correlation cusp. Substituting the expansion of Eq. (1) into the Hylleraas functional for the second-order energy and minimizing leads to many difficult integrals, so Klopper and Kutzelnigg<sup>19</sup> introduce systematic approximations that eliminate or simplify difficult integrals. These approximations become more reliable as the orbital basis set becomes more complete. Their method has been used to calculate accurate correlation energies (at the coupled-cluster as well as the MP2 level) for a variety of systems and undoubtedly represents the most successful general use of linear  $r_{ij}$  terms. The main disadvantage is that orbital basis sets that are already fairly large, such as cc-pVTZ for first-row atoms, are required for the various approximations to be reliable. It is also not necessarily obvious how to compute analytical derivatives of the MP2-R12 energy. We may finally note that the original Klopper and Kutzelnigg approach suffered from lack of invariance to unitary transformations among the occupied orbitals: this has been remedied completely by Klopper<sup>23</sup> but need not be discussed here.

A completely different set of basis functions that incorporate the interelectronic coordinate explicitly are the Gaussian-type geminals (GTGs) introduced originally by Boys<sup>24</sup> and by Singer.<sup>25</sup> The most general form of Cartesian GTG is

$$g(a,b,c,d,e,f,\alpha,\beta,\gamma,\mathbf{A},\mathbf{B}) = x_1^a y_1^b z_1^c x_2^d y_2^e z_2^f \exp(-\alpha r_{1A}^2 - \beta r_{2B}^2 - \gamma r_{12}^2), \quad (3)$$

where the electron coordinates are denoted 1 and 2 and the GTG involves two centers  $A$  and  $B$ . The GTG differs from a product of two Gaussian-type orbitals (GTOs)

$$\phi(a,b,c,\alpha,\mathbf{A})\phi(d,e,f,\beta,\mathbf{B}) = x_1^a y_1^b z_1^c x_2^d y_2^e z_2^f \exp(-\alpha r_{1A}^2 - \beta r_{2B}^2) \quad (4)$$

by the inclusion of the correlation factor  $-\gamma r_{12}^2$  in the exponential. The correlating pair function would then be expanded as

$$w_{ij}(1,2) = \sum_v c_{ij}^v g_v(1,2), \quad (5)$$

where we have collapsed all of the possible GTG index quantities into one for notational convenience. The main motivation for the use of functions such as those of Eq. (3) is that the integrals that arise in molecular calculations can be evaluated using extensions of the formulas for integrals over GTOs. All of the integrals, even three- and four-electron or higher terms, can thus be expressed either in closed form or in a form that involves a one-dimensional numerical integration or functional approximation.<sup>24,26</sup> Hence the individual integrals are not significantly more complicated than those over GTOs, and are enormously simpler than those that arise in a full implementation of linear  $r_{ij}$  approaches. And although the many-electron integrals are very numerous, like any Gaussian integrals they can be generated in batches that are completely independent of one another and are thus ideal for implementation on scalable parallel computer architectures. On the other hand, from the perspective of the two-electron cusp condition these functions appear less suitable, since they do not possess cusps. The obvious analogy is between STOs and GTOs: the latter lack the correct nuclear cusp behavior of the former. Nevertheless, experience has shown that there is a computational advantage to using GTOs, even though many GTOs may be required to give an adequate representation of a STO. The experience with GTGs has been similar:<sup>27–37</sup> these functions have been used successfully in calculations of correlation energies to high accuracy (that is, on the order of  $0.1 mE_h$ ), especially by Szalewicz and co-workers (see Refs. 30, 34, 36, and 37, for example) and recently to even higher accuracy in the work of Cencek and Rychlewski<sup>38,39</sup> on three- and four-electron systems. GTGs had been the only route to  $0.1 mE_h$  accuracy applicable to polyatomic molecules until the advent of the Klopper and Kutzelnigg approximate linear  $r_{ij}$  method.

One of the questions that immediately arises with the use of GTGs is that of the values of the nonlinear parameters in Eq. (3). This can include the choice of exponents for the “angular” terms, where these are not constrained by symmetry, as well as the Gaussian exponents and, in molecules, the centers  $A$  and  $B$ . The most common strategy has been to optimize these nonlinear parameters, which (as with any nonlinear optimization) requires considerable computational effort. Good starting guesses for the optimization are valuable, and effort has been devoted to bootstrap procedures in which a succession of calculations that begins with a small set is used to provide starting guesses for larger and larger calculations (see also Ref. 40). Another approach to generating a starting guess is to fit the term involving linear  $r_{ij}$  from the Klopper and Kutzelnigg ansatz by GTGs<sup>36</sup>

$$r_{12}\phi_i\phi_j \approx \sum_v c_v g_v. \quad (6)$$

We shall have more to say about fits of this type in this work, as our approach is closely related to this. Finally, we may note that while a complete implementation of MP2 based on GTGs requires four-electron integrals, a novel alternative to the Hylleraas functional introduced by Szalewicz and

co-workers<sup>29,30</sup> sidesteps this problem and requires at most three-electron integrals, a very valuable computational simplification.

Our purpose in the present work is to explore the use of GTGs in molecular calculations with a more modest aim than that of sub-mhartree accuracy. That is not to say we would not be interested in achieving such accuracy, but it appears at this stage that the more modest goal of mhartree accuracy is the most appropriate step beyond the use of orbital basis sets. We are particularly interested in improving the correlation energy available at, say, the valence double zeta plus polarization basis level. A set such as cc-pVDZ yields some 60% (Ne) to 75% (C) of the valence-shell correlation energy available with a given correlation treatment, and as we have discussed a basis set of this size is required anyway to obtain results close to convergence to the SCF limit for structures, etc. Going to a larger set such as cc-pVTZ recovers another 23% of the correlation energy in Ne, but the use of basis sets even this large becomes problematic in disk-based correlation treatments for large molecules, and the Ne correlation energy is still in error by 17%, which is of the order of  $56 mE_h$ ! The question we wish to answer is as follows: “How can we improve *substantially* on the 70% correlation energy we can recover with a cc-pVDZ quality basis?” That is, given that increasing the basis set is an inefficient way to recover even 90% of the correlation energy, what is our most cost-effective alternative? We will show here that a few GTGs may be used without *any* nonlinear optimization to augment basis sets of cc-pVDZ quality so that more than 90% of the correlation energy can be recovered, and that when used with larger basis sets such as cc-pVTZ it is possible to recover 98%–99%. We will first consider the helium atom using (infinite-order) variational calculations, and show how these results motivate our suggestion of a pair-function ansatz that can be applied to many-electron systems. We will then apply our approach to correlation in the neon atom and water molecule as test systems. Although most of our effort is directed toward the valence-shell correlation energy, we will also consider the issue of core correlation, since accurate total energies cannot be obtained without correlating all electrons.

All of the calculations we report have been performed using an IBM RS6000/model 350 workstation and SP-2 computer at the San Diego Supercomputer Center.

## II. CORRELATION IN THE HELIUM ATOM

Considerable effort has been devoted to correlation in the helium atom ground state and it is well known that rapid convergence can be obtained using terms in  $r_{12}$ . The six-term Hylleraas wave function<sup>18</sup> yields a total energy only  $0.4 mE_h$  above the estimated nonrelativistic limit. This result may appear surprising when one considers that the trial function

$$\Psi(1,2) = \exp[-\zeta(r_1+r_2)][1+c_1(r_1+r_2)+c_2(r_1+r_2)^2+c_3(r_1-r_2)^2+c_4r_{12}+c_5r_{12}^2](\alpha\beta-\beta\alpha) \quad (7)$$

includes only a single exponential term: the optimum single-zeta STO SCF energy for He is  $-2.847\ 66 E_h$  compared to

TABLE II. He atom variational energies using GTG fits to  $r_{12}$  and optimized GTG expansions ( $E_h$ ).

Number of GTGs	Highest GTG exponent <sup>a</sup>	Fitting range ( $a_0$ ) <sup>b</sup>	Energy
SCF energy $-2.82134$			
Hylleraas energy $-2.89112^c$			
6	81	2	$-2.88958$
6	27	2	$-2.88991$
6	9	2	$-2.82169$
6	81	5	$-2.88260$
6	27	5	$-2.89071$
6	9	5	$-2.89066$
6	81	opt <sup>d</sup>	$-2.88988$
6	27	opt <sup>d</sup>	$-2.89115$
6	9	opt <sup>d</sup>	$-2.89112$
9	2187	2	$-2.88965$
9	729	2	$-2.89099$
9	243	2	$-2.89030$
9	729	5	$-2.89075$
9	243	5	$-2.89110$
9	81	5	$-2.89108$
9	729	10	$-2.88897$
9	243	10	$-2.89102$
9	81	10	$-2.89108$
9	27	10	$-2.89099$
9	729	opt <sup>d</sup>	$-2.89118$
9	243	opt <sup>d</sup>	$-2.89124$
9	81	opt <sup>d</sup>	$-2.89124$

<sup>a</sup>Highest exponent of even-tempered sequence with ratio 3.

<sup>b</sup>GTG fit (see text) to linear  $r_{ij}$  from zero to this value.

<sup>c</sup>Variationally optimum energy for wave function of Eq. 8.

<sup>d</sup>Variationally optimum energy using this set of GTGs.

the Hartree–Fock limit of  $-2.861\ 68\ E_h$ , and anyway Hylleraas's correlation-optimized exponent gives an even worse SCF energy of  $-2.821\ 34\ E_h$ . The polynomial part of Eq. (7) thus plays a substantial role in the SCF description of the system, as well as in the correlation energy: an aspect of Hylleraas's work that tends to be overlooked in some of the literature and which we discuss at more length elsewhere. We will in fact reduce Eq. (7) to the simpler two-term expression

$$\Psi = \exp[-\zeta(r_1 + r_2)](1 + c_1 r_{12}), \quad (8)$$

partly to reduce the dimensionality of the problem but also because this forms a more logical starting point for our ultimate goal of building two-electron terms onto existing orbital-based methods. As we see from Table II, the best result we can obtain with a function of this form is  $-2.891\ 12$ , compared to  $-2.821\ 34$  at the SCF level using just the exponential term but with the correlation-optimized exponent. The exponential here is actually represented using a 10-term GTO expansion, but this does not affect the results above the  $10\ \mu E_h$  level. One immediate observation is that the  $r_{12}$  term contributes significantly to improving the SCF part of the wave function, since it lowers the energy by  $70\ mE_h$ , which is almost  $30\ mE_h$  larger than the exact correlation energy. Nevertheless, it will serve to illustrate our general approach here.

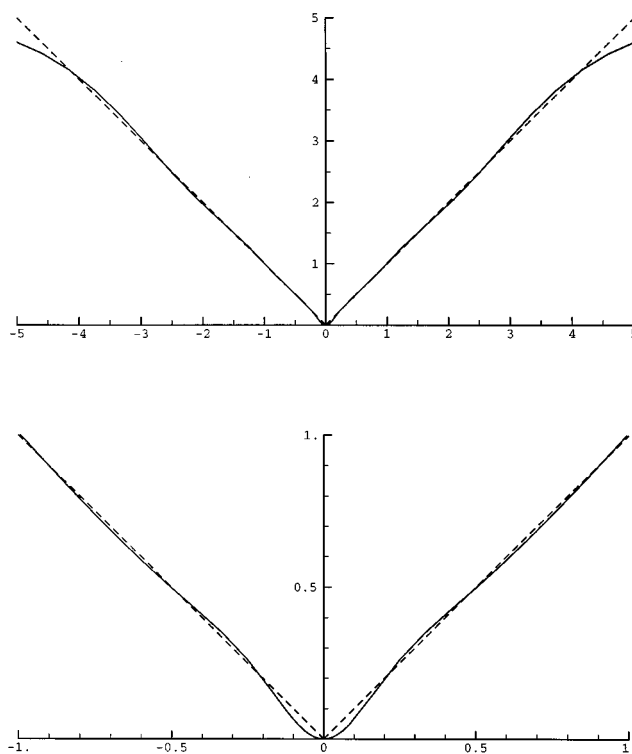


FIG. 1. Six GTG fit to  $r_{12}$  over different ranges (solid line: fit; dashed line:  $r_{12}$ ).

A first step in avoiding the explicit use of linear  $r_{12}$  would be to fit it using some more tractable functions, such as GTGs

$$r_{12} \approx \sum_{v=0} b_v [1 - \exp(-\gamma_v r_{12}^2)]. \quad (9)$$

Note that we are *not* fitting the full expression  $r_{12}\phi_{1s}^2$  here, unlike Eq. (6) above, or the work of Ref. 36. The coefficients and exponent values in Eq. (9) are chosen in some way to represent  $r_{12}$  as accurately as possible. The analogy with fitting STOs as expansions in GTOs<sup>41,42</sup> is clear. Various elaborate methods for accomplishing the latter have been suggested, including integral-based methods. We have chosen a cruder expedient, using an exponentially weighted (weight factor  $\exp[-r_{12}]$ ) least-squares procedure. The exponents  $\gamma_v$  in Eq. (9) are simply taken as an even-tempered sequence  $a/3^v$ , where  $a$  is typically a power of three: values are given in the tables. We have explored several different exponent ranges and fitting ranges. Two fits are plotted in Figs. 1 and 2. The larger fit here, involving 15 GTGs, differs imperceptibly from  $r_{12}$  over a range of  $15\ a_0$  except for a region very close to the origin. Clearly, beyond some value of  $r_{12}$  the expansion on the right-hand side of Eq. (9) will be dominated by the behavior of the GTG with the smallest exponent and will approach a constant, which is not at all the behavior of  $r_{12}$ . However, electron correlation is a short-range phenomenon (hence our use of an exponentially weighted fit) and we may assume that the long-range behavior will not matter. The results of Table II suggest that as

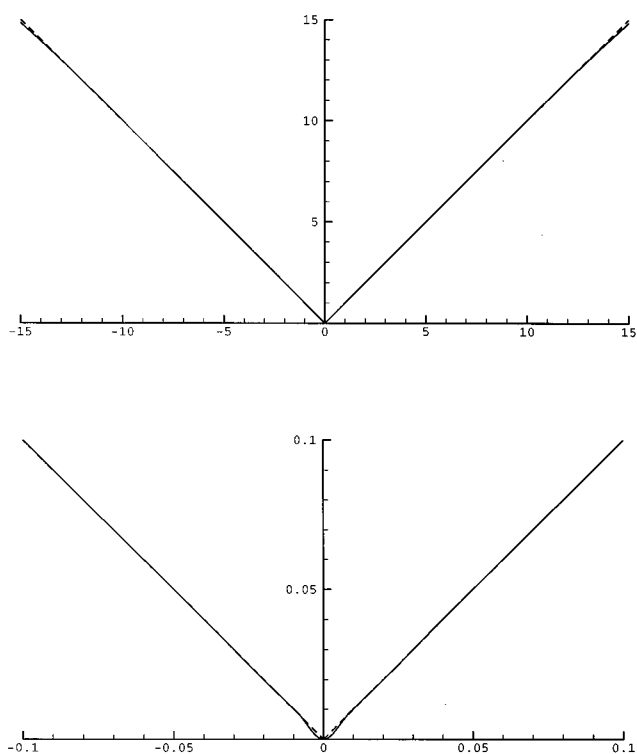


FIG. 2. Fifteen GTG fit to  $r_{12}$  over different ranges (solid line: fit; dashed line:  $r_{12}$ ).

long as the fitting range is more than  $2 a_0$  this is indeed the case. The length of the fitting expansion does not appear to be very critical: even a six-term fit introduces errors of only  $0.5 mE_h$  in the energy, while ten terms reduce the error to  $20 \mu E_h$ . The exponent range required in these fits is something of a surprise. Despite naive expectations that the most important issue would be describing the cusp (i.e., short-range behavior which would require very high exponents), there seems little need for high exponents. The best six-term fit covers an exponent range in Eq. (9) of 27–0.111 111, the best nine-term fit is from 243 to 0.037 037, but the difference in energy between these results is only  $0.4 mE_h$ . We have experimented with denser coverage of the exponent range (that is, the use of a smaller even-tempered ratio) but the results show little significant improvement. We may conclude from these experiments that it is certainly possible to represent linear  $r_{12}$  to any desired accuracy by an expansion in GTGs like Eq. (9), which may have its uses in facilitating the evaluation of many-electron integrals involving linear  $r_{ij}$  terms, just as GTO expansion methods can be used to evaluate integrals over STOs.<sup>43</sup>

The most obvious way to improve the energy obtained in a calculation with GTO fits to STOs is to optimize the coefficients of the Gaussians, by the variation principle, say, rather than constraining them by the fit. Pushing the analogy between GTO fits to STOs and GTG fits to linear  $r_{ij}$  further, then, the obvious step is to use the GTGs that appear in Eq. (9) as basis functions in themselves, with variationally opti-

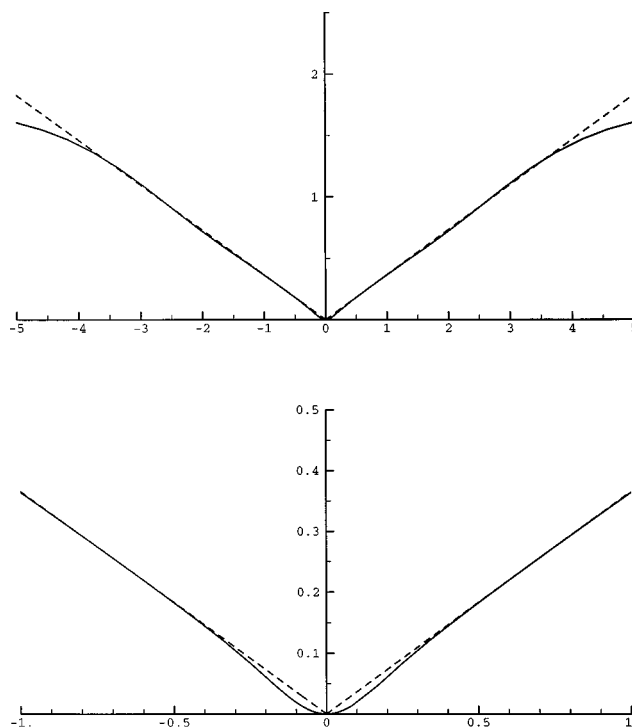


FIG. 3. Six optimized GTGs compared to variational contribution from  $r_{12}$  in He (see the text) over different ranges (solid line: calculated; dashed lines:  $r_{12}$ ).

mized coefficients. The trial wave function for He could thus be written as

$$\Psi = \exp[-\zeta(r_1 + r_2)] \left[ c_0 + \sum_v c_v \exp(-\gamma_v r_{12}^2) \right], \quad (10)$$

where the linear coefficients are variationally optimized. Results obtained in this way are also shown in Table II. Such additional flexibility produces results that are somewhat better than the fitted result alone for the best fits, and noticeably better in cases where the fits were less satisfactory. The GTG terms in the wave function are plotted together with  $c_1 r_{12}$  from Eq. (8) in Fig. 3—this shows some deviation from the linear  $r_{12}$  behavior in the cusp region, interestingly enough.

We now consider a more elaborate trial wave function, where we will see that the variational inclusion of the GTGs gives significantly better results than the use of a GTG fit to linear  $r_{ij}$ . We first recall the general remarks made in Sec. I that the use of a basis set of valence double zeta plus polarization quality was necessary to obtain molecular Hartree–Fock level results that are qualitatively converged. Such a basis set is found to yield about 60%–75% of the valence-shell correlation energy: we would like to find an efficient way to recover the remaining 25%–40%. The suggestion of Klopper and Kutzelnigg<sup>19</sup> can be viewed here as an attempt to augment a wave function for He like

$$\Psi = c_0 1s^2 + c_1 1s2s + c_2 2s^2 + c_3 (2p_x^2 + 2p_y^2 + 2p_z^2) \quad (11)$$

with a linear term to give

TABLE III. He atom variational energies using GTO and GTG basis sets ( $E_h$ ).

Number of GTGs	Highest GTG exponent <sup>a</sup>	Fitting range ( $a_0$ ) <sup>b</sup>	Energy
	SCF energy	-2.86166 <sup>c</sup>	
	CI energy	-2.89748 <sup>d</sup>	
6	27	5	-2.89853
6	27	opt <sup>e</sup>	-2.90198
9	243	5	-2.89851
9	243	opt <sup>e</sup>	-2.90201
15	19683	15	-2.89851
15	19683	opt <sup>e</sup>	-2.90201

<sup>a</sup>Highest exponent of even-tempered sequence with ratio 3.

<sup>b</sup>GTG fit (see text) to linear  $r_{ij}$  from zero to this value.

<sup>c</sup>SCF energy with ANO basis (see text).

<sup>d</sup>CI energy with ANO basis (see text and Eq. 11).

<sup>e</sup>Variationally optimum energy (Eq. 13) using this set of GTGs.

$$\Psi = c_0 1s^2 + c_1 1s2s + c_2 2s^2 + c_3(2p_x^2 + 2p_y^2 + 2p_z^2) + c_4 r_{12} 1s^2. \quad (12)$$

In the present work, we can either replace the linear term with a GTG fit as in Eq. (9), or we could increase the variational flexibility and use a form like

$$\Psi = c_0 1s^2 + c_1 1s2s + c_2 2s^2 + c_3(2p_x^2 + 2p_y^2 + 2p_z^2) + \sum_k d_k \exp(-\gamma_k r_{12}^2) 1s^2, \quad (13)$$

where the  $d_k$  and  $c_i$  are all optimized variationally. These alternatives have been tested using a large primitive GTO basis contracted to  $[2s1p]$  using atomic natural orbitals, and the results are shown in Table III. The SCF energy in this basis is essentially at the Hartree–Fock limit, so that all energy lowering due to other wave function terms represent contributions to the correlation energy. The GTO basis alone yields  $-35.8 mE_h$  for the correlation energy out of an exact correlation energy of  $-42.0 mE_h$ , or 85%. This is, of course, a considerably larger fraction of the correlation energy than would be obtained for larger systems with a basis of this quality, so in one sense He represents a better situation for GTOs alone than would larger systems. The addition of the linear  $r_{12}$  term as a fit by GTGs does *not* result in a very significant energy lowering here: the correlation energy increases in magnitude by only  $1 mE_h$ , giving 88% of the exact result. Using more elaborate fits, over a greater range of  $r_{12}$  and with more exponents, does not help and actually very slightly degrades the results, further emphasizing that the deficiencies in the original GTO-based CI wave function are more than just the failure to describe the cusp behavior. We may thus speculate that adding a linear term to a relatively small basis would not necessarily yield great improvements in the correlation energy, at least not for the typical small basis sets used in quantum chemistry. Further, attempts to refine the approximations used by Klopper and Kutzelnigg<sup>19,22</sup> so that smaller basis sets could be used in

that approach would not appear to be very fruitful, unless perhaps reoptimizing basis sets explicitly for use with linear  $r_{12}$  changes our observations here.

Much better results are obtained by augmenting the GTO basis with GTGs and optimizing their coefficients, as in Eq. (13). Results are shown in Table III. Correlation energies of more than  $-40 mE_h$  are obtained, or more than 96% of the exact result. The number of GTG correlation factors and the exponent range does not seem to be at all critical: the difference between the six-term canonical set with exponents  $\gamma_k$  of 27, 9, 3, 1, 0.333 333, and 0.111 111, and a fifteen-term set extrapolated with six larger exponents and three smaller exponents (all even-tempered with ratio three) is around  $10 \mu E_h$ . The correlation energies we obtain in this way are accurate to almost  $1 mE_h$ , an accuracy that would require multiple  $d$  and  $f$  functions to achieve with a GTO basis. In any event, our He results thus suggest that a profitable way to improve GTO basis set results may be to add a few GTGs (our canonical set of six, say) rather than to include more shells of GTOs with higher angular momentum. In Sec. III we outline a pair function approach along these lines that can be used for MP2 calculations on many-electron systems.

### III. PAIR FUNCTION ANSATZ FOR MP2

As we have noted, our helium results strongly suggest that even though we can fit linear  $r_{ij}$  using an expansion in GTGs, much better results are obtained *when augmenting small GTO sets* by allowing the weights of these geminals to be optimized. This immediately suggests adding terms such as  $\exp(-\gamma_v r_{12}^2) \phi_i \phi_j$  to the pair correlation functions to be used for many-electron systems, just like the addition of  $r_{12} \phi_i \phi_j$  in the approach of Klopper and Kutzelnigg [Eq. (1)]. However, it is not clear that the product of occupied MOs  $\phi_i \phi_j$  is necessarily the optimum factor to include when augmenting modest GTO basis sets that do not even describe the wave function well away from the correlation cusp, nor is it clear that this is the optimum choice from the perspective of computational cost. We therefore suggest a modified form of pair function ansatz

$$w_{ij} = \sum_{a>b} \phi_a \phi_b c_{ij}^{ab} + \sum_v c_{ij}^v \mathcal{Q} \exp(-\gamma_v r_{12}^2) \tilde{\phi}_i \tilde{\phi}_j. \quad (14)$$

The functions  $\tilde{\phi}_i$  could be taken identical to the occupied MOs  $\phi_i$ , but we do not require this: the tilde is used to indicate that these may differ from the corresponding occupied MOs. This allows us the possibility of using different GTO basis sets to represent the MOs  $\tilde{\phi}_i$  and  $\phi_i$ , for example. The use of Gaussian correlation factors in Eq. (14) permits the evaluation of all many-electron integrals that arise without requiring approximations. Of course, it is also possible to exploit approximations where this is desired, as in the use of the various weak orthogonality functionals and strong orthogonality forcing techniques by Szalewicz and co-workers,<sup>29,30</sup> as well as to go beyond the MP2 approximation,<sup>33,34</sup> but the latter is beyond the scope of the present work.

The use of Eq. (14) as a pair-function expansion in practical MP2 calculations requires the development of considerable computer codes to evaluate and manipulate the necessary integrals. Although there are no particular complications, this is not work to undertake lightly based only on He atom calculations as a proof of concept. We are fortunate to have access to the GEMINAL91 program of Szalwicz and collaborators,<sup>44</sup> which provides us with a more immediate way to verify the utility of our approach. We must stress that GEMINAL91 is designed for GTG calculations with full optimization of nonlinear parameters. What we propose to use it for is quite outside its design, and this will impose some constraints on our calculations. One constraint is that it is not possible to use contracted GTOs or GTGs—only primitive (i.e., uncontracted) functions may be used. Second, the pair functions must all be represented as GTGs. Thus, for example, the virtual orbital product term on the right-hand side of Eq. (14) is represented by a (strong-orthogonality projected) “GTG basis” that comprises all symmetry-allowed products of GTOs  $\chi_\mu$  in the original basis

$$\sum_{a>b} \phi_a \phi_b c_{ij}^{ab} = \sum_{a>b} \sum_{\mu\nu} c_{ij}^{ab} C_{\mu a} C_{\nu b} \chi_\mu \chi_\nu = \sum_{\mu\nu} c_{ij}^{\mu\nu} \chi_\mu \chi_\nu, \quad (15)$$

where

$$c_{ij}^{\mu\nu} = \sum_{a>b} c_{ij}^{ab} C_{\mu a} C_{\nu b} \quad (16)$$

and  $\mathbf{C}$  is the matrix of SCF orbital coefficients. Hence the orbital MP2 contribution can be expressed in terms of GTO products  $\chi_\mu \chi_\nu$ , that is, GTGs with no explicit  $r_{12}$  dependence.

The representation of the second term on the right-hand side of Eq. (14) is more complicated. Since contracted GTGs are not implemented in GEMINAL91, we must replace

$$\sum_{\nu} c_{ij}^{\nu} Q \exp(-\gamma_{\nu} r_{12}^2) \tilde{\phi}_i \tilde{\phi}_j \\ \equiv \sum_{\nu} \sum_{\mu\nu} c_{ij}^{\nu} \tilde{C}_{\mu i} \tilde{C}_{\nu j} Q \exp(-\gamma_{\nu} r_{12}^2) \tilde{\chi}_{\mu} \tilde{\chi}_{\nu}, \quad (17)$$

where  $\tilde{\chi}_{\mu}$  is the expansion basis used for the MOs  $\tilde{\phi}_i$ , with

$$\sum_{\nu} \sum'_{\mu\nu} c_{\mu\nu}^{\nu} Q \exp(-\gamma_{\nu} r_{12}^2) \chi_{\mu} \chi_{\nu}. \quad (18)$$

Note that the constraint that the GTOs appear multiplied by their SCF coefficients has been lifted. The prime on the summation in Eq. (18) indicates that the range of the summation is not required to be over all GTOs of the correct symmetry: the terms to be included are at our discretion. This is a convenient notation since in all of our calculations the GTOs used to expand the  $\tilde{\phi}_i$  have been a subset of the full GTO basis. Including all GTOs would anyway greatly increase the size of the geminal basis sets to be employed, and we have restricted the sums over GTOs in Eq. (18) to include only the GTOs that have the largest coefficients in the original MOs  $\phi_i$  and  $\phi_j$ . Full details are given in Sec. IV. We may also

TABLE IV. Ne atom MP2 pair-correlation energies ( $mE_h$ ): cc-pVDZ basis.

Pair	GTO basis	+6 GTGs <sup>a</sup>	+6 GTGs <sup>b</sup>	% <sup>c</sup>	Limit <sup>d</sup>
Valence:					
<sup>1</sup> (2s2s)	-8.5	-11.7	-11.8	98.3	-12.0
<sup>1</sup> (2s2p)	-10.2	-18.7	-19.2	95.4	-20.1
<sup>3</sup> (2s2p)	-6.8	-8.0	-8.1	91.3	-8.9
<sup>1</sup> (2p <sub>x</sub> 2p <sub>x</sub> )	-18.1	-22.2	-23.4	87.0	-26.9
<sup>1</sup> (2p <sub>x</sub> 2p <sub>y</sub> )	-11.4	-14.1	-14.8	83.9	-17.6
<sup>3</sup> (2p <sub>x</sub> 2p <sub>y</sub> )	-22.5	-25.6	-27.2	93.5	-29.1
Total	-215.5	-277.2	-290.0	90.6	-320.2
Core:					
<sup>1</sup> (1s1s)	-27.7	...	-39.0	96.9	-40.2
<sup>1</sup> (1s2s)	-2.6	...	-3.6	90.1	-4.0
<sup>3</sup> (1s2s)	-1.2	...	-1.6	98.4	-1.6
<sup>1</sup> (1s2p)	-0.5	...	-2.4	86.5	-2.7
<sup>3</sup> (1s2p)	-2.8	...	-4.5	96.4	-4.6
Total	-256.8	...	-354.6	91.4	-387.8

<sup>a</sup>Single GTO used to represent occupied MOs in Eq. 18.

<sup>b</sup>Multiple GTOs used to represent occupied MOs in Eq. 18.

<sup>c</sup>Percentage of MP2 limit recovered by 6 GTG calculation with multiple GTO representation of occupied orbitals.

<sup>d</sup>References 5, 54.

note that the use of Eq. (18) with fully optimized values of the coefficients  $c_{\mu\nu}^{\nu}$  may give a more flexible wave function, in essence including also MO terms like  $\exp(-\gamma_{\nu} r_{12}^2) \phi_a \phi_b$ , and thus may yield a lower MP2 energy than the original ansatz of Eq. (14). It is not straightforward to quantify this here, but as we show below there is reason to believe this extra flexibility contributes very little to the energy.

## IV. RESULTS USING GTGS

### A. Ne atom

The neon atom provides a good initial test case for our proposed method. There are several very accurate estimates of the valence-shell and total MP2 correlation energies which provide solid benchmarks (see Ref. 5 and references therein), and the symmetry reduces the number of distinct pairs that must be considered, as well as speeding up the calculation because all integrals are one center. Results for Ne valence-shell pair correlation energies are given in Tables IV and V. In Table IV we list the distinct pair energies obtained with the Dunning cc-pVDZ basis set<sup>2</sup> (run *uncon-*

TABLE V. Ne atom 2p<sub>x</sub><sup>2</sup> MP2 pair-correlation energy ( $mE_h$ ).

Basis	Pair energy
cc-pVDZ <sup>a</sup>	-18.1
cc-pVDZ+6 GTGs <sup>b</sup> /1 GTO per occupied MO	-22.2
cc-pVDZ+6 GTGs <sup>b</sup> /2 GTO per occupied MO	-23.4
cc-pVDZ+8 GTGs <sup>c</sup> /1 GTO per occupied MO	-22.3
cc-pVDZ+10 GTGs <sup>d</sup> /1 GTO per occupied MO	-22.3
Limit	-26.9 <sup>e</sup>

<sup>a</sup>Used uncontracted in all calculations here.

<sup>b</sup>Canonical set: exponents 27, 9, 3, 1, 0.333333, 0.111111.

<sup>c</sup>Exponents 81, 27, 9, 3, 1, 0.333333, 0.111111, 0.037037.

<sup>d</sup>Exponents 32, 16, 8, 4, 2, 1, 0.5, 0.25, 0.125, 0.0625.

<sup>e</sup>References 5, 54.



tracted and with a Cartesian  $d$  set—as noted above these are requirements in GEMINAL91). Results are given for the GTO basis alone and augmented by six GTG correlation factors with exponents of 27, 9, 3, 1, 0.333 333, and 0.111 111. Such results are denoted “+6 GTGs” in the tables: this is a convenient label although strictly speaking we are introducing six geminal correlation factors multiplying occupied MOs or approximations thereto. The number of GTGs expressed as products of correlation factors and GTO basis functions, as in Eq. (18), can be larger than six. Where GTGs are used, we have used two different sets of GTOs in Eq. (18) to represent the occupied orbitals. The single GTO approximation involves a compromise exponent that is a crude fit to the  $2s$  or  $2p$  SCF orbitals; this compromise exponent is in neither case represented in the original basis. Examination of the cc-pVDZ set itself shows that the  $2s$  and  $2p$  orbitals are both dominated by two GTOs (the outermost exponents in both cases), and in the second set of GTG calculations shown in Table IV these two  $s$  or two  $p$  GTOs were included in the expansion of Eq. (18).

The fraction of the MP2 valence-shell correlation energy recovered by the cc-pVDZ basis alone here is modest: 67%, and this reflects the use of an uncontracted set—in the usual  $[3s2p1d]$  contracted form only 58% is recovered. Adding six GTGs and using a single-term approximation to the occupied orbitals as in Eq. (18) we recover 87%, and using a more accurate two-term approximation to the occupied orbitals gives 91%. That is, we have reduced the error in the correlation energy by almost a factor of 4. It is of some interest to study the individual pair energies. The  $2s^2$  pair and the  $2s2p$  interpair singlet and triplet are all rather close to their limiting values when GTGs are included in the basis, even though the interpairs particularly show significant errors in the GTO basis alone. The  $2s2p$  singlet interpair correlation energy is substantially improved by the GTGs, since the GTO value is only about half the estimated limit, whereas the error in the value when GTGs are used is only 5%. The various  $2p^2$  pairs are not well described by the cc-pVDZ basis in comparison to pairs involving the  $2s$  orbital. The slower convergence of the  $2p^2$  pairs is already well known.<sup>34</sup> Inclusion of six GTGs once again effects a dramatic improvement in the pair energies, although the singlet pairs are still in error by about  $2 mE_h$ . For the pairs involving the  $2s$  orbital the difference between the use of single-term and two-term GTO approximations to the occupied orbitals, as in Eq. (18), is only tenths of a mhartree. For the  $2p^2$  pairs the difference is larger and exceeds  $1.5 mE_h$  in one case, but we will see later that this is not typical. We can reasonably assert that the main result of adding more GTOs is to improve the representation of the occupied orbital product, rather than describing terms such as  $\exp(-\gamma_v r_{12}^2)\phi_a\phi_b$ .

In Table V we show the convergence of the  $2p_x^2$  intra-pair correlation energy with different GTG basis sets. In addition to the results of Table IV we show the effect of using more GTGs. These are combined with single GTO approximations to the occupied orbitals. Neither the expansion of the range of geminal exponents (by adding functions with exponents of 81 and 0.037 037 at either end of the canonical

TABLE VI. Ne atom MP2 pair-correlation energies ( $mE_h$ ): cc-pVTZ basis.

Pair	GTO basis	6 GTGs	% <sup>a</sup>	Limit <sup>b</sup>
<sup>1</sup> ( $2s2s$ )	-10.3	-12.0	99.6	-12.0
<sup>1</sup> ( $2s2p$ )	-15.4	-20.0	99.1	-20.1
<sup>3</sup> ( $2s2p$ )	-8.2	-8.7	97.9	-8.9
<sup>1</sup> ( $2p_x2p_x$ )	-22.7	-26.3	97.9	-26.9
<sup>1</sup> ( $2p_x2p_y$ )	-14.1	-17.0	96.8	-17.6
<sup>3</sup> ( $2p_x2p_y$ )	-27.2	-28.6	98.3	-29.1
Total	-273.1	-314.0	98.1	-320.2

<sup>a</sup>Percentage of MP2 limit recovered by GTO basis augmented with 6 GTGs.

<sup>b</sup>References 5, 54.

even-tempered sequence) nor the use of a denser coverage of the canonical exponent range lead to significant improvement of the pair-correlation energy. Indeed, the improvement of the occupied orbital product by using more GTOs changes the pair energy by considerably more than these exponent adjustments.

Table IV also contains results for pair-correlation energies involving the Ne  $1s$  core orbital. The GTO basis is not expected to perform even as well as it does for the valence-shell pairs here, since no attempt has been made to augment the basis with the high-exponent functions needed to describe core correlation. Of course, running the GTO basis uncontracted helps, since the innermost  $p$  functions and various  $s$  functions can contribute to the correlating orbitals. The contracted cc-pVDZ basis recovers almost no core correlation at all in fact: only  $-2.1 mE_h$  from all pairs involving the  $1s$  orbital—the  $1s^2$  pair itself has a pair-correlation energy of only  $-0.25 mE_h$  in the contracted basis, compared to  $-27.7 mE_h$  in the uncontracted basis. The same six GTGs that improve the valence-shell pair energies so dramatically play a similar role here, giving a  $1s^2$  pair-correlation energy only  $1 mE_h$  from the exact result, for example. This is consistent with the observation of Klopper<sup>5</sup> that with the linear  $r_{ij}$  method it is less critical to have core-correlating GTOs in the basis, although Klopper's best results are obtained, like those here, with an uncontracted basis. It is difficult to say more without performing calculations using contracted sets augmented with GTGs, which is not possible here. Finally, we note that three GTOs (the fifth, sixth, and seventh with exponents in descending order) were used to represent the  $1s$  orbital in Eq. (18).

Our GTG sets are thus constructed by taking products of our canonical list of six GTG correlation factors and multiplying them by selected products of GTOs. The use of a smaller GTO set in GTG calculations has commonly been done in the opposite fashion, using a small GTO set to represent the Fock operator for use with a large set of GTGs.<sup>45</sup> Our approach has more in common with the first phase [use of a GTG fit to the product  $r_{12}\phi_i\phi_j$  as in Eq. (6)] of the work of Bukowski and co-workers,<sup>40</sup> where a smaller GTO set is used initially but nonlinear optimization of the GTGs is employed. We regard it as desirable to avoid nonlinear optimization even if this requires the use of larger GTG basis sets.

In Table VI we list pair-correlation energies obtained using the larger Dunning cc-pVTZ basis.<sup>2</sup> Again, the basis is

TABLE VII. Ne atom MP2 valence-shell correlation energies ( $mE_h$ ).<sup>a</sup>

Basis	Pair energy
cc-pVDZ	-185.5
cc-pVDZ (uncontracted, Cartesians)	-215.5
cc-pVDZ (uncontracted, Cartesians)+6 GTGs	-290.0
cc-pVTZ	-264.3
cc-pVTZ+linear $r_{ij}$ <sup>b</sup>	-298.8
cc-pVTZ (uncontracted, Cartesians)	-273.1
cc-pVTZ (uncontracted, Cartesians)+6 GTGs	-314.0
cc-pVTZ (uncontracted)+linear $r_{ij}$ <sup>b</sup>	-298.8
cc-pVQZ	-293.6
cc-pVQZ+linear $r_{ij}$ <sup>b</sup>	-310.0
cc-pVQZ (uncontracted)+linear $r_{ij}$ <sup>b</sup>	-312.7
cc-pV5Z	-306.2
cc-pV5Z+linear $r_{ij}$ <sup>b</sup>	-314.5
cc-pV5Z (uncontracted)+linear $r_{ij}$ <sup>b</sup>	-316.2
(15s 9p 7d 5f 3g 1h) <sup>b</sup>	-309.0
(15s 9p 7d 5f 3g 1h)+linear $r_{ij}$ <sup>c</sup>	-320.0
(18s 13p 6d 5f 4g)	-306.8
(18s 13p 6d 5f 4g 3h)	-311.8
(18s 13p 6d 5f 4g 3h 2i)	-313.8
Extended GTG set with nonlinear optimization <sup>d</sup>	-317.6
CBS extrapolation <sup>e</sup>	-317.5
Limit <sup>f</sup>	-320.2

<sup>a</sup>Spherical harmonic basis functions except as noted.

<sup>b</sup>W. Klopper (unpublished).

<sup>c</sup>Reference 5.

<sup>d</sup>Reference 34.

<sup>e</sup>Reference 14.

<sup>f</sup>References 5, 54.

used uncontracted, and Cartesian polarization functions are used. The GTO basis MP2 valence-shell correlation energy here is  $-273.1 mE_h$ , or 85% of the exact value. (Running this basis contracted as recommended by Dunning and using spherical harmonic GTOs gives a somewhat smaller correlation energy, as listed in Table VII, but the difference is less than  $9 mE_h$ , much smaller than the analogous difference for the cc-pVDZ set.) Augmenting the GTO set with six GTG correlation factors for each pair-correlation energy calculation gives a MP2 value of  $314.0 mE_h$ . This is more than 98% of the MP2 limit: an impressive result for such a simple augmentation of a medium-sized basis. In these calculations the outermost two  $s$  and/or three  $p$  GTOs are used in the expansion of Eq. (18). The individual pair-correlation energies show similar trends to those seen in the cc-pVDZ basis calculations. Pairs involving the  $2s$  orbital are very well described and the pair energies appear converged to within one or two tenths of a mhartree. Pairs involving only the  $2p$  orbitals are less well converged, but the differences are still well below  $1 mE_h$ . In another attempt to assess how the number of GTOs used in Eq. (18) affects the calculation, we have computed the  $2p_x^2$  intrapair energy using all five primitive  $p$  GTOs. The difference from the calculation with three  $p$  GTOs is less than  $0.1 mE_h$ , which again suggests that the contribution from virtual orbital product terms like  $\exp(-\gamma_v r_{12}^2) \phi_a \phi_b$  is negligible.

To summarize our Ne results and to allow a comparison with other basis sets we have listed a number of MP2 results

for the valence-shell correlation energy in Table VII. It is noteworthy that our GTG-augmented cc-pVTZ basis calculation recovers more correlation than *any* GTO basis set in Table VII, even including sets containing multiple  $i$  functions. This includes not only the correlation-consistent cc-pV5Z basis<sup>2</sup> but also the uncontracted (15s9p7d5f3g1h) basis constructed by Klopper,<sup>5</sup> which must be close to saturation in the  $d$  and  $f$  spaces at least. The MP2-R12 approach gives a result within a mhartree of the MP2 limit, although this is based on the uncontracted (15s9p7d5f3g1h) set. MP2-R12 calculations based on various correlation-consistent basis sets are also given in Table VII. Only the cc-pV5Z with linear  $r_{ij}$  terms outperforms the GTG-augmented cc-pVTZ set, but we should emphasize here that the correlation-consistent basis sets are not well suited for use in the MP2-R12 method and are not at all the optimum choice of GTO set of the given size for use with linear  $r_{ij}$ , as discussed by Klopper and co-workers.<sup>46</sup> The (18s13p6d5f4g3h2i) set of Almlöf and Taylor<sup>17</sup> should be close to saturation for the  $d$ ,  $f$ , and  $g$  spaces, and gives an idea of the contribution of  $i$  functions, which lower the energy by only  $2 mE_h$  compared to the same basis without  $i$  functions. This may be compared in turn with the energy lowering of the  $h$  functions, which is  $5 mE_h$  compared to the basis with up to  $g$  functions only. The slow convergence with angular momentum is very evident in these results. Even the set containing  $i$  functions does not quite match the result obtained with the cc-pVTZ set augmented with our six GTGs. It is hardly feasible to extrapolate the effect of adding these GTGs to the cc-pVQZ set from just the cc-pVDZ and cc-pVTZ results in Table VII, but it is certainly tempting to believe that this would give a correlation energy within  $1 mE_h$  of the valence MP2 limit.

Several methods included in the comparisons in the work by Klopper<sup>5</sup> (such as the finite element approach or partial-wave expansions) give similar or even slightly better results than MP2-R12, but these methods are not applicable to polyatomic molecules and are not listed here. The complete basis set (CBS) extrapolation<sup>12-15</sup> is a system of corrections developed by comparing computed atomic pair-correlation energies to estimated limit values. For Ne this extrapolation (which costs essentially nothing beyond the original GTO basis MP2 calculation) is in very good agreement with the MP2 limit, although one might hope that this would be the case for an atom, given the atomic origins of the extrapolation. For molecules the error in the CBS extrapolation is somewhat larger, similar in fact to the error in our GTG-augmented cc-pVTZ basis results for Ne.

## B. Water molecule

The recovery of 98% of the Ne valence-shell MP2 correlation energy by a simple extension of a cc-pVTZ basis strongly suggests that GTGs offer much promise in electronic structure calculations. A skeptical observer, however, might point to the results presented so far as being exclusively for atoms, and that a molecular example would be highly desirable to allay fears that the approach works well

TABLE VIII. H<sub>2</sub>O pair-correlation energies (mE<sub>h</sub>): cc-pVDZ basis.

Pair	GTO basis	% <sup>a</sup>	6 GTGs	% <sup>b</sup>	Limit <sup>c</sup>
<sup>1</sup> (2a <sub>1</sub> 2a <sub>1</sub> )	-10.0	75.2	-12.6	94.7	-13.3
<sup>1</sup> (1b <sub>2</sub> 1b <sub>2</sub> )	-20.6	80.5	-24.2	94.5	-25.6
<sup>1</sup> (3a <sub>1</sub> 3a <sub>1</sub> )	-18.7	72.5	-24.2	93.8	-25.8
<sup>1</sup> (1b <sub>1</sub> 1b <sub>1</sub> )	-18.4	70.0	-23.3	88.7	-26.3
<sup>1</sup> (2a <sub>1</sub> 1b <sub>2</sub> )	-13.8	64.8	-20.4	95.8	-21.3
<sup>3</sup> (2a <sub>1</sub> 1b <sub>2</sub> )	-6.9	85.2	-7.7	94.2	-8.1
<sup>1</sup> (2a <sub>1</sub> 3a <sub>1</sub> )	-10.6	59.9	-16.7	94.8	-17.7
<sup>3</sup> (2a <sub>1</sub> 3a <sub>1</sub> )	-6.8	80.0	-7.8	91.5	-8.5
<sup>1</sup> (2a <sub>1</sub> 1b <sub>1</sub> )	-10.9	57.9	-17.8	93.9	-18.9
<sup>3</sup> (2a <sub>1</sub> 1b <sub>1</sub> )	-7.2	76.6	-8.5	90.6	-9.4
<sup>1</sup> (1b <sub>2</sub> 3a <sub>1</sub> )	-13.7	77.0	-16.6	93.2	-17.8
<sup>3</sup> (1b <sub>2</sub> 3a <sub>1</sub> )	-19.8	83.2	-22.1	92.5	-23.8
<sup>1</sup> (1b <sub>2</sub> 1b <sub>1</sub> )	-9.6	65.8	-12.5	85.8	-14.6
<sup>3</sup> (1b <sub>2</sub> 1b <sub>1</sub> )	-20.8	80.9	-23.6	91.8	-25.7
<sup>1</sup> (3a <sub>1</sub> 1b <sub>1</sub> )	-10.9	64.1	-14.7	86.9	-17.0
<sup>3</sup> (3a <sub>1</sub> 1b <sub>1</sub> )	-21.0	78.7	-24.3	91.0	-26.7
Total	-219.8	73.1	-277.0	92.1	-300.5

<sup>a</sup>Percentage of MP2 limit recovered by GTO basis calculation.<sup>b</sup>Percentage of MP2 limit recovered by GTO basis augmented with 6 GTGs.<sup>c</sup>Reference 5.

only for atoms, and to demonstrate the potential for applications in molecular physics and chemistry as well as atomic physics. We have therefore computed the MP2 valence-shell correlation energy for the molecule H<sub>2</sub>O, pair energies for which are listed in Table VIII. The oxygen atom is at the coordinate origin and the hydrogen atoms are located at ( $\pm 1.430\ 432a_0$ , 0,  $1.107\ 160a_0$ ). This is the same geometry used by both Bukowski and co-workers<sup>36</sup> in their extensive optimized GTG basis calculation and by Klopper.<sup>5</sup> The GTO basis is the cc-pVDZ set of Dunning<sup>2</sup> for both O and H, run uncontracted and with Cartesian polarization functions. The occupied orbital product was expanded in GTOs as in Eq. (18): the number of GTOs needed to represent each MO was estimated by inspection of the MO coefficients, and to assist anyone trying to reproduce these calculations the exponent values and centers of the GTOs used to approximate each MO in Eq. (18) are listed in Table IX. We emphasize that all these GTOs are part of the original basis and neither their location nor their exponents were adjusted in any way.

The GTO basis alone recovers about 73% of the MP2 valence-shell limit; augmented with the canonical six GTG correlation factors this fraction rises to more than 92%. This is actually slightly *better* than the Ne result in the same basis, probably because the H<sub>2</sub>O correlation energy is smaller than that of Ne to start with, and the calculations appear to con-

TABLE IX. H<sub>2</sub>O: GTOs used in approximating the occupied orbitals.<sup>a</sup>

2a <sub>1</sub>	1b <sub>2</sub>	3a <sub>1</sub>	1b <sub>1</sub>
O(s 1.013)	O(p <sub>x</sub> 1.046)	O(s 1.013)	O(p <sub>y</sub> 1.046)
O(s 0.3023)	O(p <sub>x</sub> 0.2753)	O(s 0.3023)	O(p <sub>y</sub> 0.2753)
	H(s 0.4446)	O(p <sub>z</sub> 1.046)	
		O(p <sub>z</sub> 0.2753)	
		H(s 0.4446)	

<sup>a</sup>See Eq. 18 in the text.

verge more rapidly (the GTO basis alone also performs better for H<sub>2</sub>O than Ne). An inspection of the pair-correlation energies suggests that pairs containing the 1b<sub>1</sub> lone-pair orbital are harder to describe than the others, which is consistent with the greater difficulties of describing 2p<sup>2</sup> pairs in Ne (the H<sub>2</sub>O 1b<sub>1</sub> orbital is almost pure 2p<sub>y</sub>). For example, the 1b<sub>1</sub><sup>2</sup> intrapair energy using the GTGs is only 85% of the limit value, compared to 94% or more for the other intrapairs. The situation is similar for the interpairs. We would expect, from comparing with Ne, that the use of a cc-pVTZ basis augmented with our canonical set of GTGs might recover 99% or more of the H<sub>2</sub>O MP2 valence-shell correlation energy, but it is not feasible to test this hypothesis by mimicking the ansatz of Eq. (14) using GEMINAL91 with a basis of this size.

## V. DISCUSSION

One of the first questions that must be asked about any proposed new method is the computational cost. For the calculations listed above on Ne and H<sub>2</sub>O, those including GTGs required about 25% more computer time than those without, but this is not remotely an honest comparison because of the need to construct GTGs for the virtual orbital product terms in Eq. (14) when using GEMINAL91. This greatly inflates the time required to compute a GTO basis MP2 energy compared to conventional programs. A more accurate picture can be obtained by considering the scaling of the work required. For a MP2 method that exploits the weak orthogonality functional of Szalewicz and co-workers<sup>29,30</sup> (requiring only three-electron integrals), the integral calculation scales as  $N_{\text{GTG}}N_{\text{GTO}}^4$  and  $N_{\text{GTG}}^2N_{\text{GTO}}^2$ . If the full GTO basis were used in the construction of the GTGs in Eq. (14) (that is, all  $\tilde{\phi}_i$  are taken as  $\phi_i$ ) these expressions both reduce to  $N_{\text{GTO}}^6$ . Note that since we use the same correlation factors for each pair correlation function there is no dependence on the number of pairs here. Alternatively, we may use a reduced GTO set or some other different or approximate representation of MOs  $\tilde{\phi}_i$  in Eq. (14), similar to the spirit of the ‘‘dual basis sets’’ for correlated calculations used by Jurgens-Lutovsky and Almlöf.<sup>47</sup> In this case,  $N_{\text{GTG}}$  will depend explicitly on the number of pairs,  $n^2$  for  $n$  occupied MOs, and on the square of the number of GTOs  $\tilde{N}_{\text{GTO}}$  used to represent the  $\tilde{\phi}_i$ . The scaling would then be  $n^2N_{\text{GTO}}^2N_{\text{GTO}}^4$  and  $n^4\tilde{N}_{\text{GTO}}^4N_{\text{GTO}}^2$ . In most cases, where  $n \ll N_{\text{GTO}}$ , the former term will dominate. Note that for a given system, the work required as a larger basis set is used scales the same way for our GTG-augmented basis set as for a GTO basis:  $N_{\text{GTO}}^4$ .

Another advantage of our suggested GTG set arises in the calculation of energy derivatives. Since our GTGs have no dependence on nuclear centers other than those that already appear in the GTO basis itself, there are no complications to the expressions for the forces on the nuclei, or the harmonic force constants from other centers appearing in the GTGs. Hence energy derivatives involve no additional complications from our GTGs.

Our theoretical presentation and results here have been cast in terms of MP2 as the many-electron treatment. This is convenient as the simplest approach, but we wish to stress

that there are no fundamental restrictions preventing these GTG basis functions from being used in *any* correlation treatment that involves pair excitations of the type shown in Eq. (14), just as is the case for the ansatz of Klopper and Kutzelnigg in principle, or the general GTG treatment of Szalewicz and co-workers. Kutzelnigg and co-workers<sup>20,48</sup> have developed coupled-cluster analogues of the Klopper and Kutzelnigg method, and Szalewicz and co-workers<sup>33,34</sup> have implemented both MP3 and coupled-cluster with double excitations using pair functions expanded in arbitrary sets of GTGs. To take a historical perspective, much of this work can be viewed as practical implementations of the very general methods outlined by Sinanoğlu in his “many-electron theory” (MET) in the early 1960s.<sup>49,50</sup> This was the stimulus for the early GTG work by Pan and King,<sup>27,28</sup> for example. Sinanoğlu’s MET was extended by Silverstone and Sinanoğlu<sup>51,52</sup> to open-shell and multireference cases, providing one possible route to using functions that depend on the interelectronic distance in these situations as well. We are currently implementing many-electron integrals over GTGs in our SCF, MCSCF, and coupled-cluster molecular properties program DALTON<sup>53</sup> in order to investigate these possibilities further. This will allow us to use contracted GTO basis sets and to resolve conclusively such issues as the representation of the occupied orbital term in Eq. (14) and the ability of GTGs to describe core correlation accurately in basis sets that do not include core-correlating GTOs. Going further, the opportunity to obtain essentially basis set limit correlation energies for multireference methods is an intriguing one, and we hope our work here will stimulate other groups to consider the use of GTG basis sets in their methodological work.

## VI. CONCLUSIONS

We have shown that it is possible to achieve mhartree accuracy in pair-correlation energies with a straightforward extension of Gaussian orbital basis sets by a few functions with a Gaussian dependence on the interelectronic coordinate. In this way we are confident we can obtain more than 90% of the valence-shell correlation energy even with a modest GTO basis of split-valence plus polarization type; with larger basis sets with two or more polarization sets we expect 98%–99% of the correlation energy. We have also shown that GTG correlation factors can be used to approximate linear  $r_{ij}$  to essentially arbitrary accuracy, providing a method analogous to GTO expansions of STOs to evaluate many-electron multicenter integrals involving linear  $r_{ij}$  terms.

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