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Optimized auxiliary basis sets for explicitly correlated methods

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Auxiliary basis sets for use in explicitly correlated MP2-F12 and CCSD-F12 methods, in which three- and four-electron integrals are approximated as products of two-electron integrals through the resolution of the identity (RI), have been optimized for the elements H, B–Ne, and Al–Ar. Fully matched to the recently constructed cc-pVnZ-F12 orbital basis sets, these new auxiliary basis sets result in very small RI errors, as exemplified by the calculated atomization energies of 42 molecules at the MP2-F12 level. Their utility in calculating smooth potential energy surfaces is also demonstrated in calculations of the spectroscopic properties of several diatomic molecules. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3009271]

I. INTRODUCTION

Electron correlation treatments based on a one-electron orbital expansion of the molecular wave function are capable of yielding very high accuracy. However, when using such methods the energy converges frustratingly slowly to the complete basis set (CBS) limit as the maximum angular momentum in the orbital basis set is increased—a problem which is exacerbated by the steep computational scaling of the correlation method. The slow convergence is due to the poor description of the correlation cusp by these methods and can be remedied by the explicit inclusion of interelectronic coordinates into the wave function. This was first done by Hylleraas for the helium atom almost 80 years ago[1] but such an approach becomes intractable very quickly for larger systems, as the difficult calculation of numerous three- and four-electron integrals is necessary. The first practical implementation of this approach was carried out by Klopper and Kutzelnigg[2] at the MP2 level of theory (MP2-R12), where they employed the resolution of the identity (RI) approximation to simplify these integrals into products of no more than two-electron integrals. This initial work utilized the orbital basis set (OBS) for the RI, which required large basis sets and was still computationally costly. More recently Klopper and Samson[3] utilized a separate auxiliary basis set (ABS) to fulfill the RI approximation, which allowed for the use of relatively small orbital basis sets in explicitly correlated calculations. This was subsequently extended by Valeev,[4] who pointed out that the RI approximation is most accurate when the ABS exactly spans the OBS, and hence the ABS should at least contain the OBS. The resulting complementary ABS (CABS) approach, and, in particular, CABS+ which we will not distinguish from CABS in this paper, involves constructing the union of an ABS with the OBS, deleting linearly dependent functions through a singular valued decomposition (SVD) analysis, and then forming the orthogonal complement to the OBS for use in the RI. When combined with new nonlinear correlation factors,[5,6] as well as density fitting schemes,[7,8] local correlation treatments,[9,10] and other recent improvements,[11,12] very efficient implementations of explicitly correlated (F12) MP2 and CCSD(T) methodologies have been reported.[12–14]

The goal of the present work is to optimize accurate ABSs for use in CABS-based explicitly correlated methods. Only functions complementary to a chosen orbital basis set are actually optimized, yielding relatively small ABSs with well-controlled RI errors. The present work focuses on the cc-pVnZ-F12 (n=D, T, Q) orbital basis sets.[15] Analogous ABSs optimized for use with the aug-cc-pVnZ (n=D, T, Q, 5) series[16] will be reported separately. An additional benefit of the present approach is related to numerical issues that can arise in the general application of the CABS procedure, which can impact the smoothness of potential energy surfaces (PESs). In the usual case after the union of the ABS and OBS, the application of the SVD generally results in the deletion of a few linearly dependent basis functions based on some threshold criteria. Unfortunately there is no guarantee that the same functions are deleted at nearby points on a PES. In a few cases we have observed small discontinuities in PESs when a large ABS is utilized in this manner, which subsequently affects the accurate calculation of spectroscopic constants and properties that depend on derivatives of the PES. The direct optimization of the CABS basis set as in this work generally obviates the need to delete any linearly dependent functions and necessarily leads to smooth PESs.

II. METHODOLOGY

The general computational details of this work are almost identical to those in Ref. 15, but the most pertinent are repeated here for convenience and clarity. In all calculations, a development version (v2006.4 or v2008.2) of the MOLPRO suite of programs[17] was used. Pure spherical harmonic basis functions were used throughout, and only the valence electrons were correlated. Optimization of the exponents was performed using the Nelder–Mead simplex algorithm[18] with a convergence criterion of 10^{-7}. Using the cc-pV5Z/JKFIT ABSs of Weigend[19] for the exchange and Fock integrals and the aug-cc-pV5Z/MP2FIT basis set of Hättig[20] for the re-

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maining two-electron integrals, density fitting was employed in MP2-F12 calculations.[8,9] As the JKFIT basis sets for Ne and Ar are not available, they were obtained by extrapolating the analogous O, F and S, Cl exponents, respectively. The optimal geminal exponents, β, as determined in Ref. 15 were used throughout (0.9 for VDZ-F12, 1.0 for VTZ-F12 and 1.1 for VQZ-F12) and the 3C ansatz,[12] with the correlation factor $f_{12} = \exp(-\beta r_{12})$ fitted to an expansion of six Gaussians, was used. It should be noted at this point that tests at the MP2-F12/cc-pVTZ-F12 level of theory with $\beta = 1.4$ indicated that the accuracy of the ABSs developed in this work do not appear to depend on the choice of β.

Our goal in this work was straightforward: to augment the cc-pVnZ-F12 orbital basis sets with as few uncontracted functions as possible to minimize the RI error with respect to a given reference set. Since the CABS procedure utilizes the union of the ABS with the OBS, the present optimizations only involved the functions complementary to a given OBS. In order to determine the resulting RI errors, as well as in the definition of the optimization criterion defined below, a large reference ABS was chosen that consisted of the uncontracted 18s13p (B–Ne) and 20s15p (Al–Ar) sets of Partridge[21] combined with the $dfghi$ functions from the standard aug-cc-pV6Z basis sets.[22] Furthermore, a set of s and p diffuse functions, as well as 2 (3) tight d and 1 (2) tight f functions, were added for B–Ne (Al–Ar) in an even tempered manner. The reference ABS for hydrogen consisted of the uncontracted aug-cc-pV6Z basis set without h-type functions. A single tight p function was then added to this set. When the reference ABS was used in the optimization procedure, the default CABS thresholds in MOLPRO were utilized, namely $\max(10^{-7}, s_{\max} \times 10^{-8})$, where $s_{\max}$ is the largest eigenvalue of the CA overlap matrix.[12]

Previous work in the context of the RI-MP2 method[23] noted that ABS functions could, in principle, be optimized for the quantity $\delta\text{RI} = |E_{\text{MP2}} - E_{\text{MP2,RI}}|$, but this was not pursued due to the possibility of a more efficient approach that could utilize existing analytical gradient technology. Initial efforts in this work attempted an analogous scheme involving the absolute energy difference between MP2-F12 calculations using approximate and reference ABSs, i.e., $\delta\text{RI} = |E_{\text{MP2-F12,RI\_REF}} - E_{\text{MP2-F12,RI\_OPT}}|$. Based on our initial efforts we can indeed confirm that such a method is less than ideal, but for two practical reasons. First, as a function of the basis set exponents, the value of δRI was found to seemingly have many small discontinuities and as such both gradient-based (i.e., BFGS) and energy-based (simplex) algorithms frequently failed to converge to a minimum. In principle, this could be due to the inherent sensitivity of the reference ABS calculations to the chosen CABS thresholds. Second, and most importantly, optimizing exponents in this way seemed to introduce an explicit ansatz dependence. In preliminary optimizations, the fixed-amplitude diagonal ansatz of Ten-no[6] was used; this has the advantages of being both orbital invariant and free of geminal basis set superposition error. However, when ABSs optimized with this ansatz were used to calculate MP2-F12/3C energies,[12] the RI errors with this latter ansatz were an order of magnitude larger than those obtained using fixed amplitudes. Thus optimization di-

rectly on the energy difference seems to involve not only the accuracy of the F12 integrals but also some error cancellation from the ansatz itself.

To overcome these difficulties, a functional based on the diagonal elements of the **V** and **B** matrices encountered in F12 theory[12] was utilized:

$$\delta\text{RI} = \sum_{ij} \frac{(V_{ij,ij}^{\text{RI}} - V_{ij,ij}^{\text{RI}_{\text{ref}}})^2}{V_{ij,ij}^{\text{RI}_{\text{ref}}}} + \frac{(B_{ij,ij}^{\text{RI}} - B_{ij,ij}^{\text{RI}_{\text{ref}}})^2}{B_{ij,ij}^{\text{RI}_{\text{ref}}}}. \quad (1)$$

The **V** and **B** matrices contain the many-electron integrals approximated by the RI and the quantity in Eq. (1) is always positive. As in conventional MP2 ABS optimizations,[23] which are based on the MP2 energy expression, Eq. (1) was motivated by the energy expression for the 2*A MP2-F12 ansatz,[9] and hence δRI of Eq. (1) also has units of energy. In particular, it was also sufficiently sensitive to the accuracy of the ABS used for the RI approximation to yield well-behaved optimizations. Using Eq. (1) the ABS exponents of B–Ne and Al–Ar were optimized based solely on atomic calculations, which differed from the approach used for the cc-pVnZ-F12 orbital basis sets.[15] In addition to being much less computationally demanding, initial tests indicated that the exponents obtained in the atomic optimizations were very similar to those determined in molecular calculations.

To determine how many functions were required in the ABS for a particular choice of OBS, a similar prescription to that used in the construction of the correlation consistent orbital basis sets (including the F12 variants) was used. For each angular momentum, successive uncontracted functions were added and optimized with respect to the reference RI that was truncated to contained only functions involving the angular momentum being optimized. ABS functions were included until δRI was below a chosen threshold (which was dependent on the orbital basis set and the angular momentum of the functions being optimized). The s, p, and d functions were treated simultaneously, both to reduce the number of calculations required and to account for the strong coupling between the functions of these angular momenta. In addition, the ratio of an ABS exponent to an existing OBS exponent of the same angular momentum was constrained to be ≥ 1.5 in all cases to minimize linear dependency problems. As an example for the cc-pVTZ-F12 orbital set, the optimization of the final 4s4p4d3f2g ABS for the Ne atom proceeded as follows:

(i)   Optimize a set of 4s4p4d functions using Eq. (1) with a reference RI of size (19s14p8d) as described above.

(ii)   With the 4s4p4d exponents fixed, optimize the exponents of a set of three f-type functions with a reference RI consisting of the 4s4p4d functions from (i) and the (6f) set as described above.

(iii) With these 4s4p4d3f exponents fixed, optimize the remaining two g-type functions with a reference RI consisting of the 4s4p4d3f from (ii) and the (4g) set from above.

After the ABS sets for the first-row elements had been determined as just described, those for hydrogen were optimized using the molecules BH_3, CH_4, NH_3, and H_2O. (A

TABLE I. Number and type of functions included in the ABSs used in this work.

	H	B–Ne	Al–Ar
VDZ-F12/OptRI[a]	$3s3p2d$	$4s4p4d3f1g$	$4s4p4d3f1g$
VTZ-F12/OptRI[a]	$3s3p3d2f$	$4s4p4d3f2g$	$4s4p4d3f2g$
VQZ-F12/OptRI[a]	$3s3p3d2f1g$	$4s4p4d3f2g1h$	$4s4p4d3f2g1h$
Reference[b]	$11s7p5d4f3g$	$19s14p8d6f4g3h2i$	$21s16p9d7f4g3h2i$
VTZ/JKFIT[c]	$4s3p2d1f$	$10s7p5d2f1g$	$13s11p9d3f1g$
VQZ/JKFIT[c]	$4s3p3d2f1g$	$10s7p5d3f2g1h$	$13s11p9d4f2g1h$
aVDZ/MP2FIT[d]	$4s3p2d$	$8s6p5d3f$	$10s8p6d4f$
aVTZ/MP2FIT[d]	$5s4p3d2f$	$9s7p6d4f2g$	$11s9p8d6f3g$
aVQZ/MP2FIT[d]	$6s5p4d3f2g$	$9s8p7d6f4g2h$	$12s10p9d7f4g2h$

[a]This work.
[b]See the text.
[c]Reference 19.
[d]Reference 26.

larger test set including second-row hydrides was also investigated, but was found to yield very similar results for substantially more computational effort.) Unlike for the first- and second-row elements where the spd functions were treated together, only the s and p exponents were optimized simultaneously for H.

In order to assess the accuracy of the resulting optimized ABSs, frozen-core MP2-F12/3C benchmark calculations on the atomization energies of 42 small molecules were carried out. The geometries used for the atomization energies corresponded to the CCSD(T)/cc-pCVQZ[24] level of theory (all electrons correlated). Spectroscopic constants were also calculated for several diatomic molecules. All of the molecules used are shown in Table II. For these calculations the CABS threshold was significantly decreased to $\max(10^{-9}, s_{max} \times 10^{-9})$.

III. RESULTS AND DISCUSSION

A. Number and types of functions required in the ABS

The numbers of each type of angular momentum function used to construct the optimized ABSs, henceforth referred to as OptRI, are given in Table I where they are also compared to the current reference ABS, as well as other ABSs that have been used in literature as F12 RI basis sets. It is immediately striking how few additional functions are actually required to minimize δRI, and that even with a quadruple-ζ orbital basis set, i-type functions did not contribute appreciably either to the RI error as defined by Eq. (1), or to the difference in energies between using the reference or OptRI ABSs. This was also true when various strongly bound molecules were used in the optimizations. The development of diffuse function augmented orbital and ABSs tai-

TABLE III. RI errors (relative to the reference ABS) per correlated electron in the MP2-F12/3C correlation energies obtained with different ABSs for the 42 molecules and their associated atoms of Table II. All values are in μE_h. (MAD is the absolute deviation; σ is the standard deviation, MAX is the maximum absolute deviation).

Orbital basis	Auxiliary basis	MAD	σ	MAX
VDZ-F12	Reference[a]	(403)	(197)	(930)
	VDZ-F12/OptRI	6.5	6.7	28.7
	VTZ/JKFIT[b]	8.7	8.0	38.5
	aVDZ/MP2FIT	20.0	16.3	68.3
VTZ-F12	Reference[a]	(102)	(66)	(356)
	VTZ-F12/OptRI	4.5	3.4	12.3
	VTZ/JKFIT	4.2	4.5	19.2
	aVTZ/MP2FIT	2.3	1.8	9.8
VQZ-F12	Reference[a]	(16)	(19)	(116)
	VQZ-F12/OptRI	1.6	1.7	10.4
	VQZ/JKFIT	0.6	0.5	2.9
	aVQZ/MP2FIT	0.7	0.4	1.9

[a]Basis set truncation errors per correlated electron for this combination of orbital basis set and the reference ABS are shown. The CBS limits were defined by extrapolation of the conventional MP2 correlation energies with aug-cc-pV5Z and aug-cc-pV6Z basis sets. See the text.
[b]The VDZ/JKFIT basis set was not available.

lored for F12 methods is currently underway, and it may be found that the latter require additional functions for similarly accurate energies and properties. As shown in Table I the same number and type of functions are used in the present ABSs for both the first- and second-row elements; even though the cc-pVnZ-F12 basis sets do include an extra d function for the second-row elements compared to the first row, additional functions were found to not be required in the ABS. Presumably this is aided by the union of the ABS and OBS in the CABS procedure, which is an essential ingredient of the present auxiliary sets.

B. Correlation energies

Table III displays statistics for the RI errors in the MP2-F12/3C correlation energies (defined with respect to values obtained using the reference ABS) of the 42 molecules and their associated atoms given in Table II. In order to provide a balanced comparison between all the molecules and atoms, these results are reported on a per correlated electron basis. Also shown in Table III for comparison are the orbital basis set truncation errors per correlated electron; these calculations utilized the reference ABS. For the latter statistics the CBS limits were obtained by extrapolating the conventional MP2 correlation energies calculated with the aug-cc-pV5Z and aug-cc-pV6Z basis sets [aug-cc-pV$(n+d)$Z in the case of

TABLE II. Molecules used to benchmark the ABSs of this work.

Atomization energies	Al_2, AlH, AlN, AlP, B_2, BH_3, BN, C_2, C_2H_4, $CH_2(^1A_1)$, CH_4, Cl_2, CO, CO_2, CS_2, F_2, H_2, H_2CO, H_2CS, H_2O, H_2O_2, H_2S, H_2S_2, HCl, HCN, HF, N_2, N_2H_2, NH_3, O_2, P_2, PH_3, PF_3, PN, S_2, Si_2, $SiH_2(^1A_1)$, SiH_4, SiO, SO, SO_2, SiS
Spectroscopic constants	C_2, CS, N_2, O_2, F_2, Si_2, P_2, PN, S_2, Cl_2

second-row atoms] using a Helgaker n^{-3} two-point formula.[25] The data of Table III clearly show that the RI errors due to the use of the OptRI ABS are always at least an order of magnitude less than the orbital basis set error. The average RI errors also smoothly decrease from VDZ-F12 to VQZ-F12. The maximum RI error decreases from about 29 μE_h at the VDZ-F12/OptRI level to 10 μE_h at the VQZ-F12/OptRI level. The latter is a bit larger than expected and occurs for the Ar atom. The next largest is only about half this value. A number of tests indicated that the result for Ar was not due to just a simple deficiency in the VQZ-F12/OptRI basis set.

Also shown in Table III are the MP2-F12/3C RI error statistics obtained when using two other possible families of ABSs, the coulomb fitting sets of Weigend[19] (JKFIT) and the conventional MP2 RI sets (MP2FIT) of Weigend *et al.*[26] and Hättig.[20] These were chosen since F12 results using these sets for the RI have been previously reported in the literature. It should be noted that these basis sets were not of course optimized for use with the cc-pVnZ-F12 orbital sets or for explicitly correlated methods, so the results of Table III serve only as a rough guide toward the sensitivity of the RI errors to the chosen ABS. As also shown in Table I, these sets generally contain more functions than OptRI since they were not designed to utilize the underlying OBS. This is especially true for the second-row atoms. The RI errors per correlated electron, however, as shown in Table III are actually very similar to those of OptRI, except for the aVDZ/MP2FIT results for the VDZ-F12 basis set. It is not clear if the good results for the aVTZ/MP2FIT and aVQZ/MP2FIT basis sets implies that RI sets optimized for conventional MP2 also can serve as RI basis sets for the three- and four-electron integrals in F12 calculations, or if this is a fortuitous result due to the particular choice of orbital sets in this work. It should be noted, however, that the aVQZ/MP2FIT basis is actually very similar in size to the reference ABS of this work, particularly in regards to the higher angular momentum functions. Work is currently underway in this laboratory to optimize F12 RI basis sets for the standard aug-cc-pVnZ orbital sets and this should help further clarify this issue.

C. Atomization energies

Table IV lists both the RI and orbital basis set errors in the MP2-F12/3C correlation energy contributions to the atomization energies of the test set of 42 small molecules of Table II. These results are also presented as normal distributions in Fig. 1. The basis set errors shown for the reference RI are calculated as the difference between the MP2-F12/3C atomization energies and the estimated MP2 CBS limit. The latter was obtained by extrapolating the conventional MP2 correlation energies calculated with aug-cc-pV5Z and aug-cc-pV6Z [aug-cc-pV$(n+d)$Z for the second row] basis sets as discussed above. As shown in Table IV the average basis set error is only 0.7 kcal/mol with the VDZ-F12 basis set. The maximum error with this set, 3.8 kcal/mol, is reduced to about 2 kcal/mol if the results for SO_2 and PF_3 are removed from the statistics. Use of the VTZ-F12 basis set results in atomization energies that are all within 1 kcal/mol of their

TABLE IV. RI errors (relative to the reference ABS) in the correlation contributions to the MP2-F12/3C atomization energies obtained with different ABSs for the 42 molecules of Table II. All values are in kcal/mol (MAD is the mean absolute deviation; σ is the standard deviation; and MAX is the maximum absolute deviation).

Orbital basis	Auxiliary basis	MAD	σ	MAX
VDZ-F12	Reference[a]	(0.71)	(0.80)	(3.84)
	VDZ-F12/OptRI	0.05	0.07	0.31
	VTZ/JKFIT[b]	0.06	0.08	0.40
	aVDZ/MP2FIT	0.23	0.24	0.97
VTZ-F12	Reference[a]	(0.24)	(0.24)	(0.99)
	VTZ-F12/OptRI	0.01	0.02	0.09
	VTZ/JKFIT	0.03	0.05	0.23
	aVTZ/MP2FIT	0.01	0.01	0.06
VQZ-F12	Reference[a]	(0.15)	(0.12)	(0.47)
	VQZ-F12/OptRI	0.004	0.005	0.026
	VQZ/JKFIT	0.003	0.004	0.026
	aVQZ/MP2FIT	0.001	0.001	0.004

[a]Basis set truncation errors (correlation contribution only) for this combination of orbital basis set and the reference ABS are shown. The CBS limits were defined by extrapolation of conventional MP2 correlation energies with aug-cc-pV5Z and aug-cc-pV6Z basis sets. See the text.
[b]The VDZ/JKFIT basis set was not available.

CBS limits, while the VQZ-F12 set reduces this by another factor of 2. In particular, it is also clear from Table IV that in each case these basis set errors are at least an order of magnitude larger than the RI errors resulting from using the OptRI ABS.

Compared to the OptRI results, VTZ/JKFIT yields similar results for the VDZ-F12 orbital set while the aVDZ/MP2FIT results have RI errors about a factor of 2 larger in this case. With the VTZ-F12 orbital basis, both VTZ/JKFIT and aVTZ/MP2FIT yield results very similar to OptRI. With the VQZ-F12 basis set, the VQZ/JKFIT ABS yields nearly identical results to OptRI while the large aVQZ/MP2FIT ABS yields results nearly identical to the reference RI ABS. Taken as a whole, however, the new, smaller OptRI auxiliary sets appear to perform very satisfactorily for both absolute correlation energies and energy differences.

To determine the applicability of the new OptRI ABS sets for explicitly correlated CCSD calculations, atomization energies of the molecules of Table II were also calculated with the CCSD-F12a method of Adler *et al.*[13] for all three orbital sets employing OptRI as the ABS. For each orbital basis set the RI errors were essentially identical to the values obtained for MP2-F12 as given in Table IV and hence confirming the suitability of the OptRI ABSs for use also in CCSD-F12 calculations.

Not surprisingly there were also CPU savings from using the more compact OptRI auxiliary sets compared to either JKFIT and MP2FIT. Compared to the calculations employing MP2FIT auxiliary sets, use of the OptRI sets required an average of 33%, 18%, and 31% less CPU time for the VDZ-F12, VTZ-F12, and VQZ-F12 orbital basis sets, respectively (aVDZ, aVTZ, and aVQZ MP2FIT sets). The analogous results for the JKFIT sets (VTZ, VTZ, and VQZ JKFIT) was
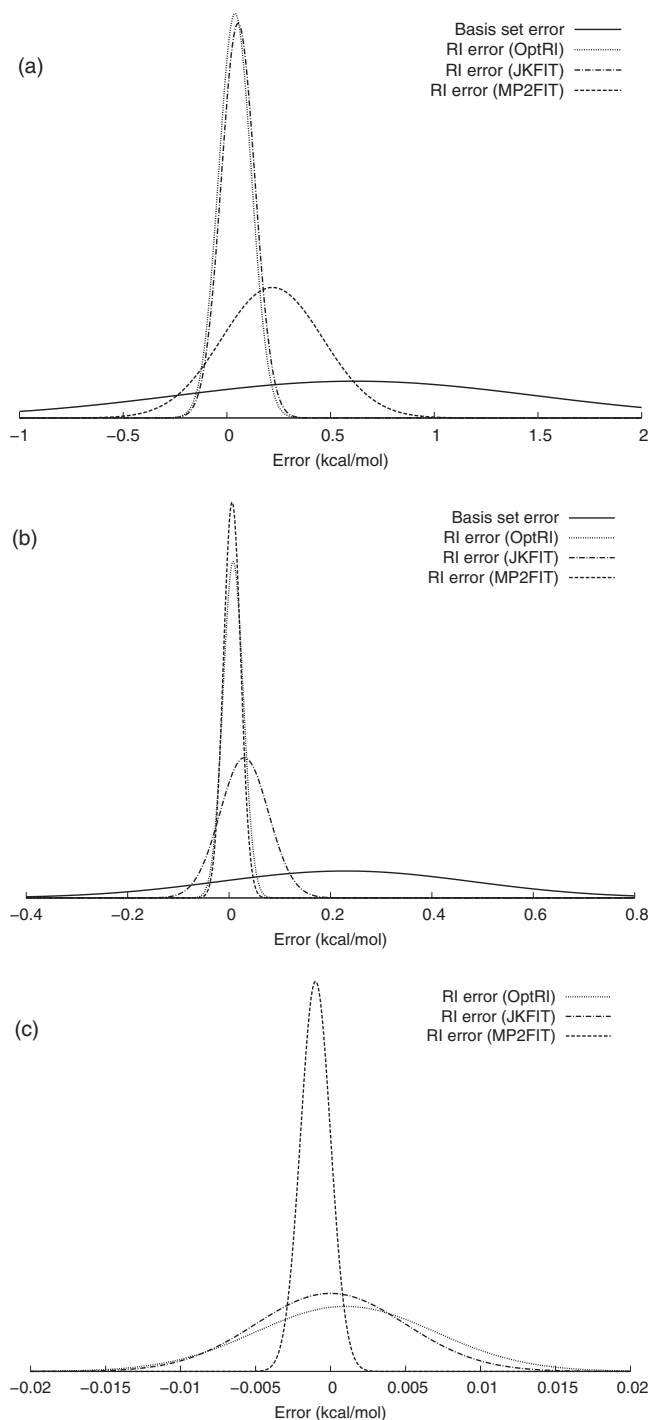
FIG. 1. Basis set and RI errors in the correlation contributions of the MP2-F12/3C atomization energies of a test set of 42 molecules (see Table II) using the (a) VDZ-F12, (b) VTZ-F12, and (c) VQZ-F12 orbital basis sets. The basis set error distribution is not shown for the VQZ-F12 set since it is more than an order of magnitude larger than the average RI errors and was not visible on this scale. RI errors with both the optimized ABSs of this work (OptRI), as well as the JKFIT and MP2FIT basis sets of Weigend et $al.$, are shown. The normal distributions are defined by $y(x)$ $=[1/(\sigma\sqrt{2\pi})]\exp\{-(1/2)[(x-\bar{x})/\sigma]^2\}$.

16%, 3%, and 9%. Compared to the calculations utilizing the large reference RI ABS, the OptRI calculations were faster on average by factors of 4.4, 2.9, and 2.1 for VDZ-F12, VTZ-F12, and VQZ-F12, respectively. All of these timings refer to just the MP2-F12/3C step of the calculations.
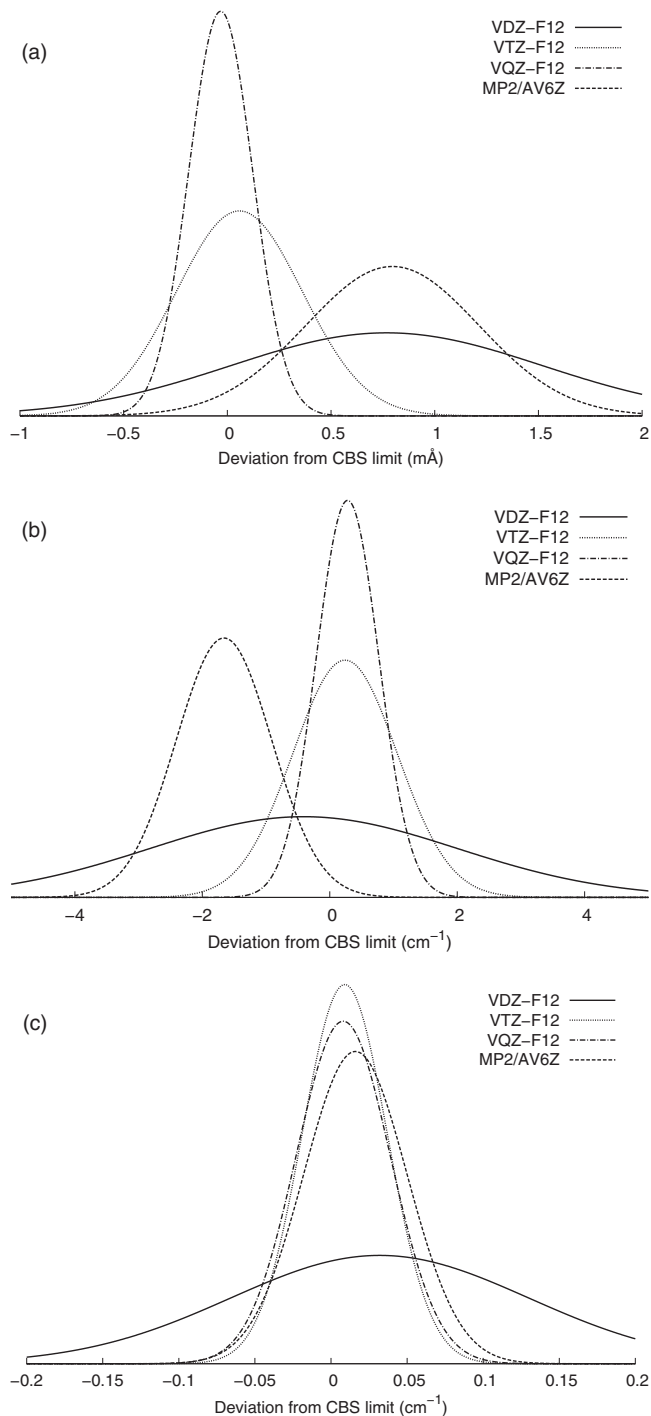

FIG. 2. MP2-F12/3C basis set errors in the spectroscopic constants (a) r_e, (b) ω_e, and (c) $\omega_e x_e$ (with respect to the MP2/CBS limit) calculated using the OptRI ABSs.

D. Spectroscopic constants

As discussed in Sec. I, one motivation for the optimization of ABSs matched to orbital basis sets is the use of explicitly correlated methods in generating smooth PESs. This is essential for accurately calculating spectroscopic constants (including geometrical parameters), as they are defined in terms of the derivatives of a potential surface. To determine whether or not F12 methods combined with our optimized ABSs yield sufficiently smooth PESs, we calculated the equilibrium bond length r_e, harmonic frequency ω_e, and an-

TABLE V. Approximate RI errors (relative to the reference ABS) in the correlation contributions to the MP2-F12/3C values of r_e and ω_e obtained with the OptRI ABS for the 10 diatomics of Table II (MAD is the mean absolute deviation; σ is the standard deviation, and MAX is the maximum absolute deviation).

Orbital basis	Auxiliary basis	r_e (mÅ)			ω_e (cm^{-1})		
		MAD	σ	MAX	MAD	σ	MAX
VDZ-F12	Reference[a]	(0.50)	(0.39)	(1.36)	(1.39)	(0.83)	(2.63)
	VDZ-F12/OptRI	0.15	0.10	0.35	0.74	0.85	2.01
VTZ-F12	Reference[a]	(0.19)	(0.18)	(0.52)	(0.54)	(0.39)	(1.31)
	VTZ-F12/OptRI	0.06	0.05	0.13	0.15	0.13	0.42
VQZ-F12	Reference[a]	(0.11)	(0.10)	(0.32)	(0.46)	(0.23)	(0.78)
	VQZ-F12/OptRI	0.02	0.02	0.07	0.06	0.08	0.24

[a]Basis set truncation errors (correlation contribution only) for this combination of orbital basis set and the reference ABS are shown.

harmonicity constant $\omega_e x_e$ for the ten diatomics listed in Table II. The constants were obtained by a Dunham analysis[27] following a polynomial interpolation of nine points located asymmetrically (from $r_e - 0.4$ a.u. to $r_e + 0.7$ a.u.) around the minimum of the potential curve. Errors in the spectroscopic constants calculated with the cc-pVnZ-F12 basis sets and OptRI auxiliary sets, relative to their CBS limits, are shown in Fig. 2. For all three spectroscopic constants, the errors decrease as expected as the size of the OBS is increased; errors at the double-ζ level are already very small and similar on average to a conventional aV6Z calculation. The CBS limit is nearly reached by performing a MP2-F12/3C calculation with the VTZ-F12 basis set. It should be noted, however, that these basis set errors include a small contribution at the HF level of theory. In each case the CBS total energies were obtained as HF/aV6Z +MP2/CBS(56), where the MP2 CBS limit correlation energies were obtained as described above. The F12 calculations in this work included the CABS single contributions to the HF, as described in Ref. 13, which significantly decreases the basis set incompleteness error at the HF level. Otherwise the basis set errors shown in Fig. 2 would be much larger than shown. This approach has the side effect, however, of mixing HF and RI errors when comparing the reference RI and OptRI results, since the former provides a slightly better HF description when using the CABS singles scheme.

In order to focus on just the RI error itself, correlation contributions to the spectroscopic constants have been defined, for example, as $r_e(\text{MP2}) - r_e(\text{HF})$. The differences in these r_e and ω_e values between the reference RI and OptRI are given in Table V. Certainly in the case of the equilibrium bond lengths the RI error is nearly negligible and much smaller than the basis set incompleteness error. The harmonic frequency is more sensitive, but the errors are only an appreciable fraction of the orbital basis set truncation error at the VDZ-F12 level. In this case the maximum difference between the reference and OptRI harmonic frequencies reaches 2 cm^{-1}. Differences of this magnitude occurred for N_2, O_2, and F_2. The differences in ω_e for all other species was less than 0.5 cm^{-1}.

IV. CONCLUSIONS

Compact RI ABSs optimized for use in explicitly correlated MP2 and CCSD(T) F12 calculations have been developed for the cc-pVnZ-F12 series of orbital basis sets. These auxiliary sets, designed for use in CABS-based calculations, exhibit very small RI errors relative to the underlying basis set error in both correlation energies and relative energies; the latter were benchmarked on the atomization energies of a number of small molecules. The new OptRI auxiliary sets were also used in the MP2-F12/3C calculation of the spectroscopic constants of a number of diatomic molecules and the results were also very promising. These sets are available for download from the author's website, as well as from the MOLPRO site.[17]-

[1] E. A. Hylleraas, Z. Phys. **54**, 347 (1929).
[2] W. Klopper and W. Kutzelnigg, J. Chem. Phys. **94**, 2020 (1991); V. Termath, W. Klopper, and W. Kutzelnigg, ibid. **94**, 2002 (1991); W. Kutzelnigg, Theor. Chim. Acta **68**, 445 (1985); W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).
[3] W. Klopper and C. C. M. Samson, J. Chem. Phys. **116**, 6397 (2002).
[4] E. Valeev, Chem. Phys. Lett. **395**, 190 (2004).
[5] W. Klopper, F. R. Manby, S. Ten-no, and E. F. Valeev, Int. Rev. Phys. Chem. **25**, 427 (2006); D. P. Tew and W. Klopper, J. Chem. Phys. **123**, 074101 (2005).
[6] S. Ten-no, Chem. Phys. Lett. **398**, 56 (2004).
[7] S. Ten-no and F. R. Manby, J. Chem. Phys. **119**, 5358 (2003).
[8] F. R. Manby, J. Chem. Phys. **119**, 4607 (2003).
[9] F. R. Manby, H.-J. Werner, T. B. Adler, and A. J. May, J. Chem. Phys. **124**, 094103 (2006).
[10] H. J. Werner, J. Chem. Phys. **129**, 101103 (2008).
[11] W. Klopper, J. Chem. Phys. **120**, 10890 (2004).
[12] H. J. Werner, T. B. Adler, and F. R. Manby, J. Chem. Phys. **126**, 164102 (2007).
[13] T. B. Adler, G. Knizia, and H. J. Werner, J. Chem. Phys. **127**, 221106 (2007).
[14] S. Höfener, F. A. Bischoff, A. Glöss, and W. Klopper, Phys. Chem. Chem. Phys. **10**, 3390 (2008); G. Knizia and H. J. Werner, J. Chem. Phys. **128**, 154103 (2008); J. Noga, S. Kedzuch, J. Simunek, and S. Ten-no, ibid. **128**, 174103 (2008); D. P. Tew, W. Klopper, C. Neiss, and C. Hättig, Phys. Chem. Chem. Phys. **9**, 1921 (2007); E. F. Valeev and T. D. Crawford, J. Chem. Phys. **128**, 244113 (2008); H.-J. Werner and F. R. Manby, ibid. **124**, 054114 (2006); S. Ten-no, Chem. Phys. Lett. **447**, 175 (2007); S. Ten-no, J. Chem. Phys. **126**, 014108 (2007)..
[15] K. A. Peterson, T. B. Adler, and H. J. Werner, J. Chem. Phys. **128**,

084102 (2008).

[16] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989); T. H. Dunning, K. A. Peterson, and A. K. Wilson, *ibid.* **114**, 9244 (2001); R. Kendall, T. H. Dunning, and R. Harrison, *ibid.* **96**, 6796 (1992); D. E. Woon and T. H. Dunning, *ibid.* **98**, 1358 (1993).

[17] MOLPRO, version 2008.2, a package of *ab initio* programs designed by H.-J. Werner and P. J. Knowles, and *et al.*, see http://www.molpro.net.

[18] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipies in FORTRAN: The Art of Scientific Computing*, 2nd ed. (Cambridge University Press, Cambridge, 1992).

[19] F. Weigend, Phys. Chem. Chem. Phys. **4**, 4285 (2002).

[20] C. Hättig, Phys. Chem. Chem. Phys. **7**, 59 (2005).

[21] H. Partridge, J. Chem. Phys. **87**, 6643 (1987); **90**, 1043 (1989).

[22] T. van Mourik and T. H. Dunning, Jr., Int. J. Quantum Chem. **76**, 205 (2000); A. K. Wilson, T. van Mourik, and T. H. Dunning, Jr., J. Mol. Struct.: THEOCHEM **388**, 339 (1996).

[23] F. Weigend, M. Häser, H. Patzelt, and R. Ahlrichs, Chem. Phys. Lett. **294**, 143 (1998).

[24] K. A. Peterson and T. H. Dunning, Jr., J. Chem. Phys. **117**, 10548 (2002); D. E. Woon and T. H. Dunning, Jr., *ibid.* **103**, 4572 (1995).

[25] T. Helgaker, W. Klopper, H. Koch, and J. Noga, J. Chem. Phys. **106**, 9639 (1997).

[26] F. Weigend, A. Kohn, and C. Hättig, J. Chem. Phys. **116**, 3175 (2002).

[27] J. L. Dunham, Phys. Rev. **41**, 721 (1932).