

Improving on the resolution of the identity in linear R12 ab initio theories

Edward F. Valeev^{a,b,*}

^a Center for Computational Molecular Science and Technology, Georgia Institute of Technology, Atlanta, GA 30332, USA

^b Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

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Abstract

Here we analyze the use of the resolution of the identity (RI) in approximating many-electron matrix elements in linear R12 theories. A modified standard approximation is proposed that involves expansion in the orthogonal complement to the span of orbital basis set (OBS). The new formulation is labeled complementary auxiliary basis set (CABS) approach. CABS MP2-R12 method has a smaller RI error vis-à-vis the standard ABS approach. Both ABS and CABS approaches are most accurate if the auxiliary basis includes OBS *explicitly*. The CABS approach found to be more numerically robust than the ABS counterpart.

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1. Introduction

Basis set incompleteness error (BSIE) is a major component of the total error in traditional wave function-based ab initio electronic structure computations. Explicitly correlated *ab initio* methods speed up the asymptotic rate of decay of BSIE with respect to the size of the basis set by including terms explicitly dependent on the interelectronic distances. Such terms are designed to correct the unphysical short- r_{ij} behavior of conventional (product) wave functions, which is the main cause of the slow convergence. Unfortunately, presence of explicitly correlated terms leads to three- and higher-electron matrix elements. Evaluation of these many-electron integrals is feasible via direct evaluation [1,2] or expansion of the correlation factor in terms of Gaussian Geminals (idea reminiscent of work by Persson and Taylor [3] and pursued by Manby and co-workers [4]). The popular linear R12 methods of Kutzelnigg, Klopper, and co-workers [5–7] avoid such matrix elements alto-

gether via the insertion of the resolution of the identity (RI). Thus only two-electron matrix elements need to be evaluated. The R12 methods, while relatively inexpensive, have repeatedly demonstrated accuracy that is often completely out of reach of the conventional methods [8–11].

Original linear R12 methods [6,7,12] employed the same basis for the orbital expansion and the RI, which meant that the preceding Hartree–Fock computation was rather expensive. Recently Klopper and Samson [13] reformulated the MP2-R12 theory to use a separate, auxiliary basis set for the RI (the ABS MP2-R12 method). We have independently implemented the method recently in a massively parallel program MPQC. Initial applications [14] hinted at several potential issues with the ABS approach, such as the error due to remaining approximations in the theory and a somewhat more technical issue of the accuracy of the RI approximation. In this work, we investigate how the RI approximation works in the context of the ABS MP2-R12 method.

In the linear R12 theories the first-order wave function is written as a sum of the standard 2-products of unoccupied 1-particle functions and the r_{12} -multiplied 2-products of occupied states:

* Corresponding author.

E-mail address: edward.valeev@chemistry.gatech.edu.

$$\psi^{(1)} = \frac{1}{2} \sum_{ij}^< d_{ab}^{ij} a_{ij}^{ab} + \frac{1}{2} \sum_{ij,kl}^< c_{kl}^{ij} \bar{R}_{\alpha\beta}^{kl} a_{ij}^{\alpha\beta}, \quad (1)$$

where the correlation operator R will be defined as:

$$R_{\alpha\beta}^{kl} = \begin{cases} r_{\alpha\beta}^{kl} & \text{if } \hat{P}\alpha = 0 \text{ or } \hat{P}\beta = 0, \\ 0 & \text{if } \hat{P}\alpha = \alpha \text{ and } \hat{P}\beta = \beta \end{cases} \quad (2)$$

(see [6,14] for complete notation). This definition corresponds to ansatz 2 of Klopper and Samson [13] and ensures orthogonality of the r_{12} -multiplied terms with respect to conventional orbital products [2,14]. It is also common to use first quantized forms in the literature on the explicitly correlated methods – here we show them for convenience:

$$|\psi^{(1)}\rangle = \sum_{ij,ab}^< d_{ab}^{ij} |ab\rangle \langle ij|\psi^{(0)}\rangle + \sum_{ij,kl}^< c_{kl}^{ij} \hat{Q}_{12} |kl\rangle r_{12} \langle ij|\psi^{(0)}\rangle. \quad (3)$$

Different choices of the correlation operator R in Eq. (1) correspond to different choices for the two-particle projector \hat{Q}_{12} in Eq. (3). Our choice (Eq. (2)) corresponds to the following two-particle projector:

$$\begin{aligned} \hat{Q}_{12} &= (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2, \\ &= 1 - \hat{O}_1 - \hat{O}_2 - \hat{P}_1 \hat{P}_2 + \hat{O}_1 \hat{P}_2 + \hat{P}_1 \hat{O}_2. \end{aligned} \quad (4)$$

Three and higher-electron matrix elements appear when the the first-order wave function is plugged into the Hylleraas functional for the second-order energy:

$$F(\psi^{(1)}) = \langle \psi^{(1)} | \hat{H}^{(0)} - E^{(0)} | \psi^{(1)} \rangle + 2 \langle \psi^{(0)} | \hat{H}^{(1)} - E^{(1)} | \psi^{(1)} \rangle. \quad (5)$$

Evaluation of matrix elements in Eq. (5) produces terms like $R_{\alpha\beta}^{kl} g_{ij}^{\alpha\beta}$ which contain three-electron integrals:

$$\begin{aligned} R_{\alpha\beta}^{kl} g_{ij}^{\alpha\beta} &= r_{\alpha\beta}^{kl} g_{ij}^{\alpha\beta} - r_{ab}^{kl} g_{ij}^{ab}, \\ &= r_{\kappa\lambda}^{kl} g_{ij}^{\kappa\lambda} - r_{\kappa m}^{kl} g_{ij}^{\kappa m} - r_{m\kappa}^{kl} g_{ij}^{m\kappa} - r_{pq}^{kl} g_{ij}^{pq} + r_{pm}^{kl} g_{ij}^{pm} + r_{mp}^{kl} g_{ij}^{mp}, \end{aligned} \quad (6)$$

$$= \delta_i^k \delta_j^l - \left(\frac{r_{12}}{r_{13}} \right)_{imj}^{klm} - \left(\frac{r_{12}}{r_{13}} \right)_{jmi}^{lkm} - r_{pq}^{kl} g_{ij}^{pq} + r_{pm}^{kl} g_{ij}^{pm} + r_{mp}^{kl} g_{ij}^{mp}. \quad (7)$$

In their ABS MP2-R12 method Klopper and Samson insert the resolution of the identity *directly* into the three-electron matrix elements in terms of a separate RI basis set $\{p'\}$, e.g.,

$$\left(\frac{r_{12}}{r_{13}} \right)_{imj}^{klm} \stackrel{\text{RI}}{\approx} (r_{12})_{p'm}^{kl} (r_{12}^{-1})_{ij}^{p'm} \equiv r_{p'm}^{kl} g_{ij}^{p'm}. \quad (9)$$

Our goal in this Letter is to investigate

- how to best construct the RI basis set, and
- whether there's a better approach to approximating the many-electron matrix elements than direct insertion of the RI via Eqs. (7) and (9).

2. Formalism

For practical purposes we will only need to consider expressions of the following type:

$$\Gamma_{ij}^{\alpha\beta} \Omega_{\alpha\beta}^{kl} - \Gamma_{ij}^{ab} \Omega_{ab}^{kl}, \quad (10)$$

in which the operator pair (Γ, Ω) is one of the following: $(r_{12}^{-1}, r_{12}), (r_{12}, r_{12}), (r_{12}^{-1}, [\hat{T}_1 + \hat{T}_2, r_{12}])$. Following Kutzelnigg [6] such expressions are rewritten in terms of complete and orbital basis set indices only:

$$\begin{aligned} \Gamma_{ij}^{\alpha\beta} \Omega_{\alpha\beta}^{kl} - \Gamma_{ij}^{ab} \Omega_{ab}^{kl} &= (\Gamma\Omega)_{ij}^{kl} - \Gamma_{ij}^{\kappa m} \Omega_{\kappa m}^{kl} - \Gamma_{ij}^{m\kappa} \Omega_{m\kappa}^{kl} \\ &\quad - \Gamma_{ij}^{pq} \Omega_{pq}^{kl} + \Gamma_{ij}^{pm} \Omega_{pm}^{kl} + \Gamma_{ij}^{mp} \Omega_{mp}^{kl}. \end{aligned} \quad (11)$$

Original evaluation of such expressions [6] assumed that the orbital basis $\{p\}$ was sufficiently complete to resolve the identity accurately:

$$\Gamma_{ij}^{\alpha\beta} \Omega_{\alpha\beta}^{kl} - \Gamma_{ij}^{ab} \Omega_{ab}^{kl} \stackrel{\text{RI}}{\approx} (\Gamma\Omega)_{ij}^{kl} - \Gamma_{ij}^{pq} \Omega_{pq}^{kl}. \quad (12)$$

This RI procedure is equivalent to replacing κ with p in Eq. (11). In first quantization this corresponds to replacing standalone projectors \hat{O}_1 and \hat{O}_2 in Eq. (4) with $\hat{O}_1 \hat{P}_2$ and $\hat{O}_2 \hat{P}_1$, respectively.

The ABS MP2-R12 method of Klopper and Samson [13], used a separate ‘auxiliary’ basis set (ABS) $\{p'\}$ to approximate matrix elements in Eq. (11):

$$\begin{aligned} \Gamma_{ij}^{\alpha\beta} \Omega_{\alpha\beta}^{kl} - \Gamma_{ij}^{ab} \Omega_{ab}^{kl} &\stackrel{\text{RI}}{\approx} (\Gamma\Omega)_{ij}^{kl} - \Gamma_{ij}^{p'm} \Omega_{p'm}^{kl} - \Gamma_{ij}^{m p'} \Omega_{m p'}^{kl} \\ &\quad - \Gamma_{ij}^{pq} \Omega_{pq}^{kl} + \Gamma_{ij}^{pm} \Omega_{pm}^{kl} + \Gamma_{ij}^{mp} \Omega_{mp}^{kl}. \end{aligned} \quad (13)$$

In first quantization we replace projectors \hat{O}_1 and \hat{O}_2 in Eq. (4) with $\hat{O}_1 \hat{P}'_2$ and $\hat{O}_2 \hat{P}'_1$, respectively. If the ABS is more appropriate for the RI than the OBS, then Eq. (13) should be more accurate than Eq. (12). When the ABS is the same as the OBS, both expressions are equivalent. When the ABS approaches completeness Eq. (13) becomes exact.

In order to understand and control the error due to the approximate RI, one must be able to approach the complete ABS limit. In atoms, partial wave analysis of these expressions indicates that an ABS complete through a certain finite orbital quantum number is often sufficient (see [6,13]). No such simplification is possible in a general molecular case. Therefore one should ask: how large of an ABS should one use and how should it be constructed?

Eq. (11) is formally rewritten as

$$\Gamma_{ij}^{\alpha\beta} \Omega_{\alpha\beta}^{kl} - \Gamma_{ij}^{ab} \Omega_{ab}^{kl} = \Gamma_{ij}^{\kappa\lambda} \Omega_{\kappa\lambda}^{kl} - \Gamma_{ij}^{pq} \Omega_{pq}^{kl} - \Gamma_{ij}^{\alpha'm} \Omega_{\alpha'm}^{kl} - \Gamma_{ij}^{m\alpha'} \Omega_{m\alpha'}^{kl}, \quad (14)$$

where set $\{\alpha'\}$ spans the orthogonal complement to the space of OBS, $\{p\}$. In other words, $\{\kappa\} = \{\alpha'\} \cup \{p\}$ and $\{\alpha\} = \{\alpha'\} \cup \{a\}$. Terms containing sums over α' indices are approximated as

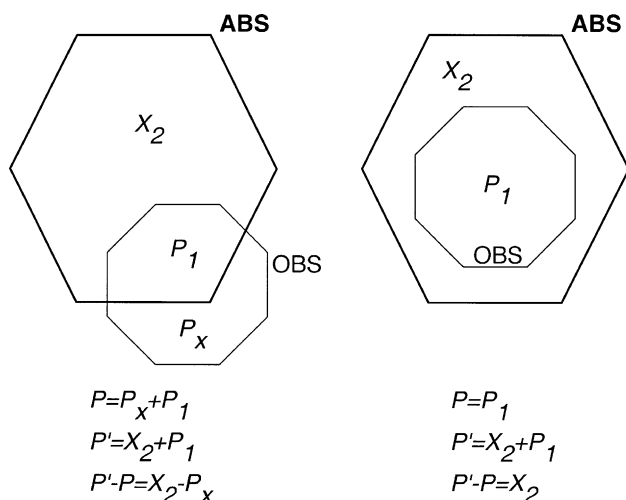


Fig. 1. Pictorial representation of projectors \hat{P} and \hat{P}' used in Klopper and Samson's ABS linear R12 methods. When ABS does not span OBS exactly (left part of the figure), the difference $\hat{P}' - \hat{P}$ (difference of areas X_2 and P_x) may be a poor approximation to the exact orthogonal complement projector $1 - \hat{P}$ (the entire area outside of the octagon). Thus, it is always preferable to approximate $1 - \hat{P}$ with the projector corresponding to area X_2 .

$$\Gamma_{ij}^{\alpha\beta} \Omega_{\alpha\beta}^{kl} - \Gamma_{ij}^{ab} \Omega_{ab}^{kl} \approx (\Gamma \Omega)_{ij}^{kl} - \Gamma_{ij}^{pq} \Omega_{pq}^{kl} - \Gamma_{ij}^{a'm} \Omega_{a'm}^{kl} - \Gamma_{ij}^{m'd} \Omega_{m'd}^{kl}, \quad (15)$$

where basis set $\{a'\}$ is a finite approximation for the space of $\{\alpha'\}$. One can interpret this approach as using $\Gamma_{ij}^{a'm} \Omega_{a'm}^{kl} + \Gamma_{ij}^{m'd} \Omega_{m'd}^{kl}$ to approximate $\Gamma_{ij}^{km} \Omega_{km}^{kl} + \Gamma_{ij}^{mk} \Omega_{mk}^{kl} - \Gamma_{ij}^{pm} \Omega_{pm}^{kl} - \Gamma_{ij}^{mp} \Omega_{mp}^{kl}$ rather than using $\Gamma_{ij}^{p'm} \Omega_{p'm}^{kl} + \Gamma_{ij}^{m'p} \Omega_{m'p}^{kl}$ to approximate $\Gamma_{ij}^{km} \Omega_{km}^{kl} + \Gamma_{ij}^{mk} \Omega_{mk}^{kl}$ in the standard ABS approach. In the language of first quantization: the ABS approach approximates the identity operator as \hat{P}' , whereas in the new approach the difference $1 - \hat{P}$ is approximated directly as an orthogonal complement projector \hat{X} .

While Eqs. (11) and (14) are equivalent, their respective approximations, Eqs. (13) and (15), are only equivalent when $\{p'\} = \{a'\} \cup \{p\}$. This means that $\{p'\}$ must span $\{p\}$ exactly, i.e., ABS must span OBS *exactly*. Thus in theory Eq. (13) is less accurate than Eq. (15) when the space of ABS does not include the space of OBS (the argument is illustrated in Fig. 1).

The MP2-R12 method which uses Eq. (15) will be called Complementary Auxiliary Basis Set (CABS) MP2-R12 method, to distinguish from the ABS MP2-R12 method of Klopper and Samson [13], which uses Eq. (13).

2.1. Construction of the complimentary auxiliary basis set $\{a'\}$

In practice one would like to construct an optimal $\{a'\}$ using an arbitrary, not necessarily orthogonal, set of functions $\{\mu'\}$, i.e., an auxiliary basis set of atom-cen-

tered Gaussian atomic orbitals (AO ABS)¹. It is always possible to orthogonalize the given AO ABS $\{\mu'\}$ to a given numerical precision. Then it is convenient to expand functions in the complementary basis set $\{a'\}$ in terms of the orthogonal functions $\{|\mu'\rangle\}$:

$$|a'\rangle = \sum_{\mu'=1}^{N'} C_{\mu'}^{a'} |\mu'\rangle. \quad (16)$$

where $|\mu'\rangle$ is a set of N' orthogonal basis functions formed by orthogonalization of the non-orthogonal $\{\mu'\}$ basis set.

We postulate that the overlap between the complementary basis set, $\{a'\}$, and the OBS, $\{p\}$, must be zero

$$\langle a'|p\rangle = 0 \quad \forall a' \in \{a'\}, \quad \forall p \in \{p\}. \quad (17)$$

Upon substitution of Eq. (16) in Eq. (17), we obtain an equation for the expansion coefficients:

$$\sum_{\mu'}^{N'} C_{\mu'}^{a'} \langle \mu'|p\rangle = 0 \quad \forall a' \in \{a'\}, \quad \forall p \in \{p\}. \quad (18)$$

We should also impose orthonormality condition on the $\{a'\}$ basis:

$$\sum_{\mu'}^{N'} \sum_{\nu'}^{N'} C_{\mu'}^{a'} C_{\nu'}^{b'} \langle \mu'|\nu'\rangle = \delta_{a'}^{b'} \quad \forall a' \in \{a'\}, \quad \forall b' \in \{a'\}. \quad (19)$$

In principle, one could solve Eqs. (18) and (19) via a straightforward Gram–Schmidt (GS) orthogonalization procedure. However, GS orthogonalization is not a robust numerical method. Thus, we avoided the GS route as follows.

Let us rewrite Eq. (18) in matrix form.

$$\mathbf{S}_{12} \mathbf{C} = 0, \quad (20)$$

where \mathbf{S}_{12} is the overlap matrix between the $\{p\}$ and $\{|\mu'\rangle\}$ sets. Thus, we need to find vectors \mathbf{C} that span null space of \mathbf{S}_{12} . Singular value decomposition (SVD) [15] of \mathbf{S}_{12} can be used to rewrite Eq. (20) as

$$\mathbf{U}_1^\dagger \Sigma_{12} \mathbf{V}_2 \mathbf{C} = 0. \quad (21)$$

where \mathbf{U}_1 and \mathbf{V}_2 are orthogonal matrices of dimensions n and N' , respectively, and Σ_{12} is a diagonal $n \times N'$ matrix of singular values. For our purposes we will assume that N' is greater than n . The numerical rank of \mathbf{S}_{12} is then $\text{rank}(\mathbf{S}_{12}) \leq n$. Hence \mathbf{V}_2 can be represented as:

$$\mathbf{V}_2 = \begin{pmatrix} \mathbf{V}_2^R \\ \mathbf{V}_2^N \end{pmatrix}, \quad (22)$$

¹ Other functional choices, such as plane waves, are possible. The choice of the basis function type does not fundamentally change our formalism.

where the two blocks are composed of $\text{rank}(\mathbf{S}_{12})$ and $N' - \text{rank}(\mathbf{S}_{12})$ rows, respectively. The desired solution \mathbf{C} is simply a transpose of \mathbf{V}_2^N :

$$\mathbf{U}_1^\dagger \mathbf{\Sigma}_{12} \mathbf{V}_2 \mathbf{V}_2^N = 0, \quad (23)$$

is true by construction. Hence our simplified procedure for constructing the complementary auxiliary basis set $\{a'\}$ is:

1. form \mathbf{S}_{12} , the overlap matrix between orthonormalized ABS, $\{|\mu'\rangle\}$, and OBS, $\{|p\rangle\}$,
2. compute SVD of \mathbf{S}_{12} : $\mathbf{S}_{12} = \mathbf{U}_1^\dagger \mathbf{\Sigma}_{12} \mathbf{V}_2$,
3. select last $N' - \text{rank}(\mathbf{S}_{12})$ rows of \mathbf{V}_2 , transpose, and transform to the $\{\mu'\}$ basis. Result is the desired matrix of coefficients in Eq. (16).

Note that $N' > n$ almost always holds in practice because it makes sense to use ABS larger than OBS.

2.2. Choice of the AO basis set for ABS

We have already discussed that for optimal accuracy of the RI approximation in the ABS approach (Eq. (13)) the ABS should span the OBS space *exactly*. In practice we found that it is extremely difficult to construct such a basis set by trial and error. It is possible that careful optimization of the AO ABS for a given AO OBS could help. However, a much simpler solution is to use a union of AO OBS and AO ABS to construct the basis set for the RI. The ‘union’ basis set has a higher number of AO functions than the ABS. Thus, the number of molecular AO integrals one has to compute in the union ABS approach is higher than in the standard ABS approach. However, the advantage is that the union basis set will span the space of OBS even with a poor choice of the AO ABS. The ‘union’ ABS approach will be referred to as ABS+.

2.3. Choice of the AO basis set for CABS

Eq. (20) implies that if the ABS does not overlap with OBS then any \mathbf{C} would automatically satisfy the equation. In other words, CABS $\{a'\}$ should ideally be constructed from an AO basis set $\{\mu'\}$ which is orthogonal (or nearly orthogonal) to OBS $\{p\}$. The exact orthogonality is impossible *a priori* for a general molecule².

Let us assume that the AO ABS $\{\mu'\}$ used to construct CABS spans some part of the OBS space. We will designate rank of the union of ABS and OBS spaces as N_U . Then rank of the orthogonal complement to OBS is

$N_C = N_U - n$. Values of N_U and N_C are determined by the choice of AO ABS, AO OBS, and the linear dependency threshold. Therefore the best CABS one could hope to construct would span the entire orthogonal complement of rank N_C . In practice, rank of CABS is significantly smaller than N_C because AO OBS and AO ABS are not exactly orthogonal to each other. The union basis set is again helpful here – it is straightforward to show that CABS of rank N_C can be *reliably* constructed using the union of AO OBS and AO ABS. Therefore, as with the standard ABS approach, one should use the union basis set for the CABS method. The ‘union’ CABS method will be referred to as CABS+.

3. Computational methods

We used the MP2-R12 method as implemented within the MPQC package (upcoming release 2.3) [16,14]. Dunning’s [17,18] augmented double- ζ correlation consistent basis set was utilized for the orbital expansion in all computations. Details of ‘universal’ uncontracted basis sets of increasing completeness X1, X2, and X3 are available from the author. BS1 basis set was used in [19]. K2 basis set was taken from an early study by Klopper [20]. K2-basis set is obtained from K2 by removing basis functions of the two highest orbital numbers from each atom. Near linear dependencies in the basis sets were handled via standard orthogonalization procedures [21], in which overlap eigenvectors that had eigenvalues smaller than 10^{-8} times the maximum overlap eigenvalue were omitted. The same linear dependence threshold was used for both OBS and ABS. The core orbitals were kept ‘frozen’ in all correlated computations.

4. Results and conclusion

We compared the accuracy of the RI in the four approaches discussed above by looking at the convergence of absolute and relative MP2-R12/A' energies with respect to the size of an AO ABS in a diverse set of systems. A small set of typical results is presented in Figs. 2–5.

The main findings are:

1. The RI error in the ABS MP2-R12 energy is significantly larger than in the corresponding CABS MP2-R12 value when a relatively small AO ABS is used. The difference is especially staggering for benzene dimer when the BS1 basis set is used.
2. When AO ABS method is very large then all methods produce nearly identical energies.
3. The ‘union’ approaches, ABS+ and CABS+, have smaller RI error than either ABS or CABS method. It is true even when we compare ABS+ and CABS+ energies with a ‘small’ AO ABS against ABS and

² In case of an atom angular momentum selection rules suggest that CABS should be composed of basis functions of angular momenta which are not represented in OBS if we assume that OBS is complete through a finite angular momentum level. For example, OBS for a second-row element should be complete in s and p-type spaces, whereas CABS should be composed of functions of d-type and higher.

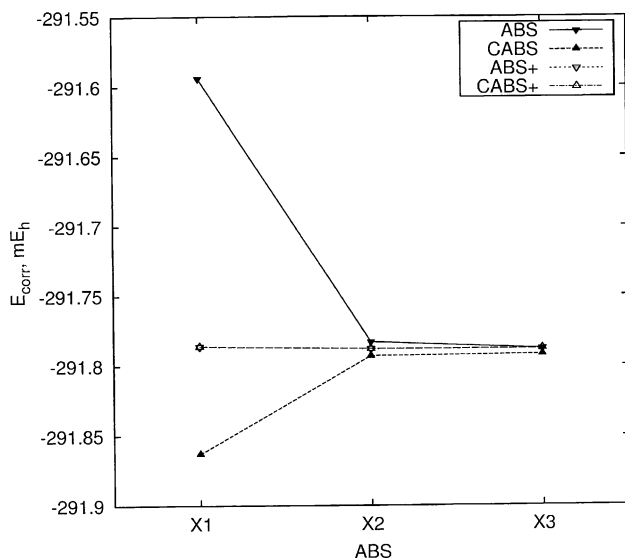


Fig. 2. ABS convergence of aug-cc-pVDZ MP2-R12/A' correlation energy of Ne computed with dual-basis approaches described in Section 2.

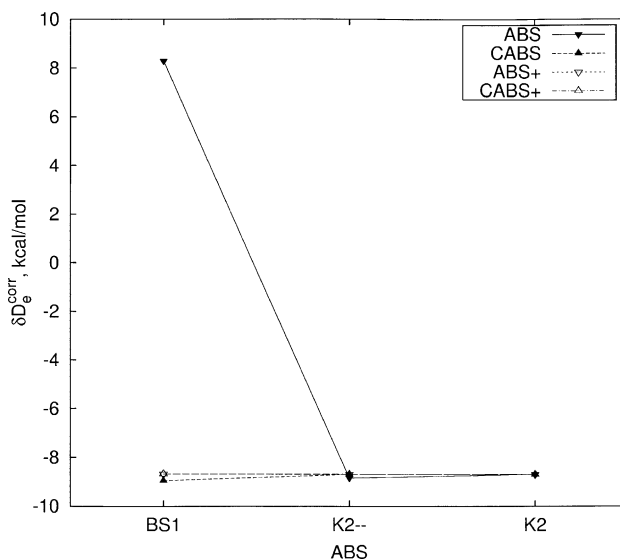


Fig. 4. ABS convergence of aug-cc-pVDZ MP2-R12/A' valence correlation contribution to the dissociation energy of benzene dimer computed with dual-basis approaches described in Section 2.

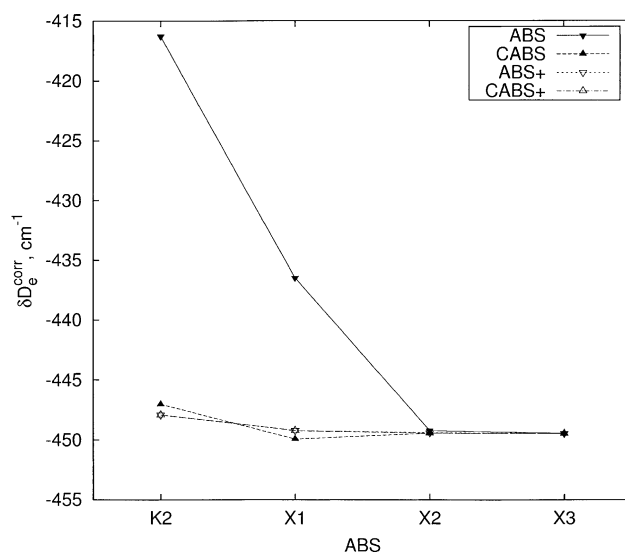


Fig. 3. ABS convergence of aug-cc-pVDZ MP2-R12/A' correlation contribution to the dissociation energy of water dimer computed with dual-basis approaches described in Section 2.

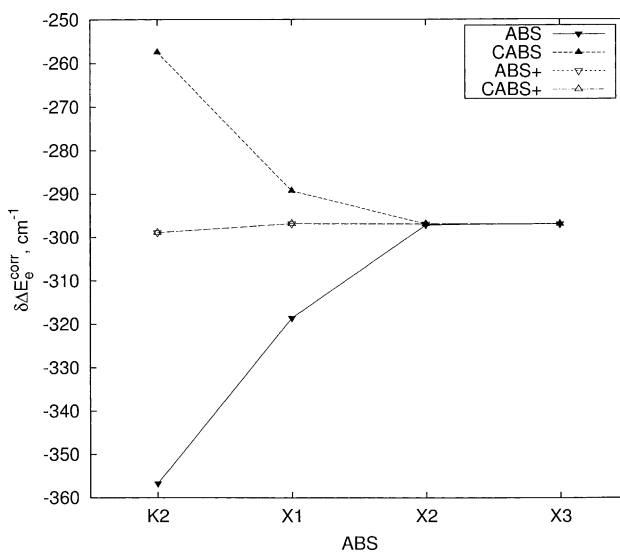


Fig. 5. ABS convergence of aug-cc-pVDZ MP2-R12/A' valence correlation contribution to the barrier of linearity of water computed with dual-basis approaches described in Section 2.

CABS calculations with a much larger AO ABS. This finding emphasizes how important it is for the RI basis set in Eq. (13) to span OBS exactly.

Note that approaches ABS+ and CABS+ are equivalent in absence of numerical round-off error. Practical tests indicate that the CABS+ approach is less sensitive to variations in the linear dependency threshold used for orthogonalization of the union basis set and thus should be preferred. A more complete investigation of numerical performance of the CABS method will be published shortly.

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