

Explicitly correlated second-order Møller–Plesset methods with auxiliary basis sets

Wim Klopper and Claire C. M. Samson

Citation: *J. Chem. Phys.* **116**, 6397 (2002); doi: 10.1063/1.1461814

View online: <http://dx.doi.org/10.1063/1.1461814>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v116/i15>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

Instruments for advanced science

Gas Analysis



- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

Surface Science



- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping

Plasma Diagnostics



- plasma source characterization
- etch and deposition process reaction kinetic studies
- analysis of neutral and radical species

Vacuum Analysis



- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

contact Hiden Analytical for further details

HIDEN
ANALYTICAL

info@hideninc.com
www.HidenAnalytical.com

CLICK to view our product catalogue 

Explicitly correlated second-order Møller–Plesset methods with auxiliary basis sets

Wim Klopper^{a)} and Claire C. M. Samson

Theoretical Chemistry Group, Debye Institute, Utrecht University, P.O. Box 80052, NL-3508 TB Utrecht, The Netherlands

(Received 28 November 2001; accepted 25 January 2002)

In explicitly correlated Møller–Plesset (MP2-R12) methods, the first-order wave function is expanded not only in terms of products of one-electron functions—that is, orbitals—but also in terms of two-electron functions that depend linearly on the interelectronic coordinates r_{ij} . With these functions, three- and four-electron integrals occur, but these integrals can be avoided by inserting a resolution of the identity (RI) in terms of the one-electron basis. In previous work, only one single basis was used for both the electronic wave function and the RI approximation. In the present work, a new computational approach is developed that uses an auxiliary basis set to represent the RI. This auxiliary basis makes it possible to employ standard basis sets in explicitly correlated MP2-R12 calculations. © 2002 American Institute of Physics.

[DOI: 10.1063/1.1461814]

I. INTRODUCTION

Beyond the Hartree–Fock level, basis-set truncation errors greatly frustrate efforts to compute highly accurate molecular electronic energies and properties.^{1–5} Such errors occur when insufficiently large basis sets of products of one-electron functions (atomic orbitals, AOs) are employed to expand the many-electron wave function. Moreover, due to the drastic increase of computation time with the size of the AO basis, it often happens that this basis cannot be increased to the size that would be required to achieve the prescribed high accuracy. Experience has shown, for example, that the computation time of a correlated electronic-structure calculation in a correlation-consistent cc-pVXZ basis grows as $\propto X^{12}$ with its cardinal number X , while basis-set truncation errors only disappear as $\propto X^{-3}$.⁶

The importance of the basis-set truncation error and the slow convergence with the size of the AO basis has been recognized for a long time, and various techniques have been developed to overcome the basis-set convergence problems. Among these, we find extrapolation and scaling techniques as well as empirical additive corrections.^{6–18} Widely used methods include the complete-basis-set (CBS) approach^{9,10} and the G3 model chemistry.^{13,14}

The basis-set truncation errors and slow convergence problems can be addressed more directly by adding two-electron basis functions to the expansion in orbital products. When such two-electron functions depend explicitly on the interelectronic distances $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, the convergence to the limit of a complete basis is significantly accelerated.^{19–23} Since 1985, various methods have been developed that employ two-electron functions that depend linearly on r_{ij} . Today, these methods are known as R12 methods.^{24–28} A key issue in these methods is that multicenter three- and four-electron integrals (and even five-electron integrals in

coupled-cluster theory) are avoided by introducing the resolution of the identity (RI) represented in the AO basis. As these many-electron integrals are avoided by virtue of the RI approximation, R12 calculations can be performed on fairly large molecules (e.g., ferrocene²⁹) and molecular complexes (e.g., benzene–neon,³⁰ water trimer, and tetramer),^{31,32} but very large AO basis sets must be employed to ensure that the RI approximation is a good one that does not introduce other types of unwanted basis-set errors.

In this article, we present a new formulation of R12 theory that utilizes an auxiliary basis set for the RI approximation. This auxiliary basis can then be chosen such that the basis-set errors due to the RI approximation become arbitrarily small (i.e., negligible in comparison with other errors). Most importantly, there will no longer be constraints on the size of the AO basis that is used to expand the molecular electronic wave function.

In Sec. II, we present the matrix elements that contribute to the MP2-R12 energy and show how they can be evaluated by introducing an auxiliary basis set. As the R12 functions can be chosen strongly orthogonal to either the full molecular orbital space (Ansatz 1) or to the occupied molecular orbital space (Ansatz 2), we derive the working equations for both cases. The computer implementations of both Ansätze are given in Sec. III. The newly developed methods are summarized in Sec. IV and numerical results are shown in Secs. V and VI, respectively, for the Ne atom and for calculations in correlation-consistent basis sets on the systems CH₂ (¹A₁), H₂O, NH₃, HF, N₂, CO, Ne, and F₂.

II. METHODOLOGY

A. The R12 Ansatz

In closed-shell explicitly correlated MP2-R12 theory, the first-order wave function is expanded not only in a basis of

^{a)}Electronic mail: w.m.klopper@chem.uu.nl. Fax: +31-30-2537504.

double excitations containing the orbital product $\varphi_a(1)\varphi_b(2)$ (as in standard MP2 theory), but also in a basis of two-electron basis functions

$$\chi_{mn}(1,2) = \hat{w}_{12} |\varphi_m(1)\varphi_n(2)\rangle, \quad (1)$$

where \hat{w}_{12} is an appropriate correlation factor (see, e.g., Ref. 23). In this article, we shall investigate two possible Ansätze for the explicitly correlated function $\chi_{mn}(1,2)$. In Ansatz **1**, the correlation factor is chosen as

$$\hat{w}_{12} = (1 - \hat{P}_1)(1 - \hat{P}_2)r_{12}, \quad (2)$$

whereas in Ansatz **2**, it is chosen as

$$\hat{w}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2)r_{12}. \quad (3)$$

Note that the correlation factor contains projection operators, which can be chosen in different manners (cf. Ref. 33). \hat{P}_1 is the one-electron projector onto the space of orthonormal spatial orbitals $\varphi_p(1)$ that is spanned by the finite basis set of N atomic orbitals (AO basis)

$$\hat{P}_1 = \sum_p |\varphi_p(1)\rangle\langle\varphi_p(1)|. \quad (4)$$

A number of n orbitals are occupied (with $2n$ electrons) in the reference Hartree–Fock function and $N - n$ orbitals are empty—or virtual. The projector \hat{O}_1 onto the occupied orbital space is given by

$$\hat{O}_1 = \sum_i |\varphi_i(1)\rangle\langle\varphi_i(1)|. \quad (5)$$

As usual, we denote occupied orbitals by the indices i, j, k, \dots , virtual orbitals by a, b, c, \dots , and arbitrary (i.e., either occupied or virtual) orbitals by p, q, r, \dots . We denote the one-electron basis $\{\varphi_p(1)\}_{p=1, \dots, N}$ as *orbital basis* and also introduce an orthonormal *auxiliary basis* $\{\varphi_{p'}(1)\}_{p'=1, \dots, N'}$ with corresponding projector

$$\hat{P}'_1 = \sum_{p'} |\varphi_{p'}(1)\rangle\langle\varphi_{p'}(1)|. \quad (6)$$

In previous MP2-R12 work, no distinction was made between the Ansätze **1** and **2**, because—after insertion of the resolution of the identity in the framework of the standard approximation—they both led to the same working equations and hence to the same numerical results. This is no longer true when the three- and four-electron integrals are computed exactly^{34,35} or when an auxiliary basis set is used. Then, the two Ansätze indeed yield different results, as we shall see below. Furthermore, it is important to realize that the Ansätze **1** and **2** are not approximations but refer to different wave function expansions.

B. Second-order pair energies

We can write the MP2-R12 correlation energy in terms of singlet ($s=0$) and triplet ($s=1$) pair energies

$$E^{(2)} = \sum_{s=0,1} (2s+1) \sum_{i \leq j} (d_{ij}^s + e_{ij}^s), \quad (7)$$

where e_{ij}^s is the conventional MP2 pair energy and d_{ij}^s the pair energy contribution from the explicitly correlated functions. In Eq. (7) it is understood that intraorbital triplet pair energies vanish, that is, $e_{ii}^1 = d_{ii}^1 = 0$.

Let us define spin-adapted vectors $\bar{\mathbf{V}}^{(ij,s)}$ and matrices $\bar{\mathbf{B}}^{(ij,s)}$ as follows:

$$\begin{aligned} \bar{\mathbf{V}}_{kl}^{(ij,s)} &= (1 + \delta_i^j)^{-1/2} (1 + \delta_k^l)^{-1/2} \\ &\quad \times (\tilde{\mathbf{V}}_{kl}^{(ij)} + (1 - 2s) \tilde{\mathbf{V}}_{lk}^{(ij)}), \end{aligned} \quad (8)$$

$$\begin{aligned} \bar{\mathbf{B}}_{kl,mn}^{(ij,s)} &= (1 + \delta_k^l)^{-1/2} (1 + \delta_m^n)^{-1/2} \\ &\quad \times (\tilde{\mathbf{B}}_{kl,mn}^{(ij)} + (1 - 2s) \tilde{\mathbf{B}}_{lk,mn}^{(ij)}), \end{aligned} \quad (9)$$

where δ_i^j is Kronecker's delta and $i \leq j, k \leq l$, and $m \leq n$ for $s=0$ and $i < j, k < l$, and $m < n$ for $s=1$. The R12 pair contributions are then given by the expression

$$d_{ij}^s = -\{\bar{\mathbf{V}}^{(ij,s)}\}^T \{\bar{\mathbf{B}}^{(ij,s)}\}^{-1} \bar{\mathbf{V}}^{(ij,s)}. \quad (10)$$

This equation has been derived in Ref. 36 and is equivalent to Eq. (15) of that paper. See also Ref. 37.

C. Matrix elements

In the MP2-R12 method, the following vector components and matrix elements must be computed:

$$\begin{aligned} \tilde{\mathbf{V}}_{kl}^{(ij)} &= V_{kl}^{(ij)} - \sum_{ab} \frac{C_{kl,ab}^{(ij)}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \\ &\quad \times \langle \varphi_a(1)\varphi_b(2) | g_{12} | \varphi_i(1)\varphi_j(2) \rangle, \end{aligned} \quad (11)$$

$$\tilde{\mathbf{B}}_{kl,mn}^{(ij)} = B_{kl,mn}^{(ij)} - \sum_{ab} \frac{C_{kl,ab}^{(ij)}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} C_{ab,mn}^{(ij)}, \quad (12)$$

where

$$\begin{aligned} V_{kl}^{(ij)} &= \langle \chi_{kl}(1,2) | g_{12} | \varphi_i(1)\varphi_j(2) \rangle \\ &= \langle \varphi_k(1)\varphi_l(2) | \hat{w}_{12}^\dagger g_{12} | \varphi_i(1)\varphi_j(2) \rangle, \end{aligned} \quad (13)$$

$$\begin{aligned} B_{kl,mn}^{(ij)} &= \langle \chi_{kl}(1,2) | \hat{f}_{12} - \varepsilon_i - \varepsilon_j | \chi_{mn}(1,2) \rangle \\ &= \langle \varphi_k(1)\varphi_l(2) | \hat{w}_{12}^\dagger (\hat{f}_{12} - \varepsilon_i - \varepsilon_j) \\ &\quad \times \hat{w}_{12} | \varphi_m(1)\varphi_n(2) \rangle, \end{aligned} \quad (14)$$

$$\begin{aligned} C_{kl,ab}^{(ij)} &= \langle \chi_{kl}(1,2) | \hat{f}_{12} - \varepsilon_i - \varepsilon_j | \varphi_a(1)\varphi_b(2) \rangle \\ &= \langle \varphi_k(1)\varphi_l(2) | \hat{w}_{12}^\dagger (\hat{f}_{12} - \varepsilon_i - \varepsilon_j) | \varphi_a(1)\varphi_b(2) \rangle, \end{aligned} \quad (15)$$

and

$$g_{12} = r_{12}^{-1}, \quad \hat{f}_{12} = \hat{F}_1 + \hat{F}_2. \quad (16)$$

\hat{F}_1 is the one-electron Fock operator and ε_i is the orbital energy of the occupied molecular orbital $\varphi_i(1)$. The explicitly correlated functions in Ansatz **1** are strongly orthogonal to all pairs of the orbital basis. As a consequence, all matrix elements $C_{kl,ab}^{(ij)}$ vanish for this Ansatz. These matrix elements describe the coupling between the doubly substituted determinants of conventional MP2 theory with the explicitly

correlated functions. These matrix elements do *not vanish* for Ansatz **2**, where the explicitly correlated functions are strongly orthogonal only to pairs of occupied orbitals. For this reason, we have defined vectors $\tilde{\mathbf{V}}^{(ij)}$ and matrices $\tilde{\mathbf{B}}^{(ij)}$ that include the coupling (zero or not) with the doubly substituted determinants.

Finally, it is useful to define the matrix

$$X_{kl,mn} = \langle \varphi_k(1)\varphi_l(2) | \hat{w}_{12}^\dagger \hat{w}_{12} | \varphi_m(1)\varphi_n(2) \rangle, \quad (17)$$

which is an intermediate quantity that is used when the $\tilde{\mathbf{B}}^{(ij)}$ matrices are computed.

D. Working equations for Ansatz 1

Let us first investigate the two-electron operator product

$$\begin{aligned} \hat{w}_{12}^\dagger g_{12} &= r_{12}(1 - \hat{P}_1)(1 - \hat{P}_2)r_{12}^{-1} \\ &= r_{12}(1 - \hat{P}_1 - \hat{P}_2 + \hat{P}_1\hat{P}_2)r_{12}^{-1}. \end{aligned} \quad (18)$$

It contains four terms. The first term is trivial, the fourth term factorizes into a product of two-electron integrals, but the second and third terms, where the operators \hat{P}_1 and \hat{P}_2 occur alone, lead to three-electron integrals. Consider, for example

$$\begin{aligned} &\langle \varphi_k(1)\varphi_l(2) | r_{12}\hat{P}_1 g_{12} | \varphi_i(1)\varphi_j(2) \rangle \\ &= \sum_p \langle \varphi_k(1)\varphi_l(2)\varphi_p(3) | r_{12}g_{23} | \varphi_p(1)\varphi_j(2)\varphi_i(3) \rangle. \end{aligned} \quad (19)$$

It has been common practice in the R12 methods to avoid these three-electron integrals by inserting the resolution of the identity (\hat{P}_2) into the integrals with a single projector

$$\hat{P}_1 \rightarrow \hat{P}_1\hat{P}_2, \quad (20)$$

and similarly by inserting \hat{P}_1

$$\hat{P}_2 \rightarrow \hat{P}_1\hat{P}_2. \quad (21)$$

This computational strategy has been termed ‘‘standard approximation’’ (SA) in previous work (the SA actually also involves a few more approximations). In the new method that we propose here, we employ an auxiliary basis $\{\varphi_{p'}(1)\}_{p'=1,\dots,N'}$ and make the substitutions

$$\hat{P}_1 \rightarrow \hat{P}_1\hat{P}'_2, \quad \hat{P}_2 \rightarrow \hat{P}'_1\hat{P}_2. \quad (22)$$

We will denote our new approach as ‘‘auxiliary basis set’’ (ABS) approximation. Thus, for the product $g_{12}\hat{w}_{12}$ in the standard and ABS approximations, we find

$$\hat{w}_{12}^\dagger g_{12} \stackrel{\text{SA}}{\approx} 1 - r_{12}\hat{P}_1\hat{P}_2 g_{12}, \quad (23)$$

and

$$\hat{w}_{12}^\dagger g_{12} \stackrel{\text{ABS}}{\approx} 1 - r_{12}\hat{P}_1\hat{P}'_2 g_{12} - r_{12}\hat{P}'_1\hat{P}_2 g_{12} + r_{12}\hat{P}_1\hat{P}_2 g_{12}, \quad (24)$$

respectively. Obviously, the matrix elements of Eq. (17) can be computed in the same manner

$$\begin{aligned} \hat{w}_{12}^\dagger \hat{w}_{12} &= \hat{w}_{12}^\dagger r_{12} \\ &\stackrel{\text{ABS}}{\approx} r_{12}^2 - r_{12}\hat{P}_1\hat{P}'_2 r_{12} - r_{12}\hat{P}'_1\hat{P}_2 r_{12} + r_{12}\hat{P}_1\hat{P}_2 r_{12}. \end{aligned} \quad (25)$$

Let us now turn to the matrix elements of Eq. (14). To evaluate these elements, we rewrite the corresponding two-electron operator as

$$\begin{aligned} \hat{w}_{12}^\dagger (\hat{f}_{12} - \varepsilon_i - \varepsilon_j) \hat{w}_{12} &= \frac{1}{2}\hat{w}_{12}^\dagger [\hat{f}_{12}, \hat{w}_{12}] + \frac{1}{2}[\hat{w}_{12}^\dagger, \hat{f}_{12}] \hat{w}_{12} \\ &\quad + \frac{1}{2}\hat{w}_{12}^\dagger \hat{w}_{12} (\hat{f}_{12} - \varepsilon_i - \varepsilon_j) \\ &\quad + \frac{1}{2}(\hat{f}_{12} - \varepsilon_i - \varepsilon_j) \hat{w}_{12}^\dagger \hat{w}_{12}. \end{aligned} \quad (26)$$

The last two terms of Eq. (26) are easily computed when we assume that the occupied orbitals are eigenfunctions of the Fock operator in the sense of the *generalized Brillouin condition* (GBC).²⁶ We then obtain

$$\begin{aligned} &\langle \varphi_k(1)\varphi_l(2) | \hat{w}_{12}^\dagger \hat{w}_{12} (\hat{f}_{12} - \varepsilon_i - \varepsilon_j) | \varphi_m(1)\varphi_n(2) \rangle \\ &\stackrel{\text{GBC}}{\approx} (\varepsilon_m + \varepsilon_n - \varepsilon_i - \varepsilon_j) X_{kl,mn}. \end{aligned} \quad (27)$$

Concerning Ansatz **1**, we furthermore assume that the *extended Brillouin condition* (EBC)²⁶ is satisfied, that is, we assume that the orbital space is closed under the Fock operator. Then

$$[\hat{f}_{12}, (1 - \hat{P}_1)(1 - \hat{P}_2)] \stackrel{\text{EBC}}{\approx} 0, \quad (28)$$

and we obtain

$$\begin{aligned} \hat{w}_{12}^\dagger [\hat{f}_{12}, \hat{w}_{12}] &\stackrel{\text{EBC}}{\approx} \hat{w}_{12}^\dagger [\hat{f}_{12}, r_{12}] \\ &= \hat{w}_{12}^\dagger [\hat{T}_1 + \hat{T}_2, r_{12}] - \hat{w}_{12}^\dagger [\hat{K}_1 + \hat{K}_2, r_{12}], \end{aligned} \quad (29)$$

where \hat{T}_1 and \hat{K}_1 are the one-electron kinetic energy and exchange operators, respectively.

The ABS approximation can now be applied to the matrix elements over the commutator of r_{12} with the kinetic energy operator

$$\begin{aligned} \hat{w}_{12}^\dagger [\hat{T}_1 + \hat{T}_2, r_{12}] &\stackrel{\text{ABS}}{\approx} r_{12}[\hat{T}_1 + \hat{T}_2, r_{12}] - r_{12}\hat{P}_1\hat{P}'_2 [\hat{T}_1 \\ &\quad + \hat{T}_2, r_{12}] - r_{12}\hat{P}'_1\hat{P}_2 [\hat{T}_1 + \hat{T}_2, r_{12}] \\ &\quad + r_{12}\hat{P}_1\hat{P}_2 [\hat{T}_1 + \hat{T}_2, r_{12}]. \end{aligned} \quad (30)$$

No further approximations are required, and the computation of the corresponding two-electron Gaussian integrals over $r_{12}[\hat{T}_1 + \hat{T}_2, r_{12}]$ and $[\hat{T}_1 + \hat{T}_2, r_{12}]$ is straightforward³⁸ when it is noted that

$$\begin{aligned} &\frac{1}{2}r_{12}[\hat{T}_1 + \hat{T}_2, r_{12}] + \frac{1}{2}[r_{12}, \hat{T}_1 + \hat{T}_2]r_{12} \\ &= \frac{1}{2}[r_{12}, [\hat{T}_1 + \hat{T}_2, r_{12}]] = 1. \end{aligned} \quad (31)$$

The matrix elements over the commutator of r_{12} with the exchange operator are more difficult, however. In the present work, we suggest to approximate these integrals by first inserting the ABS approximation into \hat{w}_{12}^\dagger

$$\hat{w}_{12}^\dagger[\hat{K}_1 + \hat{K}_2, r_{12}] \approx r_{12}[\hat{K}_1 + \hat{K}_2, r_{12}] - r_{12}\hat{P}_1\hat{P}_2'[\hat{K}_1 + \hat{K}_2, r_{12}] - r_{12}\hat{P}_1\hat{P}_2[\hat{K}_1 + \hat{K}_2, r_{12}] + r_{12}\hat{P}_1\hat{P}_2[\hat{K}_1 + \hat{K}_2, r_{12}], \quad (32)$$

and subsequently, by inserting the ABS approximation into the two-electron integrals over the operators $r_{12}[\hat{K}_1 + \hat{K}_2, r_{12}]$ and $[\hat{K}_1 + \hat{K}_2, r_{12}]$, where needed. This yields

$$\begin{aligned} \langle \varphi_k(1)\varphi_l(2) | \hat{w}_{12}^\dagger \hat{K}_1 r_{12} | \varphi_m(1)\varphi_n(2) \rangle \\ \approx \sum_{p'q'r'}^{\text{ABS}} r_{kl}^{p'q'} K_p^{r'} r_{r'q'}^{mn} - \sum_{pq'r'} r_{kl}^{pq'} K_p^{r'} r_{r'q'}^{mn} \\ - \sum_{p'q'r'} r_{kl}^{p'q'} K_p^{r'} r_{r'q'}^{mn} + \sum_{pqr'} r_{kl}^{pq} K_p^{r'} r_{r'q'}^{mn}, \end{aligned} \quad (33)$$

and

$$\langle \varphi_k(1)\varphi_l(2) | \hat{w}_{12}^\dagger r_{12} \hat{K}_1 | \varphi_m(1)\varphi_n(2) \rangle \approx \sum_{r'}^{\text{ABS}} X_{kl,r'n} K_{r'}^m, \quad (34)$$

where

$$\begin{aligned} K_p^q &= \langle \varphi_p(1) | \hat{K}_1 | \varphi_q(1) \rangle, \\ r_{pq}^{rs} &= \langle \varphi_p(1)\varphi_q(2) | r_{12} | \varphi_r(1)\varphi_s(2) \rangle. \end{aligned} \quad (35)$$

E. Working equations for Ansatz 2

The working equations for Ansatz 2 are very similar to those for Ansatz 1. In an obvious manner, the ABS approximation yields

$$\hat{w}_{12}^\dagger g_{12} \approx 1 - r_{12}\hat{O}_1\hat{P}_2'g_{12} - r_{12}\hat{P}_1\hat{O}_2g_{12} + r_{12}\hat{O}_1\hat{O}_2g_{12}, \quad (36)$$

$$\hat{w}_{12}^\dagger \hat{w}_{12} \approx r_{12}^2 - r_{12}\hat{O}_1\hat{P}_2'r_{12} - r_{12}\hat{P}_1\hat{O}_2r_{12} + r_{12}\hat{O}_1\hat{O}_2r_{12}, \quad (37)$$

for the operator products $\hat{w}_{12}^\dagger g_{12}$ and $\hat{w}_{12}^\dagger \hat{w}_{12}$, respectively.

We again employ Eqs. (26) and (27) for the computation of the elements of the matrices $\mathbf{B}^{(ij)}$. In contrast to Ansatz 1, however, we need not satisfy the EBC to arrive at Eq. (29). Rather, it is sufficient to satisfy the GBC. Since, by virtue of the GBC

$$[\hat{f}_{12}, (1 - \hat{O}_1)(1 - \hat{O}_2)] \approx 0, \quad (38)$$

we obtain

$$\begin{aligned} \hat{w}_{12}^\dagger[\hat{f}_{12}, \hat{w}_{12}] &\approx \hat{w}_{12}^\dagger[\hat{f}_{12}, r_{12}] \\ &= \hat{w}_{12}^\dagger[\hat{T}_1 + \hat{T}_2, r_{12}] - \hat{w}_{12}^\dagger[\hat{K}_1 + \hat{K}_2, r_{12}]. \end{aligned} \quad (39)$$

In the framework of the ABS approximation, the matrix elements involving the kinetic energy and exchange operators are computed according to

$$\begin{aligned} \hat{w}_{12}^\dagger[\hat{T}_1 + \hat{T}_2, r_{12}] &\approx r_{12}[\hat{T}_1 + \hat{T}_2, r_{12}] - r_{12}\hat{O}_1\hat{P}_2'[\hat{T}_1 \\ &\quad + \hat{T}_2, r_{12}] - r_{12}\hat{P}_1\hat{O}_2[\hat{T}_1 + \hat{T}_2, r_{12}] \\ &\quad + r_{12}\hat{O}_1\hat{O}_2[\hat{T}_1 + \hat{T}_2, r_{12}], \end{aligned} \quad (40)$$

$$\begin{aligned} \langle \varphi_k(1)\varphi_l(2) | \hat{w}_{12}^\dagger \hat{K}_1 r_{12} | \varphi_m(1)\varphi_n(2) \rangle \\ \approx \sum_{p'q'r'}^{\text{ABS}} r_{kl}^{p'q'} K_p^{r'} r_{r'q'}^{mn} - \sum_{iq'r'} r_{kl}^{iq'} K_i^{r'} r_{r'q'}^{mn} \\ - \sum_{p'jr'} r_{kl}^{p'j} K_p^{r'} r_{r'j}^{mn} + \sum_{ijr'} r_{kl}^{ij} K_i^{r'} r_{r'j}^{mn}, \end{aligned} \quad (41)$$

and

$$\langle \varphi_k(1)\varphi_l(2) | \hat{w}_{12}^\dagger r_{12} \hat{K}_1 | \varphi_m(1)\varphi_n(2) \rangle \approx \sum_{r'}^{\text{ABS}} X_{kl,r'n} K_{r'}^m. \quad (42)$$

Equation (42) differs from Eq. (34) only by the matrix \mathbf{X} , which contains integrals over the operator of Eq. (25) in Ansatz 1 but over the operator of Eq. (37) in Ansatz 2.

In Ansatz 2, matrix elements $C_{kl,ab}^{(ij)}$ also occur [Eq. (15)]. By virtue of the GBC, we obtain

$$\begin{aligned} C_{kl,ab}^{(ij)} &\stackrel{\text{GBC}}{\approx} \langle \varphi_k(1)\varphi_l(2) | [r_{12}, \hat{f}_{12}] | \varphi_a(1)\varphi_b(2) \rangle \\ &\quad + (\varepsilon_k + \varepsilon_l - \varepsilon_i - \varepsilon_j) r_{kl}^{ab} \\ &\stackrel{\text{ABS}}{\approx} \langle \varphi_k(1)\varphi_l(2) | [r_{12}, \hat{T}_1 + \hat{T}_2] | \varphi_a(1)\varphi_b(2) \rangle \\ &\quad + (\varepsilon_k + \varepsilon_l - \varepsilon_i - \varepsilon_j) r_{kl}^{ab} \\ &\quad + \sum_{p'} (K_k^{p'} r_{p'l}^{ab} - r_{kl}^{p'b} K_p^a) \\ &\quad + \sum_{q'} (K_l^{q'} r_{kq'}^{ab} - r_{kl}^{aq'} K_q^b). \end{aligned} \quad (43)$$

Although not necessary, one could at this point go one step further and assume that the EBC holds, that is, that the virtual orbitals are eigenfunctions of the Fock operator. Then, the $C_{kl,ab}^{(ij)}$ coupling elements simplify to

$$C_{kl,ab}^{(ij)} \stackrel{\text{EBC}}{\approx} (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j) r_{kl}^{ab}. \quad (44)$$

Following Ref. 35, we shall attach an asterisk to the method's acronym when we utilize Eq. (44). Approach 2* thus differs from approach 2 by using Eq. (44) instead of Eq. (43). We obtain for approach 2*

$$\tilde{V}_{kl}^{(ij)}(\mathbf{2}^*) \approx V_{kl}^{(ij)} - \sum_{ab}^{EBC} r_{kl}^{ab} \langle \varphi_a(1) \varphi_b(2) | g_{12} | \varphi_i(1) \varphi_j(2) \rangle, \quad (45)$$

$$\tilde{B}_{kl,mn}^{(ij)}(\mathbf{2}^*) \approx B_{kl,mn}^{(ij)} - \frac{1}{2} \sum_{ab} r_{kl}^{ab} C_{ab,mn}^{(ij)} - \frac{1}{2} \sum_{ab} r_{mn}^{ab} C_{ab,kl}^{(ij)}. \quad (46)$$

Concerning Eq. (12), we emphasize that only the matrix elements $C_{kl,ab}^{(ij)}$ are approximated according to Eq. (44), whereas the elements $C_{ab,mn}^{(ij)}$ are not, and care must be taken to symmetrize the matrices $\tilde{\mathbf{B}}^{(ij)}$ (this symmetrization is carried out by adding the corresponding two terms with weights of 1/2 each). This seems a somewhat inconsistent approach. The only reason for proceeding in this manner, however, is that we wish to define such ABS-based A and B methods that reduce to the previous approximations A and B of the original MP2-R12 work when the orbital basis $\{\varphi_p(1)\}_{p=1,\dots,N}$ is employed as the auxiliary basis. Also, Ansatz **1** reduces to the original MP2-R12 work when the orbital and auxiliary basis sets are identical.

One could speak of a $\mathbf{2}^{**}$ approach when the $C_{ab,mn}^{(ij)}$ matrix elements in Eq. (46) were also approximated according to Eq. (44), but this $\mathbf{2}^{**}$ approach is not considered in the present article. Since the $\mathbf{2}^*$ simplification is already unnecessary from a computational point of view (the approach is only briefly mentioned in the present work), we have chosen not to pursue the hypothetical $\mathbf{2}^{**}$ form at all.

III. COMPUTER IMPLEMENTATION

The new MP2-R12 methods **1**, **2**, and $\mathbf{2}^*$ have been implemented into a local version of the DALTON program,³⁹ partly by modifying and extending the code developed by Koch and co-workers for the integral-direct transformation of two-electron integrals from the AO basis into the basis of molecular orbitals.^{40–42}

When discussing the computer implementation, we shall introduce the approximations A, A', and B. In approximation B, all matrix elements are evaluated as indicated in Secs. IID and IIE. Hence, approximation B includes no other approximations than the resolution of identity in terms of the auxiliary basis set. The approximations A and A' have been described in some detail in Ref. 43 and include additional approximations concerned with the neglect of certain integrals. In approximation A', all terms are neglected that involve the exchange operator. Thus, Eqs. (33) and (34) are neglected for Ansatz **1**, and similarly, Eqs. (41) and (42) for Ansatz **2**. In addition to the terms that are neglected in approximation A', also Eq. (27) is neglected in approximation A. This term is usually much smaller than the first two terms on the right-hand side of Eq. (26).

A. Implementation of Ansatz **1**

All variants of MP2-R12 theory start with the computation of the following six types of integrals:

$$g_{ij}^{pq}, \quad g_{ij}^{p'q'}, \quad r_{ij}^{pq}, \quad r_{ij}^{p'q'}, \quad t_{ij}^{pq}, \quad t_{ij}^{p'q'}, \quad (47)$$

where r_{pq}^{rs} is given by Eq. (35), and

$$g_{pq}^{rs} = \langle \varphi_p(1) \varphi_q(2) | r_{12}^{-1} | \varphi_r(1) \varphi_s(2) \rangle, \quad (48)$$

$$t_{pq}^{rs} = \langle \varphi_p(1) \varphi_q(2) | [\hat{T}_1 + \hat{T}_2, r_{12}] | \varphi_r(1) \varphi_s(2) \rangle. \quad (49)$$

It is important to note that only integrals with *one* auxiliary function at the most occur in Eq. (47). The computational effort of a calculation with n occupied orbitals, N orbital basis functions, and N' auxiliary functions scales as nN^4 for the g_{ij}^{pq} integrals (as in conventional MP2 theory) and as $nN'N^3$ for the $g_{ij}^{p'q'}$ integrals, and the computation time required for the six integrals of Eq. (47) thus scales as $n(N+N')N^3$. With these six two-electron integrals available, as well as with the integrals

$$s_{pq}^{rs} = \langle \varphi_p(1) \varphi_q(2) | r_{12}^2 | \varphi_r(1) \varphi_s(2) \rangle, \quad (50)$$

which factorize into products of one-electron integrals, we can construct all the matrices that are needed for the approximations A and A' of R12 theory. For these approximations, the matrices $\mathbf{B}^{(ij)}$ are defined as^{36,43}

$$B_{kl,mn}^{(ij)}(\mathbf{A}) = \frac{1}{2} (T_{kl,mn} + T_{mn,kl}), \quad (51)$$

$$B_{kl,mn}^{(ij)}(\mathbf{A}') = B_{kl,mn}^{(ij)}(\mathbf{A}) + \frac{1}{2} (\varepsilon_k + \varepsilon_l + \varepsilon_m + \varepsilon_n - 2\varepsilon_i - 2\varepsilon_j) X_{kl,mn}. \quad (52)$$

Note that the matrices $\mathbf{B}^{(ij)}(\mathbf{A})$ and $\mathbf{B}^{(ij)}(\mathbf{A}')$ differ only by Eq. (27) (in symmetrized form), which is neglected in approximation A. The vectors $\mathbf{V}^{(ij)}$ and intermediates \mathbf{X} and \mathbf{T} are computed as

$$V_{kl}^{(ij)} = \delta_k^i \delta_l^j - \sum_{pq'} (r_{kl}^{pq'} g_{pq'}^{ij} + r_{lk}^{p'q'} g_{p'q'}^{ji}) + \sum_{pq} r_{kl}^{pq} g_{pq}^{ij}, \quad (53)$$

$$X_{kl,mn} = s_{kl}^{mn} - \sum_{pq'} (r_{kl}^{pq'} r_{pq'}^{mn} + r_{lk}^{p'q'} r_{p'q'}^{nm}) + \sum_{pq} r_{kl}^{pq} r_{pq}^{mn}, \quad (54)$$

$$T_{kl,mn} = \delta_k^m \delta_l^n - \sum_{pq'} (r_{kl}^{pq'} t_{pq'}^{mn} + r_{lk}^{p'q'} t_{p'q'}^{nm}) + \sum_{pq} r_{kl}^{pq} t_{pq}^{mn}. \quad (55)$$

For approximation B, we also need two-electron integrals that involve *two* orbitals of the auxiliary basis. Namely, in this approximation, we must compute the $\mathbf{B}^{(ij)}$ matrices according to

$$B_{kl,mn}^{(ij)}(\mathbf{B}) = B_{kl,mn}^{(ij)}(\mathbf{A}') + \frac{1}{2} (Q_{kl,mn} + Q_{mn,kl}) - \frac{1}{2} (P_{kl,mn} + P_{mn,kl}). \quad (56)$$

The matrix elements $Q_{kl,mn}$ represent the integrals that also occur in the original MP2-R12/B work, while the matrix elements $P_{kl,mn}$ only occur in the ABS-based approach. When the orbital and auxiliary sets are identical, the matrix elements $P_{kl,mn}$ all vanish. The elements $Q_{kl,mn}$ follow from Eq. (34), while the elements $P_{kl,mn}$ follow from Eq. (33).

The matrix elements $Q_{kl,mn}$ are most efficiently computed by introducing intermediate orbitals $\varphi_{m^*}(1)$ that are defined as

TABLE I. Overview of MP2-R12 approaches.

| Approach | GBC used? ^a | EBC used? ^b | $[\hat{K}_1 + \hat{K}_2, r_{12}]$ neglected? ^c | L'_{\max} ^d | Computing time ^e | Without ABS ^f | |
|-----------|------------------------|------------------------|---|--------------------------|-----------------------------------|--------------------------|-------------------|
| 1 | A | Yes | Yes | Yes | $L_{\max} + 2L_{\text{occ}}$ | $n(N+N')N^3$ | A |
| | A' | Yes | Yes | Yes | $L_{\max} + 2L_{\text{occ}}$ | $n(N+N')N^3$ | A' |
| | B | Yes | Yes | No | ∞ | $n(N+N')^2N^2$ | B |
| 2 | A | Yes | No | Yes | $\max(L_{\max}, 3L_{\text{occ}})$ | $n(N+N')N^3$ | None ^g |
| | A' | Yes | No | Yes | $\max(L_{\max}, 3L_{\text{occ}})$ | $n(N+N')N^3$ | None ^g |
| | B | Yes | No | No | ∞ | $n(N+N')^2N^2$ | None ^g |
| 2* | A | Yes | Yes | Yes | $3L_{\text{occ}}$ | $n(N+N')N^3$ | A |
| | A' | Yes | Yes | Yes | $3L_{\text{occ}}$ | $n(N+N')N^3$ | A' |
| | B | Yes | Yes | No | ∞ | $n(N+N')^2N^2$ | B |

^aIs the generalized Brillouin condition assumed to be satisfied?

^bIs the extended Brillouin condition assumed to be satisfied?

^cAre the $[\hat{K}_1 + \hat{K}_2, r_{12}]$ matrix elements neglected?

^d L'_{\max} is the angular momentum quantum number after which the auxiliary basis can be truncated in an atomic calculation, where L_{occ} is the highest occupied angular momentum and L_{\max} is the highest angular momentum of the orbital basis.

^e n is the number of occupied Hartree–Fock orbitals, N is the number of orbital basis functions, and N' is the number of auxiliary basis functions.

^fPrevious MP2-R12 method to which the new approach reduces when no auxiliary basis set is used.

^gThere is no previous MP2-R12 method that corresponds to this variant.

$$\varphi_{m^*}(1) = \sum_{r'} \varphi_{r'}(1) K_{r'}^m. \quad (57)$$

In terms of these orbitals, the matrix elements $Q_{kl,mn}$ are given by

$$\begin{aligned} Q_{kl,mn} = & s_{kl}^{m^*n} - \sum_{pq'} (r_{kl}^{pq'} r_{pq'}^{m^*n} + r_{lk}^{pq'} r_{pq'}^{nm^*}) + \sum_{pq} r_{kl}^{pq} r_{pq}^{m^*n} \\ & + s_{kl}^{mn^*} - \sum_{pq'} (r_{kl}^{pq'} r_{pq'}^{mn^*} + r_{lk}^{pq'} r_{pq'}^{n^*m}) \\ & + \sum_{pq} r_{kl}^{pq} r_{pq}^{mn^*} = X_{kl,m^*n} + X_{kl,mn^*}. \end{aligned} \quad (58)$$

Relative to approximations A and A', the essential extra work required for approximation B consists of the computation of the two-electron integrals $r_{m^*n}^{pq'}$, $r_{mn^*}^{pq'}$, $r_{m^*n}^{pq}$, and $r_{mn^*}^{pq}$. The computation time for this step of the calculation scales as $n(N+N')N'N^2$.

As already mentioned, the ABS approximation enables the evaluation of the integrals of Eq. (33). In our current implementation, these integrals are computed by choosing the orthonormal auxiliary basis such that the exchange matrix becomes diagonal in that space

$$K_{p'}^{q'} = \delta_{p'}^{q'} \lambda_{p'}. \quad (59)$$

Then, the following four intermediates are computed:

$$p_{p'q'}^{mn} = (\lambda_{p'} + \lambda_{q'}) r_{p'q'}^{mn}, \quad (60)$$

$$p_{p'q}^{mn} = \lambda_{p'} r_{p'q}^{mn} + \sum_{r'} K_q^{r'} r_{p'r'}^{mn}, \quad (61)$$

$$p_{pq'}^{mn} = \lambda_{q'} r_{pq'}^{mn} + \sum_{r'} K_p^{r'} r_{r'q'}^{mn}, \quad (62)$$

$$p_{pq}^{mn} = \sum_{r'} (K_p^{r'} r_{r'q}^{mn} + K_q^{r'} r_{pr'}^{mn}), \quad (63)$$

from which the matrix elements $P_{kl,mn}$ are obtained as

$$\begin{aligned} P_{kl,mn} = & \sum_{p'q'} r_{kl}^{p'q'} p_{p'q'}^{mn} - \sum_{pq'} r_{kl}^{pq'} p_{pq'}^{mn} - \sum_{p'q} r_{kl}^{p'q} p_{p'q}^{mn} \\ & + \sum_{pq} r_{kl}^{pq} p_{pq}^{mn}. \end{aligned} \quad (64)$$

Two-electron integrals must be computed that involve two functions of the auxiliary basis, both for the matrix representation of the exchange operator in the auxiliary basis ($K_p^{q'}$) and for the $r_{kl}^{p'q'}$ integrals. The corresponding computation times scale as $(N')^2N^2$ and $n(N')^2N^2$, respectively.

B. Implementation of Ansatz 2

Assuming that the integrals of Eq. (47) are available, we can compute

$$V_{kl}^{(ij)} = \delta_k^i \delta_l^j - \sum_{mq'} (r_{kl}^{mq'} g_{mq'}^{ij} + r_{lk}^{mq'} g_{mq'}^{ji}) + \sum_{mn} r_{kl}^{mn} g_{mn}^{ij}, \quad (65)$$

$$X_{kl,mn} = s_{kl}^{mn} - \sum_{iq'} (r_{kl}^{iq'} r_{iq'}^{mn} + r_{lk}^{iq'} r_{iq'}^{nm}) + \sum_{ij} r_{kl}^{ij} r_{ij}^{mn}, \quad (66)$$

$$T_{kl,mn} = \delta_k^n \delta_l^m - \sum_{iq'} (r_{kl}^{iq'} t_{iq'}^{mn} + r_{lk}^{iq'} t_{iq'}^{nm}) + \sum_{ij} r_{kl}^{ij} t_{ij}^{mn}, \quad (67)$$

as well as

$$C_{kl,ab}^{(ij)}(\text{A}) = -t_{kl}^{ab}, \quad (68)$$

$$C_{kl,ab}^{(ij)}(\text{A}') = C_{kl,ab}^{(ij)}(\text{A}) + (\varepsilon_k + \varepsilon_l - \varepsilon_i - \varepsilon_j) r_{kl}^{ab}. \quad (69)$$

We also need integrals of the type r_{kl}^{ab} to compute

TABLE II. All-electron Møller–Plesset second-order energies ($E^{(2)}$ in mE_h) of the Ne atom.

| Basis ^a | MP2 ^b | Original method | | New Ansatz 1 | | New Ansatz 2 | |
|--------------------|------------------|-----------------|---------|--------------|---------|--------------|---------|
| | | R12/A' | R12/B | R12/A' | R12/B | R12/A' | R12/B |
| <i>sp</i> | -191.99 | -688.49 | -506.95 | -361.84 | -330.37 | -362.45 | -331.33 |
| <i>spd</i> | -322.27 | -408.78 | -395.11 | -361.97 | -358.19 | -390.71 | -382.59 |
| <i>spdf</i> | -359.84 | -389.71 | -387.19 | -376.20 | -375.30 | -389.76 | -387.49 |
| <i>spdf g</i> | -374.12 | -388.62 | -387.89 | -383.27 | -382.95 | -388.67 | -387.99 |
| <i>spdf gh</i> | -379.46 | -388.29 | -388.01 | -386.13 | -385.97 | -388.35 | -388.07 |
| <i>spdf ghi</i> | -381.65 | -388.19 | -388.04 | -387.69 | -387.56 | -388.24 | -388.09 |

^aSubsets of the $20s14p11d9f7g5h3i$ basis. The $32s24p18d15f12g9h6i$ basis was applied as an auxiliary basis in all calculations.

^bConventional all-electron MP2 energy.

$$C_{kl,ab}^{(ij)}(\mathbf{B}) = C_{kl,ab}^{(ij)}(\mathbf{A}') + r_{k^*l}^{ab} + r_{kl^*}^{ab} - \sum_{r'} (r_{kl}^{r'b} K_{r'}^a + r_{kl}^{ar'} K_{r'}^b). \quad (70)$$

Hence, for the above quantities, we need two-electron integrals with only *one* auxiliary function, and no more integrals are needed for the approximations A and A'. For the more elaborate B approximation, however, we must compute two-electron integrals with *two* auxiliary functions. Namely, we need to evaluate the quantities

$$Q_{kl,mn} = X_{kl,m^*n} + X_{kl,mn^*}, \quad (71)$$

$$P_{kl,mn} = \sum_{p'q'} r_{kl}^{p'q'} P_{p'q'}^{mn} - \sum_{iq'} r_{kl}^{iq'} P_{iq'}^{mn} - \sum_{p'j} r_{kl}^{p'j} P_{p'j}^{mn} + \sum_{ij} r_{kl}^{ij} P_{ij}^{mn}, \quad (72)$$

which contribute to the matrix $\mathbf{B}^{(ij)}(\mathbf{B})$

$$B_{kl,mn}^{(ij)}(\mathbf{A}) = \frac{1}{2}(T_{kl,mn} + T_{mn,kl}), \quad (73)$$

$$B_{kl,mn}^{(ij)}(\mathbf{A}') = B_{kl,mn}^{(ij)}(\mathbf{A}) + \frac{1}{2}(\varepsilon_k + \varepsilon_l + \varepsilon_m + \varepsilon_n - 2\varepsilon_i - 2\varepsilon_j)X_{kl,mn}, \quad (74)$$

$$B_{kl,mn}^{(ij)}(\mathbf{B}) = B_{kl,mn}^{(ij)}(\mathbf{A}') + \frac{1}{2}(Q_{kl,mn} + Q_{mn,kl}) - \frac{1}{2}(P_{kl,mn} + P_{mn,kl}). \quad (75)$$

Finally, for the approximation $\xi = \mathbf{A}$, \mathbf{A}' , or \mathbf{B} , the vectors $\tilde{\mathbf{V}}^{(ij)}(\xi)$ and matrices $\tilde{\mathbf{B}}^{(ij)}(\xi)$ are computed as

$$\tilde{V}_{kl}^{(ij)}(\xi) = V_{kl}^{(ij)} - \sum_{ab} \frac{C_{kl,ab}^{(ij)}(\mathbf{B})}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} g_{ab}^{ij}, \quad (76)$$

$$\begin{aligned} \tilde{B}_{kl,mn}^{(ij)}(\xi) &= B_{kl,mn}^{(ij)}(\xi) \\ &- \frac{1}{2} \sum_{ab} \frac{C_{kl,ab}^{(ij)}(\mathbf{B})C_{ab,mn}^{(ij)}(\xi) + C_{mn,ab}^{(ij)}(\mathbf{B})C_{ab,kl}^{(ij)}(\xi)}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}. \end{aligned} \quad (77)$$

Note that the full coupling matrix of approach B, that is, $\mathbf{C}^{(ij)}(\mathbf{B})$, occurs in Eqs. (76) and (77), not only in approach B itself, but also in the approximations A and A'. Computa-

tionally, almost nothing is gained by neglecting certain terms in $\mathbf{C}^{(ij)}$. They are nonetheless neglected in the $\mathbf{C}^{(ij)}(\xi)$ matrix of Eq. (77) in an effort to remain consistent with previous R12 work. This becomes clear when we consider the 2^* approach. In this approach, the $C_{kl,ab}^{(ij)}(\mathbf{B})$ are replaced by the integrals r_{kl}^{ab}

$$\tilde{V}_{kl}^{(ij)}(\xi^*) = V_{kl}^{(ij)} - \sum_{ab} r_{kl}^{ab} g_{ab}^{ij}, \quad (78)$$

$$\begin{aligned} \tilde{B}_{kl,mn}^{(ij)}(\xi^*) &= B_{kl,mn}^{(ij)}(\xi) - \frac{1}{2} \sum_{ab} r_{kl}^{ab} C_{ab,mn}^{(ij)}(\xi) \\ &- \frac{1}{2} \sum_{ab} r_{mn}^{ab} C_{ab,kl}^{(ij)}(\xi). \end{aligned} \quad (79)$$

Due to the A and A' approximations in the matrix elements

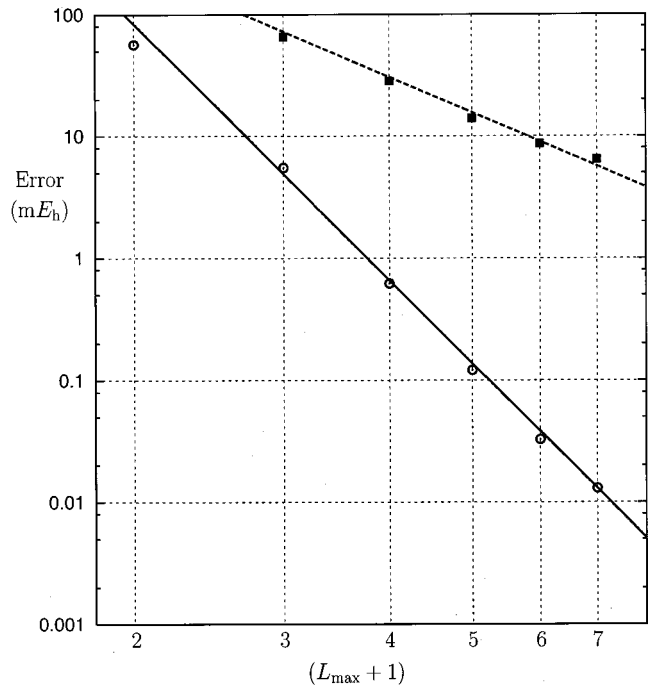


FIG. 1. Error in the all-electron second-order Møller–Plesset correlation energy of Ne as computed in subsets of the $20s14p11d9f7g5h3i$ basis. Comparison between the conventional MP2 (■) and the new MP2-R12/2B approach (○). The dashed and solid lines show $(L_{\max} + 1)^{-3}$ and $(L_{\max} + 1)^{-7}$ behavior, respectively.

TABLE III. Møller–Plesset second-order pair energies ($E^{(2)}$ in mE_h) of the Ne atom as computed by Ansatz **2**, in approximation B, in subsets of the $20s14p11d9f7g5h3i$ basis (using the auxiliary basis $32s24p18d15f12g9h6i$).

| Pair | <i>sp</i> | <i>spd</i> | <i>spdf</i> | <i>spdf g</i> | <i>spdf gh</i> | <i>spdf ghi</i> | Ref. 35 |
|------------------|-----------|------------|-------------|---------------|----------------|-----------------|---------|
| $1s^2$ (1S) | -40.140 | -40.243 | -40.252 | -40.252 | -40.252 | -40.252 | -40.252 |
| $1s2s$ (1S) | -3.831 | -3.956 | -3.971 | -3.973 | -3.974 | -3.974 | -3.974 |
| $1s2s$ (3S) | -1.534 | -1.578 | -1.582 | -1.582 | -1.582 | -1.582 | -1.582 |
| $2s^2$ (1S) | -11.906 | -12.023 | -12.036 | -12.038 | -12.039 | -12.039 | -12.038 |
| $1s2p$ (1P) | -3.631 | -7.750 | -8.132 | -8.171 | -8.176 | -8.177 | -8.176 |
| $1s2p$ (3P) | -10.636 | -13.777 | -13.901 | -13.909 | -13.910 | -13.910 | -13.911 |
| $2s2p$ (1P) | -46.566 | -59.526 | -60.341 | -60.453 | -60.476 | -60.482 | -60.472 |
| $2s2p$ (3P) | -21.732 | -26.557 | -26.694 | -26.706 | -26.708 | -26.708 | -26.708 |
| $2p^2$ (1S) | -45.286 | -45.503 | -45.550 | -45.566 | -45.571 | -45.573 | -45.565 |
| $2p^2$ (3P) | -82.192 | -87.108 | -87.317 | -87.337 | -87.340 | -87.340 | -87.341 |
| $2p^2$ (1D) | -63.874 | -84.570 | -87.714 | -87.999 | -88.047 | -88.057 | -88.042 |
| Total | -331.33 | -382.59 | -387.49 | -387.99 | -388.07 | -388.09 | -388.06 |

$C_{ab,mn}^{(ij)}(\xi)$, the approach **2*** corresponds exactly to the original MP2-R12/A and MP2-R12/A' methods when the orbital and auxiliary basis sets are identical.

IV. OVERVIEW OF MP2-R12 APPROACHES

An overview of the new MP2-R12 approaches is presented in Table I.

It is assumed in all methods that the *generalized* Brillouin condition (GBC) holds. This condition is basically satisfied in an AO basis of near-Hartree–Fock-limit quality. The *extended* Brillouin condition (EBC), which is much more difficult to satisfy than the GBC, need only be satisfied for Ansatz **1**. The EBC is not needed at all for Ansatz **2** and the approach transforms into the **2*** method when the EBC is nonetheless assumed to hold.

Approximation A (including A') is characterized by the neglect of the commutator between the exchange operators and the linear r_{12} term.⁴³

Furthermore, it is worthwhile to consider the maximum angular momentum quantum number L'_{\max} of auxiliary basis functions that contribute to the matrix elements in an atomic calculation. Auxiliary basis functions with angular momen-

tum greater than L'_{\max} do not contribute. It is seen from Table I that the auxiliary basis sets do not truncate in approximation B. This is due to the matrices **P** in Eqs. (64) and (72). Numerically, these matrices contribute little to the final energies and their contributions converge quickly with the extension of the (auxiliary) basis set. If the **P** matrices were omitted, the maximum angular momentum value L'_{\max} at which the RI can be truncated would be the same for approximations B and A (or A').

For the **2*** approach, it is found that $L'_{\max} = 3L_{\text{occ}}$. In the **2** approach itself, auxiliary functions up to L_{\max} (the highest angular momentum of the orbital basis) also contribute. This is due to the matrix elements $C_{kl,ab}^{(ij)}(\mathbf{B})$ in Eqs. (76) and (77), which are computed according to Eq. (70). Auxiliary functions up to L_{\max} contribute to the last term (i.e., the sum over r') in that equation. For Ansatz **1**, the maximum angular momentum value of the auxiliary basis is $L'_{\max} = L_{\max} + 2L_{\text{occ}}$ rather than $3L_{\text{occ}}$, as the R12 functions are chosen strongly orthogonal to orbital pairs of the full orbital basis and not only to the occupied space.

Concerning the computational effort of the new MP2-R12 calculations, it is important to realize that calculations

TABLE IV. Møller–Plesset second-order energies ($E^{(2)}$ in mE_h) of the Ne atom.

| Pair | Ref. 45 extrap. ^a | Ref. 46 extrap. ^b | Ref. 47 extrap. ^c | Ref. 48 | | Ref. 35 calc. ^f | This work calc. ^g |
|--------|---------------------------------|---------------------------------|---------------------------------|--------------------|----------------------|-------------------------------|---------------------------------|
| | | | | Calc. ^d | Extrap. ^e | | |
| $1s^2$ | -40.24 | -40.22 | -40.25 | -40.229 | -40.255 | -40.252 | -40.252 |
| $1s2s$ | -5.55 | -5.56 | -5.55 | -5.555 | -5.557 | -5.556 | -5.556 |
| $2s^2$ | -12.05 | -12.02 | -12.02 | -12.003 | -12.037 | -12.038 | -12.039 |
| $1s2p$ | -22.16 | -22.17 | -22.06 | -22.078 | -22.094 | -22.087 | -22.087 |
| $2s2p$ | -87.30 | -87.15 | -87.10 | -86.982 | -87.188 | -87.180 | -87.190 |
| $2p^2$ | -221.01 | -220.80 | -220.81 | -220.686 | -220.973 | -220.948 | -220.970 |
| Total | -388.3 | -387.9 | -387.8 | -387.53 | -388.11 | -388.06 | -388.09 |

^aWith extrapolation for $l > 6$.

^bWith extrapolation for $l > 9$.

^cRecommended values from R12 calculations and extrapolations.

^dCalculated with $l \leq 12$.

^eWith extrapolation for $l > 12$.

^fCalculated in the $20s14p11d9f7g5h$ basis.

^gCalculated by the new MP2-R12/2B method in the $20s14p11d9f7g5h3i$ orbital basis in conjunction with the $32s24p18d15f12g9h6i$ auxiliary basis.

TABLE V. Exponents of Gaussian basis functions.

| | C | N | O | F | Ne |
|----------|-------|-------|-------|-------|-------|
| <i>d</i> | 126.0 | 194.0 | 230.0 | 292.0 | 369.0 |
| | 55.0 | 83.8 | 100.0 | 127.0 | 161.0 |
| <i>f</i> | 24.1 | 37.2 | 61.6 | 88.9 | 123.0 |
| | 11.5 | 17.4 | 27.4 | 39.1 | 53.9 |
| <i>g</i> | 12.9 | 19.8 | 29.5 | 39.4 | 49.8 |
| | 5.84 | 8.74 | 12.4 | 16.3 | 20.4 |
| <i>h</i> | 4.84 | 7.06 | 10.0 | 13.4 | 17.4 |

carried out in approximation A (including A') scale only linearly with the number N' of auxiliary functions. When approximation B is used, however, the computation time grows quadratically with N' . The MP2-R12/B methods are thus significantly more time-consuming than the MP2-R12/A and MP2-R12/A' methods when $N' \gg N$. If, on the other hand, the orbital and auxiliary basis sets are identical (as in the original MP2-R12 work) or similar in size with $N' \approx N$, then the MP2-R12/B method is only ca. 30% more expensive than MP2-R12/A or MP2-R12/A'.

Finally, Table I also indicates that Ansatz 1 transforms into the original MP2-R12 approach when the orbital basis set is used for the RI approximation. Ansatz 2 does not transform into any previous method, but its 2* variant has been chosen such that it, too, transforms into the original MP2-R12 approach.

V. NUMERICAL RESULTS: THE NE ATOM

Calculations have been performed in subsets of a Gaussian basis set of the type $20s14p11d9f7g5h3i$. Its $20s14p11d9f7g5h$ subset is given in full detail in Ref. 35, and three sets of *i*-type Gaussians with exponents 6.454 503, 3.202 905, and 1.567 200 have been added to form the $20s14p11d9f7g5h3i$ basis. In conjunction with this basis, an auxiliary basis of the form $32s24p18d15f12g9h6i$ has been employed. Its $32s$ ($n_0=32$) and $24p$ ($n_1=24$) sets are even-tempered sets of the form $0.005 \times 3^{(k-1)/2}$ for $k = 1, \dots, n_l$, while the exponents of the d ($l=2$) through i sets ($l=6$) are given by the expression $(0.002l+0.003) \times 3^{(k+l-1)/2}$ for $k = 1, \dots, n_l$.

TABLE VI. Valence-shell Møller–Plesset second-order correlation energies ($E^{(2)}$ in mE_h) of the Ne atom and some small molecules as computed by the new MP2-R12 method in the correlation-consistent basis sets cc-pVXZ with $2 \leq X \leq 6$ (using the auxiliary basis $19s14p8d6f4g3h2i$ for C, N, O, F, and Ne, and $9s6p4d3f2g$ for H).

| Method | System ^a | X=2 | X=3 | X=4 | X=5 | X=6 | Limit ^b |
|--------|---|---------|---------|---------|---------|-------------------|--------------------|
| 1A' | CH ₂ (¹ A ₁) | -132.85 | -147.82 | -152.81 | -154.72 | -156.03 | -155.9 |
| | H ₂ O | -244.32 | -279.10 | -291.65 | -297.33 | -300.10 | -300.5 |
| | NH ₃ | -221.50 | -249.21 | -258.49 | -262.39 | n.a. ^c | -264.5 |
| | HF | -254.09 | -293.23 | -308.33 | -315.51 | -318.80 | -319.7 |
| | N ₂ | -355.86 | -395.27 | -410.18 | -416.71 | -419.86 | -421.0 |
| | CO | -339.30 | -377.99 | -393.03 | -399.61 | -402.80 | -403.9 |
| | Ne | -249.16 | -289.83 | -306.54 | -314.92 | -318.70 | -320.1 |
| | F ₂ | -488.24 | -561.95 | -589.77 | -603.23 | -609.32 | -611.7 |
| 2A' | CH ₂ (¹ A ₁) | -145.24 | -150.37 | -153.83 | -154.90 | -155.43 | -155.9 |
| | H ₂ O | -272.08 | -287.80 | -295.38 | -298.27 | -299.49 | -300.5 |
| | NH ₃ | -242.80 | -255.36 | -261.11 | -263.11 | n.a. ^c | -264.5 |
| | HF | -286.74 | -303.57 | -312.69 | -316.50 | -318.17 | -319.7 |
| | N ₂ | -390.28 | -405.62 | -415.38 | -418.50 | -419.96 | -421.0 |
| | CO | -374.40 | -389.19 | -398.58 | -401.69 | -402.98 | -403.9 |
| | Ne | -283.08 | -300.51 | -310.86 | -315.66 | -317.92 | -320.1 |
| | F ₂ | -553.51 | -581.53 | -598.70 | -605.72 | -608.92 | -611.7 |
| 1B | CH ₂ (¹ A ₁) | -128.79 | -146.80 | -152.37 | -154.52 | -155.89 | -155.9 |
| | H ₂ O | -236.85 | -277.39 | -290.66 | -296.88 | -299.88 | -300.5 |
| | NH ₃ | -215.72 | -247.92 | -257.82 | -262.06 | n.a. ^c | -264.5 |
| | HF | -244.21 | -290.98 | -306.94 | -314.96 | -318.57 | -319.7 |
| | N ₂ | -347.43 | -392.99 | -408.76 | -416.24 | -419.60 | -421.0 |
| | CO | -330.65 | -375.79 | -391.80 | -399.17 | -402.55 | -403.9 |
| | Ne | -236.16 | -287.00 | -304.80 | -314.30 | -318.44 | -320.1 |
| | F ₂ | -469.28 | -557.71 | -587.15 | -602.42 | -608.88 | -611.7 |
| 2B | CH ₂ (¹ A ₁) | -135.69 | -147.84 | -152.81 | -154.42 | -155.17 | -155.9 |
| | H ₂ O | -256.02 | -283.13 | -293.44 | -297.39 | -299.05 | -300.5 |
| | NH ₃ | -229.11 | -251.53 | -259.60 | -262.43 | n.a. ^c | -264.5 |
| | HF | -268.44 | -297.95 | -310.26 | -315.39 | -317.59 | -319.7 |
| | N ₂ | -372.17 | -400.25 | -412.97 | -417.46 | -419.44 | -421.0 |
| | CO | -355.50 | -383.64 | -396.24 | -400.70 | -402.49 | -403.9 |
| | Ne | -263.47 | -294.35 | -308.13 | -314.41 | -317.24 | -320.1 |
| | F ₂ | -518.79 | -571.05 | -594.05 | -603.68 | -607.88 | -611.7 |

^aFixed geometries and reference energies were taken from Refs. 51, 52.

^bAverage of MP2-R12/A and MP2-R12/B energies from Refs. 51, 52.

^cNot available.

TABLE VII. Valence-shell Møller–Plesset second-order correlation energies ($E^{(2)}$ in mE_h) of the Ne atom and some small molecules as computed by the new MP2-R12 method in the *augmented* correlation-consistent basis sets aug-cc-pVXZ with $2 \leq X \leq 6$ (same auxiliary basis as in Table VI).

| Method | System ^a | X=2 | X=3 | X=4 | X=5 | X=6 | Limit ^b |
|--------|---|---------|---------|---------|---------|-------------------|--------------------|
| 1A' | CH ₂ (¹ A ₁) | -135.63 | -149.23 | -153.42 | -155.07 | -156.32 | -155.9 |
| | H ₂ O | -256.61 | -283.92 | -293.88 | -298.29 | -300.62 | -300.5 |
| | NH ₃ | -230.09 | -252.70 | -260.08 | -263.11 | n.a. ^c | -264.5 |
| | HF | -267.54 | -298.70 | -310.79 | -316.60 | -319.52 | -319.7 |
| | N ₂ | -362.16 | -398.94 | -411.92 | -417.68 | -420.57 | -421.0 |
| | CO | -346.39 | -381.21 | -394.50 | -400.47 | -403.47 | -403.9 |
| | Ne | -260.48 | -294.90 | -308.59 | -316.00 | -319.46 | -320.1 |
| | F ₂ | -509.94 | -570.97 | -593.49 | -605.19 | -610.71 | -611.7 |
| 2A' | CH ₂ (¹ A ₁) | -147.25 | -152.42 | -154.74 | -155.48 | -155.75 | -155.9 |
| | H ₂ O | -278.56 | -292.91 | -297.90 | -299.56 | -300.09 | -300.5 |
| | NH ₃ | -248.15 | -258.91 | -262.76 | -263.90 | n.a. ^c | -264.5 |
| | HF | -292.94 | -310.47 | -316.36 | -318.49 | -319.20 | -319.7 |
| | N ₂ | -392.43 | -409.77 | -417.16 | -419.54 | -420.40 | -421.0 |
| | CO | -376.37 | -392.58 | -399.97 | -402.40 | -403.28 | -403.9 |
| | Ne | -288.49 | -309.31 | -315.85 | -318.59 | -319.48 | -320.1 |
| | F ₂ | -560.14 | -593.34 | -604.64 | -609.05 | -610.55 | -611.7 |
| 1B | CH ₂ (¹ A ₁) | -132.61 | -148.43 | -153.08 | -154.93 | -156.21 | -155.9 |
| | H ₂ O | -251.04 | -282.54 | -293.16 | -297.92 | -300.40 | -300.5 |
| | NH ₃ | -225.75 | -251.66 | -259.63 | -262.89 | n.a. ^c | -264.5 |
| | HF | -260.61 | -296.96 | -309.77 | -316.17 | -319.31 | -319.7 |
| | N ₂ | -355.28 | -397.11 | -410.72 | -417.29 | -420.34 | -421.0 |
| | CO | -339.63 | -379.46 | -393.53 | -400.12 | -403.25 | -403.9 |
| | Ne | -252.63 | -292.94 | -307.29 | -315.52 | -319.24 | -320.1 |
| | F ₂ | -497.19 | -567.86 | -591.47 | -600.23 | -610.29 | -611.7 |
| 2B | CH ₂ (¹ A ₁) | -141.03 | -151.01 | -154.25 | -155.30 | -155.66 | -155.9 |
| | H ₂ O | -269.05 | -290.36 | -296.89 | -299.14 | -299.89 | -300.5 |
| | NH ₃ | -239.87 | -256.88 | -262.06 | -263.62 | n.a. ^c | -264.5 |
| | HF | -282.06 | -307.39 | -315.01 | -317.98 | -319.00 | -319.7 |
| | N ₂ | -379.44 | -406.22 | -415.60 | -419.01 | -420.18 | -421.0 |
| | CO | -363.50 | -389.09 | -398.52 | -401.89 | -403.05 | -403.9 |
| | Ne | -276.65 | -305.76 | -314.16 | -318.00 | -319.25 | -320.1 |
| | F ₂ | -539.93 | -587.74 | -601.79 | -608.09 | -610.15 | -611.7 |

^{a,b,c}As for Table VI.

Table II shows the all-electron second-order correlation energies of Ne that are obtained in the subsets $20s14p$, $20s14p11d$, $20s14p11d9f$, and so on, by means of conventional MP2 calculations, the original MP2-R12 method, and by means of the new Ansätze **1** and **2**. In the sp subset, the original MP2-R12 energies are clearly not variational. In approximations A' and B, energies of -688.5 and $-506.95 mE_h$ are obtained, respectively, which are much too low. This behavior is the result of using the $20s14p$ orbital basis for the RI approximation in these original MP2-R12 calculations, and is not observed when the large auxiliary basis set is employed.

Furthermore, Ansatz **2** appears to be clearly superior to Ansatz **1**.

In approximation 2A', there is a tendency to overshoot the magnitude of the correlation energy due to the neglect of exchange terms, and the results appear to converge from below towards the basis-set limit. The MP2-R12/2B energies converge from above, and the convergence is rapid in both cases. Figure 1, which depicts the error of the computed MP2 energy with respect to an estimated basis-set limit energy of $-388.107 mE_h$, compares the convergence of the MP2-R12/2B approach with conventional MP2 calculations. It seems that the MP2-R12/2B results can be well described

in terms of an $(L_{\max}+1)^{-7}$ dependence, which is a much faster convergence than the conventional $(L_{\max}+1)^{-3}$ behavior.⁴⁴

Table III displays the individual singlet and triplet pair energies of the MP2-R12/2B calculations shown in Table II, in comparison with the results of Ref. 35. In the work of Wind *et al.*,³⁵ the same $20s14p11d9f7g5h$ was used as in the present work, three-electron integrals were evaluated exactly (i.e., without RI approximation), but the wave function Ansatz was slightly different from the present work (i.e., not orbital-invariant³⁶). Nevertheless, the agreement between the results of Ref. 35 and the column under *spdfgh* is striking—the maximum deviation is only $6 \mu E_h$. In view of this excellent agreement, we are confident that our MP2-R12/2B pair energies in the $20s14p11d9f7g5h3i$ basis are the most accurate, directly computed Ne pair energies to date.

A comparison between our present calculations and selected literature data^{45–48} is presented in Table IV. Our results agree closely (to within $7 \mu E_h$) with the accurate but extrapolated pair energies of Flores.⁴⁸ It is remarkable that a calculation in terms of a partial-wave expansion with partial waves up to $l=12$ is in error by ca. $0.6 mE_h$, and that an extrapolation for $l>12$ is needed to improve the accuracy

TABLE VIII. All-electron Møller–Plesset second-order correlation energies ($E^{(2)}$ in mE_h) of the Ne atom and some small molecules as computed by the new MP2-R12 method in the *core–valence* correlation-consistent basis sets cc-pCVXZ with $2 \leq X \leq 5$ (using the auxiliary basis $19s14p10d8f6g4h2i$ for C, N, O, F, and Ne, and $9s6p4d3f2g$ for H).

| Method | System ^a | X=2 | X=3 | X=4 | X=5 | Limit ^b |
|--------|---|---------|---------|---------|---------|--------------------|
| 1A' | CH ₂ (¹ A ₁) | −182.72 | −199.54 | −206.34 | −209.01 | −209.9 |
| | H ₂ O | −295.51 | −338.97 | −352.99 | −359.04 | −362.1 |
| | NH ₃ | −270.83 | −305.45 | −316.32 | −320.91 | −322.9 |
| | HF | −306.66 | −356.96 | −373.43 | −380.54 | −384.6 |
| | N ₂ | −455.48 | −506.91 | −525.24 | −532.91 | −536.9 |
| | CO | −438.48 | −490.02 | −508.55 | −515.88 | −519.7 |
| | Ne | −302.89 | −357.46 | −375.21 | −380.30 | −388.1 |
| | F ₂ | −593.47 | −690.09 | −718.74 | −732.61 | −740.6 |
| 2A' | CH ₂ (¹ A ₁) | −198.69 | −205.50 | −208.96 | −209.31 | −209.9 |
| | H ₂ O | −337.74 | −353.83 | −358.49 | −360.53 | −362.1 |
| | NH ₃ | −303.28 | −316.43 | −320.32 | −321.93 | −322.9 |
| | HF | −358.77 | −374.27 | −379.35 | −381.65 | −384.6 |
| | N ₂ | −509.90 | −527.57 | −533.64 | −536.06 | −536.9 |
| | CO | −491.97 | −510.78 | −517.03 | −519.04 | −519.7 |
| | Ne | −233.73 | −368.48 | −381.17 | −386.37 | −388.1 |
| | F ₂ | −692.40 | −722.36 | −731.48 | −736.90 | −740.6 |
| 1B | CH ₂ (¹ A ₁) | −175.04 | −198.54 | −205.80 | −208.75 | −209.9 |
| | H ₂ O | −286.26 | −337.17 | −351.87 | −358.50 | −362.1 |
| | NH ₃ | −264.39 | −303.93 | −315.87 | −320.52 | −322.9 |
| | HF | −295.15 | −355.15 | −371.93 | −379.90 | −384.6 |
| | N ₂ | −445.56 | −504.91 | −522.52 | −532.55 | −536.9 |
| | CO | −427.77 | −487.90 | −506.78 | −515.36 | −519.7 |
| | Ne | −288.45 | −355.56 | −373.26 | −382.57 | −388.1 |
| | F ₂ | −571.54 | −685.68 | −716.62 | −731.57 | −740.6 |
| 2B | CH ₂ (¹ A ₁) | −186.34 | −202.00 | −207.17 | −208.66 | −209.9 |
| | H ₂ O | −318.09 | −348.09 | −356.62 | −360.12 | −362.1 |
| | NH ₃ | −286.76 | −311.75 | −319.08 | −321.05 | −322.9 |
| | HF | −335.14 | −367.53 | −375.76 | −381.79 | −384.6 |
| | N ₂ | −484.91 | −518.92 | −530.15 | −534.81 | −536.9 |
| | CO | −467.19 | −503.39 | −513.69 | −517.79 | −519.7 |
| | Ne | −343.67 | −374.48 | −377.23 | −384.14 | −388.1 |
| | F ₂ | −649.88 | −709.27 | −725.05 | −735.14 | −740.6 |

^{a,b}As for Table VI.

to the microhartree level.^{48,49} The new MP2-R12/2B approach yields this level of accuracy without the need for extrapolations.

VI. NUMERICAL RESULTS: MOLECULES

A. Geometries and basis sets

All molecular structures were kept fixed throughout the present study. These fixed structures correspond to equilibrium geometries that were optimized at the CCSD(T)(FULL)/cc-pCVQZ level (FULL means that all electrons were correlated). They were taken from Ref. 50 and are identical to the structures used in Refs. 51 and 52.

The (augmented) polarized valence correlation-consistent basis sets (aug-)cc-pVXZ are used as orbital basis^{53–59} when only the valence shell is correlated, in conjunction with the auxiliary basis $19s14p8d6f4g3h2i$ for C, N, O, F, and Ne, and $9s6p4d3f2g$ for H. The latter sets for C, N, O, F, and Ne were obtained by adding the two *i*-type sets of the aug-cc-pV6Z basis to the basis sets of Ref. 51. For H, the two *g*-type sets of the aug-cc-pV5Z basis were added to the basis set of Ref. 51.

The (augmented) polarized core–valence correlation-consistent basis sets (aug-)cc-pCVXZ are used as orbital basis^{57,59} when all orbitals are correlated, in conjunction with the auxiliary basis $19s14p10d8f6g4h2i$ for C, N, O, F, and Ne, and $9s6p4d3f2g$ for H. These auxiliary basis sets for all-electron correlated calculations were obtained from the above-mentioned auxiliary basis sets for valence shell correlated calculations by adding *d*-, *f*-, *g*-, and *h*-type Gaussians. The exponents of these Gaussians are given in Table V.

B. Results

The results of the calculations on small molecules are collected in Table VI (valence–shell correlation in cc-pVXZ basis sets), Table VII (valence–shell correlation in aug-cc-pVXZ basis sets), Table VIII (all-electron correlation in cc-pCVXZ basis sets), and Table IX (all-electron correlation in aug-cc-pCVXZ basis sets). For the NH₃ molecule, the calculations in the cc-pV6Z, aug-cc-pV6Z, and aug-cc-pV5Z basis were not feasible with the computer hardware currently available to us.

Again, we observe that Ansatz 2 is superior to Ansatz 1, except for the largest basis sets (aug-)cc-pV6Z and (aug-)cc-

TABLE IX. All-electron Møller–Plesset second-order correlation energies ($E^{(2)}$ in mE_h) of the Ne atom and some small molecules as computed by the new MP2-R12 method in the *augmented core–valence* correlation-consistent basis sets aug-cc-pCVXZ with $2 \leq X \leq 5$ (same auxiliary basis as in Table VIII).

| Method | System ^a | X=2 | X=3 | X=4 | X=5 | Limit ^b |
|--------|---|---------|---------|---------|-------------------|--------------------|
| 1A' | CH ₂ (¹ A ₁) | -184.44 | -200.84 | -206.92 | -209.35 | -209.9 |
| | H ₂ O | -307.31 | -343.58 | -355.12 | -359.98 | -362.1 |
| | NH ₃ | -279.14 | -309.24 | -317.87 | n.a. ^c | -322.9 |
| | HF | -319.07 | -362.21 | -375.75 | -381.61 | -384.6 |
| | N ₂ | -462.61 | -510.77 | -526.94 | -534.05 | -536.9 |
| | CO | -445.71 | -492.00 | -509.70 | -516.73 | -519.7 |
| | Ne | -312.28 | -362.35 | -377.35 | -384.46 | -388.1 |
| | F ₂ | -612.01 | -697.65 | -722.36 | -734.58 | -740.6 |
| 2A' | CH ₂ (¹ A ₁) | -201.21 | -207.52 | -209.48 | -209.87 | -209.9 |
| | H ₂ O | -363.30 | -359.64 | -361.72 | -362.15 | -362.1 |
| | NH ₃ | -309.59 | -320.11 | -322.55 | n.a. ^c | -322.9 |
| | HF | -360.00 | -380.58 | -383.94 | -384.67 | -384.6 |
| | N ₂ | -514.07 | -531.80 | -536.01 | -537.83 | -536.9 |
| | CO | -496.35 | -514.46 | -518.93 | -519.84 | -519.7 |
| | Ne | -367.65 | -383.94 | -386.87 | -388.44 | -388.1 |
| | F ₂ | -705.67 | -734.93 | -739.08 | -740.78 | -740.6 |
| 1B | CH ₂ (¹ A ₁) | -179.19 | -199.41 | -206.51 | -209.17 | -209.9 |
| | H ₂ O | -300.08 | -341.67 | -354.34 | -359.53 | -362.1 |
| | NH ₃ | -274.46 | -307.44 | -317.93 | n.a. ^c | -322.9 |
| | HF | -310.49 | -360.10 | -375.08 | -381.09 | -384.6 |
| | N ₂ | -453.30 | -508.65 | -525.56 | -533.55 | -536.9 |
| | CO | -436.84 | -490.99 | -508.46 | -516.31 | -519.7 |
| | Ne | -302.91 | -360.07 | -375.88 | -383.92 | -388.1 |
| | F ₂ | -597.25 | -693.62 | -721.87 | -733.60 | -740.6 |
| 2B | CH ₂ (¹ A ₁) | -192.61 | -205.38 | -208.81 | -209.61 | -209.9 |
| | H ₂ O | -332.51 | -355.84 | -360.17 | -361.37 | -362.1 |
| | NH ₃ | -297.91 | -317.31 | -321.49 | n.a. ^c | -322.9 |
| | HF | -358.09 | -378.22 | -381.77 | -383.57 | -384.6 |
| | N ₂ | -494.01 | -526.73 | -533.46 | -536.19 | -536.9 |
| | CO | -477.58 | -509.52 | -516.22 | -519.16 | -519.7 |
| | Ne | -342.47 | -378.00 | -386.16 | -387.25 | -388.1 |
| | F ₂ | -676.34 | -726.93 | -734.72 | -739.44 | -740.6 |

^{a,b}As for Table VIII.^cNot available.

pCV5Z. For these set, however, the differences are small.

As usual, the energies of approximation A' are more negative than those of approximation B. Since the MP2-R12/A' calculations in the correlation-consistent basis sets do not overshoot the magnitude of the second-order energy—as happened before in Sec. V for the Ne atom—the MP2-R12/A' energies are found closer to the estimated basis-set limits than the MP2-R12/B results. Note, however, that this better agreement is to some extent fortuitous. It is based on a cancellation of errors, as certain matrix elements are neglected in approximations A and A'. No matrix elements are neglected in approximation B.

Table X summarizes the results of Tables VI through IX by reporting the percentage of the second-order Møller–Plesset correlation energy that is recovered by the various methods. See also Figs. 2 and 3.

Even in the largest basis sets, the conventional MP2 approach does not succeed in recovering more than 98% of the basis-set limit second-order energy, and it is clear from Figs. 2 and 3 that it seems rather difficult to recover the remaining 2%.

TABLE X. Average percentage of the valence–shell (cc-pVXZ and aug-cc-pVXZ results) and all-electron (cc-pCVXZ and aug-cc-pCVXZ results) second-order Møller–Plesset correlation energy that is recovered by the various approaches.

| Basis | X | MP2 | 1A' | 2A' | 1B | 2B | |
|----------|--------------|------|-------|-------|------|------|------|
| cc-pVXZ | 2 | 67.2 | 82.0 | 91.2 | 79.3 | 85.8 | |
| | 3 | 86.8 | 92.9 | 95.7 | 92.3 | 94.1 | |
| | 4 | 93.9 | 97.0 | 98.2 | 96.7 | 97.6 | |
| | 5 | 96.8 | 98.9 | 99.2 | 98.7 | 98.9 | |
| | 6 | 98.0 | 99.7 | 99.6 | 99.7 | 99.5 | |
| | aug-cc-pVXZ | 2 | 72.0 | 84.9 | 92.6 | 83.0 | 89.2 |
| 3 | | 88.8 | 94.2 | 97.3 | 93.7 | 96.4 | |
| 4 | | 94.8 | 97.6 | 99.0 | 97.3 | 98.7 | |
| 5 | | 97.3 | 99.2 | 99.6 | 99.0 | 99.5 | |
| 6 | | 98.3 | 100.0 | 99.8 | 99.9 | 99.8 | |
| cc-pCVXZ | | 2 | 66.7 | 82.5 | 89.8 | 79.7 | 88.6 |
| | 3 | 87.6 | 93.8 | 97.5 | 93.3 | 96.3 | |
| | 4 | 94.5 | 97.5 | 99.0 | 97.2 | 98.3 | |
| | 5 | 97.2 | 99.1 | 99.6 | 99.0 | 99.4 | |
| | aug-cc-pCVXZ | 2 | 70.7 | 84.6 | 95.9 | 82.6 | 91.6 |
| | | 3 | 89.1 | 94.7 | 99.1 | 94.2 | 98.1 |
| 4 | | 95.3 | 98.0 | 99.8 | 97.8 | 99.4 | |
| 5 | | 97.5 | 99.4 | 100.0 | 99.2 | 99.8 | |

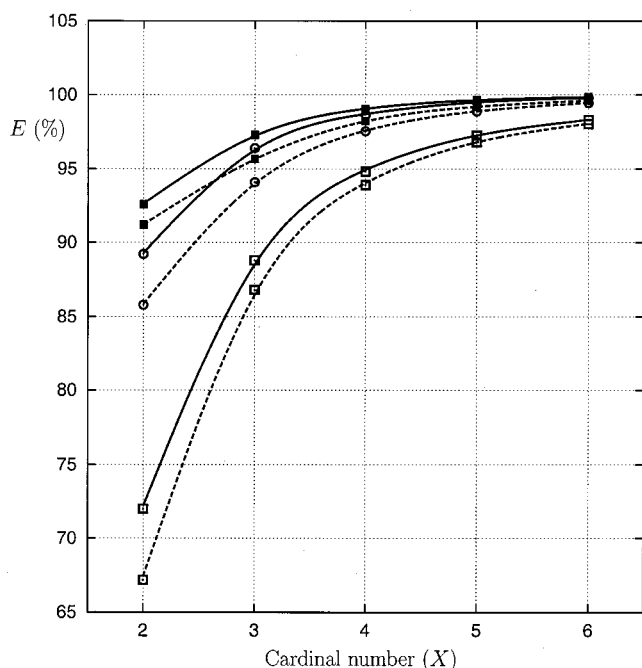


FIG. 2. Average percentage of the valence-shell second-order Møller-Plesset correlation energy that is recovered by the standard MP2 (\square) and new MP2-R12/2A' (\blacksquare) and MP2-R12/2B (\circ) methods in the cc-pVXZ (dashed lines) and aug-cc-pVXZ (solid lines) basis sets.

With the MP2-R12 methods, this level of accuracy (98%) is already reached in basis sets with cardinal number $X=4$ (valence-shell correlation) or $X=3$ (all-electron correlation). Concerning this comparison, it is noted that the computation time for these MP2-R12 calculations is significantly shorter than for the conventional MP2 calculations in the (aug-)cc-pV6Z and (aug-)cc-pCV5Z basis sets.

VII. CONCLUSION

By using an auxiliary basis set for the RI approximation in R12 theory, we have developed new MP2-R12 methods that can be employed for calculations in standard basis sets. In the present work, we have chosen to keep this auxiliary basis large and constant for all calculations in the correlation-consistent basis sets, and the auxiliary basis was thus chosen notably larger than the largest correlation-consistent basis. For calculations in small standard basis sets, aiming at describing ca. 95% of the correlation energy, for example, such large auxiliary basis sets are probably not needed, and it seems worthwhile to investigate the effect of the auxiliary basis on the computed energies in more detail and to optimize suitable auxiliary basis sets for use in conjunction with selected correlation-consistent or other standard Gaussian basis sets. Work along these lines is in progress.

It also seems worthwhile to investigate the convergence of the R12 calculations in correlation-consistent basis sets in more detail. In conventional calculations, this convergence goes as X^{-3} .¹ For R12 calculations, a convergence close to X^{-7} should be achievable for the principal expansion,²⁶ that is, for basis sets with correlation-consistent composition. The calculations on the Ne atom, for instance, showed a conver-

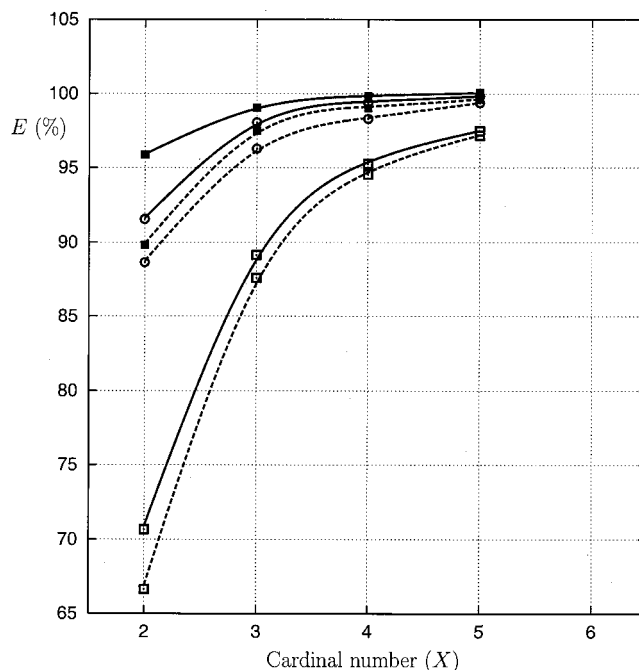


FIG. 3. Average percentage of the all-electron second-order Møller-Plesset correlation energy that is recovered by the standard MP2 (\square) and new MP2-R12/2A' (\blacksquare) and MP2-R12/2B (\circ) methods in the cc-pCVXZ (dashed lines) and aug-cc-pCVXZ (solid lines) basis sets.

gence of the form $(L_{\max}+1)^{-7}$ (Fig. 1). To obtain this convergence rate, however, the exponents of the Gaussian functions must be reoptimized for use in R12 theory. Today, their exponents are optimized for calculations without R12 terms.

When an auxiliary basis set is used, two different Ansätze can be distinguished in R12 theory: **1** versus **2**. In general, Ansatz **2** outperforms **1**, and Ansatz **2** is recommended for future work with the new ABS-based MP2-R12 method.

When all matrix elements are computed (approximation B), the computation times of the new approaches grow quadratically with the number of auxiliary basis functions. When certain exchange terms are neglected, however, the scaling becomes only linear (approximations A and A'). This is an important advantage of the approximations A and A'.

Work is in progress to implement computational methods that utilize auxiliary basis sets in explicitly correlated coupled-cluster theory (CC-R12).

ACKNOWLEDGMENTS

The research of W.K. has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences. The calculations were performed on SGI Origin 2000 R12000 computers at Utrecht University and at Academic Computing Services Amsterdam (SARA). We gratefully acknowledge partial support from COST Chemistry Action D9 (Working Group 13/98) and a generous grant of computing time from National Computing Facilities (NCF) Foundation.

¹T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, Chichester, 2000).

²K. L. Bak, P. Jørgensen, J. Olsen, T. Helgaker, and W. Klopper, *J. Chem. Phys.* **112**, 9229 (2000).

- ³T. H. Dunning, Jr., *J. Phys. Chem. A* **104**, 9062 (2000).
- ⁴T. Helgaker, W. Klopper, A. Halkier, K. L. Bak, P. Jørgensen, and J. Olsen, in *Understanding Chemical Reactivity*, Vol. 22, Quantum-Mechanical Prediction of Thermochemical Data, edited by J. Cioslowski (Kluwer Academic, Dordrecht, 2001), pp. 1–30.
- ⁵K. L. Bak, A. Halkier, P. Jørgensen, J. Olsen, T. Helgaker, and W. Klopper, *J. Mol. Struct.* **567–568**, 375 (2001).
- ⁶T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Chem. Phys.* **106**, 9639 (1997).
- ⁷D. Feller and K. A. Peterson, *J. Chem. Phys.* **108**, 154 (1998).
- ⁸D. Feller and K. A. Peterson, *J. Chem. Phys.* **110**, 8384 (1999).
- ⁹J. W. Ochterski, G. A. Petersson, and J. A. Montgomery, Jr., *J. Chem. Phys.* **104**, 2598 (1996).
- ¹⁰G. A. Petersson and M. J. Frisch, *J. Phys. Chem. A* **104**, 2183 (2000).
- ¹¹P. L. Fast, M. L. Sánchez, and D. G. Truhlar, *J. Chem. Phys.* **111**, 2921 (1999).
- ¹²J. M. Rodgers, P. L. Fast, and D. G. Truhlar, *J. Chem. Phys.* **112**, 3141 (2000).
- ¹³L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- ¹⁴L. A. Curtiss, P. C. Redfern, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **114**, 108 (2001).
- ¹⁵J. M. L. Martin and G. de Oliveira, *J. Chem. Phys.* **111**, 1843 (1999).
- ¹⁶S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114**, 6014 (2001).
- ¹⁷A. G. Császár, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **108**, 9751 (1998).
- ¹⁸A. G. Császár and M. L. Leininger, *J. Chem. Phys.* **114**, 5491 (2001).
- ¹⁹W. Cencek and J. Rychlewski, *J. Chem. Phys.* **102**, 2533 (1995).
- ²⁰B. J. Persson and P. R. Taylor, *J. Chem. Phys.* **105**, 5915 (1996).
- ²¹R. J. Gdanitz, *J. Chem. Phys.* **110**, 706 (1999).
- ²²R. Bukowski, B. Jeziorski, and K. Szalewicz, *J. Chem. Phys.* **110**, 4165 (1999).
- ²³W. Klopper, in *The Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner (Wiley, Chichester, 1998), pp. 2351–2375.
- ²⁴W. Kutzelnigg, *Theor. Chim. Acta* **68**, 445 (1985).
- ²⁵W. Klopper and W. Kutzelnigg, *Chem. Phys. Lett.* **134**, 17 (1987).
- ²⁶W. Kutzelnigg and W. Klopper, *J. Chem. Phys.* **94**, 1985 (1991).
- ²⁷J. Noga and W. Kutzelnigg, *J. Chem. Phys.* **101**, 7738 (1994).
- ²⁸J. Noga, W. Klopper, and W. Kutzelnigg, in *Recent Advances in Computational Chemistry*, Vol. 3, Recent Advances in Coupled-Cluster Methods, edited by R. J. Bartlett (World Scientific, Singapore, 1997), pp. 1–48.
- ²⁹W. Klopper and H. P. Lüthi, *Chem. Phys. Lett.* **262**, 546 (1996).
- ³⁰W. Klopper, H. P. Lüthi, Th. Brupbacher, and A. Bauder, *J. Chem. Phys.* **101**, 9747 (1994).
- ³¹W. Klopper, M. Schütz, H. P. Lüthi, and S. Leutwyler, *J. Chem. Phys.* **103**, 1085 (1995).
- ³²M. Schütz, W. Klopper, H. P. Lüthi, and S. Leutwyler, *J. Chem. Phys.* **103**, 6114 (1995).
- ³³R. J. Gdanitz and R. Röhse, *Int. J. Quantum Chem.* **55**, 147 (1996).
- ³⁴P. Wind, T. Helgaker, and W. Klopper, *Theor. Chem. Acc.* **106**, 280 (2001).
- ³⁵P. Wind, T. Helgaker, and W. Klopper, *Theor. Chem. Acc.* **107**, 173 (2002).
- ³⁶W. Klopper, *Chem. Phys. Lett.* **186**, 583 (1991).
- ³⁷W. Klopper and J. Almlöf, *J. Chem. Phys.* **99**, 5167 (1993).
- ³⁸W. Klopper and R. Röhse, *Theor. Chim. Acta* **83**, 441 (1992).
- ³⁹T. Helgaker, H. J. Aa. Jensen, P. Jørgensen *et al.*, DALTON program, version 1.1.
- ⁴⁰H. Koch, O. Christiansen, R. Kobayashi, P. Jørgensen, and T. Helgaker, *Chem. Phys. Lett.* **228**, 233 (1994).
- ⁴¹H. Koch, A. Sánchez de Merás, T. Helgaker, and O. Christiansen, *J. Chem. Phys.* **104**, 4157 (1996).
- ⁴²H. Koch, P. Jørgensen, and T. Helgaker, *J. Chem. Phys.* **104**, 9528 (1996).
- ⁴³W. Klopper, W. Kutzelnigg, H. Müller, J. Noga, and S. Vogtner, *Top. Curr. Chem.* **203**, 21 (1999).
- ⁴⁴W. Kutzelnigg and J. D. Morgan III, *J. Chem. Phys.* **96**, 4484 (1992).
- ⁴⁵I. Lindgren and S. Salomonson, *Phys. Scr.* **21**, 335 (1980).
- ⁴⁶K. Jankowski and P. Malinowski, *Phys. Rev. A* **21**, 45 (1980).
- ⁴⁷V. Termath, W. Klopper, and W. Kutzelnigg, *J. Chem. Phys.* **94**, 2002 (1991).
- ⁴⁸J. R. Flores, *Phys. Rev. A* **46**, 6063 (1992).
- ⁴⁹J. R. Flores and D. Kolb, *J. Phys. B* **32**, 779 (1999).
- ⁵⁰K. L. Bak, J. Gauss, P. Jørgensen, J. Olsen, T. Helgaker, and J. F. Stanton, *J. Chem. Phys.* **114**, 6548 (2001).
- ⁵¹W. Klopper, *Mol. Phys.* **99**, 481 (2001).
- ⁵²W. Klopper, C. C. M. Samson, G. Tarczay, and A. G. Császár, *J. Comput. Chem.* **22**, 1306 (2001).
- ⁵³T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ⁵⁴R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- ⁵⁵D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **98**, 1358 (1993).
- ⁵⁶D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 2975 (1994).
- ⁵⁷D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **103**, 4572 (1995).
- ⁵⁸A. K. Wilson, T. van Mourik, and T. H. Dunning, Jr., *J. Mol. Struct.: THEOCHEM* **388**, 339 (1996).
- ⁵⁹The basis-set parameters were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 10/12/01, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830.