A hybrid scheme for the resolution-of-the-identity approximation in second-order Møller–Plesset linear-r12 perturbation theory

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A hybrid scheme for the resolution-of-the-identity approximation in second-order Møller–Plesset linear-r_{12} perturbation theory

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In the framework of second-order Møller–Plesset linear-r_{12} (MP2-R12) perturbation theory, a method is developed and implemented that uses an auxiliary basis set for the resolution-of-the-identity (RI) approximation for the three- and four-electron integrals. In contrast to previous work, the two-electron integrals that must be evaluated never involve more than *one* auxiliary basis function. The new method therefore scales linearly with the number of auxiliary basis functions and is much more efficient than the previous one, which scaled quadratically. A general formulation of MP2-R12 theory is presented for various ansätze, approximations, and orbitals (canonical or localized). The new method is assessed by computations of the valence-shell second-order Møller–Plesset correlation energy of a few small closed-shell systems. The preliminary calculations indicate that the difference between the new and previous methods is about one order of magnitude smaller than the errors that occur due to basis-set truncations and RI approximations and under the assumptions of generalized and extended Brillouin conditions. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1742904]

I. INTRODUCTION

The second-order Møller–Plesset linear-r_{12} (MP2-R12) method was introduced in 1987.[1] It was derived in the framework of closed-shell second-order Møller–Plesset perturbation theory by expanding the first-order pair function $u_{ij}^{(1)}(1,2)$ in a basis of (a) orbital products $|ab\rangle$ and (b) functions that depend linearly on the interelectronic coordinate $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$,

$$u_{ij}^{(1)}(1,2)=t_{ab}^{ij}|ab\rangle+c_{ij}(1-\hat{O}_1)(1-\hat{O}_2)r_{12}|ij\rangle. \quad (1)$$

Here, $\hat{O}_1$ is the projector onto the space spanned by the occupied spin orbitals $\{\varphi_k(1)\}_{k=1}^n$. $|pq\rangle$ is a short-hand notation for the two-electron determinant

$$|pq\rangle=|\varphi_p\varphi_q|=\frac{1}{\sqrt{2}}\{\varphi_p(1)\varphi_q(2)-\varphi_q(1)\varphi_p(2)\}, \quad (2)$$

and throughout this paper, we assume implicit summation over repeated indices. Occupied spin orbitals are indicated by the indices $i,j,k,\ldots$, empty (virtual) ones by $a,b,c,\ldots$, and arbitrary ones by $p,q,r,\ldots$.

In 1991, the method was also implemented by Bearpark *et al.* in terms of Eq. (1),[2] but in the same year, the method was extended by the present author to the form[3]

$$u_{ij}^{(1)}(1,2)=t_{ab}^{ij}|ab\rangle+c_{kl}^{ij}(1-\hat{O}_1)(1-\hat{O}_2)r_{12}|kl\rangle. \quad (3)$$

The MP2-R12 method based on Eq. (3) is invariant to unitary transformations among the occupied spin orbitals, whereas the original method based on Eq. (1) was not. An integral-semidirect computer code, the SORE program

(second-order R12 energy),[4] was developed in 1991 on the basis of Eq. (3), invoking an approximation to the many-electron integrals called standard approximation A (MP2-R12/A method). This program was recently parallelized and extended to include the standard approximation B as well (MP2-R12/B method).[5]

Since 2000, a similar MP2-R12 program has been developed by Valeev and Schaefer,[6–8] and impressive results have been obtained with their code.[9–11]

Furthermore, the MP2-R12/A and MP2-R12/B energies are computed as intermediate results by the coupled-cluster linear-r_{12} methods, not only for closed-shell systems but also for unrestricted Hartree–Fock and restricted open-shell Hartree–Fock references.[12–16]

Recent work has been concerned with the evaluation of the many-electron integrals, partly eliminating or modifying the standard approximations of R12 theory. Wind *et al.* have computed the main three-electron integrals exactly for atoms,[17] and Manby[18] and Ten-no and Manby[19] have investigated alternative insertions of the (approximate) resolution of the identity (RI) as well as further approximations to reduce the complexity of the two-electron integrals of R12 theory to the computation of three-center integrals.

So far, the various implementations of MP2-R12 theory have all used the main basis of atomic orbitals for the RI approximations of that theory. Only very recently, we have proposed to use another, auxiliary basis set for that purpose.[20]

The present paper is concerned with the utilization of an auxiliary basis $\{\chi_{\mu'}(1)\}_{\mu'=1}^{n'}$, which defines a set of orthonormal spin orbitals $\varphi_{p'}$. Here and throughout the paper, primed indices refer to orbitals of the auxiliary basis. It be-

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comes clear in Ref. 20 that the MP2-R12/A method requires two-electron integrals of the type $(\mu\nu|\kappa\lambda')$, where only one function (λ') belongs to the auxiliary basis. In contrast to this single auxiliary function, the MP2-R12/B method requires two-electron integrals of the types $(\mu\nu|\kappa'\lambda')$ and $(\mu\nu'|\kappa\lambda')$ with *two* functions of the auxiliary basis.

However, we shall show in the present work that it is possible to design an MP2-R12/B method that requires nothing more complicated than two-electron integrals that involve *only one* auxiliary basis function. As the auxiliary basis is usually large, this leads to substantial savings of both computation time and data storage. The new approach is denoted the "hybrid MP2-R12/B" method, as it employs the new approach (with an auxiliary basis) for the terms of the MP2-R12/A method but the old approach (without an auxiliary basis) for the extra, post-MP2-R12/A terms that occur in the MP2-R12/B method.

The present paper is organized as follows: The theory is presented in Sec. II, computational details are given in Sec. III, and numerical results are presented and discussed in Sec. IV. The conclusions of the present work are summarized in Sec. V.

II. THEORY

In this section, we present the MP2-R12 method in a spin-orbital formalism, using the notations of Refs. 15 and 20. The theory is like usual second-order Møller–Plesset perturbation theory, with the exception that it uses pair functions of the form

$$u_{ij}^{(1)}(1,2) = t_{ab}^{ij}|ab\rangle + c_{kl}^{ij}\hat{w}_{12}|kl\rangle, \tag{4}$$

with $\hat{w}_{12} = \hat{Q}_{12}r_{12}$. The projector $\hat{Q}_{12}$ is defined in the following.

When an auxiliary basis is used, two different ansätze (**1** and **2**) can be made (Sec. II A), and the MP2-R12 energy and amplitude equations are given in a general and compact form (Sec. II B). The standard approximations A, A′, and B differ by the neglect of certain terms. These approximations and also the approach **2*** are explained in Sec. II C. The post-MP2-R12/A terms can be computed efficiently by virtue of intermediate orbitals, and the new hybrid approach consists of expanding these intermediate orbitals not always in the auxiliary basis but partly also in the main orbital basis (Sec. II D). Section II ends with remarks on the computation of the matrices **P** and **L** (Sec. II E).

A. Ansätze 1 and 2

The projection operator $\hat{Q}_{12}$ is defined differently for the ansätze **1** and **2**. With ansatz **1**, it contains the projection onto the full spin-orbital basis, whereas with ansatz **2**, it contains the projection onto the space of occupied spin orbitals. Hence,

$$\text{ansatze } \mathbf{1}: \quad \hat{Q}_{12} = (1-\hat{P}_1)(1-\hat{P}_2), \tag{5}$$

$$\text{ansatze } \mathbf{2}: \quad \hat{Q}_{12} = (1-\hat{O}_1)(1-\hat{O}_2), \tag{6}$$

where $\hat{P}_1 = |\varphi_p(1)\rangle\langle\varphi_p(1)|$ and $\hat{O}_1 = |\varphi_i(1)\rangle\langle\varphi_i(1)|$ and similarly for $\hat{P}_2$ and $\hat{O}_2$. Without using an auxiliary basis for

the RI approximation, the two ansätze **1** and **2** lead to the same working equations and to the same numerical results. Distinct results only occur with an auxiliary basis or when the many-electron integrals are computed exactly.[17]

B. MP2-R12 equations

In order to arrive at compact equations, we collect the amplitudes t_{ab}^{ij} and c_{kl}^{ij} into the matrices **T** and **C**, respectively, and define further the following matrices:

$$\bar{V}_{mn}^{kl} = \langle mn|g_{12}\hat{w}_{12}|kl\rangle, \tag{7}$$

$$\bar{X}_{mn}^{kl} = \langle mn|\hat{w}_{12}^{\dagger}r_{12}|kl\rangle, \tag{8}$$

$$\bar{F}_{mn}^{kl} = \langle mn|\hat{w}_{12}^{\dagger}(\hat{f}_1+\hat{f}_2)\hat{w}_{12}|kl\rangle, \tag{9}$$

$$\bar{E}_{mn}^{ab} = \langle mn|\hat{w}_{12}^{\dagger}(\hat{f}_1+\hat{f}_2)|ab\rangle, \tag{10}$$

$$\bar{W}_{mn}^{ab} = \langle mn|\hat{w}_{12}^{\dagger}|ab\rangle, \tag{11}$$

$$\bar{G}_{mn}^{ab} = \langle mn|g_{12}|ab\rangle. \tag{12}$$

In the above-presented equations, $\hat{f}_1$ and $\hat{f}_2$ are the Fock operators acting on the coordinates of electrons 1 and 2, respectively, and $g_{12} = r_{12}^{-1}$ is the electron repulsion operator. The MP2-R12 correlation energy can now be expressed as

$$E_{\text{MP2-R12}}^{(2)} = \frac{1}{4}\text{Tr}(\mathbf{GT}+\mathbf{VC}), \tag{13}$$

and the MP2-R12 amplitude equations can be written in terms of two coupled equations,

$$\{\mathbf{f}_v,\mathbf{T}\} - \{\mathbf{T},\mathbf{f}_o\} + \mathbf{E}^T\mathbf{C} - \mathbf{W}^T\{\mathbf{C},\mathbf{f}_o\} + \mathbf{G}^T = \mathbf{0}, \tag{14}$$

$$\mathbf{FC} - \mathbf{X}\{\mathbf{C},\mathbf{f}_o\} + \mathbf{ET} - \mathbf{W}\{\mathbf{T},\mathbf{f}_o\} + \mathbf{V}^T = \mathbf{0}. \tag{15}$$

Terms of the type $\{\mathbf{A},\mathbf{f}_o\}$ or $\{\mathbf{f}_v,\mathbf{A}\}$ refer to 1-index transformations of the 4-index intermediate **A** with the occupied–occupied ($\mathbf{f}_o$) or virtual–virtual ($\mathbf{f}_v$) blocks of the Fock matrix

$$\mathbf{f} = \begin{bmatrix} \mathbf{f}_o & 0 \\ 0 & \mathbf{f}_v \end{bmatrix}. \tag{16}$$

Specifically,

$$\{\mathbf{C},\mathbf{f}_o\}_{kl}^{ij} = c_{kl}^{oj}f_o^i + c_{kl}^{io}f_o^j, \tag{17}$$

$$\{\mathbf{f}_o,\mathbf{C}\}_{kl}^{ij} = f_k^o c_{ol}^{ij} + f_l^o c_{ko}^{ij}, \tag{18}$$

$$\{\mathbf{T},\mathbf{f}_o\}_{ab}^{ij} = t_{ab}^{oj}f_o^i + t_{ab}^{io}f_o^j, \tag{19}$$

$$\{\mathbf{f}_v,\mathbf{T}\}_{ab}^{ij} = f_a^c t_{cb}^{ij} + f_b^c t_{ac}^{ij}, \tag{20}$$

$$\{\mathbf{f}_o,\mathbf{W}\}_{kl}^{ab} = f_k^o\bar{W}_{ol}^{ab} + f_l^o\bar{W}_{ko}^{ab}, \tag{21}$$

$$\{\mathbf{W},\mathbf{f}_v\}_{kl}^{ab} = \bar{W}_{kl}^{cb}f_a^c + \bar{W}_{kl}^{ac}f_b^c. \tag{22}$$

Equations (13)–(15) are valid for both canonical and localized molecular orbitals, as the Fock matrix Eq. (16) is only required to be block-diagonal.

C. Standard approximations A, A′, and B

The key idea of the standard approximations of linear-r_{12} theory is to rewrite the integrals that involve products of r_{12} with Fock operators. For example, consider the matrix elements $\bar{E}_{mn}^{ab}$ of Eq. (10). These can be rewritten as

$$\bar{E}_{mn}^{ab} = \langle mn|[\hat{w}_{12}^{\dagger},\hat{f}_1+\hat{f}_2]|ab\rangle + \langle mn|(\hat{f}_1+\hat{f}_2)\hat{w}_{12}^{\dagger}|ab\rangle$$

$$= \langle mn|[r_{12}\hat{Q}_{12},\hat{f}_1+\hat{f}_2]|ab\rangle$$

$$+ \langle mn|(\hat{f}_1+\hat{f}_2)r_{12}\hat{Q}_{12}|ab\rangle. \quad (23)$$

Under the assumption that $[\hat{Q}_{12},\hat{f}_1+\hat{f}_2]=0$, we obtain

$$\bar{E}_{mn}^{ab} = \langle mn|[r_{12},\hat{f}_1+\hat{f}_2]\hat{Q}_{12}|ab\rangle + \langle mn|(\hat{f}_1+\hat{f}_2)r_{12}\hat{Q}_{12}|ab\rangle$$

$$= \bar{U}_{mn}^{ab} + \bar{K}_{mn}^{ab} - \bar{L}_{mn}^{ab} + f_k^o \bar{W}_{ol}^{ab} + f_l^o \bar{W}_{ko}^{ab}, \quad (24)$$

with

$$\bar{U}_{mn}^{ab} = \langle mn|[r_{12},\hat{t}_1+\hat{t}_2]\hat{Q}_{12}|ab\rangle, \quad (25)$$

$$\bar{K}_{mn}^{ab} = \langle mn|(\hat{k}_1+\hat{k}_2)r_{12}\hat{Q}_{12}|ab\rangle, \quad (26)$$

$$\bar{L}_{mn}^{ab} = \langle mn|r_{12}(\hat{k}_1+\hat{k}_2)\hat{Q}_{12}|ab\rangle. \quad (27)$$

The only parts of the Fock operator $\hat{f}_\mu$ that do not commute with r_{12} are the kinetic energy operator $\hat{t}_\mu$ and the exchange operator $\hat{k}_\mu$ ($\mu=1,2$). To arrive at Eq. (24), we assume for ansatz **1** that the space of all spin orbitals is closed under the Fock operator (extended Brillouin condition) and for ansatz **2** that the space of occupied spin orbitals is closed under the Fock operator (generalized Brillouin condition).[20]

Analogous to

$$\mathbf{E} = \mathbf{U} + \mathbf{K} - \mathbf{L} + \{\mathbf{f}_o, \mathbf{W}\}, \quad (28)$$

we obtain

$$\mathbf{F} = \mathbf{B} + \mathbf{Q} - \mathbf{P} + \tfrac{1}{2}\{\mathbf{f}_o, \mathbf{X}\} + \tfrac{1}{2}\{\mathbf{X},\mathbf{f}_o\}, \quad (29)$$

with

$$\bar{B}_{mn}^{kl} = \frac{1}{2}\langle mn|\hat{w}_{12}^{\dagger}[\hat{t}_1+\hat{t}_2,r_{12}] + [r_{12},\hat{t}_1+\hat{t}_2]\hat{w}_{12}|kl\rangle, \quad (30)$$

$$\bar{P}_{mn}^{kl} = \frac{1}{2}\langle mn|\hat{w}_{12}^{\dagger}(\hat{k}_1+\hat{k}_2)r_{12} + r_{12}(\hat{k}_1+\hat{k}_2)\hat{w}_{12}|kl\rangle, \quad (31)$$

$$\bar{Q}_{mn}^{kl} = \frac{1}{2}\langle mn|\hat{w}_{12}^{\dagger}r_{12}(\hat{k}_1+\hat{k}_2) + (\hat{k}_1+\hat{k}_2)r_{12}\hat{w}_{12}|kl\rangle. \quad (32)$$

In ansatz **1**, the projector $\hat{Q}_{12}$ is the projector onto the full orbital basis. Hence, $\hat{Q}_{12}|ab\rangle=0$ and therefore $\mathbf{E}=\mathbf{0}$. Moreover, not only $\mathbf{E}=\mathbf{0}$, but also $\mathbf{W}=\mathbf{U}=\mathbf{K}=\mathbf{L}=\mathbf{0}$ in ansatz **1**. In ansatz **2**, however, $\mathbf{E}$ is nonzero and must be evaluated.

In Refs. 17 and 20, we have introduced the approach **2***, where $\mathbf{E}^T$ in Eq. (14) is not computed according to Eq. (28) but rather from the equation $\mathbf{E}=\{\mathbf{W},\mathbf{f}_v\}$. It is important to note that the latter equation is used to simplify Eq. (14) but not Eq. (15). This **2*** approach may seem artificial or arbi-

trary, but the reason to restrict the simplification to Eq. (14) is that, by doing so, the results from the **2*** approach become identical to those of the original MP2-R12 methods when the auxiliary basis set is chosen to be identical with the main orbital basis.[20] In the present paper, results are presented not only for the **1** and **2** approaches but also for the **2*** approach. To summarize, the matrix $\mathbf{E}^T$ in Eq. (14) is computed as follows in the various approaches:

$$\text{Ansatz } \mathbf{1}: \quad \mathbf{E}^T = \mathbf{0}^T, \quad (33)$$

$$\text{Ansatz } \mathbf{2}: \quad \mathbf{E}^T = \mathbf{U}^T + \mathbf{K}^T - \mathbf{L}^T + \{\mathbf{W}^T,\mathbf{f}_o\}, \quad (34)$$

$$\text{Ansatz } \mathbf{2}^*: \quad \mathbf{E}^T = \{\mathbf{f}_v, \mathbf{W}^T\}. \quad (35)$$

Up to this point, the formulation of MP2-R12 theory has been completely general. The various approximations A, A′, and B of linear r_{12} theory are obtained when certain terms are neglected.[21] These approximations are defined by rewriting Eq. (15) as follows:[15,20,21]

$$\text{MP2-R12/A:} \quad \mathbf{BC} + \mathbf{UT} + \mathbf{V}^T = \mathbf{0}, \quad (36)$$

$$\text{MP2-R12/A':} \quad \mathbf{BC} + \tfrac{1}{2}\{\mathbf{f}_o,\mathbf{X}\}\mathbf{C} + \tfrac{1}{2}\{\mathbf{X},\mathbf{f}_o\}\mathbf{C} - \mathbf{X}\{\mathbf{C},\mathbf{f}_o\}$$

$$+ \mathbf{UT} + \{\mathbf{f}_o,\mathbf{W}\}\mathbf{T} - \mathbf{W}\{\mathbf{T},\mathbf{f}_o\} + \mathbf{V}^T = \mathbf{0}. \quad (37)$$

$$\text{MP2-R12/B:} \quad (\mathbf{B} + \mathbf{Q} - \mathbf{P})\mathbf{C} + \tfrac{1}{2}\{\mathbf{f}_o,\mathbf{X}\}\mathbf{C}$$

$$+ \tfrac{1}{2}\{\mathbf{X},\mathbf{f}_o\}\mathbf{C} - \mathbf{X}\{\mathbf{C},\mathbf{f}_o\} + (\mathbf{U} + \mathbf{K} - \mathbf{L})\mathbf{T}$$

$$+ \{\mathbf{f}_o,\mathbf{W}\}\mathbf{T} - \mathbf{W}\{\mathbf{T},\mathbf{f}_o\} + \mathbf{V}^T = \mathbf{0}. \quad (38)$$

Without auxiliary basis, approximation B is only $\sim 25\%$ more time-consuming than approximation A. If an auxiliary basis is used, however, approximation B becomes much more expensive than A because it requires two-electron integrals with two indices belonging to the auxiliary basis. Only one index belongs to the auxiliary basis in approximation A. Approximation B is more reliable than approximation A, in particular when an auxiliary basis is used. It then contains all terms, in contrast to A, where some terms are omitted. Both approximations are useful because it has turned out that the results of approximation A usually converge from below to the basis-set limit while the results of B have thus far always converged from above. Therefore, approximations A and B appear to provide upper and lower bounds to the basis-set limit MP2 correlation energy.

D. Intermediate orbitals

The evaluation of the matrix elements of the preceeding sections involves three- and four-electron integrals, which are approximated by inserting the resolution of the identity in an auxiliary basis (RI approximation). We shall not give details here (cf. Ref. 20) but instead focus on the computation of the matrices that occur in the MP2-R12/B model.

The computation of the matrices $\mathbf{Q}$ and $\mathbf{K}$ is straightforward when we introduce the *intermediate* orbitals[20]

$$\varphi_{m*} = \sum_{p'} \varphi_{p'} K_m^{p'}, \tag{39}$$

$$K_m^{p'} = \sum_i \langle \varphi_m(1)\varphi_i(2)|g_{12}|\varphi_i(1)\varphi_{p'}(2)\rangle, \tag{40}$$

in terms of which we obtain

$$\bar{Q}_{mn}^{kl} = \frac{1}{2}(\bar{X}_{mn}^{k*l} + \bar{X}_{mn}^{kl*} + \bar{X}_{m*n}^{kl} + \bar{X}_{mn*}^{kl}) \tag{41}$$

and

$$\bar{K}_{mn}^{ab} = \bar{W}_{m*n}^{ab} + \bar{W}_{mn*}^{ab}. \tag{42}$$

Although straightforward, we note that the computation of the matrix $\mathbf{Q}$ requires the evaluation of two-electron integrals with up to *two* auxiliary basis functions. Consider, for example,

$$\bar{X}_{mn}^{k*l} = \langle mn|\hat{w}_{12}^\dagger r_{12}|k*l\rangle = \langle mn|r_{12}^2|k*l\rangle - \hat{r}_{mn}^{\mu q'} r_{\mu q'}^{k*l}$$
$$- \hat{r}_{mn}^{p'\nu} r_{p'\nu}^{k*l} + \hat{r}_{mn}^{\mu\nu} r_{\mu\nu}^{k*l}, \tag{43}$$

where $\mu, \nu \equiv p, q$ for ansatz **1** and $\mu, \nu \equiv i, j$ for ansatz **2**. The integrals $r_{\mu q'}^{k*l}$ and $r_{p'\nu}^{k*l}$ involve *two* auxiliary basis functions, since the intermediate orbital φ_{k*} is expanded in the auxiliary basis according to Eq. (39).

This observation has motivated us to investigate a new scheme, which we denote the "hybrid" scheme. In this hybrid scheme, the intermediate orbitals for $\mathbf{K}$ are expanded in the auxiliary basis $\{\varphi_{p'}\}$ as before, but the intermediate orbitals for $\mathbf{Q}$ are expanded in the orbital basis $\{\varphi_p\}$. Hence, we construct a second set of intermediate orbitals,

$$\varphi_{m\circ} = \sum_p \varphi_p K_m^p, \tag{44}$$

$$K_m^p = \sum_i \langle \varphi_m(1)\varphi_i(2)|g_{12}|\varphi_i(1)\varphi_p(2)\rangle, \tag{45}$$

and compute $\mathbf{Q}$ from

$$\bar{Q}_{mn}^{kl} = \frac{1}{2}(\bar{X}_{mn}^{k\circ l} + \bar{X}_{mn}^{kl\circ} + \bar{X}_{m\circ n}^{kl} + \bar{X}_{mn\circ}^{kl}), \tag{46}$$

rather than from the intermediate orbitals φ_{m*}. It is important to note that the matrix $\mathbf{K}$ remains unchanged in the new hybrid scheme.

E. The matrices P and L

We have so far only considered the matrices $\mathbf{Q}$ and $\mathbf{K}$, not $\mathbf{P}$ and $\mathbf{L}$. Concerning the hybrid approach, nothing needs to be done about $\mathbf{L}$, since it is either zero (ansatz **1**) or it involves integrals with only one auxiliary function at the most, as desired (ansatz **2**),

$$\bar{L}_{mn}^{ab} = \bar{r}_{mn}^{p'b} K_{p'}^a + \bar{r}_{mn}^{aq'} K_{q'}^b, \quad \text{for ansatz } \mathbf{2}. \tag{47}$$

The matrix $\mathbf{P}$ was originally given by[15,20]

TABLE I. Nuclear Cartesian coordinates in a_0.

Molecule	Atom	x	y	z
CH$_2$ ($^1A_1$)	C	0.000 000 0	0.000 000 0	−0.189 234 3
	H	1.625 683 1	0.000 000 0	1.126 590 4
	H	−1.625 683 1	0.000 000 0	1.126 590 4
H$_2$O	O	0.000 000 0	0.000 000 0	−0.124 309 0
	H	1.427 450 2	0.000 000 0	0.986 437 0
	H	−1.427 450 2	0.000 000 0	0.986 437 0
NH$_3$	N	0.000 000 0	0.000 000 0	0.000 000 0
	H	1.766 326 0	0.000 000 0	0.728 948 1
	H	−0.883 163 0	1.529 683 2	0.728 948 1
	H	−0.883 163 0	−1.529 683 2	0.728 948 1
HF	F	0.000 000 0	0.000 000 0	0.000 000 0
	H	0.000 000 0	0.000 000 0	1.730 552 9
N$_2$	N	0.000 000 0	0.000 000 0	1.037 572 1
	N	0.000 000 0	0.000 000 0	−1.037 572 1
CO	C	0.000 000 0	0.000 000 0	1.218 843 3
	O	0.000 000 0	0.000 000 0	−0.914 423 4
F$_2$	F	0.000 000 0	0.000 000 0	1.333 518 7
	F	0.000 000 0	0.000 000 0	−1.333 518 7

$$\begin{aligned}
\bar{P}_{mn}^{kl} = \frac{1}{2}(& \bar{r}_{mn}^{p'q'} K_{p'}^{r'} \bar{r}_{r'q'}^{kl} - \bar{r}_{mn}^{\mu q'} K_\mu^{r'} \bar{r}_{r'q'}^{kl} - \bar{r}_{mn}^{p'\nu} K_{p'}^{r'} \bar{r}_{r'\nu}^{kl} \\
& + \bar{r}_{mn}^{\mu\nu} K_\mu^{r'} \bar{r}_{r'\nu}^{kl} + \bar{r}_{mn}^{p'q'} K_{q'}^{r'} \bar{r}_{p'r'}^{kl} - \bar{r}_{mn}^{\mu q'} K_{q'}^{r'} \bar{r}_{\mu r'}^{kl} \\
& - \bar{r}_{mn}^{p'\nu} K_\nu^{r'} \bar{r}_{p'r'}^{kl} + \bar{r}_{mn}^{\mu\nu} K_\nu^{r'} \bar{r}_{\mu r'}^{kl} + \bar{r}_{mn}^{r'q'} K_{r'}^{p'} \bar{r}_{p'q'}^{kl} \\
& - \bar{r}_{mn}^{r'q'} K_{r'}^\mu \bar{r}_{\mu q'}^{kl} - \bar{r}_{mn}^{r'\nu} K_{r'}^{p'} \bar{r}_{p'\nu}^{kl} + \bar{r}_{mn}^{r'\nu} K_{r'}^\mu \bar{r}_{\mu\nu}^{kl} \\
& + \bar{r}_{mn}^{p'r'} K_{r'}^{q'} \bar{r}_{p'q'}^{kl} - \bar{r}_{mn}^{\mu r'} K_{r'}^{q'} \bar{r}_{\mu q'}^{kl} - \bar{r}_{mn}^{p'r'} K_{r'}^\nu \bar{r}_{p'\nu}^{kl} \\
& + \bar{r}_{mn}^{\mu r'} K_{r'}^\nu \bar{r}_{\mu\nu}^{kl}),
\end{aligned} \tag{48}$$

where $\mu, \nu \equiv p, q$ for ansatz **1** and $\mu, \nu \equiv i, j$ for ansatz **2**. The energy contributions originating from $\mathbf{P}$ have been extremely small in all of the previous calculations, and when we replace some of the primed indices (which refer to auxiliary orbitals) by the standard orbital indices in the spirit of the new hybrid scheme, the matrix $\mathbf{P}$ vanishes completely. Hence, in this scheme, the computation of $\mathbf{P}$ is omitted.

III. COMPUTATIONAL DETAILS

The geometries of the seven molecules are identical to those used in previous work.[20] The Cartesian coordinates are given in Table I to enable a complete reproduction of the numerical results, if desired. All calculations were performed in the augmented correlation-consistent polarized valence X-tuple zeta basis sets (aug-cc-pVXZ) of Kendall, Dunning, and Harrison,[22,23] with $X = 2, 3, 4, 5$. Only the valence orbitals were correlated (frozen-core approximation), and the auxiliary basis set of Ref. 20 ($19s14p8d6f4g3h2i$ for C, N, O, F, and Ne, and $9s6p4d3f2g$ for H) was used for the RI approximation of MP2-R12 theory. The sextuple-zeta basis with $X = 6$ was not considered as orbital basis, since this basis is virtually as large as the auxiliary basis set, yielding like results for the full and hybrid MP2-R12/B methods. The new hybrid MP2-R12/B scheme has been implemented into the DALTON program, which was used for all of the calculations of the present work.[24]

TABLE II. Valence-shell Møller–Plesset second-order correlation energies ($-E^{(2)}$ in mE_h) as obtained from the MP2-R12/B method using various approximations.

System	Limit	Basis	1B		2B		2B*	
			Hybrid	Full	Hybrid	Full	Hybrid	Full
$CH_2(^1A_1)$	155.9	aug-cc-pVDZ	131.99	132.61	139.02	141.03	138.44	140.28
		aug-cc-pVTZ	148.25	148.43	150.67	151.01	150.44	150.67
		aug-cc-pVTZ	148.42	148.40	150.70	150.99	150.44	150.62
		aug-cc-pV5Z	154.86	154.93	155.26	155.30	155.10	155.13
H_2O	300.5	aug-cc-pVDZ	249.45	251.04	266.11	269.05	265.88	268.60
		aug-cc-pVTZ	282.21	282.54	289.69	290.36	289.61	290.11
		aug-cc-pVQZ	292.89	293.16	296.53	296.89	296.41	296.64
		aug-cc-pV5Z	297.80	297.92	299.05	299.14	298.82	298.88
NH_3	264.5	aug-cc-pVDZ	224.62	225.75	237.15	239.87	236.88	239.37
		aug-cc-pVTZ	251.63	251.66	256.49	256.88	256.43	256.68
		aug-cc-pVQZ	259.55	259.63	261.90	262.06	261.82	261.88
		aug-cc-pV5Z	262.83	262.89	263.58	263.59	263.40	263.41
HF	319.7	aug-cc-pVDZ	258.64	260.61	278.95	282.06	278.95	281.93
		aug-cc-pVTZ	296.44	296.96	306.51	307.39	306.48	307.14
		aug-cc-pVQZ	309.39	309.77	314.51	315.01	314.33	314.67
		aug-cc-pV5Z	316.09	316.17	317.92	317.98	317.63	317.66
N_2	421.0	aug-cc-pVDZ	353.46	355.28	374.67	379.44	371.85	375.98
		aug-cc-pVTZ	396.84	397.11	405.22	406.22	404.64	405.30
		aug-cc-pVQZ	410.31	410.72	415.03	415.60	414.64	415.04
		aug-cc-pV5Z	417.08	417.29	418.86	419.01	418.43	418.54
CO	403.9	aug-cc-pVDZ	337.81	339.63	358.97	363.50	356.45	360.30
		aug-cc-pVTZ	379.27	379.46	388.11	389.09	387.68	388.39
		aug-cc-pVQZ	393.03	393.53	397.93	398.52	397.63	398.04
		aug-cc-pV5Z	400.00	400.12	401.80	401.89	401.39	401.45
Ne	320.1	aug-cc-pVDZ	250.40	252.63	273.51	276.65	274.31	277.56
		aug-cc-pVTZ	292.43	292.94	304.80	305.76	304.58	305.32
		aug-cc-pVQZ	306.97	307.29	313.60	314.16	313.35	313.72
		aug-cc-pV5Z	315.43	315.52	317.93	318.00	317.54	317.57
F_2	611.7	aug-cc-pVDZ	493.49	497.19	533.41	539.93	532.72	538.88
		aug-cc-pVTZ	567.09	567.97	585.94	587.74	585.69	586.97
		aug-cc-pVQZ	590.86	591.47	600.84	601.79	600.24	600.89
		aug-cc-pV5Z	604.49	604.44	608.10	608.09	607.46	607.38

IV. RESULTS AND DISCUSSION

We have computed the valence-shell Møller–Plesset second-order correlation energies of the Ne atom and the molecules CH_2 (in its $^1A_1$ state), H_2O, NH_3, HF, N_2, CO, and F_2 in the fixed geometries of Table I. These are the same systems as studied in Ref. 20. The results are collected in Table II, which shows the energies obtained from the approaches **1**, **2**, and **2*** in the standard approximation B. The energies obtained from the approach of Ref. 20 (under the header "Full") are compared with the energies from the new hybrid scheme (under the header "Hybrid"). The estimated basis-set limits are those of Ref. 20.

Table II shows that, except maybe in the aug-cc-pVDZ basis, the differences between the full and hybrid approaches are indeed very small. Most important, these differences are much smaller than the errors due to other approximations, assumptions, or truncations. This is documented in Table III and Fig. 1, which show the differences between the full MP2-R12/B results and the estimated basis-set limit (Δ_{limit}), the differences between the full MP2-R12/B results and the corresponding MP2-R12/A calculations (Δ_{A-B}), and the differences between the full MP2-R12/B and hybrid MP2-R12/B results (Δ_{Hybrid}) for the approaches **1**, **2**, **2*** and for

the basis sets aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z.

Table II and Fig. I show that Δ_{hybrid} is at least one order of magnitude smaller than Δ_{limit}, and also much smaller (almost an order of magnitude) than the difference between the standard approximations A and B. Hence, it appears perfectly reasonable to apply the new hybrid approach.

TABLE III. Mean absolute deviations (in mE_h) of the full R12/B results with respect to the basis set limit (Δ_{limit}), with respect to the R12/A approximation (Δ_{A-B}), and with respect to the hybrid approach (Δ_{hybrid}).

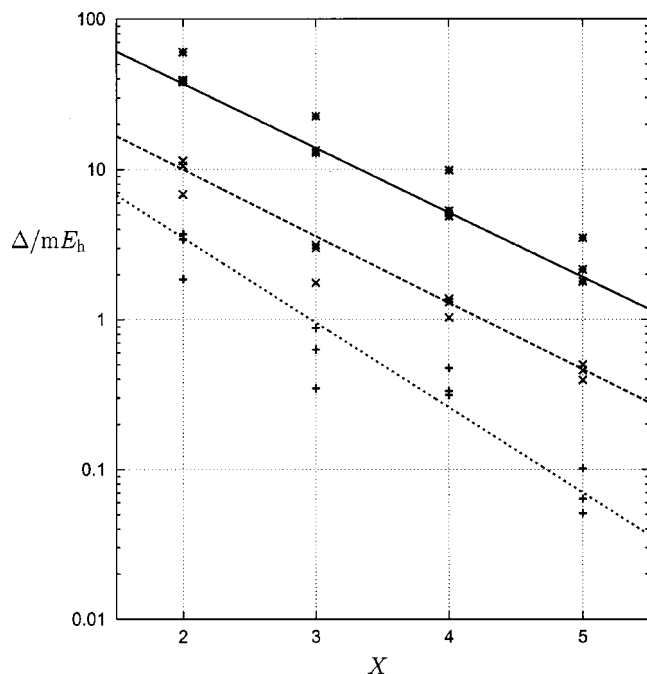| Error	Ansatz	$X=2$	$X=3$	$X=4$	$X=5$
Δ_{limit}	**1**	60.32	22.54	9.83	3.50
	2	38.22	12.85	4.88	1.79
	2*	39.30	13.34	5.30	2.16
Δ_{A-B}	**1**	6.83	1.76	1.03	0.39
	2	11.38	3.14	1.38	0.50
	2*	10.54	2.99	1.31	0.46
Δ_{hybrid}	**1**	1.86	0.35	0.33	0.10
	2	3.72	0.88	0.47	0.06
	2*	3.43	0.63	0.31	0.05

FIG. 1. Three types of mean absolute deviations (Δ in mE_h) are displayed as function of the aug-cc-pVXZ basis with $X = 2,3,4,5$. These deviations are, respectively, the difference between the full R12/B results and the estimated basis-set limit (Δ_{limit}, *), the difference between the approximations A and B ($\Delta_{\text{A-B}}$, ×), and the difference between the full and hybrid R12/B results (Δ_{hybrid}, +). The mean absolute deviations for eight molecular systems are shown for the ansätze **1**, **2**, and **2*** by three like symbols per X and Δ. To guide the eye, straight lines fitted to the average of the **2** and **2*** results are also given. See also Table III.

V. CONCLUSIONS

For the standard approximation B of linear-r_{12} theory, we have proposed and investigated a new hybrid scheme, which can be applied when an auxiliary basis is used for the RI approximation. It has appeared possible to use the (large) auxiliary basis for the RI approximation in all of the integrals that contribute to the MP2-R12/A model and to use the (small) orbital basis for the RI approximation in all of the integrals that occur beyond the MP2-R12/A model, that is, for MP2-R12/B. A comparison between valence-shell second-order correlation energies of some small systems indicates that the difference between the full and hybrid MP2-R12/B results is negligible, being an order of magnitude smaller than the errors due to other approximations. By virtue of the new hybrid scheme, the MP2-R12/A and MP2-R12/B methods never require the computation of two-electron integrals with more than one function from the auxiliary basis. Hence, computation times and data storage requirements grow only linearly with the size of the auxiliary basis, which translates into substantial savings in comparison with the full MP2-R12/B approach of Ref. 20.

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