Alternative Formulation of the Matrix Elements in MP2-R12 Theory

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ABSTRACT: A formulation of MP2-R12 theory is presented leading to simplified matrix elements in the R12 part. The resulting formulas are free from the integrals over the commutator of the kinetic operator with inter-electronic distance, which means a substantial decreasing of the computational demands. The use of an auxiliary basis set for the resolution of identity is discussed. First results using the standard approximation are compared with the former variants of MP2-R12 for CH_2, CH_4, NH_3, H_2O, HF, CO, CH_3OH, N_2, and F_2. The results show that the new formulation is not only less demanding, but also preferred concerning the convergence properties toward the basis set limit.   © 2005 Wiley Periodicals, Inc. Int J Quantum Chem 105: 929–936, 2005

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Introduction

It has been known for about 75 years that in order to achieve the proper behavior of the wave function for inter-electronic distances close to zero, one has to introduce the inter-electronic coordinate r_{12} into the wave function expansions explicitly [1]. It is the improper description of the correlation cusp [2] that causes frustratingly slow convergence of the traditional configuration space based wave function expansions with the size of the employed one-electron basis set. The main practical limitation related to direct inclusion and exact treatment of r_{12} in the wave function is the occurrence of many-electron integrals in the final working equations, which would make the calculations prohibitive for most, but very small systems. Nevertheless, several attempts to tackle this problem have been made (for a review, see e.g., Refs. [3, 4]).

So far, the most practical explicitly correlated approaches proved to be those based on the R12 theory that originates in the work of Kutzelnigg [5]. Taking the helium atom as an example, this author showed that to satisfy the electron–electron cusp

condition [2], and thus to enhance the convergence of the calculated energy with respect to increasing the basis set by functions with higher and higher angular momenta (ℓ), it was sufficient to extend the usual (conventional) wave function expansion by augmenting the reference determinant by a single linear r_{12} term. Although such an ansatz would not give rise to practical algorithms for many electron systems either, later introduced constraints and approximations led to avoiding the need of evaluation of the difficult three- and four-electron integrals [6]. Yet, the resulting R12 approaches provide, at least formally, a much faster convergence with respect to the highest angular momentum function included in the computational basis set (L). Depending on the approximation, the error is proportional to $(L+1)^{-5}$ or $(L+1)^{-7}$, vs. $(L+1)^{-3}$ for the conventional wave function expansions in the configuration space [6, 8].

Most closely related to the original work [5] is the orbital-non-invariant MP2-R12 theory [8]. Soon after, MP2-R12 was improved to its orbital invariant formulation by Klopper [9]. The formulation within the coupled cluster theory (CC-R12) [10–13] resembles some features of the transcorrelated Hamiltonian of Boys and Handy [14], though, with a different correlation function, which led to more practical method. CC-R12 in its CCSD(T)-R12 variant proved to be very accurate, and, with the given orbital basis set, its computational complexity is only slightly different from the conventional calculation [15].

Until recently, the R12 theories were formulated in what is called "the standard approximation" (SA) [6], which assumes that the finite spin orbital space is closed under the Fock operator, i.e., assuming not only the generalized Brillouin condition (GBC)

$$f_i^\alpha = 0, \tag{1}$$

but also the extended Brillouin condition (EBC)

$$f_p^\alpha = 0, \tag{2}$$

where i and p denote occupied and arbitrary spin orbitals within the finite computational basis, respectively, whereas α denotes orbitals from the orthogonal complement to the latter basis. At the same time, SA assumes that the resolution of identity can be well represented within the given computational basis set. The SA constraints imply that

this basis has to be saturated at least at the level of $3L_{occ}$, where L_{occ} is the highest angular momentum involved in the occupied spin orbitals.

Alternatively, one can use an auxiliary basis set for the resolution of identity with the aim to weaken this strong basis set requirement. This has been implemented recently within the MP2-R12 theory, using diverse variants [16–20].

In this work we present the MP2-R12 from a different perspective, within the second quantized formalism with normal ordering with respect to the reference. We do not apply any a priori approximations in order to evaluate the necessary matrix elements. Instead, we formulate the theory exactly (using a complete basis) and apply approximations to the final matrix elements. As a result, it turns out that, unlike in the previous formulations, the integrals over the commutator of the kinetic operator with r_{12} are not needed. At the level of MP2-R12, this means a computational acceleration by a factor of at least two. First, we formulate the theory and derive the matrix elements using auxiliary basis set for the resolution of identity. We briefly discuss the minimum requirements for the auxiliary set. In the last section, we have tested this alternative approach using the standard approximation.

Theory

In the following we will denote occupied orbitals as $i, j, \ldots, o$; virtual spin orbitals within the computational basis as a, b, c; and arbitrary spin orbitals within the computational basis as p, q, r, s. Greek letters $\kappa, \lambda, \mu, \nu$ denote any spin orbitals within the complete basis, and α, β, γ, the spin orbitals from the complete basis that are outside the final computational one. (Note that in the early formulation [6, 11], the Greek letters $\alpha, \beta, \cdots$ denoted spin orbitals within the full virtual space.) The basis set is assumed to be orthonormal. We will use a tensor notation for the integrals over any n-body operator $\hat{o}_n$,

$$o_{\kappa_1 \cdots \kappa_n}^{\lambda_1 \cdots \lambda_n} = \langle \kappa_1 \cdots \kappa_n | \hat{o}_n | \lambda_1 \cdots \lambda_n \rangle, \tag{3}$$

as well as for integral products. Einstein summation convention is considered throughout, i.e., summations run over all indices that do not appear on both sides of the equations.

Let $|\Phi\rangle$ be our reference determinant (Fermi vacuum). We will work with normal ordered n-body replacement operators

$$\tilde{a}_{\kappa_1\kappa_2\cdots\kappa_n}^{\lambda_1\lambda_2\cdots\lambda_n} = (\tilde{a}_{\lambda_1\lambda_2\cdots\lambda_n}^{\kappa_1\kappa_2\cdots\kappa_n})^\dagger = \{a_{\lambda_1}^\dagger a_{\lambda_2}^\dagger \cdots a_{\lambda_n}^\dagger a_{\kappa_n} \cdots a_{\kappa_2} a_{\kappa_1}\}, \tag{4}$$

where $a_\lambda^\dagger$ and a_κ are the creation and annihilation operators, respectively. The braces in Eq. (4) denote the normal order with respect to $|\Phi\rangle$. Accordingly, the normal ordered Hamiltonian is given as

$$\hat{H}_N = \hat{H} - \langle\Phi|\hat{H}|\Phi\rangle = \hat{F}_N + \hat{W}_N, \tag{5}$$

$$\hat{F}_N = f_\kappa^\lambda \tilde{a}_\lambda^\kappa = (h_\kappa^\lambda + \bar{g}_{\kappa i}^{\lambda i})\tilde{a}_\lambda^\kappa, \tag{6}$$

$$\hat{W}_N = \tfrac{1}{4}\bar{g}_{\kappa\lambda}^{\mu\nu}\tilde{a}_{\mu\nu}^{\kappa\lambda}, \tag{7}$$

where $\hat{h}$ is the usual one-electron Hamiltonian, $\hat{f}$ the Fock operator, and $\hat{g} = r_{12}^{-1}$. For our purpose (vide infra), it will be useful to rewrite $\hat{f}$ through different contributions as

$$\hat{f} = \hat{t} + \hat{v} + \hat{j} - \hat{k}, \tag{8}$$

with $\hat{t}$ the kinetic energy operator, $\hat{v}$ the nuclear potential, and $\hat{j}$ and $\hat{k}$ being the Coulomb and exchange operators. Greek letters in Eqs. (6) and (7) emphasize that the second-quantized Hamiltonian is exact if it is defined in terms of a complete basis set. Similarly, the operator of inter-electronic coordinates in normal ordered form reads

$$\hat{r}_N = \sum_{p>q} r_{pq} - \left\langle\Phi\left|\sum_{p<q} r_{pq}\right|\Phi\right\rangle = \tfrac{1}{4}\bar{r}_{\mu\nu}^{\kappa\lambda}\tilde{a}_{\kappa\lambda}^{\mu\nu} + \bar{r}_{\mu i}^{\kappa i}\tilde{a}_\kappa^\mu. \tag{9}$$

Action of $\hat{r}_N$ on $|\Phi\rangle$ yields

$$\hat{r}_N|\Phi\rangle = \left(\tfrac{1}{4}\bar{r}_{ab}^{ij}\tilde{a}_{ij}^{ab} + \tfrac{1}{4}\bar{r}_{\alpha\beta}^{ij}\tilde{a}_{ij}^{\alpha\beta} + \tfrac{1}{2}\bar{r}_{a\beta}^{ij}\tilde{a}_{ij}^{a\beta} + \bar{r}_{aj}^{ij}\tilde{a}_i^a \right.$$
$$\left. + \bar{r}_{\alpha j}^{ij}\tilde{a}_i^\alpha\right)|\Phi\rangle, \tag{10}$$

where we have used the fact that only terms with excitation operators survive. The terms that do not contain Greek indices obviously involve substituted determinants —single and double excitations— used to expand the wave function in the conventional configuration space. Hence, it is desirable to outproject these contributions.

We can introduce particular pseudo-excitation operators for what can be called r_{12} double excitations or r_{12} single excitations [12]

$$\tilde{\mathcal{R}}_{ij}^{kl} = \tilde{a}_{ij}^{kl}(\tfrac{1}{2}\bar{r}_{\alpha\beta}^{kl}\tilde{a}_{kl}^{\alpha\beta} + \bar{r}_{a\beta}^{kl}\tilde{a}_{kl}^{a\beta}), \tag{11}$$

$$\tilde{\mathcal{R}}_i^k = \tilde{a}_i^k\bar{r}_{\alpha j}^{kj}\tilde{a}_k^\alpha. \tag{12}$$

Further, one can associate these operators with scalar amplitudes (c_{kl}^{ij}, c_k^i) and define a global r_{12}-excitation operator

$$\hat{\mathcal{R}} = \hat{\mathcal{R}}_1 + \hat{\mathcal{R}}_2 = c_k^i\tilde{\mathcal{R}}_i^k + \tfrac{1}{4}c_{kl}^{ij}\tilde{\mathcal{R}}_{ij}^{kl}. \tag{13}$$

Let us recall that at the second order many body perturbation theory level with Møller–Plesset splitting of the Hamiltonian (MP2-R12) the contribution from $\hat{\mathcal{R}}$ is completely decoupled from the usual (conventional) contribution, i.e.,

$$E_{\text{MP2-R12}} = E_{\text{MP2}} + E_{\text{R12}}^{(2)}, \tag{14}$$

where

$$E_{\text{R12}}^{(2)} = \langle\Phi|\hat{W}_N\hat{\mathcal{R}}^{(1)}|\Phi\rangle = \tfrac{1}{4}\bar{V}_{ij}^{kl}c_{kl}^{ij}. \tag{15}$$

$\mathcal{R}^{(1)}$ is the first-order contribution to $\hat{\mathcal{R}}$ [11]. In the present study, we restrict ourselves to closed-shell RHF reference. Consequently, $\hat{\mathcal{R}}^{(1)} \equiv \hat{\mathcal{R}}_2^{(1)}$. Because we shall only deal with the first-order wave function, we use $c_{kl}^{ij(1)} \equiv c_{kl}^{ij}$. In Eq. (15)

$$\bar{V}_{ij}^{kl} = \langle\Phi|\hat{W}_N\tilde{\mathcal{R}}_{ij}^{kl}|\Phi\rangle. \tag{16}$$

Using the fact that

$$\sum_\alpha = \sum_\kappa - \sum_p, \tag{17}$$

one easily gets

$$\bar{V}_{ij}^{kl} = \tfrac{1}{2}\bar{g}_{ij}^{\alpha\beta}\bar{r}_{\alpha\beta}^{kl} + \bar{g}_{ij}^{\alpha b}\bar{r}_{\alpha b}^{kl} = \tfrac{1}{2}\bar{g}_{ij}^{\kappa\lambda}\bar{r}_{\kappa\lambda}^{kl} - \bar{g}_{ij}^{\kappa q}\bar{r}_{\kappa q}^{kl}$$
$$+ \tfrac{1}{2}\bar{g}_{ij}^{pq}\bar{r}_{pq}^{kl} + \bar{g}_{ij}^{\kappa b}\bar{r}_{\kappa b}^{kl} - \bar{g}_{ij}^{pb}\bar{r}_{pb}^{kl}. \tag{18}$$

The first term of the right-hand side gives $(\overline{gr})_{ij}^{kl} = \delta_i^k\delta_j^l - \delta_i^l\delta_j^k = \bar{\delta}_{ij}^{kl}$. In an exact treatment, the second and fourth terms give rise to three electron integrals. This is avoided within the "standard approximation" by replacing the summation over κ (the resolution of identity) by the summation over the actual set of molecular spin orbitals. Instead, one can approximate the resolution of identity by an auxiliary set as first implemented by Klopper and Samson [16] with a slightly different ansatz for $\hat{\mathcal{R}}$. An equivalent ansatz as here was used by Valeev [20] and quite recently as well by Fliegl et al. [21]. In

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the following discussion, we shall denote the auxiliary set by p', q', etc. At the same time, we automatically assume that the main computational basis is a subset of the auxiliary one, which is highly recommended [20]. Part of the auxiliary basis that forms an orthogonal complement to the computational one will be denoted by p'', q'', and so on. Equation (18) then reads

$$\bar{V}_{ij}^{kl} \overset{\text{aux}}{=} \delta_{ij}^{kl} - \bar{g}_{ij}^{mq''}\bar{r}_{mq''}^{kl} - \tfrac{1}{2}\bar{g}_{ij}^{pq}\bar{r}_{pq}^{kl}. \quad (19)$$

From this result, it is easily seen that, at least for atoms, the second term vanishes due to symmetry reasons if the computational basis is saturated at the level of $3L_{\text{occ}}$.

The coefficients c_{kl}^{ij} from Eq. (15) can be calculated from the set of equations [11]:

$$\langle\Phi|(\tilde{\mathcal{R}}_{kl}^{ij})^{\dagger}\hat{F}_N\hat{\mathcal{R}}^{(1)}|\Phi\rangle + \langle\Phi|(\tilde{\mathcal{R}}_{kl}^{ij})^{\dagger}\hat{W}_N|\Phi\rangle = 0, \quad (20)$$

more explicitly given as

$$\tfrac{1}{2}\bar{B}_{ij}^{mn}c_{mn}^{kl} - \tfrac{1}{2}\bar{X}_{ij}^{mn}(c_{mn}^{ol}f_o^k + c_{mn}^{ko}f_o^l) + (\bar{V}_{ij}^{kl})^{\dagger} = 0. \quad (21)$$

The first term originates from the virtual–virtual block of $\hat{F}_N$ and the second term from the occupied–occupied one. Matrix elements

$$\bar{X}_{ij}^{kl} = \langle\Phi|(\tilde{\mathcal{R}}_{kl}^{ij})^{\dagger}\tilde{\mathcal{R}}_{ij}^{kl}|\Phi\rangle, \quad (22)$$

are evaluated in a similar manner as V in Eqs. (18) and (19), leading to

$$\bar{X}_{ij}^{kl} = \tfrac{1}{2}\bar{r}_{ij}^{\alpha\beta}\bar{r}_{\alpha\beta}^{kl} + \bar{r}_{ij}^{\alpha b}\bar{r}_{\alpha b}^{kl}$$

$$\overset{\text{aux}}{=} (\bar{r^2})_{ij}^{kl} - \bar{r}_{ij}^{mq''}\bar{r}_{mq''}^{kl} - \tfrac{1}{2}\bar{r}_{ij}^{pq}\bar{r}_{pq}^{kl} \quad (23)$$

Evaluation of matrix elements

$$\bar{B}_{ij}^{kl} = \langle\Phi|(\tilde{\mathcal{R}}_{kl}^{ij})^{\dagger}(f_d^c\tilde{a}_c^a + f_a^\gamma\tilde{a}_\gamma^a + f_c^c\tilde{\alpha}_c^\alpha + f_\alpha^\gamma\tilde{\alpha}_\gamma^\alpha)\tilde{\mathcal{R}}_{ij}^{kl}|\Phi\rangle, \quad (24)$$

is more difficult. Earlier derivations were based on a tricky way of using the commutator $[\hat{f}, r_{12}]$ and a priori assuming the GBC. This led to final formulas that involved integrals over $[\hat{t}, r_{12}]$ in both the standard approximation "R12-A" and "R12-B" variants [6], as well as within the mentioned auxiliary basis set approximations [16, 18–20]. If we do not apply any a priori approximations and simply use the relation Eq. (17), we get

$$\bar{B}_{ij}^{kl} = \bar{r}_{ij}^{\alpha\beta}f_\alpha^\gamma\bar{r}_{\gamma\beta}^{kl} + \bar{r}_{ij}^{\alpha b}f_\alpha^\gamma\bar{r}_{\gamma b}^{kl} + \bar{r}_{ij}^{a\beta}f_a^\gamma\bar{r}_{\gamma\beta}^{kl} + \bar{r}_{ij}^{\alpha\beta}f_\alpha^c\bar{r}_{c\beta}^{kl}$$
$$+ \bar{r}_{ij}^{a\beta}f_a^c\bar{r}_{c\beta}^{kl} \quad (25)$$

$$= \bar{r}_{ij}^{\kappa\lambda}f_\kappa^\mu\bar{r}_{\mu\lambda}^{kl} \quad (26)$$

$$+ \bar{r}_{ij}^{\kappa b}f_\kappa^\mu\bar{r}_{\mu b}^{kl} - \bar{r}_{ij}^{\kappa q}f_\kappa^\mu\bar{r}_{\mu q}^{kl} \quad (27)$$

$$+ \bar{r}_{ij}^{p\lambda}f_p^c\bar{r}_{r\lambda}^{kl} - \bar{r}_{ij}^{a\lambda}f_a^c\bar{r}_{r\lambda}^{kl} - \bar{r}_{ij}^{p\lambda}f_p^c\bar{r}_{c\lambda}^{kl} + \bar{r}_{ij}^{a\lambda}f_a^c\bar{r}_{c\lambda}^{kl} \quad (28)$$

$$- \bar{r}_{ij}^{p\lambda}f_p^\mu\bar{r}_{\mu\lambda}^{kl} + \bar{r}_{ij}^{a\lambda}f_a^\mu\bar{r}_{\mu\lambda}^{kl} - \bar{r}_{ij}^{\kappa\lambda}f_\kappa^c\bar{r}_{r\lambda}^{kl} + \bar{r}_{ij}^{\kappa\lambda}f_\kappa^c\bar{r}_{c\lambda}^{kl} \quad (29)$$

$$+ \bar{r}_{ij}^{pq}f_p^\mu\bar{r}_{\mu q}^{kl} - \bar{r}_{ij}^{aq}f_a^\mu\bar{r}_{\mu q}^{kl} + \bar{r}_{ij}^{\kappa q}f_\kappa^c\bar{r}_{rq}^{kl} - \bar{r}_{ij}^{\kappa q}f_\kappa^c\bar{r}_{cq}^{kl} \quad (30)$$

$$- \bar{r}_{ij}^{pb}f_p^\mu\bar{r}_{\mu b}^{kl} - \bar{r}_{ij}^{\kappa b}f_\kappa^c\bar{r}_{rb}^{kl} + \bar{r}_{ij}^{pb}f_p^c\bar{r}_{rb}^{kl} \quad (31)$$

$$- \bar{r}_{ij}^{pq}f_p^c\bar{r}_{rq}^{kl} + \bar{r}_{ij}^{pq}f_p^c\bar{r}_{cq}^{kl} + \bar{r}_{ij}^{aq}f_a^c\bar{r}_{rq}^{kl} - \bar{r}_{ij}^{aq}f_a^c\bar{r}_{cq}^{kl}. \quad (32)$$

Realizing that

$$-\sum_{p,r}\bar{r}_{ij}^{pq}f_p^c\bar{r}_{rq}^{kl} = -\sum_{m,n}\bar{r}_{ij}^{mq}f_m^\rho\bar{r}_{nq}^{kl} - \sum_{m,c}\bar{r}_{ij}^{mq}f_m^c\bar{r}_{cq}^{kl} - \sum_{a,c}\bar{r}_{ij}^{aq}f_a^c\bar{r}_{rq}^{kl},$$
$$(33)$$

the contributions from (32) are reduced to the following term:

$$(32): -\bar{r}_{ij}^{mq}f_m^\rho\bar{r}_{nq}^{kl}. \quad (34)$$

Further simplifications of similar kind yield

$$(27): -\bar{r}_{ij}^{\kappa m}f_\kappa^\mu\bar{r}_{\mu m}^{kl} \quad (35)$$

$$(28) + (34): +\bar{r}_{ij}^{m\beta}f_m^\rho\bar{r}_{n\beta}^{kl} \quad (36)$$

$$(29) + (30): -\bar{r}_{ij}^{m\beta}f_m^\mu\bar{r}_{\mu\beta}^{kl} - \bar{r}_{ij}^{\kappa\beta}f_\kappa^n\bar{r}_{m\beta}^{kl} \quad (37)$$

$$(31): -\bar{r}_{ij}^{pb}f_p^\gamma\bar{r}_{\gamma b}^{kl} - \bar{r}_{ij}^{\alpha b}f_\alpha^c\bar{r}_{rb}^{kl} - \bar{r}_{ij}^{pb}f_p^c\bar{r}_{rb}^{kl}. \quad (38)$$

Term (26) can be rewritten as

$$\bar{r}_{ij}^{\kappa\lambda}f_\kappa^\mu\bar{r}_{\mu\lambda}^{kl} = \langle ij|r_{12}\hat{f}r_{12}|kl\rangle$$

$$= \langle ij|\tfrac{1}{2}[r_{12}, [\hat{f}, r_{12}]]|kl\rangle + \tfrac{1}{2}\langle ij|[\hat{f}, r_{12}^2]_+|kl\rangle. \quad (39)$$

For all the parts of $\hat{f}$ that commute with r_{12} (i.e., $\hat{v}$ and $\hat{j}$), the first term on the right-hand side clearly disappears. For the kinetic energy operator, one can use the identity

$$\langle ij|\tfrac{1}{2}[r_{12}[\hat{t}, r_{12}]]|kl\rangle = \bar{\delta}_{ij}^{kl}. \quad (40)$$

Hence, for $(\hat{f} + \hat{k})$ we have

$$\bar{r}_{ij}^{\kappa\lambda}(f + k)_{\kappa}^{\mu}\bar{r}_{\mu\lambda}^{kl} = \bar{\delta}_{ij}^{kl} + \langle ij|\tfrac{1}{2}[r_{12}^2, (\hat{f} + \hat{k})]_+|kl\rangle$$

$$= \bar{\delta}_{ij}^{kl} + \tfrac{1}{2}[(\overline{r^2})_{ij}^{kl}(f + k)_{\kappa}^{k} + (\overline{r^2})_{ij}^{k\lambda}(f + k)_{\lambda}^{l}]$$

$$+ \tfrac{1}{2}[(f + k)_i^{\mu}(\overline{r^2})_{\mu j}^{kl} + (f + k)_j^{\nu}(\overline{r^2})_{i\nu}^{kl}]. \quad (41)$$

Using (35)–(41) and replacing the summations over the complete set by an auxiliary basis set results in

$$\bar{B}_{ij}^{kl} \overset{\text{aux}}{=} \bar{\delta}_{ij}^{kl} + \tfrac{1}{2}[(\overline{r^2})_{ij}^{p'l}(f + k)_{p'}^{k} + (\overline{r^2})_{ij}^{kp'}(f + k)_{p'}^{l} + \text{h.c.}]$$

$$- \bar{r}_{ij}^{p'q'}k_{p'}^{r'}\bar{r}_{r'q'}^{kl} - \bar{r}_{ij}^{p'm}f_{p'}^{t}\bar{r}_{r'm}^{kl} + \bar{r}_{ij}^{mq'}f_m^t\bar{r}_{nq'}^{kl} - \bar{r}_{ij}^{pb}f_p^t\bar{r}_{rb}^{kl}$$

$$- (\bar{r}_{ij}^{mq''}f_m^t\bar{r}_{p'q''}^{kl} + \bar{r}_{ij}^{p''b}f_{p''}^t\bar{r}_{qb}^{kl} + \text{h.c.}), \quad (42)$$

where h.c. means hermitian conjugates of the terms explicitly given within the brackets and parentheses.

Besides using the auxiliary basis set instead of the complete basis, no approximation has been applied. We can now analyze individual contributions and discuss the requirements for the auxiliary basis set. As previously [6], these considerations will be exactly valid for atoms, although computational experience during the last decade proved them for molecules as well.

The terms in brackets and the first term in parentheses vanish as soon as p' is of higher angular momentum than L_{occ}, second term in parentheses vanishes for p' with $\ell > L$ and $\bar{r}_{ij}^{mq''}$ disappear for q'' with $\ell > 3L_{\text{occ}}$. The L-expansion for the remaining contribution from $\bar{r}_{ij}^{p'q'}k_{p'}^{r'}\bar{r}_{r'q'}^{kl}$ formally does not terminate, but the truncation error goes as $(L'+1)^{-7}$, where L' is the highest ℓ included in the auxiliary set. It follows that one needs an auxiliary set saturated at least at the level of $3L_{\text{occ}}$ or L, depending on which is higher. If one wants to use the standard approximation and does not want to use a special auxiliary set, the same is required for the computational basis. We have used such an approach in our preliminary test calculations presented in the next section. We shall refer to it as approximation R12-C.

Test Calculations

The new approach has been tested for a set of molecules including CH_2, CH_4, NH_3, H_2O, HF, CO, CH_3OH, N_2, and F_2. Except for CH_3OH, the molec-

ular calculations were carried out at geometries optimized at the CCSD(T)/cc-pCVQZ level [22]. The calculations for CH_3OH were performed using the frozen core MP2/ccpVTZ optimized geometry [23] (antiperiplanar conformation). We employed recently constructed R12-suited basis sets of $9s6p4d3f$ for hydrogen [24] and $19s14p8d6f4g3h$ [25] for other atoms. To see the convergence behavior toward the basis set limit, we have also used subsets of the latter bases, step by step skipping the highest angular momentum functions. All electrons have been correlated, except for methanol, when the $1s$ electrons on C and O were not involved in the correlation treatment.

Total energies with both standard approximations B and C are given in Table I. It is seen that the differences between R12/B and R12/C values decrease with the larger basis set, as expected from the theoretical analysis. Quite encouraging is the fact that the results with the new approach C seem to converge faster to the basis set limit than those with R12/B.

Figure 1 provides an overall statistical picture on the energies given in Table I. Here, normal distributions of relative deviations from the estimated limits are depicted. The energy limit was taken as a sum of Hartree–Fock (HF) energy with the largest basis set and a two-point extrapolation of the correlation energy from the g/f and h/f results, assuming an $(L+1)^{-7}$ dependence. Since the HF results were still not at the limit, we have taken total energy deviations, although relative to the correlation energy extrapolations. L values were taken from the heavier atoms. Of course, there are other ways to estimate the energy limits, but for our purpose this was not so important since we can compare the convergence behavior of the two methods with respect to any reference.

The whole range of errors in Figure 1 is within 0.4%, which means that the differences are fairly small. Nevertheless, smaller intervals between the peaks for MP2-R12/C show a slightly faster convergence toward the limit values than it is for R12/B. Figure 2 depicts the mean relative errors $(\bar{\Delta}_r)$ of the MP2-R12 energies as functions of $(L+1)^{-7}$. Perfect linearity for R12/B is fully in accord with the theoretical dependence. The R12/C dependence is close to linear in that scale, too, although not as perfectly. A smaller slope and slip at g/f indicate little faster convergence than $\propto (L+1)^{-7}$. Extrapolations for $L \to \infty$ differ by about 0.03%, which is acceptable. Recall that for R12/C, the extrapolated value has actually been set to zero; thus,

TABLE I

Total energies at MP2-R12 level using standard approximations B and C.*

Basis	$E_{\text{MP2-R12/B}}/E_h$	$E_{\text{MP2-R12/C}}/E_h$	$\Delta_{\text{B-C}}/mE_h$
	CH_4		
f/p	−40.488495	−40.489186	0.691
f/d	−40.490235	−40.490807	0.572
g/d	−40.490668	−40.490960	0.292
g/f	−40.490836	−40.491027	0.191
h/d	−40.490848	−40.491013	0.165
h/f	−40.490937	−40.491040	0.103
	CH_2		
f/p	−39.104435	−39.104755	0.320
f/d	−39.105281	−39.105543	0.262
g/d	−39.105575	−39.105737	0.162
g/f	−39.105664	−39.105805	0.141
h/d	−39.105695	−39.105794	0.099
h/f	−39.105748	−39.105813	0.065
	HF		
f/p	−100.453719	−100.454236	0.517
f/d	−100.454267	−100.454612	0.345
g/d	−100.455015	−100.455192	0.177
g/f	−100.455052	−100.455215	0.163
h/d	−100.455225	−100.455345	0.120
h/f	−100.455243	−100.455346	0.103
	H_2O		
f/p	−76.427276	−76.428101	0.825
f/d	−76.428359	−76.428933	0.574
g/d	−76.429014	−76.429325	0.311
g/f	−76.429103	−76.429387	0.284
h/d	−76.429254	−76.429486	0.232
h/f	−76.429303	−76.429492	0.189
	NH_3		
f/p	−56.545369	−56.546069	0.700
f/d	−56.546801	−56.547296	0.495
g/d	−56.547297	−56.547592	0.295
g/f	−56.547424	−56.547645	0.221
h/d	−56.547492	−56.547701	0.209
h/f	−56.547565	−56.547712	0.147
	CH_3OH		
f/p	−115.582945	−115.584993	2.048
f/d	−115.584733	−115.586446	1.713
g/d	−115.586078	−115.586932	0.854
g/f	−115.586259	−115.586985	0.726
h/f	−115.586601	−115.587017	0.416
N_2			
f	−109.528333	−109.529139	0.806
g	−109.529495	−109.529989	0.494
h	−109.529782	−109.529995	0.213
	CO		
f	−113.308794	−113.309789	0.995
g	−113.310011	−113.310531	0.520
h	−113.310338	−113.310532	0.194
	F_2		
f	−199.511819	−199.513307	1.488
g	−199.513518	−199.513950	0.432
h	−199.513909	−199.514114	0.205

* Subsets of 19s14p8d6f4g3h basis set for nonhydrogen atoms and 9s6p4d3f for hydrogen are employed up to the angular momentum functions as indicated in the first column.
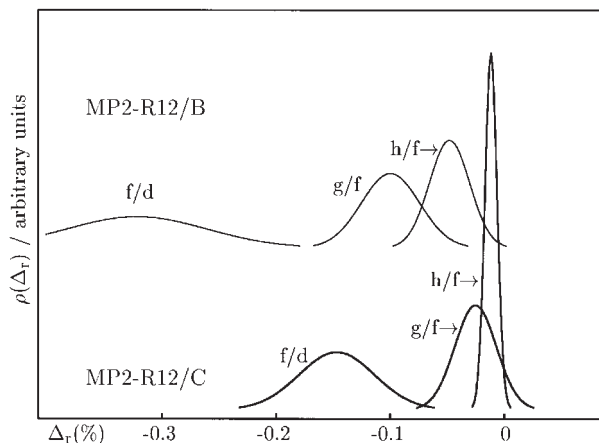

FIGURE 1. Normal distributions $\rho(\Delta_r)$ of the relative errors (Δ_r) of the MP2-R12 energies for CH_2, CH_4, NH_3, H_2O, HF, CO, CH_3OH, N_2, and F_2. Errors are with respect to g/f–h/f two-point extrapolations of the correlation energies as described in text.

what has to be seriously considered are merely the differences.

In Table II, individual contributions to the MP2-R12 correlation energy for variants R12/A, R12/B, and R12/C are given. MP2-R12/A, whose error goes as $\propto (L+1)^{-5}$ [6, 9], is known usually to overshoot the correlation energy, and the limit is usually achieved from below, whereas with R12/B the situation is opposite. Interestingly, for our set of molecules, the variant R12/C provided $E_{R12}^{(2)}$ values be-
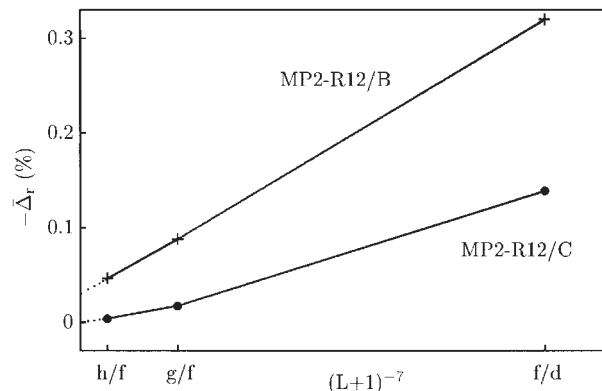

FIGURE 2. Mean relative error ($\bar{\Delta}_r$) of the MP2-R12 energies as a function of $(L+1)^{-7}$. Calculated for a set of CH_2, CH_4, NH_3, H_2O, HF, CO, CH_3OH, N_2, and F_2 molecules. Errors are with respect to g/f–h/f two-point extrapolations of the correlation energies as described in text.

TABLE II
Contributions to MP2-R12 correlation energies calculated with different variants of standard approximation.*

Basis	E_{MP2}/E_h	$E^{(2)}_{R12/A}/E_h$	$E^{(2)}_{R12/B}/E_h$	$E^{(2)}_{R12/C}/E_h$
		CH_4		
f/p	−0.255091	−0.019600	−0.016784	−0.017474
f/d	−0.261032	−0.013416	−0.012244	−0.012817
g/d	−0.264059	−0.010277	−0.009618	−0.009910
g/f	−0.265373	−0.008941	−0.008458	−0.008649
h/d	−0.265551	−0.008743	−0.008294	−0.008459
h/f	−0.266335	−0.007954	−0.007591	−0.007695
		CH_2		
f/p	−0.195454	−0.015237	−0.013148	−0.013468
f/d	−0.198702	−0.011672	−0.010593	−0.010855
g/d	−0.201698	−0.008403	−0.007875	−0.008037
g/f	−0.202462	−0.007601	−0.007193	−0.007334
h/d	−0.203022	−0.007000	−0.006666	−0.006765
h/f	−0.203450	−0.006571	−0.006287	−0.006351
		HF		
f/p	−0.356896	−0.029102	−0.026248	−0.026765
f/d	−0.358387	−0.027502	−0.025120	−0.025465
g/d	−0.368694	−0.016382	−0.015520	−0.015698
g/f	−0.369001	−0.016062	−0.015244	−0.015408
h/d	−0.372278	−0.012582	−0.012128	−0.012248
h/f	−0.372398	−0.012467	−0.012024	−0.012126
		H_2O		
f/p	−0.337640	−0.025646	−0.022620	−0.023446
f/d	−0.340967	−0.022058	−0.020060	−0.020634
g/d	−0.348649	−0.013805	−0.012979	−0.013291
g/f	−0.349343	−0.013080	−0.012360	−0.012644
h/d	−0.351512	−0.010785	−0.010328	−0.010560
h/f	−0.351827	−0.010483	−0.010056	−0.010245
		NH_3		
f/p	−0.301526	−0.022251	−0.019346	−0.020045
f/d	−0.306343	−0.017122	−0.015598	−0.016093
g/d	−0.311494	−0.011623	−0.010891	−0.011186
g/f	−0.312460	−0.010632	−0.010040	−0.010260
h/d	−0.313928	−0.009051	−0.008633	−0.008842
h/f	−0.314427	−0.008562	−0.008200	−0.008348
		CH_3OH		
f/p	−0.451694	−0.034978	−0.030166	−0.032215
f/d	−0.457626	−0.028778	−0.025612	−0.027325
g/d	−0.468924	−0.016733	−0.015505	−0.016358
g/f	−0.470247	−0.015391	−0.014345	−0.015071
h/f	−0.473957	−0.011545	−0.010953	−0.011369
		N_2		
f	−0.508384	−0.030553	−0.027118	−0.027924
g	−0.519812	−0.017618	−0.016629	−0.017122
h	−0.524066	−0.013111	−0.012640	−0.012846
		CO		
f	−0.489927	−0.031671	−0.028280	−0.029330
g	−0.501680	−0.018587	−0.017540	−0.018080
h	−0.505460	−0.014648	−0.014071	−0.014265
		F_2		
f	−0.691042	−0.052353	−0.047457	−0.048945
g	−0.711439	−0.030138	−0.028595	−0.028993
h	−0.718058	−0.023140	−0.022347	−0.022552

* Basis sets as in Table I.

tween R12/A and R12/B. Consequently, the errors were closer to zero.

Conclusions

Using the second quantization formalism for MP2-R12 without a priori approximations, we have arrived at an alternative expression for the final matrix elements used in the calculation. Unlike in previous derivations, it appears that integrals over the commutator of the kinetic operator with the operator of inter-electronic distance, $[\hat{t}, r_{12}]$, are not necessarily needed both within the standard approximation and within the auxiliary basis approach for the resolution of identity. This gives rise to a substantial computational saving, since the pertinent integrals were not only demanding as such, but due to the nonhermicity of the commutator, one needed twice as many of them.

The new method, denoted as variant R12/C, has been tested for a set of 9 molecules including CH_2, CH_4, NH_3, H_2O, HF, CO, CH_3OH, N_2, and F_2 using the standard approximation. Our results indicate that the convergence behavior toward the basis set limit might be even more favorable than it was with the former variant R12/B. Although these preliminary results are encouraging, more tests are necessary to fully assess the approach. It appears to be a challenging alternative together with the use of auxiliary basis set at coupled cluster level. Work in this direction is in progress.

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