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Second-order Møller–Plesset perturbation theory with terms linear in the interelectronic coordinates and exact evaluation of three-electron integrals

Peter Wind[1], **Wim Klopper**[2], **Trygve Helgaker**[3]

[1] Institute of Chemistry, University of Tromsø, 9037 Tromsø, Norway
[2] Theoretical Chemistry Group, Debye Institute, Utrecht University, P.O. Box 80052, 3508 TB Utrecht, The Netherlands
[3] Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, 0315 Oslo, Norway

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Abstract. The second-order correlation energy of Møller–Plesset perturbation theory is computed for the neon atom using a wave function that depends explicitly on the interelectronic coordinates (MP2-R12). The resolution-of-identity (RI) approximation, which is invoked in the standard formulation of MP2-R12 theory, is largely avoided by rigorously computing the necessary three-electron integrals. The basis-set limit for the second-order correlation energy is reached to within 0.1 mE_h. A comparison with the conventional RI-based MP2-R12 method shows that only three-electron integrals over *s* and *p* orbitals need to be computed exactly, indicating that the RI approximation can be safely used for integrals involving orbitals of higher angular momentum.

Key words: Neon atom – Second-order energy – Interelectronic coordinates – Three-electron integrals – Strong orthogonality

1 Introduction

Most ab initio methods represent the electronic wave function by a linear combination of products of one-electron functions; however, since the early work of Hylleraas and Slater in the 1920s, it has been known that such functions give a poor description of the correlation cusp [1, 2]. For example, as a result of the poor representation of the cusp, it is exceedingly difficult to converge total atomization energies to an error of less than 1 kJ/mol using a product wave function [3]. For an accurate quantitative description of the correlation cusp (and small errors in the calculated energies), the cusp is better described by an explicitly correlated wave function, i.e., by a wave function that depends explicitly on the interelectronic distances.

Among the different explicitly correlated models that have been proposed, the R12 method [4] has several appealing features, being applicable to relatively large molecules. The principal advantage of this method is the scheme by which the costly evaluation of three- and four-electron integrals is avoided. A key ingredient is the use of the resolution of the identity (RI) to split the three-electron integrals into linear combinations of products of two-electron integrals. Formally, use of the RI assumes that the one-electron basis is complete – at least up to angular momentum $\ell = 3\ell_\mathrm{occupied}$ [5].

In practical calculations, this condition is never satisfied and it becomes important to study the limitations of this approximation. Recently, an efficient algorithm for the exact evaluation of certain one-center three-electron integrals was proposed [6]. Several terms in the R12 method can now be computed using either the RI approximation or the exact three-electron integrals, making it possible to study directly the consequences of the RI approximation.

The bulk of this article consists of two sections. We derive the necessary formulas for the calculation of the second-order Mϕller–Plesset (MP2) correlation energy using explicitly correlated functions, with and without the use of the RI approximation, in Sect. 2. Next, in Sect. 3, we present calculations on the neon atom, comparing the different R12 approximations to the MP2 energy with one another and also with energies obtained by other methods.

2 The MP2-R12 method

We here derive the equations of the MP2-R12 method without the simplifications that occur when the RI approximation is introduced as in the original method [7, 8].

2.1 The MP2-R12 ansatz

Assuming that all operators and basis functions are real, we start from the second-order Hylleraas functional

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Correspondence to: W. Klopper

$$J_{\mathrm{H}}(\psi) = 2\langle\psi|H^{(1)} - E^{(1)}|\phi\rangle + \langle\psi|H^{(0)} - E^{(0)}|\psi\rangle \ . \tag{1}$$

Here, $H^{(0)}$ is the zeroth-order Hamiltonian, which we take as the n-electron Fock operator

$$H^{(0)} = \sum_{i=1}^{n} F_i \ , \tag{2}$$

and ϕ is the n-electron restricted Hartree–Fock wave function constructed from a set of canonical spin orbitals with orbital energies ε_p,

$$\langle\varphi_p|F_1|\varphi_q\rangle = \delta_{pq}\varepsilon_p \ . \tag{3}$$

The perturbation operator is defined in the usual manner as $H^{(1)} = H - H^{(0)}$.

We now minimize the Hylleraas functional in a finite space of conventional Slater determinants augmented with explicitly correlated many-electron functions. As ϕ is the restricted Hartree–Fock wave function, the Hylleraas functional separates into a sum of pair contributions,

$$\begin{aligned} J_{\mathrm{H}}(\psi) &= \sum_{i<j} f(u_{ij}); \\ f(u_{ij}) &= 2\langle[ij]|r_{12}^{-1}|u_{ij}\rangle + \langle u_{ij}|F_1 + F_2 - \varepsilon_i - \varepsilon_j|u_{ij}\rangle \ , \end{aligned} \tag{4}$$

where $[ij]$ denotes an antisymmetric two-electron function of the form

$$[pq] = 2^{-1/2}\{\varphi_p(1)\varphi_q(2) - \varphi_q(1)\varphi_p(2)\} \ . \tag{5}$$

Thus, in addition to the standard linear combination of doubly excited determinants $[ab]$, each first-order two-electron function u_{ij} contains an explicitly correlated part that is linear in the interelectronic distance $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$,

$$u_{ij} = c_{ij}w_{ij} + \sum_{a<b} c_{ij}^{ab}[ab] \equiv \tfrac{1}{2}c_{ij}Q_{12}r_{12}[ij] + \sum_{a<b} c_{ij}^{ab}[ab] \ . \tag{6}$$

Here, Q_{12} is an appropriate projection operator, which we shall take as the strong-orthogonality (SO) projector

$$Q_{12} = (1 - O_1)(1 - O_2) = 1 - O_1 - O_2 + O_1O_2 \ , \tag{7}$$

where O_1 and O_2 are projectors onto the one-electron occupied orbital space,

$$O_1 = \sum_i |\varphi_i(1)\rangle\langle\varphi_i(1)| \ . \tag{8}$$

Note that the SO projector has the following properties

$$Q_{12}[ij] = 0; \quad Q_{12}[aj] = 0; \quad Q_{12}[ab] = [ab] \ . \tag{9}$$

As we shall see, the presence of $Q_{12}r_{12}$ in the pair function (Eq. 6) leads to three- and four-electron integrals, whose exact evaluation is nontrivial but may be avoided by invoking the generalized Brillouin theorem and the RI approximation.

2.2 The MP2-R12 energy

Minimizing the Hylleraas functional with respect to the coefficients c_{ij} and c_{ij}^{ab}, we find that the variational problem gives the following solution for the MP2 energy:

$$J_{\mathrm{H}}(\psi) = \sum_{i<j} f(u_{ij}) = \sum_{i<j}\left(e_{ij} + f_{ij}\right) \ , \tag{10}$$

where

$$e_{ij} = -\sum_{a<b} \frac{\langle[ij]|r_{12}^{-1}|[ab]\rangle^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \tag{11}$$

is the conventional MP2 pair energy, whereas f_{ij} represents a correction due to the explicitly correlated function,

$$f_{ij} = -N_{ij}^2/D_{ij} \ , \tag{12}$$

with

$$N_{ij} = \langle[ij]|r_{12}^{-1}|w_{ij}\rangle - \sum_{a<b} \frac{\langle[ij]|r_{12}^{-1}|[ab]\rangle\langle[ab]|F_1 + F_2 - \varepsilon_i - \varepsilon_j|w_{ij}\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \ , \tag{13}$$

$$D_{ij} = \langle w_{ij}|F_1 + F_2 - \varepsilon_i - \varepsilon_j|w_{ij}\rangle - \sum_{a<b} \frac{\langle w_{ij}|F_1 + F_2 - \varepsilon_i - \varepsilon_j|[ab]\rangle^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \ . \tag{14}$$

As seen by inserting the w_{ij} term and by expanding the SO operator and the exchange operator, the matrix elements $\langle[ij]|r_{12}^{-1}|w_{ij}\rangle$ and $\langle[ab]|F_1 + F_2 - \varepsilon_i - \varepsilon_j|w_{ij}\rangle$ contain up to three-electron integrals, whereas the matrix element $\langle w_{ij}|F_1 + F_2 - \varepsilon_i - \varepsilon_j|w_{ij}\rangle$ involves up to four-electron integrals.

Up to this point, our development of MP2-R12 theory has been exact within a given (finite) one-electron basis set. In the following, we shall invoke a series of approximations, designed to simplify the algebra needed for the evaluation of the R12 correction to the MP2 energy – in particular, by avoiding the calculation of the four-electron integrals and some or all of the three-electron integrals.

2.3 The R12-SO approximation

Let us assume that the occupied orbitals are exact eigenfunctions of the zeroth-order Hamiltonian (generalized Brillouin condition of Ref. [8]),

$$F_1\varphi_i(1) \approx \varepsilon_i\varphi_i(1) \ . \tag{15}$$

Within this approximation, the SO projector commutes with the Fock operators,

$$[F_1 + F_2, Q_{12}] \approx 0 \ , \tag{16}$$

and we obtain [8]

$$\begin{aligned} (F_1 + F_2 - \varepsilon_i - \varepsilon_j)w_{ij} &= \tfrac{1}{2}(F_1 + F_2 - \varepsilon_i - \varepsilon_j)Q_{12}r_{12}[ij] \\ &\approx \tfrac{1}{2}Q_{12}[F_1 + F_2, r_{12}][ij] \ . \end{aligned} \tag{17}$$

By introducing the approximate relation Eq. (17) in the various matrix elements of Eqs. (13) and (14), we arrive at the following R12-SO correction to the MP2 energy:

$$f_{ij}^{\mathrm{R12-SO}} = -V_{ij}^2/B_{ij} \ , \tag{18}$$

where

$$V_{ij} = \langle[ij]|r_{12}^{-1}Q_{12}\left(r_{12} - \sum_{a<b}\frac{|[ab]\rangle\langle[ab]|}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}[F_1 + F_2, r_{12}]\right)|[ij]\rangle \ , \tag{19}$$

$$\begin{aligned} B_{ij} = \langle[ij]|[r_{12}, F_1 \\ + F_2]Q_{12}\left(r_{12} - \sum_{a<b}\frac{|[ab]\rangle\langle[ab]|}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}[F_1 + F_2, r_{12}]\right)|[ij]\rangle \ . \end{aligned} \tag{20}$$

Apart from some further simplification involving the exchange part of the Fock operator (see Sect. 2.5), this is the expression used to calculate the R12-SO energies reported in Sect. 3.

2.4 The R12-SO approximation*

In deriving the R12-SO approximation, we assumed that the occupied canonical orbitals are exact eigenfunctions of the Fock operator. We now make the stronger assumption that also the virtual canonical orbitals are exact eigenfunctions of F_1 in the sense of what has been termed the extended Brillouin condition [8],

$$F_1\varphi_a(1) \approx \varepsilon_a\varphi_i(1) \ . \tag{21}$$

This allows us to make the identification

$$\sum_{a<b}\frac{|[ab]\rangle\langle[ab]|}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}[F_1 + F_2, r_{12}]|[ij]\rangle \approx \sum_{a<b}|[ab]\rangle\langle[ab]|r_{12}|[ij]\rangle \ , \tag{22}$$

which gives us the R12-SO* correction to the MP2 energy,

$$f_{ij}^{\mathrm{R12-SO^*}} = -\frac{\langle[ij]|r_{12}^{-1}Q_{12}(1 - V_{12})r_{12}|[ij]\rangle^2}{\langle[ij]|[r_{12}, F_1 + F_2]Q_{12}(1 - V_{12})r_{12}|[ij]\rangle} \ . \tag{23}$$

Table 1. 7s5p3d2f Gaussian basis set

s	Contraction		p	Contraction	d	f
99920.0000	0.000086	0.000020	99.6800	0.006566	6.4710	4.6570
14960.0000	0.000669	0.000158	23.1500	0.045979	2.2130	1.5240
3399.0000	0.003518	0.000824	7.1080		0.7470	
958.9000	0.014667	0.003500	2.4410			
311.2000	0.050962	0.012233	0.8339			
111.7000	0.143744	0.037017	0.2662			
43.3200	0.304562	0.086113				
17.8000						
7.5030						
2.3370						
0.9001						
0.3301						

Here,

$$V_{12} = \sum_{a<b} |[ab]\rangle\langle[ab]| \tag{24}$$

is the projector onto the finite two-electron space spanned by the virtual orbitals.

In passing, we note that by replacing the SO projector Q_{12} everywhere by $Q_{12}(1 - V_{12})$, the R12-SO* energy may be derived in a manner that closely resembles that of the R12-SO energy. Specifically, we then invoke the ansatz

$$u_{ij} = c_{ij}w_{ij} + \sum_{a<b} c_{ij}^{ab}[ab] \equiv \tfrac{1}{2}c_{ij}Q_{12}(1 - V_{12})r_{12}[ij] + \sum_{a<b} c_{ij}^{ab}[ab] \tag{25}$$

under the assumption

$$[F_1 + F_2, Q_{12}(1 - V_{12})] \approx 0 \ , \tag{26}$$

rather than Eq. (6) under the assumption Eq. (16). The presence of the projector $(1 - V_{12})$ in Eq. (25) makes the explicitly correlated part of the wave function rigorously orthogonal to the virtual excitation space spanned by $[ab]$.

Finally, we note that the difference between Eq. (23) and the original MP2-R12 method [7] is that in the original method the projector product $Q_{12}(1 - V_{12})$ is approximated as [9]

$$Q_{12}(1 - V_{12}) \approx 1 - \sum_{p<q} |[pq]\rangle\langle[pq]| \ . \tag{27}$$

Again, we may view this approximation as arising from the ansatz Eq. (25), having first made the substitution Eq. (27) and having neglected the SO constraint.

2.5 The commutator of the Fock operator with the interelectronic distance

Let us now consider the commutator $[F_1 + F_2, r_{12}]$. The Fock operator F_1 has three contributions: the kinetic-energy operator T_1, the Coulomb operator J_1, and the (negative) exchange operator $-K_1$. Since the Coulomb operator is multiplicative, it commutes with r_{12} and we obtain

$$[F_1 + F_2, r_{12}] = [T_1 + T_2, r_{12}] - [K_1 + K_2, r_{12}] \ . \tag{28}$$

The commutator with the kinetic-energy operator gives rise to a new two-electron operator, which we denote by U_{12},

$$[T_1 + T_2, r_{12}] = -\frac{2}{r_{12}} - \frac{(\vec{r}_1 - \vec{r}_2) \cdot (\vec{\nabla}_1 - \vec{\nabla}_2)}{r_{12}} \equiv -\frac{2}{r_{12}} + 2U_{12} \ . \tag{29}$$

Certain exchange terms do not simplify and still lead to four-electron integrals. To restrict ourselves to three-electron integrals, we apply the RI approximation to the terms

$$\begin{aligned} &[K_1 + K_2, r_{12}]Q_{12}r_{12} \\ &\quad \approx (K_1P_1r_{12} + K_2P_2r_{12} - r_{12}P_1K_1 - r_{12}P_2K_2)Q_{12}r_{12} \ , \end{aligned} \tag{30}$$

where P_1 is the projector onto the finite one-electron basis set,

$$P_1 = \sum_p |\varphi_p(1)\rangle\langle\varphi_p(1)| \ . \tag{31}$$

This approximation avoids all four-electron integrals as well as three-electron integrals of the type $r_{12}r_{13}r_{23}^{-1}$. Note that the RI approximation is inserted only into the first commutator in Eq. (20) or into the commutator in Eq. (23).

We observe that our expressions require the computation of three types of three-electron integrals: $\langle pqr|r_{13}^{-1}r_{12}|stu\rangle$, $\langle pqr|r_{13}U_{12}|stu\rangle$, and $\langle pqr|r_{13}r_{12}|stu\rangle$. For Gaussians, the second integrals are essentially of the same type as the first ones. The evaluation of the third type of integrals may also be related to the first type. A method for the efficient calculation of these integrals in the case of a one-center basis has been presented elsewhere [6].

3 Calculations of the neon atom

3.1 Basis sets and computational details

The contracted 7s5p3d2f basis set was obtained from Dunning's cc-pVQZ basis [10] by removing the g functions and adding some primitive s and p functions, (Table 1).[1] The uncontracted 20s14p11d9f7g5h basis set in Table 2 was derived from Partridge's 18s13p basis [11] by adding two diffuse s functions (with exponents 0.10 and 0.05) and one diffuse p shell (with exponent 0.05). The exponents ζ_ℓ of the 11d9f7g5h part of the basis were obtained by multiplying selected exponents ζ_1 of the 14p set by the factor $(2\ell + 3)/5$ [12]. With the 14p exponents sorted in decreasing order, the exponents 3–13, 5–13, 7–13, and 8–12 were used for the d, f, g, and h sets, respectively. Only the spherical components of the basis sets were used.

In our calculations, we used spin- and symmetry-adapted singlet and triplet pairs rather than antisymmetrized pairs of spin orbitals. This means that, for the $2p^2$ pair energy of neon, we consider ^{1}S, ^{1}D, and ^{3}P pairs rather than Cartesian $2p_x^2$ and $2p_x2p_y$ spin–orbital pairs. Finally, we note that we have nowhere employed the orbital-invariant generalization of the MP2-R12 method [13]; all the results were obtained with the ansatz Eq. (6).

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[1] The basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 1/29/01, 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, WA 99352, USA. Contact David Feller or Karen Schuchardt for further information

3.2 Calculations in small basis sets

Let us first consider calculations in a medium-sized basis constructed from a 12s6p3d2f Gaussian basis, comparing the results obtained with the conventional MP2 method and other explicitly correlated models (Table 3). The original MP2-R12/A model [7] makes use of only two-electron integrals and corresponds to Eq. (23) but with the SO operator replaced by Eq. (27) and with all terms involving the exchange commutator neglected; the MP2-R12/B model is similar to MP2-R12/A but includes some of the exchange-operator terms [8]; the MP2-R12-SO model uses Eq. (18) for the calculation of the second-order correlation energy.

By comparing the energies in Table 3, we note that different MP2-R12-SO methods converge much more smoothly than the standard MP2-R12 energies. Moreover, the differences between the various MP2-R12-SO levels are negligible compared with the differences relative to the standard MP2-R12 method and the conventional (orbital-based) MP2 method. Also, even in the very small 7s5p basis, the MP2-R12-SO energies constitute a vast improvement on the orbital-based MP2 energy, reducing the error in the correlation energy by a factor of 0.5.

It is also interesting to note that whereas the original MP2-R12 energy overshoots the correlation energy (at least for small basis sets), the MP2-R12-SO energies converge from above, just like the orbital-based MP2 energy. The overshooting by the MP2-R12 method occurs because of the neglect of the SO constraint in this method. Indeed, the relaxation of this constraint is the single most important effect of the RI approximation in the standard R12 method. For larger basis sets, the effects on the final results are much smaller, as demonstrated in Sect. 3.4.

3.3 The RI approximation for high-angular-momentum functions only

The evaluation of the full set of three-electron integrals is time-consuming. Clearly, we would be able to treat much larger basis sets if only a subset of the three-electron integrals is calculated explicitly. In the last column of Table 3, only three-electron integrals over s and p functions were computed exactly whereas the remaining three-electron integrals were computed using the RI approximation. While this approach reduces drastically the number of integrals to be computed, it has a very small effect on the solution. This behavior can be understood by looking more closely at the terms in Eqs. (19) and (20).

Table 2. 20s14p11d9f7g5h Gaussian basis set

s	p	d	f	g	h
2598845.0	3257.3130	350.746340	73.1402640	19.2774296	11.2172086
389291.20	771.04600	134.265222	33.1370820	9.49148420	5.59390260
88614.780	250.53310	56.8868720	15.7724424	4.73330220	2.77585100
25103.590	95.903730	25.7732860	7.76575980	2.34879700	1.35824000
8190.9100	40.633480	12.2674552	3.87270180	1.14928000	0.65219180
2957.4970	18.409490	6.04003540	1.92174300	0.55185460	
1153.7430	8.7624680	3.01210140	0.94032000	0.25455760	
478.68000	4.3143110	1.49468900	0.45151740		
208.86450	2.1515010	0.73136000	0.20827440		
94.993240	1.0676350	0.35118020			
44.686810	0.5224000	0.16199120			
21.623280	0.2508430				
10.694420	0.1157080				
5.3116890	0.0500000				
2.4260420					
1.1181120					
0.5073780					
0.2239600					
0.1000000					
0.0500000					

Table 3. Second-order correlation energy ($-E/\mathrm{m}E_\mathrm{h}$) of the neon atom. Comparison of different methods

Basis	MP2	MP2-R12/A[a]	MP2-R12/B[b]	MP2-R12-SO[c]	MP2-R12-SO*[d]	MP2-R12-SO(sp)[e]
7s5p	184.031	652.159	488.908	307.528	307.884	307.528
7s5p3d	304.504	394.617	372.412	366.006	366.988	365.816
7s5p3d2f	336.379	376.212	365.948	371.036	370.932	371.047

[a] Original MP2-R12/A method as defined in Ref. [7]
[b] Original MP2-R12/B method as defined in Ref. [8]
[c] Eqs. (18), (19), (20)
[d] Eq. (23)
[e] Eqs. (18), (19), (20), but with exact three-electron integrals only over s and p functions

Table 4. Second-order correlation energy ($-E/\mathrm{m}E_\mathrm{h}$) of the neon atom. Convergence with respect to the size of the basis

Basis	MP2	MP2-R12/A[a]	MP2-R12/B[b]	MP2-R12-SO(sp)[c]
20s14p	191.992	653.039	492.416	309.448
20s14p11d	322.266	407.909	394.374	380.318
20s14p11d9f	359.835	389.621	387.096	387.124
20s14p11d9f7g	374.115	388.598	387.869	387.912
20s14p11d9f7g5h	379.455	388.285	387.999	388.061

[a] Original MP2-R12/A method as defined in Ref. [7]

[b] MP2-R12/B method as defined in Ref. [8]

[c] Eqs. (18), (19), (20), but with exact three-electron integrals only over s and p functions

The only terms involving three-electron integrals over high-ℓ virtual orbitals are integrals over the exchange operator, which plays only a secondary role in the equations. In fact, in the MP2-R12/A model, the exchange terms are neglected altogether [8]. The most important terms involving the exchange operator – they are included in the MP2-R12/B model – occur in the evaluation of $\langle[ij]|K_1P_1r_{12}Q_{12}r_{12}|[ij]\rangle$ and $\langle[ij]|K_1P_1r_{12}|[ab]\rangle$. However, a closer examination shows that if the occupied orbitals are only of s or p types, then the terms of higher angular momentum do not contribute (by orthogonality since K_1 is adjacent to $[ij]$). The other terms that involve the exchange operator, $\langle[ij]|r_{12}P_1K_1Q_{12}r_{12}|[ij]\rangle$ and $\langle[ij]|r_{12}P_1K_1|[ab]\rangle$, do in fact involve integrals over high-ℓ orbitals. However, in Ref. [8], it was shown that these contributions are very small – they are neglected in the original MP2-R12/B model.

3.4 Calculations in large basis sets

Having established in Sect. 3.3 that we may safely ignore all three-electron integrals except those involving s and p functions, we may proceed to carry out calculations in much larger basis sets (Tables 4, 5, 6). Our best result of $-388.06\ \mathrm{m}E_\mathrm{h}$ is, to our knowledge, the most accurate, rigorous (i.e., nonextrapolated) value obtained for the second-order correlation energy of neon. It can be compared with results obtained by numerical methods [14], where $-383.55\ \mathrm{m}E_\mathrm{h}$ was obtained including up to i functions and $-388.31\ \mathrm{m}E_\mathrm{h}$ with extrapolation. Using a finite-elements method with angular extrapolations, Flores obtained $-388.11\ \mathrm{m}E_\mathrm{h}$ [16] and Flores and Kolb obtained $-388.13\ \mathrm{m}E_\mathrm{h}$ [17]. A similar extrapolation of our results would be meaningless since most of the error arises from the incompleteness of basis functions of low angular momentum, demonstrating the efficiency by which the R12 method includes the contributions of the functions of high angular momentum. For comparison, we also quote the results obtained with the standard MP2 method in the cc-pCVXZ basis [18] with $2 \leq X \leq 6$: -228.3, -329.1, -361.5, -374.1, and $-379.8\ \mathrm{m}E_\mathrm{h}$; two-point extrapolation from the last two energies yields $-387.6\ \mathrm{m}E_\mathrm{h}$. We also add that the orbital-invariant CCSD-R12/B method in the same 20s14p11d9f7g5h basis gives a value of $-383.90\ \mathrm{m}E_\mathrm{h}$ for the correlation energy, of which $-7.27\ \mathrm{m}E_\mathrm{h}$ is due to the R12 terms.

Table 5. Pair contributions ($-E/\mathrm{m}E_\mathrm{h}$) to the second-order correlation energy of the neon atom, computed in the 20s14p11d9f7g5h basis

Pair	MP2-R12-SO(sp)	R12-SO(sp)[a]	c_{ij}
$1s^2$ (^{1}S)	40.252	1.100	0.94
$1s2s$ (^{1}S)	3.974	0.090	0.93
$1s2s$ (^{3}S)	1.582	0.010	0.44
$2s^2$ (^{1}S)	12.038	0.384	0.94
$1s2p$ (^{1}P)	8.176	0.386	0.91
$1s2p$ (^{3}P)	13.911	0.048	0.45
$2s2p$ (^{1}P)	60.472	2.575	0.92
$2s2p$ (^{3}P)	26.708	0.105	0.46
$2p^2$ (^{1}S)	45.565	0.961	0.90
$2p^2$ (^{3}P)	87.341	0.192	0.46
$2p^2$ (^{1}D)	88.042	2.754	0.92

[a] R12 contribution

Clearly, the inclusion of the explicitly correlated functions improves the convergence dramatically. If f functions are included, the differences between the MP2-R12-SO and MP2-R12/B energies become negligible. illustrating the "$\ell_\mathrm{max} \geq 3\ell_\mathrm{occupied}$" rule.

On comparing the MP2-R12 and MP2-R12-SO energies in the 7s5p3d2f basis in Table 3, we find that the effect of the RI approximation is small. When the basis is almost complete up to f functions (Table 4), the RI approximation gives rise to negligible errors (compared with the exact evaluation of three-electron integrals); when only s, p, and d functions are retained, the results are still not unreasonable.

3.5 Calculations in standard Gaussian basis sets

When this article was submitted for publication, a referee remarked that it would be interesting to investigate the performance of the R12-SO approximation for standard Gaussian basis sets – in particular, for small sets such as cc-pVDZ or cc-pVTZ. We agree but note that R12-SO calculations in small basis sets are only partly useful since the RI approximation is still applied to the integrals arising from the exchange commutator (see Eq. 30). In the cc-pVDZ basis, for example, the energy is contaminated by about 4–5 $\mathrm{m}E_\mathrm{h}$ owing to the RI approximation in the exchange commutator. To compute meaningful R12 energies (i.e., energies without RI contamination) with small basis sets, we decided to employ a very large auxiliary basis of the

Table 6. Pair contributions ($-E/\mathrm{m}E_\mathrm{h}$) to the second-order correlation energy of the neon atom

Pair	Ref. [14] extrapolation[a]	Ref. [15] extrapolation[b]	Ref. [5] extrapolation[c]	Ref. [16]		This work calculated[f]
				Calculated[d]	Extrapolation[e]	
$1s^2$	40.24	40.22	40.25	40.229	40.255	40.252
$1s2s$	5.55	5.56	5.55	5.555	5.557	5.556
$2s^2$	12.05	12.02	12.02	12.003	12.037	12.038
$1s2p$	22.16	22.17	22.06	22.078	22.094	22.087
$2s2p$	87.30	87.15	87.10	86.982	87.188	87.180
$2p^2$	221.01	220.80	220.81	220.686	220.973	220.948
Total	388.3	387.9	387.8	387.53	388.11	388.06

[a] With extrapolation for $\ell > 6$
[b] With extrapolation for $\ell > 9$
[c] Recommended values from R12 calculations and extrapolations
[d] Calculated with $\ell \leq 12$
[e] With extrapolation for $\ell > 12$
[f] MP2-R12-SO(sp) energies calculated in the 20s14p11d9f7g5h basis of Table 2

Table 7. Valence-shell and all-electron second-order correlation energies ($-E/\mathrm{m}E_\mathrm{h}$) of the neon atom, computed in a standard Gaussian basis

Basis	Valence-shell			All-electron		
	MP2	MP2-R12-SO*	MP2-R12-SO	MP2	MP2-R12-SO*	MP2-R12-SO
cc-pVDZ	185.5	253.1	261.7	187.6	298.0	306.6
cc-pVTZ	264.3	287.5	292.7	277.3	338.7	343.1
cc-pVQZ	293.6	306.4	307.7	326.3	365.0	365.9
cc-pV5Z	306.2	313.4	313.9	346.1	375.4	375.2
cc-pV6Z	311.8	316.7	316.9	358.1	380.7	380.3
aug-cc-pVDZ	206.9	278.4	277.4	209.1	323.6	322.7
aug-cc-pVTZ	272.5	305.0	305.4	285.9	356.4	356.1
aug-cc-pVQZ	297.2	314.2	314.8	330.0	373.0	373.2
aug-cc-pV5Z	308.0	317.5	318.0	348.0	379.5	379.3
aug-cc-pV6Z	312.9	318.9	319.2	359.2	382.7	382.6
cc-pCVDZ	190.3	257.2	265.0	228.3	309.3	318.7
cc-pCVTZ	271.6	293.9	298.4	329.1	357.6	362.4
cc-pCVQZ	297.5	308.9	310.3	361.5	375.6	377.1
cc-pCV5Z	308.1	314.9	315.3	374.1	382.3	382.7
VTZ(2d1f)[a]	261.6	287.8	291.5	280.8	339.7	343.5
6-31G*	150.3	252.9	252.8	151.4	298.1	298.0
6-311 + +(3d1f)	265.7	302.6	305.2	289.7	356.5	359.8
cc-pVDZ (unc.,Car.)[b]	215.7	269.4	278.2	256.9	327.4	336.2
cc-pVTZ (unc.,Car.)[b]	273.2	294.7	298.9	323.4	357.9	361.8
Limit	320.2			388.1		

[a] VTZ basis [20] augmented with 2d1f set of cc-pVTZ basis
[b] Uncontracted basis with Cartesian d and f sets, as in Ref. [21]

form 32s24p18d15f12g9h6i for the remaining RI approximation[2]. The resulting energies can be regarded as obtained by a method where all (four-electron as well as three-electron) integrals are computed exactly.

There is one particular case, however, where the RI approximation is not needed at all. Consider the R12-SO* approximation as defined by Eq. (23). In the present work, all integrals in Eq. (23) are computed analytically except those involving the exchange commutators arising from $[F_1 + F_2, r_{12}]$, for which the RI approximation is still used (Eq. 30). Hence, if we neglect these exchange commutators in our model, RI-free results are obtained. Since this approach is closely related to the "standard approximation A" of MP2-R12 theory [8], we denote it the R12-SO*/A approximation. In the cc-pVDZ basis, the R12-SO*/A second-order energy is -317.6362 mE_h. Note that all the integrals that contribute to this energy were computed analytically.

In principle, when all three-electron integrals are computed analytically, the R12-SO* and R12-SO calculations (without standard approximation A) use the auxiliary RI basis only for the exchange commutators; however, in such calculations, we may utilize the same large RI basis for the three-electron integrals as well, giving an R12-SO*/A energy of -317.6308 mE_h. Thus, the effect of using this auxiliary basis to approximate all three-electron integrals is less than 0.01 mE_h. Since it is

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[2] The 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 $k = 1, \ldots, n_\ell$ while the exponents of the d ($\ell = 2$) through i sets ($\ell = 6$) are given by the expression $(0.002\ell + 0.003) \times 3^{(k+\ell-1)/2}$ for $k = 1, \ldots, n_\ell$

sufficient to compute the energies to within 0.1 mE_h, we decided to employ the auxiliary RI basis in all the calculations reported in Table 7, saving large amounts of computer time and making possible the investigation of a variety of standard Gaussian basis sets. In these fully RI based R12 calculations, a molecular rather than atomic code was used; it employs Cartesian spin–orbital pairs such as $2p_x^2$ and $2p_x 2p_y$.

In Table 7, we have listed the valence and all-electron second-order energies for various standard basis sets, in particular, for the correlation-consistent sets cc-pVXZ [10], aug-cc-pVXZ [19], and cc-pCVXZ [18]. In the standard orbital-based treatment, triple-zeta basis sets [e.g., cc-pVTZ, aug-cc-pVTZ, cc-pCVTZ, VTZ(2d1f), and 6-311++G(3d1f)] recover 80–85% of the valence correlation energy. By contrast, the R12-SO approach recovers 90–95% of the energy, reducing the error by a factor of 0.5. The same reduction is observed for the other basis sets in Table 7 but the improvements are more pronounced for $X \geq 5$. For all basis sets in the table, the average error reduction due to explicit correlation is about 40 and 35% at the valence-only and all-electron levels, respectively.

Table 7 also includes results for the uncontracted Cartesian cc-pVDZ and cc-pVTZ basis sets, as employed in the Gaussian-geminal calculations of Ref. [21]. At the valence R12-SO level, 86.8% of the correlation energy is recovered with the uncontracted cc-pVDZ basis and 93.3% with the uncontracted cc-pVTZ basis. In Ref. [21], 90.6 and 98.1%, respectively, of the correlation energy were recovered using six (independent) Gaussian geminals rather than a single linear r_{12} term. Clearly, with more variational (linear) parameters, a larger proportion of the correlation energy is recovered.

4 Conclusions

The test calculations presented here were restricted to the neon atom; however, since the correlation cusp is only weakly dependent on the chemical environment, most of our conclusions should be valid for other many-electron systems as well. Of course, in molecular systems, orbitals of higher angular momentum are partly occupied and higher-order functions are required in the basis. In this sense, more test calculations would be useful.

Even with a rather small basis, the effects of the standard RI approximation are small. This is an important result since for molecular calculations the completeness condition is never well satisfied.

We conclude that the standard RI approximation is a good one and that the conventional R12 method with approximation of integrals by way of the RI approximation is a robust method. Theoretical arguments for the use of the RI approximation were given in Ref. [8] and the method has been succesfully applied for a long time; therefore these conclusions are not unexpected. However, it was nevertheless important to quantify the effects of the RI approximation in a direct way.

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References

1. Hylleraas EA (1929) Z Phys 54: 347
2. Slater JC (1928) Phys Rev 31: 333
3. Helgaker T, Jørgensen P, Olsen J (2000) Molecular electronic-structure theory. Wiley, Chichester
4. Kutzelnigg W (1985) Theor Chim Acta 68: 445
5. Termath V, Klopper W, Kutzelnigg W (1991) J Chem Phys 94: 2002
6. Wind P, Helgaker T, Klopper W (2001) Theor Chem Acc 106: 280
7. Klopper W, Kutzelnigg W (1987) Chem Phys Lett 134: 17
8. Kutzelnigg W, Klopper W (1991) J Chem Phys 94: 1985
9. Klopper W, Kutzelnigg W (1990) J Phys Chem 94: 5630
10. Dunning TH Jr (1989) J Chem Phys 90: 1007
11. Partridge H (1989) J Chem Phys 90: 1043
12. Klopper W, Kutzelnigg W (1991) J Chem Phys 94: 2020
13. Klopper W (1991) Chem Phys Lett 186: 583
14. Lindgren I, Salomonson S (1980) Phys Scr 21: 335
15. Jankowski K, Malinowski P (1980) Phys Rev A 21: 45
16. Flores JR (1992) Phys Rev A 46: 6063
17. Flores JR, Kolb D (1999) J Phys B 32: 779
18. Woon DE, Dunning TH Jr (1995) J Chem Phys 103: 4572
19. Woon DE, Dunning TH Jr (1994) J Chem Phys 100: 2975
20. Schäfer A, Huber C, Ahlrichs R (1994) J Chem Phys 100: 5829
21. Persson BJ, Taylor PR (1996) J Chem Phys 105: 5915