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Efficient evaluation of one-center three-electron Gaussian integrals

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Abstract. An algorithm is presented for the efficient evaluation of two types of one-center three-electron Gaussian integrals. These integrals are required to avoid the resolution-of-identity (RI) approximation in explicitly correlated linear R12 methods. Without the RI approximation, it is possible to enforce rigorously the strong orthogonality of the second-order Møller–Plesset R12 ansatz. A test calculation is performed using atomic Gaussian-type orbitals of the neon atom.

Key words: Explicitly correlated methods – R12 methods – Møller–Plesset–R12 calculations – Three-electron integrals – Resolution-of-identity approximation

1 Introduction

The advantages of using explicitly correlated basis functions in molecular electronic calculations have been recognized for many years. Compared with the more conventional products of one-electron functions, the use of basis functions with terms depending explicitly on the interelectronic coordinates can improve significantly the rate of convergence of the wave-function expansion.

Various explicitly correlated ansätze have been proposed. The explicitly correlated Gaussian [1] and Gaussian geminal approaches (with [2] or without [3] optimization of the Gaussian exponents) have been applied to small systems and have provided extremely accurate results. The R12 method [4, 5] has demonstrated its usefulness in particular for relatively large systems. The principal advantage of this method is the scheme by which the expensive evaluation of integrals involving more than two electrons is avoided. A key ingredient of this approach is the use of the resolution of the identity (RI) to factorize the three-electron integrals into linear

combinations of products of two-electron integrals. Concerning the RI approximation, the one-electron basis set should be complete up to the finite angular momentum quantum number $\ell = 3\ell_{\text{occupied}}$ [6]. Experience has shown that, for medium-sized basis sets, this does not cause major problems. Nevertheless, in a molecule, atomic orbitals of all ℓ have partial occupations. Furthermore, for heavy atoms with occupied *d* or *f* shells, the justification of the RI approximation in terms of low-angular-momentum functions is not obvious [7].

In this context, the exact evaluation of three-electron integrals would be useful. First, it will make possible the direct investigation of the errors incurred by the use of the RI approximation. Second, in molecular calculations, it may be possible to include some exactly evaluated three-electron integrals as improvements on the conventional R12 method.

The main obstacles associated with the exact evaluation of all three-electron integrals are the large number of such integrals and their complicated evaluation. A simplification can be achieved by restricting the calculation to one-center integrals. The three-electron integrals can then be calculated for medium-sized basis sets (containing 50–100 Gaussians) and convergence properties can be tested on atoms.

Algorithms for the evaluation of one-center three-electron integrals have already been proposed. For example, in Ref. [8] general algorithms are given for Slater-type orbitals and spherical-harmonic expansions. We know of no applications, however, of similar algorithms for medium-sized Gaussian basis sets.

We present here an efficient method for the evaluation of two types of three-electron integrals. As will be shown elsewhere, these integrals are sufficient for removing the deficiencies introduced by the RI approximation. The efficiency of the method enables us to use relatively large basis sets.

Our method is based on the expansion of overlap distributions in Hermite Gaussians, widely used for the evaluation of two-electron integrals in the McMurchie–Davidson scheme [9]. An advantage of this scheme is that it may be extended from one-center to six-center

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integrals, although the computational cost would obviously be much higher. Indeed, explicit schemes based on this approach have already been exposed for the calculation of three-electron integrals in the case of Gaussian geminals [3]. The connection between the two approaches can be seen by observing Eq. (25) later. In the Gaussian-geminal approach, the integration over t in Eq. (25) is avoided; instead, t corresponds to a constant geminal exponent. The principal advantage of the geminal approach is that the elementary integral derivatives can be (relatively simply) evaluated also for multicenter integrals [3, 10].

2 Evaluation of one-center three-electron integrals

In this section we present a method for the evaluation of three-electron integrals of the type

$$\begin{aligned} I_{II} &= \left\langle \mu\nu\lambda \left| \frac{1}{r_{13}} \frac{1}{r_{12}} \right| \theta\phi\kappa \right\rangle \\ &= \int \int \int \chi_\mu(\mathbf{r}_1) \chi_\nu(\mathbf{r}_2) \chi_\lambda(\mathbf{r}_3) \frac{1}{r_{13}} \frac{1}{r_{12}} \chi_\theta(\mathbf{r}_1) \chi_\phi(\mathbf{r}_2) \chi_\kappa(\mathbf{r}_3) \\ &\quad \mathbf{d}\mathbf{r}_1 \mathbf{d}\mathbf{r}_2 \mathbf{d}\mathbf{r}_3, \end{aligned} \quad (1)$$

$$\begin{aligned} I_{IR} &= \left\langle \mu\nu\lambda \left| \frac{1}{r_{13}} r_{12} \right| \theta\phi\kappa \right\rangle \\ &= \int \int \int \chi_\mu(\mathbf{r}_1) \chi_\nu(\mathbf{r}_2) \chi_\lambda(\mathbf{r}_3) \frac{1}{r_{13}} r_{12} \chi_\theta(\mathbf{r}_1) \chi_\phi(\mathbf{r}_2) \chi_\kappa(\mathbf{r}_3) \\ &\quad \mathbf{d}\mathbf{r}_1 \mathbf{d}\mathbf{r}_2 \mathbf{d}\mathbf{r}_3, \end{aligned} \quad (2)$$

$$\begin{aligned} I_{RR} &= \langle \mu\nu\lambda | r_{13}r_{12} | \theta\phi\kappa \rangle \\ &= \int \int \int \chi_\mu(\mathbf{r}_1) \chi_\nu(\mathbf{r}_2) \chi_\lambda(\mathbf{r}_3) r_{13}r_{12} \chi_\theta(\mathbf{r}_1) \chi_\phi(\mathbf{r}_2) \chi_\kappa(\mathbf{r}_3) \\ &\quad \mathbf{d}\mathbf{r}_1 \mathbf{d}\mathbf{r}_2 \mathbf{d}\mathbf{r}_3. \end{aligned} \quad (3)$$

In these expressions, the bra Gaussian orbitals are given by

$$\chi_\mu(\mathbf{r}_1) = x_{1P}^{n_{\mu x}} y_{1P}^{n_{\mu y}} z_{1P}^{n_{\mu z}} \exp(-\alpha_\mu r_{1P}^2), \quad (4)$$

$$\chi_\nu(\mathbf{r}_2) = x_{2P}^{n_{\nu x}} y_{2P}^{n_{\nu y}} z_{2P}^{n_{\nu z}} \exp(-\beta_\nu r_{2P}^2), \quad (5)$$

$$\chi_\lambda(\mathbf{r}_3) = x_{3P}^{n_{\lambda x}} y_{3P}^{n_{\lambda y}} z_{3P}^{n_{\lambda z}} \exp(-\gamma_\lambda r_{3P}^2), \quad (6)$$

where r_{1P} , r_{2P} , and r_{3P} are the norms of the position vectors

$$\mathbf{r}_{1P} = \mathbf{r}_1 - \mathbf{P}_1, \quad (7)$$

$$\mathbf{r}_{2P} = \mathbf{r}_2 - \mathbf{P}_2, \quad (8)$$

$$\mathbf{r}_{3P} = \mathbf{r}_3 - \mathbf{P}_3, \quad (9)$$

and similarly for the ket Gaussians. Since we consider the evaluation of one-center integrals, the three centers \mathbf{P}_1 , \mathbf{P}_2 , and \mathbf{P}_3 are the same; however, for the purpose of deriving the expressions for the evaluation of the integrals, we shall need to distinguish between the centers \mathbf{P}_1 , \mathbf{P}_2 , and \mathbf{P}_3 of the orbitals of the three electrons.

Of the three types of integrals (Eqs. 1–3), only I_{IR} and I_{RR} are of direct interest in the context of explicitly correlated methods; however, since the evaluation of I_{IR} and I_{RR} is easily related to the evaluation of I_{II} , we shall first discuss the evaluation of I_{II} .

2.1. Evaluation of $r_{13}^{-1}r_{12}^{-1}$ integrals

On combining the bra and ket Gaussians, Eq. (1) becomes

$$\begin{aligned} I_{II} &= \int \int \int x_{1P}^{n_{x1}} y_{1P}^{n_{y1}} z_{1P}^{n_{z1}} x_{2P}^{n_{x2}} y_{2P}^{n_{y2}} z_{2P}^{n_{z2}} x_{3P}^{n_{x3}} y_{3P}^{n_{y3}} z_{3P}^{n_{z3}} \\ &\quad \times \frac{\exp(-\alpha r_{1P}^2 - \beta r_{2P}^2 - \gamma r_{3P}^2)}{r_{13}r_{12}} \mathbf{d}\mathbf{r}_1 \mathbf{d}\mathbf{r}_2 \mathbf{d}\mathbf{r}_3, \end{aligned} \quad (10)$$

where we have introduced the total exponents

$$\alpha = \alpha_\mu + \alpha_\theta, \quad (11)$$

$$\beta = \beta_\nu + \beta_\phi, \quad (12)$$

$$\gamma = \gamma_\lambda + \gamma_\kappa, \quad (13)$$

and the total Cartesian quantum numbers

$$n_{x1} = n_{\mu x} + n_{\theta x}, \quad (14)$$

$$n_{y1} = n_{\mu y} + n_{\theta y}, \quad (15)$$

⋮

$$n_{z3} = n_{\lambda z} + n_{\kappa z}. \quad (16)$$

Next, following the procedure of McMurchie and Davidson for one- and two-electron integrals, we expand the Cartesian Gaussians in Hermite Gaussians, for example,

$$\begin{aligned} x_{1P}^{n_x} \exp(-\alpha x_{1P}^2) &= \sum_{t=0}^{n_x} E_t^{n_x} \left(\frac{\partial}{\partial P_x} \right)^t \\ &\quad \times \exp[-\alpha(x_1 - P_x)^2]. \end{aligned} \quad (17)$$

The expansion coefficients $E_t^{n_x}$ that appear in this expression can be calculated by recurrence relations. Since in our case the Cartesian and Hermite Gaussians are centered at the same position, these become particularly simple,

$$E_0^0 = 1, \quad (18)$$

$$E_t^n = \frac{1}{2\alpha} E_{t-1}^{n-1} + (t+1) E_{t+1}^{n-1}. \quad (19)$$

In terms of integrals over Hermite Gaussians, we now obtain

$$I_{II} = \sum_{\text{tuv}} E_{t_1}^{n_{x1}} E_{u_1}^{n_{y1}} E_{v_1}^{n_{z1}} E_{t_2}^{n_{x2}} E_{u_2}^{n_{y2}} E_{v_2}^{n_{z2}} E_{t_3}^{n_{x3}} E_{u_3}^{n_{y3}} E_{v_3}^{n_{z3}} R_{\text{tuv}}. \quad (20)$$

where the Hermite integrals are defined as

$$R_{\text{tuv}} = \int \int \int \left(\frac{\partial}{\partial P_{x_1}} \right)^{t_1} \cdots \left(\frac{\partial}{\partial P_{z_3}} \right)^{v_3} \times \frac{\exp(-\alpha r_{1P}^2 - \beta r_{2P}^2 - \gamma r_{3P}^2)}{r_{13} r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 . \quad (21)$$

By taking the differentiations outside the integration (Leibniz theorem), we obtain

$$R_{\text{tuv}} = \left(\frac{\partial}{\partial P_{x_1}} \right)^{t_1} \cdots \left(\frac{\partial}{\partial P_{z_3}} \right)^{v_3} R_{000} , \quad (22)$$

where the basic, undifferentiated integral is given by

$$R_{000} = \int \int \int \frac{\exp(-\alpha r_{1P}^2 - \beta r_{2P}^2 - \gamma r_{3P}^2)}{r_{13} r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 . \quad (23)$$

Our strategy will now be to obtain a simple expression for the integral Eq. (23) and then to obtain the remaining Hermite integrals by differentiation according to Eq. (21). To evaluate R_{000} , we follow Boys and introduce the identity

$$\frac{1}{r_{13}} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp(-r_{13}^2 u^2) du , \quad (24)$$

and similarly for r_{12}^{-1} . This gives us the following 11-dimensional integral:

$$R_{000} = \frac{4}{\pi} \int \int \int \int \int \int \exp(-\alpha r_{1P}^2 - \beta r_{2P}^2 - \gamma r_{3P}^2 - r_{12}^2 t^2 - r_{13}^2 u^2) dt du d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 , \quad (25)$$

whose integration over the nine spatial coordinates is trivial. By carrying out these integrations and making the substitutions $(t^2)/(\beta + t^2) \rightarrow t^2$ and $(u^2)/(\gamma + u^2) \rightarrow u^2$, we obtain

$$R_{000} = \frac{4\pi^{\frac{7}{2}}}{\beta\gamma} \int_0^1 \int_0^1 \frac{\exp\left(-\frac{\alpha\beta t^2 P_{12}^2 + \alpha\gamma u^2 P_{13}^2 + \beta\gamma t^2 u^2 P_{23}^2}{\alpha + \beta t^2 + \gamma u^2}\right)}{(\alpha + \beta t^2 + \gamma u^2)^{\frac{3}{2}}} dt du . \quad (26)$$

Note that both integration limits are from 0 to 1.

2.2. Expansion of the Hermite integrals R_{tuv} in elementary integrals

The integrals R_{tuv} are obtained by successively differentiating the basic integral R_{000} in Eq. (26). This produces a linear combination of elementary integrals of the type

$$I_{NML}^{abc} = 4\pi^{\frac{7}{2}} \alpha^{2L-M-N} \beta^{N-1} \gamma^{M-1} X_{12}^{a_1} X_{13}^{a_2} X_{23}^{a_3} Y_{12}^{b_1} Y_{13}^{b_2} Y_{23}^{b_3} Z_{12}^{c_1} Z_{13}^{c_2} Z_{23}^{c_3} \times \int_0^1 \int_0^1 \frac{t^{2N} u^{2M} \exp\left(-\frac{\alpha\beta t^2 P_{12}^2 + \alpha\gamma u^2 P_{13}^2 + \beta\gamma t^2 u^2 P_{23}^2}{\alpha + \beta t^2 + \gamma u^2}\right)}{(\alpha + \beta t^2 + \gamma u^2)^{\frac{3}{2}+L}} dt du , \quad (27)$$

where X_{12} , Y_{12} , and Z_{12} are the three Cartesian components of the vector

$$\mathbf{P}_{12} = \mathbf{P}_1 - \mathbf{P}_2 , \quad (28)$$

and similarly for the components of \mathbf{P}_{13} and \mathbf{P}_{23} . Since we are concerned with one-center integrals, only integrals of the type

$$I_{NML} = (I_{NML}^{000})_{\mathbf{P}_1=\mathbf{P}_2=\mathbf{P}_3} \quad (29)$$

will contribute, but for the purpose of deriving expressions for the calculation of the integrals, it will be necessary to consider the full set of integrals in Eq. (27). We therefore expand the Hermite integrals as follows:

$$R_{\text{tuv}} = \sum_{NML} \sum_{abc} C_{N_x M_x L_x}^{ta} C_{N_y M_y L_y}^{ub} C_{N_z M_z L_z}^{vc} I_{NML}^{abc} , \quad (30)$$

where we have used the notation

$$N = N_x + N_y + N_z , \quad (31)$$

$$M = M_x + M_y + M_z , \quad (32)$$

$$L = L_x + L_y + L_z . \quad (33)$$

Since all dependence on exponents and coordinates has been included in the integrals I_{NML}^{abc} in Eq. (27), the expansion coefficients in Eq. (30) are independent of the exponents and coordinates (and thus are the same for the three Cartesian directions). By considering some low-order special cases, it becomes clear that the coefficients are even integers (positive, negative, or zero).

Let us consider the recursive evaluation of the expansion coefficients. By differentiating Eq. (30) with respect to P_{x_1} , we obtain the two equivalent expressions

$$R_{t_1+1, t_2, t_3, uv} = \sum_{NML} \sum_{abc} C_{N_x M_x L_x}^{t_1+1, t_2, t_3, a} C_{N_y M_y L_y}^{ub} C_{N_z M_z L_z}^{vc} I_{NML}^{abc} \quad (34)$$

$$= \sum_{NML} \sum_{abc} C_{N_x M_x L_x}^{ta} C_{N_y M_y L_y}^{ub} C_{N_z M_z L_z}^{vc} \frac{\partial I_{NML}^{abc}}{\partial P_{x_1}} , \quad (35)$$

where the derivatives of the elementary integrals Eq. (27) are given by

$$\frac{\partial I_{NML}^{abc}}{\partial P_{x_1}} = a_1 I_{NML}^{a_1-1, a_2, a_3, b, c} + a_2 I_{NML}^{a_1, a_2-1, a_3, b, c} - 2I_{N+1, M, L+1}^{a_1+1, a_2, a_3, b, c} - 2I_{N, M+1, L+1}^{a_1, a_2+1, a_3, b, c} . \quad (36)$$

On inserting Eq. (36) into Eq. (35), substituting dummy indices, and comparing with Eq. (34), we obtain

$$C_{N_x M_x L_x}^{t_1+1, t_2, t_3, a} = (a_1 + 1) C_{N_x M_x L_x}^{t, a_1+1, a_2, a_3} + (a_2 + 1) C_{N_x M_x L_x}^{t, a_1, a_2+1, a_3} - 2C_{N_x-1, M_x, L_x-1}^{t, a_1-1, a_2, a_3} - 2C_{N_x, M_x-1, L_x-1}^{t, a_1, a_2-1, a_3} , \quad (37)$$

$$C_{N_x M_x L_x}^{t_1, t_2+1, t_3, a} = -(a_1 + 1) C_{N_x M_x L_x}^{t, a_1+1, a_2, a_3} + (a_3 + 1) C_{N_x M_x L_x}^{t, a_1, a_2, a_3+1} + 2C_{N_x-1, M_x, L_x-1}^{t, a_1-1, a_2, a_3} - 2C_{N_x-1, M_x-1, L_x-1}^{t, a_1, a_2-1, a_3-1} , \quad (38)$$

$$C_{N_x M_x L_x}^{t_1, t_2, t_3+1, a} = -(a_2 + 1)C_{N_x M_x L_x}^{t_1, a_1, a_2+1, a_3} - (a_3 + 1)C_{N_x M_x L_x}^{t_1, a_1, a_2, a_3+1} \\ + 2C_{N_x M_x-1, L_x-1}^{t_1, a_1, a_2-1, a_3} + 2C_{N_x-1, M_x-1, L_x-1}^{t_1, a_1, a_2, a_3-1} , \quad (39)$$

where we have included the corresponding recurrence relations for t_2 and t_3 . By beginning with the element

$$C_{000}^{000000} = 1 , \quad (40)$$

and noting that the coefficients vanish if any of the indices become negative, we may generate the full set of expansion coefficients by recursion. In practice, many of the expansion coefficients are zero. In fact, for a coefficient to be nonzero, $t_1 + t_2 + t_3$ must be an even integer and the following conditions must be satisfied:

$$\max(N_x, M_x) \leq L_x = \frac{t_1 + t_2 + t_3}{2} \leq N_x + M_x . \quad (41)$$

Since the number of nonzero coefficients is rather small and is independent of the exponents and the Cartesian directions, the coefficients may be calculated and stored once and for all, that is, there is no need to recompute them for each individual integral.

2.3. Expansion of the Cartesian integrals I_{II} in elementary integrals

Having established the transformations from elementary to Hermite integrals (Eq. 30) and from Hermite to Cartesian integrals (Eq. 20), we are now ready to consider the direct transformation from elementary to Cartesian integrals. By substituting into Eq. (20) the expansion Eq. (30), we obtain

$$I_{II} = \sum_{tuv} \sum_{NLM} E_{t_1}^{n_{x_1}} E_{u_1}^{n_{y_1}} E_{v_1}^{n_{z_1}} E_{t_2}^{n_{x_2}} E_{u_2}^{n_{y_2}} E_{v_2}^{n_{z_2}} E_{t_3}^{n_{x_3}} E_{u_3}^{n_{y_3}} E_{v_3}^{n_{z_3}} \\ \times C_{N_x M_x L_x}^{t_1 t_2 t_3} C_{N_y M_y L_y}^{u_1 u_2 u_3} C_{N_z M_z L_z}^{v_1 v_2 v_3} I_{NML} . \quad (42)$$

For an efficient evaluation, we combine the expansion coefficients for each Cartesian direction and obtain

$$F_{N_x M_x L_x}^{n_{x_1} n_{x_2} n_{x_3}} = \sum_{t_1} E_{t_1}^{n_{x_1}} \sum_{t_2} E_{t_2}^{n_{x_2}} \sum_{t_3} E_{t_3}^{n_{x_3}} C_{N_x M_x L_x}^{t_1 t_2 t_3} , \quad (43)$$

where we have indicated that the coefficients are best evaluated by three partial summations, one for each electronic coordinate. Since the Hermite-to-Cartesian expansion coefficients depend on the exponents (Eq. 19), this transformation must be carried out separately for each new batch of integrals. In terms of these coefficients, we obtain the following expression for the Cartesian integrals:

$$I_{II} = \sum_{NLM} F_{N_x M_x L_x}^{n_{x_1} n_{x_2} n_{x_3}} F_{N_y M_y L_y}^{n_{y_1} n_{y_2} n_{y_3}} F_{N_z M_z L_z}^{n_{z_1} n_{z_2} n_{z_3}} I_{NML} . \quad (44)$$

It only remains to consider the evaluation of the elementary integrals I_{NML} . However, we first note the following restrictions on the summation indices:

$$N_x \leq \frac{n_{x_1} + n_{x_3}}{2} , \quad (45)$$

$$M_x \leq \frac{n_{x_2} + n_{x_3}}{2} , \quad (46)$$

$$L_x \leq \frac{n_{x_1} + n_{x_2} + n_{x_3}}{2} , \quad (47)$$

$$\max(N_x, M_x) \leq L_x \leq N_x + M_x . \quad (48)$$

The summation over the indices $N_x, M_x, L_x, N_y, M_y, L_y, N_z, M_z, L_z$ can be factorized by first summing over $N_y, M_y, L_y, N_z, M_z, L_z$ and then over $N_x, M_x, L_x, N_y + N_z, M_y + M_z, L_y + L_z$. This is still the most time-consuming part of the calculation. It is difficult to give an expression for the number of nonzero terms in Eq. (44), but the conditions on the indices ensure that the number of nonzero terms is not too large.

2.4. Inclusion of the r_{12}^2 factor

We shall now compute the integrals Eqs. (2) and (3) by including the factors r_{12}^2 and r_{13}^2 . The factor r_{12}^2 can be introduced by considering the integral

$$R_{000, a} = \frac{4}{\pi} \int \int \int \int \int \exp[-\alpha r_{1P}^2 - \beta r_{2P}^2 - \gamma r_{3P}^2 - r_{12}^2 \\ \times (t^2 - a) - r_{13}^2 u^2] dt du d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 . \quad (49)$$

After the integration over the nine spatial coordinates, we substitute $(t^2 - a)/(\beta + t^2 - a) \rightarrow t^2$ and take the derivative with respect to a for $a = 0$. We obtain

$$P_{NML} = \frac{1}{2\beta} I_{NML} - \frac{1}{2\alpha} I_{N-1, ML} , \quad \text{for } N \geq 1 , \quad (50)$$

$$P_{NML} = \frac{1}{\beta} I_{NML} - \left(\frac{3}{2} + L\right) \left(\frac{1}{\alpha\beta} I_{N+1, M, L+1} - \frac{1}{\alpha^2} I_{NM, L+1}\right) , \quad \text{for } N = 0 . \quad (51)$$

The integral Eq. (2) can then be expressed as

$$I_{IR} = \sum_{NML} F_{N_x M_x L_x}^{n_{x_1} n_{x_2} n_{x_3}} F_{N_y M_y L_y}^{n_{y_1} n_{y_2} n_{y_3}} F_{N_z M_z L_z}^{n_{z_1} n_{z_2} n_{z_3}} P_{NML} . \quad (52)$$

The integral Eq. (3) can be derived in a similar manner to give

$$I_{IRR} = \sum_{NML} F_{N_x M_x L_x}^{n_{x_1} n_{x_2} n_{x_3}} F_{N_y M_y L_y}^{n_{y_1} n_{y_2} n_{y_3}} F_{N_z M_z L_z}^{n_{z_1} n_{z_2} n_{z_3}} Q_{NML} , \quad (53)$$

with

$$Q_{NML} = \frac{1}{2\gamma} P_{NML} - \frac{1}{2\alpha} P_{N, M-1, L} , \quad \text{for } M \geq 1 , \quad (54)$$

$$Q_{NML} = \frac{1}{\gamma} P_{NML} - \left(\frac{3}{2} + L\right) \\ \times \left(\frac{1}{\alpha\gamma} P_{N, M+1, L+1} - \frac{1}{\alpha^2} P_{NM, L+1}\right) , \quad \text{for } M = 0 . \quad (55)$$

The expansion coefficients are the same for Eqs. (44), (52), and (53), and should be computed together.

3 Test calculations

We computed the three-electron integrals that occur in second-order Møller–Plesset (MP2)–R12 calculations on the neon atom, both to assess the correctness and efficiency of our integral-evaluation scheme and to gain some preliminary insight into the quality of the RI approximation in linear R12 theory.

In linear R12 theory, the following (spin-free) two-electron functions occur

$$\Psi_{ij}^{r_{12}}(\mathbf{r}_1, \mathbf{r}_2) = (1 - P_1 P_2) r_{12} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) , \quad (56)$$

Where ϕ_i and ϕ_j are occupied orbitals, and P_1 and P_2 are projectors onto the finite basis used in the calculation:

$$P_1 = \sum_{\chi_\mu \in \text{basis}} |\chi_\mu(\mathbf{r}_1)\rangle \langle \chi_\mu(\mathbf{r}_1)| . \quad (57)$$

However, the two-electron functions of this ansatz are not strongly orthogonal to the occupied orbitals. A correct, strongly orthogonal ansatz requires the following two-electron functions

$$\Psi_{ij}^{r_{12}^{\text{SO}}}(\mathbf{r}_1, \mathbf{r}_2) = (1 - Q_1)(1 - Q_2)(1 - P_1 P_2) r_{12} \\ \times \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) , \quad (58)$$

where Q_1 and Q_2 are projectors onto the occupied orbital space:

$$Q_1 = \sum_{\phi_k \in \text{occupied}} |\phi_k(\mathbf{r}_1)\rangle \langle \phi_k(\mathbf{r}_1)| . \quad (59)$$

One of the major effects of the RI approximation is to replace the strongly orthogonal ansatz (Eq. 58) by the simpler form (Eq. 56). With the exact evaluation of one-center three-electron integrals now possible, we can compare directly the two ansätze. We do this by comparing the norms of Eqs. (58) and (56), which involve three-electron integrals over occupied orbitals and the operator product $r_{12} \times r_{13}$.

In our calculations, we used three different basis sets (Table 1). The largest basis (basis 1) contains the functions 20s14p11d9f and corresponds to the 18s13p basis of Partridge [11] supplemented with two diffuse s-type functions with exponents 0.1 and 0.05, one diffuse p set with exponent 0.05, and the 11d9f set of Noga et al. [12]. The two smaller basis sets, basis 2 (20s11p7d5f) and basis 3 (20s8p7d5f) have the same s functions, but fewer functions of higher angular momentum.

The norm of Eqs. (58) and (56) is compared for different valence orbital pairs of the neon atom in basis 1 in Table 2. The differences between the two ansätze are very small. We therefore expect the resulting differences in the calculated energies to be only a few percent of the R12 basis-set truncation correction. Since, in this basis, the R12 correction itself is a small part of the total energy, the resulting error due to the RI approximation is certainly negligible. This is not unexpected, because it has been shown (cf. Ref. [6]) that if the occupied orbitals have an angular momentum quantum number not larger than ℓ_{occupied} then the RI approximation becomes exact if the one-electron basis is complete up to $\ell = 3\ell_{\text{occupied}}$. For the neon atom, this means that it is sufficient to have a basis complete up to f-type functions. In practical calculations, this completeness condition is never met. It is therefore crucial to study the RI approximation for a smaller basis.

The results of the two ansätze in the smaller basis 2 (20s11p7d5f) are compared in Table 3; in this basis, the error is still small. However, if we try to reduce the size of the basis further, the results deteriorate dramatically. Thus, the results in Table 4 are obtained by using slightly sparser p functions in basis 3 (20s8p7d5f). Although the Hartree–Fock and MP2 energies are essentially unaffected by this change in the basis (Table 5), Eq. (56) is strongly modified and is no longer a good approximation to Eq. (58), demonstrating that it is necessary to select carefully basis sets in calculations that rely on the RI approximation.

Table 1. Basis sets 1 (20s14p11d9f), 2 (20s11p7d5f), and 3 (20s8p7d5f)

20s 1 + 2 + 3	14p 1	11p 2	8p 3	11d 1	7d 2 + 3	9f 1	5f 2 + 3
2598845.0	3257.313	132.79	109.35	350.7463400	15.46	73.1402640	4.68
389291.20	771.0460	60.36	36.45	134.2652220	7.02	33.1370820	2.12
88614.780	250.5331	27.43	12.15	56.8868720	3.19	15.7724424	0.96
25103.590	95.90373	12.47	4.05	25.7732860	1.45	7.7657598	0.44
8190.9100	40.63348	5.66	1.35	12.2674552	0.66	3.8727018	0.20
2957.4970	18.40949	2.57	0.45	6.0400354	0.30	1.9217430	
1153.7430	8.762468	1.17	0.15	3.0121014	0.14	0.9403200	
478.68000	4.314311	0.53	0.05	1.4946890		0.4515174	
208.86450	2.151501	0.24		0.7313600		0.2082744	
94.993240	1.067635	0.11		0.3511802			
44.686810	0.522400	0.05		0.1619912			
21.623280	0.250843						
10.694420	0.115708						
5.3116980	0.050000						
2.4260420							
1.1181120							
0.5073780							
0.2239600							
0.1000000							
0.0500000							

Table 2. Comparison of the norm of two ansätze for various electron-pair functions of the neon atom, computed in the 20s14p11d9f basis

Orbital pair	$\ \Psi^{r_{12}SO}\ ^2$	$\ \Psi^{r_{12}}\ ^2$	Relative difference (%)
$2s^2 \ ^1S$	1.2572×10^{-4}	1.2686×10^{-4}	0.91
$2s2p \ ^1P$	5.8072×10^{-4}	5.8164×10^{-4}	0.16
$2s2p \ ^3P$	9.6584×10^{-5}	9.7590×10^{-5}	1.00
$2p^2 \ ^1S$	6.2996×10^{-4}	6.3054×10^{-4}	0.09
$2p^2 \ ^3P$	1.4979×10^{-4}	1.5035×10^{-4}	0.37
$2p^2 \ ^1D$	5.5027×10^{-4}	5.5096×10^{-4}	0.13

Table 3. Comparison of the norm of two ansätze for various electron-pair functions of the neon atom, computed in the 20s11p7d5f basis

Orbital pair	$\ \Psi^{r_{12}SO}\ ^2$	$\ \Psi^{r_{12}}\ ^2$	Relative difference (%)
$2s^2 \ ^1S$	1.300×10^{-4}	1.313×10^{-4}	0.96
$2s2p \ ^1P$	5.888×10^{-4}	5.906×10^{-4}	0.30
$2s2p \ ^3P$	1.010×10^{-4}	1.039×10^{-4}	2.90
$2p^2 \ ^1S$	6.476×10^{-4}	6.491×10^{-4}	0.23
$2p^2 \ ^3P$	1.577×10^{-4}	1.592×10^{-4}	0.92
$2p^2 \ ^1D$	5.583×10^{-4}	5.652×10^{-4}	1.24

Table 4. Comparison of the norm of two ansätze for various electron-pair functions of the neon atom, computed in the 20s8p7d5f basis

Orbital pair	$\ \Psi^{r_{12}SO}\ ^2$	$\ \Psi^{r_{12}}\ ^2$	Relative difference (%)
$2s^2 \ ^1S$	1.513×10^{-4}	1.836×10^{-4}	21
$2s2p \ ^1P$	6.303×10^{-4}	7.979×10^{-4}	27
$2s2p \ ^3P$	1.195×10^{-4}	2.186×10^{-4}	83
$2p^2 \ ^1S$	6.826×10^{-4}	9.397×10^{-4}	38
$2p^2 \ ^3P$	1.687×10^{-4}	4.029×10^{-4}	139
$2p^2 \ ^1D$	5.788×10^{-4}	8.277×10^{-4}	43

Table 5. Hartree–Fock and second-order Møller–Plesset (MP2) energies (E_h) in three different basis sets

	20s14p11d9f	20s11p7d5f	20s8p7d5f
$E_{\text{Hartree-Fock}}$	-128.54709	-128.54628	-128.54433
E_{MP2}	-0.35984	-0.35218	-0.35082
$E_{\text{MP2-R12/A}}$	-0.38967	-0.38876	-0.38810

4 Concluding remarks

In our calculations, we tested the RI approximation through its effect on the strong orthogonality condition. The RI approximation is also used to approximate other terms. In fact, four-electron integrals also appear in explicitly correlated R12 theory. Nevertheless, it is expected that the neglect of the strong orthogonality condition is the most important error introduced by the RI approximation. Our results show that the completeness condition in the RI approximation does not require unreasonably large basis sets. Still, it is interesting to note that the border where the RI approximation collapses is rather sharp.

Practical calculations with the R12 method have proved to give impressive results, even when the basis is too small to justify strictly the use of the RI approximation. It would therefore be of interest to study in more detail all the terms involved in an explicitly correlated calculation. Such a study is under way.

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Appendix

In this appendix, we evaluate the elementary integrals

$$I_{NML} = 4\pi^{\frac{7}{2}} \alpha^{2L-M-N} \beta^{N-1} \gamma^{M-1} \times \int_0^1 \int_0^1 \frac{t^{2N} u^{2M}}{(\alpha + \beta t^2 + \gamma u^2)^{\frac{3}{2}+L}} dt du, \quad (\text{A1})$$

with the constraint

$$\max(N, M) \leq L \leq N + M + 2. \quad (\text{A2})$$

Integration by parts yields

$$(2M+1)I_{NML} = \frac{2}{\alpha} \left(L + \frac{3}{2} \right) I_{N, M+1, L+1} + \alpha^{2L-M-N} \beta^{N-1} \gamma^{M-1} J_{NL}(\alpha + \gamma, \beta) \quad (\text{A3})$$

$$(2N+1)I_{NML} = \frac{2}{\alpha} \left(L + \frac{3}{2} \right) I_{N+1, M, L+1} + \alpha^{2L-M-N} \beta^{N-1} \gamma^{M-1} J_{ML}(\alpha + \beta, \gamma) \quad (\text{A4})$$

with

$$J_{NL}(a, b) = 4\pi^{\frac{7}{2}} \int_0^1 \frac{t^{2N}}{(a + bt^2)^{\frac{3}{2}+L}} dt. \quad (\text{A5})$$

Let us assume that the integrals $J_{NL}(a, b)$ are known for all N and L . Then, we can compute I_{NML} by recursion using Eqs. (A3) and (A4). To start these recursions, we need the integrals I_{0J0} for all J as well as I_{001} and I_{002} . These integrals are computed as follows:

$$I_{000} = \frac{4\pi^{\frac{7}{2}}}{\beta\gamma} \int_0^1 \int_0^1 \frac{1}{(\alpha + \beta t^2 + \gamma u^2)^{\frac{3}{2}}} dt du = \frac{4\pi^{\frac{7}{2}}}{\beta\gamma} \frac{1}{\sqrt{\alpha\beta\gamma}} \arctan \sqrt{\frac{\beta\gamma}{\alpha(\alpha + \beta + \gamma)}}, \quad (\text{A6})$$

$$\begin{aligned}
I_{001} &= \frac{4\pi^{\frac{7}{2}}\alpha^2}{\beta\gamma} \int_0^1 \int_0^1 \frac{1}{(\alpha + \beta t^2 + \gamma u^2)^{\frac{5}{2}}} dt du \\
&= \frac{4\pi^{\frac{7}{2}}\alpha}{3\beta\gamma} \left[\frac{\arctan \sqrt{\frac{\beta\gamma}{\alpha(\alpha+\beta+\gamma)}}}{\sqrt{\alpha\beta\gamma}} \right. \\
&\quad \left. + \frac{\alpha + (\alpha + \beta + \gamma)}{\sqrt{(\alpha + \beta + \gamma)(\beta\gamma + \alpha(\alpha + \beta + \gamma))}} \right], \quad (A7)
\end{aligned}$$

$$\begin{aligned}
I_{002} &= \frac{4\pi^{\frac{7}{2}}\alpha^4}{\beta\gamma} \int_0^1 \int_0^1 \frac{1}{(\alpha + \beta t^2 + \gamma u^2)^{\frac{7}{2}}} dt du \\
&= \frac{4\pi^{\frac{7}{2}}\alpha^2}{5\beta\gamma} \left[\frac{\arctan \sqrt{\frac{\beta\gamma}{\alpha(\alpha+\beta+\gamma)}}}{\sqrt{\alpha\beta\gamma}} \right. \\
&\quad + \frac{12\alpha^4 + 26\alpha^3(\beta + \gamma) + 3\beta\gamma(\beta + \gamma)^2}{3(\alpha + \beta + \gamma)\sqrt{(\alpha + \beta + \gamma)(\beta\gamma + \alpha(\alpha + \beta + \gamma))}^2} \\
&\quad \left. + \frac{\alpha(\beta + \gamma)(5\beta^2 + 16\beta\gamma + 5\gamma^2) + \alpha^2(19\beta^2 + 42\beta\gamma + 19\gamma^2)}{3(\alpha + \beta + \gamma)\sqrt{(\alpha + \beta + \gamma)(\beta\gamma + \alpha(\alpha + \beta + \gamma))}^2} \right], \quad (A8)
\end{aligned}$$

$$I_{0J0} = 4\pi^{\frac{7}{2}}\alpha^{-J}\beta^{-1}\gamma^{J-1} \int_0^1 \int_0^1 \frac{u^{2J}}{(\alpha + \beta t^2 + \gamma u^2)^{\frac{5}{2}}} dt du. \quad (A9)$$

We write

$$I_{0J0} = 4\pi^{\frac{7}{2}}\alpha^{-J}\beta^{-1}\gamma^{J-1}L_J, \quad (A10)$$

and integrate over t , leading to

$$L_J = \int_0^1 \frac{u^{2J}}{(\alpha + \gamma u^2)(\alpha + \beta + \gamma u^2)^{\frac{5}{2}}} du. \quad (A11)$$

Substitution of $x^2 = \frac{\alpha + \beta + \gamma}{\alpha + \beta + \gamma u^2} u^2$ into L_J gives

$$\begin{aligned}
L_J &= (\alpha + \beta)^J \sqrt{\alpha + \beta + \gamma} \\
&\quad \times \int_0^1 \left(\frac{x^2}{\alpha + \beta + \gamma - \gamma x^2} \right)^J \frac{1}{\alpha(\alpha + \beta + \gamma) + \beta\gamma x^2} dx, \quad (A12)
\end{aligned}$$

which can be rewritten to give

$$\begin{aligned}
\gamma L_J &= -\alpha L_{J-1} + (\alpha + \beta)^{J-1} \sqrt{\alpha + \beta + \gamma} \\
&\quad \times \int_0^1 \frac{x^{2J-2}}{(\alpha + \beta + \gamma - \gamma x^2)^J} dx. \quad (A13)
\end{aligned}$$

The second term contains an integral of the type

$$M_{KL} = \int_0^1 \frac{x^{2L}}{(a - bx^2)^K} dx, \quad \text{with } L \geq K - 1. \quad (A14)$$

for which integration by parts yields

$$2b(K - 1)M_{KL} = \frac{1}{(a - b)^{K-1}} - (2L - 1)M_{K-1,L-1}. \quad (A15)$$

The integrals M_{KL} are thus computed recursively in conjunction with

$$M_{00} = 1, \quad (A16)$$

$$M_{10} = \int_0^1 \frac{1}{a - bx^2} dx = \frac{1}{2\sqrt{ab}} \ln \left(\frac{\sqrt{a} + \sqrt{b}}{\sqrt{a} - \sqrt{b}} \right), \quad (A17)$$

$$M_{1L} = \frac{a}{b} M_{1,L-1} - \frac{1}{b(2L - 1)}, \quad (A18)$$

where $a > b > 0$.

Finally, the integrals $J_{NL}(a, b)$ are computed from

$$J_{NL}(a, b) = 4\pi^{\frac{7}{2}} \frac{a^{N-L-1}}{(a + b)^{L+\frac{1}{2}}} \int_0^1 \frac{x^{2N}}{(a + b - bx^2)^{N-L}} dx, \quad (A19)$$

by virtue of the substitution $x^2 = (a + b)/(a + bt^2)t^2$. If $N - L$ is negative the integral reduces to an integral over a polynomial; otherwise, $J_{NL}(a, b)$ is similar to M_{KL} .

Integration by parts can be unstable. The convergence of the series in Eqs. (A3) and (A4) is as $[\gamma/(\alpha + \gamma)]^i$ or $[\beta/(\alpha + \beta)]^i$. For large α , downward recursion is unstable, but in this case a numerically stable infinite upward recursion gives a rapidly convergent series with only positive terms.

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