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Computation of two-electron Gaussian integrals for wave functions including the correlation factor $r_{12}\exp(-\gamma r_{12}^2)$

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Abstract

Explicitly correlated molecular electronic-structure calculations with the damped correlation factor $r_{12}\exp(-\gamma r_{12}^2)$ require two-electron integrals that are different from the already implemented R12 integrals. The aim of such a correlation factor, which combines the interelectronic distance with a Gaussian-type function, is to avoid integrals with large interelectronic distances, thus making it possible to use R12 methods for large molecular systems. In particular, an important perspective of the new correlation factor is to be able to utilize *local-correlation techniques* for explicitly correlated wave functions, such that computation times will asymptotically scale linearly with the size of the molecule. For the development of such techniques, the correlation factor must be restricted to the (physically meaningful) short range of the correlation cusp of the Coulomb hole. In the present paper, the evaluation of all two-electron integrals needed for damped-R12 theory is described, as implemented in a local version of the Dalton program.

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1. Introduction

Most *ab initio* methods represent the electronic wave function by a linear combination of products of one-electron functions, which do not describe accurately the Coulomb hole and which cannot represent the electron-correlation cusp [1–5]. The R12 method improves this description by using two-electron basis functions of the form $f_{12}\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)$, where $\psi_i(\mathbf{r}_1)$ and $\psi_j(\mathbf{r}_2)$ are molecular spin-orbitals and f_{12} a correlation factor.

So far, the only correlation factor explored in R12 theory is the interelectronic distance $f_{12} = r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. In combination with several types of approximations designed to remove the three- and four-electron integrals involved [6–8], this factor has given very accurate results for a variety of small and medium-sized molecules. Nevertheless, use of the linear r_{12} factor, which does not vanish for large electronic separations, becomes awkward for large molecules. For such systems, therefore, we wish to investigate the correlation factor $f_{12} = r_{12}\exp(-\gamma r_{12}^2)$,

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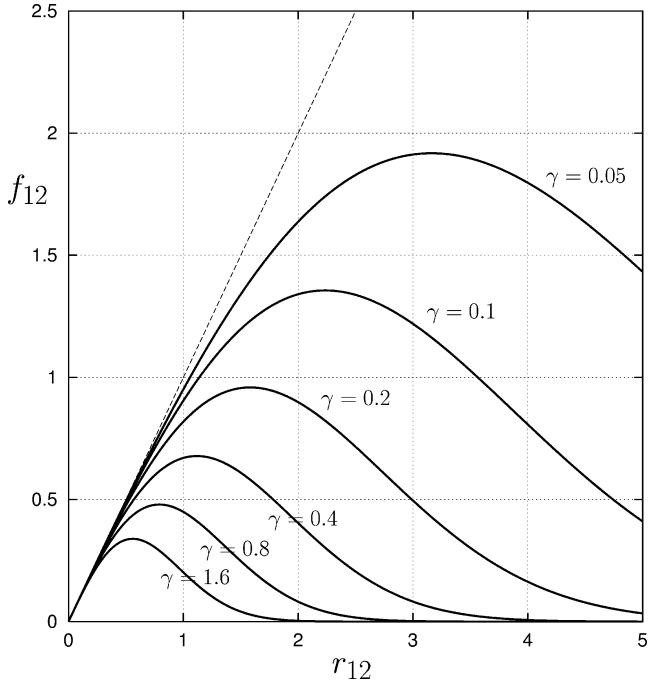

Fig. 1. Correlation factor $f_{12} = r_{12}\exp(-\gamma r_{12}^2)$ for various values of γ.

which vanishes for large separations between the electrons—see Fig. 1. Rather than expanding the correlation factor in a basis of Gaussian geminals alone [9–11], which also vanish for large r_{12}, we wish to investigate products of the linear r_{12} factor with such Gaussians.

Clearly, with the introduction of a new correlation factor, we must develop a scheme for the calculation of two-electron integrals involving this factor. The scheme presented in this paper is based on the McMurchie–Davidson method for the evaluation of one- and two-electron integrals over Gaussian atomic orbitals [12]. As demonstrated here, none of the five nonstandard two-electron integrals that arise from the use of the damped r_{12} factors require much more effort than do the usual two-electron integrals over Gaussian functions, indicating that the damped-R12 method will be practicable for large systems. Indeed, the particular damping function chosen for our correlation factor—that is, the Gaussian factor $\exp(-\gamma r_{12}^2)$—was selected with computational ease in mind. Other damping factors such as the complementary error function $\mathrm{erfc}(\gamma r_{12})$ are possible but lead to a more complicated integral evaluation.

2. Integral evaluation

We begin our discussion of two-electron integral evaluation by examining the overall structure of the integrals in Section 2.1. Next, in Section 2.2, we introduce the McMurchie–Davidson expansion of overlap distributions in Hermite functions followed by the expansion of Cartesian integrals in Hermite integrals in Section 2.3. Finally, the recursive evaluation of the spherical and nonspherical Hermite integrals is treated in Sections 2.4 and 2.5.

2.1. Structure of the Cartesian two-electron damped-R12 integrals

Within the standard approximations of R12 theory, there are six different two-electron integrals to be evaluated. The integrals I_1 and I_2 originate from the Coulomb repulsion:

$$I_1 = \big(ab\big|r_{12}^{-1}\big|cd\big) = \iint \psi_a^*(\mathbf{r}_1)\psi_c^*(\mathbf{r}_2)r_{12}^{-1}\psi_b(\mathbf{r}_1)\psi_d(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2, \tag{1}$$

$$I_2 = \big(ab\big|r_{12}^{-1}f_{12}\big|cd\big) = \big(ab\big|\exp\big(-\gamma r_{12}^2\big)\big|cd\big) = \iint \psi_a^*(\mathbf{r}_1)\psi_c^*(\mathbf{r}_2)\exp\big(-\gamma r_{12}^2\big)\psi_b(\mathbf{r}_1)\psi_d(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2; \tag{2}$$

the integrals I_3 and I_4 are overlap integrals:

$$\begin{aligned} I_3 &= (ab|\,f_{12}|cd) = \big(ab\big|r_{12}\exp\big(-\gamma r_{12}^2\big)\big|cd\big) \\ &= \iint \psi_a^*(\mathbf{r}_1)\psi_c^*(\mathbf{r}_2)r_{12}\exp\big(-\gamma r_{12}^2\big)\psi_b(\mathbf{r}_1)\psi_d(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2, \end{aligned} \tag{3}$$

$$\begin{aligned} I_4 &= (ab|\,f_{12}f'_{12}|cd) = \big(ab\big|r_{12}^2\exp\big(-(\gamma+\gamma')r_{12}^2\big)\big|cd\big) \\ &= \iint \psi_a^*(\mathbf{r}_1)\psi_c^*(\mathbf{r}_2)r_{12}^2\exp\big(-(\gamma+\gamma')r_{12}^2\big)\psi_b(\mathbf{r}_1)\psi_d(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2; \end{aligned} \tag{4}$$

and the integrals I_5 and I_6 involve commutators with the kinetic-energy operator $\widehat{T}$:

$$\begin{aligned} I_5 &= (ab|[f_{12},\widehat{T}_1]|cd) = \big(ab\big|\big[r_{12}\exp\big(-\gamma r_{12}^2\big),\widehat{T}_1\big]\big|cd\big) \\ &= \iint \psi_a^*(\mathbf{r}_1)\psi_c^*(\mathbf{r}_2)\big[r_{12}\exp\big(-\gamma r_{12}^2\big),\widehat{T}_1\big]\psi_b(\mathbf{r}_1)\psi_d(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2, \end{aligned} \tag{5}$$

$$\begin{aligned} I_6 &= \big(ab\big|\big[[f_{12},\widehat{T}_1],f'_{12}\big]\big|cd\big) = \big(ab\big|\big[\big[r_{12}\exp\big(-\gamma r_{12}^2\big),\widehat{T}_1\big],r_{12}\exp\big(-\gamma' r_{12}^2\big)\big]\big|cd\big) \\ &= \iint \psi_a^*(\mathbf{r}_1)\psi_c^*(\mathbf{r}_2)\big[\big[r_{12}\exp\big(-\gamma r_{12}^2\big),\widehat{T}_1\big],r_{12}\exp\big(-\gamma' r_{12}^2\big)\big]\psi_b(\mathbf{r}_1)\psi_d(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2. \end{aligned} \tag{6}$$

For flexibility in the choice of the correlation factor, two different exponents γ and γ' and thus two different correlation factors $f_{12} = r_{12}\exp(-\gamma r_{12}^2)$ and $f'_{12} = r_{12}\exp(-\gamma' r_{12}^2)$ have been introduced in I_4 and I_6.

Before we begin our discussion of the evaluation of the damped-R12 integrals, a few general remarks on their structure are in order. In the following, we assume that the integration is over real, primitive Cartesian orbitals with exponents a, b, c, and d centered on **A**, **B**, **C**, and **D**, respectively:

$$\psi_a(\mathbf{r}_1,a,\mathbf{A}) = x_{1A}^i y_{1A}^k z_{1A}^m \exp\big(-ar_{1A}^2\big), \tag{7}$$

$$\psi_b(\mathbf{r}_1,b,\mathbf{B}) = x_{1B}^j y_{1B}^l z_{1B}^n \exp\big(-br_{1B}^2\big), \tag{8}$$

$$\psi_c(\mathbf{r}_2,c,\mathbf{C}) = x_{2C}^{i'} y_{2C}^{k'} z_{2C}^{m'} \exp\big(-cr_{2C}^2\big), \tag{9}$$

$$\psi_d(\mathbf{r}_2,d,\mathbf{D}) = x_{2D}^{j'} y_{2D}^{l'} z_{2D}^{n'} \exp\big(-dr_{2D}^2\big). \tag{10}$$

The transformation of integrals to a symmetrized, contracted spherical-harmonic basis may be carried out in the same manner as for the usual two-electron integrals I_1 and is not discussed further here.

Next, we observe that the integrals involving the kinetic-energy operator can be expressed in the following manner [13]:

$$\begin{aligned} I_5 &= \tfrac{1}{2}\big(ab\big|\nabla_1^2 r_{12}\exp\big(-\gamma r_{12}^2\big) - r_{12}\exp\big(-\gamma r_{12}^2\big)\nabla_1^2\big|cd\big) \\ &= \tfrac{1}{2}\big(\big(\nabla_1^2 a\big)b - a\big(\nabla_1^2 b\big)\big|r_{12}\exp\big(-\gamma r_{12}^2\big)\big|cd\big) \\ &= \tfrac{1}{2}\big(\nabla_A^2 - \nabla_B^2\big)I_3, \end{aligned} \tag{11}$$

$$\begin{aligned} I_6 &= \big(ab\big|\big(\boldsymbol{\nabla}_1 f_{12}\big)\cdot\big(\boldsymbol{\nabla}_1 f'_{12}\big)\big|cd\big) \\ &= \big(ab\big|\big(1-2\gamma r_{12}^2\big)\big(1-2\gamma' r_{12}^2\big)\exp\big[-(\gamma+\gamma')r_{12}^2\big]\big|cd\big), \end{aligned} \tag{12}$$

where $\boldsymbol{\nabla}_1$ is the gradient operator with respect to the coordinates of the first electron and whereas $\boldsymbol{\nabla}_A$ and $\boldsymbol{\nabla}_B$ denote gradients with respect to **A** and **B**, respectively. Comparing these expressions for I_5 and I_6 with those for

$I_2 - I_4$ in Eqs. (2)–(4), we conclude that all two-electron integrals needed in damped-R12 theory can be computed from integrals over the operators $r_{12}^k \exp(-\beta r_{12}^2)$ with $k = 0, 1, 2, 4$ and $\beta = \gamma$ or $\beta = \gamma + \gamma'$. We note, however, that the I_5 integrals are obtained as second derivatives of the integrals I_3; as we shall see, the evaluation of I_5 according to Eq. (11) can be carried out in an efficient manner, requiring not much more effort than the evaluation of the other damped-R12 integrals.

In the standard R12 approach, the correlation factor f_{12} is chosen to be equal to r_{12}. In this special case, the integral I_2 need not to be evaluated since the operator in I_2 reduces to $r_{12}^{-1} r_{12} = 1$. Also, the integral I_4 over r_{12}^2 factorizes into products of one-electron integrals and the operator I_6 reduces to $[[r_{12}, \widehat{T}_1], r_{12}] = 1$. With the use of the new, damped correlation factor, these simplifications do not occur.

2.2. Expansion of Cartesian overlap distributions in Hermite functions

In our evaluation of two-electron integrals, we adopt the McMurchie–Davidson scheme [12], expanding the Cartesian overlap distributions in Hermite integrals. In this approach, we write the overlap distribution $\psi_a(\mathbf{r}_1, a, \mathbf{A})\psi_b(\mathbf{r}_1, b, \mathbf{B})$ as a linear combination of Hermite functions

$$\Lambda_{tuv}(\mathbf{r}_1, p, \mathbf{P}) = \frac{\mathrm{d}^t}{\mathrm{d}P_x^t} \frac{\mathrm{d}^u}{\mathrm{d}P_y^u} \frac{\mathrm{d}^v}{\mathrm{d}P_z^v} \exp\bigl(-p r_{1P}^2\bigr), \tag{13}$$

with exponent p and centered at $\mathbf{P}$,

$$p = a + b, \tag{14}$$

$$\mathbf{P} = \frac{a\mathbf{A} + b\mathbf{B}}{p}, \tag{15}$$

in the following manner [12]:

$$\psi_a(\mathbf{r}_1, a, \mathbf{A})\psi_b(\mathbf{r}_1, b, \mathbf{B}) = \sum_{t=0}^{i+j} E_t^{ij} \sum_{u=0}^{k+l} E_u^{kl} \sum_{v=0}^{m+n} E_v^{mn} \Lambda_{tuv}(\mathbf{r}_1, p, \mathbf{P}) = \sum_{tuv} E_{tuv}^{ab} \Lambda_{tuv}(\mathbf{r}_1, p, \mathbf{P}). \tag{16}$$

As demonstrated in Ref. [14], the expansion coefficients E_t^{ij} of the first electron may be evaluated from the following two-term recurrence relations

$$E_0^{00} = \exp\left(-\frac{ab}{a+b} X_{AB}^2\right), \tag{17}$$

$$E_0^{i+1,j} = -\frac{b}{p} X_{AB} E_0^{ij} + E_1^{ij}, \tag{18}$$

$$E_0^{i,j+1} = \frac{a}{p} X_{AB} E_0^{ij} + E_1^{ij}, \tag{19}$$

$$E_t^{ij} = \frac{1}{2pt}\bigl(i E_{t-1}^{i-1,j} + j E_{t-1}^{i,j-1}\bigr), \tag{20}$$

and likewise for E_u^{kl} and E_v^{mn}. Similar relations may be used for the second electron. In the original McMurchie–Davidson method, three-term recurrence relations are used for these coefficients [12]. Similarly, we may expand the overlap distribution of the second electron as

$$\psi_c(\mathbf{r}_2, c, \mathbf{C})\psi_d(\mathbf{r}_2, d, \mathbf{D}) = \sum_{\tau\upsilon\phi} E_{\tau\upsilon\phi}^{cd} \Lambda_{\tau\upsilon\phi}(\mathbf{r}_2, q, \mathbf{Q}) \tag{21}$$

where $q = c + d$ and $\mathbf{Q} = (c\mathbf{C} + d\mathbf{D})/q$, and where the coefficients $E_{\tau\upsilon\phi}^{cd}$ of the second electron are different from the coefficients E_{tuv}^{ab} of the first electron.

2.3. Expansion of Cartesian integrals in Hermite integrals

We now introduce the following basic two-electron integrals over spherical Gaussian functions with centers at **P** and **Q**:

$$D_k(\beta) = \int\int \exp\bigl(-pr_{1P}^2\bigr)\exp\bigl(-qr_{2Q}^2\bigr)r_{12}^k\exp\bigl(-\beta r_{12}^2\bigr)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2. \tag{22}$$

Inserting the Hermite expansions of the overlap distributions Eqs. (16) and (21) in the integrals (1)–(4) and (6), we obtain

$$I_k = \sum_{tuv} E_{tuv}^{ab} \sum_{\tau\upsilon\phi}(-1)^{\tau+\upsilon+\phi} E_{\tau\upsilon\phi}^{cd} R_k^{t+\tau,u+\upsilon,v+\phi}, \quad k = 1, 2, 3, 4, 6; \tag{23}$$

with

$$R_1^{tuv} = \frac{\mathrm{d}^t}{\mathrm{d}P_x^t}\frac{\mathrm{d}^u}{\mathrm{d}P_y^u}\frac{\mathrm{d}^v}{\mathrm{d}P_z^v} D_{-1}(0), \tag{24}$$

$$R_2^{tuv} = \frac{\mathrm{d}^t}{\mathrm{d}P_x^t}\frac{\mathrm{d}^u}{\mathrm{d}P_y^u}\frac{\mathrm{d}^v}{\mathrm{d}P_z^v} D_0(\gamma), \tag{25}$$

$$R_3^{tuv} = \frac{\mathrm{d}^t}{\mathrm{d}P_x^t}\frac{\mathrm{d}^u}{\mathrm{d}P_y^u}\frac{\mathrm{d}^v}{\mathrm{d}P_z^v} D_1(\gamma), \tag{26}$$

$$R_4^{tuv} = \frac{\mathrm{d}^t}{\mathrm{d}P_x^t}\frac{\mathrm{d}^u}{\mathrm{d}P_y^u}\frac{\mathrm{d}^v}{\mathrm{d}P_z^v} D_2(\gamma+\gamma'), \tag{27}$$

$$R_6^{tuv} = \frac{\mathrm{d}^t}{\mathrm{d}P_x^t}\frac{\mathrm{d}^u}{\mathrm{d}P_y^u}\frac{\mathrm{d}^v}{\mathrm{d}P_z^v}\bigl[D_0(\gamma+\gamma') - 2(\gamma+\gamma')D_2(\gamma+\gamma') + 4\gamma\gamma' D_4(\gamma+\gamma')\bigr]. \tag{28}$$

To obtain these expressions, we have taken the differentiation operators with respect to the components of **P** and **Q** outside the integration and invoked the translational invariance of the integrals to replace derivatives with respect to **Q** by derivatives with respect to $-\mathbf{P}$.

The integrals I_5 in Eq. (11) require special attention. By substituting Eq. (23) in Eq. (11), we obtain:

$$I_5 = \frac{1}{2}\bigl(\nabla_A^2 - \nabla_B^2\bigr)\sum_{tuv} E_{tuv}^{ab} \sum_{\tau\upsilon\phi}(-1)^{\tau+\upsilon+\phi} E_{\tau\upsilon\phi}^{cd} R_3^{t+\tau,u+\upsilon,v+\phi}. \tag{29}$$

Since the coefficients E_{tuv}^{ab} depend only on $\mathbf{A}-\mathbf{B}$ and the integrals R_3^{tuv} only on **P**, it is advantageous to express I_5 in terms of derivatives with respect to these coordinates rather than with respect to **A** and **B** [15]. From the relations

$$\frac{\mathrm{d}}{\mathrm{d}A_x} = \frac{a}{p}\frac{\mathrm{d}}{\mathrm{d}P_x} + \frac{\mathrm{d}}{\mathrm{d}X_{AB}}, \tag{30}$$

$$\frac{\mathrm{d}}{\mathrm{d}B_x} = \frac{b}{p}\frac{\mathrm{d}}{\mathrm{d}P_x} - \frac{\mathrm{d}}{\mathrm{d}X_{AB}}, \tag{31}$$

where X_{AB} is the x component of $\mathbf{A}-\mathbf{B}$, we then obtain [13]:

$$\begin{aligned} I_5 = {} & \frac{a-b}{2p}\sum_{tuv} E_{tuv}^{ab} \sum_{\tau\upsilon\phi}(-1)^{\tau+\upsilon+\phi} E_{\tau\upsilon\phi}^{cd} \nabla_P^2 R_3^{t+\tau,u+\upsilon,v+\phi} \\ & + \sum_{tuv} \nabla_X E_{tuv}^{ab} \cdot \sum_{\tau\upsilon\phi}(-1)^{\tau+\upsilon+\phi} E_{\tau\upsilon\phi}^{cd} \nabla_P R_3^{t+\tau,u+\upsilon,v+\phi}. \end{aligned} \tag{32}$$

The derivatives of the Hermite integrals (26) are given by

$$\nabla_P R_3^{tuv} = \left[R_3^{t+1,u,v}, R_3^{t,u+1,v}, R_3^{t,u,v+1}\right]^{\mathrm{T}}, \tag{33}$$

$$\nabla_P^2 R_3^{tuv} = R_3^{t+2,u,v} + R_3^{t,u+2,v} + R_3^{t,u,v+2}, \tag{34}$$

while the elements of $\nabla_X E_t^{ij}$ are obtained from recurrence relations obtained by differentiating Eqs. (17)–(20). For the x component, for example, we obtain for the coefficients

$$F_t^{ij} = \frac{\mathrm{d}E_t^{ij}}{\mathrm{d}X_{AB}} \tag{35}$$

the recurrence relations

$$F_0^{00} = -\frac{2ab}{p} X_{AB} E_0^{00}, \tag{36}$$

$$F_0^{i+1,j} = -\frac{b}{p} X_{AB} F_0^{ij} + F_1^{ij} - \frac{b}{p} E_0^{i,j}, \tag{37}$$

$$F_0^{i,j+1} = \frac{a}{p} X_{AB} F_0^{ij} + F_1^{ij} + \frac{a}{p} E_0^{i,j}, \tag{38}$$

$$F_t^{ij} = \frac{1}{2pt}\left(i F_{t-1}^{i-1,j} + j F_{t-1}^{i,j-1}\right), \tag{39}$$

and similarly for the y and z components.

2.4. Evaluation of the spherical Hermite integrals

In the present section, we consider the evaluation of the spherical Hermite integrals $D_k(\beta)$ of Eq. (22). We begin by noting the following relations among these integrals:

$$D_{k+1}(\beta) = -D'_{k-1}(\beta), \tag{40}$$

$$D_{2k-1}(\beta) = \frac{2}{\sqrt{\pi}} \int_0^\infty D_{2k}\left(\beta + t^2\right) \mathrm{d}t. \tag{41}$$

The first relation is obtained straightforwardly by differentiation of Eq. (22); the second relation follows by introducing in Eq. (22) the integral transform

$$\frac{1}{r_{12}} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp\left(-t^2 r_{12}^2\right) \mathrm{d}t, \tag{42}$$

as pioneered by Boys for the two-electron repulsion integrals [16]. We may therefore generate the necessary integrals $D_k(\beta)$ by explicit integration for $D_0(\beta)$, followed by application of Eqs. (40) and (41) to yield the remaining integrals.

The overlap integral $D_0(\beta)$ is easily evaluated as it contains only Gaussian functions. By integrating over the x, y, and z coordinates separately,

$$\begin{aligned} D_0(\beta) = {} & \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left[-p(x_1 - P_x)^2 - q(x_2 - Q_x)^2 - \beta(x_1 - x_2)^2\right] \mathrm{d}x_1\,\mathrm{d}x_2 \\ & \times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left[-p(y_1 - P_y)^2 - q(y_2 - Q_y)^2 - \beta(y_1 - y_2)^2\right] \mathrm{d}y_1\,\mathrm{d}y_2 \end{aligned}$$

$$\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left[-p(z_1-P_z)^2 - q(z_2-Q_z)^2 - \beta(z_1-z_2)^2\right] \mathrm{d}z_1\,\mathrm{d}z_2, \tag{43}$$

and introducing the reduced exponent

$$\alpha = \frac{pq}{p+q}, \tag{44}$$

we obtain

$$D_0(\beta) = \left(\frac{\pi^2}{pq}\right)^{3/2}\left(\frac{\alpha}{\alpha+\beta}\right)^{3/2} \exp\left(-\frac{\alpha\beta}{\alpha+\beta}R_{PQ}^2\right), \tag{45}$$

$$D_2(\beta) = \left(\frac{3}{2} + \frac{\alpha^2}{\alpha+\beta}R_{PQ}^2\right)\frac{D_0(\beta)}{\alpha+\beta}, \tag{46}$$

$$D_4(\beta) = \left[\frac{15}{4} + \frac{5\alpha^2}{\alpha+\beta}R_{PQ}^2 + \frac{\alpha^4}{(\alpha+\beta)^2}R_{PQ}^4\right]\frac{D_0(\beta)}{(\alpha+\beta)^2}, \tag{47}$$

where we have applied Eq. (40) to yield $D_2(\beta)$ and $D_4(\beta)$. The even-order integrals $D_{2n}(\beta)$ are thus easily evaluated in closed form.

To calculate the odd-order spherical integrals $D_{2n-1}(\beta)$, we begin by deriving an expression for $D_{-1}(\beta)$, from which we next generate $D_1(\beta)$ by differentiation according to Eq. (40). From Eqs. (41) and (45), we obtain

$$D_{-1}(\beta) = \frac{2}{\sqrt{\pi}}\left(\frac{\pi^2}{pq}\right)^{3/2}\int_0^{\infty}\left(\frac{\alpha}{\alpha+\beta+t^2}\right)^{3/2} \exp\left(-\alpha R_{PQ}^2\frac{\beta+t^2}{\alpha+\beta+t^2}\right)\mathrm{d}t. \tag{48}$$

The variable substitution

$$u^2 = \frac{t^2}{\alpha+\beta+t^2} \tag{49}$$

gives

$$\mathrm{d}t = (\alpha+\beta)^{-1}\left(\alpha+\beta+t^2\right)^{3/2}\mathrm{d}u, \tag{50}$$

with integration limits 0 and 1 for u. Integral (48) then becomes

$$D_{-1}(\beta) = 2\sqrt{\frac{\alpha+\beta}{\pi}}F_0\left(\frac{\alpha^2}{\alpha+\beta}R_{PQ}^2\right)D_0(\beta), \tag{51}$$

where we have introduced the Boys function of order n:

$$F_n(x) = \int_0^1 \exp\left(-xt^2\right)t^{2n}\,\mathrm{d}t. \tag{52}$$

Finally, differentiation of D_{-1} with respect to β according to Eq. (40) and use of the relations

$$F_n'(x) = -F_{n+1}(x), \tag{53}$$

$$F_n'(x) = \frac{\exp(-x) - (2n+1)F_n(x)}{2x}, \tag{54}$$

yields:

$$D_1(\beta) = \left[\exp\left(-\frac{\alpha^2}{\alpha+\beta}R_{PQ}^2\right) + \left(1 + \frac{2\alpha^2}{\alpha+\beta}R_{PQ}^2\right)F_0\left(\frac{\alpha^2}{\alpha+\beta}R_{PQ}^2\right)\right]\frac{D_0(\beta)}{\sqrt{\pi(\alpha+\beta)}}. \tag{55}$$

For a more compact representation of the integrals, we introduce

$$\overline{R}_{PQ}^2 = \frac{\alpha}{\alpha+\beta} R_{PQ}^2, \tag{56}$$

and obtain for the damped integrals:

$$D_0(\beta) = \left(\frac{\pi^2}{pq}\right)^{3/2} \left(\frac{\alpha}{\alpha+\beta}\right)^{3/2} \exp\bigl(-\beta \overline{R}_{PQ}^2\bigr), \tag{57}$$

$$D_2(\beta) = \left(\frac{\pi^2}{pq}\right)^{3/2} \left(\overline{R}_{PQ}^2 + \frac{3}{2\alpha}\right) \left(\frac{\alpha}{\alpha+\beta}\right)^{5/2} \exp\bigl(-\beta \overline{R}_{PQ}^2\bigr), \tag{58}$$

$$D_4(\beta) = \left(\frac{\pi^2}{pq}\right)^{3/2} \left(\overline{R}_{PQ}^4 + \frac{5}{\alpha}\overline{R}_{PQ}^2 + \frac{15}{4\alpha^2}\right) \left(\frac{\alpha}{\alpha+\beta}\right)^{7/2} \exp\bigl(-\beta \overline{R}_{PQ}^2\bigr), \tag{59}$$

$$D_{-1}(\beta) = \left(\frac{\pi^2}{pq}\right)^{3/2} \sqrt{\frac{4\alpha}{\pi}}\, F_0\bigl(\alpha \overline{R}_{PQ}^2\bigr) \left(\frac{\alpha}{\alpha+\beta}\right) \exp\bigl(-\beta \overline{R}_{PQ}^2\bigr), \tag{60}$$

$$\begin{aligned} D_1(\beta) = {} & \left(\frac{\pi^2}{pq}\right)^{3/2} \sqrt{\frac{4\alpha}{\pi}} \left[\left(\overline{R}_{PQ}^2 + \frac{1}{2\alpha}\right) F_0\bigl(\alpha \overline{R}_{PQ}^2\bigr) + \frac{1}{2\alpha} \exp\bigl(-\alpha \overline{R}_{PQ}^2\bigr)\right] \\ & \times \left(\frac{\alpha}{\alpha+\beta}\right)^2 \exp\bigl(-\beta \overline{R}_{PQ}^2\bigr). \end{aligned} \tag{61}$$

In the special case when $\beta = 0$ (no damping), $\overline{R}_{PQ}^2$ becomes R_{PQ}^2 and the two last factors in each integral become equal to one.

2.5. Evaluation of nonspherical Hermite integrals

To evaluate the nonspherical Hermite integrals (24)–(28) from the spherical integrals discussed in Section 2.4, we first introduce the auxiliary integrals

$$H_{tuv}^{mn}(\mu,\nu) = \frac{\mathrm{d}^t}{\mathrm{d}P_x^t} \frac{\mathrm{d}^u}{\mathrm{d}P_y^u} \frac{\mathrm{d}^v}{\mathrm{d}P_z^v} \frac{\mathrm{d}^m}{\mathrm{d}\mu^m} \exp\bigl(-\mu R_{PQ}^2\bigr) F_n\bigl(\nu R_{PQ}^2\bigr) \tag{62}$$

which correspond to the Boys function (52) damped by a Gaussian. Inserting the expressions (57)–(61) in Eqs. (24)–(28), we obtain:

$$R_1^{tuv} = \left(\frac{\pi^2}{pq}\right)^{3/2} \sqrt{\frac{4\alpha}{\pi}}\, H_{tuv}^{00}(0,\alpha), \tag{63}$$

$$R_2^{tuv} = \left(\frac{\pi^2}{pq}\right)^{3/2} \left(\frac{\alpha}{\alpha+\gamma}\right)^{3/2} H_{tuv}^{00}\left(\frac{\alpha\gamma}{\alpha+\gamma}, 0\right), \tag{64}$$

$$\begin{aligned} R_3^{tuv} = {} & \left(\frac{\pi^2}{pq}\right)^{3/2} \sqrt{\frac{4\alpha}{\pi}} \left(\frac{\alpha}{\alpha+\gamma}\right)^2 \\ & \times \left[\frac{1}{2\alpha} H_{tuv}^{00}(\alpha,0) + \frac{1}{2\alpha} H_{tuv}^{00}\left(\frac{\alpha\gamma}{\alpha+\gamma}, \frac{\alpha^2}{\alpha+\gamma}\right) - \frac{\alpha}{\alpha+\gamma} H_{tuv}^{10}\left(\frac{\alpha\gamma}{\alpha+\gamma}, \frac{\alpha^2}{\alpha+\gamma}\right)\right], \end{aligned} \tag{65}$$

$$\begin{aligned} R_4^{tuv} = {} & \left(\frac{\pi^2}{pq}\right)^{3/2} \left(\frac{\alpha}{\alpha+\gamma+\gamma'}\right)^{5/2} \\ & \times \left[\frac{3}{2\alpha} H_{tuv}^{00}\left(\frac{\alpha\gamma+\alpha\gamma'}{\alpha+\gamma+\gamma'}, 0\right) - \frac{\alpha}{\alpha+\gamma+\gamma'} H_{tuv}^{10}\left(\frac{\alpha\gamma+\alpha\gamma'}{\alpha+\gamma+\gamma'}, 0\right)\right], \end{aligned} \tag{66}$$

$$R_6^{tuv} = \left(\frac{\pi^2}{pq}\right)^{3/2}\left(\frac{\alpha}{\alpha+\gamma+\gamma'}\right)^{3/2}\left\{\left[1-\frac{3(\gamma+\gamma')}{\alpha+\gamma+\gamma'}+\frac{15\gamma\gamma'}{(\alpha+\gamma+\gamma')^2}\right]H_{tuv}^{00}\left(\frac{\alpha\gamma+\alpha\gamma'}{\alpha+\gamma+\gamma'},0\right)\right.$$
$$+2\left[\gamma+\gamma'-\frac{10\gamma\gamma'}{\alpha+\gamma+\gamma'}\right]\left(\frac{\alpha}{\alpha+\gamma+\gamma'}\right)^2 H_{tuv}^{10}\left(\frac{\alpha\gamma+\alpha\gamma'}{\alpha+\gamma+\gamma'},0\right)$$
$$\left.+4\gamma\gamma'\left(\frac{\alpha}{\alpha+\gamma+\gamma'}\right)^4 H_{tuv}^{20}\left(\frac{\alpha\gamma+\alpha\gamma'}{\alpha+\gamma+\gamma'},0\right)\right\}. \tag{67}$$

Clearly, the integrals R_k^{tuv} needed for the evaluation of the damped-R12 integrals are simple linear combinations of the damped Hermite integrals (62), whose recursive evaluation is now considered.

To determine recurrence relations for the damped Hermite integrals, we proceed as follows:

$$H_{t+1,u,v}^{mn} = \frac{\mathrm{d}^t}{\mathrm{d}P_x^t}\frac{\mathrm{d}^u}{\mathrm{d}P_y^u}\frac{\mathrm{d}^v}{\mathrm{d}P_z^v}\frac{\mathrm{d}^m}{\mathrm{d}\mu^m}\frac{\mathrm{d}}{\mathrm{d}P_x}\exp\left(-\mu R_{PQ}^2\right)F_n\left(\nu R_{PQ}^2\right) \tag{68}$$

$$= -2\frac{\mathrm{d}^t}{\mathrm{d}P_x^t}\frac{\mathrm{d}^m}{\mathrm{d}\mu^m}\mu X_{PQ}H_{0uv}^{0n} - 2\nu\frac{\mathrm{d}^t}{\mathrm{d}P_x^t}X_{PQ}H_{0uv}^{m,n+1}. \tag{69}$$

By making use of the relations

$$\frac{\mathrm{d}^t}{\mathrm{d}P_x^t}X_{PQ} = t\frac{\mathrm{d}^{t-1}}{\mathrm{d}P_x^{t-1}} + X_{PQ}\frac{\mathrm{d}^t}{\mathrm{d}P_x^t}, \tag{70}$$

$$\frac{\mathrm{d}^m}{\mathrm{d}\mu^m}\mu = m\frac{\mathrm{d}^{m-1}}{\mathrm{d}\mu^{m-1}} + \mu\frac{\mathrm{d}^m}{\mathrm{d}\mu^m}, \tag{71}$$

we obtain:

$$H_{t+1,u,v}^{mn} = -2\left(t\frac{\mathrm{d}^{t-1}}{\mathrm{d}P_x^{t-1}} + X_{PQ}\frac{\mathrm{d}^t}{\mathrm{d}P_x^t}\right)\left(m\frac{\mathrm{d}^{m-1}}{\mathrm{d}\mu^{m-1}} + \mu\frac{\mathrm{d}^m}{\mathrm{d}\mu^m}\right)H_{0uv}^{0n} - 2\nu\left(t\frac{\mathrm{d}^{t-1}}{\mathrm{d}P_x^{t-1}} + X_{PQ}\frac{\mathrm{d}^t}{\mathrm{d}P_x^t}\right)H_{0uv}^{m,n+1}$$
$$= -2tmH_{t-1,u,v}^{m-1,n} - 2t\mu H_{t-1,u,v}^{mn} - 2X_{PQ}mH_{tuv}^{m-1,n} - 2X_{PQ}\mu H_{tuv}^{mn}$$
$$-2\nu tH_{t-1,u,v}^{m,n+1} - 2\nu X_{PQ}H_{tuv}^{m,n+1}. \tag{72}$$

Similar relations may be established for increments in u and v, giving the following three sets of six-term recurrence relations:

$$H_{t+1,u,v}^{mn}(\mu,\nu) = -2\mu\left[tH_{t-1,u,v}^{mn}(\mu,\nu) + X_{PQ}H_{tuv}^{mn}(\mu,\nu)\right]$$
$$-2m\left[tH_{t-1,u,v}^{m-1,n}(\mu,\nu) + X_{PQ}H_{tuv}^{m-1,n}(\mu,\nu)\right]$$
$$-2\nu\left[tH_{t-1,u,v}^{m,n+1}(\mu,\nu) + X_{PQ}H_{tuv}^{m,n+1}(\mu,\nu)\right], \tag{73}$$

$$H_{t,u+1,v}^{mn}(\mu,\nu) = -2\mu\left[uH_{t,u-1,v}^{mn}(\mu,\nu) + Y_{PQ}H_{tuv}^{mn}(\mu,\nu)\right]$$
$$-2m\left[uH_{t,u-1,v}^{m-1,n}(\mu,\nu) + Y_{PQ}H_{tuv}^{m-1,n}(\mu,\nu)\right]$$
$$-2\nu\left[uH_{t,u-1,v}^{m,n+1}(\mu,\nu) + Y_{PQ}H_{tuv}^{m,n+1}(\mu,\nu)\right], \tag{74}$$

$$H_{t,u,v+1}^{mn}(\mu,\nu) = -2\mu\left[vH_{t,u,v-1}^{mn}(\mu,\nu) + Z_{PQ}H_{tuv}^{mn}(\mu,\nu)\right]$$
$$-2m\left[vH_{t,u,v-1}^{m-1,n}(\mu,\nu) + Z_{PQ}H_{tuv}^{m-1,n}(\mu,\nu)\right]$$
$$-2\nu\left[vH_{t,u,v-1}^{m,n+1}(\mu,\nu) + Z_{PQ}H_{tuv}^{m,n+1}(\mu,\nu)\right]. \tag{75}$$

Using these recurrence relations, we may generate all the necessary integrals H_{tuv}^{mn}, starting from the source integrals

$$H_{000}^{mn}(\mu,\nu) = (-1)^m R_{PQ}^{2m}\exp\left(-\mu R_{PQ}^2\right)F_n\left(\nu R_{PQ}^2\right). \tag{76}$$

The evaluation of the Boys function $F_n(\nu R_{PQ}^2)$ may be carried out as discussed in Ref. [14].

Although the recurrence relations Eqs. (73)–(75) look rather complicated, some simplifications occur in important special cases. For example, whenever one of the two arguments μ or ν to $H_{tuv}^{mn}(\mu,\nu)$ is zero—as happens in many cases in Eqs. (63)–(67)—the six-term recurrence relations reduce to four-term recurrences. We also note that, in the evaluation of the Hermite integrals (63)–(67), only integrals of the type $H_{tuv}^{m0}(\mu,\nu)$ are needed. The integrals $H_{tuv}^{mn}(\mu,\nu)$ with $n>0$ were introduced only because they arise upon differentiation of $H_{tuv}^{m0}(\mu,\nu)$, playing the role of intermediates in the recurrence relations (73)–(75). Finally, it should be realized that, in the application of the recurrence relations (73)–(75), all integrals $H_{tuv}^{k,n}$ with $k<m$ and all integrals $H_{tuv}^{m,k}$ with $k>n$ must be evaluated before the integrals H_{tuv}^{mn} are attempted.

3. Conclusion

All integrals discussed in this paper have been implemented in a local version of the Dalton [17] program and will be used to investigate explicitly correlated methods for large molecular systems. For small systems, some preliminary calculations on systems such as H_2O, CO and F_2 have shown that the computation time does not differ significantly from previous R12 methods. For large systems, however, the new correlation factor is expected to reduce dramatically the number of significant integrals, thereby making the calculations more efficient.

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