Analytic Evaluation for Integrals of Product Gaussians with Different Moments of Distance Operators $(R_{C1}^{-n}R_{D1}^{-m}, R_{C1}^{-n}r_{12}^{-m}$ and $r_{12}^{-n}r_{13}^{-m}$ with n, m=0,1,2), Useful in Coulomb Integrals for One, Two and Three-Electron Operators

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Abstract. In the title, where R stands for nucleus-electron and r for electron-electron distances in practice of computation chemistry or physics, the (n,m)=(0,0) case is trivial, the (n,m)=(1,0) and (0,1) cases are well known, fundamental milestone in integration and widely used, as well as based on Laplace transformation with integrand $\exp(-a^2t^2)$. The rest of the cases are new and need the other Laplace transformation with integrand $\exp(-a^2t)$ also, as well as the necessity of a two dimensional version of Boys function comes up in case. These analytic expressions (up to Gaussian function integrand) are useful for manipulation with higher moments of inter-electronic distances, for example in correlation calculations. The equations derived help to evaluate the important Coulomb integrals

$$\int\rho(\mathbf{r}_1)R_{C1}^{-n}R_{D1}^{-m}d\mathbf{r}_1,$$
$$\int\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)R_{C1}^{-n}r_{12}^{-m}d\mathbf{r}_1d\mathbf{r}_2,$$
$$\int\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\rho(\mathbf{r}_3)r_{12}^{-n}r_{13}^{-m}d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3,$$

where $\rho(\mathbf{r}_i)$, called one-electron density, is a linear combination of Gaussian functions of position vector variable $\mathbf{r}_i$, capable to describe the electron clouds in molecules, solids or any media/ensemble of materials.

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INTRODUCTION

The Coulomb interaction between two charges in classical physics is $Q_1Q_2r_{12}^{-n}$, and is one of the most important fundamental interactions in nature. The power "n" has the rigorous value 2 describing the force, while as a consequence, the n=1 yields the energy. For electron-electron interactions, the exact theory says that the Coulomb interaction energy is represented by the two-electron energy operator r_{12}^{-1}.

Using GTO functions, which is

$$G_{Ai}(a,nx,ny,nz)\equiv (x_i-R_{Ax})^{nx}(y_i-R_{Ay})^{ny}(z_i-R_{Az})^{nz}\exp(-a|\mathbf{r}_i-\mathbf{R}_A|^2) \tag{1}$$

with a>0 and nx, ny, nz $\geq$0 benefiting its important property such as $G_{Ai}(a,nx,ny,nz)G_{Bi}(b,mx,my,mz)$ is also (a sum of) GTO, the Coulomb interaction energy for molecular systems is expressed finally with the linear combination of the famous integral

$$\int G_{A1}G_{B2}\, r_{12}^{-1}d\mathbf{r}_1d\mathbf{r}_2. \tag{2}$$

In Eq.1 we use double letters for polarization powers i.e., nx, ny and nz to avoid "index in index", nx=0,1,2,… are the s, p, d-like orbitals, etc.. The analytic evaluation [1-3] of the integral in Eq.2 has been fundamental and a mile stone in the history of computation chemistry. It is an important building block for the solution of the Schrödinger (partial differential) equation of many variables $(\mathbf{r}_1,…,\mathbf{r}_N)$, which still needs correction terms for its approximate solutions today. By this reason, in view of the extreme power of series expansion (trigonometric Fourier, polynomial Taylor, Pade, etc.) in numerical calculations, the

$$\int G_{A1}G_{B2}\, r_{12}^{-2}d\mathbf{r}_1d\mathbf{r}_2 \quad \text{as well as} \quad \int G_{A1}G_{B2}G_{C3}r_{12}^{-n}\, r_{13}^{-m}d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3 \tag{3}$$

with n,m=1,2 important terms have also come up in computation chemistry, for example, what we can call higher moments with respect to inter-electronic distances r_{ij}, though their analytical evaluations have not been provided yet. Another key to improve the existing Coulomb energy approximations is the use of e.g.

$$\{ \int [\rho(\mathbf{r}_1)]^p [\rho(\mathbf{r}_2)]^q r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 \}^t \qquad (4)$$

non-local moment expansion for correlation effects. Only approximate numerical expressions are available for evaluation, for example, for the second one in Eq.3 (or see equation 52 in ref.[4] with m=-n=1) the

$$<ijm|r_{12}^{-n} r_{13}^{-m}|kml> \approx \Sigma_p <ij|r_{12}^{-n}|pm><pm|r_{12}^{-m}|kl> , \qquad (5)$$

where the bracket notation [1-2] is used along without reducing product Gaussians to single Gaussians, as well as the GTO basis set {p} for expansion has to be a "good quality" for adequate approximation.

Not only two or three-electron integrals (Eqs.2-5), but (less effective) one-electron integrals

$$\int G_{A1} R_{C1}^{-2} d\mathbf{r}_1 \qquad (6)$$

can also be used as candidates, or the more general

$$\{ \int \rho^p R_{C1}^{-n} d\mathbf{r}_1 \}^t . \qquad (7)$$

Furthermore, if derivatives appear, such as $\int (\partial\rho(\mathbf{r}_1)/\partial x_1)^p R_{C1}^{-n} d\mathbf{r}_1$, $\int (\partial\rho(\mathbf{r}_1)/\partial x_1)^p \rho(\mathbf{r}_2)^q r_{12}^{-n} d\mathbf{r}_1 d\mathbf{r}_2$ or many other algebraic possibilities (recall that derivatives of ρ are used frequently even by empirical reasons, e.g. in the generalized gradient approximations), and ρ is given as linear combination of Gaussians, analytical evaluation of Eqs.3-7 are fundamental building blocks for analytical integral evaluation, since not only the products, but the derivatives of Gaussians in Eq.1 are Gaussians.

More general one-electron and the mixed case two-electron Coulomb integrals with $R_{C1}^{-n} R_{D1}^{-m}$ and $R_{C1}^{-n} r_{12}^{-m}$, resp.: These cases come up not only mathematically after the above cases, but in computation for electronic structures as well. Not going into too much details, we outline one way only as example: Applying the Hamiltonian twice for the ground state wave function simply yields $H^2 \Psi_0 = E_{0,electr} H \Psi_0 = E_{0,electr}^2 \Psi_0$, or $<\Psi_0|H^2|\Psi_0> = E_{0,electr}^2$. The H^2 preserves the linearity and hermetic property from operator H, and if e.g. HF-SCF single determinant S_0 approximates Ψ_0 via variation principle from $<S_0|H|S_0>$, the approximation $(<S_0|H^2|S_0>)^{1/2} \approx E_{0,electr}$ is better than $<S_0|H|S_0> \approx E_{0,electr}$, coming from basic linear algebraic properties of linear operators for the ground state. However, H^2 yields very hectic terms, the H_{ne}^2, $H_{ne}H_{ee}$ and H_{ee}^2 products show up, for example, yielding Coulomb operators belonging to the types indicated. Using $<S_0|H^2 S_0> = <HS_0|HS_0>$, the right side keeps the algorithm away from operators like $\nabla_1^2 r_{12}^{-1}$ at least.

Below, we use common notations, abbreviations and definitions: $F_L(v) \equiv \int_{(0,1)} \exp(-vt^2) t^{2L} dt$, the Boys function, L=0,1,2,...; GTO = primitive Gaussian-type atomic orbital, the $G_{Ai}(a,nx,ny,nz)$ in Eq.1; $\mathbf{R}_A \equiv$ (R_{Ax}, R_{Ay}, R_{Az}) or (x_A, y_A, z_A)= 3 dimension position (spatial) vector of (fixed) nucleus A; $R_{AB} \equiv |\mathbf{R}_A-\mathbf{R}_B|$= nucleus-nucleus distance; $R_{Ai} \equiv |\mathbf{R}_A-\mathbf{r}_i|$= nucleus-electron distance; $\mathbf{r}_i \equiv (x_i,y_i,z_i)$= 3 dimension position (spatial) vector of (moving) electron i; $r_{ij} \equiv |\mathbf{r}_i-\mathbf{r}_j|$= electron-electron distance.

One-electron spherical Coulomb integral for R_{C1}^{-2}

Now $R_{C1} \equiv |\mathbf{R}_C-\mathbf{r}_1|$ and $R_{P1} \equiv |\mathbf{R}_P-\mathbf{r}_1|$, and we evaluate the one-electron spherical Coulomb integral for $G_{P1}(p,0,0,0)= \exp(-p R_{P1}^2)$ in Eq.1 analytically, i.e. the

$$V_{P,C}^{(n)} \equiv \int_{(R3)} \exp(-p R_{P1}^2) R_{C1}^{-n} d\mathbf{r}_1 , \qquad (8)$$

for which n=1 is well known and 2 is a new expression below. The idea comes from the Laplace transformation for n= 1 and 2 respectively as

$$R_{C1}^{-1} = \pi^{-1/2} \int_{(-\infty,\infty)} \exp(-R_{C1}^2 t^2) dt , \qquad (9)$$

$$R_{C1}^{-2} = \int_{(-\infty,0)} \exp(R_{C1}^2 t) dt = \int_{(0,\infty)} \exp(-R_{C1}^2 t) dt . \qquad (10)$$

In this way (using Appendixes 1-2 after the e.g. middle part in Eq.10) the

$V_{P,C}^{(2)} = \int_{(-\infty,0)} \int_{(R3)} \exp(-p R_{P1}^2) \exp(R_{C1}^2 t) d\mathbf{r}_1 dt = \int_{(-\infty,0)} \int_{(R3)} \exp(pt(p-t)^{-1} R_{CP}^2) \exp((t-p)R_{S1}^2) d\mathbf{r}_1 dt =$
$\int_{(-\infty,0)} (\pi/(p-t))^{3/2} \exp(pt(p-t)^{-1} R_{CP}^2) dt$. Using u:=t/(p-t) changes the domain t in $(-\infty,0) \to$ u in (-1,0), $V_{P,C}^{(2)} =$ $\pi^{3/2} p^{-1/2} \int_{(-1,0)} (u+1)^{-1/2} \exp(p R_{CP}^2 u) du$, and using w:= $(u+1)^{1/2}$ changes the domain u in $(-1,0) \to$ w in (0,1) and yields

$$V_{P,C}^{(2)} = (2\pi^{3/2}/p^{1/2}) \int_{(0,1)} \exp(p R_{CP}^2 (w^2-1)) dw = (2\pi^{3/2}/p^{1/2}) e^{-v} F_0(-v) , \qquad (11)$$

where $F_0(v)$ is Boys function with $v \equiv p R_{CP}^2$. For Eq.11 the immediate minor/major values come from $1 \le$ $\exp(pR_{CP}^2 w^2) \le \exp(v \equiv pR_{CP}^2)$ if $0 \le w \le 1$ as

$$0 < \exp(-v) < [p^{1/2}/(2\pi^{3/2})] V_{P,C}^{(2)} < 1, \qquad (12)$$

and for a comparison, we recall the well known expression [5] for n=1

$$V_{P,C}^{(1)} = (2\pi/p) \int_{(0,1)} \exp(-p R_{CP}^2 w^2) dw = (2\pi/p)F_0(v) \qquad (13)$$

with immediate minor/major values

$$0 < \exp(-v) \; < \; [p/(2\pi)] \; V_{P,C}^{(1)} \; < \; 1. \tag{14}$$

Note that point $\mathbf{R}_S$ can be calculated by the m=2 case in Appendix 2, but its particular value drops, because integral value in Appendix 1 is invariant by shifting a Gaussian in R3 space. Eqs.12 and 14 tell that up to normalization factor with p, the $V_{P,C}^{(1)}$ and $V_{P,C}^{(2)}$ are in same range, roughly in (0,1). The ratio of the two is easily obtained when $R_{CP}=0$, then the integrands become unity, and

$$V_{P,C}^{(2)}(R_{CP}=0)/\; V_{P,C}^{(1)}(R_{CP}=0)= (2\pi^{3/2}/p^{1/2})/(2\pi/p)= (\pi p)^{1/2} \tag{15}$$

as well as for n=1 and 2 the $\lim V_{P,C}^{(n)}=0$ if $R_{CP}\to\infty$.

Note that the integral is the type $\int\exp(-w^2)dw$ in Eq.13, a frequent expression coming up in physics, but contrary, the $\int\exp(w^2)dw$ has come up in Eq.11. The latter is infinite on domain $(0,\infty)$, otherwise similar algebraic blocks have come up in Eqs.8-14 for n=1 vs. 2, which is not surprising; but, the evaluation of $F_0(v)$ differs significantly from $F_0(-v)$. Integration in Eq.13 can be related to the "erf" function (i.e. for $F_0(v>0)$) in a calculation which is standard in programming, but lacks analytical expression, as well as the "erf" is inbuilt function in program languages like FORTRAN. However, integration in Eq.11 cannot be related to any inbuilt function like "erf", but its evaluation numerically belongs to standard devices, mainly because the integrand is a simple monotonic elementary function.

Note that, 1., The algebraic keys are in Eqs.9-10 and Appendix 2 to evaluate Eq.8 analytically - up to Gaussian function $\exp(\pm w^2)$ in the integrand. If not GTO but Slater-type atomic orbitals ($|\mathbf{r}_i\text{-}\mathbf{R}_A|^2 \to |\mathbf{r}_i\text{-}\mathbf{R}_A|$ replacement) is used in Eq.1, i.e. not R_{P1}^2 but R_{P1} shows up in the power of Eq.8, the evaluation for the corresponding integral in Eq.8 is far more difficult, stemming from the fact that the convenient device in Appendix 2 cannot be used. A simple escape route is to use the approximation $\exp(-pR_{P1})\approx \Sigma_{(i)}c_i G_{P1}(a_i,0,0,0)$, which is well known in molecular structure calculations, see the idea of STO-3G basis sets and higher levels in which one does not even need many terms in the summation but, in fact in this way, one loses the desired complete analytical evaluation for the original integral $\int_{(R3)}\exp(-pR_{P1})R_{C1}^{-n} d\mathbf{r}_1$. 2., In Eqs.9-10 the power correspondence in the integrand and integral value for n=1 vs. 2 is $R_{C1}^{-1} \leftrightarrow R_{C1}^{2}$ vs. $R_{C1}^{-2} \leftrightarrow R_{C1}^{2}$, what is the seed of trick for analytical evaluation, and may indicates the way for further generalizations. 3., Fast, accurate and fully numerical integration for one-electron Coulomb integrals in Eq.8 is available for any n≥1 integer and non-integer values of n, the general numerical integral scheme is widely used in DFT correlation calculations based on Voronoi polygons, Lebedev spherical integration and Becke' scheme in R3, see references in ref.[6]. However, this numerical process is definitely not applicable for two and three-electron Coulomb integrals in R6 or R9, respectively because it is slow in computation; the reason being that the at least K=1000 points for numerical integration becomes K^2 or K^3, respectively, that is, the computation time is K or K^2 times longer, respectively.

One-electron non-spherical Coulomb integral for R_{C1}^{-2}

If the more general $G_{P1}(p,nx,ny,nz)$ is used, Eq.8 generates the analytical evaluation as a seed, and no further trick needed than Eqs.9-10, the only formula necessary is how to shift the center of polynomials (Appendix 3, the alternative is Appendix 4). We use the notations $^{full}V_{P,C}^{(n)}$ and $V_{P,C}^{(n)}$, the former stands for any (spherical and non-spherical, nx+ny+nz≥0) quantum number, while the latter denotes the simplest spherical (1s-like) case, nx=ny=nz=0. With the help of Appendixes 1 and 3, we show the evaluation for

$$^{full}V_{P,C}^{(2)}\equiv \int_{(R3)} G_{P1}(p,nx1,ny1,nz1) \; R_{P1}^{-2} \, d\mathbf{r}_1 \; . \tag{16}$$

With short hand abbreviations (for sum and multiplication operators)

$$\Sigma_1 \equiv \Sigma_{i1=0}^{\;nx1}\Sigma_{j1=0}^{\;ny1}\Sigma_{k1=0}^{\;nz1} \binom{nx1}{i1}\binom{ny1}{j1}\binom{nz1}{k1} \quad \text{for even i1, j1, k1 only} \tag{17}$$

$$n1 \equiv nx1+ny1+nz1 \tag{18}$$

$$m1 \equiv i1+j1+k1 \tag{19}$$

$$\Gamma_1\equiv \Gamma((i1+1)/2)\; \Gamma((j1+1)/2)\; \Gamma((k1+1)/2) \tag{20}$$

$$D \equiv (x_P-x_C)^{nx1-i1}(y_P-y_C)^{ny1-j1}(z_P-z_C)^{nz1-k1} \tag{21}$$

one obtains

$$^{full}V_{P,C}^{(2)}= 2\Sigma_1\Gamma_1 D\; p^{-(m1+1)/2} \int_{(0,1)} (w^2-1)^{n1-m1}\, w^{m1} \exp(p\, R_{CP}^2(w^2-1))\, dw \; . \tag{22}$$

If n1=0, then Eq.22 reduces to Eq.11 as expected. Since m1 is always even via Eq.17, it yields that integrand in Eq.22 is always linear combination of $w^{2L}\exp(p\, R_{CP}^2(w^2-1))$ for L=0,1,2,…, i.e. Boys function can be recalled again as in Eq.11, that is, $e^{-v}F_L(-v)$ with $v\equiv p\, R_{CP}^2$.

The expression for n=1 (in R_{C1}^{-n}) comes out in analogous way, and the final expression is

$$^{full}V_{P,C}{}^{(1)} = 2p^{-1}\pi^{-1/2}\Sigma_1\Gamma_1 D \ p^{-m1/2}\int_{(0,1)}(-w^2)^{n1-m1} (1-w^2)^{m1/2} \exp(-p \ R_{CP}{}^2 \ w^2) \ dw. \tag{23}$$

Eq.23 reduces to Eq.13 if n1=0 in Eq.18 as expected, and since powers of w^2 appear, it makes the linear combination of Boys functions $F_L(v)$ with $v \equiv p \ R_{CP}{}^2$. De-convolution of Boys functions from $F_L(\pm v)$ to $F_0(\pm v)$ can be found in Appendix 5. Note that D in Eq.21 dynamically provides signs.

One-electron spherical Coulomb integral for $R_{C1}{}^{-n}R_{D1}{}^{-m}$ with n, m=1,2

We evaluate analytically the one-electron spherical Coulomb integral

$$V_{P,CD}{}^{(n,m)} \equiv \int_{(R3)}\exp(-pR_{P1}{}^2)R_{C1}{}^{-n}R_{D1}{}^{-m}d\mathbf{r}_1 . \tag{24}$$

Let us take the example of (n,m)= (1,2), the algorithm is straightforward for other cases of (n,m). Using Eq.9 and e.g. the far right side in Eq.10, as well as Appendixes 1-2, finally

$$V_{P,CD}{}^{(1,2)} = \pi\int_{t=(-\infty,\infty)}\int_{u=(0,\infty)}g^{-3/2}\exp(-f/g)dudt \tag{25}$$

$$g \equiv p + t^2 + u \tag{26}$$

$$f \equiv p \ t^2 \ R_{PC}{}^2 + p \ u \ R_{PD}{}^2 + u \ t^2 \ R_{CD}{}^2 . \tag{27}$$

Like for Eq.11 or Eq.13, by simple substitution one can end up with $\int_{(0,1)}\int_{(0,1)}(\dots)dtdu$ integration.

Two and three-electron spherical Coulomb integrals:
Two-electron spherical Coulomb integral for $r_{12}{}^{-2}$, the (n,m)=(2,0) or (0,2) case

$$V_{PQ}{}^{(n)} \equiv \int_{(R6)} \exp(-p \ R_{P1}{}^2) \exp(-q \ R_{Q2}{}^2) \ r_{12}{}^{-n} \ d\mathbf{r}_1 d\mathbf{r}_2 \tag{28}$$

is considered, for which n=1 is well known and 2 is a new expression below. Re-indexing Eq.11 and 13 for C→2 and R→r (i.e. electron 2 takes the role of nucleus C algebraically) yields

$$V_{P,C}{}^{(2)} = \int_{(R3)} \exp(-p \ R_{P1}{}^2)r_{12}{}^{-2} \ d\mathbf{r}_1 = (2\pi^{3/2}/p^{1/2}) \int_{(0,1)}\exp(p \ R_{P2}{}^2 \ (w^2-1))dw, \tag{29}$$

$$V_{P,C}{}^{(1)} = \int_{(R3)} \exp(-p \ R_{P1}{}^2)r_{12}{}^{-1} \ d\mathbf{r}_1 = (2\pi/p) \int_{(0,1)}\exp(-p \ R_{P2}{}^2 \ w^2)dw . \tag{30}$$

Finally, with $v \equiv pqR_{PQ}{}^2/(p+q)$

$$V_{PQ}{}^{(2)} = 2\pi^3(pq)^{-1/2}(p+q)^{-1}\int_{(0,1)} \exp(v(w^2-1))dw = (2\pi^3(pq)^{-1/2}(p+q)^{-1})e^{-v}F_0(-v), \tag{31}$$

where $F_0(v)$ is the Boys function, and the immediate minor/major values come from $1 \leq \exp(vw^2) \leq \exp(v)$ if $0 \leq w \leq 1$ as

$$0 < \exp(-v) \ < \ [(pq)^{1/2}(p+q)/(2\pi^3)]V_{PQ}{}^{(2)} \ < \ 1. \tag{32}$$

For comparison, we recall the well known expression for n=1 as

$$V_{PQ}{}^{(1)} = (2\pi^{5/2}/(pq)) \int_{(0,c)} \exp(-pqR_{PQ}{}^2 \ w^2)dw \tag{33}$$

with $c \equiv (p+q)^{-1/2}$ in the integration domain, it can also be expressed with Boys or "erf" functions, and the immediate minor/major values (from w:=c vs. 0 in the integrand)

$$0 < \exp(-v) \ < \ [pq(p+q)^{1/2}/(2\pi^{5/2})]V_{PQ}{}^{(1)} \ < \ 1. \tag{34}$$

In Eqs.31-34 the expressions are symmetric to interchange of p and q, as expected. The ratio of the two is easily obtained when $R_{PQ}=0$, then the integrands become unity, and

$$V_{PQ}{}^{(2)}(R_{PQ}=0)/ \ V_{PQ}{}^{(1)}(R_{PQ}=0)= (2\pi^3(pq)^{-1/2}(p+q)^{-1}/(2c\pi^{5/2}/(pq))= (\pi pq/(p+q))^{1/2} \tag{35}$$

as well as for n=1 and 2 the $\lim V_{PQ}{}^{(n)}=0$ if $R_{PQ}\to\infty$.

Two-electron spherical Coulomb integral for the mixed term $R_{C1}{}^{-n}r_{12}{}^{-m}$ with n, m=1,2

$$\int_{(R6)}\exp(-pR_{P1}{}^2)\exp(-qR_{Q2}{}^2)R_{C1}{}^{-1}r_{12}{}^{-1}d\mathbf{r}_1 d\mathbf{r}_2 = (2\pi^2/q)\int_{u=(0,1)}\int_{t=(-\infty,\infty)} g^{-3/2}\exp(-f/g) \ dtdu \tag{36}$$

$$f \equiv pqR_{PQ}{}^2u^2 + pR_{PC}{}^2t^2 + qR_{QC}{}^2u^2t^2 \tag{37}$$

$$g \equiv p + qu^2 + t^2 \tag{38}$$

Alternatively, with $\mathbf{R}_W = (p\mathbf{R}_P + qu^2\mathbf{R}_Q)/(p+qu^2)$ and Boys function

$$\int_{(R6)}\exp(-pR_{P1}{}^2)\exp(-qR_{Q2}{}^2)R_{C1}{}^{-1}r_{12}{}^{-1}d\mathbf{r}_1 d\mathbf{r}_2 = (4\pi^2/q)\int_{(0,1)}F_0(gR_{WC}{}^2)g^{-1}\exp(-f/g)du \tag{39}$$

$$f \equiv pqR_{PQ}{}^2u^2 \tag{40}$$

$$g \equiv p + qu^2 , \tag{41}$$

where R_{WC} depends on u as $gR_{WC}{}^2 = (p+qu^2)|\mathbf{R}_W - \mathbf{R}_C|^2 = |p\mathbf{R}_P + qu^2\mathbf{R}_Q - g\mathbf{R}_C|^2$. Eqs.39-41 vs. Eqs.36-38 shows us something about the two dimensional version of the Boys function, see below. The algorithm is straightforward for other cases of (n,m).

Three-electron spherical Coulomb integral for $r_{12}^{-n}r_{13}^{-m}$ with n,m=1,2

$$V_{PQS}^{(n,m)} \equiv \int_{(R9)} \exp(-p\,R_{P1}^2)\,\exp(-q\,R_{Q2}^2)\,\exp(-s\,R_{S3}^2)\,r_{12}^{-n}r_{13}^{-m}\,d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \qquad (42)$$

Eqs.29 and 30 provide the key substitutions for integrating out with $\mathbf{r}_2$ and $\mathbf{r}_3$. For example, for n=m=1,

$$V_Q^{(n=1)} = \int_{(R3)}\exp(-qR_{Q2}^2)r_{12}^{-1}d\mathbf{r}_2 = (2\pi/q)\int_{(0,1)}\exp(-qR_{Q1}^2 u^2)du = (2\pi/q)F_0(qR_{Q1}^2), \qquad (43)$$

$$V_S^{(m=1)} = \int_{(R3)}\exp(-sR_{S3}^2)r_{13}^{-1}d\mathbf{r}_3 = (2\pi/s)\int_{(0,1)}\exp(-sR_{S1}^2 t^2)dt = (2\pi/s)F_0(sR_{S1}^2). \qquad (44)$$

Eqs.42-44 and Appendixes 1-2 yield finally

$$V_{PQS}^{(1,1)} = (4\pi^{7/2}/(qs))\int_{(0,1)}\int_{(0,1)} g^{-3/2}\exp(-f/g)du\,dt \qquad (45)$$

$$f \equiv pqR_{PQ}^2 u^2 + psR_{PS}^2 t^2 + qsR_{QS}^2 u^2 t^2 \qquad (46)$$

$$g \equiv p + qu^2 + st^2 . \qquad (47)$$

This integration can be done numerically, see next section, which is still more stable and more reliable than Eq.5 because the latter is basis set choice dependent and much more complex. For n and/or m=2 cases not Eq.30 but Eq.29 must be applied analogously to evaluate Eq.42, the algorithm is straightforward again.

The way to Eqs.45-47 was to apply Eqs.43-44, then Appendixes 1-2, yielding two dimensional integral on the unit square. Another way, analogous to Eqs.39-41 yielding one dimensional integral on the unit segment is to apply only Eq.43 and not Eq.44 or vice versa, then Appendixes 1-2, and then Eq.33. Finally, with $\mathbf{R}_V \equiv (p\mathbf{R}_P + qu^2\mathbf{R}_Q)/(p + qu^2)$ one obtains

$$V_{PQS}^{(1,1)} = (4\pi^{7/2}/(qs)) \int_{(0,1)} h(u)\, g^{-1}\exp(-f/g)\,du \qquad (48)$$

$$h(u) \equiv \int_{(0,c)}\exp(-g\,s\,R_{VS}^2 w^2)dw \qquad (49)$$

$$c \equiv (g+s)^{-1/2} \qquad (50)$$

$$f \equiv pqR_{PQ}^2 u^2 \qquad (51)$$

$$g \equiv p + qu^2 . \qquad (52)$$

Eqs.45-47 and Eqs.48-52 both yield the same value for $V_{PQS}^{(1,1)}$, of course, as well as h(u) in Eq.49 is the pre-stage of Boys function F_0 as in Eq.33. Here again as above, Eqs.48-52 can be considered as the two dimensional version of Boys function wherein a one dimensional Boys function is in the integrand. See Appendix 6 how Coulomb operator $r_{12}^{-n}r_{13}^{-m}$ can come up.

The two dimensional Boys function, its pre-equation and integration

If we consider the right hand side of Eq.39 or Eq.48 as a kind of two dimensional Boys function, one can see that a one dimensional Boys function appears in its integrand. We draw attention to the fact, that at the beginning, i.e. in "seed equations" Eqs.11 and 13 we obtained the one dimensional Boys function F_0 via the term $g^{-3/2}\exp(-f/g)$ in the integrand as a pre-equation, (recall the derivation in middle stage e.g. as $V_{P,C}^{(2)} = \pi^{3/2}\int_{(-\infty,0)}g^{-3/2}\exp(f/g)dt$ with $f \equiv pR_{CP}^2 t$ and $g \equiv p-t$), and when the two dimensional cases came up, the same term showed up in the integrand again, but instead of function set {f(t), g(t)}, the {f(u,t), g(u,t)}, see Eqs.25-27, 36-38 and Eqs.45-47. The $g^{-3/2}\exp(f/g)$ is the core part of integrands for all cases in the main title of this work. Finer property is that, $f=f((-u)^K,(-t)^L)$ and $g=g((-u)^K,(-t)^L)$ are 2nd and 1st order polynomials, respectively, with respect to $(-u)^K$ and $(-t)^L$, where K, L = 1 or 2; wherein the middle part of Eq.10 has been used, alternatively, with the far right side of Eq.10 the -u→u and -t→t transformations should be done in this sentence. The K, L= 1 generates $\exp(w^2)$, while the 2 generates $\exp(-w^2)$ type Gaussians in the integrand.

Appendix 1: For m= 1 and 2, the $\int_{(0,\infty)} x^n \exp(-ax_1^m)dx_1 = \Gamma[(n+1)/m]/(m\,a^{(n+1)/m})$ holds for a>0. If m=2 and n=0 $\Rightarrow$ $\int_{(R3)}\exp(-ar_1^2)d\mathbf{r}_1 = (\int_{(-\infty,\infty)}\exp(-ax_1^2)dx_1)^3 = (\pi/a)^{3/2}$. If m=2 $\Rightarrow$ $\int_{(-\infty,\infty)} x^n \exp(-ax_1^2)dx_1 = \Gamma[(n+1)/2]/a^{(n+1)/2}$ for even n, but zero if n is odd. The gamma function is $\Gamma[n+1]= n!$ for n=0,1,2,…, with $\Gamma[1/2] = \pi^{1/2}$ and $\Gamma[n+1/2] = 1\times3\times5\times\ldots(2n-1)\,\pi^{1/2}/2^n$ for n=1,2,… . The $erf(x) \equiv 2\pi^{-1/2}\int_{(0,x)}\exp(-w^2)dw$, for which $erf(\infty)=1$.

Appendix 2: The product of two Gaussians, $G_{J1}(p_J,0,0,0)$ with J=1,…,m=2 is another Gaussian centered somewhere on the line connecting the original Gaussians, but a more general expression for m>2 comes from the elementary

$$\Sigma_J p_J R_{J1}^2 = (\Sigma_J p_J) R_{W1}^2 + (\Sigma_J \Sigma_K p_J p_K R_{JK}^2)/(2\Sigma_J p_J) \qquad (53)$$

$$\mathbf{R}_W \equiv (\Sigma_J p_J \mathbf{R}_J)/(\Sigma_J p_J) \qquad (54)$$

where $\Sigma_{J\,or\,K} \equiv \Sigma_{(J\,or\,K=1\,to\,m)}$ and $R_{J1} \equiv |\mathbf{R}_J - \mathbf{r}_1|$ for $\exp(\Sigma_J c_J) = \Pi_{(J=1\,to\,m)}\exp(c_J)$, keeping in mind that $R_{JJ}=0$, and the m centers do not have to be collinear. For m=2, this reduces to

$$p R_{P1}^2 + q R_{Q1}^2 = (p+q) R_{W1}^2 + pqR_{PQ}^2/(p+q) \tag{55}$$

yielding the well known and widely used

$$G_{P1}(p,0,0,0) \, G_{Q1}(q,0,0,0) = G_{W1}(p+q,0,0,0)exp(-pqR_{pq}^2/(p+q)) . \tag{56}$$

We also need the case m=3, which explicitly reads as

$$p R_{P1}^2 + q R_{Q1}^2 + s R_{S1}^2 = (p+q+s) R_{W1}^2 + (pqR_{PQ}^2+psR_{PS}^2+qsR_{QS}^2)/(p+q+s) . \tag{57}$$

Only the $G_{W1}(p+q+s,0,0,0)$ depends on electron coordinate r_1 in Eqs.A56-57, not the other multiplier, indicating that the product of Gaussians decomposes to (sum of) individual Gaussians, (s=0 reduces Eq.57 to Eq.56).

Appendix 3: Given a single power term polynomial at R_P, we need to rearrange or shift it to a given point R_S. For variable x, this rearrangement is $(x–x_P)^n = \Sigma_{i=0 \text{ to } n} c_i (x–x_S)^i$, which can be solved systematically and immediately for c_i by the consecutive equation system obtained from the 0,1,…n^{th} derivative of both sides at x:= x_S, yielding

$$POLY(x,P,S,n) \equiv (x-x_P)^n = \Sigma_{i=0 \text{ to } n} (^n_i)(x_S-x_P)^{n-i} (x-x_S)^i , \tag{58}$$

where $(^n_i)=n!/(i!(n-i)!)$. If $x_S=0$, it reduces to the simpler well known binomial formula as $(x–x_P)^n = \Sigma_{i=0 \text{ to } n} (^n_i)(-x_P)^{n-i}x^i$.

Appendix 4: The Hermite Gaussians are defined as

$$H_{Ai}(a,t,u,v) \equiv (\partial/\partial R_{Ax})^t(\partial/\partial R_{Ay})^u(\partial/\partial R_{Az})^v exp(-a|r_i-R_A|^2) , \tag{59}$$

and $H_{Ai}(a,2,0,0) = (\partial/\partial R_{Ax})^2 exp(-a R_{Ai}^2) = (\partial/\partial R_{Ax})[-2a (R_{Ax} -x_i) exp(-a R_{Ai}^2)] =$
$-2a exp(-a R_{Ai}^2) + 4a^2(R_{Ax} -x_i)^2 exp(-a R_{Ai}^2) = -2aG_{Ai}(a,0,0,0) + 4a^2G_{Ai}(a,2,0,0)$ is an example that Hermite Gaussians are linear combination of Cartesian Gaussians.

Appendix 5: De-convolution of Boys functions from $F_L(v) \equiv \int_{(0,1)} exp(-vt^2)t^{2L}dt$ to $F_0(v) = \int_{(0,1)} exp(-vt^2)dt$ for v>0 and v≤0 comes from the help of partial integration ($\int f'g=[fg]-\int fg'$) on interval [0,1] with $f'=t^M$, M≠-1 and $g=exp(-vt^2)$, and K:=M+2 thereafter. After elementary calculus:

$$2v\int_{(0,1)}t^K exp(-vt^2)dt = (K-1)\int_{(0,1)}t^{K-2} exp(-vt^2)dt - exp(-v) \tag{60}$$

for K=0,-1, ±2, ±3, ±4,…, i.e. any integer except 1, and v is any real number, i.e. v>0 and v≤0. (For K=1 the $2v\int_{(0,1)}t exp(-vt^2)dt = 1-exp(-v)$ by $\int g' exp(g(t))dt = exp(g(t))$.) In Boys functions the K=2L ≥0 is even, so K=1 is jumped, and with K:=2L+2 Eq.60 yields

$$2vF_{L+1}(v) = (2L+1)F_L(v) – exp(-v) . \tag{61}$$

The value of L recursively goes down to zero, and the value of $F_0(v)$ is needed only at the end. The v=0 case is trivial and the v>0 is well known in the literature but, the v<0 cases are also needed for cases described in the main title of this work.

Appendix 6: The cardinality in the set generated by electron-electron repulsion operator $H_{ee}^2 = (\Sigma_{i=1,N} \Sigma_{j=i+1...N} r_{ij}^{-1})^2$ comes from elementary combinatorics. H_{ee} contains $(^N_2)=N(N-1)/2$ and H_{ee}^2 contains $N^2(N-1)^2/4$ terms. In relation to integration with single Slater determinant, it contains three kinds of terms: r_{12}^{-2}, $r_{12}^{-1}r_{13}^{-1}$ and $r_{12}^{-1}r_{34}^{-1}$ as

$$<S*|H_{ee}^2|S> = (^N_2)\{<S*|r_{12}^{-2}|S> +2(N-2)<S*|r_{12}^{-1}r_{13}^{-1}|S> +(^{N-2}_2)<S*|r_{12}^{-1}r_{34}^{-1}|S>\} . \tag{62}$$

The control sum $(^N_2) +2(N-2)(^N_2) + (^N_2)(^{N-2}_2) = N^2(N-1)^2/4$ holds, as well as the magnitude of cardinality of individual terms on the right in Eq.62 are N^2, N^3 and N^4, respectively.

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