On the Computation of Two-center Coulomb Integrals over Slater Type Orbitals Using the Poisson Equation

Sedat Gümüş

Department of Physics, Education Faculty, Ondokuz Mayis University, 05189 Amasya, Turkey

Reprint requests to Prof. S. G.; E-mail: sedatg@omu.edu.tr

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In this paper, a new analytical formula has been derived for the two-center Coulomb integrals over Slater type orbitals using the Poisson equation. The obtained results from constructed computer program for the presented formula have been compared with the available literature and it is seen that the efficiency of the presented algorithm for a wide range of quantum numbers, orbital exponents and internuclear distances is satisfactory.

Key words: Coulomb Integral; Slater Type Orbital; Poisson Equation; Overlap Integral.

1. Introduction

The evaluation of multicenter integrals excess is a basic step used for determining the ab initio and density functional theory molecular structure calculations. As is well-known, the ab initio calculations using linear combination of atomic orbitals (LCAO) approach strongly depend on the choice of the basis functions for the electronic distributions they provide. A good atomic orbital basis should decay exponentially for large distances [1] and also satisfy Kato's conditions for analytical solution of the approximate Schrödinger equation [2].

In the literature, the most commonly used basis sets are Slater type orbitals (STOs) and Gaussian type orbitals (GTOs). Ab initio calculations are carried out mostly by using GTOs due to the fact that numerous multicenter integrals over GTOs can be evaluated easily. Unfortunately, GTOs fail to satisfy the above mathematical conditions for atomic electronic distributions. Strictly speaking, STOs are potentially overcomplete basis sets suitable for electronic structure calculations of atomic and molecular systems. On the other hand, the use of STOs has been prevented by the fact that their multicenter integrals are extremely difficult to evaluate for polyatomic molecules. A detailed discussion and historical developments for multicenter integrals over STOs can be found in [3 – 7] and quotations therein.

As can be seen clearly from the literature, during to the last four decades, several groups have improved different methods such as the Zeta functions method [8], the elliptical coordinates method [9], the Fourier transform method [10], the Gaussian transform method [11], and one-center expansion methods [12 – 14] for the evaluation of multicenter integrals. However, the calculation of the electronic structure of polyatomic systems (not necessarily linear) was not achieved. On the other hand, this situation is changing at the present and might be inverted in the near future due to the advance in applied mathematics and computer science [3 – 7, 15 – 17].

From now on, several software packages are available to solve the problems surrounding ab initio and density functional theory over STOs. As the requisite integrals have been evaluated analytically, STOP package (*S*later *T*ype *O*rbital *P*ackage) was developed for ab initio SCF molecular properties [18]. SMILES (*S*later *M*olecular *I*ntegrals for *L*arge *E*lectronic *S*ystems) has suggested various basis sets, geometry optimization and CI. The electronic structure of polyatomic molecules employing up to about four hundred Slater functions of s, p, d, f, g and h types can be calculated with an acceptable cost by the present version of SMILES. The more recent excellent paper by Rico et. al. [3] is advised for the reader interested in the calculation of molecular properties using STOs.

One of the most important types of multicenter integrals is the two-center Coulomb integral what has to be calculated accurately and efficiently. During the calculation procedure, the number of these integrals ranges from hundreds of thousands, in small systems, to millions in medium size when LCAO-MO approximation is employed in the calculations. At the same time, these type of integrals also contribute to the total energy of the molecule which requires to a precision sufficient for small fraction changes to be evaluated. In practice, an error in the range of $10^{-8}-10^{-10}$ in integrals will deteriorate the energy by an amount of 10^{-3} atomic units.

The Coulomb integrals, C, can be related to the Overlap integrals, S, by the Poisson equation $\nabla^2 C = -4\pi S$ [9h, k]. On the other hand, although this approach is mathematically delicate, it has not been applied to the Coulomb integrals except for the early works of Ruedenberg et al. [9h, k] and the recent works of Hierse and Oppeneer [16] and Steinborn and Weniger [17]. Even though there are many successful analytical formulas on the two-center Coulomb integrals over STOs in the literature, several difficulties appear in the calculations. These difficulties appear especially for nearly equal or equal orbital exponents, small or higher internuclear distances.

The aim of this paper is twofold. The first one is to present a new analytical formula for the calculation of two-center Coulomb integrals running in a wide range of quantum numbers, orbital exponents and internuclear distances by means of the Poisson equation. The second one is to propose a reliable reference for testing the results of the other alternative algorithms. Atomic units (a. u.) will be used throughout this paper.

2. General Definitions

The two-center Coulomb integrals are defined as follows:

$$
\begin{aligned}
&C^{n_2 l_2 m_2, n'_2 l'_2 m'_2}_{n_1 l_1 m_1, n'_2 l'_1 m'_1}(\zeta_1, \zeta'_1, \zeta_2, \zeta'_2; R) \\
&= \int\int \chi^*_{n_1 l_1 m_1}(\zeta_1, \vec{r}_{1a}) \chi_{n'_1 l'_1 m'_1}(\zeta'_1, \vec{r}_{1a}) \\
&\qquad \cdot \frac{1}{r_{12}} \chi^*_{n_2 l_2 m_2}(\zeta_2, \vec{r}_{2b}) \chi_{n'_2 l'_2 m'_2}(\zeta'_2, \vec{r}_{2b}) \mathrm{d}V_1 \mathrm{d}V_2,
\end{aligned}
\tag{1}
$$

where R is the internuclear distance and χ are normalized complex or real STOs.

A STO is given by

$$
\chi_{nlm}(\zeta, \vec{r}) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}} r^{n-1} e^{-\zeta r} S_{lm}(\theta, \varphi). \tag{2}
$$

Here ζ is the orbital exponent and the function $S_{lm}(\theta, \varphi)$ is complex or real spherical harmonic defined by [19]:

$$
S_{lm}(\theta, \varphi) = P_{l|m|}(\cos\theta) \Phi_m(\varphi), \tag{3}
$$

where $\Phi_m(\varphi)$ is an orthonormal function given by

$$
\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{\mathrm{i}m\varphi} \tag{4a}
$$

for complex spherical harmonic and

$$
\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}} \begin{cases} \cos m\varphi & \text{for } m \geq 0, \\ \sin |m|\varphi & \text{for } m < 0, \end{cases} \tag{4b}
$$

for real spherical harmonic. In (3), P_{lm} is the normalized associated Legendre function and can be defined by Rodrigues' formula [9j] as

$$
\begin{aligned}
P_{lm}(\cos\theta) &= W_{lm}(1-\cos^2\theta)^{\frac{m}{2}} \\
&\quad \cdot \sum_{i=0}^{l-m} A^i_{lm}(\cos\theta + 1)^i (\cos\theta - 1)^{l-m-i},
\end{aligned}
\tag{5}
$$

with

$$
W_{lm} = \left[\frac{(2l+1)F_\lambda(l+m)}{2^{2l+1}F_m(l)}\right]^{1/2}, \tag{6a}
$$

$$
A^i_{lm} = F_i(l) F_{i+m}(l). \tag{6b}
$$

In (6), the quantity $F_i(j) = \frac{j!}{i!(j-i)!}$ is an usual binomial coefficient.

The later step we work on is to try to evaluate the two-center Coulomb integral by means of Poisson equation [9g, h],

$$
\nabla^2 C = -4\pi S, \tag{7}
$$

where

$$
S^{n_2 l_2 m_2, n'_2 l'_2 m'_2}_{n_1 l_1 m_1, n'_1 l'_1 m'_1}(\zeta_1, \zeta'_1, \zeta_2, \zeta'_2) = \int \chi^*_{n_1 l_1 m_1}(\zeta_1, \vec{r}_{1a}) \chi_{n'_1 l'_1 m'_1}(\zeta'_1, \vec{r}_{1a}) \chi^*_{n_2 l_2 m_2}(\zeta_2, \vec{r}_{1b}) \chi_{n'_2 l'_2 m'_2}(\zeta'_2, \vec{r}_{1b}) \mathrm{d}V_1 \tag{8}
$$

and the differentiations in ∇^2 refer to the components of the internuclear distance.

The S integral in (8) can be rewritten by means of the product of same center atomic orbitals, that is, the one-center charge density and two-center overlap integrals as follows:

$$S = \frac{1}{4\pi} {}^{(2)}\sum_{LL'} \sum_{MM'} W(n_1 l_1 m_1, n_1' l_1' m_1', NLM, \zeta_1, \zeta_1', z_1) W(n_2 l_2 m_2, n_2' l_2' m_2', N'L'M', \zeta_2, \zeta_2', z_2) \cdot S_{NLM,N'L'M'}(z_1, z_2; R), \tag{9}$$

where the one-center charge density [20a] is

$$W(nlm, n'l'm', NLM, \zeta, \zeta', z) = \frac{z^{3/2} F_{n'}(N)}{2^N n} \left[\frac{(2L+1) F_N(2N)}{2 F_n(2n) F_{n'}(2n')}\right]^{1/2} C^{L|M|}(lm, l'm') A^M_{mm'} \cdot \delta_{N,n+n'-1} (1+t)^{n+1/2} (1-t)^{n'+1/2}, \tag{10}$$

where $N = n_1 + n_1' - 1$, $N' = n_2 + n_2' - 1$, $z_1 = \zeta_1 + \zeta_1'$, $z_2 = \zeta_2 + \zeta_2'$, $t = \frac{\zeta - \zeta'}{\zeta + \zeta'}$ and the exact definitions of the Gaunt coefficients $C^{L|M|}(lm, l'm')$ and $A^M_{mm'}$ can be found in [20b]. The summations over L and M vary between the limit of $|l_1 - l_2| \le L \le l_1 + l_2$, $-L \le M \le L$, respectively, and ${}^{(2)}\sum$ indicates running in steps of two. The overlap integrals $S_{NLM,N'L'M'}$ in (9) are defined by

$$S_{NLM,N'L'M'}(z_1, z_2; R) = \int \mathrm{d}V_1 \chi^*_{NLM}(z_1, \vec{r}_{1a}) \chi_{N'L'M'}(z_2, \vec{r}_{1b}). \tag{11}$$

3. The Derivation of Two-center Coulomb Integrals Using the Poisson Equation

The two-center Coulomb integrals in (1) can be reduced to one-dimensional quadrature over the two-center overlap integrals as the following form [9g, h]:

$$\begin{aligned} C = {}^{(2)}\sum_{L,L'} \sum_{M,M'} & W(n_1 l_1 m_1, n_1' l_1' m_1', NLM, \zeta_1, \zeta_1', z_1) W(n_2 l_2 m_2, n_2' l_2' m_2', N'L'M', \zeta_2, \zeta_2', z_2) \\ & \cdot {}^{(2)}\sum_{L_a} \sum_{M_a} J^{L_a 0}(LM, L'-M') J^{L_a 0}(LM_a, L'-M_a) \left[R^{-L_a-1} \int_0^R \mathrm{d}R' R'^{(L_a+2)} S_{NLM_a,N'L'M_a}(R'z_1 R'z_2) \right. \\ & \left. + R^{L_a} \int_R^\infty \mathrm{d}R' R'^{(-L_a+1)} S_{NLM_a,N'L'M_a}(R'z_1 R'z_2) \right], \end{aligned} \tag{12}$$

where $S_{NLM_a,N'L'M_a}$ are the two-center overlap integrals for which we will use the analytical formula presented in our previous paper [21].

The limit values of L_a and M_a quantum numbers are

$$|L - L'| \le L_a \le L + L', -\mathrm{Min}(L, L') \le M_a \le \mathrm{Min}(L, L'), \tag{13}$$

respectively. Therefore, taking into account the integration of (12), we have the expression for the two-center Coulomb integrals over STOs as follows:

$$\begin{aligned} C = {}^{(2)}\sum_{LL'} \sum_{MM'} & W(n_1 l_1 m_1, n_1' l_1' m_1', NLM, \zeta_1, \zeta_1', z_1) W(n_2 l_2 m_2, n_2' l_2' m_2', N'L'M', \zeta_2, \zeta_2', z_2) \\ & \cdot {}^{(2)}\sum_{L_a} \sum_{M_a} J^{L_a 0}(LM, L'-M') J^{L_a 0}(LM_a, L'-M_a) T^{L_a M_a}_{NL,N'L'}(p_a, p_b, p, u; R). \end{aligned} \tag{14}$$

Here, the function of $T^{L_aM_a}_{NL,N'L'}$ in (14) is defined as

$$T^{L_aM_a}_{NL,N'L'}(p_a,p_b,p,u;R) = (-1)^{L'-M_a}R^2\frac{p_a^{N+1/2}p_b^{N'+1/2}}{p^{N+N'+1}} \cdot \sum_{i,i'}\sum_{j,j'}\sum_{k,s}F_s(L'+i-i'+j,L+i'-i+j')Q^k_{ii',jj'}(NL,N'L',M_a;p)\left[I^{(0;1)(1;\infty)}_{\sigma,s}(pu,u)+I^{(1;\infty)(1,\infty)}_{\mu,s}(pu,u)\right], \tag{15}$$

where σ, μ, p_a, p_b, p, and u are as follows:

$$\sigma = L_a+j+j'+k+2,\ \mu = -L_a+j+j'+k+1,\ p_a = z_1R,\ p_b = z_2R,\ p = \frac{1}{2}(p_a+p_b),\ u = \frac{(z_1-z_2)}{(z_1+z_2)}. \tag{16}$$

$J^{L_aM_a}(LM,L'M')$ in (14) is the well-known Wigner 3j coefficient, in which $M_a+M+M'=0$.

In (15), the symbol $F_m(N,N')$ is the generalized binomial coefficient and defined by [20b]

$$F_m(N,N') = \sum_{\sigma=\frac{1}{2}[(m-N)+|m-N|]}^{\min(m,N')}(-1)^\sigma F_{m-\sigma}(N)F_\sigma(N'). \tag{17}$$

In (15), the quantity $Q^k_{ii',jj'}$ is defined as

$$Q^k_{ii',jj'}(NL,N'L',M_a;p) = q_{ij}(NLM_a;p)q_{i'j'}(N'L'M_a;p)F_k(i+i'+M_a)(N+N'-j-j'-k)!(2p)^k \tag{18}$$

with

$$q_{ij}(NLM_a;p) = (-1)^{L-i}\frac{W_{LM_a}}{\sqrt{(2N)!}}A^i_{LM_a}F_j(N-L)p^j \tag{19}$$

and the summation indices i, i', j, j', k and s run as follows:

$$0 \le i \le (L-M_a),\ 0 \le i' \le (L'-M_a), \tag{20a}$$

$$0 \le j \le (N-L),\ 0 \le j' \le (N'-L'), \tag{20b}$$

$$0 \le k \le i+i'+M_a,\ 0 \le s \le L+L'+j+j'. \tag{20c}$$

4. Auxiliary Functions

The functions $I^{(0;1)(1;\infty)}_{\sigma,s}(\alpha,\beta)$ and $I^{(1;\infty)(1;\infty)}_{\sigma,s}(\alpha,\beta)$ in (15) can be expressed in terms of auxiliary functions $B^{(0;1)(1;\infty)}_{\sigma,s}$ and $B^{(1;\infty)(1;\infty)}_{\sigma,s}$ defined by Magnasco and Rapallo [22e]:

$$I^{(0;1)(1,\infty)}_{\sigma,s}(\alpha,\beta) = (-1)^{s+1}B^{(0;1)(1;\infty)}_{\sigma,s}(-\alpha,\beta) - B^{(0;1)(1;\infty)}_{\sigma,s}(\alpha,\beta), \tag{21a}$$

$$I^{(1;\infty)(1;\infty)}_{\sigma,s}(\alpha,\beta) = (-1)^{s+1}B^{(1;\infty)(1;\infty)}_{\sigma,s}(-\alpha,\beta) - B^{(1;\infty)(1;\infty)}_{\sigma,s}(\alpha,\beta), \tag{21b}$$

where

$$B^{(0;1)(1;\infty)}_{\sigma,s}(\alpha,\beta) = s!\sum_{j=0}^{s}\frac{A^{(0;1)}_{\sigma-j-1}(\alpha+\beta)}{(s-j)!(\alpha)^{j+1}} \tag{22}$$

for $\sigma \ge 0$, $s \ge 0$, and $s \le \sigma-1$;

$$B^{(1;\infty)(1;\infty)}_{\sigma,s}(\alpha,\beta) = s!\sum_{j=0}^{s}\frac{(\alpha)^{j-s-1}A^{(1;\infty)}_{\sigma-s+j-1}(\alpha+\beta)}{j!} \tag{23}$$

for $\sigma \ge 0$, $s \ge 0$, and $\sigma \ge s+1$;

$$B^{(1;\infty)(1;\infty)}_{\sigma,s}(\alpha,\beta) = \frac{s!}{(\alpha)^{\sigma+1}}\left\{\sum_{j=0}^{s-\sigma}\frac{E_{j+1}(\alpha+\beta)}{(s-\sigma-j)!(\alpha)^j} + \sum_{j=0}^{\sigma-1}\frac{(\alpha)^{j+1}A^{(1;\infty)}_j(\alpha+\beta)}{(j+s-\sigma+1)!}\right\} \tag{24}$$

Table 1. Comparative values of two-center Coulomb integrals for various quantum numbers with molecular parameters.

n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	n_3	l_3	m_3	ζ_3	n_4	l_4	m_4	ζ_4	R	Equation (14)	Equation (14)	Literature
																	Turbo Pascal results	Mathematica results	
1	0	0	0.99	1	0	0	0.99	1	0	0	1.01	1	0	0	1.01	0.01	0.624 916 670 583 001 E-0	0.624 916 670 583 008 814 983 455 183 84 E-0	0.624 916 671 027 413 E-0[a]
1	0	0	5.2	1	0	0	5.2	2	0	0	4.1	2	0	0	4.1	0.2	0.182 289 255 375 066 E+1	0.182 289 255 375 066 268 097 062 499 9 E+1	0.182 289 255 4 E+1[d]
1	0	0	5.2	1	0	0	5.2	2	0	0	4.1	2	0	0	4.1	100	1.000 000 000 000 000 18 E-2	1.000 000 000 000 000 000 000 000 0 E-2	0.999 999 999 999 997 E-2[e]
2	0	0	0.8	2	0	0	0.9	2	0	0	1.1	2	0	0	1.2	0.2	3.459 836 479 166 103 E-1	3.459 836 479 166 103 675 050 707 535 55 E-1	3.459 836 113 655 93 E-1[b]
1	0	0	5.2	2	1	0	3.1	2	0	0	4.1	3	2	0	2.5	0.2	-0.236 064 302 092 E-0	-0.236 064 302 092 006 371 569 414 924 8 E-0	-0.203 568 853 8 E-0[d]
1	0	0	5.2	2	1	0	3.1	2	0	0	4.1	3	2	0	2.5	20	7.832 887 076 581 409 01 E-7	7.832 887 076 575 685 124 205 6 E-7	7.832 887 076 575 67 E-7[e]
2	1	0	0.8	2	1	0	0.9	2	0	0	1.1	2	0	0	1.2	2	3.247 564 480 254 982 54 E-1	3.247 564 480 254 982 286 583 702 334 11 E-1	3.247 564 355 700 19 E-1[b]
3	2	2	10.0	3	2	2	5.0	2	1	1	6.0	2	1	1	4.0	0.8	6.338 241 311 523 E-1	6.338 241 311 523 816 529 759 504 477 87 E-1	6.338 241 859 901 91 E-1[b]
3	2	2	10.0	3	2	2	5.0	2	1	1	6.0	2	1	1	4.0	20	2.988 628 717 976 E-2	2.988 628 717 976 153 455 620 301 604 2 E-2	2.988 628 717 976 15 E-2[e]
4	2	2	7.0	4	2	2	2.1	2	1	1	5.6	2	1	1	2.8	0.1	1.735 E-2	1.736 518 356 251 406 118 544 498 731 58 E-1	1.736 518 356 251 41 E-1[e]
4	3	0	0.8	1	0	0	0.9	3	2	0	1.1	1	0	0	1.2	20	2.071 524 286 355 E-6	2.071 524 286 373 192 386 622 072 E-6	2.071 538 566 684 38 E-6[c]
4	3	0	0.8	1	0	0	0.9	3	2	0	1.1	1	0	0	1.2	100	1.325 782 449 E-10	1.325 782 470 936 295 456 13 E-10	1.711 599 185 48 E-10[a]
4	3	0	3.5	4	3	1	2.6	7	0	0	0.5	3	2	1	3.0	20	3.221 258 E-10	3.221 258 083 611 678 142 0 E-10	-3.221 258 083 611 67 E-10[e]
5	0	0	1.0	3	2	0	3.0	4	2	1	2.0	4	1	1	4.0	8.0	4.883 580 812 E-5	4.883 580 814 037 952 760 183 173 E-5	4.883 580 814 E-5[c]
5	1	0	0.6	5	1	0	1.2	5	0	0	3.0	5	0	0	4.2	2.0	8.526 916 911 162 E-2	8.526 916 911 162 949 000 584 018 201 5 E-2	8.526 916 911 163 10 E-2[e]
5	2	1	7	4	2	1	5	4	2	1	6	4	2	1	2	2.4	1.157 078 779 E-0	1.157 078 770 704 021 084 339 788 925 19 E-0	1.157 078 725 263 078 E-0[b]
5	3	2	3	4	3	2	2	4	2	2	8	4	2	2	5	0.4	0.412 425 608 391 E-0	0.412 425 608 390 551 638 457 590 825 479 E-0	0.412 425 206 364 181 E-0[b]
1	0	0	5.2	10	2	0	0.2	2	0	0	4.1	3	2	0	2.5	20	7.342 E-20	7.527 285 480 E-20	—
10	2	0	0.2	2	1	0	3.1	3	1	1	1.5	3	2	1	3.0	0.2	-0.125 014 E-11	-0.125 016 847 625 996 669 6 E-11	-0.125 016 847 6 E-11[d]
10	2	0	0.2	10	2	0	0.2	5	1	0	0.6	7	0	0	0.5	0.2	-4.903 852 E-6	-4.903 878 581 791 862 392 573 35 E-6	—
10	2	0	0.2	10	2	0	0.2	5	1	0	0.6	7	0	0	0.5	8.5	-0.225 291 889 365 E-3	-0.225 291 889 365 543 605 537 045 73 E-3	-0.225 291 889 6 E-3[d]
10	2	0	0.2	10	2	0	0.2	5	1	0	0.6	7	0	0	0.5	25	-8.349 418 795 939 E-4	-8.349 418 795 953 265 164 545 499 76 E-4	—

[a] Ref. [20a]; [b] Ref. [25]; [c] Ref. [22c]; [d] Ref. [22e]; [e] Ref. [26].

for $\sigma \geq 0$, $s \geq 0$ and $0 \leq \sigma \leq s$;

$$B_{\sigma,s}^{(1;\infty)(1;\infty)}(\alpha,\beta) = s! \sum_{j=0}^{s} \frac{E_{|\sigma|+j+1}(\alpha+\beta)}{(s-j)!(\alpha)^{j+1}} \quad (25)$$

for $\sigma < 0$, $s \geq 0$.

When α is equal to zero, the auxiliary functions take the following forms:

$$I_{\sigma,s}^{(0;1)(1;\infty)}(0,\beta) = A_{\sigma-1}^{(0;1)}(\beta)\left(\frac{1+(-1)^s}{1+s}\right) \sigma \geq 0, \quad (26)$$

$$I_{\sigma,s}^{(1;\infty)(1;\infty)}(0,\beta) = A_{\sigma}^{(1;\infty)}(\beta)\left(\frac{1+(-1)^s}{1+s}\right) \sigma \geq 0, \quad (27)$$

$$I_{\sigma,s}^{(1;\infty)(1;\infty)}(0,\beta) = E_{|\sigma|}(\beta)\left(\frac{1+(-1)^s}{1+s}\right) \sigma \leq 0. \quad (28)$$

The functions $A_n^{(0;1)}$ and E_n in the above equations are evaluated as follows [22d, e]:

$$A_n^{(0;1)}(\beta) = n! \exp(-\beta) \sum_{k=0}^{\infty} \frac{\beta^k}{(n+k+1)!} \text{ for } n \geq \beta, \quad (29)$$

$$A_n^{(0;1)}(\beta) = \frac{n! - \Gamma(n+1,\beta)}{\beta^{n+1}} \text{ for } n < \beta, \quad (30)$$

where Γ is the incomplete gamma function and if n is integer and positive, and β is real and positive $E_n(\beta)$,

$$E_n(\beta) = \int_1^{\infty} \mathrm{d}t \frac{\exp(-\beta t)}{t^n}. \quad (31)$$

We can calculate E_n by means of the recursive formula [19]:

$$(n-1)E_n(\beta) = \exp(-\beta) - \beta E_{n-1}(\beta). \quad (32)$$

In (32), the starting term $E_1(\beta)$ has been calculated using the Gaussian quadrature method [22d].

5. Results and Discussion

A new analytical formula for two-center Coulomb integrals over STOs has been derived using the Poisson equation. For the evaluation of two-center Coulomb integrals presented in (14), computer programs have been constructed using Mathematica 5.0 [23] and Turbo Pascal 7.0 programming languages. The obtained results are tested over a wide range of orbital exponent, internuclear distances and also for different quantum sets.

It is well-known that the conventional programming languages, such as Turbo Pascal and Fortran cause a catastrophic loss of accuracy when they process on terms of equal and opposite sign in magnitude. Therefore, the symbolic computation such as Mathematica or Maple programming language is widely used to test the result from the implementations of the programs constructed by the conventional programming languages. However, as the symbolic calculations increase the computational cost abnormally, the conventional programming languages are preferred to calculate the molecular properties in the computational quantum chemistry instead. In this manner, the excellent review paper by Barnett et al. [24] is advised for reading.

The comparative values of two-center Coulomb integrals over STOs are listed in Table 1 for wide changes in molecular parameters. In listing the computer results by Mathematica and Turbo Pascal for two-center Coulomb integrals, Turbo Pascal results have been truncated to the first or second figure affected by error due to the fact that the Mathematica results are more accurate than the Turbo Pascal ones. As can be seen clearly from Table 1, the results from Turbo Pascal computer program development for (14) are in good agreement with the previous works [20a, 22c, 22e, 25, 26]. Numerical accuracy for significant figures of the result usually changes from 10 to 20 digits. The reliability of our program is checked in two ways. Firstly, we compared our values with the obtained ones from the computer program constructed for two-center Coulomb integrals by Jones [27], for which magnetic quantum numbers are equal to zero. It is seen that our values agree well with Jones'. Secondly, the obtained results for the two-center Coulomb integrals over STOs were the same as those of one-center Coulomb integrals over STOs while the internuclear distance R approaches to zero.

The CPU times for each integral did not contain in Table 1 because of the fact that the type and capacity of the computer used in the calculations would affect the CPU times. Since the author is inexperienced in efficient programming, it is difficult to arrive at the correct time estimate. However, the typical CPU time with Turbo Pascal code for a whole set of integrals collected in Table 1 is about 3.5 milliseconds measured on a Pentium III PC at 800 MHz provided with 128 MB of RAM.

As a consequence, the presented formula for two-center Coulomb integrals over STOs gives satisfactory results and therefore can be used in molecular orbital calculations. Works are in progress for the calculation of other two-electron integrals over STOs and some primarily results will be reported in short.

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