ORIGINAL PAPER

ON THE EXACT EVALUATION OF INTERMOLECULAR ELECTROSTATIC INTERACTION ENERGY IN A MOLECULAR COORDINATE SYSTEM

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Abstract. *We propose an effective general approach for accurately calculating the electron-electron, nuclear-electron and nuclear-nuclear Coulomb electrostatic interaction energies. Since these interaction energies are fundamental terms in the ab initio, density function and semi-empirical theories, their general examination will make an important contribution to the accurate calculation of the physical and chemical properties of atoms and molecules. It is well known that electron-electron, nuclear-electron and nuclear-nuclear Coulomb electrostatic interaction energies can be reduced to basic two-center Coulomb integrals. The analytical calculation of electrostatic interaction energies with respect to basic two-center Coulomb integrals over Slater type orbitals (STOs) in molecular coordinate systems allows for the routine evaluation of molecular structures and their related properties. In this study, we introduce a new full analytical algorithm for calculating the basic two-center Coulomb integrals over STOs using Guseinov's auxiliary functions, especially the interactions between electrons. The auxiliary functions are calculated by using the exact recurrence relations developed by Guseinov. Our new approach is successfully tested on data from previously published studies, and can be recommended for the evaluation of related problems in atomic and molecular physics.*

Keywords: *basic two-center Coulomb integrals; electrostatic interaction energies; charge density; auxiliary functions.*

1. INTRODUCTION

There are many fields and applications in which electrostatic interactions are used; the most important of these are problems in molecular dynamics simulations of polar fluids, protein structure calculations, the modeling of macromolecules, and atomic and molecular structure calculations. For example, molecular recognition and chemical and biological activity are known to related to electrostatic interactions, and may be critical to achieving a physical model of solvation effects such as solvation energies and molecular properties [1-5]. In view of this, the accurate modeling and determination of solvation methods for the interactions between molecules are of prime importance.

It is well known that electrons are very light particles and that their behaviors within atomic and molecular systems must be described from the perspective of quantum mechanical computational methods. The large difference in mass between the electrons and the nucleus offers scientists computational opportunities to solve for the terms of the Hamilton operator in the Schrödinger equation [6-8]. When solving problems involving differential equations, the

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separation of variables method has been used to produce less complicated equations; however, for many particle systems, separation is not possible and a many-body problem can be transformed into a pseudo one-particle system by taking into account the average interaction. If we are interested in exact analytical definitions of electron distributions in detail, without reference to experimental data, we need to take into account all of the dynamics of a many-electron system [6-11].

Separating the nuclear and electronic variables occurring in the Hamilton operator is a useful approximation for avoiding this difficulty. Due to the difference in mass between the nucleus and an electron, the electronic wave function depends only the position of the nucleus rather than its velocity. Based on this, the Born-Oppenheimer method was introduced, which deals with a potential energy surface where electrons move within its field [12, 13]. By neglecting some interactions, the Schrödinger equation can be exactly solved for hydrogen-like atoms. In addition, molecular orbital theory is a well-known approximation method that can be used to calculate the electronic structures of multi-electron atoms and molecules. Many theoretical approximate methods have been developed in molecular orbital theory [14]. One of the most commonly used of these methods is the Hartree-Fock-Roothaan (HFR) method, which is based on the linear combination of atomic orbitals (LCAO) approach [15-19]. The HFR method uses the self-consistent field (SCF) theory, which is based on independent particle models. We note that for any state of a single configuration which has any symmetry in the open shells, the open shell HFR theory [20-27] is not general. To eliminate these drawbacks of the HFR theory, a combined open shell Hartree-Fock-Roothaan (CHFR) theory of atomic-molecular and nuclear systems has been suggested [28, 29].

Scientists have previously attempted to solve the Schrödinger equation for many-body systems for all atoms and molecules, and in each case have started with the problem of the main force holding the nucleus and electron together, which is the Coulomb interaction. The Coulomb electron-electron, nuclear-electron and nuclear-nuclear interactions are all needed to calculate the electrostatic interaction energies. Notice that the electron-electron, nuclear-electron and nuclear-nuclear interactions can generally be defined as basic two-center Coulomb integrals [30-38]. The main goal of this study is to calculate the basic two-center Coulomb integrals over STOs using auxiliary functions occurring in intermolecular electrostatic interaction energies. In addition, as can be seen from the studies of Guseinov [39-46], the calculations of the multi-center molecular integrals occurring in the CHFR equations can be reduced to the basic two-center Coulomb integrals over STOs. Hence, fast and accurate analytical evaluations for basic two-center Coulomb integrals are very important in molecular structure calculations. In the literature, there are several calculation methods for basic two-center Coulomb integrals which have allowed other scientists to improve their studies in this field [31-49]. When all the developments and different approximations are considered, the evaluation of the Coulomb interactions becomes more straightforward. Analytical treatments of the intermolecular electrostatic interaction energies through the use of different algorithms have been important in terms of increasing the efficiency and accuracy. From previous studies, it can easily be seen that the evaluation of the electron-electron term is the most difficult problem to solve analytically [36-38]. To overcome this difficulty, the basic two-center Coulomb integrals of the electron-electron interaction must be calculated accurately, using effective approaches.

In view of this, we propose an alternative analytical evaluation method for the basic two-center Coulomb integrals over STOs in a molecular coordinate system using auxiliary functions. Our test results show good agreement with the data in the literature. We believe that this study will be valuable for future work in this field.

2. MATERIALS AND METHODS

The two-center Coulomb integrals occurring in the HFR equations evaluated in this study are defined as follows [48]:

$$I^{aa,bb}_{p_1p_1',p_2p_2'}\left(\zeta_1,\zeta_1',\zeta_2,\zeta_2';\vec{R}_{ab}\right)=\int \chi^{*}_{p_1}\left(\zeta_1,\vec{r}_{a1}\right)\chi_{p_1'}\left(\zeta_1',\vec{r}_{a1}\right)\frac{1}{r_{21}}\chi_{p_2}\left(\zeta_2,\vec{r}_{b2}\right)\chi^{*}_{p_2'}\left(\zeta_2',\vec{r}_{b2}\right)dv_1dv_2\,, \qquad (1)$$

where $p_1\equiv n_1l_1m_1$, $p_1'\equiv n_1'l_1'm_1'$, $p_2\equiv n_2l_2m_2$, $p_2'\equiv n_2'l_2'm_2'$, $\vec{R}_{ab}=\vec{R}_b-\vec{R}_a$ and the $\chi_{p_2}\left(\zeta_2,\vec{r}_{b2}\right)$ terms are the well-known STOs expressed as [49]:

$$\chi_{nlm}\left(\zeta,\vec{r}\right)=\left(2\zeta\right)^{n+\frac{1}{2}}\left[\left(2n\right)!\right]^{-\frac{1}{2}}\quad r^{n-1}e^{-\zeta\, r}S_{lm}(\theta,\varphi)\,. \qquad (2)$$

Here, the complex and real spherical harmonics S_{lm} are determined by

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

where $P_{l|m|}$ are the normalized associated Legendre functions [50, 51]. For complex spherical harmonics (SHs),

$$\Phi_m(\varphi)=\frac{1}{\sqrt{2\pi}}e^{im\varphi}\,, \qquad (4)$$

and for real spherical harmonics,

$$\Phi_m(\varphi)=\frac{1}{\sqrt{\pi(1+\delta_{m0})}}\begin{cases}\cos|m|\varphi & for\quad m\geq 0\\ \sin|m|\varphi & for\quad m<0\end{cases}\,. \qquad (5)$$

It should be noted that our definition of the phases for the complex spherical harmonics $\left(Y^{*}_{lm}=Y_{l-m}\right)$ differs from the Condon-Shortley phases [52] in terms of the sign. In order to evaluate the two-center Coulomb integrals, we use an expansion of the one-center electron charge density [53]:

$$\begin{aligned}&I^{aa,bb}_{p_1p_1',p_2p_2'}\left(\zeta_1,\zeta_1',\zeta_2,\zeta_2';\vec{R}_{ab}\right)\\&\quad=\sum_{l=0}^{n-1}\sum_{m=-l}^{l}W^{*}_{p_1p_1'p}\left(\zeta_1,\zeta_1',z\right)\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}W_{p_2p_2'p'}\left(\zeta_2,\zeta_2',z'\right)J_{pp'}\left(z,z';\vec{R}_{ab}\right).\end{aligned} \qquad (6)$$

Here, $z=\zeta_1+\zeta_1'$, $z'=\zeta_2+\zeta_2'$ and the $W^{*}_{p_1p_1'p}\left(\zeta_1,\zeta_1',z\right)$ terms are the charge density expansion coefficients, defined in general form as:

$$W_{nlm,n'l'm',\mu\nu\sigma}(\zeta,\zeta',z)$$
$$=\frac{z\sqrt{z}}{2^{\mu}}\frac{F_{n'}(\mu)}{n}\left[\frac{2l+1}{2}\frac{F_{\mu}(2\mu)}{F_n(2n)F_{n'}(2n')}\right]^{1/2}(1+t)^{n+\frac{1}{2}}(1-t)^{n'+\frac{1}{2}}C^{\nu|\sigma|}(lm,l'm')A^{\sigma}_{mm'}\delta_{\mu,n+n'-1}\quad . \tag{7}$$

The generalized Gaunt coefficients $C^{\nu|\sigma|}(lm,l'm')$ and $A^{\sigma}_{mm'}$ in Eq. (7) are determined by the following relationships [54]:

$$C^{L|M|}(lm,\ l'm')=\begin{cases}C^{L}(lm,\ l'm') & for\quad |M|=|m-m'|\\ C^{L}(lm,\ l'-m') & for\quad |M|=|m+m'|\end{cases},$$
(8)

$$A^{M}_{mm'}=\begin{cases}\frac{1}{\sqrt{2}}(2-|\eta^{m-m'}_{mm'}|)^{1/2}\quad \delta_{M,\ \varepsilon|m-m'|}\quad +\frac{1}{\sqrt{2}}\eta^{m+m'}_{mm'}\delta_{M,\ \varepsilon|m+m'|} & for\quad real\quad STO's\\ \delta_{M,\ m-m'} & for\quad complex\quad STO's\end{cases}. \tag{9}$$

See Ref. [54] for exact definitions of the quantities $\eta^{m\pm m'}_{mm'}$ *and* $\varepsilon=\varepsilon_{mm'}$.

In Eq. (6), the term $J_{pp'}(z,z';R_{ab})$ is the basic two-center Coulomb integral in a molecular coordinate system, which can be defined in integral form as follows:

$$J_{pp'}(\zeta,\zeta';R)=\frac{1}{4\pi}\int\chi^{*}_{p}(\zeta,r_{a1})\frac{1}{r_{21}}\chi_{p'}(\zeta',r_{b2})dv_1dv_2\quad . \tag{10}$$

Through the use of the Guseinov rotational function, the basic two-center Coulomb integral in a lined-up coordinate system can be written as follows:

$$J_{nlm,n'l'm'}(\zeta,\zeta';\vec{R})=\sum_{\lambda=0}^{\min(l,l')}T^{\lambda}_{lm,l'm'}(\theta,\varphi)J_{nl\lambda,n'l'\lambda}(\zeta,\zeta';R). \tag{11}$$

Here, $T^{\lambda}_{lm,l'm'}(\theta,\varphi)$ is the Guseinov rotational function (see Refs. [55-57] for an exact definition) and $J_{nl\lambda,n'l'\lambda}(\zeta,\zeta';R)$ is the lined-up basic two-center Coulomb integral which can be defined as [46]:

$$J_{nl\lambda,n'l'\lambda}(\zeta,\zeta';R_{ab})=\frac{2^{n+n'+1}(l+1)!F_n(n+l+1)\,p'^{n'}\sqrt{pp'}}{[F_n(2n)(2n')!]^{1/2}(2l+1)\zeta^2p^l}\sum_{\alpha\beta q}g^{q}_{\alpha\beta}(l\lambda,l'\lambda)$$
$$\times\begin{cases}Q^{q}_{|l+\alpha|,n'-\beta}(p';-p')-\sum_{s=0}^{n+l}\frac{\gamma^{l}_{s}(n)}{s!}p^{s}Q^{q}_{|l+\alpha|+s,n'-\beta}(p_{ab},p_{ab}t_{ab}) & for\ l+\alpha\le 0\\ G^{q}_{-(l+\alpha),n'-\beta}(p,p',-p')-\sum_{s=l+\alpha}^{n+l}\frac{\gamma^{l}_{s}(n)}{s!}p^{s}Q^{q}_{s-(l+\alpha),n'-\beta}(p_{ab},p_{ab}t_{ab}) & for\ l+\alpha>0,\end{cases} \tag{12}$$

where

$$\vec{R}=\vec{R}_{ab},\ p=\frac{1}{2}\zeta R,$$

$$p' = \frac{1}{2}\zeta' R\,,\ p_{ab} = p + p'\,,$$

$$t_{ab} = \frac{p - p'}{p + p'},$$

and

$$\gamma_s^l(\mathrm{n}) = 1 - \frac{F_{2l+1}(s)}{F_{n-l}(n+l+1)}\ .$$

In Eqs. (13) and (14), $p_a > 0, p > 0$ and $-p \le pt \le p$. The indices n, s, and q are all nonnegative integers.

It can be seen from Eq. (12) that giving reliable formulas for the auxiliary functions Q_{ns}^q, G_{-ns}^q and $g_{\alpha\beta}^q$ is very important for the accurate calculation of the basic two-center Coulomb integral. The auxiliary functions appearing in Eq. (12) are given by [45, 46]:

$$Q_{ns}^q(p, pt) = \int_1^\infty \int_{-1}^1 (\mu\nu)^q (\mu+\nu)^n (\mu-\nu)^s \times e^{-p\mu - pt\nu} d\mu d\nu \quad , \tag{13}$$

$$G_{-ns}^q(p_a; p, pt) = \int_1^\infty \int_{-1}^1 \frac{(\mu\nu)^q (\mu-\nu)^s}{(\mu+\nu)^n} \times \left(1 - e^{-p_a(\mu+\nu)} \sum_{k=0}^{n-1} \frac{[p_a(\mu+\nu)]^k}{k!}\right), \times e^{-p\mu - pt\nu} d\mu d\nu \tag{14}$$

$$g_{\alpha\beta}^q(l\lambda, l'\lambda) = g_{\alpha\beta}^0(l\lambda, l'\lambda)\,\mathrm{F}_q(\alpha+\lambda, \beta-\lambda)\,, \tag{15}$$

$$g_{\alpha\beta}^0(l\lambda, l'\lambda) = \left[\sum_{i=0}^{\lambda} (-1)^i F_i(\lambda) D_{\alpha+2\lambda-2i}^{l\lambda}\right] D_\beta^{l'\lambda}\ , \tag{16}$$

$$D_\beta^{l\lambda} = \frac{(-1)^{(l-\beta)/2}}{2^l} \left[\frac{2l+1}{2} \frac{F_l(l+\lambda)}{F_\lambda(l)}\right]^{1/2} F_{(l-\beta)/2}(l) F_{\beta-\lambda}(l+\beta)\,. \tag{17}$$

With the help of the auxiliary functions A_k and B_k, the expression for the Q_{ns}^q function can be defined as [45]:

$$Q_{ns}^q(p, pt) = \sum_{k=0}^{n+s} F_k(n,s) A_{q+n+s-k}(p) B_{q+k}(pt)\,. \tag{18}$$

For special cases, an alternative efficient formula for the Q_{ns}^q function is given as [45]:

$$Q_{ns}^{q}(p,pt)=\begin{cases}\sum_{k=0}^{n+s}F_k(n,s)A_{q+n+s-k}(p)\left[h_{q+k+1}(pt)+(-1)^{q+k}h_{q+k+1}(-pt)\right] & pt\neq 0\\ \sum_{k=0}^{n+s}F_k(n,s)A_{q+n+s-k}(p)\dfrac{\left[1+(-1)^{q+k}\right]}{q+k+1} & pt=0\end{cases}. \tag{19}$$

The $F_m(N,N')$ functions in Eqs. (18) and (19) are the generalized binomial coefficients defined by the following relations:

$$F_m(N,N')=\sum_{\sigma=\frac{1}{2}\left[(m-N)+|m-N|\right]}^{\min(m,N')}(-1)^{\sigma}F_{m-\sigma}(N)F_{\sigma}(N'), \tag{20}$$

$$F_m(n)=F_m(n,0)=n!/m!(n-m)!\ . \tag{21}$$

The recursive formulas for the G_{-ns}^{q} function can be expressed as follows [45]:

$$\begin{aligned}2(n-1)G_{-ns}^{q}=&-(p+pt)G_{-n+1s}^{q}+qG_{-n+2s}^{q-1}-q\frac{p_a^{n-2}}{(n-2)!}Q_{0s}^{q-1}(p_{ab},p_{ab}t_{ab})\\&+M_{-n+1s}^{q}-L_{-n+1s}^{q}+(-1)^{q}E_{-n+1s}^{q}\end{aligned}. \tag{22}$$

By applying partial integration with respect to ν *and* μ, the recursive relations for M_{-ns}^{q}, L_{-ns}^{q} *and* E_{-ns}^{q} can be established as:

$$\begin{aligned}(n-1)M_{-ns}^{q}=&-ptM_{-n+1s}^{q}-sM_{-n+1s-1}^{q}+qM_{-n+1s}^{q-1}\\&+\frac{p_a^{n-1}}{(n-1)!}\left[(-1)^{q}2^{s}e^{-p+pt}-\delta_{s0}(n-1)h_{n-1}(2p_a)e^{-p-pt}\right]\end{aligned} \tag{23}$$

$$(n-1)L_{-ns}^{q}=-pL_{-n+1s}^{q}+sL_{-n+1s-1}^{q}+qL_{-n+1s}^{q-1}+\delta_{s0}\frac{p_a^{n-1}}{(n-1)!}h_{n-1}(2p_a)e^{-p-pt} \tag{24}$$

$$(n-1)E_{-ns}^{q}=-pE_{-n+1s}^{q}+sE_{-n+1s-1}^{q}+qE_{-n+1s}^{q-1}+2^{s}\frac{p_a^{n-1}}{(n-1)!}e^{-p+pt}\quad , \tag{25}$$

respectively, where

$$h_{\sigma}(x)=\begin{cases}-A_{\sigma-1}(x)+f_{\sigma}(x) & for\quad x\neq 0,\ \sigma\neq 0\\ Ei(-x)-\ln|x| & for\quad x\neq 0,\ \sigma=0\\ 1/\sigma & for\quad x=0,\ \sigma\neq 0\\ C & for\quad x=0,\ \sigma=0\end{cases} \tag{26}$$

$$f_\sigma(x)=\begin{cases}\dfrac{(\sigma-1)!}{x^\sigma} & for \quad x\neq 0,\ \sigma\neq 0\\ -\ln|x| & for \quad x\neq 0,\ \sigma=0\end{cases} \tag{27}$$

where C is the Euler constant and $Ei(-x)$ is an exponential integral determined by [51]:

$$Ei(-x)=-\int_x^\infty \frac{e^{-t}}{t}dt\,. \tag{28}$$

Using the equation $G^q_{-1s}=\dfrac{\partial^{2q}}{\partial p^q\partial(pt)^q}G^0_{-1s}$, we can get the following expression:

$$G^q_{-1s}(p_a,p,pt)=\sum_{\sigma=0}^{s+q}\eta^q_{s\sigma}\{A_{s+2q-\sigma}(p-pt)[h_\sigma(2pt)-h_\sigma(2p_a+2pt)-(-1)^\sigma(f_\sigma(2p) - f_\sigma(2p_a+2p))]-(-1)^s A_{s+2q-\sigma}(-p+pt)[A_{\sigma-1}(2p)-A_{\sigma-1}(2p_a+2p)]\} \tag{29}$$

where

$$\eta^q_{s\sigma}=(-1)^\sigma\sum_{k=0}^{q}2^k F_k(q)F_{\sigma-k}(s)\,, \tag{30}$$

$$A_{-1}(x)=\int_1^\infty \mu^{-1}e^{-x\mu}d\mu=-Ei(-x)\ . \tag{31}$$

The expressions for the functions M^q_{-1s}, L^q_{-1s} *and* E^q_{-1s} can be easily obtained. For this purpose, we perform calculations analogous to those for the auxiliary functions G^q_{-1s}, which can be given as:

$$M^q_{-1s}(p_a,p,pt)=e^{-p+pt}\sum_{\sigma=0}^{s+q}\eta^q_{s\sigma}[h_\sigma(2pt)-h_\sigma(2p_a+2pt)]\,, \tag{32}$$

$$L^q_{-1s}(p_a,p,pt)=(-1)^s e^{p-pt}\sum_{\sigma=0}^{s+q}\eta^q_{s\sigma}[A_{\sigma-1}(2p)-A_{\sigma-1}(2p_a+2p)]\,, \tag{33}$$

$$E^q_{-1s}(p_a,p,pt)=(-1)^q e^{-p+pt}\sum_{\sigma=0}^{s+q}(-1)^\sigma\eta^q_{s\sigma}[f_\sigma(2p)-f_\sigma(2p_a+2p)]\,. \tag{34}$$

It is clear from Eq. (12) that the basic two-center Coulomb integral can be easily calculated using the auxiliary functions, which have no restrictions on their application.

3. RESULTS AND DISCUSSION

Since the electrostatic interactions are found to be a key factor in determining reliable structural information, the modeling of electrostatic interactions in different fields is very important. It is well known that the many-body theories of the electronic structure of atoms and molecules are very complex, and require additional computational approaches. One of the most widely used methods is HFR theory, which has been shown in the literature to give an acceptable accuracy. This theory depends on an independent particle model in which all interactions are taken into consideration in an average fashion. The literature contains various theoretical and semi-empirical methods which allow the HFR approximation to be used to solve many-body electronic structure problems. In this study, we have introduced a new calculation method for basic two-center Coulomb integrals using auxiliary functions, especially the interactions between electrons.

It is clear from previous studies that the basic two-center Coulomb integrals are important for calculating the atomic and molecular properties [36-38]. In Ref. [37], Nguyen et al. proposed a precise calculation method using Löwdin α functions. Based on the accurate calculation of the basic two-center Coulomb integral over STOs, they calculated the electrostatic interaction energy between two continuous molecular charge distributions with high precision [38]. In a molecular coordinate system, the suggested approximations for accurate analytical calculations of basic two-center Coulomb integrals sustain its difficulties and deficiencies. Hence, deriving reliable methods for the evaluation of basic two-center Coulomb integrals is an important problem. In this study, we have suggested a full analytical algorithm for basic two-center Coulomb integrals using the Guseinov Q_{ns}^{q} and G_{-ns}^{q} auxiliary functions. It can be seen from Eq. (6) that the two-center Coulomb integrals can be expressed based on the basic two-center Coulomb integrals. Since there are no comparable solutions for the basic two-center Coulomb integrals in the literature, we have proved the accuracy of our method using two-center Coulomb integral solutions. The results of our calculations of the two-center Coulomb integrals arising in the LiH molecule in a molecular coordinate system, and a comparison with the results reported by Prof. I. Shavitt, are given in Table 1.

Table 1. The comparative values of two-center Coulomb integrals $I^{aa,bb}$ in molecular coordinate system (in a.u.)

$(n_1 l_1 m_1)(n_1 l_1' m_1')/(n_2 l_2 m_2)(n_2' l_2' m_2')$	**This study**	**I.Shavitt's Results**
$(100)_{Li}$ $(100)_{Li}$ / $(100)_{H}$ $(100)_{H}$	6.42923011411776 E-01	6.4292301 E-01
$(100)_{Li}$ $(100)_{Li}$ / $(211)_{H}$ $(211)_{H}$	5.2875283894770 E-01	5.2875184 E-01
$(100)_{Li}$ $(100)_{Li}$ / $(211)_{H}$ $(21{-}1)_{H}$	2.62916489254298 E-02	2.629165 E-02
$(100)_{Li}$ $(100)_{Li}$ / $(21{-}1)_{H}$ $(21{-}1)_{H}$	5.68189312403252 E-01	5.6818931 E-01
$(211)_{Li}$ $(211)_{Li}$ / $(21{-}1)_{H}$ $(21{-}1)_{H}$	4.75866356920393 E-01	4.7586636 E-01
$(211)_{Li}$ $(211)_{Li}$ / $(211)_{H}$ $(211)_{H}$	4.79993860724975 E-01	4.7999386 E-01
$(210)_{Li}$ $(210)_{Li}$ / $(211)_{H}$ $(211)_{H}$	4.61321486782034 E-01	4.6132149 E-01
$(210)_{Li}$ $(210)_{Li}$ / $(211)_{H}$ $(210)_{H}$	3.22419243252908 E-03	3.22419 E-03
$(211)_{Li}$ $(211)_{Li}$ / $(311)_{H}$ $(311)_{H}$	4.15340385129991 E-01	4.1534039 E-01
$(211)_{Li}$ $(21{-}1)_{Li}$ / $(311)_{H}$ $(311)_{H}$	-1.71070506207756 E-03	-1.71070 E-03
$(211)_{Li}$ $(21{-}1)_{Li}$ / $(31{-}1)_{H}$ $(31{-}1)_{H}$	-4.65313979074467 E-04	-4.6531 E-04
$(322)_{Li}$ $(322)_{Li}$ / $(322)_{H}$ $(322)_{H}$	3.72323271632354 E-01	3.7232327 E-01
$(322)_{Li}$ $(322)_{Li}$ / $(32{-}2)_{H}$ $(32{-}2)_{H}$	3.71471468071404 E-01	3.7147147 E-01
$(322)_{Li}$ $(322)_{Li}$ / $(322)_{H}$ $(32{-}1)_{H}$	-3.16264467119299 E-03	-3.16264 E-03
$(32{-}2)_{Li}$ $(32{-}2)_{Li}$ / $(32{-}1)_{H}$ $(32{-}1)_{H}$	3.55486892754802 E-01	3.5548689 E-01

We note that since Prof. I.I. Guseinov was a Fulbright Scholar in 1985, he had the opportunity to work with Prof. I. Shavitt at Ohio State University, and shared a great deal of scientific information and data via private communications during this period. The calculation results given in Table 1 are based on these shared data. We remember Prof. I. Shavitt, one of the pioneers of quantum chemistry, with deep respect. In this paper, the atomic coordinates (*x*, *y*, *z*) and parameters (in a.u.) for the *LiH* molecule are assumed to be *Li*(0,0,0), *H*(0.5,1.0,0.7), $\zeta_{Li} = \zeta_H = 1.5$. It is clear from Table 1 that our results are in good agreement with the given data. Based on this, we can conclude that our calculation results for the basic two-center Coulomb integrals are also correct. We present calculation results for the basic two-center Coulomb integrals in Table 2 for arbitrary quantum sets and intermolecular distances. To the best of our knowledge, this study is the first to give calculation results for basic two-center Coulomb integrals in a molecular coordinate system.

Table 2. The values of basic two-center Coulomb integrals $J_{nlm,n'l'm'}\left(\zeta,\zeta';\vec{R}\right)$ in molecular coordinate system (in a.u.)

n	l	m	ζ	n'	l'	m'	ζ'	R	θ	φ	**Eq. (12)**
1	0	0	3	1	0	0	3	1.3	$\pi/3$	$\pi/4$	3.841558313832543 E-01
2	1	1	3.8	2	0	0	4.6	0.6	$2\pi/3$	$3\pi/4$	6.83875826690048 E-02
2	1	1	5.6	2	1	1	6.8	3.1	$\pi/2$	π	-1.9179687946892312E-03
2	1	-1	8.7	2	1	-1	9.8	2.4	π	$3\pi/4$	2.758897931991839 E-04
3	2	-1	10.2	2	1	1	2.3	0.004	$\pi/3$	$5\pi/4$	-7.491204672424577 E-10
3	2	2	2.3	3	2	2	2.5	3.6	$2\pi/3$	$3\pi/2$	1.6336202976281054 E-02
4	2	-1	10.6	4	2	-1	1.6	5.5	$5\pi/6$	$7\pi/4$	-2.654403921224302 E-04
4	2	2	13.4	4	2	2	10.8	2.4	π	2π	2.2218647776528384 E-05
4	2	2	13.4	4	2	2	10.8	0.2	π	2π	1.6080869906802815 E-02
4	3	-3	9.6	4	3	-2	4.4	0.006	$\pi/7$	$2\pi/5$	1.1060467631603868 E-05
4	3	3	9.6	3	2	2	4.4	7.1	$2\pi/7$	$3\pi/5$	7.722156806219806 E-07
4	3	3	16.3	4	3	3	11.7	0.07	$3\pi/7$	$4\pi/5$	6.478264999191043 E-03
5	4	3	7.8	4	3	3	2.7	10.6	$4\pi/7$	$6\pi/5$	-4.480882221214228 E-07
5	4	4	17.8	5	4	4	15.9	15.8	$5\pi/7$	π	6.256545092201997 E-05
6	5	5	8.3	6	4	4	2.9	1.5	$5\pi/7$	π	6.429862814343103 E-04
7	5	5	13.1	6	4	4	13.6	2.1	$6\pi/7$	$6\pi/5$	-1.1734523283710374 E-07
8	4	3	9.6	7	4	4	9.6	6.2	$6\pi/7$	$6\pi/5$	3.744537010398973 E-06
6	5	5	9.3	6	5	5	10.3	4.6	$3\pi/4$	$7\pi/5$	-3.4434439500935504 E-07
5	3	-3	15.2	5	3	3	19.6	0.4	$7\pi/8$	$8\pi/5$	1.7117759518718334 E-06

To compute the basic two-center Coulomb integrals, the coefficients $F_m(n)$, $F_m(N,N')$, M^q_{-ns}, L^q_{-ns} *and* E^q_{-ns} are repeatedly used. To reduce the time need to compute the multicenter matrix elements which appear in the CHFR equation and intermolecular

electrostatic interactions, we suggest a common storage method for these coefficients with the same selection rule. For quick calculations, $F_m(n), F_m(N,N'), M^q_{-ns}$, L^q_{-ns} *and* E^q_{-ns} are stored in the memory of the computer. Based on the special relations given here, the positions of certain coefficients and quantities $F_m(n)$, $F_m(N,N'), M^q_{-ns}$, L^q_{-ns} *and* E^q_{-ns} are considered in order to put these coefficients and quantities into or to get them back from the computer memory. The analytical method suggested in this study for evaluating basic two-center Coulomb integrals is valid for arbitrary quantum sets and intermolecular distances in a molecular coordinate system. The proposed method was implemented in the Turbo Pascal 7.0 programming language and yielded high performance.

4. CONCLUSION

In this study calculation method for the basic two-center Coulomb integral appearing in the intermolecular electrostatic interaction energy has been suggested in molecular coordinate system. The novelty of this study lies in the use of a full analytical calculation method in a molecular coordinate system with no restrictions on its use. We believe that this will benefit future studies of the electrostatic interaction energy.

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