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AN ANALYTICAL METHOD FOR CALCULATING MULTICENTRE INTEGRALS BUILT UP FROM GTF-S II.

ABSTRACT: *This paper is the continuation of [1] discussing the analytical evaluation of three-centre one-electron potential integrals made up of primitive GTF-S and Bardsley's pseudopotential.*

In [1], [2], [3], [4] and [5] we have suggested an analytical method for the unified evaluation of multicentre potential integrals made up of primitive GTF-S and polarizational pseudopotential members. The main steps of the method have been presented mainly in [1], [4], [5]. This paper is the continuation of [1] discussing the analytical evaluation of three-centre one-electron potential integrals made up of primitive GTF-S and Bardsley's pseudopotential.

In [1] we have pointed out that the value of

$\mathrm{int}(-\infty \le x \le +\infty)\ \ \exp(-x^2)\left[(p-\Gamma x)^2+d^2\right]^{-2^{*}}$ is necessary to the analytical evaluation of the matrix elements of Bardsley's pseudopotential formed with primitive GTF-S. Here p, Γ,d are real numbers.

In calculating the above-mentioned integral first we are going to apply Fourier's cosinus- and sinus transforms defined by the

$$F(k) = \int_0^\infty f(x) \cos(kx)\, dx \qquad (39a)$$

$$f(x) = \frac{2}{\pi} \int_0^\infty F(k) \cos(kx)\, dk \qquad (39b)$$ and

$$F(k) = \int_0^\infty f(x) \sin(kx)\, dx \qquad (40a)$$

* $\text{int}(-\infty \le x \le +\infty)\exp(-x^2)\left[(p-\Gamma x)^2+d^2\right]^{-2} \equiv \int_a^b \frac{e^{-x^2}}{[(p-\Gamma x)^2+d^2]^a}\, dx$

$$f(x) = \frac{2}{\pi} \int_0^\infty F(k) \sin(kx)\, dk \qquad (40b)$$ equations

The integrability and the continuity of $f(x)$ and $F(k)$ from 0 to $+\infty$ are the necessary conditions of the existence of the (39a), (39b), (40a), (40b) equations. Moreover (39a), (39b) demand the $f(x)=f(-x)$ equality whereas (40a), (40b) demand the $f(x)=-f(-x)$ one.

If we want to calculate an integral of $\text{int}(-\infty \le x \le +\infty)f(x,p)$ form by means of Fourier's cosinus- and sinus transforms with respect to p it is useful to express $f(x,p)$ as a sum of a gerade and an ungerade function of p:

$$f(x,p) = f_{g(p)}(x,p) + f_{ug(p)}(x,p) \qquad (41)$$

$$f_{g(p)}(x,p)=[f(x,p)+f(x,-p)]2^{-1}, f_{ug(p)}(x,p)=[f(x,p)-f(x,-p)]2^{-1} \qquad (42a\text{-}b)$$

$$\int_{-\infty}^{+\infty} f(p,x)dx = \int_{-\infty}^{+\infty} f_{g(p)}(x,p)dx + \int_{-\infty}^{+\infty} f_{ug(p)}(x,p)dx \qquad (43)$$

First let us deal with the calculation of the first member in the right-side of (43). As $f_{g(p)}(x,p)$ is a gerade function of p, $\text{int}(-\infty \le x \le +\infty)f_{g(p)}(x,p)$ is also a gerade function of p, because if $F(p)=\text{int}(a \le x \le b)f(x,p)$, then $F(-p)=\text{int}(a \le x \le b)f(x,-p)$ moreover in case of $f(x,p)=f(x,-p)$ for each x and p $F(p)=F(-p)$. Let $\Phi(k)$ be equal to

$$\mathrm{int}(0 \le p \le \infty)\left[\mathrm{int}(-\infty \le x \le +\infty) f_{g(p)}(x,p)\right] \qquad (44a)$$

then $\mathrm{int}(-\infty \le x \le +\infty) f_{g(p)}(x,p) = \frac{2}{\pi}\mathrm{int}(0 \le k \le \infty)\ \Phi(k)\cos(pk)$ (44b)

If calculating $\Phi(k)$ and that of its inverse are simpler than the direct evaluation of $\mathrm{int}(-\infty \le x \le +\infty) f_{g(p)}(x,p)$ it is useful to apply to the calculation of $\mathrm{int}(-\infty \le x \le +\infty) f_{g(p)}(x,p)$:

$$\int_0^{\infty}\left[\int_{-\infty}^{+\infty} f_{g(p)}(x,p)dx\right]\cos(kp)dp = \int_{-\infty}^{+\infty}\left[\int_0^{\infty} f_{g(p)}(x,p)\cos(kp)dp\right]dx =$$

$$= \int_{-\infty}^{+\infty}\left[\frac{1}{2}\int_{-\infty}^{+\infty} f_{g(p)}(x,p)\cos(kp)dp\right]dx = \int_{-\infty}^{+\infty}\left[\frac{1}{2}\,\mathrm{Re}\int_{-\infty}^{+\infty} f_{g(p)}(x,p)e^{ikp}dp\right]dx \qquad (45)$$

It is to be seen that the first task is to evaluate $\int_{-\infty}^{+\infty} f_{g(p)}(x,p)e^{ikp}dp$. Taking into account the (41), (42a), (42b), (43), (44a), (44b), (45), (46) equations, the remark concerning the first task in calculating the right side of (45) moreover taking into account also the continuity and the integrability of $\mathrm{int}(-\infty \le x \le +\infty) f_{g(p)}(x,p)$ with respect to p from 0 to $+\infty$ and the continuity and integrability of $\Phi(k)$ with respect to k from 0 to $+\infty$ we can see that we have to evaluate the

$$\int_{-\infty}^{+\infty} f_{g(p)}(x,p)e^{ikp}dp = \frac{1}{2}\left[\int_{-\infty}^{+\infty}\exp(-x^2)\cdot\exp(ikp)\cdot\right.$$

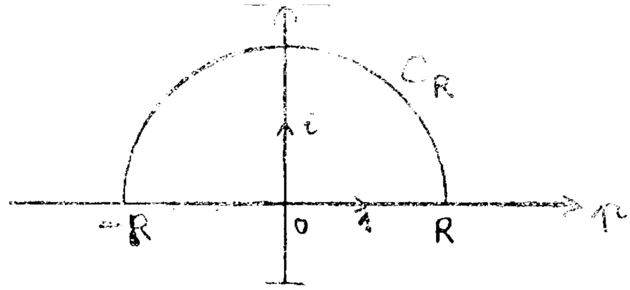
$$\cdot\left[(p-\Gamma x)^2+d^2\right]^{-2}dp + \int_{-\infty}^{+\infty}\exp(-x^2)\cdot\exp(ikp)\cdot$$

$$\left.\cdot\left[(p+\Gamma x)^2+d^2\right]^{-2}dp\right] \text{ expression,} \qquad (47)$$

For the sake of calculating the first member in the right side of (47) let us consider the

$$\oint_{G_R}\exp(ikz)\left[(z-\Gamma x)^2+d^2\right]^{-2}dz$$

integral where k>0 because it is the parameter of Fourier's cosinus transform with respect to p and G_R is the curve to be seen below:



$$G_R = [-R, R] \cup C_R$$

$$z = p + ir$$

$$\oint_{G_R} \frac{e^{-x^2}\, e^{ikz}}{[(z-\Gamma x)^2+d^2]^2}\, dz = \int_{-R}^{R} \frac{e^{-x^2}\, e^{ikp}}{[(p-\Gamma x)^2+d^2]^2}\, dp \; +$$

$$+ \int_{C_R} \frac{e^{-x^2}\, e^{ikz}}{[(z-\Gamma x)^2+d^2]^2}\, dz \qquad (48)$$

$$\lim_{R\to\infty} \oint_{G_R} \frac{e^{-x^2}\, e^{ikz}}{[(z-\Gamma x)^2+d^2]^2}\, dz = \int_{-\infty}^{+\infty} \frac{e^{-x^2}\, e^{ikp}}{[(p-\Gamma x)^2+d^2]^2}\, dp \qquad (49)$$

that results from

$$\lim_{R\to\infty} \int_{-R}^{R} \frac{e^{-x^2}\, e^{ikp}}{[(p-\Gamma x)^2+d^2]^2}\, dp \equiv \int_{-\infty}^{+\infty} \frac{e^{-x^2}\, e^{ikp}}{[(p-\Gamma x)^2+d^2]^2}\, dp \qquad \text{(50a) and}$$

$$\left| \int_{C_R} \frac{e^{-x^2}\, e^{ikz}}{[(z-\Gamma x)^2+d^2]^2}\, dz \right| \le \max_{z\in C_R} \left| \frac{e^{-x^2}\, e^{ikz}}{[(z-\Gamma x)^2+d^2]^2} \right| \cdot \pi R \qquad (50b)$$

(50b) is the application of the

$$\left| \int_{\gamma} f(z)\,dz \right| \le \max_{z\in\gamma} \left\{ |f(z)| \right\} \cdot l(\gamma) \qquad (51)$$

relation that is Cauchy's estimation where $l(\gamma)$ is the length of the curve γ. The denominator of the fraction in the right side of (50b) is equal to zero if $z = \Gamma x + id$ and accordingly in case of $R = \sqrt{(\Gamma x)^2 + d^2}$ and $\varphi = \text{arc tg}\, [d \cdot (\Gamma x)^{-1}]$. Since $|\exp(ikR \cos\varphi)| = 1$ in any case, $|\exp(-kR \sin\varphi)| \le 1$ along C_R if $k \ge 0$ and the numerator of the fraction is a linear function of R while the denominator is a polynomial of R of degree 4 not being equal to zero along C_R if $R > \sqrt{(\Gamma x)^2+d^2}$ the values of the denominator converge to $+\infty$ more quickly than that of the numerator if $R\to\infty$. That is why the values of the fraction converge to zero if $R\to\infty$. Thus the integral in the left side of (50b) has to converge to zero if $R\to\infty$.

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