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

Abstract: In this paper we explain the principles of an analytical method for calculating multicentre potential integrals built up from Gaussian basis functions. The method is based upon the theory of complex variable functions and the Fourier series form solutions of the two dimensional Laplace-equation. The multicentre integrals built up from Slater-type basis functions will be treated in the second part of the paper.

Note before the introduction: As almost each work from [3] to [12] in the referred literature contains the principles of the main part of the introduction in details we refer to books or articles only in a few cases in order to avoid the interruption of the text with references in many instances.

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Introduction: Let us consider a pair of two valence electrons a quantum mechanical system, which is the chemical bonding pair of a diatomic molecule. Let other valence electrons not be in the above-mentioned chemical bond. It is possible to construct the Hamilton operator of this electron pair if we choose the following work-hypotheses of the suitable ones. If the other electrons of the molecule are not valence electrons but so called core electrons belonging to either one or the other nucleus their effect on either of the valence electrons can be taken into account together with the influence of that nucleus they belong to. The effective potential of a system consisting of a nucleus and its core electrons can be expressed approximately with the aid of many pseudopotentials. [1]

These pseudopotentials can be derived from the statistical theory of atoms or from the wave mechanics. [1],[2],[3]
In the case of a valence electron mentioned above the effect of a nucleus and its core electrons on the valence electron can be given - among others - with the following pseudopotential form:

$$V(r)=V_{lr}(r)+V_{sr}(r),$$

$$V_{lr}(r) = -\frac{Z_c}{r} - \frac{\alpha_d}{2\left(r^2+d^2\right)^2} - \frac{\alpha_q}{2\left(r^2+d^2\right)^3}$$

$$V_{sr}(r) = \sum_l A_l r^p \exp\left(-\xi_l r^q\right).$$

In these formulas $V_{lr}(r)$ given by Bardsley[4] is a "long range" pseudopotential while V_{sr} is a "short range" one. The "r" variable means the distances between the nucleus and the points of the three-dimensional space. Z_C is the effective number of the elementary positive charges in the system of the nucleus and its core electrons. The $d, \xi_l, \alpha_d, \alpha_q, A_l$ quantities are atomic constants, p and q are integers.

The first member of V_{lr} is the effective potential of the nucleus and its core electrons affecting on the valence electrons of the atom, when it is not chemically bound to another one. The second and third members of $V_{lr}(r)$ are the consequences of the fact that the atoms chemically bound to each other and having different electronegativities polarize the atomic cores of each other, in consequence of which the atomic cores take effect on the valence electrons not with a pure Coulomb-type pseudopotential, but with a modified potential compared to the Coulomb-type one. If we put the origin of the system of co-ordinates in the nucleus of the first atom the Hamilton operator of the system of the two valence electrons has the following form in atomic units:

$$\hat{H} = -\frac{1}{2}\left(\Delta_1+\Delta_2\right) - \frac{Z_c(1)}{r_1} - \frac{Z_c(1)}{r_2} - \frac{Z_c(2)}{|\bar{R}_2-\bar{r}_1|} - \frac{Z_c(2)}{|\bar{R}_2-\bar{r}_2|} +$$

$$+ \frac{1}{|\bar{r}_1-\bar{r}_2|} - \frac{\alpha_d(1)}{2\left(r_1^2+d_1^2\right)^2} - \frac{\alpha_d(1)}{2\left(r_2^2+d_1^2\right)^2} - \frac{\alpha_d\,(2)}{2\left[\left(\bar{R}_2-\bar{r}_1\right)^2+d_2^2\right]^2} -$$

$$- \frac{\alpha_d\,(2)}{2\left[\left(\bar{R}_2-\bar{r}_2\right)^2+d_2^2\right]^2} - \frac{\alpha_q(1)}{2\left(r_1^2+d_1^2\right)^3} - \frac{\alpha_q(1)}{2\left(r_2^2+d_1^2\right)^3} -$$

$$- \frac{\alpha_q (2)}{2\left[\left(\bar{R}_2-\bar{r}_1\right)^2+d_2^2\right]^3} - \frac{\alpha_q (2)}{2\left[\left(\bar{R}_2-\bar{r}_2\right)^2+d_2^2\right]^3} +$$

$$+ \sum_l A_l (1)\, r_1^{p_1} \exp\left[-\xi_l (1)\, r_1^{q_1}\right] + \sum_l A_l (1)\, r_2^{p_1} \exp\left[-\xi_l (1)\, r_2^{q_1}\right] +$$

$$+ \sum_l A_l (2) \left|\bar{R}_2-\bar{r}_1\right|^{p_2} \exp\left[-\xi_l (2) \left|\bar{R}_2-\bar{r}_1\right|^{p_2}\right] +$$

$$+ \sum_l A_l (2) \left|\bar{R}_2-\bar{r}_2\right|^{p_2} \exp\left[-\xi_l (2) \left|\bar{R}_2-\bar{r}_2\right|^{p_2}\right] \qquad (1)$$

where $\bar{R}_2 = \left(X_2, Y_2, Z_2\right)$ is the position vector of the second nucleus, $r_1 = |\bar{r}_1|$, $r_2 = |\bar{r}_2|$ where $\bar{r}_1 = \left(x_1, y_1, z_1\right)$, $\bar{r}_2 = \left(x_2, y_2, z_2\right)$,
that are the position vectors of the corresponding electrons.

When the two-electron system is in the n-th stationary state its state-function having the $\bar{r}_1$, $\bar{r}_2$ position-vectors, the s_1, s_2 spin-co-ordinates and the t time-variable as arguments can be written in the following form according to the non-relativistic quantum-mechanical theory of the many-body problem:

$$\psi_n \left(\bar{r}_1, \bar{r}_2, s_1, s_2, t\right) = \psi_n \left(\bar{r}_1, \bar{r}_2, s_1, s_2\right) \exp\left[- \frac{2\Pi\sqrt{-1}}{h} E_n t\right], \qquad (2)$$

where h is the Planck-constant, E_n is the energy of the system satisfying the following equation too:

$$E_n = \int_{\infty} \psi_n^* \left(\bar{r}_1, \bar{r}_2, s_1, s_2\right) \hat{H} \psi_n \left(\bar{r}_1, \bar{r}_2, s_1, s_2\right) d\tau \text{ ,} \tag{3}$$

where $d\tau$ is the volume element in the configuration space of the system including the spin-co-ordinates of the electrons. The integral in (3) must be taken over the complete domain of all the variables. In the integration there is always included also a summation on the spin coordinates. $\psi_n\left(\bar{r}_1, \bar{r}_2, s_1, s_2\right)$ is to be expressed with a linear combination of innumerable Slater-determinants of the second order built up from one-electron functions of $\psi(\bar{r}, s)$ type:

21. $$\psi_n\left(\bar{r}_1, \bar{r}_2, s_1, s_2\right) = \sum_{i=1}^{\infty} C_i \Phi_i \left(\bar{r}_1, \bar{r}_2, s_1, s_2\right) \text{ ,} \tag{4a}$$

22. $$\Phi_i = \begin{vmatrix} \psi_{i\,I}\left(\bar{r}_1, s_1\right) & \psi_{i\,II}\left(\bar{r}_1, s_1\right) \\ \psi_{i\,I}\left(\bar{r}_2, s_2\right) & \psi_{i\,II}\left(\bar{r}_2, s_2\right) \end{vmatrix} \tag{4b}$$

where i denotes the i-th repetitionless second-class combination of an innumerable discrete sequence of one-electron $\psi(\bar{r}, s)$ functions, and the I,II indeces denote the first and the second member of the i-th combination of the $\psi(\bar{r}, s)$ one-electron functions

As $\psi_n\left(\bar{r}_1,\bar{r}_2,s_1,s_2,t\right)$ has to be normalized with the norm 1, $\psi_n\left(\bar{r}_1,\bar{r}_2,s_1,s_2\right)$ must also be normalized with the same norm. That is why the Φ_i determinants are to be built up from normalized $\psi(\bar{r},s)$ functions. The most general form of these $\psi(\bar{r},s)$ functions is the following:

$$\psi(\bar{r},s) = \psi_+(\bar{r})\alpha + \psi_-(\bar{r})\beta , \qquad (5)$$

where $\psi_+(\bar{r})$ and $\psi_-(\bar{r})$ have to satisfy the

$$\int_\infty \left[\psi_+^*(\bar{r})\psi_+(\bar{r}) + \psi_-^*(\bar{r})\psi_-(\bar{r})\right] d^3\bar{r} = 1 \qquad (6)$$

condition, α and β are the basic spin-functions forming an orthonormal function-system. In the spinor representation given by Pauli

$$\alpha = \begin{pmatrix}1\\0\end{pmatrix}, \qquad \beta = \begin{pmatrix}0\\1\end{pmatrix}.$$

The $\psi_+(\bar{r})$ and $\psi_-(\bar{r})$ functions of (4a) are usually unknown. In order to reduce the number of the unknown functions in (4a) the $\psi(\bar{r},s)$ ones are frequently written in the following forms that are less general and flexible than the form of $\psi(\bar{r},s)$ in (5):

$$\psi(\bar{r},s) = \begin{cases} \varphi_\alpha(\bar{r})\alpha \\ \varphi_\beta(\bar{r})\beta \end{cases}$$

Let each determinant in (4b) be built up from the $\psi(\bar{r},s)$ functions of the form given in (7). Thus the sum in (4a) can contain - among others- such determinants in which $\varphi_\alpha(\bar{r}) \equiv \varphi_\beta(\bar{r})$. Let Φ_j and Φ_k be such determinants:

$$\Phi_j = \begin{vmatrix} \varphi_j\left(\bar{r}_1\right)\alpha(1) & \varphi_j\left(\bar{r}_1\right)\beta(1) \\ \varphi_j\left(\bar{r}_2\right)\alpha(2) & \varphi_j\left(\bar{r}_2\right)\beta(2) \end{vmatrix}, \qquad (8a)$$

$$\Phi_k = \begin{vmatrix} \varphi_k\left(\bar{r}_1\right)\alpha(1) & \varphi_k\left(\bar{r}_1\right)\beta(1) \\ \varphi_k\left(\bar{r}_2\right)\alpha(2) & \varphi_k\left(\bar{r}_2\right)\beta(2) \end{vmatrix}. \qquad (8b)$$

According to (3) and (4a):

$$E_n = \int_\infty \sum_{i=1}^{\infty} c_i^* \Phi_i^* \hat{H} \sum_{l=1}^{\infty} c_l \Phi_l \, d\tau =$$

$$= \int_\infty \sum_{i=1}^{\infty} \sum_{l=1}^{\infty} c_i^* c_l \Phi_i \hat{H} \Phi_l \, d\tau =$$

$$= \sum_{i=1}^{\infty} \sum_{l=1}^{\infty} c_i^* c_l \int_\infty \Phi_i^* \hat{H} \Phi_l \, d\tau = \qquad (9)$$

Let us examine the $\int_\infty \Phi_i^* \hat{H} \Phi_l \, d\tau$ integral in that case when i=j, ℓ=k from (8a) and (8b).

$$\int_\infty \Phi_j^* \hat{H} \Phi_k \, d\tau = \int_\infty \begin{vmatrix} \varphi_j(\bar{r}_1)\alpha(1) & \varphi_j(\bar{r}_1)\beta(1) \\ \varphi_j(\bar{r}_2)\alpha(2) & \varphi_j(\bar{r}_2)\beta(2) \end{vmatrix} \hat{H} \begin{vmatrix} \varphi_k(\bar{r}_1)\alpha(1) & \varphi_k(\bar{r}_1)\beta(1) \\ \varphi_k(\bar{r}_2)\alpha(2) & \varphi_k(\bar{r}_2)\beta(2) \end{vmatrix} d\tau =$$

$$= \int_\infty \left[\varphi_j(\bar{r}_1)\varphi_j(\bar{r}_2)\alpha(1)\beta(2) - \varphi_j(\bar{r}_1)\varphi_j(\bar{r}_2)\alpha(2)\beta(1)\right]^* .$$

$$. \ \hat{H}\left[\varphi_k(\bar{r}_1)\varphi_k(\bar{r}_2)\alpha(1)\beta(2) - \varphi_k(\bar{r}_1)\varphi_k(\bar{r}_2)\alpha(2)\beta(1)\right] d\tau =$$

$$=\int_{\infty}\left[\varphi_j\left(\bar{r}_1\right)\varphi_j\left(\bar{r}_2\right)\alpha(1)\beta(2)\right]^{*}\hat{H}\left[\varphi_k\left(\bar{r}_1\right)\varphi_k\left(\bar{r}_2\right)\alpha(1)\beta(2)\right]d\tau\ -$$

$$-\int_{\infty}\left[\varphi_j\left(\bar{r}_1\right)\varphi_j\left(\bar{r}_2\right)\alpha(1)\beta(2)\right]^{*}\hat{H}\left[\varphi_k\left(\bar{r}_1\right)\varphi_k\left(\bar{r}_2\right)\alpha(2)\beta(1)\right]d\tau\ -$$

$$-\int_{\infty}\left[\varphi_j\left(\bar{r}_1\right)\varphi_j\left(\bar{r}_2\right)\alpha(2)\beta(1)\right]^{*}\hat{H}\left[\varphi_k\left(\bar{r}_1\right)\varphi_k\left(\bar{r}_2\right)\alpha(1)\beta(2)\right]d\tau\ +$$

$$\tag{10}$$

$$+\int_{\infty}\left[\varphi_j\left(\bar{r}_1\right)\varphi_j\left(\bar{r}_2\right)\alpha(2)\beta(1)\right]^{*}\hat{H}\left[\varphi_k\left(\bar{r}_1\right)\varphi_k\left(\bar{r}_2\right)\alpha(2)\beta(1)\right]d\tau$$

Taking into account the fact that the $\alpha(1),\beta(1)$ and $\alpha(2),\beta(2)$ spin-function pairs are separately orthonormal function-systems we get from (10):

$$\int_{\infty}\Phi_j^{*}\,\hat{H}\,\Phi_k d\tau = 2\int_{\infty}\int_{\infty}\varphi_j^{*}\left(\bar{r}_1\right)\varphi_j^{*}\left(\bar{r}_2\right)\,\hat{H}\,\left[\varphi_k\left(\bar{r}_1\right)\varphi_k\left(\bar{r}_2\right)\right]d^3\bar{r}_1 d^3\bar{r}_2 \tag{11}$$

H being a sum of operators the right-hand side of (11) is a sum of integrals. Let us consider the following member of this sum satisfying the undermentioned equation:

$$\int_{\infty}\int_{\infty}\varphi_j^{*}\left(\bar{r}_1\right)\varphi_j\left(\bar{r}_2\right)\frac{\alpha_d(2)}{\left[\left(\bar{R}_2-\bar{r}_1\right)^2+d_2^2\right]^2}\varphi_k\left(\bar{r}_1\right)\varphi_k\left(\bar{r}_2\right)d^3\bar{r}_1 d^3\bar{r}_2 =$$

$$=\int_{\infty}\varphi_j\left(\bar{r}_1\right)\frac{\alpha_d(2)}{\left[\left(\bar{R}_2-\bar{r}_1\right)^2+d_2^2\right]^2}\,\varphi_k\left(\bar{r}_1\right)d^3\bar{r}_1\cdot\int_{\infty}\varphi_j\left(\bar{r}_2\right)\varphi_k\left(\bar{r}_2\right)d^3\bar{r}_2 \qquad (12)$$

Let us investigate the first integral-factor in the right-hand side of (12). Let $\varphi_j\left(\bar{r}_1\right)$ and $\varphi_k\left(\bar{r}_1\right)$ be real functions. $\varphi_j\left(\bar{r}_1\right)$ and $\varphi_k\left(\bar{r}_1\right)$ can be written in the form of the linear combination of Gaussian-functions:

$$\varphi_j\left(\bar{r}_1\right) = \sum_p c_{jp}\left(\frac{2\alpha_{jp}}{\Pi}\right)^{\frac{3}{4}} \exp\left[-\alpha_{jp}\left(\bar{r}_1-\bar{R}_p\right)^2\right] \qquad (13a)$$

$$\varphi_k\left(\bar{r}_1\right) = \sum_q c_{kq}\left(\frac{2\alpha_{kq}}{\Pi}\right)^{\frac{3}{4}} \exp\left[-\alpha_{kq}\left(\bar{r}_1-\bar{R}_q\right)^2\right] \qquad (13b)$$

where $c_{jp}, c_{kq}, \alpha_{jp}, \alpha_{kq}$ are real constants. Putting (13a) and (13b) in the first integral-factor of (12) we get:

$$\int_{\infty}\varphi_j\left(\bar{r}_1\right)\frac{\alpha_d(2)}{\left[\left(\bar{R}_2-\bar{r}_1\right)^2+d_2^2\right]^2}\,\varphi_k\left(\bar{r}_1\right)d^3\bar{r}_1 =$$

$$= \int_{\infty}\sum_p c_{jp}\left(\frac{2\alpha_{jp}}{\Pi}\right)^{\frac{3}{4}} \exp\left[-\alpha_{jp}\left(\bar{r}_1-\bar{R}_p\right)^2\right]\frac{\alpha_d(2)}{\left[\left(\bar{R}_2-\bar{r}_1\right)^2+d_2^2\right]^2}\;\cdot$$

$$\cdot\;\sum_q c_{kq}\left(\frac{2\alpha_{kq}}{\Pi}\right)^{\frac{3}{4}} \exp\left[-\alpha_{kq}\left(\bar{r}_1-\bar{R}_q\right)^2\right]d^3\bar{r}_1\,. \qquad (14)$$

This integral is also equal to a sum of integrals. The general member of this sum is the following:

$$\cdot \int_{\infty} c_{jp} c_{kq} \left[\frac{4\alpha_{jp}\alpha_{kq}}{\Pi^2}\right]^{\frac{3}{4}} \exp\left\{-\left[\alpha_{jp}\left(\bar{R}_p-\bar{r}_1\right)^2+\alpha_{kq}\left(\bar{R}_q-\bar{r}_1\right)^2\right]\right\} \cdot$$

$$\cdot \frac{\alpha_d(2)}{\left[\left(\bar{R}_2-\bar{r}_1\right)^2+d_2^2\right]^2} d^3\bar{r}_1 . \qquad (15)$$

In this part of the paper we want to give a method for the beginning of the calculation of this integral.

Treatment: First let us express the exponent with the components of the $\bar{R}_p, \bar{R}_q, \bar{r}_1$ vectors:

$$-\left[\alpha_{jp}\left(\bar{R}_p-\bar{r}_1\right)^2+\alpha_{kq}\left(\bar{R}_q-\bar{r}_1\right)^2\right]=-\alpha_{jp}\left[\left(X_p-x_1\right)^2+\left(Y_p-y_1\right)^2+\left(Z_p-z_1\right)^2\right]-$$

$$-\alpha_{kq}\left[\left(X_q-x_1\right)^2+\left(Y_q-y_1\right)^2+\left(Z_q-z_1\right)^2\right]. \qquad (16)$$

It will be sufficient to investigate in details only the members of (15) depending on x_1 because the members depending separately on x_1, y_1, or z_1 have the same structure.

$$\alpha_{jp}\left(X_p-x_1\right)^2-\alpha_{kq}\left(X_q-x_1\right)^2= -\alpha_{jp}\left(X_p^2-2X_px_1+x_1^2\right)-\alpha_{kq}\left(X_q^2-2X_qx_1+x_1^2\right)=$$

$$= -\left(\alpha_{jp}X_p^2 - 2\alpha_{jp}X_px_1 + \alpha_{jp}x_1^2 + \alpha_{kq}X_q^2 - 2\alpha_{kq}X_qx_1 + \alpha_{kq}x_1^2\right)=$$

$$= -\left[\left(\alpha_{jp}+\alpha_{kq}\right)x_1^2-2\left(\alpha_{jp}X_p+\alpha_{kq}X_q\right)x_1+\alpha_{jp}X_p^2+\alpha_{kq}X_q^2\right]=$$

$$= -\left(\alpha_{jp}+\alpha_{kq}\right)\left[x_1^2-\frac{2\left(\alpha_{jp}X_p+\alpha_{kq}X_q\right)}{\alpha_{jp}+\alpha_{kq}}x_1+\frac{\alpha_{jp}X_p^2+\alpha_{kq}X_q^2}{\alpha_{jp}+\alpha_{kq}}\right]=$$

$$= -\left(\alpha_{jp}+\alpha_{kq}\right)\left[\left(x_1-\frac{\alpha_{jp}X_p+\alpha_{kq}X_q}{\alpha_{jp}+\alpha_{kq}}\right)^2+\frac{\alpha_{jp}X_p^2+\alpha_{kq}X_q^2}{\alpha_{jp}+\alpha_{kq}}-\right.$$

$$\left.-\left(\frac{\alpha_{jp}X_p+\alpha_{kq}X_q}{\alpha_{jp}+\alpha_{kq}}\right)^2\right] = -\left(\alpha_{jp}+\alpha_{kq}\right)\left(x_1-\frac{\alpha_{jp}X_p+\alpha_{kq}X_q}{\alpha_{jp}+\alpha_{kq}}\right)^2+$$

$$+\frac{\left(\alpha_{jp}X_p+\alpha_{kq}X_q\right)^2}{\alpha_{jp}+\alpha_{kq}}-\left(\alpha_{jp}X_p^2+\alpha_{kq}X_q^2\right). \qquad (17)$$

Now we can see that introducing the

$$\xi = x_1-\frac{\alpha_{jp}X_p+\alpha_{kq}X_q}{\alpha_{jp}+\alpha_{kq}} \qquad (18a)$$

$$\eta = y_1-\frac{\alpha_{jp}Y_p+\alpha_{kq}Y_q}{\alpha_{jp}+\alpha_{kq}} \qquad (18b)$$

$$\zeta = z_1 - \frac{\alpha_{jp} Z_p + \alpha_{kq} Z_q}{\alpha_{jp} + \alpha_{kq}} \qquad (18c)$$

arguments in place of x_1, y_1, z_1 the exponential function factor in the integrandus is to be written in the

$$\exp\left[-\left(\alpha_{jp}+\alpha_{kq}\right)\left(\xi^2+\eta^2+\zeta^2\right)\right. \quad \text{form.}$$

The integral in (15) expressed with the $\xi, \eta, \zeta,$ arguments gets a constant multiplier in front of the sign of the integration:

$$\exp\left[\frac{\left(\alpha_{jp}X_p+\alpha_{kq}X_q\right)^2+\left(\alpha_{jp}Y_p+\alpha_{kq}Y_q\right)^2+\left(\alpha_{jp}Z_p+\alpha_{kq}Z_q\right)^2}{\alpha_{jp}+\alpha_{kq}}+\right.$$

$$-\left(\alpha_{jp}X_p^2+\alpha_{kq}X_q^2\right)-\left(\alpha_{jp}Y_p^2+\alpha_{kq}Y_q^2\right)-\left(\alpha_{jp}Z_p^2+\alpha_{kq}Z_q^2\right)$$

rising only from the (17) expression of the exponent because from (18) we get the

$dx_1 = d\xi$ (19a), $dy_1 = d\eta$ (19b), $dz_1 = d\zeta$ (19c)

equations not giving constant multipliers to be written in front of the sign of the integration.

Introducing the

$$\xi' = \left(\alpha_{jp} + \alpha_{kq}\right)^{\frac{1}{2}} \xi \qquad (20a)$$

$$\eta' = \left(\alpha_{jp} + \alpha_{kq}\right)^{\frac{1}{2}} \eta \qquad (20b)$$

$$\zeta' = \left(\alpha_{jp} + \alpha_{kq}\right)^{\frac{1}{2}} \zeta \qquad (20c)$$

arguments in place of ξ, η, ζ the form of the exponential factor in the integrandus will be simpler:

$$\exp\left[-\left(\xi'^2 + \eta'^2 + \zeta'^2\right]\right.$$

From (20) we get:

$$d\xi = \left(\alpha_{jp}+\alpha_{kq}\right)^{-\frac{1}{2}} d\xi' \qquad (21a)$$

$$d\eta = \left(\alpha_{jp}+\alpha_{kq}\right)^{-\frac{1}{2}} d\eta' \qquad (21b)$$

$$d\zeta = \left(\alpha_{jp}+\alpha_{kq}\right)^{-\frac{1}{2}} d\zeta' \qquad (21c)$$

Taking into account (18) and (21) we can write:

$$dx_1 = \left(\alpha_{jp}+\alpha_{kq}\right)^{-\frac{1}{2}} d\xi' \qquad (22a)$$

$$dy_1 = \left(\alpha_{jp}+\alpha_{kq}\right)^{-\frac{1}{2}} d\eta' \qquad (22b)$$

$$dz_1 = \left(\alpha_{jp}+\alpha_{kq}\right)^{-\frac{1}{2}} d\zeta' \qquad (22c)$$

(21) gives another constant multiplier accompanying to the first one mentioned between (17) and (18):

$$\left(\alpha_{jp}+\alpha_{kq}\right)^{-\frac{3}{2}}.$$

Now let us transform the "polarizational" part of the integrandus. Its original form is:

$$\frac{\alpha_d(2)}{\left[\left(\bar{R}_2-\bar{r}_1\right)^2+d_2^2\right]^2} = \frac{\alpha_d(2)}{\left[\left(X_2-x_1\right)^2+\left(Y_2-y_1\right)^2+\left(Z_2-z_1\right)^2+d_2^2\right]^2} \qquad (23)$$

Applying the

$$\xi' = \left(\alpha_{jp}+\alpha_{kq}\right)^{\frac{1}{2}} \left[x_1 - \frac{\alpha_{jp}X_p+\alpha_{kq}X_q}{\alpha_{jp}+\alpha_{kq}}\right] \qquad (24a)$$

$$\eta' = \left(\alpha_{jp}+\alpha_{kq}\right)^{\frac{1}{2}} \left[y_1 - \frac{\alpha_{jp}Y_p+\alpha_{kq}Y_q}{\alpha_{jp}+\alpha_{kq}}\right] \qquad (24b)$$

$$\zeta' = \left(\alpha_{jp}+\alpha_{kq}\right)^{\frac{1}{2}} \left[z_1 - \frac{\alpha_{jp}Z_p+\alpha_{kq}Z_q}{\alpha_{jp}+\alpha_{kq}}\right] \qquad (24c)$$

formulas rising from (18) and (20) in (22) we get for the right side of (23):

$$\frac{\alpha_d(2)}{\left\{\left[X_2-\frac{1}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\left(\xi'+\frac{\alpha_{jp}X_p+\alpha_{kq}X_q}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\right)\right]^2+\right.}$$

$$\frac{\alpha_d(2)}{+\left[Y_2-\frac{1}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\left(\eta'+\frac{\alpha_{jp}Y_p+\alpha_{kq}Y_q}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\right)\right]^2}$$

$$\frac{\alpha_d \ (2)}{+\left[Z_2-\frac{1}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\left[\zeta'+\frac{\alpha_{jp}Z_p+\alpha_{kq}Z_q}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\right]\right]^2+d^2\Bigg\}^2} \qquad (25)$$

Multiplying (25) with $\exp\left[-\left(\xi'^2+\eta'^2+\zeta'^2\right)\right]$ we get the form of the integrandus expressed with the ξ', η', ζ' arguments and not containing any constant multipliers in front of the sign of the integration. Further on we will disregard the constant multipliers because it is possible to expound the principles of the beginning of the calculation disregarding them.

The integration in (15) was $\int_\infty f\left(\bar{r}_1\right)d^3\bar{r}_1$ - type and we have transformed it to the $\int_\infty F(\bar{\rho})d^3\bar{\rho}$ form, where $\bar{\rho} = \left(\xi', \eta', \zeta'\right)$, $d^3\bar{\rho} = d\xi' . d\eta' . d\zeta'$; The $\int_\infty F(\bar{\rho})d^3\bar{\rho}$ integration means simple integrations on the ξ', η', ζ' arguments from $-\infty$ to $+\infty$ in each case. It is allowed to begin the integration with that variable we want to, because the limits of the three single integrations are constants. So let us begin with the integration on ξ'. In this case the two other variables are to be considered as constants. The form of the integral on ξ' is the following:

$$\int_{-\infty}^{+\infty} \frac{\alpha_d(2)\ \exp\left[-\left(\eta'^2+\zeta'^2\right)\right]\exp\left[-\xi'^2\right]}{\left\{\left[X_2-\frac{1}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\left(\xi'+\frac{\alpha_{jp}X_p+\alpha_{kq}X_q}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\right)\right]^2+d'^2\right\}^2}\, d\xi' \qquad (26)$$

where

$$d'^2 = \left[Y_2-\frac{1}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\left(\eta'+\frac{\alpha_{jp}Y_p+\alpha_{kq}Y_q}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\right)\right]^2 +$$

$$+\left[Z_2-\frac{1}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\left(\zeta'+\frac{\alpha_{jp}Z_p+\alpha_{kq}Z_q}{\sqrt{\alpha_{jp}+\alpha_{kq}}}\right)\right]^2+d^2 \geq d^2 \qquad (27)$$

Let us introduce the following notations:

$$\Gamma \ \underline{\underline{\text{def}}}.\ \frac{1}{\sqrt{\alpha_{jp}+\alpha_{kq}}} \quad (28a), \qquad \Gamma_x \ \underline{\underline{\text{def}}}.-\ \frac{\alpha_{jp}X_p+\alpha_{kq}X_q}{\alpha_{jp}+\alpha_{kq}} \quad (28b)$$

Using these notations the integral in (26) has the following form:

$$\int_{-\infty}^{+\infty} \frac{\alpha_d(2)\exp\left[-\left(\eta'^2+\zeta'^2\right)\right]\exp\left[-\xi'^2\right]}{\left[\left(X_2 - \Gamma\xi' + \Gamma_x\right)^2 + d'^2\right]^2} d\xi' \qquad (29)$$

Let us introduce the ϑ notation with the following definition:

$\vartheta = X_2 + \Gamma_x$. With this notation the integral in (29) can be written in the following form:

$$\int_{-\infty}^{+\infty} \frac{\alpha_d(2)\exp\left[-\left(\eta'^2+\zeta'^2\right)\right]\exp\left[-\xi'^2\right]}{\left[\left(\vartheta - \Gamma\xi'\right)^2 + d'^2\right]^2} d\xi' \qquad (30)$$

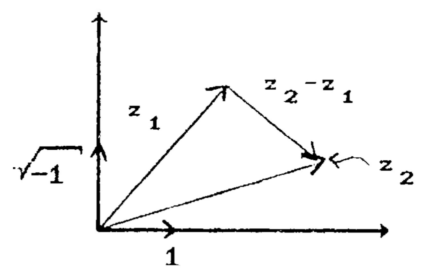
First we have to solve the problem of the calculation of the integral of the following-type:

$$\int_{\infty}^{+\infty} \frac{\exp\left[-\xi'^2\right]}{\left[\left(\vartheta - \Gamma\xi'\right)^2 + d'^2\right]^2} d\xi' \qquad (31)$$

If we solve the problem of the calculation of this integral, then multiplying the result with $\exp\left[-\left(\eta'^2+\zeta'^2\right)\right]$ we can continue the integration on η' or in the other case on ζ' . Now let us deal with the integral in (31). This integral can be calculated approximately with the method of the numerical analysis. In this case we ought to apply the Hermite-Gauss integration formula approaching the value of the integral with a sum. With this technique we could calculate the original $\int_{\infty} \cdots d^3\bar{r}$ integral applying the Hermite-Gauss-formula three times. But in this article we want to explain the beginning of an analytical method.

In mathematics one of the methods for calculating definite real integrals is based upon the so-called residuum-theorem of the theory of complex variable functions. In some cases we can use a simpler form of this theorem, the Cauchy-theorem. Let us begin with showing the possibilities and the conditions of applying Cauchy's theorem for calculating definite real integrals.

Let $z = x+\sqrt{-1}\,.\,y \equiv x+iy,$ where x,y are real numbers. x is the real part of z while iy is the imaginary one. Consisting of two parts z is called a complex number. The complex numbers can be described as the vectors of the complex Gauss-Argand number-plane:



If $z_1=x_1\pm iy_1$, $z_2=x_2\pm iy_2$, then

$$z_1 \pm z_2 = \left(x_1\pm x_2\right)+i\left(y_1\pm y_2\right), \tag{32a}$$

$$z_1 \cdot z_2 = \left(x_1+iy_1\right)\cdot\left(x_2+iy_2\right) =$$

$$= x_1x_2+ix_1y_2+iy_1x_2-y_1y_2 =$$

$$= \left(x_1x_2-y_1y_2\right) + i\left(x_1y_2+x_2y_1\right) \tag{32b}$$

according to the definitions of the summation and the multiplication of complex numbers.

Let f(z) be a function of z projecting the complex number-plane onto itself. As the values of f(z) are complex numbers f(z) consists of a real and an imaginary part:

$$f(z) = u(x,y)+iv(x,y) , \tag{33}$$

where u(x,y) and v(x,y) are real functions.

$\int\limits_{a\,(G)}^{b} f(z)dz$ means a complex integral of the f(z) function that must be taken on the complex number-plane along the G curve between its a and b points:

$$\int\limits_{a\,(G)}^{b} f(z)dz = \int\limits_{a\,(G)}^{b} \left[u(x,y)+iv(x,y)\right]d(x+iy) =$$

$$= \int\limits_{a\,(G)}^{b} \left[u(x,y)+iv(x,y)\right]dx + \int\limits_{a\,(G)}^{b} \left[u(x,y)+iv(x,y)\right]d(iy) =$$

$$= \int_{a\,(G)}^{b} u(x,y)dx + i\int_{a\,(G)}^{b} v(x,y)dx + i\int_{a\,(G)}^{b} u(x,y)dy - \int_{a\,(G)}^{b} v(x,y)dy =$$

$$= \int_{a\,(G)}^{b} \left[u(x,y)dx - v(x,y)dy\right] + i\int_{a\,(G)}^{b} \left[u(x,y)dx + v(x,y)dx\right], \qquad (34)$$

where we have used (32a) and (32b).

It is to be seen that a complex integral of a complex variable function can be calculated with the aid of real integrals.

Let G be a closed curve of the complex number-plane and let f(z) be analytical on the set consisting of all points of the closed G curve and also in all points of the region of the plane bordered by this curve. In this case

$$\oint_{(G)} f(z)dz = 0. \qquad (35)$$

This is Cauchy's theorem. The analyticy of f(z) on a set means that

$$\left|f'(z)\right| = \left|\lim_{h \to 0} \frac{f(z+h)-f(z)}{h}\right| \neq +\infty \qquad (36)$$

exists in each point of the set, where h means complex numbers. The operation defined in (36) is called the complex derivation of f(z).

Cauchy and Riemann have proved that f'(z) exists in the z point only in that case if the $\frac{\partial u}{\partial x}$, $\frac{\partial u}{\partial y}$ $\frac{\partial v}{\partial x}$, $\frac{\partial v}{\partial y}$, partial derivatives exist in this point and satisfy the so-called Cauchy-Riemann equations:

$$\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y}\ , \quad \frac{\partial u}{\partial y} = -\frac{\partial v}{\partial x} \qquad (37)$$

How can we calculate $\int_a^b f(x)dx$ using Cauchy's theorem? First we have to write z in place of x in f(x) then we have to form the $\oint f(z)dz$ integral along a closed G curve containing the $[a,b]$ interval of the x-axis. If f(z) is analytical along G and within the region of the plane bordered by G we can write using (35) and the z=x,if y=0 equation:

$$\oint_{(G)} f(z)dz = \int_{\substack{z_1\\(G_1)}}^{z_2} f(z)dz + \int_{\substack{z_2\\(G_2)}}^{z_3} f(z)dz + \dots + \int_{\substack{z_k\\(G_k)}}^{z_{k+1}} f(z)dz +$$

$$+ \int_a^b f(x)dx + \dots + \int_{\substack{z_{n-1}\\(G_{n-1})}}^{z_n} f(z)dz = 0, \qquad (38)$$

where $G_1 \cup G_2 \cup \dots \cup G_k \cup \dots \cup [a,b] \cup \dots \cup G_{n-1} = G.$

(U is the sign of forming the union of sets.)

If we can calculate the values of the integrals of the sum in the right-hand side of (36) except $\int_a^b f(x)dx$ with simple analytical methods,

the (38) equation gives us an analytical formula for the value of

$\int_a^b f(x)dx$.

The application of this method and that of the two-dimensional Laplace-equation for the calculation of the integral in (31) will be treated in the second part of this paper.

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