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Note

The Derivatives of Single-Center Integrals Involving Gaussian Functions

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In an »*ab initio*« calculation of harmonic force constants from a single-center wave function, derivatives of various one- and two-electron integrals are required. Using Slater orbitals as basic functions, the derivatives of single-center integrals were evaluated in analytical form by Bishop and Randić[1]. Since wider applications of Gaussian orbitals in molecular calculations may be anticipated, we have undertaken to derive formulae for the derivatives of these integrals using Gaussian functions as a basis.

We consider first overlap and normalization integrals. These are of the form:

$$I_1(n, \zeta) = \int_0^\infty r^n e^{-\zeta r^2} dr = \frac{1}{2}\, \Gamma\left(\frac{n+1}{2}\right) \Big/ \zeta^{\frac{n+1}{2}}$$

The derivatives with respect to n and ζ are:

$$\frac{\partial I_1(n, \zeta)}{\partial n} = [I_1(n, \zeta)/2] \left[\psi\left(\frac{n+1}{2}\right) - \ln \zeta\right]$$

$$\frac{\delta^2 I_1(n, \zeta)}{\partial n^2} = [I_1(n, \zeta)/4] \left[\left\{\psi\left(\frac{n+1}{2}\right) - \ln \zeta\right\}^2 + \psi'\left(\frac{n+1}{2}\right)\right]$$

$$\frac{\partial I_1(n, \zeta)}{\partial \zeta} = - I_1(n+2, \zeta)$$

where $\psi(n)$ and $\psi'(n)$ are digamma and trigamma functions respectively defined in the same way as the first and second logarithmic derivatives of a gamma function:

$$\psi(n) = \frac{d}{dn} \ln \Gamma(n) \quad \text{and} \quad \psi'(n) = \frac{d}{dn}\, \psi(n)$$

These functions are discussed earlier[1] and also in the references cited therein.

The one-electron integrals take the form:

$$I_2(n, \zeta, k, R) = \int_0^\infty \frac{r_<^k}{r_>^{k+1}}\, e^{-\zeta r^2} r^n dr$$

where $r_<$ and $r_>$ are the lesser and greater of r and R respectively. This integral can be expressed as follows:

$$I_2(n,\zeta,k,R)=\frac{1}{2}\left[\frac{\varrho}{\zeta}\right]^{\frac{n}{2}}\left[\varrho^{\frac{k-n}{2}}\,\Gamma\left(\frac{n-k}{2}\right)+F\left(\varrho,\frac{n+k-1}{2}\right)-F\left(\varrho,\frac{n-k-2}{2}\right)\right]$$

Here $\varrho=\zeta R^2$ and $F(x,p)$ is an auxilliary function defined as:

$$F(x,p)=x^{-p-1}\int_0^x t^p e^{-t}\,dt$$

Using the relationship:

$$x\,F(x,p)=p\,F(x,p-1)-e^{-x}$$

and

$$\frac{\partial F(x,p)}{\partial x}=-F(x,p+1)$$

the derivatives $\frac{\partial I_2}{\partial R}$ and $\frac{\partial^2 I_2}{\partial R^2}$ may be again expressed in a form similar to that given by Bishop and Randić[1]:

$$\frac{\partial I_2(n,\zeta,k,R)}{\partial R}=\frac{1}{2}\left[\frac{\varrho}{\zeta}\right]^{\frac{n-1}{2}}\left[k\,\varrho^{\frac{k-n}{2}}\,\Gamma\left(\frac{n-k}{2}\right)-\right.$$

$$\left.-k\,F\left(\varrho,\frac{n-k-2}{2}\right)-(k+1)\,F\left(\varrho,\frac{n+k-1}{2}\right)\right]$$

$$\frac{\partial^2 I_2(n,\zeta,k,R)}{\partial R^2}=\frac{1}{2}\left[\frac{\varrho}{\zeta}\right]^{\frac{n}{2}-1}\left[k(k-1)\,\varrho^{\frac{k-n}{2}}\,\Gamma\left(\frac{n-k}{2}\right)+\right.$$

$$\left.+k(1-k)\,F\left(\varrho,\frac{n-k-2}{2}\right)+(k+1)(k+2)\,F\left(\varrho,\frac{n+k-1}{2}\right)-2(2k+1)\,e^{-\varrho}\right]$$

Derivatives of I_2 with respect to n are easily found if $\frac{\partial F}{\partial p}$ and $\frac{\partial^2 F}{\partial p^2}$ are known. The latter ones are already quoted.[1]

Finally:

$$\frac{\partial I_2(n,\zeta,k,R)}{\partial \zeta}=-I_2(n+2,\zeta,k,R)$$

The two-electron integrals, which are of the form:

$$I_3(n_1,\zeta_1,n_2,\zeta_2,k)=\int_0^\infty\int_0^\infty r_1^{n_1}\,e^{-2\zeta_1 r_1^2}\,\frac{r_<^k}{r_>^{k+1}}\,r_2^{n_2}\,e^{-2\zeta_2 r_2^2}\,dr_1\,dr_2$$

where $r_<$, $r_>$, are the lesser and greater of r_1 and r_2 respectively, can be split into two parts:

$$I_3^{(1)}=\int_0^\infty dr_1\,r_1^{n_1-k-1}\,e^{-2\zeta_1 r_1^2}\int_0^{r_1} dr_2\,r_2^{n_2+k}\,e^{-2\zeta_2 r_2^2}$$

and

$$I_3^{(2)}=\int_0^\infty dr_1\,r_1^{n_1+k}\,e^{-2\zeta_1 r_1^2}\int_{r_1}^\infty dr_2\,r_2^{n_2-k-1}\,e^{-2\zeta_2 r_2^2}$$

The substitution:

$$r_1=[x(1-t)/2\,\zeta_1]^{1/2}\qquad r_2=[x\,t/2\,\zeta_2]^{1/2}$$

yields

$$I_3^{(1)} = \frac{1}{4} A \left(\frac{n_1 - k}{2}, \zeta_1, \frac{n_2 + k + 1}{2}, \zeta_2 \right) J_\alpha \left(\frac{n_2 + k + 1}{2}, \frac{n_1 - k}{2} \right)$$

where

$$A (p, \zeta_1, q, \zeta_2) = \frac{\Gamma (p) \Gamma (q)}{(2 \zeta_1)^p (2 \zeta_2)^q}$$

$$J_\alpha (p, q) = \int_0^\alpha t^{p-1} (1 - t)^{q-1} \, dt / B (p, q)$$

$\alpha = \zeta_2/(\zeta_1 + \zeta_2)$, and $B (p, q)$ is Euler's integral of the first kind or Beta function:

$$B (p, q) = \frac{\Gamma (p) \Gamma (q)}{\Gamma (p + q)}$$

Similarly:

$$I_3^{(2)} = \frac{1}{4} A \left(\frac{n_1 + k + 1}{2}, \zeta_1, \frac{n_2 - k}{2}, \zeta_2 \right) J_{1-\alpha} \left(\frac{n_1 + k + 1}{2}, \frac{n_2 - k}{2} \right)$$

which can be simply obtained by the permutation of indices *1* and *2* of n and ζ of the first integral. Derivatives of I_3 require the derivative of I_α. These are discussed[1] and will not be repeated here. In the last formula in ref. 1 a minus sign is missing and the expression should read:

$$\frac{\partial^2 c}{\partial p \, \partial q} = - \sum_{j=1}^{\infty} x^j (p + j)^{-2}$$

All the formulae for the derivatives obtained for Gaussian orbitals resemble the corresponding expressions when Slater type orbitals are used, the only difference being the values of the parameters which appear in the auxiliary and gamma functions and their coefficients.

We have also considered more general functions of the form:

$$f (n, \zeta, s) = r^n e^{-\zeta r^s}$$

The formulae for the integrals I_1, I_2 and I_3, and their derivatives can be derived in a similar way. For example:

$$I_1 (n, \zeta, s) = \frac{1}{s} \Gamma \left(\frac{n+1}{s} \right) \Big/ \zeta^{\frac{n+1}{s}}$$

$$I_2 (n, \zeta, k, R, s) = \frac{1}{s} \left[\frac{\varrho}{\zeta} \right]^{\frac{n}{s}} \left[\varrho^{\frac{k-n}{s}} \Gamma \left(\frac{n-k}{s} \right) + F \left(\varrho, \frac{n+k+1-s}{s} \right) - \right.$$

$$\left. - F \left(\varrho, \frac{n-k-s}{s} \right) \right]$$

$$I_3^{(1)} (n_1, \zeta_1, n_2, \zeta_2, s) = \frac{1}{s^2} A \left(\frac{n_1 - k}{s}, \zeta_1, \frac{n_2 + k + 1}{s}, \zeta_2 \right) \cdot$$

$$\cdot J_\alpha \left(\frac{n_2 + k + 1}{s}, \frac{n_1 - k}{s} \right)$$

which reduce to known formulae for Slater and Gaussian orbitals when $s = 1$ and $s = 2$ respectively. Work on the derivatives of many-center integrals is in progress.

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REFERENCES

1. D. M. Bishop and M. Randić, *J. Chem. Phys.* **44** (1966) 2480.

IZVOD

Derivacije nekih integrala jednog centra s Gaussovim funkcijama

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Izvedene su formule za derivacije po parametrima nekih integrala jednog centra s Gaussovim funkcijama. Dobiveni rezultati su slični odgovarajućim izrazima za Slaterove funkcije. Promatran je i slučaj općenitijih funkcija oblika $f = r^n e^{-\zeta r^s}$ koje u sebi sadrže Slaterove i Gaussove orbitale kao specijalne slučajeve.

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