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Relationes

Semi-Asymptotic Evaluation of Certain Three-Center Two-Electron Integrals*

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Two-electron repulsion integrals between a two-center charge distribution and a charge distribution about a third center, which do not appreciably interpenetrate, are shown to be given to useful accuracy by numerical differentiation of certain three-center one-electron integrals. This method also may be used to evaluate integrals of this type for which the Mulliken or Sklar approximations are inapplicable.

In the theoretical study of polyatomic molecules many two-electron, three-center hybrid integrals (AB | CC′) occur, wherein the two-center charge distribution (AB) and the one-center charge distribution (CC′) are essentially non-penetrating. Such integrals can be evaluated by standard techniques with arbitrarily high accuracy [1] or estimated by such as the Mulliken [2] or Sklar [3] approximation, provided the two-center overlap integral S(AB) does not vanish identically. We point out a numerical technique for evaluating this type of integral, which makes use of an existing facility to compute three-center, one-electron nuclear attraction integrals.

Write the integral $I = (\mathrm{AB}\,|\,\mathrm{CC}')$ as

$$I = \int \chi_{\mathrm{A}}(1)\,\chi_{\mathrm{B}}(1)\,\{\int \chi_{\mathrm{C}}(2)\,\chi'_{\mathrm{C}}(2)\,dv_2/r_{12}\}\,dv_1\ ; \tag{1}$$

$\chi_i(\mu)$ is a function assigned to center i having the general form

$$\chi_i(\mu) = R_n(r_\mu)\,S_{lm}(\theta_\mu, \phi_\mu) \tag{2}$$

for coordinate system μ. $S_{lm}(\theta_\mu, \phi_\mu)$ is a normalized real spherical harmonic and $R_n(r_\mu)$ is a suitable radial function. In what follows, we shall take $\chi_i(\mu)$ to be a normalized Slater-Type-Orbital (STO) with integral principal quantum number n and orbital exponent ζ. Generalizations to other radial function dependences will be obvious. See Fig. 1 for details of the coordinate systems.

As shown for instance by Roothaan [4], a one-center charge distribution may be expanded according to

$$\chi_{\mathrm{C}}(\mu)\,\chi'_{\mathrm{C}}(\mu) = \sum_{L,M} \alpha_{L,M}\,f_{N,L}(r_\mu)\,S_{L,M}(\theta_\mu, \phi_\mu)\,. \tag{3}$$

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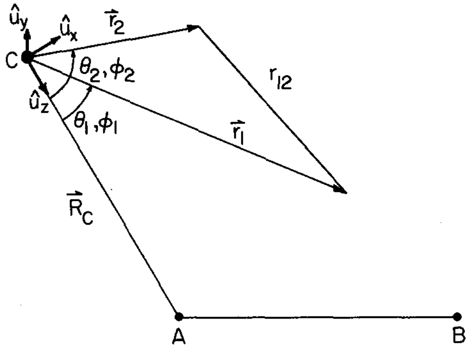

Fig. 1. Definition of coordinate systems. $\boldsymbol{u}_y$ is perpendicular to the BAC plane

The coefficients $\alpha_{L,M}$ are zero except when $0 \leqq L, |M| \leqq l + l'$;

$$f_{N,L}(r) = \left(\frac{2L+1}{4\pi}\right)^{\frac{1}{2}} \frac{2^L(2\bar{\zeta})^{N+2}}{(N+L+1)!} r^{N-1} \exp(-2\bar{\zeta}r),$$

where $N = n + n' - 1$ and $2\bar{\zeta} = \zeta + \zeta'$. Alternatively, Eq. (3) can be expressed in terms of homogeneous polynomials of Cartesian coordinates:

$$\chi_C(\mu)\,\chi'_C(\mu) = \sum_{p,q,t} \beta_{pqt} f_{N,L}(r_\mu)\, x_\mu^p y_\mu^q z_\mu^t r_\mu^{-L} \tag{3'}$$

with $p + q + t = L$.

Inserting Eq. (3) into Eq. (1) yields

$$I = \sum_{L,M} \alpha_{L,M} \int \chi_A(1)\,\chi_B(1)\, V_{L,M}(1)\, dv_1 \tag{4}$$

with

$$V_{L,M}(1) = \int f_{N,L}(r_2)\, S_{L,M}(\theta_2, \phi_2)\, dv_2/r_{12}\,.$$

At large distances $f_{N,L}(r)\, S_{L,M}(\theta, \phi)$ behaves as a multipole of order 2^L and magnitude $\bar{\zeta}^{-L}$. These circumstances occur when $(\bar{\zeta}r_1)^{N+L}\exp(-2\bar{\zeta}r_1) \ll 1$, and then

$$V_{L,M}(1) \to \bar{\zeta}^{-L} r_1^{-L-1}\, S_{L,M}(\theta_1, \phi_1)\,. \tag{5}$$

Now Eq. (4) becomes

$$I = \sum_{L,M} \alpha_{L,M} \bar{\zeta}^{-L} \int \chi_A(1)\,\chi_B(1)\, S_{L,M}(\theta_1, \phi_1)\, r_1^{-L-1}\, dv_1\,. \tag{6}$$

The alternate substitution of Eq. (3′) into Eq. (1) yields

$$I = \sum_{p,q,t} \beta_{pqt} \bar{\zeta}^{-L} \int \chi_A(1)\,\chi_B(1)\, x_1^p y_1^q z_1^t r_1^{-2L-1}\, dv_1\,. \tag{6'}$$

Each integral in Eq. (6) or (6′) may be written in terms of derivatives of three-center nuclear attraction integrals

$$U_{pqt}(\boldsymbol{R}_c) = \frac{\partial^p}{\partial x^p} \frac{\partial^q}{\partial y^q} \frac{\partial^t}{\partial z^t} \int \chi_A(1)\,\chi_B(1)\, r_1^{-1}\, dv_1\,. \tag{7}$$

The procedure suggested here involves computing the integral in (7) at sufficient points $\boldsymbol{R}_c + \boldsymbol{\delta}$ in the neighborhood of point C to effect a *numerical* evaluation of (7) at point C. Let

$$U(\boldsymbol{R}_c + \boldsymbol{\delta}) = \int \chi_A(1)\, \chi_B(1)\, |\boldsymbol{r}_1 - \boldsymbol{\delta}|^{-1}\, dv_1$$

with

$$\boldsymbol{\delta} = \delta_x \boldsymbol{u}_x + \delta_y \boldsymbol{u}_y + \delta_z \boldsymbol{u}_z .$$

Then, for example,

$$U_{020}(\boldsymbol{R}_C) = \delta_y^{-2}\, [U(\boldsymbol{R}_C + \delta_y \boldsymbol{u}_y) - 2U(\boldsymbol{R}_C) + U(\boldsymbol{R}_C - \delta_y \boldsymbol{u}_y)] \; ;$$

and the integral

$$I = (\chi_A(1)\, \chi_B(1) \,|\, 2py_C(2)\; 2py_C(2))$$

is evaluated according to

$$\begin{aligned} I &= \int \chi_A(1)\, \chi_B(1) \left[r_1^{-1} + \frac{6!}{10(4!)\zeta^2} \left(\frac{3y_1^2 - r_1^2}{2r_1^5} \right) \right] dv_1 \\ I &= U(\boldsymbol{R}_C) + (3/2)\, \zeta^{-2}\, U_{020}(\boldsymbol{R}_C) , \end{aligned} \tag{8}$$

where ζ is the orbital exponent of the $2py$ STO.

This procedure has been tested using the two-center coulomb and the three-center hybrid integrals $(2py_A(1)\, 2py_B(1) \,|\, 2py_C(2))$ calculated by Karplus and Shavitt [5] for the pi-electron repulsion in benzene. The $2p\pi$ STO orbital exponent (1.590) and C–C distance (2.6320755 a.u.) as used in Ref. [5] were taken. The Table presents the exact values, the monopole ($L=0$) contribution and the complete calculation by Eq. (8), various errors, the distance R_{cent} between centroids of the (AB) and (CC′) charge distributions, all arranged according to the value of the "convergence criterion" $\varrho^3 \exp(-2\varrho)$, with $\varrho = \bar{\zeta} R_{\text{cent}}$. The three-center nuclear attraction integrals required were computed accurate to within $\pm 2 \times 10^{-6}$ a.u.; the differences occuring in $U_{020}(\boldsymbol{R}_C)$, however, are at least an order of magnitude more accurate. δ_y was set to 0.1 a.u.

It is seen from these results that the present method yields errors only in the fifth decimal place when $\varrho^3 \exp(-2\varrho) < 10^{-3}$, and that the percent errors are (as expected) proportional to that quantity. When R_{cent} is smaller, interpenetration of the two charge distributions leads to much larger errors, which are all positive though smaller in magnitude than those from the Mulliken or the Sklar approximations.

For evaluating integrals of this class, therefore, the method appears to give reasonably accurate results at a cost of calculating but several three-center nuclear attraction integrals. As well, it affords a method (useful even in smaller ranges of R_{cent}) for reliably approximating integrals which, because the $\chi_A(1)\, \chi_B(1)$ charge distribution in Eq. (1) has a vanishing overlap integral, do not yield to the Mulliken or the Sklar approximations.

Table. *π-electron repulsion integrals (in a. u.) for the benzene molecule*

Integral AB CC	Accurate Values[a]	Monopole Contribution	Eq. (8)	Error from Eq. (8) × 10^6	Percent Errors: Mulliken Approx.[a]	Percent Errors: Sklar Approx.[a]	Percent Errors: Eq. (8)	$\varrho^3 \exp(-2\varrho)$	$\frac{R_{cent}}{R_{C-C}}$
26 11	0.016131	0.016806	0.018313	2182	−20.04	+19.30	+13.53	0.139	0.50
25 11	0.005416	0.005546	0.005588	172	−11.61	+ 8.59	+ 3.18	0.0170	1.00
22 11	0.331838	0.347820	0.337555	5717	—	—	+ 1.72	0.0170	1.00
23 11	0.068193	0.070148	0.068588	365	+ 2.97	+ 0.799	+ 0.535	0.00477	1.25
24 11	0.010001	0.010232	0.010089	88	− 0.03	+ 2.77	+ 0.880	0.00264	1.32
35 11	0.008846	0.009021	0.008866	20	− 8.43	+ 4.16	+ 0.226	0.000873	1.50
33 11	0.208385	0.213090	0.208434	48	—	—	+ 0.023	0.000192	1.73
34 11	0.051664	0.052659	0.051674	10	− 1.64	+ 1.10	+ 0.019	0.000120	1.80
44 11	0.182605	0.185897	0.182614	9	—	—	+ 0.005	0.000032	2.00

[a] Values of the three-center hybrid integrals and their approximations are taken from Ref. [5].

References

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