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# Note on an Integral of A. F. Saturno

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A simple derivation is given of an integral discussed by Saturno in connection with certain atomic inter-electron repulsion integrals. This derivation extends the method to any type of atomic orbital, and it can be used to derive the values of similar Coulomb integrals when the two atomic centres are a distance $R$ apart.

In a recent paper in this journal [1] Saturno has proposed a simple electrostatic model for the one-centre Coulomb integral $(pp|pp)$, where $p$ is a standard normalized Slater-type atomic orbital

$$\chi_p = N_{lm\zeta}\, r^l\, e^{-\zeta r}\, Y_{lm}(\theta, \phi) \tag{1}$$

and $N^2_{lm\zeta} = (2\zeta)^{2l+3}/(2l+2)!$, and $Y_{lm}$ is itself normalized on the surface of a sphere.

The integral to be evaluated is

$$V_{pp} = \iint \chi_p^2(1)\, \chi_p^2(2)\, (r_1 + r_2)^{-1}\, d\tau_1\, d\tau_2 \tag{2}$$

$$= \frac{2\zeta}{[(2l+2)!]^2} \int_0^\infty\!\!\int x^{2l+2}\, e^{-x}\, y^{2l+2}\, e^{-y}\, \frac{dx\, dy}{x+y}. \tag{3}$$

The purpose of this note is 1) to provide a very simple method for evaluating (3), which avoids all use of incomplete gamma functions and exponential integrals such as occur in the method used by Saturno; 2) to show that the new method can be used for much more general atomic orbitals than Slater-type ones; 3) to indicate how by the same method, we can also evaluate the two-centre Coulomb integral $(pp|qq)$ where $p$ and $q$ are similar atomic orbitals on different centres $A$ and $B$ separated by a distance $R$; and 4) to evaluate $(pp|qq)$ where $p$ and $q$ are different orbitals on the same or different atoms.

1) If, in (3) we write

$$\frac{1}{x+y} = \int_0^\infty e^{-t(x+y)}\, dt \tag{4}$$

the integrations over $x$ and $y$ are immediate, and we find that

$$V_{pp} = \frac{2\zeta}{[(2l+2)!]^2} \int_0^\infty \frac{(2l+2)!}{(t+1)^{2l+3}} \cdot \frac{(2l+2)!}{(t+1)^{2l+3}}\, dt = \frac{2\zeta}{4l+5} \tag{5}$$

as found with much more trouble by Saturno.

2) In general we write (2) in the form

$$V_{pp} = \int_0^\infty dt \int \chi_p^2(1)\, \chi_p^2(2)\, e^{-t(r_1+r_2)}\, d\tau_1\, d\tau_2$$
$$= \int_0^\infty \{F_p(t)\}^2\, dt \tag{6}$$

where

$$F_p(t) = \int \chi_p^2(1)\, e^{-tr_1}\, d\tau_1\,. \tag{7}$$

The integrations in (6) and (7) are usually elementary, whatever the analytic form of $\chi_p$. Moreover, even self-consistent-field orbitals can be chosen if numerical methods are used. It should therefore be possible to extend Saturno's discussion of $(pp|pp)$ to include different choices of $\chi_p$.

3) If $\chi_p$ and $\chi_q$ are similar normalized orbitals on centres $A$ and $B$, a distance $R$ apart, the generalization of Saturno's model leads to the evaluation of

$$(pp|qq) = \iint \chi_p^2(1)\, \chi_q^2(2)\, (r_1 + r_2 + R)^{-1}\, d\tau_1\, d\tau_2\,. \tag{8}$$

Using a simple extension of (4) this may be written

$$(pp|qq) = \int_0^\infty F_p(t)\, F_q(t)\, e^{-tR}\, dt$$
$$= \int_0^\infty \{F_p(t)\}^2\, e^{-tR}\, dt \tag{9}$$

where $F_p$ (and $F_q$) are defined as in (7).

The integration (9) can always be completed numerically if necessary. But if we adopt the Slater form (1) for $\chi_p$ and $\chi_q$

$$(pp|qq) = \int_0^\infty \frac{(2\zeta)^{4l+6}}{(2\zeta + t)^{4l+6}}\, e^{-tR}\, dt$$
$$= 2\zeta\, e^{2\zeta R}\, E_{4l+6}(2\zeta R)$$

where $E_n(x)$ is the generalized exponential integral [2] defined by

$$E_n(x) = \int_1^\infty e^{-xt}\, t^{-n}\, dt\,.$$

Some numerical values of this function are available [3].

4) If $p$ and $q$ are now different orbitals on atoms $A$ and $B$, Eq. (9) still applies, with $F_p(t) \neq F_q(t)$; but the final integration may need to be completed numerically. However, even in this case it presents no particular difficulty.

## References

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