THE CALCULATION OF OVERLAP INTEGRALS BETWEEN
SLATER-TYPE ORBITALS WITH NEARLY EQUAL EXPONENTS

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It is shown that the usual formulas for the auxilary functions $B_n(\alpha)$, necessary for the calculation of overlap integrals, give inaccurate results for small values of α. Attention is drawn to better methods.

In calculating overlap integrals between Slater-type orbitals, e.g. from the master formulas of Mulliken et al. [1], one needs values for the auxiliary functions $B_n(\alpha)$ defined by

$$B_n(\alpha) = \int_{-1}^{1} x^n e^{-\alpha x} dx. \qquad (1)$$

The B_n's are given explicitly by

$$B_n(\alpha) = \frac{n!}{\alpha^{n+1}} \left[e^{\alpha} \sum_{k=0}^{n} \frac{(-\alpha)^k}{k!} - e^{-\alpha} \sum_{k=0}^{n} \frac{\alpha^k}{k!} \right]. \qquad (2)$$

But

$$B_n(0) = \begin{cases} \dfrac{2}{n+1} & \text{if } n \text{ is even}; \\ 0 & \text{if } n \text{ is odd}. \end{cases} \qquad (3)$$

Therefore, Mulliken et al. give besides the general formula for each overlap integral another one for the case $\alpha = 0$. Alternatively a recursion formula can be used:

$$B_n(\alpha) = \frac{1}{\alpha} \left[n B_{n-1}(\alpha) - e^{-\alpha} + (-1)^n e^{\alpha} \right]. \qquad (4)$$

Apart from a few exceptions [2-4] it is often not realised that both eq. (2) and (4) give inaccurate results for small values of α. In such a case the use of eq. (2) involves the subtraction of two large quantities with a resulting loss in significant figures. The same problem is implicitly present in the recursion formula (4). The actual situation depends on the word length of the computer, the value of n and the smallness of α. For second-row elements values of $\alpha < 0.1$ can easily arise when slightly different exponents are used for 2s- and 2p-orbitals. For example, in calculating the 2s-2pσ overlap between two double-bonded carbon atoms using the best atomic single exponents of Clementi and Raimondi [5], we have $\alpha \approx 0.05$. Some values of $B_n(0.05)$ are given in table 1. With increasing n important deviations from the accurate values occur, and for $n > 4$ not even the leading figure is correct. Although this should be evident to anybody con-

Table 1
Some values of $B_n(0.05)$ computed with 11 figures and rounded to 7. Parentheses contain powers of 10

	eq. (2)	eq. (4)	accurate
B_0	2. 000 833 (0)	2. 000 833 (0)	2. 000 833 (0)
$-B_1$	3. 334 166 (-2)	3. 334 166 (-2)	3. 334 167 (-2)
B_2	6. 671 669 (-1)	6. 671 670 (-1)	6. 671 667 (-1)
$-B_3$	1. 999 998 (-2)	1. 999 274 (-2)	2. 000 595 (-2)
B_4	4. 019 470 (-1)	4. 014 146 (-1)	4. 003 572 (-1)
$-B_5$	7. 812 500 (-3)	8. 982 866 (-2)	1. 429 034 (-2)
B_6	4. 000 000 (0)	1. 297 433 (1)	2. 859 921 (-1)

cerned with molecular computations, many pro-grammes from the Quantum Chemistry Pro-gramme Exchange show that this is not generally true.

Corbató [2] has given a complicated procedure in which he uses the relation of the B_n's to the spehrical Bessel functions in order to circum-vent these problems. However, a much simpler solution to the problem was given by Zener and Guillemin [6] as early as 1929. They expanded the exponential function in eq. (1) directly to give

even n:

$$B_n(\alpha) = 2 \sum_{k=0}^{\infty} \frac{\alpha^k}{k!(k+n+1)} \qquad (k = \text{even}) ; \qquad (5)$$

odd n:

$$B_n(\alpha) = -2 \sum_{k=1}^{\infty} \frac{\alpha^k}{k!(k+n+1)} \qquad (k = \text{odd}) . \qquad (6)$$

Using these expressions terms of the same sign are added together so that the B_n's can be calcu-lated to any desired accuracy. Furthermore eqs. (5) and (6) are equally valid for $\alpha = 0$, and there is no need for a special formula for the overlap integral to cover this case. Therefore the eas-iest correct way to evaluate the B_n's is probably to use the series (5) and (6) for $\alpha < 1$, in which region there is a rapid convergence, and the re-cursion formula (4) for $\alpha > 1$. The choice of $\alpha = 1$ is arbitrary, of course. In our computations with 11 figures eqs. (2) or (4) still give 8 signif-icant figures for $B_4(1)$, but only 3 for $B_{10}(1)$. Thus the given procedure is acceptable for sec-ond-row atoms where $n \leqslant 4$. If B_n's for higher values of n are required it is necessary to ex-tend the use of eqs. (5) and (6) to values of $\alpha > 1$, or alternatively the loss of significant figures in applying eq. (4) can be circumvented by using the recursion formula downwards (decreasing n). In that case eqs. (5) or (6) can be used to calculate the starting value. Used in this way the recur-sion formula applies to the case $\alpha = 0$ as well.

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