PRAMANA — journal of physics
© Indian Academy of Sciences
Vol. 61, No. 4
October 2003
pp. C779–C780

Comment: "On the computation of molecular auxiliary functions A_n and B_n"

FRANK E HARRIS
Department of Physics, University of Utah, Salt Lake City, UT 84112, USA
Quantum Theory Project, University of Florida, P.O. Box 118435, Gainesville, FL 32611, USA
Email: harris@qtp.ufl.edu

Abstract. Guseinov, Mamedov, Kara and Orbay (*Pramana – J. Phys.* **56**, 691 (2001)) propose methods for evaluating the molecular auxiliary functions $A_n(p)$ and $B_n(pt)$ for the range $17 \leq n \leq 60$ and $25 \leq pt \leq 60$. However, their procedure for $A_n(p)$ is not new, and that for $B_n(pt)$ is less efficient for their target range than another well-known method. Their approach does have merit for smaller non-zero values of pt. Two minor errors in table 1 of their paper are also identified.

Keywords. Molecular auxiliary functions; overlap integrals.

PACS Nos 02.30.Gp; 02.90.+p

In a recent paper in this journal, Guseinov, Mamedov, Kara and Orbay [1] (hereafter GMKO) discuss the evaluation of the auxiliary functions $A_n(p)$ and $B_n(pt)$ which arise in electronic structure studies of molecules [2]. GMKO claim that the methods discussed in their paper constitute an improvement in the technology for evaluation of these integrals in the range $17 \leq n \leq 60$ and $25 \leq pt \leq 60$. But, for that target range, GMKO's method for the B_n is less effective than a straightforward procedure which has been known for many years. There is, however, a range of smaller pt for which GMKO's approach is competitive.

Taking first $A_n(p)$, generation by upward recurrence (as used by GMKO) is not new; it has been the approach taken ever since 1929 [3], and it is numerically stable for all positive values of p. GMKO's statement, attributed to Flodmark [4], that 'Computation of $A_n(p)$ for small internuclear distances is very difficult', is neither correct nor what Flodmark wrote. Flodmark was referring to the fact that upward recursion was not a satisfactory way to generate the $B_n(pt)$ for small non-zero pt.

For $B_n(pt)$ at large pt, GMKO's suggestion of generation by downward recurrence in n is of extremely limited value. For example, differencing error in the recurrence relation causes for $pt = 60$ a loss of nine significant figures by the time B_{17} is reached starting from an accurate value of B_{60}, so that, using 16S arithmetic (precision 16 significant digits, about that of 8-byte floating-point computation), B_{17} is only given to 7S. On the other hand, upward recurrence from B_0 at 16S yields all B_n through $n = 60$ to 16 figures. Since GMKO's prescription for obtaining an accurate value of B_{60} requires downward recursion from an initial value of B_N approximated by B_0 for some $N \geq 136$, it is for $pt = 60$ that is both more efficient and more accurate just to recur upward from $n = 0$. Similar observations will apply to all larger pt values.

As pt is decreased, downward recurrence stays accurate longer, but even at $pt = 40$, 16S upward recurrence yields B_{60} at 15S, while 16S downward recurrence (starting from B_{110} set to B_0) produces only 11S accuracy for B_{17}. A further decrease, to $pt = 30$, leads to a situation in which 16S downward recurrence (starting from B_{98} set to B_0) does give better results than upward recurrence for $n > 25$, but even in this case upward recurrence yields B_{60} to 10S. Finally, at $pt = 25$, 16S downward recurrence is superior for $n \geq 20$, while 16S upward recurrence gives B_{60} to 6S. If now one considers that the B_n of large n are to be used in the context of expansions that will be nearing convergence by $n = 60$, it becomes evident that accuracy for smaller n is more important than accuracy at larger n, and upward recurrence will be the preferred method for GMKO's entire target range.

GMKO's procedure will, however, be useful for values of pt which are smaller than those in their target range. For $|pt| < 6$, downward recurrence with 16S computation can yield all B_n for $n \leq 60$ to about 15S. For pt between about 6 and 25, accurate results for $n \leq 60$ via 16S computation will require both upward and downward recurrence; the simplest prescription will be to recur upward until $n > |pt|$, recurring downward to obtain the remaining B_n.

For persons wanting to use the entries in GMKO's table 1, we identify two errors (probably caused by transcription of accurate data for incorrect n) for $pt = 30$. Corrected values of B_n for this pt value are:

$$n = 50 \quad +1.32535806779393E+11,$$
$$n = 55 \quad -1.24765593904292E+11.$$

References

[1] I I Guseinov, B A Mamedov, M Kara and M Orbay, *Pramana – J. Phys.* **56**, 691 (2001)
[2] R S Mulliken, C A Rieke, D Orloff and H Orloff, *J. Chem. Phys.* **17**, 1248 (1949)
[3] C Zener and V Guillemin, *Phys. Rev.* **34**, 999 (1929)
[4] S Flodmark, *Arkiv. Fys.* **11**, 417 (1957)