NASA-CR-197982

IN-72-TM
42533

A multi-region radial integration scheme

Leslie A. Barnes *
Eloret Institute
Palo Alto
California 94303

Abstract

In this preliminary report, a multi-region radial integration is compared to the recently proposed method due to Handy *et al.*. Preliminary results for small systems indicate that the new integration scheme is generally comparable to and sometimes better than that of Handy *et al.*, although this conclusion is by no means firm. Work for larger systems is continuing.

(NASA-CR-197982) A MULTI-REGION RADIAL INTEGRATION SCHEME Preliminary Report (Eloret Corp.) 12 p

N95-23408

Unclas

G3/72 0042583

*Mailing Address: NASA Ames Research Center, Moffett Field, California 94035-1000

1 Introduction

There is recently a great deal of interest in the testing and application of Density Functional techniques for use in molecular calculations. The complicated functional forms used in this theory preclude analytical integration, so that numerical methods must be used. Recently, Handy *et al.*[1] proposed a radial integration based on the Euler-Maclaurin summation giving good results for a number of systems. However, it is worthwhile investigating other methods since for accurate calculations many quadrature points are required in general, even with the Euler-Maclaurin technique. In addition, on problem with the Euler-Maclaurin scheme is that there is little control over the location of additional quadrature points. For example, this scheme is very efficient for atoms, but in a molecular context additional points are required for an integration which is comparable to the atomic case. These additional points should ideally be placed in the valence region. However, with the Euler-Maclaurin scheme points must be placed throughout the entire region. This problem is bypassed with a multiregion integration.

The advantage of the multiregion integration is the control of the placement of additional quadrature points in the molecular situation. In general, we determine an accurate quadrature for the constituent atoms or small molecular fragments. In the molecular situation we then only need to add points to the valence region(s), and increase the accuracy of the angular quadrature, in order to be able to produce an accurate molecular quadrature. One disadvantage of the multiregion integration is a possible increase in errors due to the accumulation of errors from the individual regions.

Here we investigate the efficiency of a multi-region integration similar to that previously proposed by Te Velde and Baerends [2] and also Thakar [3]. One difference in the current work is the use of a change of variables due to McLean and Yoshimine [4] which allows for efficient placement of the quadrature points by mapping the region $[a, m, b]$ onto the region $[-1, 0, 1]$, where a and b are the endpoints of the region, and m is any point between a and b. This mapping takes the form

$$x = c_1 + c_2(1 + \beta)/(1 - \beta t).$$

The constants c_1, c_2 and β are completely determined by the mapping $a \rightarrow -1$, $m \rightarrow 0$, and $b \rightarrow 1$. This mapping may be used for all ranges except the doubly infinite range (-∞, ∞), providing appropriate limiting forms are used for special cases.

The regions used here are based on the atomic charge density, in a spirit similar

to that used by Thakar [3]. However, rather than using a general rule based on the atomic number by which to determine the regions, we use the atomic charge density directly. The function $r^2 * \rho(r)$ is generated numerically, and analysed for maxima, minima and points of inflection. In general, the regions we define are based on these points, in particular the points a and b map onto two minima in the charge density, and the point m maps onto the maximum in between these. These three points define a shell, and the mapping ensures an optimal distribution of quadrature points in the region. Generally we have one region for each shell, with the valence shell being split into an inner and outer parts at the point of inflection of the valence shell (see also Thakar), and the innermost (core) region into two at the first point of inflection. Although this scheme may seem somewhat complicated, in fact it is straightforward to generate the required regions and tabulate them for any atom.

For the inner regions we use a standard Gauss-Legendre quadrature, whereas for the outer region we use a shifted Gauss-Laguerre scheme based on the weight function $e^{-\alpha r}$, where α is related to the highest occupied MO eigenvalue (or the IP) by $\alpha = 2(\sqrt{-2\epsilon_i})$ (see also Thakar [3]).

The other details of the integration are very similar to that proposed by Handy *et al.* [1]. We use a product scheme for the angular integration identical to that of Handy *et al.*, including the use of the angular crowding parameter K_θ. The single center integration scheme of Becke [5] is used, but we use the cutoff function due to Handy *et al.*, with standard Bragg-Slater radii.

We consider three systems here - Ne, Cu and CO. We compare the Euler-Maclaurin to the current multiregion integration for all four systems. We consider integration of the total charge density only here, at the SCF level of approximation, since Handy *et al.* [1] showed that this gives a good indication of the overall performance of an integration scheme. For Ne, we use the Dunning [6] [5*s*4*p*] contracted Gaussian basis set. For carbon and oxygen we use the correlation consistent polarized valence triple zeta (cc-pVTZ) basis sets of Dunning. For Cu we use a $(20s\ 15p\ 10d\ 6f\ 4g)/[6+1s\ 5+1p\ 4d\ 2f\ 1g]$ basis set derived from the large primitive set of Partridge [7], contracted by Bauschlicher using the atomic natural orbital (ANO) approach. The C–O bond length is 2.2 a.u. in all cases.

The calculations were carried out using the Seward integral program and the Sweden SCF program on the Cray YMP-C90 at NASA Ames research center.

2 Results and Discussion

For Ne atom, the results for the Euler-Maclaurin integration are given in Table 1. We give the number of points used in the radial integration, the number of points including those discarded due to the radial cutoff (in parentheses), the radial factor m_r (Handy *et al.* [1], Eqn. 6), and the total error in the integrated charge density. Our results for this are very similar to Handy *et al.*, as expected, with a very accurate radial integration attained with 72 radial points. In Table 2, we give the results from the multiregion integration, with the number of points in each region given. In region 5 we also indicate the number of points including those discarded due to the radial cutoff, in parentheses. Overall, more radial points are required for the multi-region integration, although the integration is still accurate. For example, if one used a value for m_r in the Euler-Maclaurin integration which was not optimal, then the results could be worse than for the multi-region integration.

In Table 3, we give the results for the integration of Cu atom in a large ANO basis set, for three different numbers of radial points. One trend to be noted is that a higher m_r value is needed for Cu than Ne as more radial points are added, and more radial points are needed to achieve a similar absolute accuracy. As noted by Handy *et al.* this is because the numerical integration only gives a certain *relative* error rather than absolute error in the integration. We note that for Cu atom ($4s^1$) it is necessary to integrate out a long way (22 a.u.) due to the very diffuse nature of the $4s$ orbital, and that sometimes a higher value of m_r can be necessary than that recommended than Handy *et al.* to obtain optimum results.

The multi-region results of Tables 4 and 5 compare quite well with the Euler-Maclaurin results, although again it seems that more points are necessary for the multi-region scheme, depending on the m_r value used for in the Euler-Maclaurin scheme. We note that the inner regions for the multi-region scheme are very compact, due to the higher atomic number in this case, and that quite a few radial points are necessary to describe the density accurately in this compact region. However, this does not necessarily translate to a lot of points in a molecular calculation, since the number of angular points needed in the inner regions is much smaller than in the valence regions.

Finally we consider the CO molecule (Tables 6–8). We use the same number of angular points in for the Euler-Maclaurin and the multi-region integrations (n_θ=42, n_ϕ=84), and the same Bragg-Slater radii in each case (r_C=1.32281 a.u., r_O=1.13383 a.u.). Overall, it seems that it is possible for the Euler-Maclaurin scheme

to outperform the multi-radial scheme if the right values of m_r and m_μ (the angular factor [1]) are chosen. However, these differ significantly from the "standard" values recommended by Handy *et al.*, m_r=2 or 3 and m_μ=10 or 11. For these values, we see that the multi-region scheme is either equivalent to or better than the Euler-Maclaurin scheme in efficiency. Another interesting point from Tables 6 and 8 is that it is not just the total number of radial points which is important, but also the spread of these points along r, as this affects the total number of points through the angular factors. For example, the spread of radial points in the Euler-Maclaurin scheme is approximately linear on a logarithmic scale, apart from the very short and long range regions. Changing the factor m_r changes the slope of this logarithmic plot, so that for higher values of m_r there are more points in the core region and more points in the long range regions, leading to fewer points overall, since there are fewer angular points in the core region and the long range points are discarded due to the radial cutoff. Thus for the Euler-Maclaurin scheme, very different total numbers of points are realized for m_r=3 versus m_r=4, even though the nominal number of radial points is the same in each case.

For the multi-region scheme, two sets of results are presented for CO (Table 8), differing in the number of points in the valence and outer regions, and with the total number of points being very comparable to the best results found for the Euler-Maclaurin scheme. One advantage of the multi-region scheme is that we are able to take a set of integration parameters from a similar atom (for example, those for Ne in this case), and then place more radial points in the valence and outer valence regions in order to attain higher accuracy. This can be seen to be an effective way to add points for CO.

Overall, it seems that neither integration scheme is clearly superior in the molecular situation, based on the current results. More and larger systems need to be studied in order to establish whether the multi-region integration scheme proposed here is significantly better to the widely used Euler-Maclaurin scheme of Handy *et al.*[1]

3 Acknowledgements

L.A.B was supported by NASA grant number NCC-2-741. Helpful discussions with D. W. Schwenke, H. Partridge and A. D. McLean are acknowledged. The provision of a subroutine to facilitate the McLean-Yoshimine change of variable by A. D. McLean is acknowledged.

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Table 1: Euler-Maclaurin integration of Ne atom (r_{max}=15.0 a.u.)

n_r	m_r	$\Delta\rho(r)$
66(70)	1	$3.0\text{x}10^{-5}$
56(70)	2	$3.1\text{x}10^{-10}$
50(70)	3	$8.8\text{x}10^{-10}$
47(70)	4	$7.1\text{x}10^{-7}$
94(100)	1	$6.6\text{x}10^{-6}$
72(100)	2	$9.1\text{x}10^{-13}$
80(100)	3	$3.8\text{x}10^{-11}$
67(100)	4	$9.1\text{x}10^{-11}$

Table 2: Multiregion integration of Ne atom (r_{max}=15.0 a.u.)

n_r(region)					Total n_r	$\Delta\rho(r)$
1	2	3	4	5		
10	15	12	16	3(3)	56(56)	$5\text{x}10^{-9}$
15	20	24	24	11(16)	94(99)	$1\text{x}10^{-12}$

Table 3: Euler-Maclaurin integration of Cu atom (r_{max}=22.0 a.u.)

n_r	m_r	$\Delta\rho(r)$
47(64)	2	$6.0\text{x}10^{-6}$
43(64)	3	$6.4\text{x}10^{-8}$
40(64)	4	$7.6\text{x}10^{-6}$
71(96)	2	$5.2\text{x}10^{-9}$
64(96)	3	$1.4\text{x}10^{-10}$
60(96)	4	$4.4\text{x}10^{-10}$
95(128)	2	$6.5\text{x}10^{-9}$
86(128)	3	$4.9\text{x}10^{-12}$
80(128)	4	$1.1\text{x}10^{-13}$
77(128)	5	$1.1\text{x}10^{-10}$

Table 4: Regions for Cu atom (a.u.)

	a	m	b
1	0.000	0.005	0.010
2	0.010	0.038	0.077
3	0.077	0.170	0.380
4	0.380	0.630	0.940
5	0.940	2.500	6.000
6	6.000	—	22.000

Table 5: Multiregion integration of Cu atom (r_{max}=22.0 a.u.)

n_r(region)						Total n_r	$\Delta\rho(r)$
1	2	3	4	5	6		
15	15	15	10	20	15(9)	84(90)	$2.2\text{x}10^{-9}$
20	15	15	10	20	11(20)	91(100)	$6.7\text{x}10^{-11}$
25	20	20	15	25	11(20)	117(130)	$1.4\text{x}10^{-12}$

Table 6: Euler-Maclaurin integration of CO molecule (n_θ=42, radbs=1.32281,1.13383 a.u. n_ϕ=84, r_{max}=15.0 a.u.). Note: same value of m_μ and m_r used for C and O.

n_r	N_{grid}	m_r	m_μ	$\Delta\rho(r)$
132,134 (192,192)	60902,62666	3	10	$1.3\text{x}10^{-9}$
132,134 (192,192)	60902,62666	3	11	$3.0\text{x}10^{-10}$
132,134 (192,192)	60902,62666	3	12	$2.8\text{x}10^{-11}$
132,134 (192,192)	60902,62666	3	13	$9.8\text{x}10^{-12}$
132,134 (192,192)	60902,62666	3	14	$2.5\text{x}10^{-11}$
148,150 (192,192)	87162,88926	2	10	$2.1\text{x}10^{-10}$
148,150 (192,192)	87162,88926	2	11	$8.7\text{x}10^{-11}$
148,150 (192,192)	87162,88926	2	12	$3.9\text{x}10^{-11}$
148,150 (192,192)	87162,88926	2	13	$2.2\text{x}10^{-11}$
148,150 (192,192)	87162,88926	2	14	$1.6\text{x}10^{-11}$
148,150 (192,192)	87162,88926	2	15	$1.7\text{x}10^{-11}$
124,125 (192,192)	47228,48110	4	11	$8.7\text{x}10^{-9}$
124,125 (192,192)	47228,48110	4	12	$5.4\text{x}10^{-9}$
124,125 (192,192)	47228,48110	4	13	$1.8\text{x}10^{-9}$
124,125 (192,192)	47228,48110	4	14	$5.2\text{x}10^{-10}$
124,125 (192,192)	47228,48110	4	15	$1.5\text{x}10^{-9}$

Table 7: Regions for CO molecule (a.u.)

	a	m	b
		C	
1	0.00	0.025	0.05
2	0.05	0.17	0.63
3	0.63	1.27	1.90
4	1.90	4.0	6.0
5	6.0	—	15.0
		O	
1	0.0	0.02	0.04
2	0.04	0.12	0.41
3	0.41	0.83	1.37
4	1.37	4.0	6.0
5	6.0	—	15.0

Table 8: Multiregion integration of CO molecule (r_{max}=15.0 a.u.)

n_r(region)					Total n_r	N_{grid}	m_μ	$\Delta\rho(r)$
1	2	3	4	5				
15	20	24	24	7(16)	90(99)	58078,56944	12	$3.0\text{x}10^{-9}$
15	20	24	24	7(16)	90(99)	58078,56944	13	$1.0\text{x}10^{-10}$
15	20	24	24	7(16)	90(99)	58078,56944	14	$1.4\text{x}10^{-9}$
15	20	24	24	9(24)	92(107)	59842,58708	13	$8.3\text{x}10^{-11}$
15	20	24	24	11(32)	94(115)	61606,60472	13	$8.3\text{x}10^{-11}$
15	20	24	32	9(24)	100(115)	66898,65764	13	$5.7\text{x}10^{-11}$
15	20	24	40	9(24)	108(123)	73954,72820	13	$1.0\text{x}10^{-11}$
15	20	24	40	9(24)	108(123)	73954,72820	12	$1.4\text{x}10^{-11}$
15	20	24	40	9(24)	108(123)	73954,72820	14	$1.2\text{x}10^{-11}$