Theoret. Chim. Acta (Berl.) 37, 275—283 (1975)

Numerical Integration Techniques for Quantum Chemistry

The Role of Periodization in the Calculation of Electronic Integrals

J. P. Daudey, S. Diner, and R. Savinelli
Institut de Biologie Physico-Chimique, Paris

Received May 7, 1974 / December 3, 1974

Korobov theory for multidimensional numerical integration is used to evaluate electronic integrals. This paper shows the important role played by periodization techniques. Singularity (r_{12}^{-1}) in the bielectronic six-dimensional integrals is removed through a twofold three-dimensional integration. Results are presented for atomic integrals involving Slater type atomic orbitals.

Key words: Korobov numerical integration – Numerical integration, Korobov theory for ~

1. Introduction

In a recent paper from this laboratory, numerical integration techniques were used to evaluate matrix elements of the Hamiltonian between localized molecular orbitals [1]. For bielectronic integrals a six-dimensional Korobov integration grid was used, without an explicit removal of the singularity r_{12}^{-1} in the integrand. Although the results were satisfactory, a full advantage of Korobov theory was not taken. Recently, Handy and Boys [2] have studied the effect of periodization for some one-dimensional integrals ("periodization" in our sense is identical to "reduction of boundary conditions" in the paper of Handy and Boys). After a brief account of some general theoretical results dealing with the convergence of numerical integration for some classes of functions, we investigate the efficiency of periodization techniques for integrals used in quantum chemical calculations (with the difficult problem of r_{12}^{-1} singularity), and we give some practical results for atomic integrals involving Slater type orbitals.

2. Role of Periodization in Multidimensional Integration Methods

For a one-dimensional function with a derivative of order $2k+1$, there is a well-known theorem:

"Let $g(x) \in C^{(2k+1)}[a, b]$, $g'(a)=g'(b)$, $g'''(a)=g'''(b)$, $g^{(2k-1)}(a)=g^{(2k-1)}(b)$ and let $|g^{(2k+1)}(x)| \leqq M$ for $a \leqq x \leqq b$.

If T_n designates the trapezoidal sum, that is, if:

$$T_n(g)=h[g(a)/2+g(a+h)+\cdots+g(a+(n-1)h)+g(b)/2], \quad h=(b-a)/n,$$

then $|\int_b^a g(x)\,dx - T_n(g)| \leqq C/n^{2k+1}$. The constant C is independent of n and may be taken as: $C = M(b-a)^{2k+2}2^{-2k}\pi^{-2k-1}\zeta(2k+1)$ where $\zeta(k) = \Sigma_{j=1}^{\infty} j^{-k}$ is the Riemann zeta function" ([3], p. 55).

Various modern multidimensional integration methods [4–7] can be considered as a generalization of this theorem to multidimensional functions[1]. Let us introduce the class $\tilde{D}_n^\alpha$ of functions $f(x_1, \ldots, x_n)$ such that:

– the partial derivatives $\partial^k f/\partial x_1^{k_1} \ldots \partial x_n^{k_n}$ $(0 \leqq k \leqq \alpha n,\ 0 \leqq k_r \leqq \alpha n,\ r = 1, \ldots, n)$ are continuous and bounded in the whole space.

– f and the preceding partial derivatives have the same unit period.

Bakhvalov theorem [8] proves that for $f \in \tilde{D}_n^\alpha$, the best integration grid is the uniform one (uniform subdivision of the n-hypercube) which provides an error $\mathcal{O}(1/N^\alpha)$. For functions with a less pronounced periodic character, the uniform grid is far from being a good rule. Korobov [4] has demonstrated that it is nevertheless possible to find good integration rules for classes larger than $\tilde{D}_n^\alpha$. Let us introduce $H_n^\alpha(C)$, class of functions $f(x_1, \ldots, x_n)$ such that the partial derivatives $\partial^k f/\partial x_1^{k_1} \ldots \partial x_n^{k_n}$ $(0 \leqq k \leqq \alpha n,\ 0 \leqq k_r \leqq \alpha,\ r = 1, \ldots, n)$ are continuous and bounded by C. $\tilde{H}_n^\alpha(C)$ is the subset of $H_n^\alpha(C)$ of functions g for which g and its partial derivatives are periodic with a unit period. For $g \in \tilde{H}_n^\alpha(C)$, Korobov has determined integration grids for which the error is $\mathcal{O}(\mathrm{Log}^{\alpha n} N/N^\alpha)$. Moreover he has shown that for every function $f \in H_n^\alpha(C)$, it is always possible to find $g \in \tilde{H}_n^\beta(C')$ $(\beta \leqq \alpha)$ such that $\int_0^1 dx_1 \int_0^1 dx_2 \ldots \int_0^1 dx_n\ f(x_1, x_2, \ldots, x_n) = \int_0^1 dx_1 \int_0^1 dx_2 \ldots \int_0^1 dx_n\ g(x_1, x_2, \ldots, x_n)$. Finding g from f is what we call "periodization of f".

3. Periodization Techniques

The key lemma proved by Korobov [4] is:

If $g(x_1, x_2, \ldots, x_n) \in H_n^\alpha(C)$, $\alpha \geqq 2$, and if $[\partial^k g/\partial x_r^k]_{x_r=0} = [\partial^k g/\partial x_r^k]_{x_r=1}$ $(r = 1, \ldots, n,\ k = 0, 1, \ldots, \beta-2,\ 2 \leqq \beta \leqq \alpha)$, then $g(\{x_1\}, \{x_2\}, \ldots, \{x_n\})$ (where $\{x\}$ means fractional part of x) belongs to $\tilde{H}_n^\beta(C')$. Therefore starting from f belonging to $H_n^\alpha(C)$, the periodization is the determination of g satisfying to the conditions of the preceding lemma and giving the same integral as f over the unit hypercube.

A simple periodization corresponds to $\beta = 2$, and means that g must take the same value at the frontier of the unit n-hypercube. This can be done with a simple change of variables:

$$g(x_1, x_2, \ldots, x_n) = f(\Phi(x_1), \Phi(x_2), \ldots, \Phi(x_n))\, \Phi'(x_1)\, \Phi'(x_2), \ldots, \Phi'(x_n) \qquad (1)$$

with $\Phi(x) = \sin^2(\pi x/2)$.

A complete periodization of order $\beta - 2$ can be achieved in different ways. The simplest one uses the formula (1) with:

$$\Phi(x) = (2j-1)\, C_{2j-2}^{j-1} \int_0^x (t(1-t))^{j-1}\, dt, \qquad j = \beta - 2\,.$$

The same procedure is used by Handy and Boys [2]. Such a periodization is not very expensive (in computing time) and this paper will mainly illustrate its

---

[1] For a short presentation of Korobov Theory, see Stroud, A. H.: Approximate calculation of multiple integrals. Englewood Cliffs, New Jersey: Prentice Hall 1972. In Ref. [10], Zaremba gives a slightly different presentation of Korobov theory.

effects (K periodization). It has a serious drawback: nothing warrants that g belongs to a class $\tilde{H}_n^\beta(C')$ with $C' \leqq C$. If $C' \gg C$, the precision of the numerical integration can be significantly lowered.

This difficulty can be in principle overcome with another periodization process. This periodization technique has been proposed by Korobov [4] and illustrated by Zaremba [9, 10] and Maisonneuve [11] (Z periodization).

Let

$$g_r(x_1, \ldots, x_n) = g_{r-1}(x_1, \ldots, x_n) + \sum_{k_r=0}^{\beta-2} \sum_{\varepsilon_r=0}^{1} P_{k_r,\varepsilon_r}(x_r)\,(\partial^k g_{r-1}/\partial x_r^{k_r})_{x_r=\varepsilon_r} \tag{2}$$

with $g_0(x_1, \ldots, x_n) = f(x_1, \ldots, x_n)$ where $P_{m,\varepsilon}(x) = (-1)^\varepsilon B_{m+1}(x)/(m+1)$, $B_m(x)$ being Bernouilli polynomials. $g_n(x_1, \ldots, x_n)$ provides a complete periodization of order $\beta - 2$ but involves some partial derivatives of f at the frontier of the unit n-hypercube and this transformation is time consuming. Its effectiveness will be examined on a simple case.

4. Removal of Singularity for Bielectronic Integrals

The general type of bielectronic integrals arising in quantum chemical calculations is:

$$I = (ab|r_{12}^{-1}|cd) = \int \varphi_a(1)\,\varphi_b(1)\,r_{12}^{-1}\,\varphi_c(2)\,\varphi_d(2)\,dv_1\,dv_2 = \int f(1)\,r_{12}^{-1}\,g(2)\,dv_1\,dv_2$$

where φ_a, φ_b, φ_c, φ_d are molecular or atomic orbitals. In our previous work [1], we have calculated molecular bielectronic integrals of that type *by a direct six-dimensional integration.* We merely eliminated some "dangerous points" with a very crude procedure [12]. Many authors (Ellis [13], Boys and Handy [14], Goodisman and Secrest [15]) have pointed out the importance of the r_{12}^{-1} singularity for the convergence of the numerical integration. There are a lot of transformations which suppress the singularity, but we may keep in mind that (a) the sampling points must be as much as possible concentrated in the region where the integrand takes its significant values, (b) after the removal of the singularity, the modified integrand is only a continuous function and nothing can be said for the successive derivatives. We shall see in the next section that it seems difficult to fulfil the conditions imposed in Korobov theory for integrals used in quantum chemistry calculations. However, and fortunately, the following "numerical experiments" prove that precision can be improved by a judicious elimination of singularity and periodization techniques.

The removal of r_{12}^{-1} singularity is simplified by a first decomposition of six-dimensional integration into two successive three-dimensional integrations:

$I = \int f(1)\,V(1)\,dv_1$, where $V(1) = \int g(2)\,r_{12}^{-1}\,dv_2$. We have tried different methods for the numerical integration of V. In the first one we used for electron 2 polar coordinates centered on electron 1. But it was impossible with this transformation to determine sampling points adapted to the distribution of electron 2 (see convergence in the first column of Table 1). In a second method we used the Neumann expansion of r_{12}^{-1}. $V(1)$ is then expressed as:

$$V(1) = \int_0^{r_1} g(2)\,N(r_2/r_1)\,dv_2 + \int_{r_1}^{\infty} g(2)\,N(r_1/r_2)\,dv_2\,,$$

Table 1. Comparison between different ways for removing the singularity in the potential integral for a monocentric $1s\,1s$ Slater type distribution [$\xi(1s) = 1.265$, distance $= 1.55$ a.u., exact value $= 0.752250$ a.u.]. Absolute errors appear in the table. Numerical integration is performed using simple periodization. N is the number of points of the integration grid

N	Method 1 Polar coordinates	Method 2 Neuman expansion	Method 3 Prolate spheroidal coordinates
101	−0.01040	0.00656	0.00224
199	+0.00905	0.00061	0.00021
307	−0.00246	0.00643	0.00017
523	0.00183	0.00901	0.00004

where $N(x)$ is a limited Neuman expansion. The results were not encouraging (second column of Table 1) and periodization had no noticeable effect on convergence. Moreover it appears from a work of Schaefer [16] that it is necessary to use a large expansion to obtain sufficient accuracy and this is a serious drawback. The third way we tried and kept for subsequent calculations was to introduce a prolate spheroidal coordinate system with one of the foci on the electron 1 and the other on a "central" point of the distribution of electron 2. This transformation deletes the singularity and concentrates the sampling points in a well adapted region. The results obtained (last column of Table 1) are much better than those obtained with others methods. However the partial derivatives of the transformed integrand $g(\xi, \eta, \varphi)$ are continuous but no longer bounded at the frontier of the unit hypercube. (For instance, special form of g excepted, $\partial g/\partial\xi \to \infty$, $\xi \to 1$.) Therefore, we cannot apply Z periodization to an arbitrary g. K periodization can be used but nothing warrants its efficiency in each case.

5. Effect of *K* Periodization

We have studied the effect of K periodization for different types of integrals used in a quantum chemical calculation of energy.

5.1. Overlap Integrals

$$S = \int \chi_a(1)\,\chi_b(1)\,dv_1\,.$$

If $a = b$, polar coordinates r, θ, φ centered on the nucleus are transformed as $t = 1/(r+1)$, $u = \theta/\pi$ and $w = \varphi/2\pi$ in order to map the integration domain over the unit hypercube.

If $a = b$, prolate spheroidal coordinates ξ, η, φ along the line ab are transformed as $t = 1/\xi$, $u = (\eta + 1)/2$, $w = \varphi/2\pi$.

In both cases, the integrand is completely periodic with respect to w and we have only to perform the periodization for t and u. In Table 2, we have displayed complete results for a monocentric overlap integral and for a bicentric one. We can make the following comments, valid for all types of integrals:

There is an optimal degree of periodization, different for t and u. As we have mentionned before (Part 2) starting from $f \in H_3^\alpha(C)$, K periodization gives $g \in \tilde{H}_3^\beta(C')$.

Table 2. Absolute errors (in units 10^{-5} a.u.) for overlap integrals, corresponding to different degrees of K periodization. The upper tables correspond to the monocentric overlap between 1s and 2s Slater type orbitals [$\xi(1s)=7.663$, $\xi(2s)=2.250$, exact value $=0.231145112$]. The lower tables correspond to the bicentric overlap between 1s and 2p Slater type orbitals [$\xi(1s)=1.268$, $\xi(2p)=2.214$, exact value $=0.39408778$]. N is the number of points used in the integration formula. α_t, α_u are the degrees of K periodization

α_t / α_u	1	2	3	4	5	6	α_t / α_u	1	2	3	4	5	6
$N=101$							$N=199$						
1	206	139	53	15	68	113	1	0.9	8	9	8	4	0.4
2	22	13	2	5	11	16	2	0.2	0.07	0.08	0.06	0.008	0.05
3	7	4	*0.6*	2	4	5	3	0.2	0.0027	0.002	0.002	0.0039	0.006
4	20	12	1.6	6	11	16	4	0.2	*0.0001*	*0.0001*	0.0003	0.0007	0.0011
5	87	51	7	26	50	68	5	0.2	0.0001	0.0001	0.0012	0.0058	0.0064
6	245	145	20	73	142	193	6	0.2	0.0004	0.0014	0.02	0.04	0.04
1	74	500	706	817	853	926	1	45	138	239	276	265	235
2	131	221	261	286	302	312	2	52	10	8	11	10	9
3	50	41	57	62	63	63	3	43	16	0.37	0.49	0.13	0.41
4	98	34	29	101	119	132	4	38	17	0.23	0.19	0.22	0.20
5	156	55	*15*	03	142	190	5	33	18	0.17	*0.12*	0.16	0.08
6	191	141	29	102	225	333	6	28	18	0.18	*0.12*	0.21	0.20

Table 3. Absolute errors (in units 10^{-5} a.u.) for kinetic integrals with respect to different degrees of K periodization and different interpolation formulas. The left table was obtained for a (1s, 1s) monocentric kinetic integral [$\xi(1s)=1.268$, exact value $=0.004964850$] and the right table was obtained for a (1s, 2s) kinetic integral [$\xi(1s)=7.663$, $\xi(2s)=2.250$, exact value $=-0.933751880$]. On the first line is the result obtained by numerical integration with the exact analytical derivatives, on the three following lines (F_1, F_2, F_3) are the results obtained with interpolation formulas (see 5.2). α indicates the periodization degree in the special case $\alpha=\alpha_t=\alpha_u$

$N=199$	$\alpha=1$	$\alpha=2$	$\alpha=3$	$\alpha=4$	$N=199$	$\alpha=1$	$\alpha=2$	$\alpha=3$	$\alpha=4$
A	2.38	-5.61	0.01	0.02	A	-82.71	0.0008	0.00026	0.00012
F_1	2.20	-5.79	0.19	0.15	F_1	-3.49	79.18	79.18	79.17
F_2	2.38	-5.61	0.01	0.02	F_2	-82.72	0.0006	0.00024	0.00015
F_3	2.38	-5.61	0.01	0.02	F_3	-82.72	0.0007	0.00022	0.00013

With a small number of points in the integration formula (our case), the increase of C may annihilate the increase of convergence produced by periodization.

The optimal degrees of periodization are linked to the type of integrand, i.e. the type of distribution involved. The leading factor seems to be the monocentric or bicentric character.

5.2. Kinetic Integrals

$$T = -\int \chi_a(1)\, \nabla^2/2\, \chi_b(1)\, dv_1 \, .$$

In this case an additional difficulty is the numerical calculation of the derivatives. It is convenient to rewrite $T=1/2\int \nabla\chi_a(1)\,\nabla\chi_b(1)\,dv_1$, where $\nabla\chi$ is the gradient of χ. To test the precision of numerical differentiation, we have compared

Table 4. Absolute errors (in units 10^{-5} a.u.) for potential integrals corresponding to different degrees of K periodization. The upper tables correspond to the potential created by a monocentric distribution $(1s, 2s)$ [$\xi(1s) = 7.663$, $\xi(2s) = 2.250$, $d = 1.0$ a.u., exact value $= 0.230070522$ a.u.]. The lower tables correspond to the potential created by a bicentric distribution $(1s, 2s)$ [$\xi(1s) = 1.268$, $\xi(2s) = 2.250$, distance from $1s$ center $= 1.65$ a.u., distance from $2s$ center $= 2$ a.u., exact value $= 0.26522010$ a.u.]. N is the number of points in the integration formula. α_t, α_u are the degrees of K periodization

1	2	3	4	5	6	α_t \ α_u	1	2	3	4	5	6
$N = 101$						$N = 199$						
198	575	811	971	1095	1199	1	273	147	264	327	352	355
127	206	381	500	588	655	2	182	8	7	11	15	19
378	46	86	100	103	100	3	153	7	0.9	0.8	1	1
600	47	60	140	201	245	4	131	8	0.3	0.1	0.1	0.1
671	213	139	45	45	126	5	101	9	0.1	0.07	0.02	0.01
616	322	321	239	134	28	6	71	10	0.03	0.06	0.01	0.006
238	555	866	1085	1264	1412	1	62	128	225	291	330	353
112	102	53	83	67	17	2	38	28	26	41	62	85
104	174	65	22	52	36	3	46	23	3	9	17	22
126	226	157	81	52	59	4	76	30	6	21	37	59
123	317	339	320	325	347	5	97	31	23	62	106	155
127	456	587	642	694	745	6	104	20	48	110	179	251

the results of different interpolation formulas with that of the analytical formula. Interpolation formulas used are:

$$F_1\colon\ \partial f/\partial x(x_0) = (f(x_0 + h) - f(x_0))/h$$

$$F_2\colon\ \partial f/\partial x(x_0) = (f(x_0 + h) - f(x_0 - h))/2h$$

$$F_3\colon\ \partial f/\partial x(x_0) = (f(x_0 + 2h) - 2f(x_0) + f(x_0 - 2h))/2h\,,$$

where h is an adjustable parameter. For a judicious choice of h ($h = 0.001$ for radial variables, $h = 1°$ for angular variables) formula F_2 provides good results (Table 3).

5.3. *Potential Integrals*

The coordinate transformation is that described in Part 4. With a very limited number of points, it is possible to obtain a reasonable accuracy. Although the conditions of K periodization are not completely fulfilled (see Part 4), an increase of periodization up to $\alpha = 3,4$ improves seriously the accuracy.

5.4. *Bielectronic Integrals*

We have first studied the convergence with respect to integration on electron 1, i.e. $\int \chi_a(1)\, \chi_b(1)\, V(1) dv_1$, where V is calculated analytically. The convergence is similar to that observed for overlap integrals (somewhat slower, Table 5). Secondly, for the same type of integrals we have investigated the influence of the numerical integration of V on the final precision. We have used, for numerical integration on electron 1, the best result of Table 5. Results in Table 6 indicate that a careful integration of potential does not greatly influence the final precision.

Table 5. Absolute errors (in units 10^{-5} a.u.) for bielectronic integrals $\int \chi_a(1)\, \chi_b(1)\, V(1) dv_1$ where $V(1)$, potential created by a monocentric distribution $(1s, 1s)$ $(\xi(1s) = 1.268)$ is evaluated analytically. The upper tables correspond to a monocentric distribution $(1s_a(1), 1s_a(1))$ the lower tables correspond to a bicentric distribution $(1s_a(1), 1s_b(1))$. Exact values are 0.01289257 a.u. (upper tables) and 0.34320456 a.u. (lower tables)

$\alpha_{u_1} \backslash \alpha_{t_1}$	1	2	3	4	$\alpha_{u_1} \backslash \alpha_{t_1}$	1	2	3	4
$N_1 = 101$					$N_1 = 199$				
1	53	323	546	605	1	3	0.02	3	35
2	− 3	− 41	− 59	− 74	2	−0.4	0.08	2	0.1
3	−10	8	− 21	−174	3	0.3	0.09	−2	5
4	20	29	− 30	−173	4	0.09	0.2	0.9	3
1	4	− 18	− 12	− 23	1	−2	−2	−2	− 3
2	− 3	− 0.5	3	6	2	−1	−0.3	−2	− 5
3	− 3	10	13	19	3	−1	−0.9	−5	−11
4	− 8	9	− 16	25	4	−2	−3	−9	−17

Table 6. Absolute errors (in units 10^{-5} a.u.) for the bielectronic integrals defined in Table 5 $\int \chi_a(1)\, \chi_b(1) \cdot V(1) dv_1$ where $V(1)$ is calculated numerically. In all cases the integration relative to electron 1 correspond to the best result in Table 5 ($N_1 = 199$, $\alpha_{t_1} = \alpha_{u_1} = 2$) and in this table are displayed absolute errors corresponding to different K periodization degrees $(\alpha_{t_2}, \alpha_{u_2})$ and different grids (N_2) for the numerical calculation of V

$\alpha_{u_2} \backslash \alpha_{t_2}$	3	4	$\alpha_{u_2} \backslash \alpha_{t_2}$	3	4	5
$N_2 = 101$			$N_2 = 199$			
2	1.0	1.6	3	0.09	0.12	0.16
3	2.5	1.7	4	0.06	0.24	0.10
2	+5.6	−2.4	3	−1.2	−3.6	−4.5
3	−7.8	−1.3	4	+0.4	−0.7	−0.9

Table 7. Absolute errors (in units 10^{-5} a.u.) for the bielectronic integral $(1s_a(1)\, 2p_b(1)/r_{12}^{-1}/1s_c(2)\, 1s_d(2))$. The periodization degrees are limited to $\alpha_{t_1} = \alpha_{u_1} = \alpha_1$ and $\alpha_{t_2} = \alpha_{u_2} = \alpha_2$. Exact value is 0.0436757 a.u.

$\alpha_2 \backslash \alpha_1$	1	2	3	4	$\alpha_2 \backslash \alpha_1$	1	2	3	4
$N_1 = 101$ $N_2 = 101$					$N_1 = 199$ $N_2 = 199$				
1	−89	−50	−60	−46	1	−35	−6	−15	−47
2	−60	− 5	+12	+11	2	−40	−0.8	− 3	−11
3	−32	+ 2	−13	−56	3	− 7	−1	− 4	−18
4	−45	−28	−23	−47	4	−26	−8	−10	−35

Finally, we have calculated four center atomic integrals (Table 7). The best choice of α for integration on electron 1 and electron 2 does not lead systematically to the best final result, there are possible cancellations of errors between the two successive approximate integrations.

Table 8. Absolute errors (in units 10^{-5} a.u.) corresponding to different degrees of Z periodization. The potential is created by a $(1s, 1s)$ distribution [$\xi(1s) = 1.260$, $d = 1.38$ a.u., exact value $= 0.66343575$ a.u.]. N is the number of points and α is the periodization degree defined in formula (2) of Part 3

α \ N	21	35	78	101	135	199
1	8044	666	855	501	255	34
2	206	103	11	6	5	4
3	175	45	4	9	1	0.3
4	98	31	3	0.1	0.3	0.08

6. Effect of *Z* Periodization

Z periodization presents a great advantage over *K* periodization: an increase of *Z* periodization degree leads to a regular increase of convergence. Some specific results reported for integrals where *Z* periodization was tractable (see Part 4 for details) clearly illustrate this fact and the real efficiency of *Z* periodization. However it requires a lengthy calculation of various derivatives, in general by numerical techniques. Nevertheless the additive structure of the transformation formula (formula (2) of Part 3) may allow a very crude estimation of derivatives without a great loss in accuracy. We have compared, in the study of *Z* periodization, optimal grids given by Zaremba [10] and Korobov [4] and we have obtained similar results for a similar number of points (Table 8).

7. Conclusion

It appears from this work that the use of periodization techniques leads to numerical integration procedures far more efficient than traditional multidimensional rules (product of unidimensional rules, Monte Carlo method ...) and would improve methods (Haselgrove [5], Conroy [6] ...) similar to that of Korobov. A first periodization technique proposed by Korobov [4] (*K* periodization) is simple and unexpensive, but an optimal degree of periodization must be empirically determined for each integral type. This seems to be feasible. A second periodization technique proposed by Korobov [4] and Zaremba [10] has the great advantage of a regular and rapid convergence of the numerical integration. In practice it can be expensive and its real usefulness remains to be investigated.

Appendix

We shall recall briefly the way for the determination of the integration grids. The integration formula is:

$$\int_0^1\int_0^1\int_0^1 f(x_1, x_2, x_3)dx_1\,dx_2\,dx_3 = 1/N \sum_{k=1}^{N} g(\{a_1 k/N\}, \{a_2 k/N\}, \{a_3 k/N\})$$

where $\{x\}$ means fractional part of x and a_1, a_2, a_3 are the so called optimal coefficients for the integration grid with N points.

Table 9. Optimal coefficients for a three dimensional integration corresponding to the definition of Zaremba (a_2 and a_3) and Korobov (a'_2 and a'_3). In both cases $a_1 = 1$

N	a_2	a_3	a'_2	a'_3
21	3	8		
26	8	12		
44	14	20		
66	9	23		
78	10	25		
86	30	40		
98	16	44		
101			40	85
135	29	42		
142	14	37		
185	26	64		
199			30	104
214	32	78		
301	36	92		
307			75	99

Korobov [4] has proposed a systematic way for the determination of the optimal coefficients (see [1]) in which there is the following constraint: $a_1 = 1$, $a_3 = a_2^2$. Zaremba and Maisonneuve [9–11] have shown that the determination of optimal coefficients without constraints is feasible for small dimensions (3,4 variables). Optimal coefficients according to Korobov and Zaremba for three variables are gathered in Table 9.

References

1. Daudey, J. P., Diner, S.: Intern. J. Quantum Chem. **6**, 575 (1972)
2. Handy, N. C., Boys, S. F.: Theoret. Chim. Acta (Berl.) **31**, 195 (1973)
3. Davis, P. J., Rabinowitz, P.: Numerical integration. New York and Toronto: Blaisdell Publication 1967
4. Korobov, N. M.: Teoretikochislovye Metody v Priblizhennom Analize (Number theoretic methods in approximate analysis). Moskow: Gosudartstvennoe Izdatel'stvo Fiziko-matematicheckoi Literatury 1963
5. Haselgrove, C. B.: Math. Computation **15**, 323 (1961)
6. Hlawka, E.: Monatsh. Math. **66**, 140 (1962)
7. Conroy, H.: J. Chem. Phys. **41**, 1327 (1964)
8. Bakhvalov, N. S.: Vest. Mosk. Univ. **4**, 3 (1959)
9. Zaremba, S. K.: Aequationes mathematicae **4**, 11 (1970)
10. Zaremba, S. K.: In: Applications of number theory to numerical analysis, S. K. Zaremba. Ed., p. 39. New York and London: Academic Press 1972
11. Maisonneuve, D.: In: Applications of number theory to numerical analysis, S. K. Zaremba. Ed., p. 121. New York and London: Academic Press 1972
12. Davis, P. J., Rabinowitz, P., Siam, J.: Numer. Anal. B, **2**, 367 (1965)
13. Ellis, D. E.: Intern. J. Quantum Chem. **2** S, 35 (1968)
14. Boys, S. F., Handy, N. C.: Proc. Roy. Soc. A **311**, 309 (1969)
15. Goodisman, J., Secrest, D.: J. Chem. Phys. **45**, 1515 (1966)
16. Schaefer, H. F.: J. Chem. Phys. **52**, 6241 (1970)

Dr. J. P. Daudey
Institut de Biologie Physico-Chimique
Laboratoire de Biochimie
Théorique associé au C.N.R.S.
13, Rue P. et M. Curie
Paris V, France