Relationes

On the Evaluation of Molecular Integrals by Three Dimensional Numerical Integration in Spherical Polar Coordinates

M. Kleiner*

Department of Chemistry, The University of Sheffield, England

The dependence of three dimensional numerical integration procedures in spherical polar coordinates on choice of frame of reference is examined for certain molecular integrals. Strong dependence on axial alignment is found for short internuclear distance, and diffuse quadratures, but the results improve significantly for large distances and finer integration grids. The implications of this dependence to invariance against choice of frame of reference are examined in an SCF study on water.

Key words: Molecular integrals by numerical integration.

Introduction

In molecular calculations it is customary to introduce a discrete basis ϕ and to compute matrix elements of an operator over this basis [1]. The problem of actual evaluation of such matrix elements becomes one of computing molecular integrals. Several computationally fast methods exist for analytical treatment of the problem [2], but a severe drawback for all of them arises from their dependence on the particular basis ϕ and the specific form of the operator. This imposes a development of a separate procedure for each basis and operator. On the other hand, one may evaluate molecular integrals on the basis of the definition of an integral as a Riemann sum, thus circumventing in principle the necessity for closed analytical expressions. In this way only the values of the integrand at certain points are required, but for acceptable accuracy the number of points is large, so that the method is too slow to be of practical value. The usefulness of this approach is enhanced by employing orthogonal polynomial techniques, which efficiently decrease the number of points required to achieve certain preset accuracy, thus rendering a method of numerical integration of practical utility.

Numerical Integration

The problem of approximating an integral by numerical integration is represented in (1)[1]

$$\int_a^b w(x) f(x) dx \approx \sum_{i=1}^n A_i f(x_i).$$ (1)

---

* Present address: Chemical Physics Department, The Weizmann Institute Rehovot, Israel.

[1] This reads: approximate the integral of $f(X)$ with respect to weight function $w(X)$ over $[a, b]$ by the n term sum on the right of (1).

When in (1) the X_i's refer to roots of orthogonal polynomials, (1) becomes a Gaussian quadrature formula and mathematical theorems assure generality and practical utility of the method[2]. It is further known that the degree of an n point Gauss formula is $2n-1$, and since any continuous function can be approximated by a polynomial (uniform convergence, theorem of Weierstrass), this means that the approximation in (1) becomes exact for any continuous $f(x)$ if n is sufficiently large. Although (1) is still a slow procedure, even with the help of orthogonal polynomials, its generality and suitability for fast "Brute force" electronic computing make it an attractive possibility in molecular calculations [3]. In the course of developing a computing procedure in this laboratory, it became necessary to evaluate integrals of certain potential operators by means of three dimensional numerical integration in spherical polar coordinates. It turns out that under normal conditions the results of integration are not invariant towards choice of coordinate system.

Because such invariance is important for the outcome of molecular calculations, and because of its relevance to numerical integration in general, we investigate this point in some detail.

Method of Calculation

Let ϕ_A and ϕ_B be basis functions centered on A and B. We compute the following integral:

$$\int\limits_{\text{space}} \phi_A^*(x_1) V(r_1, r_2, \cdots, r_n; x_1) \phi_B(x_1) dx_1$$

$$= \int\limits_0^\infty \int\limits_0^\pi \int\limits_0^{2\pi} \phi_A^*(r_{1A}; \theta_{1A}; \varphi_{1A}) V(r_1, r_2, \cdots, r_n; r_{1A}; \theta_{1A}; \varphi_{1A}) \phi_B(r_{1B}; \theta_{1B}; \varphi_{1B}) \quad (2)$$

$$\cdot r_A^2 \cdot \sin\theta_A \cdot dr_A \cdot d\theta_A \cdot d\varphi_A .$$

In (2), $(r_{1A}; \theta_{1A}; \varphi_{1A})$ are the coordinates of point x_1 relative to local coordinate system centered on A (see Fig. 1).

Since ϕ_B is defined relative to local B, it takes its value at x_1 by some $(r_{1B}; \theta_{1B}; \varphi_{1B})$.

Furthermore, if $V(r_1, r_2, \cdots, r_n; x_1) = -\sum\limits_{v=1}^n \dfrac{Zv}{r_{v,1}}$ we have for example, the usual molecular nuclear attraction operator.

We first note that all values of functions in (2) (including ϕ_B) can be expressed relative to a single local coordinate system situated at A. Let the origin of B have coordinates $(X; Y; Z)$ relative to A (always derivable from input information in molecular calculations) then point X_1 has coordinates relative to center B

$$(x_B; y_B; z_B) = [(x_a - X); (y_a - Y); (z_a - Z)] \quad (3)$$

---

[2] 1. *(existence theorem).* For any interval $[a, b]$, any $w(X) \geqq 0$ defined on $[a, b]$ and any n in (1) there exists a *unique* orthogonal polynomial $P_n(X)$. (uniqueness up to a multiplicative constant).

2. [*Theorem on Roots of $P_n(X)$*]. Let $P_n(X)$ be the nth degree orthogonal polynomial for a given $[a, b]$ and $w(x)$, then all the roots of $P_n(X)$ are distinct, real and inside $[a, b]$.
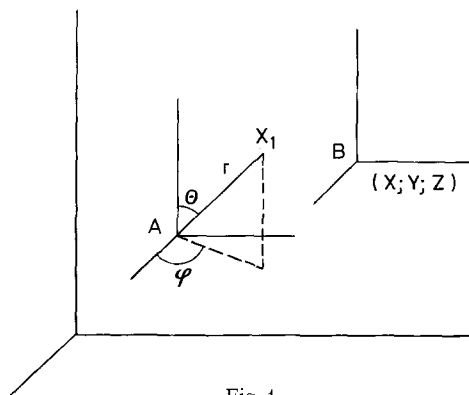
Fig. 1

where

$$x_a = r \cdot \sin\theta \cdot \cos\varphi$$

$$y_a = r \cdot \sin\theta \cdot \sin\varphi$$

$$z_a = r \cdot \cos\varphi .$$

In (3) we have expressed coordinates of any point relative to local B by its values relative to local A, thus enabling us to compute integrals of type (2) by a single numerical integration grid centered at A. This establishes the general applicability of the procedure. For the invariance point in question which affects integral (2) it is sufficient to have both functions centered at A (i.e. $A = B$); this simplifies the numerical analysis. In practical applications the integrand in (2) is first transformed to bring the limits of integration to the limits of the proper quadrature range and also to account for the weight function in case in (1) $w(x) \neq 1$. For integral (2) one uses:

Integration	Range	Range of quadrature	Weight	Variable transformation
r	$(0; \infty)$	$(0; \infty)$	e^{-r}	$r = x$
θ	$(0; \pi)$	$(-1; 1)$	1	$\theta = (x+1)\pi/2$
φ	$(0; \pi)$	$(-1; 1)$	1	$\varphi = (x+1)\pi/2$
φ	$(\pi; 2\pi)$	$(-1; 1)$	1	$\varphi = (x+3)\pi/2$

where in the last column X refers to the value of the *quadrature point*. The integral of the transformed variables (with $B = A$) now to be approximated has the following form:

$$\int_0^\infty \int_{-1}^1 \int_{-1}^1 \phi_A^{*T}(r;\theta;\varphi) V(r_1,\cdots,r_n;r;\theta;\varphi) \phi_A'^{T}(r;\theta;\varphi) \mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\varphi$$

$$\approx \sum_{i=1}^{n_i} \sum_{j=1}^{n_j} \sum_{k=1}^{n_k} A_i A_j A_k \psi(i,j,k) . \tag{4}$$

In (4) $\psi(i,j,k)$ is the value of the integrand at r, θ, φ quadrature points and the A's are the corresponding weights.

Results

The numerical calculation was performed for diatomic fluorine with STO's possessing Clementi-Raimondi [4] exponents. For fluorine $Z = 9.0$ and the potential function takes the form:

$$V(r_1, r_2; r; \theta; \varphi) = -9.0 \left[\frac{1}{r_{A,1}} + \frac{1}{r_{B,1}} \right] \tag{5}$$

The calculation is repeated with the diatomic axis aligned on the X, Y, and Z axes successively and with different internuclear distances for each alignment. The angular (θ, φ) integration is always relative to the same fixed Z axis in any alignment. Since in all calculations the pure one center contribution due to $1/r_{A,1}$ are evaluated exactly by closed expressions, this part becomes an additive constant in all numerical values listed in the tables below, and the discrepancies between integrals which ought to have the same value arise from the $\int \frac{\phi_A^*(1) \phi_A'(1) d\tau_1}{r_{B,1}}$ part which is evaluated by numerical integration.

The results of the calculations are compared for the following integrals:

Integral		Axial alignment
$\langle 2S \| V(r_1, r_2; x_1) \| 2S \rangle$		x, y, z
$\langle 2P\sigma \| V(r_1, r_2; x_1) \| 2P\sigma \rangle =$	$\begin{cases} \langle 2P_x \| V \| 2P_x \rangle \\ \langle 2P_y \| V \| 2P_y \rangle \\ \langle 2P_z \| V \| 2P_z \rangle \end{cases}$	x y z
$\langle 2S \| V(r_1, r_2; x_1) \| 2P\sigma \rangle =$	$\begin{cases} \langle 2S \| V \| 2P_x \rangle \\ \langle 2S \| V \| 2P_y \rangle \\ \langle 2S \| V \| 2P_z \rangle \end{cases}$	x y z
$\langle 2P\pi \| V(r_1, r_2; x_1) \| 2P\pi \rangle =$	$\begin{cases} \langle 2P_y^x \| V \| 2P_y^x \rangle \\ \langle 2P_z^y \| V \| 2P_z^y \rangle \\ \langle 2P_x^z \| V \| 2P_x^z \rangle \end{cases}$	z x y

Discussion

Examination of integral Tables 1–4 indicates the following general features:

1) Accuracy of a given integral generally improves though not monotonically with increase in the number of quadrature points. This is a trivial result. At the same time, within each category, the integrals for different axial alignment differ markedly (most pronounced for the 8 point quadratures).

2) It is noticeable that the X and Z axis alignment usually produce the most accurate integrals[3], whereas the Y axis alignment does not do this to the same extent.

---

[3] The absolute accuracy of the integrals computed here depends on a singularity correction which is applicable to integrals with potential of type (5). This problem is dealt with by a procedure to be published [5]. Because of the symmetry of the P and S sets of atomic functions, all integrals of certain type reported here have the same correction. Thus differences within a certain category in the tables are due to the integration process.

Table 1[a]

$\langle 2S|V(r_1,r_2;x_1)|2S\rangle$

D(a.u.)	Ref. (exact)	24 × 24 × 24			16 × 16 × 16			8 × 8 × 8		
		X	Y	Z	X	Y	Z	X	Y	Z
1.0	−19.627763	−19.61781	−19.61521	−19.62207	−19.62815	−19.61288	−19.67251	−19.52605	−19.49822	−19.58680
2.0	−16.024449	−16.02383	−16.02324	−16.02563	−16.02211	−16.02102	−16.02466	−16.01051	−16.00660	−16.02426
3.0	−14.536960	−14.53691	−14.53689	−14.53695	−14.53684	−14.53680	−14.53698	−14.53615	−14.53581	−14.53698
6.0	−13.037100	−13.03709	−13.03709	−13.03709	−13.03709	−13.03709	−13.03709	−13.03709	−13.03709	−13.03710

Table 2

$\langle 2P\sigma|V(r_1,r_2;x_1)|2P\sigma\rangle$

D(a.u.)	Ref.	24 × 24 × 24			16 × 16 × 16			8 × 8 × 8		
		X	Y	Z	X	Y	Z	X	Y	Z
1.0	−21.338947	−21.31433	−21.30549	−21.32865	−21.33644	−21.29009	−21.47150	−21.02357	−20.93103	−21.22705
2.0	−16.452712	−16.45084	−16.44897	−16.45689	−16.44552	−16.44198	−16.45404	−16.40762	−16.39423	−16.45007
3.0	−14.628329	−14.62820	−14.62815	−14.62836	−14.62795	−14.62782	−14.62839	−14.62542	−14.62413	−14.62833
6.0	−12.994223	−12.99421	−12.99421	−12.99421	−12.99422	−12.99422	−12.99422	−12.99421	−12.99420	−12.99422

Table 3

$\langle 2P\sigma|V(r_1,r_2;x_1)|2S\rangle$

D(a.u.)	Ref.	24 × 24 × 24			16 × 16 × 16			8 × 8 × 8		
		X	Y	Z	X	Y	Z	X	Y	Z
1.0	−3.359090	−3.343390	−3.33859	−3.35116	−3.35876	−3.33214	−3.43621	−3.18013	−3.12939	−3.29129
2.0	−1.247256	−1.24621	−1.24515	−1.24951	−1.24318	−1.24120	−1.24784	−1.22223	−1.21501	−1.24633
3.0	−0.564239	−0.56418	−0.56414	−0.56426	−0.56403	−0.56396	−0.56429	−0.56271	−0.56266	−0.56426
6.0	−0.141123	−0.14112	−0.14112	−0.14112	−0.14112	−0.14112	−0.14112	−0.14112	−0.14112	−0.14112

a X, Y, Z refer to axial alignment; n × n × n to number of points in R, θ, φ integration respectively; Exact integrals by the Browne–Miller method (Technical Report, Molecular Physics group, University of Texas at Austin, January 1962, unpublished) orbital data: 1s (8.6501); 2s (2.5638); 2P (2.5500) [4].

Table 4[a]

$\langle 2P\pi|V(r_1,r_2;x_1)|2P\pi\rangle$

D(a.u.)	Ref.	24 × 24 × 24						8 × 8 × 8					
		X/Y	X/Z	Y/X	Y/Z	Z/X	Z/Y	X/Y	X/Z	Y/X	Y/Z	Z/X	Z/Y
1.0	−18.655788	−18.65568	−18.65588	−18.65599	−18.65590	−18.65574	−18.65579	−18.66404	−18.67007	−18.64975	−18.67699	−18.65630	−18.65630
2.0	−15.716353	−15.71633	−15.71635	−15.71638	−15.71636	−15.71634	−15.71634	−15.71761	−15.71882	−15.71512	−15.71929	−15.71619	−15.71619
3.0	−14.398110	−14.39809	−14.39809	−14.39810	−14.39809	−14.39809	−14.39809	−14.39831	−14.39852	−14.39799	−14.39861	−14.39810	−14.39810
6.0	−12.965388	−12.96538	−12.96538	−12.96538	−12.96538	−12.96538	−12.96538	−12.96538	−12.96538	−12.96538	−12.96539	−12.96538	−12.96538

a Upper XYZ refer to axial alignment; lower XYZ refer to type of integral.

3) An important feature of the numerical results is that accuracy is improved with increase in internuclear distances. While at $D = 1.0$ the individual differences for X, Y, Z alignment are large, these become smaller at $D = 3.0$ and virtually disappear at $D = 6.0$ a. u.

This point indicates that for metals and large organic molecules where bond distances are large this may be a procedure of acceptable accuracy even with small quadratures. The pertinence of these observations for a small molecule, e.g. H_2O, is further discussed in the appendix.

The origin of the dependence on axial alignment and internuclear distance may be explained (for simplicity for case $\phi_A = \phi'_A = 2s$) as follows:

Z Axis Alignment

For each D and θ (Fig. 2) the φ integration defines points on a circle with Radius $R \cdot \sin\theta$ equidistant (r) from point B. Thus the φ integration for each (D, θ) becomes *exactly* proportional to $\sum_{i=1}^{n} \frac{1}{r_i} = \frac{n}{r}$, n being the number of points in the φ quadrature.
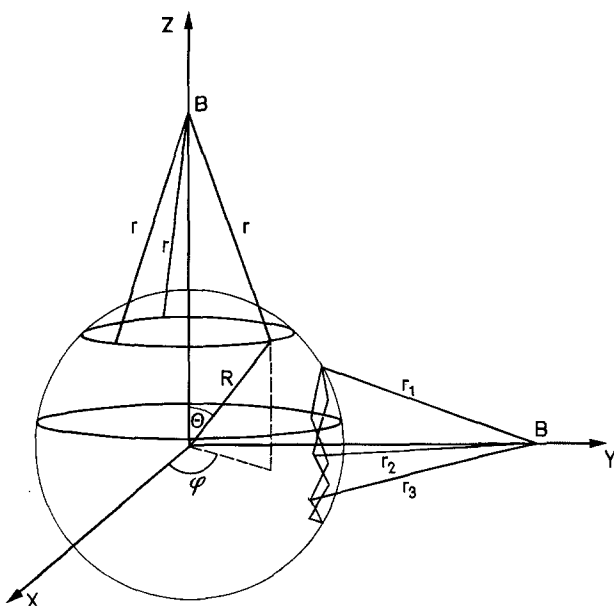

Fig. 2

Y Axis Alignment

The (R, θ, φ) points are defined *as before*, but we are not guaranteed a set of n points with $r_1 = r_2 = \cdots r_n$ as before. The integral value is approximately proportional to $\sum_{i=1}^{n} \frac{1}{r_i} \approx \frac{n}{r_i}$ and the differences between the two alignments Z and Y are

being smoothed as either $n \to \infty$ or $r_i \to \infty$, which explain the observations in points 1, 3 made above.

An immediately obvious remedy to the situation is to rotate the coordinate system so that the Z axis relative to which the φ integration is performed always lies along the line connecting the nuclei. This would mean a back transformation of the integral value to the original frame, which is computationally expensive. In practice for most systems this refinement is not worth the extra effort.

Appendix

The effect of choice of coordinate system on the invariance of the total energy is examined for H_2O, a molecule which is sensitive to the above discussed procedure due to short bond distances ($R_{OH} = 1.8103$ a.u. $\theta = 105°$). All parameters are those of Merrifield and Pitzer [6] whose result serve as reference (all integrals believed accurate to 10^{-6} a.u.).

In the present study all two electron integrals were computed by least squares fit of 6 Gaussians to each slater orbital [7].

The following picture emerges from the SCF study (all values in Hartrees).

Table 5

Symmetry	Ref. [6]	$C_2 = Z(\sigma_h = YZ)$ quadratures		$C_2 = X(\sigma_h = XY)$ quadratures		$C_2 = Y(\sigma_h = YZ)$ quadratures	
		8	16	8	16	8	16
a1	− 20.5046	− 20.4454	− 20.5261	− 20.4384	− 20.5166	− 20.4601	− 20.5344
a1	− 1.2981	− 1.2655	− 1.3035	− 1.2604	− 1.2991	− 1.2781	− 1.3072
b2	− 0.6386	− 0.6034	− 0.6504	− 0.5956	− 0.6448	− 0.6198	− 0.6554
a1	− 0.4715	− 0.4397	− 0.4824	− 0.4341	− 0.4773	− 0.4483	− 0.4867
b1	− 0.4251	− 0.3928	− 0.4362	− 0.3904	− 0.4313	− 0.4016	− 0.4407
a1	0.4013	0.4999	0.3994	0.5111	0.4098	0.4618	0.3916
b2	0.5909	0.6858	0.5632	0.7114	0.5767	0.6395	0.5520
E_{total}	−75.6556	−75.5776	−75.6704	−75.5567	−75.6589	−75.6233	−75.6797

With 8 point quadratures the results are obviously not invariant to choice of axial alignment but the picture improves with 16 points and for approximate calculation choice of a 24 point quadrature may make these differences insignificant. It is encouraging that even for this sensitive case of H_2O with very short bond lengths the orbital symmetries and energies give the correct picture already with 8 point quadratures.

References

1. Roothaan, C. C. J.: Rev. Mod. Phys. **23**, 69 (1951)
2. Alder, B., Fernbach, S., Rotzenberg, M. (Eds.): Methods of Computational Physics, Vol. 2. New York: Academic Press 1963
3a. Magnusson, E. A., Zauli, C.: Proc. Phys. Soc. **78**, 53 (1961)
3b Guidotti, C. *et al.:* La ricerca Scientifica anno 33, serie 2, parte II – A, Vol. 3, n. 2, p. 185, Roma, Marzo 1963 and subsequent papers

3c. Wahl, A. C., Land, R. H.: Int. J. Quant. Chem. **Is**, 375 (1967); – J. Chem. Phys. **50**, 4725 (1969)
3d. Daudey, C. J. P., Diner, S.: Int. J. Quant. Chem. VI 575 (1972) and references cited therein
4. Clementi, E., Raimondi, D. L.: J. Chem. Phys. **38**, 2686 (1963)
5. Kleiner, M., McWeeny, R.: to be published
6. Pitzer, R. M., Merrifield, D. P.: J. Chem. Phys. **52**, 4782 (1970)
7. O-ohata, K., Taketa, H., Huzinaga, S.: J. Phys. Soc. Jap. **21**, 2306 (1966)

Dr. M. Kleiner
Chemical Physics Dept.
The Weizmann Institute of Sciences
P.O.B. 26
Rehovot, Israel