

Ab-initio Hartree–Fock self-consistent-field calculations— An indigenous development of computer programs

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Abstract. A set of indigenously developed computer programs for ab-initio Hartree–Fock calculations on both closed- and open-shell molecules have been described. These programs have been written for calculations using GTO basis sets. Integral formulae have been taken from Taketa *et al* [8]. Structures and functions of the programs have been discussed. These programs have been extensively tested. Molecular integrals over GTO basis sets have been chosen for tests and as numerical examples in this paper. Results of calculations using very accurate minimal bases have been given for methane. Time taken for these computations in a CDC Cyber 180/840 machine has been indicated. Trends in the calculations have also been illustrated by employing 4-gaussian expansions for the STO's and by varying the basis size for LiH and BH⁺.

Keywords. Hartree–Fock; ab-initio; program development; open shell.

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1. Introduction

The quantitative bonding theory developed by theoretical chemists and physicists is mature. A small collection of flexible and powerful techniques, exercised with caution and insight, gives a full and subtle account of structural details and chemical reactivity for a wide range of molecules. Among these techniques, the Hartree–Fock theory [1,2] and Hartree–Fock–Roothaan self-consistent-field calculations [3] together occupy a central position, a position revered as the mean field or the one-electron approximation. The theory and the technique of calculation are not new. What is new in this article is the algorithm for an indigenously prepared computer program for the ab-initio, nonrelativistic, Hartree–Fock self-consistent-field calculation on closed- and open-shell molecules using gaussian basis sets [4]. A few newly computed results are also given.

The programs developed can be easily extended for nonrelativistic configuration interaction calculations, and with suitable considerations, for relativistic Hartree–Fock and relativistic correlation treatments. These extensions will be described in a series of papers to be published in the near future.

The calculations involved are under two major and one minor approximations. The major approximations are theoretical in nature. These are (i) the Born–Oppenheimer approximation and (ii) the neglect of the polarization of mass [5]. The minor approximation is rather technical in nature. It is assumed that the Hartree–Fock orbitals are given by linear combinations of the basis functions employed. Since only a finite number of basis functions will be in use in one calculation, the description

of the Hartree–Fock orbitals as linear expansions in the basis set is by no means complete. That is, the calculated functions will be approximate Hartree–Fock orbitals. The Hartree–Fock equations are essentially second-order differential equations that can be solved by numerical integration techniques to any desired degree of accuracy in total energy. Such numerical calculations were performed for atoms [6]. Results of these numerical calculations are very close to the exact solutions of the atomic Hartree–Fock equations, and the same results are said to be in the Hartree–Fock limit. Results obtained from a calculation with analytical basis functions can be compared with the near Hartree–Fock results, the differences serving as a measure of the accuracy of the “analytical” calculation. This accuracy can be improved by extending the basis set, that is, by using more basis functions. The basis set truncation error can also be reduced by improving the basis function, that is, by optimizing the GTO’s and by increasing the number of optimized GTO’s in each basis function [7].

This article is arranged as follows. The GTO basis set is described in § 2. Calculation of integrals over basis functions is described in § 3. The discussion involves the nature of integrals, the calculation of these integrals over gaussians as prescribed by Taketa *et al* [8] and the calculation of integrals in the atomic case. Structures of the programs developed are described in detail in § 4. Computed results for a few molecules (CH_4 , LiH and BH^+) are discussed in § 5 and A few remarks on the trend of calculations are included.

2. GTO basis set

The gaussian functions to be used as input are of the form

$$g_i^{in} = N_i r^{-l_i} e^{-\alpha_i r^2} \bar{Y}_{l_i} \quad (1)$$

where \bar{Y}_{l_i} is a real spherical harmonics of type

$$\bar{Y}_{l_i} = N_Y \sum_{l=0}^{l_i} \sum_{m=0}^{(l_i-l)} \eta_{l,m,l_i-l-m} r^{-l_i} x^l y^m z^{(l_i-l-m)} \quad (2)$$

and N_i is the normalization constant of the radial function,

$$N_i = \frac{2^{l_i+7/4} \alpha_i^{l_i/2+3/4}}{\pi^{1/4} [(2l_i+1)!]^{1/2}} \quad (3)$$

For instance, for the d_{z^2} gaussian

$$\bar{Y} = (5/16\pi)^{1/2} \frac{2z^2 - x^2 - y^2}{r^2}, \quad (4)$$

$l_i = 2$ and $N_Y = (5/16\pi)^{1/2}$; here the only nonvanishing coefficients are $\eta_{2,0,0} (= -1)$, $\eta_{0,2,0} (= -1)$ and $\eta_{0,0,2} (= 2)$.

Hence the input gaussians can be written as

$$g_i^{in} = \sum_j g_j c_{ji} \quad (5)$$

where g_j is a cartesian gaussian of the form

$$g_j = x^l y^m z^{l_i-l-m} e^{-\alpha_j r^2}, \quad (6)$$

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c_{ji} is given by

$$c_{ji} = N_i N_Y \eta_{l,m,l-l-m}, \quad (7)$$

and the sum over the index j in (5) covers the sum over all possible combinations of l and m with nonvanishing coefficients (η 's).

The basis functions are of the form

$$\phi_\mu = \sum_i g_i^{in} a_{i\mu}. \quad (8)$$

The input involves coordinates of the centre of the gaussians g_i^{in} , angular type representing the l, m and $(l-l-m)$ values, exponent α_i and coefficient a_i . The initial program converts the basis function into a linear combination of cartesian gaussians,

$$\phi_\mu = \sum_j g_j d_{j\mu}. \quad (9)$$

One can easily see that the coefficient $d_{j\mu}$ of the cartesian gaussian g_j is given by

$$d_{j\mu} = \sum_i c_{ji} a_{i\mu}. \quad (10)$$

These coefficients of the cartesian gaussians are calculated and printed.

3. Calculation of integrals

Types of integrals

The integrals involved in a nonrelativistic Hartree-Fock calculation are as follows:

- (i) Overlap integrals, $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$
- (ii) Kinetic energy integrals, $T_{\mu\nu} = -\frac{1}{2} \langle \phi_\mu | \nabla^2 | \phi_\nu \rangle$
- (iii) Nuclear attraction integrals, $V_{\mu\nu} = -Z_m \left\langle \phi_\mu \left| \frac{1}{|\mathbf{r} - \mathbf{R}_m|} \right| \phi_\nu \right\rangle$
- (iv) Electron repulsion integrals,

$$(\mu\nu|\sigma\delta) = \int d\mathbf{v}_1 \int d\mathbf{v}_2 \phi_\mu(\mathbf{r}_1) \phi_\sigma(\mathbf{r}_2) r_{12}^{-1} \phi_\nu(\mathbf{r}_1) \phi_\delta(\mathbf{r}_2).$$

Calculation

Following (6), the GTO g_j centered at atom A is written as

$$g_j(A) = x_A^l y_A^m z_A^n \exp(-\alpha_j r_A^2). \quad (11)$$

The coordinates x_A, y_A and z_A are components of the position vector \mathbf{r}_A relative to the centre of the atom A . Then we have

$$S_{\mu\nu} = \sum_{i,j} d_{i\mu} d_{j\nu} \langle g_i | g_j \rangle, \quad (12)$$

$$T_{\mu\nu} = -1/2 \sum_{i,j} d_{i\mu} d_{j\nu} \langle g_i | \nabla^2 | g_j \rangle,$$

$$V_{\mu\nu}^m = -Z_m \sum_{i,j} d_{i\mu} d_{j\nu} \left\langle g_i \left| \frac{1}{|\mathbf{r} - \mathbf{R}_m|} \right| g_j \right\rangle,$$

$$(\mu\nu|\sigma\delta) = \sum_{ijkl} d_{i\mu} d_{j\nu} d_{k\sigma} d_{l\delta} \langle g_i g_j | g_k g_l \rangle.$$

Calculation of the integrals $\langle g_i | g_j \rangle$, $\langle g_i | \nabla^2 | g_j \rangle$, $\left\langle g_i \left| \frac{1}{|\mathbf{r} - \mathbf{R}_m|} \right| g_j \right\rangle$ and $(g_i g_j | g_k g_l)$ has been discussed by Taketa *et al* [8] and the formulae derived have been used in the preparation of the first two computer programs. The working equations have been assembled in Appendix I. For a full derivation of these equations refer [8].

Integrals (iii) and (iv) involve functions G and H (equations 8 and 11 in Appendix I). Explicit forms for the functions G and H have been calculated by Taketa *et al* up to the combinations $l_1 + l_2 = 4$ and $(l_1 = 2, l_2 = 2)$ respectively. Our systematics for computing G and H functions for these values of l_1 and l_2 as well as higher values are given in tables 1 and 2.

Atomic calculations

For calculations on atoms or atomic ions, the formulae become much simplified. So it is useful to separate the atomic calculations from the main body of the programs. This requires only one (or two) additional subroutine (s).

The atomic simplification arises from two observations: (i) the factor f_j given by (3) of Appendix I reduces to

$$f_j = \delta_{j, l_1 + l_2} \tag{13}$$

for $0 \leq j \leq l_1 + l_2$, and (ii) there is only one nucleus that can be conveniently located at the origin so that $R_A = R_B = R_C = R_D = R_P = R_Q = 0$. We get the following simplified expressions.

1. Overlap integral

$$\begin{aligned} \langle g_1 | g_2 \rangle &= 0, \text{ if any of the sums } (l_1 + l_2), (m_1 + m_2) \text{ and } (n_1 + n_2) \text{ is odd,} \\ &= \left(\frac{\pi}{\gamma}\right)^{3/2} \frac{(l_1 + l_2 - 1)!! (m_1 + m_2 - 1)!! (n_1 + n_2 - 1)!!}{(2\gamma)^{(l_1 + m_1 + n_1 + l_2 + m_2 + n_2)/2}} \text{ otherwise.} \end{aligned} \tag{14}$$

2. Kinetic energy integral

$$\begin{aligned} &(-1/2) \langle g_1 | \nabla^2 | g_2 \rangle \\ &= 0, \text{ if any of the sums } (l_1 + l_2), (m_1 + m_2) \text{ and } (n_1 + n_2) \text{ is odd} \\ &= \left(\alpha_2 [2(l_2 + m_2 + n_2) + 3] - \frac{\alpha_2^2}{\gamma} [l_1 + l_2 + m_1 + m_2 + n_1 + n_2 + 3] \right. \\ &\quad \left. - \gamma \left[\frac{l_2(l_2 - 1)}{(l_1 + l_2 - 1)} + \frac{m_2(m_2 - 1)}{(m_1 + m_2 - 1)} + \frac{n_2(n_2 - 1)}{(n_1 + n_2 - 1)} \right] \right) \langle g_1 | g_2 \rangle \text{ otherwise.} \end{aligned} \tag{15}$$

3. Nuclear attraction energy integrals

$$\begin{aligned} &\left\langle g_1 \left| -\frac{Z}{r} \right| g_2 \right\rangle \\ &= 0, \text{ if any of the sums } (l_1 + l_2), (m_1 + m_2) \text{ and } (n_1 + n_2) \text{ is odd} \\ &= -\frac{2\pi Z}{\gamma} \sum_{I=0}^{l_2 + l_2} \sum_{J=0}^{m_1 + m_2} \sum_{K=0}^{n_1 + n_2} G_{Ix} G_{Jy} G_{Kz} / [2(I + J + K) + 1] \text{ otherwise,} \end{aligned} \tag{16}$$

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Table 1. Algorithm for preparing G_x functions for various $(l_1 + l_2)$. The parameter p is given by $p = X_p - X_C$. In each expression G_{ix} represents the expression for G_{ix} for the preceding $l_1 + l_2$. The parameter $f_{l_1+l_2}$ is 1 for every $(l_1 + l_2)$.

$(l_1 + l_2)$	l	$G_l(l_1, l_2, x_A - x_p, x_B - x_p, p)$
0	0	f_0
1	0	G_{0x}
	1	$-f_1 p$
2	0	$G_{0x} + f_2/2\gamma$
	1	$G_{1x} - f_2/2\gamma$
	2	$f_2 p^2$
3	0	G_{0x}
	1	$G_{1x} - 3f_3 p/2\gamma$
	2	$G_{2x} + 3f_3 p/2\gamma$
	3	$-f_3 p^3$
4	0	$G_{0x} + 3f_4/4\gamma^2$
	1	$G_{1x} - 3f_4/2\gamma^2$
	2	$G_{2x} + 3f_4 p^2/\gamma + 3f_4/4\gamma^2$
	3	$G_{3x} - 3f_4 p^2/\gamma$
	4	$f_4 p^4$
5	0	G_{0x}
	1	$G_{1x} - 15f_5 p/4\gamma^2$
	2	$G_{2x} + 15f_5 p/2\gamma^2$
	3	$G_{3x} - 15f_5 p/4\gamma^2 - 5f_5 p^3/\gamma$
	4	$G_{4x} + 5f_5 p^3/\gamma$
	5	$-f_5 p^5$
6	0	$G_{0x} + 15f_6/8\gamma^3$
	1	$G_{1x} - 45f_6/8\gamma^3$
	2	$G_{2x} + 45f_6 p^2/4\gamma^2 + 45f_6/8\gamma^3$
	3	$G_{3x} - 45f_6 p^2/2\gamma^2 - 15f_6/8\gamma^3$
	4	$G_{4x} + 15f_6 p^4/2\gamma + 45f_6 p^2/4\gamma^2$
	5	$G_{5x} - 15f_6 p^4/2\gamma$
	6	$f_6 p^6$
7	0	G_{0x}
	1	$G_{1x} - 105f_7 p/8\gamma^3$
	2	$G_{2x} + 315f_7 p/8\gamma^3$
	3	$G_{3x} - 105f_7 p^3/4\gamma^2 - 315f_7 p/8\gamma^3$
	4	$G_{4x} + 105f_7 p^3/2\gamma^2 + 105f_7 p/8\gamma^3$
	5	$G_{5x} - 21f_7 p^5/2\gamma - 105f_7 p^3/4\gamma^2$
	6	$G_{6x} + 21f_7 p^5/2\gamma$
	7	$-f_7 p^7$
8	0	$G_{0x} + 105f_8/16\gamma^4$
	1	$G_{1x} - 105f_8/4\gamma^4$
	2	$G_{2x} + 105f_8 p^2/2\gamma^3 + 315f_8/8\gamma^4$
	3	$G_{3x} - 315f_8 p^2/2\gamma^3 - 105f_8/4\gamma^4$
	4	$G_{4x} + 105f_8 p^4/2\gamma^2 + 315f_8 p^2/2\gamma^3 + 105f_8/16\gamma^4$
	5	$G_{5x} - 105f_8 p^4/\gamma^2 - 105f_8 p^2/2\gamma^3$
	6	$G_{6x} + 14f_8 p^6/\gamma + 105f_8 p^4/2\gamma^2$
	7	$G_{7x} - 14f_8 p^6/\gamma$
	8	$f_8 p^8$

Table 2. Algorithm for preparing H_L functions for various $(l_1 + l_2)$. In each expression H_L represents the expression for H_L for the preceding $l_1 + l_2$. The parameter $f_{l_1+l_2}$ is 1 for every $(l_1 + l_2)$.

$(l_1 + l_2)$	L	$H_L(l_1, l_2, a, b, \gamma)$
0	0	f_0
1	0	H_0
	1	$f_1/4\gamma$
2	0	$H_0 + f_2/2\gamma$
	1	H_1
	2	$f_2/(4\gamma)^2$
3	0	H_0
	1	$H_1 + 6f_3/(4\gamma)^2$
	2	H_2
	3	$f_3/(4\gamma)^3$
4	0	$H_0 + 12f_4/(4\gamma)^2$
	1	H_1
	2	$H_2 + 12f_4/(4\gamma)^3$
	3	H_3
	4	$f_4/(4\gamma)^4$
5	0	H_0
	1	$H_1 + 60f_5/(4\gamma)^3$
	2	H_2
	3	$H_3 + 20f_5/(4\gamma)^4$
	4	H_4
	5	$f_5/(4\gamma)^5$
6	0	$H_0 + 120f_6/(4\gamma)^3$
	1	H_1
	2	$H_2 + 180f_6/(4\gamma)^4$
	3	H_3
	4	$H_4 + 30f_6/(4\gamma)^5$
	5	H_5
	6	$f_6/(4\gamma)^6$
7	0	H_0
	1	$H_1 + 840f_7/(4\gamma)^4$
	2	H_2
	3	$H_3 + 420f_7/(4\gamma)^5$
	4	H_4
	5	$H_5 + 42f_7/(4\gamma)^6$
	6	H_6
	7	$f_7/(4\gamma)^7$
8	0	$H_0 + 1680f_8/(4\gamma)^4$
	1	H_1
	2	$H_2 + 3360f_8/(4\gamma)^5$
	3	H_3
	4	$H_4 + 840f_8/(4\gamma)^6$
	5	H_5
	6	$H_6 + 56f_8/(4\gamma)^7$
	7	H_7
	8	$f_8/(4\gamma)^8$

where

$$G_{Ix} = \frac{(-1)^I (l_1 + l_2)!}{\left(\frac{l_1 + l_2}{2} - I\right)! I! (4\gamma)^{(l_1 + l_2)/2}} \quad (17)$$

etc.

4. Electron repulsion integrals

$$(g_1 g_2 | g_3 g_4) = \frac{2\pi^2}{\gamma_1 + \gamma_2} \left(\frac{\pi}{\gamma_1 + \gamma_2}\right)^{1/2} \sum_{I,J,K} C_{Ix} C_{Jy} C_{Kz} / (2[I + J + K] + 1) \quad (18)$$

where

$$C_{Ix} = \sum_L^{(l_1 + l_2)} \sum_M^{(l_2 + l_3)}_{(L+M=2I)} H_L(l_1, l_2, 0, 0, \gamma_1) (-1)^{I-L} H_M(l_3, l_4, 0, 0, \gamma_2) \times \frac{(2I)!}{I! [(\gamma_1 + \gamma_2)/4\gamma_1\gamma_2]^I} \quad (19)$$

and

$$H_L = \frac{(l_1 + l_2)!}{[(l_1 + l_2 - L)/2]! L! (4\gamma_1)^{(l_1 + l_2 + L)/2}} \quad (20)$$

4. Program structures

Plan: The development of these programs has been completely indigenous. The whole scheme of calculation is covered by three programs to be executed successively, and the option is kept open for the execution of two more programs for the calculation of molecular properties and the configuration interaction treatment. The plan is exhibited in figure 1. The order of execution is indicated by arrows. Output of any

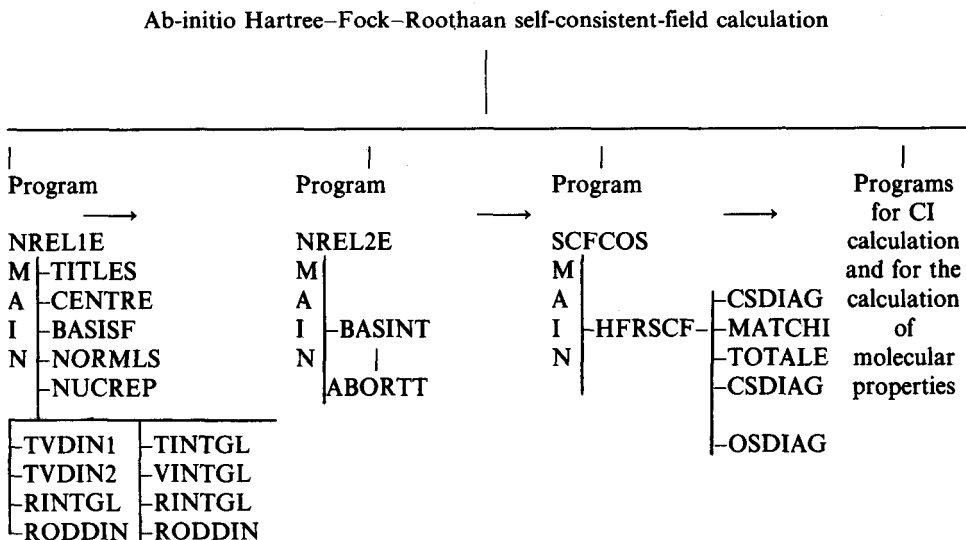


Figure 1. Scheme for carrying out ab-initio Hartree-Fock self-consistent-field calculations on closed- and open-shell molecules by using the GTO basis sets and the calling sequences for subroutines in the programs used.

program is to be used in all subsequent executions. Thus output of NREL1E is used in executing NREL2E, SCFCOS and FUTURE, etc. Functions of the programs are as follows.

Functions

- NREL1E** Calculates the nonrelativistic one-electron integrals, viz., (i) overlap integrals, (ii) kinetic energy integrals (integrals of $-2^{-1}\nabla^2$), (iii) electron-nuclear attractive potential energy integrals (integrals of $-Z_n|\mathbf{r}_i - \mathbf{R}_n|^{-1}$), and optionally (for atoms) (iv) r^n integrals (where $n = -3, -2, -1, 1, 2, 4, 6$) over nonrelativistic basis functions.
- NREL2E** Calculates the nonrelativistic two-electron integrals, that is, two-electron repulsion integrals (integrals of r_{12}^{-1}) over nonrelativistic basis functions.
- SCFCOS** Carries out the Hartree-Fock-Roothaan Self-Consistent-Field calculations, and optionally (for atoms) calculates the $\langle r^n \rangle$ expectation values for (atomic) orbitals.
- FUTURE** The two aspects covered by these programs are (i) the calculation of molecular properties and (ii) configurations interaction treatment. The SDCl program has already been developed [9]. The full CI and molecular properties packages will be reported in the near future.

Subroutines of the first three programs are listed in table 3. Their functions are explained in the following.

Program NREL1E

Nonrelativistic one-electron integrals are calculated with the help of 13 subroutines in addition to the main program.

- ABORTT** aborts execution in case of emergencies.
- BASISF** reads specifications for the GTO basis.
- CENTER** reads specifications for the centres of basis functions.
- CONVRT** carries out (optionally) conversions necessary for a valence-electron calculation instead of an all-electron calculation.
- MAIN**
- NORMLS** normalizes the basis functions.
- NUCREP** calculates internuclear repulsion energy.
- RINTGL** calculates r^n matrices where n is even (optionally, for atomic cases).

Table 3. List of subroutines.

Program ¹	Subroutine
NREL1E (1712)	ABORTT, BASISF, CENTER, CONVRT, MAIN, NORMLS, NUCREP, RINTGL, RODDIN, TINTGL, TITLES, TVDIN1, TVDIN2, VINTGL
NREL2E (1172)	ABORTT, BASINT, MAIN
SCFCOS (1249)	CSDIAG, HFRSCF, MAIN, MATCHI, OSDIAG, TOTALE

¹Total number of statements is indicated in paranthesis under the name of each program.

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RODDIN	calculates r^n matrices where n is odd (optionally, for atomic cases).
TINTGL	calculates kinetic energy matrix.
TITLES	reads the heading of the job.
TVDIN1,	optionally performs atomic calculations, avoiding NORMLS,
TVDIN2	TINTGL and VINTGL: each of these subroutines can be written to completion while a TV dinner is cooked, hence the nomenclature.
VINTGL	calculates nuclear attraction energy matrix.

Program NREL2E

Nonrelativistic two-electron integrals are calculated.

ABORTT	aborts execution.
BASINT	calculates two-electron integrals over basis functions.
MAIN	

Program SCFCOS

Hartree-Fock-Roothaan SCF treatment is carried out for closed and open shell molecules.

CSDIAG	diagonalizes the closed-shell Fock matrix.
HFRSCF	carries out the SCF calculations.
MAIN	
MATCHI	matches indices for two-electron integrals and selects the stored values for preparing Fock matrices.
OSDIAG	diagonalizes the open-shell Fock matrix.
TOTALE	calculates total energy in every SCF loop.

Test

All the molecular integrals quoted in tables 1-5 in the paper of Taketa *et al* [8] have been computed and verified.

5. Concluding remarks

The difficulties in calculations employing the GTO basis sets are well known [8]. The main difficulty is the need to compute about $(1/8)N^4$ basic summands for two-electron integrals where N is the total number of gaussians. This is coupled with the problem of slow convergence of the calculated results as the number of terms in the expansion of each basis function increases. The advantages of using the GTO basis are that an exact analytical expression is available for each integral and the computation of these expressions is reasonably fast.

For illustration I show in table 4(a) one-electron integrals for π electrons in the benzene molecule with C-C distance 2.6320755 a.u. For the $2p_z$ orbital of carbon atom I have used 8-, 11-, and 13-gaussian expansions calculated by Partridge [10]. Pi-electron repulsion integrals are given in table 4(b). The performance of the expansions due to Partridge is gratifying. The 13-gaussian expansion represents the atomic Hartree-Fock limit and obviously the values calculated with this expansion are the accurate values for integrals over $2p_z$ orbitals of carbon atoms with the chosen molecular geometry. Trends in the calculated values parallel the trends in the radial

Table 4(a). One-electron integrals: $2p\pi - 2p\pi$ for the benzene molecule (a. u.).

Integrals	Partridge basis set		
	8p	11p	13p
$\langle 2p_{za} 2p_{zb} \rangle$			
12	0.3228027	0.3228235	0.3228243
13	0.0805732	0.0806314	0.0806334
14	0.0466768	0.0467444	0.0467467
$-(1/2)\langle 2p_{za} \nabla^2 2p_{zb} \rangle$			
11	1.2536583	1.2536686	1.2536697
12	0.1053507	0.1053380	0.1053378
13	0.0048302	0.0048334	0.0048336
14	0.0001659	0.0001652	0.0001628
$\sum_c \left\langle 2p_{za} \left \frac{1}{r_c} \right 2p_{zb} \right\rangle$			
11	2.072825	2.072813	2.072813
12	0.6044734	0.6044812	0.6044816
13	0.1458726	0.1459341	0.1459359
14	0.0839891	0.0840590	0.0840600

Table 4(b). Pi-electron repulsion integrals for the benzene molecule (a.u.). Carbon-carbon bond distance used is 2.6320755 a.u.

Integrals	Partridge basis set*		
	8p	11p	13p
11 11	0.5775441	0.5775322	0.5775317
11 12	0.1376486	0.1376476	0.1376476
11 13	0.0260711	0.0266185	0.0266188
11 14	0.0142159	0.0142275	0.0142277
11 22	0.0454505	0.0434194	0.0429192
11 23	0.0092344	0.0092377	0.0092378
11 24	0.0045394	0.0045432	0.0045433
11 25	0.0075520	0.0075555	0.0075556
11 26	0.0342107	0.0342116	0.0342116
11 33	0.0022881	0.0022879	0.0023143
11 34	0.0011852	0.0011866	0.0011867
11 35	0.0018567	0.0018582	0.0018583
11 44	0.0007190	0.0007200	0.0007210
12 12	0.3210676	0.3210609	0.3210606
12 13	0.0822259	0.0822270	0.0822271
12 14	0.0198691	0.0198782	0.0198785
12 15	0.0132073	0.0132180	0.0132183
12 16	0.0295130	0.0295222	0.0295225
12 34	0.0021339	0.0021355	0.0021356
12 35	0.0011913	0.0011927	0.0011927
12 43	0.0043401	0.0043436	0.0043437
12 45	0.0007078	0.0007089	0.0007089

(Continued)

Table 4(b). (Continued)

Integrals	Partridge basis set ^a		
	8p	11p	13p
12 53	0.0061509	0.0061539	0.0061540
12 63	0.0234139	0.0234152	0.0234152
13 13	0.2058286	0.2058256	0.2058255
13 14	0.0630221	0.0630237	0.0630237
13 15	0.0176700	0.0176782	0.0176785
13 64	0.0206595	0.0206608	0.0206609
14 14	0.1808739	0.1808717	0.1808716
Time (seconds) ^b	180	578	1028

(a) Ref. [10]

(b) CDC Cyber 180/840 machine (with about 1 MFLOPS available speed for computation) was used.

Table 5. Calculated radial moments of 2p orbitals of carbon atom.

	Partridge basis set [10]		
	8p	11p	13p
$\langle r^{-2} \rangle$	0.8919758	0.8920567	0.8920611
$\langle r^{-1} \rangle$	0.7835025	0.7835024	0.7835025
$\langle r \rangle$	1.714385	1.714490	1.714494
$\langle r^2 \rangle$	3.745603	3.746742	3.746793

moments for the 2p orbitals of carbon atom in table 5. Integrals given in tables 4(a) and 4(b) can be directly used in a suitable (all-electron, effective potential or π -electron) calculation. The last entries in table 4(b) refer to the time taken for each computation in a CDC Cyber 180/840 machine installed in IIT Bombay. The machine offers an effective computing speed of about 1 million floating point operations per second.

Preliminary results on the methane molecule are given in table 6(a). The basis sets used have been minimal (carbon: 1s, 2s and 2p functions; hydrogen 1s function) but elaborate, that is, near exact Hartree-Fock solutions for atoms. The first set consists of 13S8P bases for carbon [10] and STO-10G basis for hydrogen [11]. The second set has 18S13P bases for carbon [10] and a STO-12G basis (modified from the STO-10G basis) for hydrogen [4]. The C-H distance has been taken to be 1.093 Å [12]. A tetrahedral geometry has been adopted. A break-up for the time taken in different steps of these calculations is also shown in this table. Table 6(b) shows the radial moments of the atomic orbitals used in the basis sets.

We choose to give some sample results on the LiH and BH⁺ molecules here. LiH is a closed-shell molecule and BH⁺ is an open-shell molecular ion. Experimental bond lengths have been chosen in both the cases ($R_{\text{LiH}} = 3.015$ bohr; $R_{\text{BH}^+} = 2.296$ bohr) such that a comparison can be made between the presently computed values and results available in the literature. The present calculations are based on 4-gaussian expansions of STO's. Exponents of the STO's have been taken from Cade and Huo

Table 6(a). Computed results for the methane molecule (tetrahedral geometry; C-H bond length = 1.093 Å or 2.06547 bohr). All energy values are in hartree.

	Basis I ^a	Basis II ^b
Total energy (E)	-40.0552448	-40.0553007
V/T^c	-2.0198969	-2.0198935
Orbital energies (ϵ)		
1A ₁	-11.386921	-11.386976
2A ₁	-1.004501	-1.004535
1T ₂	-0.606479	-0.606517
Time in seconds ^d		
1-electron integrals	146	203
2-electron integrals	576	1485
SCF calculation	40	36

(a) Partridge 13S8P basis for carbon and STO-10G expansion for hydrogen 1s orbital: total number of gaussians is 90.

(b) Partridge 18S13P basis for carbon and STO-12G expansion for hydrogen 1s orbital: total number of gaussians is 122.

(c) V/T is the ratio of potential and kinetic energies.

(d) Time taken by a CDC Cyber 180/840 machine.

Table 6(b). Radial moments of atomic orbitals.

	Basis I	Basis II
$\langle r^{-2} \rangle$		
C 1s	65.227519	65.232129
C 2s	3.255063	3.254940
C 2p	0.891976	0.892061
H 1s	1.999600	1.999860
$\langle r^{-1} \rangle$		
C 1s	5.664434	5.664437
C 2s	0.896807	0.896798
C 2p	0.783502	0.783502
H 1s	0.999993	0.999994
$\langle r \rangle$		
C 1s	0.268442	0.268443
C 2s	1.589225	1.589341
C 2p	1.714385	1.714494
H 1s	1.500006	1.500005
$\langle r^2 \rangle$		
C 1s	0.097198	0.097199
C 2s	3.051006	3.052031
C 2p	3.745603	3.746793
H 1s	3.000023	3.000019

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[13]. The calculations of Cade and Huo involve very large STO bases and their results are of high quality, near the Hartree–Fock limit for each molecule.

The minimal basis results on LiH were given earlier [4]. These results are surprisingly good, which is obviously an outcome of employing the near Hartree–Fock atomic orbitals due to Partridge [10] as basis functions. These are shown alongside the presently calculated values in table 7. One of the present calculations has been performed with 4-gaussian expansions for 1s, 1s', 2s, 2s', 3s and 2p STO's of Li and 1s, 1s', 2s and 2p STO's of H (Basis I). The second calculation has utilized 4-gaussian expansions for 2p', 2p'' and 3p STO's of Li in addition to the basis functions used in the first calculation (Basis II). Results from these calculations are compared with those computed by Cade and Huo [13] using a STO basis set (1s, 1s', 2s, 2s', 3s, 2p, 2p', 2p'', 3p and also 3d, 3d' and 4f STO's for Li; 1s, 1s', 2s, and 2p STO's for H). Differences

Table 7. Computed results for LiH. The bond length employed is 3.015 bohr. All energies are in hartree.

	Minimal Basis ^a	Present calculations			Cade and Huo ^c
		Minimal STO-4G ^b	Basis I ^b	Basis II ^b	
Li					
Basis	1s, 2s	1s, 2s	1s, 1s', 2s, 2s', 3s, 2p	1s, 1s', 2s, 2s', 3s, 2p, 2p', 2p'', 3p	1s, 1s', 2s, 2s', 3s, 2p, 2p', 2p'', 3p, 3d, 3d', 4f
$\langle r^{-2} \rangle$					
1s	14.8885	12.3788	14.5807	14.5807	
2s	0.4354	1.0797	0.5597	0.5597	
2p	—	—	0.1793	0.0983	
$\langle r^{-1} \rangle$					
1s	2.6850	2.5166	2.6817	2.6817	
2s	0.3454	0.5186	0.3999	0.3999	
2p	—	—	0.3680	0.2796	
$\langle r \rangle$					
1s	0.5731	0.5947	0.5748	0.5748	
2s	3.8736	2.7823	3.2321	3.2321	
2p	—	—	3.3928	4.2002	
$\langle r^2 \rangle$					
1s	0.4468	0.4711	0.4503	0.4503	
2s	17.7376	8.9909	11.7342	11.7342	
2p	—	—	13.8123	20.0973	
H					
Basis	1s	1s	1s, 1s', 2s, 2p	1s, 1s', 2s, 2p	1s, 1s', 2s, 2p
$\langle r^{-2} \rangle$					
1s	1.9999	1.5346	1.9517	1.9517	
$\langle r^{-1} \rangle$					
1s	1.0000	0.8861	0.9903	0.9903	
$\langle r \rangle$					
1s	1.5000	1.6893	1.5442	1.5442	
$\langle r^2 \rangle$					
1s	3.0000	3.8011	3.2420	3.2420	
Molecular results					
<i>E</i>	-7.96039	-7.9061	-7.9713	-7.9732	-7.98731
<i>V/T</i> ^d	-1.98615	-2.0939	-1.9960	-1.9960	-1.99950
$\epsilon_{1\sigma}$	-2.46882	-2.4538	-2.4429	-2.4355	-2.44525
$\epsilon_{2\sigma}$	-0.29481	-0.2844	-0.2974	-0.2968	-0.30172

(a) This minimal basis calculation had used Partridge's 18S basis for Li and a 12-gaussian expansion for H 1s orbital [4].

(b) Each STO was expanded into a linear sum of four gaussians.

(c) STO calculation by Cade and Huo [13].

(d) *V/T* is the ratio of potential and kinetic energies.

from the results of Cade and Huo are mainly attributable to the very approximate nature of the 4-gaussian expansions and to a lesser extent to the absence of the 3*d*, 3*d'* and 4*f* basis functions.

For BH⁺ we have taken similar expansions for 1*s*, 1*s'*, 2*s*, 2*s'*, 3*s* and 2*p* STO's of B (Basis I) and additionally 2*p'*, 2*p''* and 2*p'''* STO's of B (Basis II). The hydrogen basis remains as before but the exponents differ. The minimal basis calculation has been carried out using the B.²P (18*s* 13*p*) basis set due to Partridge and a 12-gaussian expansion for the 1*s* orbital of hydrogen. The calculated values are shown along with the values from the STO calculation of Cade and Huo in table 8.

The results computed for both the molecules using the first basis sets show encouraging improvements over the minimal STO-4G results. In each case the total

Table 8. Computed results for BH⁺. The bond length employed is 2.296 bohr. All energies are in hartree.

	Minimal Basis ^a	Present calculations			Cade and Huo ^c
		Minimal STO-4G ^b	Basis I ^b	Basis II ^b	
B	1 <i>s</i> , 2 <i>s</i>	1 <i>s</i> , 2 <i>s</i> ,	1 <i>s</i> , 1 <i>s'</i> , 2 <i>s</i> ,	1 <i>s</i> , 1 <i>s'</i> , 2 <i>s</i> ,	1 <i>s</i> , 1 <i>s'</i> , 2 <i>s</i> ,
Basis	2 <i>p</i>	2 <i>p</i>	2 <i>s'</i> , 3 <i>s</i> , 2 <i>p</i>	2 <i>s'</i> , 3 <i>s</i> , 2 <i>p</i> , 2 <i>p'</i> , 2 <i>p''</i> , 2 <i>p'''</i>	2 <i>s'</i> , 3 <i>s</i> , 2 <i>p</i> , 2 <i>p'</i> , 2 <i>p''</i> , 2 <i>p'''</i> , 3 <i>d</i> , 3 <i>d'</i> , 4 <i>f</i>
$\langle r^{-2} \rangle$					
1 <i>s</i>	44.5364	30.1466	43.6587	43.6587	
2 <i>s</i>	2.0243	0.9289	2.0868	1.6123	
2 <i>p</i>	0.5299	0.2738	0.2738	1.2361	
$\langle r^{-1} \rangle$					
1 <i>s</i>	4.6743	3.9339	4.6745	4.6601	
2 <i>s</i>	0.7129	0.5696	0.7351	0.6525	
2 <i>p</i>	0.6050	0.4548	0.4548	1.1999	
$\langle r \rangle$					
1 <i>s</i>	0.3259	0.3796	0.3261	0.3278	
2 <i>s</i>	1.9771	2.2402	1.8990	2.0955	
2 <i>p</i>	2.2048	2.7452	2.7452	2.7468	
$\langle r^2 \rangle$					
1 <i>s</i>	0.1434	0.1943	0.1439	0.1457	
2 <i>s</i>	4.7091	5.7989	4.2748	5.1636	
2 <i>p</i>	6.1461	9.0423	9.0423	6.1500	
H	1 <i>s</i>	1 <i>s</i>	1 <i>s</i> , 1 <i>s'</i> , 2 <i>s</i> ,	1 <i>s</i> , 1 <i>s'</i> , 2 <i>s</i> ,	1 <i>s</i> , 1 <i>s'</i> , 2 <i>s</i> ,
Basis			2 <i>p</i>	2 <i>p</i>	2 <i>p</i>
$\langle r^{-2} \rangle$					
1 <i>s</i>	1.9999	2.7239	2.0181	2.0181	
$\langle r^{-1} \rangle$					
1 <i>s</i>	1.0000	1.1805	1.0218	1.0218	
$\langle r \rangle$					
1 <i>s</i>	1.5000	1.2679	1.4425	1.4425	
$\langle r^{-2} \rangle$					
1 <i>s</i>	3.0000	2.1415	2.7116	2.7116	
Molecular results					
<i>E</i>	-24.71738	-23.9268	-24.6898	-24.7829	-24.82064
<i>V/T</i> ^d	-2.02667	-2.4027	-2.0051	-2.0004	-2.00122
$\epsilon_{1\sigma}$	-8.31101	-8.4302	-8.2368	-8.0985	-8.10898
$\epsilon_{2\sigma}$	-1.01561	-1.0077	-1.0141	-0.9759	-0.97699
$\epsilon_{3\sigma}$	-0.83275	-0.7768	-0.7439	-0.8201	-0.81953

(a) This minimal basis calculation used Partridge's 18S13P basis for B and a 12-gaussian expansion for H 1*s* orbital.

(b) Each STO was expanded into a linear sum of four gaussians.

(c) STO calculation by Cade and Huo [13].

(d) *V/T* is the ratio of potential and kinetic energies.

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energy computed by using the set of near Hartree–Fock atomic orbitals differs by a large amount from that computed by using the minimal STO-4G basis set, indicating the importance of a large, more accurate expansion for each STO. The gross inadequacy of the minimal STO-4G basis set is also reflected by the large (20%) deviation of the virial ratio in table 8. The poor quality of the basis functions (atomic valence functions) is evident from the radial moments shown in the same table. An interesting observation is that for BH^+ the minimal Partridge basis calculation gives a total energy that is even superior to the value calculated using Basis I. Values computed by using the second basis sets are closed to the STO results of Cade and Huo [13]. The differences can be made smaller by using a larger expansion for each STO and using STO's of symmetries d and f . A few standard GTO expansions have been determined by Ohata *et al* [11]. These can be of invaluable assistance in carrying out ab-initio calculations on molecules of lighter elements.

Note added while revising the manuscript: The author could not directly compare the speed of the present programs with that of GAUSSIAN. The execution for LiH with basis 6–311g** (24 basis functions, 39 gaussian primitives) gave results ($E = -7.98577$, $V/T = -2.0003$, $\varepsilon_{1\sigma} = -2.44759$, $\varepsilon_{2\sigma} = -0.30154$) in agreement with the results of GAUSSIAN 90 for LiH with bond length 1.595 Å. The GAUSSIAN 90 results were obtained from Ewig and Trindle. The time taken was as follows: 219 cp seconds using Cyber (with speed about 1 MFLOPS) for the calculation of two-electron integrals; about 2.8 s using IBM RS/6000 550 system (speed 15–20 MFLOPS) and about 11.6 s using Silicon Graphics 4D/35 (speed 5–10 MFLOPS) for the whole execution of GAUSSIAN 90. This indicates that the generation of two-electron integrals by the present program is 3–4 times slower. But the 6–311g** basis is very nicely suited for GAUSSIAN as s and p orbitals of lithium atom have been given common exponents, whereas in the programs reported here no provision has been made for exploiting this situation. So the speed of computing the two-electron integrals over general basis functions is expected to be comparable to the speed of GAUSSIAN. The disc memory required for the execution in Cyber was about 3.5 MB compared to about 6 MB required for the execution of GAUSSIAN.

Appendix A

Integrals over gaussians

(1) The overlap integral between gaussians g_1 on atom A and g_2 on atom B with exponents α_1 and α_2 respectively is given by [8]

$$\begin{aligned} \langle g_1 | g_2 \rangle &= \left(\frac{\pi}{\gamma} \right)^{3/2} \exp(-\alpha_1 \alpha_2 R_{AB}^2 / \gamma) \\ &\times \sum_{i=0}^{(l_1 + l_2)/2} f_{2i}(l_1, l_2, X_A - X_P, X_B - X_P) \frac{(2i-1)!!}{(2\gamma)^i} \\ &\times \sum_{j=0}^{(m_1 + m_2)/2} f_{2j}(m_1, m_2, Y_A - Y_P, Y_B - Y_P) \frac{(2j-1)!!}{(2\gamma)^j} \\ &\times \sum_{k=0}^{(n_1 + n_2)/2} f_{2k}(n_1, n_2, Z_A - Z_P, Z_B - Z_P) \frac{(2k-1)!!}{(2\gamma)^k} \end{aligned} \quad (\text{A1})$$

where \mathbf{R}_A , \mathbf{R}_B , etc. denote the position vectors for the centres of atoms A, B, etc.,

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R_{AB} is the distance between atom centres A and B,

$$\gamma = \alpha_1 + \alpha_2, \quad (\text{A2})$$

$$\mathbf{R}_p = (\alpha_1 \mathbf{R}_A + \alpha_2 \mathbf{R}_B) / \gamma,$$

$$(2i - 1)!! = (2i)! / [2^i i!],$$

and $[N]$ represents the largest integer less than or equal to N . The factor f_j is the coefficient of X_p^j in the product $X_A^{l_1} X_B^{l_2}$,

$$X_A^{l_1} X_B^{l_2} = \sum_{j=0}^{l_1+l_2} f_j(l_1, l_2, X_A - X_p, X_B - X_p) X_p^j \quad (\text{A3})$$

such that

$$f_j(l_1, l_2, X_A - X_p, X_B - X_p) = \sum_{k_1=0}^{l_1} \sum_{\substack{k_2=0 \\ (k_1+k_2=j)}}^{l_2} \binom{l_1}{k_1} \binom{l_2}{k_2} (X_A - X_p)^{l_1-k_1} (X_B - X_p)^{l_2-k_2}. \quad (\text{A4})$$

(2) The kinetic energy integral is calculated to be [8]

$$\begin{aligned} \langle g_1 | (-1/2) \nabla^2 | g_2 \rangle &= \alpha_2 [2(l_2 + m_2 + n_2) + 3] s(l_1, m_1, n_1; l_2, m_2, n_2) \\ &\quad - 2\alpha_2^2 [s(l_1, m_1, n_1; l_2 + 2, m_2, n_2) + s(l_1, m_1, n_1; l_2, m_2 + 2, n_2) \\ &\quad + s(l_1, m_1, n_1; l_2, m_2, n_2 + 2)] \\ &\quad - 2^{-1} [l_2(l_2 - 1) s(l_1, m_1, n_1; l_2 - 2, m_2, n_2) \\ &\quad + m_2(m_2 - 1) s(l_1, m_1, n_1; l_2, m_2 - 2, n_2) \\ &\quad + n_2(n_2 - 1) s(l_1, m_1, n_1; l_2, m_2, n_2 - 2)] \end{aligned} \quad (\text{A5})$$

where s is the overlap integral over the two gaussians represented by the quantum numbers involved.

(3) The nuclear attraction integral has been calculated as [8]

$$\begin{aligned} \left\langle g_1 \left| \frac{1}{|\mathbf{r} - \mathbf{R}_C|} \right| g_2 \right\rangle &= \frac{2\pi}{\gamma} \exp(-\alpha_1 \alpha_2 R_{AB}^2 / \gamma) \sum_{I=0}^{l_1+l_2} \sum_{J=0}^{m_1+m_2} \sum_{K=0}^{n_1+n_2} G_{Ix} G_{Jy} G_{Kz} F_{I+J+K}(\gamma |R_p - R_C|^2) \end{aligned} \quad (\text{A6})$$

where

$$F_L(t) = \int_0^1 x^{2L} \exp(-tx^2) dx \quad (\text{A7})$$

and

$$\begin{aligned} G_{Ix} &= \sum_{i=0}^{(l_1+l_2)} \sum_{\substack{r=0 \\ (i-2r-u=l)}}^{[i/2]} \sum_{u=0}^{[(i-2r)/2]} (-1)^i f_i(l_1, l_2, X_A - X_p, X_B - X_p) \\ &\quad \frac{(-1)^u i! (X_p - X_C)^{i-2r-2u}}{r! u! (i-2r-2u)! (4\gamma)^{r+u}} \end{aligned} \quad (\text{A8})$$

etc.

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(4) The electron repulsion integral over gaussians g_1 on atom A, g_2 on atom B, g_3 on atom C and g_4 on atom D and with exponents $\alpha_1, \alpha_2, \alpha_3$ and α_4 respectively is obtained as [8]

$$(g_1 g_2 | g_3 g_4) = \frac{2\pi^2}{\gamma_1 + \gamma_2} \left(\frac{\pi}{\gamma_1 + \gamma_2} \right)^{1/2} \exp \left[-\frac{\alpha_1 \alpha_2 R_{AB}^2}{\gamma_1} - \frac{\alpha_3 \alpha_4 R_{CD}^2}{\gamma_2} \right] \sum_{I,J,K} C_{Ix} C_{Jy} C_{Kz} F_{I+J+K} \left(\frac{\gamma_1 + \gamma_2}{\gamma_1 \gamma_2} R_{PQ}^2 \right) \quad (A9)$$

where

$$\gamma_1 = \alpha_1 + \alpha_2,$$

$$\gamma_2 = \alpha_3 + \alpha_4$$

and

$$\mathbf{R}_Q = (\alpha_3 \mathbf{R}_C + \alpha_4 \mathbf{R}_D) / \gamma_2.$$

The term C_I is given by

$$C_I = \sum_{\substack{(l_1+l_2) \\ L}} \sum_{\substack{(l_3+l_4) \\ M}} \sum_u H_L(l_1, l_2, X_A - X_P, X_B - X_P, \gamma_1) (-1)^M H_M(l_3, l_4, X_C - X_Q, X_D - X_Q, \gamma_2) \times \frac{(L+M)! (-1)^u (X_Q - X_P)^{(L+M-2u)}}{u! (L+M-2u)! ((\gamma_1 + \gamma_2) / 4 \gamma_1 \gamma_2)^{L+M-u}} \quad (A10)$$

where

$$H_L(l_1, l_2, a, b, \gamma) = \sum_{\substack{i=0 \\ (i-2r=L)}}^{(l_1+l_2)} \sum_{r=0}^{[i/2]} \frac{i! f_i(l_1, l_2, a, b, \gamma)}{r! (i-2r)! (4\gamma)^{i-r}} \quad (A11)$$

Integrals for atomic computations (given in § 3) are calculated from these expressions.

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