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Electronic Structure of Large Molecular Systems

E. CLEMENTI[1] AND D. R. DAVIS

International Business Machine Corporation,
San Jose Research Laboratory, California

ABSTRACT

Computations of the electronic structure for molecules with more than 4 to 5 atoms have been traditionally based on semi-empirical techniques. In this paper, a general computer program is described for computations of Self-Consistent Field-Molecular Orbital wave functions for molecules of any geometry and with a large number of nuclei and electrons. The molecular orbitals are linear expansions of symmetry-adapted functions; the latter are linear combinations of so-called "contracted Gaussians." The "contracted Gaussian set" is a linear expansion of standard gaussian functions, with expansion coefficients obtained from atomic computation with Gaussian set. The use of "contracted Gaussians" decreases drastically the number of matrix elements over symmetry orbitals, and makes the size of the "contracted Gaussian set" comparable with the size of a Slater-type (exponential) basis set. Special provisions are included in the program for the elimination or approximation, or both, of integrals smaller than a preassigned threshold. With these innovations over traditional computations with standard Gaussian function, it is quite feasible to compute large molecular systems.

The computer program, written as a preliminary version for the IBM 7094 computer (and now in process of conversion for the IBM System 360), can handle a maximum of 800 Gaussian functions distributed on 50 centers. Gaussian functions are restricted to *s*, *p*, *d*, and *f* type. In order to gain computer speed, *s* and *p* functions are computed with special formulas given in the Appendix.

Average computational time for 4 center integrals over *s* Gaussian (uncontracted) functions is 0.6 milliseconds. This time increases for *p* type approximately to 2.6 milliseconds. For many-center integrals involving *d* and *f* functions, the computing time is rather large, about 25 and 50 milliseconds, respectively. The computational time

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[1] Presently Visiting Professorial Lecturer, Department of Chemistry, University of Chicago (address: Department of Physics, LMSS).

here quoted is somewhat higher than the time needed in standard computations, since no integral, however small, has been neglected or approximated in the time quoted above.

The program has been used for problems involving no more than 44×10^6 million twoelectron integrals. Larger computations can be done with our present program; however, one should consider the use of computers possibly with faster C.P.U. and certainly with larger core memory than the IBM 7094-Mod. I.

From our preliminary computations, and taking into account both the structure and limits of our present version of the program as well as newly announced high-speed computer specifications, we feel confident in stating that within the next 2 to 4 years "a priori" computations for molecules with about 100–150 electrons and 5–20 atoms will be considered "routine" effort in theoretical chemistry.

I. INTRODUCTION

Attempts to construct theoretically the electronic structure of molecular systems are nearly as old as the Schrödinger equation. Since the beginning of quantum chemistry, two approaches have predominated in the field, namely, the valence bond theory [1] and the molecular orbital theory [2]. The search for new approximations to the Schrödinger equation continues. Presently the use of higher-order perturbation is being actively reconsidered, for example, at the University of Wisconsin [3] and Uppsala [4]. Well-known many-body formalisms like those of Brueckner [5] and Bethe-Goldstone [6] are readapted and quantitatively tested for atomic systems (see, i.e., Kelly [7], Nesbet [8], and Sinanǒglu [9]).

Parallel to this search for new techniques, at present mainly concerned with the electronic correlation energy of light atoms, there has been serious effort in the numerical analysis and large-scale programming, necessary to quantitatively verify the accuracy of theoretical schemes. Since the elegant review by Roothaan [10] of the molecular orbital self-consistent field technique, it was realized that a "bottleneck" of quantum chemistry is the numerical intricacy of the problem, in particular of many-center integrals [11].

With the advent of computers, a rapid growth was experienced and a first set of numerical successes was obtained [12]. Due to the numerical complexity of the problem, however, the field was polarized in two directions; one was aimed at exact (*ab initio*) computations and was by necessity restricted to systems with very few electrons; the other was aimed directly at large molecular systems and was by necessity restricted to the use of semi-empirical or frankly totally empirical models. By 1959 this division was so marked as to be formally christened by Coulson [13].

It is the aim of this paper to give evidence that such a distinction should disappear in the near future, at least for molecules with about one or two dozens of atoms. Admittedly, this is a very modest size if one considers macromolecules; however, the majority of molecules are built up from molecular fragments approximately of the size we can now compute. In the following we shall report on the numerical techniques underlying a new molecular program written for the IBM 7094. The recent announcement of computers superior both in core size and logic speed to the IBM 7094 gives additional support to our optimism on the feasibility of rigorous computation of the electronic structure of large molecules. The method which we have adopted is the molecular orbital, self-consistent field method [14] with Gaussian-type functions [15].

II. General Outline of the Problem

As an atomic orbital (AO) represents the density of an electron in an atom, so do the molecular orbitals (MO) in molecules. As the Hartree–Fock technique [16] constructs optimal AO's, so the matrix Hartree–Fock [14] techniques construct optimal MO's for a given basis set. The MO's are obtained as linear combination of functions centered at the atomic nucleus of molecules. These functions, however, are of Gaussian form [13].

The Hamiltonian for the problem is

$$\mathscr{H} = \sum_{i,a} \left(-\frac{1}{2} \nabla_i^2 - \frac{Z_a}{r_i} \right) + \sum_{i,j} \frac{1}{r_{ij}} - \sum_{a,b} \frac{Z_a Z_b}{R_{ab}} . \tag{2.1}$$

The first term is the kinetic operator for the ith electron, the second term is the potential between the ith electron and the nuclear charge Z on center a, the third term is the electron-electron potential between the ith and jth electrons, and the last term is the nuclear potential with Z_a and Z_b the nuclear charges (assumed point charges) and R_{ab} the internuclear distance.

The first and second term are subsequantly referred to as the one-electron hamiltonian, the second is referred to as the two-electron hamiltonian, and the last term is clearly a constant for a given geometrical configuration. Atomic units are used in this paper.

The wave function Ψ for the problem is the standard antisymmetrized product (Pauli principle) of spin-orbitals. Since the hamiltonian (2.1) is spin-independent, the spin-orbitals are a simple product of a spin function and an orbital (spatial) function.

The orbitals are obtained by solving the Hartree–Fock equations (self-consistent field, SCF, equations), which are approximate solutions to the hamiltonian (2.1). When the wave function is obtained, the energy is given by the standard relation

$$E = \frac{\langle \Psi | \mathscr{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{2.2}$$

For a given molecular system, a given geometrical configuration and a given electronic configuration and state, each molecular orbital, Φ, is characterized by an index λ, which specifies the irreducible representation of the point group for the molecule in consideration, and by a second index i which identifies the ith MO of the λth irreducible representation. Since we have selected to work with real functions, an n-degenerate representation is described by a n dimensional set of real orbitals.

The MO's are expanded in terms of symmetry adapted functions. These, in general, are the smallest linear combination of atomic functions, which transform as an irreducible representation of the molecular point group. Therefore, if we designate by φ the symmetry-adapted functions and by χ the Gaussian functions, a symmetry function and a molecular orbital are expanded as

$$\varphi_{\lambda q} = \sum_r d_{\lambda q r} \chi_r \tag{2.3}$$

$$\varphi_{\lambda i} = \sum_q c_{\lambda i q} \varphi_{\lambda q}. \tag{2.4}$$

The $d_{\lambda qr}$ are coefficients selected as to insure that the χ_r transform properly. The $c_{\lambda iq}$ are the expansion coefficients for the molecular orbital $\Phi_{\lambda i}$ and are variationally obtained in the self-consistent field technique. The expansion coefficients $c_{\lambda iq}$ give rise to a vector $\mathbf{c}_{\lambda i}$.

The molecular orbitals, Φ's, are orthogonal by definition when they belong to different irreducible representation. In addition, the set of molecular orbitals of a given irreducible representation are constrained to be orthogonal among themselves. The symmetry-adapted functions, φ, are by construction orthogonal to each other when they belong to different irreducible representations.

In our program, there is a hierarchy of functions. The lowest type are standard Gaussian functions, χ, centered in general, *but not necessarily*, on one of the atomic nuclei. The second are linear combinations of Gaussian, on one center the "contracted Gaussian set," where the linear expansion coefficients are taken from educated guesses, based on the atomic orbital expansion coefficients of atomic computations (see Section IV). The choice of uncontracted (single) Gaussian or contracted (linear combination) Gaussian set is an input option. The third set of functions, are the symmetry functions; these are expanded either in terms of uncontracted Gaussian functions or in terms of the contracted Gaussian set, or in terms of both, free and contracted. Finally, the last set of functions are the molecular orbitals, clearly variational combinations of symmetry-adapted functions.

It should be noted that symmetry functions for a given molecule can be constructed in a variety of ways. One can use complex or real symmetry functions; we choose the latter because of ease in programming. Since the symmetry orbital expansion coefficients $d_{\lambda q r}$ are input parameters, we have the freedom to use the smallest possible set of Gaussian functions in constructing the $\varphi_{\lambda q}$ or larger sets. For example, if one is interested in computing molecular interaction, with the interacting molecules at such distances that only dipole-dipole type of interactions is important, then one might select the option to use the molecular orbitals of previously computed separated molecules as symmetry-adapted functions for the system of interacting molecules.

In the following, the term "Gaussian set" will be used to indicate both the contracted and uncontracted Gaussian functions, unless otherwise specified; and the term "symmetry functions" will be used both for minimal symmetry combinations or more complex ones, unless otherwise specified.

With this in mind, let us indicate with $S_{\lambda pq}$ the orthogonality matrix element

$$S_{\lambda pq} = \langle \varphi_{\lambda p} \mid \varphi_{\lambda q} \rangle \equiv \langle \varphi_{\lambda q} \mid \varphi_{\lambda p} \rangle \tag{2.5}$$

which can be considered the element of a real symmetryc matrix $\mathbf{S}_\lambda$, the orthogonality matrix. Then the orthogonality constraints for the molecular orbitals of a given irreducible representation are

$$\mathbf{c}_{\lambda i}^{+} \mathbf{S}_\lambda \mathbf{c}_{\lambda j} = \delta_{ij} \tag{2.6}$$

The vectors $\mathbf{c}$, subjected to the constraint (2.6), define the following density matrices

$$D_{i\lambda} = N_{i\lambda} c_{i\lambda} c_{i\lambda}^{+} \tag{2.7a}$$

$$D_{c\lambda} = \sum_i{}' D_{i\lambda} \tag{2.7b}$$

$$D_{o\lambda} = \sum_i{}'' D_{i\lambda} \tag{2.7c}$$

$$D_{T\lambda} = D_{c\lambda} + D_{o\lambda}, \tag{2.7d}$$

where $N_{i\lambda}$ is the occupation numbers, and the subscripts c, o, and T refer to closed, open, and total, respectively. $D_{i\lambda}$ is the density matrix for the ith molecular orbital of the λth irreducible representation, and $D_{c\lambda}$ and $D_{o\lambda}$ are the closed and open shell density matrices. The Σ' and Σ'' summation are over closed or open orbitals, respectively.

The expansion coefficients $\mathbf{c}$, are obtained by solving the SCF equations

$$F_c\mathbf{c} = \varepsilon\,\mathbf{Sc} \tag{2.8}$$

$$F_o c = \varepsilon\,\mathbf{Sc} \tag{2.9}$$

where the, ε's are the eigenvalues (orbital energies), $\mathbf{c}$'s are the eigenvectors (expansion coefficient), and F_o and F_c are the Hartree-Fock hamiltonians, defined respectively as

$$F_c = \mathscr{h} + \mathscr{P}D_T + [N_{o\lambda}/(N_{c\lambda} - N_{o\lambda})]\sum_i{}''[S_\lambda c_{i\lambda}(\mathscr{Q}D_o c_{i\lambda})^\dagger + D_o\mathbf{c}_{i\lambda}(S_\lambda c_{i\lambda})^+] \tag{2.10}$$

$$\begin{aligned} F_o = \mathscr{h} + \mathscr{P}D_T - \mathscr{Q}D_o + [N_{c\lambda}/(N_{c\lambda} - N_{o\lambda})]\,\Sigma'[\mathbf{S}_\lambda c_{i\lambda}(D_o c_{i\lambda})^\dagger \\ + D_o c_{i\lambda}(S_\lambda c_{i\lambda})^+], \end{aligned} \tag{2.11}$$

where $\mathscr{h}$ is the one electron part of the total hamiltonian (2.1); and $\mathscr{P}$ and $\mathscr{Q}$ are the closed and open shell supermatrices, respectively, which represent the electron-electron interaction of closed-closed and closed-open, and open-open shells. Details on the constructions of these supermatrices can be obtained, for example, from Roothaan and Bagus' work [14].

It has been pointed out [14] that the eigenvalue problem (2.8) and (2.9) can be solved directly without transforming it into the problem

$$F_c'c = \varepsilon\,\mathbf{c} \tag{2.12}$$

$$F_o'c = \varepsilon\,c \tag{2.13}$$

where the overlap matrix S of (2.10) and (2.11) are transformed into unit matrices. This is certainly the case for the lowest configuration of atomic systems. There a "somewhat decent approximation to the vector $\mathbf{c}$," given as input, is sufficient in order to successfully use "single-vector techniques" like the one proposed by Sack [14]. However, in molecular cases, especially with Gaussian sets, there are new difficulties not present in atomic systems. For example, it is clear that in a hydrocarbon there is a large number of nearly degenerate orbitals. This is simply the result of the fact that the splitting of the orbital levels of equivalent atoms from an exact degenerate set (no interaction) to a nearly degenerate set (molecular interaction) is in general small. Preliminary numerical experimentation on H_6

indicates that the "input trial vectors should be as good as to have two to three significant figure accuracy, compared to the final vectors." We have therefore used Jacobi diagonalization followed by Sack single-vector diagonalization. (This approach was used on previous atomic programs from the University of Chicago.) The test on whether to continue with the Jacobi process or to initiate the single-vector diagonalization process is based on the two-electron energy convergency. The total energy is given by the relation

$$E = \mathscr{h}^{+}D_T + \tfrac{1}{2}D_T{}^{+}\mathscr{P}D_T - \tfrac{1}{2}D_o{}^{+}\mathscr{Q}D_o + E_N = E_1 + E_2 + E_N \tag{2.14}$$

where the first term is the one-electron energy, the second and third are the two-electron energies, and E_N is the nuclear-nuclear repulsion energy. Let us analyze the convergency of E_1, E_2, and E for the specific case of the Ne atom (Table I).

TABLE I

CONVERGENCE OF THE ONE-ELECTRON, TWO-ELECTRON, AND TOTAL ENERGY IN THE NE ATOM

E_1	E_2	E	Cycle No.
−148.77154	30.115002	−118.65654	2
−193.71428	67.981011	−125.73327	3
−171.84472	44.507845	−127.33687	4
−186.95863	58.734003	−128.22462	5
−179.91135	51.464291	−128.45506	6
−183.81116	55.289364	−128.52179	7
−181.93076	53.392240	−128.53830	8
−182.41809	53.874465	−128.54362	10
−182.53927	53.995312	−128.54396	12
−182.56965	54.025668	−128.54398	14
−182.57924	54.035258	−128.54398	18
−182.57981	54.035821	−128.54398	22
−182.57988	54.035900	−128.54398	26
−182.57987	54.035883	−128.54398	30
−182.57986	54.035883	−128.54398	34

The last column gives the number of times we have solved the SCF equations (both iterative and extrapolation techniques are used). From Table I, one can see that, in the specific case in question, the total energy E has converged in 12 cycles, the one-electron energy has converged in 22 cycles, and the two-electron energy has converged in 30 cycles. Analysis on the density matrix indicates that seven-figure convergency on E_2 guarantees, *in general*, 6–7 figure convergency on the density matrix.

When this level of convergency is obtained, one can optimally continue with a single-vector diagonalization routine. This is done mostly to ensure convergency on the virtual (unoccupied) orbitals, since the E_1 or E_2 do not guarantee any convergency on these. There is an additional program option which allows the program user to specify a given number of additional Jacobi passes after convergency on E_2. This option has been inserted in the program after having experienced that the "trial" vector supplied by Jacobi diagonalization, even after full convergency on E_2, might sometimes not be a "decent" guess of the virtual orbitals for the Sack single-vector diagonalization.

III. General Formulas for the Matrix Elements

In this section we give the analytical solutions for the matrix elements needed in the SCF computation. No derivations will be given here since these are partially available in several publications. The reader is referred to the works of Boys [15], Shavitt [17], Harrison [18], Krauss [21], Harris [20], and Wright [19] for additional information. The following analytical solutions were derived by Huzinaga [22].

The uncontracted Gaussian function, χ, on a center A is defined as

$$\begin{aligned}\chi(A, \alpha, l, m, n) &= (A, \alpha, l, m, n)\\ &= (x - A_x)^l (y - A_y)^m (z - A_z)^n \exp(-\alpha r_A^2) \qquad (3.1)\\ &= x_A^l y_A^m z_A^n \exp(-\alpha r_A^2)\,.\end{aligned}$$

In defining the integrals over Gaussian functions, the following auxiliary functions are used:

$$f_j(l, m, a, b) = \sum_{i=\max(o,j-m)}^{i=\min(j,l)} \binom{l}{i} \binom{m}{j-i} a^{l-i} b^{n+i-j} \qquad (3.2)$$

$$F_\nu(t) = \int_0^1 u^{2\nu} \exp(-tu^2)du \quad (t > 0, \nu = 0, 1, 2 \ldots). \qquad (3.3)$$

This is a form of the Incomplete Gamma Function and is evaluated in the program, depending on the range of the argument t, by asymptotic expansions, recursion formulas, or tabular interpolations.

The normalization factor for the Gaussian function (3.1) is:

$$N\alpha = \left[\left(\frac{\pi}{2a}\right)^{3/2} \frac{(2l-1)!!\,(2m-1)!!\,(2n-1)!!}{2^{2(l+m+n)}\alpha^{(l+m+n)}}\right]^{-1/2}. \tag{3.4}$$

In the formulas which follow, all coordinate systems on various centers are parallel and right-handed.

The Overlap Integral

$$\begin{aligned}&\langle A, \alpha_1, l_1, m_1, n_1 \mid B, d_2, l_2, m_2, n_2\rangle \\ &= N_1N_2\left(\frac{\pi}{\alpha_1+\alpha_2}\right)^{3/2} \exp\left(-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}\,\overline{AB}^2\right) \Sigma_x\Sigma_y\Sigma_z\,,\end{aligned} \tag{3.5}$$

where

$$\Sigma_x = \sum_{i=0}^{[\frac{1}{2}(l_1+l_2)]} f_{2i}(l_1, l_2, \overline{PA}_x, \overline{PB}_x)\cdot\frac{(2i-1)!!}{{}_2i(\alpha_1+\alpha_2)^i}$$

and Σ_y, Σ_z are similarly defined in terms of the corresponding exponents and components in the y- and z-directions.

The convention $\overline{R_1R_2} = \vec{R} - \vec{R}_2$ applies throughout, and the point P appearing in (3.5) and the following formulas is the center of the new Gaussian function, the product of the Gaussians on A and B:

$$P_i = \frac{\alpha_1A_i + \alpha_2B_i}{\alpha_1+\alpha_2}\quad i = x, y, z\,. \tag{3.6}$$

The Kinetic Integral

$$\begin{aligned}&\langle A, \alpha_1, l_1, m_1, n_1 \mid -\tfrac{1}{2}\nabla^2 \mid B, \alpha_2, l_2, m_2, n_2\rangle \\ &= N_1N_2[\alpha_2\{2(l_2+m_2+n_2)+3\}\langle A, \alpha_1, l_1, m_1, n_1 \mid B, \alpha_2, l_2, m_2n_2\rangle \\ &\quad - 2\alpha_2{}^2\{\langle A, \alpha_1, l_1, m_1, n_1 \mid B, \alpha_2, l_2+2, m_2, n_2\rangle \\ &\qquad + \langle A, \alpha_1, l_1, m_1, n_1 \mid B, \alpha_2, l_2, m_2+2, n_2\rangle \\ &\qquad + \langle A, \alpha_1, l_1, m_1, n_1 \mid B, \alpha_2, l_2, m_2, n_2+2\rangle\} \\ &\quad - \tfrac{1}{2}\{l_2(l_2-1)\langle A, \alpha_1, l_1, m_1, n_1 \mid B, \alpha_2, l_2-2, m_2, n_2\rangle \\ &\qquad + m_2(m_2-1)\langle A, \alpha_1, l_1, m_1, n_1 \mid B, \alpha_2, l_2, m_2-2, n_2\rangle \\ &\qquad + n_2(n_2-1)\langle A, \alpha_1, l_1, m_1, n_1 \mid B, \alpha_2, l_2, m_2, n_2-2\rangle\}]\,.\end{aligned} \tag{3.7}$$

The Nuclear Attraction Integral

$$
\begin{aligned}
&\sum_c \left\langle A, \alpha_1, l_1, m_1, n_1 \left| \frac{1}{r_c} \right| B, \alpha_2, l_2, m_2, n_2 \right\rangle \\
&= N_1 N_2 \left(\frac{2\pi}{\alpha_1 + \alpha_2} \right) \exp\left(- \frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} \overline{AB}^2 \right) \\
&\quad \times \sum_{i,r,u} A_{i,r,u}(l_1, l_2, A_x, B_x, C_x, \gamma) \\
&\quad \times \sum_{j,s,v} A_{j,s,v}(m_1, m_2, A_y, B_y, C_y, \gamma) \\
&\quad \times \sum_{k,t,w} A_{k,t,w}(n_1, n_2, A_x, B_x, C_x, \gamma)\, F_\nu(\gamma \cdot \overline{CP}^2),
\end{aligned}
\tag{3.8}
$$

where

$$\gamma = \alpha_1 + \alpha_2 ; \qquad \varepsilon = \frac{1}{4\gamma}$$

$$\nu = i + j + k - 2(r + s + t) - u - v - w$$

$$A_{i,u,r} = (-)^i f_i(l_1, l_2, \overline{PA}_x, \overline{PB}_x)\, \frac{(-)^u i!(CP_x)^{i-2(r+u)} \varepsilon^{r+u}}{r!u!(i - 2r - 2u)!}.$$

$A_{j,s,v}$, $A_{k,t,w}$ are similarly defined in terms of the y- and z-components. The summations in (3.8) are over the following ranges:

$$
\begin{array}{lll}
i = 0 \to l_1 + l_2 & j = 0 \to m_1 + m_2 & k = 0 \to n_1 + n_2 \\
r = 0 \to [i/2] & s = 0 \to [j/2] & t = 0 \to [k/2] \\
u = 0 \to [i - 2r)/2] & v = 0 \to [(j - 2s)/2] & w = 0 \to [(k - 2t)/2].
\end{array}
$$

Here, as throughout this paper, the notation $[k]$ is used to denote the largest integer $\leq k$.

The Electron Repulsion Integral

$$
\begin{aligned}
&\left\langle (A, \alpha_1, l_1, m_1, n_1), (B, \alpha_2, l_2, m_2, n_2) \left| \frac{1}{r_{12}} \right| (C, \alpha_3, l_3, m_3, n_3), (D, \alpha_4, l_4, m_4, n_4) \right\rangle \\
&= N_1 N_2 N_3 N_4 \frac{2\pi^2}{\gamma_1 \gamma_2} \left(\frac{\pi}{\gamma_1 + \gamma_2} \right)^{1/2} \exp\left(- \frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} \overline{AB}^2 - \frac{\alpha_3 \alpha_4}{\alpha_3 + \alpha_4} CD^2 \right) \\
&\quad \times \sum_{i_1, i_2, r_1, r_2, u} B_{i_1, i_2, r_1, r_2, u} \sum_{j_1, j_2, s_1, s_2, v} B_{j_1, j_2, s_1, s_2, v} \\
&\quad \times \sum_{k_1, k_2, t_1, t_2, w} B_{k_1, k_2, t_1, t_2, w} F_\nu\left(\frac{\overline{PQ}^2}{4\delta} \right)
\end{aligned}
$$

where:

$$\gamma_1 = \alpha_1 + \alpha_2\,; \qquad \gamma_2 = \alpha_3 + \alpha_4\,; \qquad \delta = \frac{1}{4}\left(\frac{1}{\gamma_1} + \frac{1}{\gamma_2}\right)$$

$$Qi = \frac{\alpha_3 C_i + \alpha_4 D_i}{\alpha_3 + \alpha_4} \qquad i = x,\ y,\ z$$

$$\nu = i_1 + i_2 + j_i + j_2 + k_1 + k_2 - 2(r_1 + r_2 + s_1 + s_2 + t_1 + t_2) - u - v - w$$

$$\begin{aligned} B_{i_1,i_2,r_1,r_2,u} &= B_{i_1,i_2,r_1,r_2,u}(l_1\,, l_2\,, A_x\,, B_x\,, P_x\,, \gamma_1 \mid l_3\,, l_4\,, C_x\,, D_x\,, Q_x\,, \gamma_2) \\ &= (-)^{i_2} f_{i_1}(l_1\,, l_2\,, \overline{PA}_x\,, \overline{PB}_x) f_{i_2}(l_3\,, l_4\,, \overline{QC}_x\,, \overline{QD}_x) \\ &\quad \times \frac{i_1!\,i_2! \qquad \gamma_1^{\,r_1}\gamma_2^{\,r_2} \qquad (2\delta)^{2(r_1+_2r)}}{\gamma_1^{\,i_1}\gamma_2^{\,i_2}(4\delta)^{i_1+i_2} r_1!\,r_2!\,(i_1 - 2r_1)!\,(i_2 - 2r_2)!} \\ &\quad \times \frac{[i_1 + i_2 - 2r_1 - 2r_2]!\,(-)^4\,\overline{PQ}_x^{\,i_1+i_2-2(r_1+r_2+u)}\delta^u}{u!\,[i_1 + i_2 - 2(r_1 + r_2 + u)]!}\,. \end{aligned}$$

$B_{j_1,j_2,s_1,s_2,t}$ and $B_{k_1,k_2,t_1,t_2,w}$ are similarly defined in terms of the y- and z-components, respectively.

The summations in 3.10 are over the following ranges:

$$\left.\begin{array}{lll} i_1 & = 0 & l_1 + l_2 \\ i_2 & = 0 & l_3 + l_4 \\ r_1 & = 0 & [i_1/2] \\ r_2 & = 0 & [i_2/2] \\ u & = 0 & \left[\dfrac{i_1 + i_2}{2} - r_1 - r_2\right] \end{array}\right\} \text{and similarly for the indices of the summations over the } y\text{- and } z\text{-components.}$$

IV. CONTRACTION

In an SCF computation, the number of two-electron integrals (one center or many centers) is proportional to the fourth power of the numbers of atomic functions. To adequately describe an atom of the first period with s and p electrons, one needs 9–12 s-type Gaussian functions and 5–6 p-type Gaussian functions. Therefore such an atom, when in a molecule, will be described by about 30 Gaussian functions (10 of s-type, 5 of p_x-type, 5 of p_y-type, 5 of p_z-type, plus some d- and f-type). The corresponding number of Slater-type functions is about 20 (4–5 of s-type, 3 of p_x-type, 3 of p_y-type, 3 of p_z-type, plus some d- and f-type).

[redacted] functions. These integrals are then transformed into integrals over symmetry-adapted functions; no matter what transformation technique is used, the computational time required for the transformation is proportional to the size of the integral list. Availability of large core memory certainly ameliorates the situation but does not eliminate the complexity of the transformation. Alternatively, one could compute directly the integrals over the symmetry-adapted functions, therefore eliminating the need for the transformations. However, in this case one will either compute a redundant number of integrals over the Gaussian function, or carry a very long "integral request" list.

These difficulties can be overcome by replacing the individual Gaussians with some appropriate linear combination of Gaussian such as to reduce and therefore "contract" the number of stored integrals. This has been suggested for large molecular computations some time ago by one of us [23]. Now we have implemented this suggestion, and from our preliminary results it appears that one can finally compute rather accurately large molecular systems.

Two possible schemes are available for contracting the original basis set. On one hand one could use as the contracted set the atomic orbitals of the separated atom. In this case one would start with as many contracted functions as the orbitals of the component atoms in their ground state. Computationally, one would construct the integrals over the atomic orbitals, making use of the atomic expansion coefficients. The drawback of this scheme is that the atomic orbitals are in general poor representations for molecular functions, except for the inner shells.

A second possibility is to analyze the Gaussian functions of the atomic orbitals and make appropriate linear combinations of the atomic functions. For an illustration of this technique, let us consider the Ne(^{1}S) atom. We shall compare the result of a standard, but optimal, basis set obtained by Huzinaga [22] with the results obtained with a "contracted set." Huzinaga's set consists of 11 Gaussian functions of *s*-type, and 7 Gaussian functions of *p*-type. We shall designate the *s*-function as $\chi_1 \cdots$ to χ_{11}, and the 7 *p*-functions as $\chi_{12} \cdots$ to χ_{18}. The orbital exponents and expansion coefficients of Huzinaga's computation are given in Table II.

The total energy is -128.5447 a.u. By simply inspecting the orbital exponents and the expansion coefficients, it is clear that (a) a number of Gaussian are needed only in order to represent the 1s cusp (the very high orbital exponents), and (b) that several Gaussians belong only to the 2s orbital, and the small coefficient in the 1s is present for orthogonality requirements. Therefore, the set of 18 Gaussians can be contracted to a smaller set, a "contracted" set.

TABLE II

NE ATOM: UNCONTRACTED GAUSSIAN SET, ORBITAL ENERGIES, AND EXPANSION COEFFICIENTS (TOTAL ENERGY, − 128.5447 a.u.)

	Orbital exponent	1*s* Orbital	2*s* Orbital		Orbital exponent	2*p* Orbital
χ_1	47870.2	.00021	−.00005	χ_{12}	129.802	.00426
χ_2	7385.83	.00162	−.00038	χ_{13}	30.4192	.03061
χ_3	1660.18	.00863	−.00206	χ_{14}	9.62151	.11927
χ_4	460.539	.03617	−.00856	χ_{15}	3.54645	.26912
χ_5	146.038	.12134	−.03097	χ_{16}	1.41435	.35733
χ_6	50.4137	.30702	−.08388	χ_{17}	.578893	.33183
χ_7	18.7165	.43944	−.17194	χ_{18}	.216044	.16084
χ_8	7.39702	.22518	−.10947		ε	−.84999
χ_9	2.6768	.01554	.37643			
χ_{10}	.775195	−.00230	.57102			
χ_{11}	.29176	.00095	.20449			
	ε	−32.772	−1.9300			

For example, we could use the following set, and re-perform an SCF computation with it:

$$\begin{aligned}
\chi_1' &= .00021\,\chi_1 + .00162\,\chi_2\\
\chi_2' &= .00863\,\chi_3 + .03617\,\chi_4\\
\chi_3' &= .12194\,\chi_5 + .30702\,\chi_6\\
\chi_4' &= .43944\,\chi_7 + .22518\,\chi_8\\
\chi_5' &= \chi_9\\
\chi_6' &= .57102\,\chi_{10} + .20449\,\chi_{11}\\
\chi_7' &= .00426\,\chi_{12} + .03061\,\chi_{13}\\
\chi_8' &= .11927\,\chi_{14} + .26912\,\chi_{15}\\
\chi_9' &= .35733\,\chi_{16} + .33183\,\chi_{17}\\
\chi_{10}' &= \chi_{18}.
\end{aligned}$$

Table III shows the results for orbital energies, total energies, and the new expansion coefficients.

TABLE III

CONTRACTED SET FOR NE ATOM

	$1s$ Orbital	$2s$ Orbital		$2p$ Orbital
χ_1'	.001747	−.000416	χ_7'	.033118
χ_2'	.043015	−.010125	χ_8	.366407
χ_3'	.41259	−.107915	χ_9	.651301
χ_4'	.647292	−.267860	χ_{10}	.160667
χ_5'	.0145941	.363564	ε	−.85091
χ_6'	−.000715	.757529		
ε	−32.7711	−1.93016	$E = -128.5440$	

The total energy for the contracted set, χ', is − 128.5440. Let us contract even more and use the following contracted set for a new SCF computation:

$$\begin{aligned}
\chi_1'' &= .00021\,\chi_1 + .00162\,\chi_2 + .00863\,\chi_3 \\
\chi_2'' &= .03617\,\chi_4 + .12194\,\chi_5 + .307012\,\chi_6 \\
\chi_3'' &= .43944\,\chi_7 + .22518\,\chi_8 \\
\chi_4'' &= .37643\,\chi_9 + .57102\,\chi_{10} + .20443\,\chi_{11} \\
\chi_5'' &= .00426\,\chi_{12} + .03061\,\chi_{13} + .11927\,\chi_{14} \\
\chi_6'' &= .26912\,\chi_{15} + .35733\,\chi_{16} \\
\chi_7'' &= .16084\,\chi_{17} + .33183\,\chi_{18}.
\end{aligned}$$

The recomputed orbital energies are − 32.76031 for 1s, − 1.92977 for 2s, and − .848104 for $2p$; and the total energy is − 128.5412 a.u.

Table IV summarizes the above analysis and gives, the total energies, the orbital energies, the number of two-electron integrals for each type of set, and the equivalent number of two-electron integrals (the $2p$ orbitals were considered to be subdivided in $2p_x$, $2p_y$, $2p_z$, as they are in most molecules).

In Table IV, we have reported in the last column the number of elements in the $\mathscr{P}$ matrix. It is noted that the number of integrals is much larger, since (a) we compute all the distinct and possible integrals which can be derived from the basis set, (b) the $\mathscr{P}$ supermatrix contains both coulomb and exchange integrals.

A final example of the usefulness of the contracted set is reported for the N_2

TABLE IV

COMPARISON OF CONTRACTED AND UNCONTRACTED SETS

Type	Total energy	$\varepsilon(1s)$	$\varepsilon(2s)$	$\varepsilon(2p)$	No. of s basis	No. of p basis	No. of $\mathscr{P}$ elements
χ set	−128.5447	−32.772	−1.9300	−.84999	11	7,7,7	11325
χ' set	−128.54398	−32.771	−1.9301	−.85091	6	4,4,4	861
χ'' set	−128.54114	−32.700	−1.9298	−.84810	4	3,3,3	406

molecule. Again we started with Huzinzga's N(^{3}P) atomic computation [24] with 11 s-type Gaussian and 7 p-type Gaussians. This set was contracted to 4 functions of s-type and 2 of p-type. The computed total energy is − 108.81163 a.u. This contracted set of 4 contracted s-type Gaussian and 2 contracted Gaussian of $2p$-type is equal in number to a double-zeta Slater-type set [23]. However, a Slater double-zeta-type set gives an energy of − 108.79508 a.u., or 0.01655 a.u. higher than the Gaussian contracted set.

Before concluding our remarks on the contraction, we wish to point out that one can optimize the contracted set by performing, for a given selected contracted set, a series of atomic computations whereby the contraction coefficients are optimized (instead of the orbital exponents as usual). This first requires an optimal uncontracted basis set and then new optimization on the contraction coefficients. Work is in progress for the programming of this problem.

From the above results on the Ne atom and N_2 molecule where direct comparison with Slater-type functions can be made, and from computations on H_2O, C_2H_6, and H_6, we have performed, we tentatively conclude that the basis set with more than 150–200 functions must necessarily resort to some "contraction" technique, otherwise the handling of integrals becomes a very expensive process in terms of computational time.

V. PROGRAM ORGANIZATION

In this section we shall briefly outline the organization of the program [25]. There are three logically distinct sections in the program.

The *first* is computation of the integrals either over contracted or uncontracted Gaussian function, or a mixture of both. For integrals involving s and *p* Gaussians, special time-saving function routines have been obtained (see Appendix). For integrals with a *d* or *f* function, the general formulas (see Section IV) are used. The computation is over all the possible combinations of Gaussian functions.

It is noted that we compute more integrals than needed for the SCF computations. This is done because we are in the process of including a superposition of configuration routines in our program. There are a variety of techniques which allow one to obtain the integrals in a faster way. As it was pointed out by one of us [23], many integrals are exceedingly small and could be safely neglected; others are small and could be approximated. Provision for such techniques are included in the program. However, we shall defer any additional discussion on this point until we know how safe these simplifications are. It is noted in this regard that, in a computation with 10–20 million nonzero integrals, most likely more than 20–30% of these could be neglected or approximated. But it will take some very careful analysis to ensure that the approximated computation will represent long-range effects as accurately as the full computation with no approximation.

The *second* part of the program is the construction of the supermatrices needed in SCF computations. This is a transformation from integrals over Gaussian functions to integrals over symmetry orbitals. This section of the program is logically straightforward, although time-consuming.

The *third* part of the program is the SCF proper. Some of the details of this program section have been discussed previously (Section II).

In the *coding process* are the superposition configuration and a number of routines dealing with expectation values other than the energy.

A maximum number of 75 orbitals is allowed in the present version (this restriction will be removed in the IBM-360 version of the processes). A maximum of 800 uncontracted functions, centered on 50 different positions (of arbitrary geometry), is allowed. The maximum number of simple Gaussian functions in a contracted function is eight. This number is more than sufficient, according to our still limited experience.

VI. CONCLUSIONS

Preliminary computations [26] on H_2O, N_2, C_2H_6 (eclipsed, staggered, 20° rotation, 40° rotation), H_6, and C_4NH_5 indicate that the program can be readily [illegible] of the SCF section of the program. Accordingly, the program is in the process of being rewritten for the IBM System 360.

For very large systems with several hundreds of Gaussian functions, one will have to resort to the use of approximation in the integrals, especially the small ones.

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APPENDIX

Special Formulas for the Matrix Elements of s- and p-Type.

In the formulas of this section, the subscripts i, j, k, and l define the axis of a p-type orbital function, and each is to be replaced with the value x or y or z as appropriate.

The Overlap Integral

$$S^{oo}(a, b) = \langle S_a \mid S_b \rangle = N_1 N_2 \left(\frac{\pi}{\alpha_1 + \alpha_2} \right)^{3/2} \exp \left(- \frac{a \quad b}{a + b} \overline{AB}^2 \right)$$

$$S^{io}(a, b) = \langle P_{ia} \mid S_b \rangle = \frac{-b}{a + b} (A_i - B_i) S^{oo}(a, b)$$

$$S^{oj}(a, b) = \langle S_a \mid P_{jb} \rangle = \frac{a}{a + b} (A_j - B_j) S^{oo}(a, b)$$

$$S^{ij}(a, b) = \langle P_{ia} \mid P_{jb} \rangle = \left\{ \frac{1}{2(a + b)} \delta_{ij} - \frac{ab}{(a + b)^2} (A_i - B_i)(A_j - B_j) \right\} S^{oo}(a, b).$$

Here, as throughout this section, δ_{ij} is the Kronecker delta.

The Kinetic Integral

We first define a set of functions:

$$K^{oo}(a, b) = \frac{3ab}{a + b} - \frac{2a^2b^2}{(a + b)^2} \overline{AB}^2$$

$$K^{io}(a, b) = -\frac{2ab^2}{(a+b)^2}(A_i - B_i)$$

$$K^{oj}(a, b) = \frac{2a^2b}{(a+b)^2}(A_j - B_j)$$

$$K^{ij}(a, b) = \frac{ab}{(a+b)^2}\delta_{ij}.$$

In terms of these K-functions and the S-functions given above, the kinetic integrals are defined as follows:

$$\begin{aligned}
T^{oo}(a, b) &= \langle S_a \mid -\tfrac{1}{2}\Delta \mid S_b\rangle = K^{oo}(a, b)S^{oo}(a, b)\\
T^{io}(a, b) &= \langle P_{ia} \mid -\tfrac{1}{2}\Delta \mid S_b\rangle = K^{io}(a, b)S^{oo}(a, b) + K^{oo}(a, b)S^{io}(a, b)\\
T^{oj}(a, b) &= \langle S_a \mid -\tfrac{1}{2}\Delta \mid P_{jb}\rangle = K^{oj}(a, b)S^{oo}(a, b) + K^{oo}(a, b)S^{oj}(a, b)\\
T^{ij}(a, b) &= \langle P_{ia} \mid -\tfrac{1}{2}\Delta \mid P_{jb}\rangle = K^{ij}(a, b)S^{oo}(a, b) + K^{io}(a, b)S^{oj}(a, b)\\
&\qquad + K^{oj}(a, b)S^{io}(a, b) + K^{oo}(a, b)S^{ij}(a, b).
\end{aligned}$$

The Nuclear Attraction Integral

Again we define a set of intermediate functions. These use the Incomplete Gamma Function defined in (3.4). In each case the argument, $t = (a + b)\,\overline{PC}^2$, is used where P is defined as in (3.7):

$$L^{oo}(c; a, b) = F_o(t)$$

$$L^{io}(c; a, b) = L^{oi}(c; a, b) = (C_i - P_i)F_i(t)$$

$$L^{ij}(c; a, b) = (P_i - C_i)(P_j - C_j)F_2(t) - \frac{1}{2(a+b)}\delta_{ij}F_1(t).$$

The nuclear attraction integrals may now be defined:

$$V^{oo}(a, b) = \left\langle S_a \left| \frac{1}{r_c} \right| S_b \right\rangle = \theta \sum_c S^{oo}(a, b)L^{oo}(c; a, b)$$

$$V^{io}(a, b) = \left\langle P_{ia} \left| \frac{1}{r_c} \right| S_b \right\rangle = \theta \sum_c \{S^{io}(a, b)L^{oo}(c; a, b) + S^{oo}(a, b)L^{io}(c; a, b)\}$$

$$V^{oj}(a, b) = \left\langle S_a \left| \frac{1}{r_c} \right| P_{jb} \right\rangle = \theta \sum_c \{S^{oj}(a, b)L^{oo}(c; a, b) + S^{oo}(a, b)L^{oj}(c; a, b)\}$$

$$\begin{aligned}
V^{ij}(a, b) = \left\langle P_{ia} \left| \frac{1}{r_c} \right| P_{jb} \right\rangle &= \theta \sum_c \{S^{ij}(a, b)L^{oo}(c; a, b) + S^{io}(a, b)L^{oj}(c; a, b)\\
&\qquad + S^{oj}(a, b)L^{io}(c; a, b) + S^{oo}(a, b)L^{ij}(c; a, b)\}
\end{aligned}$$

where

$$\theta = \frac{2}{\pi^{1/2}}(a+b)^{1/2}.$$

Note that every additive term of these formulas contains either explicitly or implicitly the term $S^{oo}(a, b)$. Thus all normalization factors are included by the definition of this term. This applies also to the formulas for the kinetic integrals.

The Electron Repulsion Integral

In this case also the special formulas are simplified by first defining a set of intermediate functions. In these formulas the centers P and Q are defined as in Section III. The argument of the Incomplete Gamma Function in these formulas is

$$t = \frac{(a+b)(c+d)}{(a+b+c+d)}\overline{PQ}^2 .$$

To abbreviate these formulas, the following conventions are used throughout:

$$S_1 = a+b; \quad S_2 = c+d; \quad S_4 = S_1 + S_2 = a+b+c+d.$$

The intermediate functions are defined as:

$$G^{oooo}(t) = F_o(t)$$

$$G^{iooo}(t) = G^{oioo}(t) = \frac{S_2}{S_4}(P_i - Q_i)F_1(t)$$

$$G^{ooio}(t) = G^{oooi}(t) = \frac{S_1}{S_4}(P_i - Q_i)F_1(t)$$

$$G^{ijoo}(t) = \frac{S_2}{S_4}\left\{\frac{S_2}{S_4}(P_i - Q_i)(P_j - Q_j)F_2(t) - \delta_{ij}\frac{1}{2S_1}F_1(t)\right\}$$

$$G^{ooij}(t) = \frac{S_1}{S_4}\left\{\frac{S_1}{S_4}(P_i - Q_i)(P_j - Q_j)F_2(t) - \delta_{ij}\frac{1}{2S_2}F_1(t)\right\}$$

$$\begin{aligned} G^{iojo}(t) &= G^{oijo}(t) = G^{oioj}(t) = G^{iooj}(t) \\ &= \frac{-1}{S_4}\left\{\frac{S_1S_2}{S_4}(P_i - Q_i)(P_j - Q_j)F_2(t) - \frac{1}{2}\delta_{ij}F_1(t)\right\} \end{aligned}$$

$$\begin{aligned} G^{ijko}(t) &= G^{ijok}(t) = \frac{S_2}{S_4^2}\left\{\frac{S_1S_2}{S_4}(P_i - Q_i)(P_j - Q_j)(P_k - Q_k)F_3(t)\right. \\ &\left. - \tfrac{1}{2}[\delta_{ij}(P_k - Q_k) + \delta_{ik}(P_j - Q_j) + \delta_{jk}(P_i - Q_i)]F_2(t)\right\} \end{aligned}$$

$$G^{oijk}(t) = G^{iojk}(t) = \frac{-S_1}{S_4{}^2}\{(P_i - Q_i)(P_j - Q_j)(P_k - Q_k)F_3(t)$$

$$- \tfrac{1}{2}[\delta_{ij}(P_k - Q_k) + \delta_{ik}(P_j - Q_j) + \delta_{jk}(P_i - Q_i)]F_2(t)\}$$

$$G^{ijkl}(t) = \frac{1}{S_4{}^2}\left\{\frac{S_1{}^2 S_2{}^2}{S_4{}^2}(P_i Q_i)(P_j - Q_j)(P_k - Q_k)(P_l - Q_l)F_4(t)\right.$$

$$- \frac{1}{2}\,\frac{S_1 S_2}{S_4}[\delta_{ij}(P_k - Q_k)(P_l - Q_l) + \delta_{ik}(P_j - Q_j)(P_l - Q_l)$$

$$+ \delta_{il}(P_j - Q_j)(P_k - Q_k) + \delta_{ik}(P_i - Q_i)(P_l - Q_l)$$

$$+ \delta_{jl}(P_i - Q_i)(P_k - Q_k) + \delta_{kl}(P_i - Q_i)(P_j - Q_j)]F_3(t)$$

$$\left. + \tfrac{1}{4}\,\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}]F_2(t)\right\}.$$

The electron repulsion integrals can now be defined in terms of the G-functions and the S-functions, normalization factors again being included by the explicit or implicit use of the product $S^{oo}(a, b)S^{oo}(c, d)$. An abbreviated notation will be introduced whose meaning will be apparent to the reader. The multiplicative term Λ appearing in each formula is defined as:

$$\Lambda = 2\left(\frac{S_1 S_2}{\pi S_4}\right)^{1/2}$$

$$\langle S_a\, S_b \mid S_c\, S_d\rangle = \left\langle S_a S_b \left| \frac{1}{r_{12}} \right| S_c S_d \right\rangle = \Lambda\, S^{oo}(a, b) S^{oo}(c, d) G^{oooo}(t)$$

$$= \Lambda\, S^{oo}_{ab}\, S^{oo}_{cd}\, G^{oooo}$$

$$\langle P_{ia} S_b \mid S_c\, S_d\rangle = \Lambda\, \{S^{io}_{ab}\, S^{oo}_{cd}\, G^{oooo} + S^{oo}_{ab}\, S^{oo}_{cd}\, G^{iooo}\}$$

$$\langle P_{ia} S_b \mid P_{kc} S_d\rangle = \Lambda\, \{S^{io}_{ab}[S^{ko}_{cd}\, G^{oooo} + S^{oo}_{cd}\, G^{ooko}] + S^{oo}_{ab}[S^{oo}_{cd}\, G^{ioko} + S^{ko}_{cd}\, G^{iooo}]\}$$

$$\langle P_{ia} P_{jb} \mid S_c\, S_d\rangle = \Lambda\, \{S^{ij}_{ab}\, S^{oo}_{cd}\, G^{oooo} + S^{io}_{ab}\, S^{oo}_{cd}\, G^{ojoo}$$

$$+ S^{oj}_{ab}\, S^{oo}_{cd}\, G^{iooo} + S^{oo}_{ab}\, S^{oo}_{cd}\, G^{ijoo}\}$$

$$\langle P_{ia} P_{jb} \mid P_{kc} S_d\rangle = \Lambda\, \{S^{ij}_{ab}[S^{ko}_{cd}\, G^{oooo} + S^{oo}_{cd}\, G^{ooko}] + S^{io}_{ab}[S^{ko}_{cd}\, G^{ojoo} + S^{oo}_{cd}\, G^{ojko}]$$

$$+ S^{oj}_{ab}[S^{ko}_{cd}\, G^{iooo} + S^{oo}_{cd}\, G^{ioko}] + S^{oo}_{ab}[S^{ko}_{cd}\, G^{ijoo} + S^{oo}_{cd}\, G^{ijko}]\}$$

$$\langle P_{ia} P_{jb} \mid P_{kc} P_{ld}\rangle = \Lambda\, \{S^{ij}_{ab}[S^{kl}_{cd}\, G^{oooo} + S^{ko}_{cd}\, G^{oool} + S^{ol}_{cd}\, G^{ooko} + S^{oo}_{cd}\, G^{ookl}]$$

$$+ S^{io}_{ab}[S^{kl}_{cd}\, G^{ojoo} + S^{ko}_{cd}\, G^{ojol} + S^{ol}_{cd}\, G^{ojko} + S^{oo}_{cd}\, G^{ojkl}]$$

$$+ S^{oj}_{ab}[S^{kl}_{cd}\, G^{iooo} + S^{ko}_{cd}\, G^{iool} + S^{ol}_{cd}\, G^{ioko} + S^{oo}_{cd}\, G^{iokl}]$$

$$+ S^{oo}_{ab}[S^{kl}_{cd}\, G^{ijoo} + S^{ko}_{cd}\, G^{ijol} + S^{ol}_{cd}\, G^{ijko} + S^{oo}_{cd}\, G^{ijkl}]\}.$$

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