The quantitative study of the electronic states of molecules always involves the evaluation of very large numbers of ~~and~~ integrals. These integrals are just the matrix elements of the relevant operators associated with the kinetic and potential energies of the electrons, taken between basis functions used to represent the wave functions of the electrons in the molecule. The number and complexity of the molecular integrals is such that the development of theories of valency in any kind of quantitative form was effectively ~~blocked~~ halted until the advent of modern computers. While this "bottleneck" has now been largely (but not completely) broken for diatomic molecules, the problem remains for polyatomic systems.

The basis functions used in molecular ~~orbital~~ calculations are almost always simple analytic functions, chosen to represent the motion of the electrons in the vicinity of one of the nuclei which constitute the molecule. The most common form is $\approx f(r) X_l^m(\theta, \phi)$ in which the polar coordinates $r, \theta, \phi$ are measured relative to a local reference frame with origin at one of the atomic nuclei, and $X_l^m(\theta, \phi)$ is a cubic harmonic (see Section 2). The form of the radial function propounded by Slater (1930), $f(r) \approx r^{n-1} \exp(-zr)$ where $n$ is an integer $(= l+1, l+2, \ldots,)$ and $z$ an adjustable parameter (the screening constant), satisfies the relevant boundary conditions as $r \to \infty$ and $r \to 0$ for the potentials ~~experienced~~ experienced by an electron in a molecule. Thus a Slater-type orbital (STO) centred on atom A and expressed in the coordinate system with origin at the same centre is of the form

$$\phi_p(\underset{\sim}{r}_a) = R(n_p, z_p)\, r_a^{n_p-1} e^{-z_p r_a} X_{l_p}^{m_p}(\theta_a, \phi_a), \qquad (1.4)$$

where $R(n_p, z_p)$ is the appropriate normalization constant (see Section 2). Function (1.4) clearly possesses no radial

nodes, and in order to reproduce the oscillations required in an actual wave function, a linear combination of several of these basis functions is necessary. Other forms for $f(r)$ may be used, and are briefly considered below.

The operators corresponding to the kinetic and electron-nuclear attraction terms of the Hamiltonian (energy) are sums of one-electron contributions, and the evaluation of their matrix elements in any basis gives rise to 3-dimensional integrals. In the case of Slater orbitals, two of the integrations (over angular coordinates) can readily be carried out analytically. However the operator corresponding to the electron-electron repulsion is a sum of two-electron terms, and the corresponding molecular integrals are six-dimensional. Analytic integration over the angular coordinates usually reduces these to two dimensional form which must then be evaluated by quadrature. Since the STO's are sited at different nuclei, these integrals are in addition multicentred. The kinetic energy integrals are never more than two-centres while electron-nuclear attraction integrals may involve up three centres. The electron repulsions integrals however may include up to four distinct nuclear centres.

Apart from the intrinsic difficulty (this) ↓ ~~[illegible]~~ causes in evaluating the integrals themselves, the problem is further compounded by the fact that the values of the multicentre integrals obviously depend upon the relative positions of the nuclei. For any change in the nuclear geometry, the integrals must all be recalculated It is therefore a formidable task to generate the potential energy surface of a molecule point by point in this manner. Even for a simple triatomic molecule, the number (almost) of energy points needed is so large as to stretch beyond the capabilities of even the most powerful computers available.

This problem can be greatly alleviated if one calculates for each nuclear geometry not just the total energy but also the gradients of the energy with respect to changes in the relative nuclear positions. For then interpolation between energy points is considerably more accurate, and far fewer points are needed. The theory for calculating energy gradients was developed by Gerratt and Mills (1968) for closed-shell Hartree-Fock functions and recently extended to arbitrary M.O.-C.I. wave functions by Tachibana et al. (1978). However implementation of the theory requires the calculation of new types of multi-centre integrals in which the gradients of the basis functions with respect to nuclear positions now occur.

The computation of molecular integrals which include derivatives of the form $\partial \chi_p / \partial R_i^{\alpha}$, where $R_i^{\alpha}$ is the $\alpha$ component ($\alpha = x, y$ or $z$) of the position vector $\underset{\sim}{R}_i$ of nucleus $i$, enables one also to evaluate the matrix elements of the non-adiabatic interactions between different electronic states. This is a scarcely touched field from a computational viewpoint, but is of much current and experimental interest in the study of dynamical processes in molecules.

Besides the integrals which occur in the evaluation of the total energy, it is important also to consider integrals associated with operators corresponding to other experimental observables. Thus integrals over operators corresponding to multipole moments enable one to calculate the expectation value of the dipole, quadrupole, ..., etc., moments of the molecule in a given electronic state, or the appropriate transition moments between two different electronic states. These operators are sums of one-electron contributions, the general form of each contribution being a regular solid harmonic $Y_\ell^m(r, \theta, \phi) = r^\ell X_\ell^m(\theta, \phi)$ (See Section 2 and

$(r, \theta, \phi)$

Appendix A). Other molecular properties such as forces and field gradients are expressed as irregular solid harmonics $Y_\ell^m(r,\theta,\phi) = r^{-\ell-1} X_\ell^m(\theta,\phi)$ which possess a radial singularity at the origin. The potential of electron-nuclear attraction is just the first member of this series of operators, corresponding to $\ell = m = 0$.

The inclusion of relativistic effects is frequently important in the study of electronic states of molecules with unpaired electrons. For molecules composed of light atoms only, the Hamiltonian corresponding to such interactions, $\mathcal{H}_{s.o.}$, can be written as a sum of spin-orbit, spin-spin and orbit-orbit coupling terms. These operators also involve one- and two electron contributions and give rise to characteristic multi-centre molecular integrals. Their evaluation is even more difficult than the "conventional" types of integral introduced above. Indeed there is at the time of writing no general program in existence for the calculation of the multicentre integrals over Slater orbitals which arise from spin-orbit and spin-spin interactions, but only for the diatomic case (Sunk, 1975). The matrix elements of orbit-orbit interactions have only ever been evaluated for atomic systems.

An alternative to the Slater form of the radial part of the basis functions are the functions $f(r) \propto r^{n-1} \exp(-\alpha r^2)$ : the so-called Gaussian orbitals, first suggested by Boys (1950). Functions of this type are appropriate for potentials which decrease to zero as $r \to 0$ and increase indefinitely as $r \to \infty$. They therefore hardly seem appropriate for atomic and molecular systems, and indeed linear combinations of many of them are needed to obtain functions which approximately satisfy the correct boundary conditions. The main advantage of Gaussian functions is that multicentre integrals involving them are

very much easier to evaluate than the corresponding integrals involving STO's (see e.g. Shavitt, 1963). In addition the operators corresponding to the electronic kinetic ~~and~~ energy and potential energy of nuclear attraction happen to emphasize parts of the radial function in the general vicinity of the nuclei where the shortcomings of the Gaussian functions are at their least. Consequently good results for ground state energies are obtainable using a manageable number of this type of basis function, and indeed Gaussian orbitals are in widespread use. However it is important not to lose sight of their ~~das~~ fundamental inadequacies. [illegible] These manifest themselves in the calculation of expectation values of operators other than that corresponding to total energy. Multipole moments, intermolecular interaction energies and electron-molecule collision processes all emphasize the outer portions of the ground state electronic wave function, and are poorly or inadequately represented by Gaussian-based functions. Furthermore these deficiencies are greatly magnified in excited electronic states. At the other extreme, the operators corresponding to forces ~~and~~ field gradients emphasize parts of the wave function very close to the nuclei, and these are also poorly represented by Gaussian [illegible] orbitals, unless ~~a~~ very many of them are employed. (and spin-orbit coupling)

The purpose of the present series of articles is to address ourselves to the problem of calculating multicentre integrals over Slater orbitals. We do so from a particular standpoint: the use of the zeta function expansion, originated by Coulson (1937) and developed by Barnett and Coulson (1951; Barnett, 1963). The fundamental characteristic of this method is the expansion of all STO's on the various centres about a single, unique, centre, [illegible] enabling the integrations to be

carried out in spherical polar coordinates, with origin at that nucleus.

The main alternative to the zeta function expansion is the Gaussian-transform method which is described by Kern and Karplus (1965), and embodied in a set of programs written by R. M. Stevens of Harvard University for calculating total energies. The evaluation of forces and field gradients in polyatomic molecules using the Gaussian transform technique has also been reported by Flygare et al. (1966).

However the outstanding merit of the Barnett–Coulson method is the simplicity and directness with which any type of integral can be formulated. Its only disadvantage is that the expansion for multicentre integrals sometimes converges rather slowly. But as first noted by Peterson and McKoy (1967), this is dramatically improved by the application of certain term-by-term transformations due to Wynn (1956).

We consider a wide range of operators: indeed all those introduced above with the exception of those arising from relativistic interactions. We emphasize that the techniques described in this series of papers have been embodied in a set of programs (undergone) ~~which have~~ carefully (optimization) ~~optimized~~ over a ~~many~~ number of years. Paper I is devoted to the development of techniques for the compact transfer of a Slater orbital from one centre to another. This undertaking is completed in Paper II and extended to cover the important case of transfer of gradients of STO's with respect to nuclear displacements. The application of the Shanks-Wynn transformation to accelerate convergence of the expansions is also fully described in II, together with certain ancillary techniques of list-generation and indexed retrieval. After these lengthy but necessary preliminaries, ~~Papers~~ III and IV

(Papers)

are devoted to the evaluation of multicentre one electron integrals over operators expressed as regular and irregular solid harmonics* Lastly Paper V deals with the two-electron integrals.

The central theme of the present Paper is therefore is the development of the original Barnett-Coulson expansion into a form enabling the radial part of a Slater orbital to be transferred efficiently to any other centre in a polyatomic molecule of arbitrary geometry. [Continue on line 14, page 4§: "The angular part...

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* (Footnote of page 3: The use of ellipsoidal coordinates...)