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Mr. P. C. Johnson NOT IN

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SEMI-ANNUAL PROGRESS REPORT
NUMBER 73 JULY 15, 1970

SOLID-STATE AND MOLECULAR
THEORY GROUP

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OF TECHNOLOGY
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SURVEY

In the first contribution to this report, Smith and Johnson continue their application of the scattered wave method of computing molecular wave functions to the SO_4^{2-} ion. This represents the first time this method, which avoids the calculation of multicenter integrals has been carried to self consistency.

Professor DeCicco in his contribution discusses computational aspects of the APW method and in particular proposes the interpolation of the APW determinant as means of finding surfaces of constant energy and densities of states.

In the remaining two contributions, John Connolly gives corrections and additions to his article in the last report and Professor Gilmore continues his discussions of properties of the continuous groups.

As the last item in this report you should find a form to be returned to enable us to update our mailing list. This seems an appropriate time to revise our list since the character of the investigations reported has widened. Professor Scully's work on laser physics and quantum optics, and Professor Stanley's work on statistical physics and phase transitions have already appeared in some of our earlier reports and will be appearing in future reports.

SCF MOLECULAR-ORBITAL STUDIES OF THE SULFATE ION BY THE SCATTERED-WAVE MODEL

F. C. Smith, Jr. and K. H. Johnson

Introduction

In previous publications and reports^{1,2}, we have introduced a self-consistent-field scattered-wave (SCF-SW) model for the electronic structures of polyatomic molecules. In the present report, we discuss the results of molecular-orbital calculations for the dinegative sulfate ion (SO_4^{2-}) on the basis of this approach.

A determination of the molecular orbitals of a polyatomic cluster such as SO_4^{2-} is complicated, first of all, by its ionicity, by the presence of several "inner" electron shells, and, when conventional SCF-LCAO methods of quantum chemistry are used, the necessity of having to compute many multicenter integrals or equivalent Hartree-Fock matrix elements. Furthermore, the sulfate complex is not stable in free space, i.e., the gaseous phase, but typically exists as the anion in an ionic crystal, (e.g., K_2SO_4). Experimental information on the sulfate ion can be extracted from the results of measurements on such crystals (e.g., ESR³ and chemical shift⁴ data). Thus in order to calculate sulfate molecular orbitals which are potentially relevant to observed chemical and physical properties, it is essential for one to include, explicitly or implicitly, the stabilizing effects of the crystal environment.

Ab initio Hartree-Fock SCF-LCAO molecular-orbital calculations of the sulfate ion have recently been published⁵. Also available in the literature are the results of approximate SCF-LCAO⁶, SCCEI-LCAO⁷, CNDO⁸, and Wolfsberg-Helmholz (WH) type⁹ calculations on SO_4^{2-} . Because of the differences among such LCAO methods, e.g., the choices of atomic orbital basis functions and the approximations to multicenter integrals, the results of these calculations are not in close agreement with each other. This inconsistency is evident in the comparison of LCAO orbital energies and electronic charge dis-

tributions of SO_4^{2-} shown in Tables VIII and IX, respectively.

The ab initio SCF-LCAO work is reported to have required a total of 7.5 hours of computational time on a large-scale computer, most of it involved in the evaluation of multicenter integrals over the component atomic orbitals (a small Gaussian basis set including sulfur 3d orbitals). There are no multicenter integrals in the SCF-SW approach. As we shall demonstrate, stable molecular orbitals can be calculated for SO_4^{2-} by the latter technique with relatively little computational effort (a few minutes on an IBM 360 Mod. 65 computer), including sulfur-s, p, d, oxygen-s, p, and higher partial-wave components in the SW basis set. It will be shown that the SCF-SW results are similar to those calculated with the ab initio SCF-LCAO method⁵ with respect to the ordering of the occupied valence and core orbitals and with respect to the magnitudes of the core-orbital energies. An analysis of the electronic charge distribution in the sulfate ion on the basis of the SCF-SW model is also described in this report, followed by a discussion of the dependence of the results on the choices of local exchange potential and stabilizing charge.

The SCF-SW Model^{1,2}

Consider the sulfate ion in its equilibrium tetrahedral configuration, as illustrated schematically in Fig. 1. In the SCF-SW model, we partition the space of the molecule into three contiguous regions:

- I. Intraatomic: the region within nonoverlapping spheres centered on the constituent sulfur and oxygen atoms.
- II. Interatomic: the region between the inner atomic spheres and an outer sphere (the "Watson sphere") centered on the sulfur atom and surrounding the entire cluster.
- III. Outeratomic: the region outside the Watson sphere.

These artificial spherical boundaries are most generally assumed to be touching. The atomic spheres are pictured as being relatively small in Fig. 1 for the purpose of illustration only. The actual sphere radii depend on the nature of the model Hartree-Fock potential chosen to initiate the SCF-SW calculation.

At an arbitrary point \vec{r} of the molecule, the initial model potential is represented as a superposition

$$V(\vec{r}) = V^S(|\vec{r} - \vec{R}_0|) + \sum_{j=1}^4 V^O(|\vec{r} - \vec{R}_j|) \quad (1)$$

of spherically symmetric Hartree-Fock-Slater free-atom and free-ion potentials centered at \vec{R}_j ($j=0, \dots, 4$; \vec{R}_0 = center of cluster), including the Slater $X\alpha$ ¹⁰ statistical approximation

$$V_{X\alpha}(\vec{r}) = -6\alpha [(3/8\pi) \rho(\vec{r})]^{1/3} \quad (2)$$

to exchange correlation. The latter depends only on the local electronic charge density $\rho(\vec{r})$ and on the choice of exchange coefficient α . Particular values of $\alpha = 1$ and $\alpha = 2/3$ have been tested (see below). The superposition (1) is then spherically averaged within each atomic sphere j and in the outeratomic region (III). In region (II), the starting potential is that based on a constant charge density equal to the average value of the true charge density over the interatomic volume.

To stabilize the orbitals of SO_4^{2-} we have added a contribution to the potential similar to that originally adopted by Watson¹¹ for the calculation of free-ion Hartree-Fock wavefunctions. We distribute a positive charge uniformly around the outer spherical boundary separating the interatomic and outeratomic regions. This "Watson sphere" is therefore a crude approximation to the stabilizing effects of a crystal environment. Charges of +2 (as indicated in Fig. 1) and +1 have both been tested.

In Tables I through III we have listed (in Rydbergs and at every fourth radial mesh point) the respective intraatomic and outeratomic potentials used to start the SCF-SW calculation. These potentials are based on a choice of $X\alpha$ parameter $\alpha = 1$ and stabilizing charge of +2. Included for comparison in the same Tables are the final SCF potentials. The sulfur and oxygen spheres are assumed to be touching at respective radii where the corresponding starting potentials are equal. The Watson sphere is then assumed to be tangent to the oxygen spheres. The equilibrium S-O bond length in SO_4^{2-} is 1.44 \AA ¹². The sphere radii based on this bond length and on the starting potentials in Tables I through III are listed in Table IV, along with the initial and SCF average interatomic potentials. It is important to note that discontinuities of the potential across the boundaries separating the intra-, and inter-, and outeratomic regions do not imply discontinuities in the molecular-orbital wavefunctions. Continuity of the wavefunctions and their first derivatives is ensured through the scattered-wave formalism (described below).

The partitioning of the space of the molecule into bounded regions of spherically averaged potential allows one to introduce a rapidly convergent, composite partial-wave representation of the molecular orbitals. Within each atomic sphere j of radius b_j (sulfur: $j = 0$; oxygen: $j = 1, 2, 3, 4$), we expand the orbital wavefunctions in the single-center form

$$\psi_I^j(\vec{r}) = \sum_L C_L^j R_L^j(E; r) Y_L(\vec{r}) \quad (0 < r \leq b_j) \quad (3)$$

where $L = (\ell, m)$ is the partial-wave (angular-momentum) index, C_L^j are partial-wave coefficients (to be determined) and $Y_L(\vec{r})$ are real spherical harmonics. The functions $R_L^j(E; r)$ are solutions of the radial Schrödinger equation

$$\left[-\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{\ell(\ell+1)}{r^2} + V^j(r) - E \right] R_L^j(E; r) = 0 \quad (4)$$

for the spherical average $V^j(r)$ of the superposition (1) with respect to the j^{th} atomic site (e.g., the potentials in Tables I through III). The radial functions must be finite at the origin $r = 0$ of each atomic sphere. The solutions are generated by outward numerical integration of Eq. (4), using the Noumerov technique¹³, for each trial energy parameter E and partial-wave component l .

In the outeratomic region the orbitals are expanded with respect to the center of the cluster in the representation

$$\psi_{\text{III}}(\vec{r}) = \sum_L D_L^0 R_L^{\text{out}}(E; r) Y_L(\vec{r}) \quad (b_W \leq r < \infty) \quad (5)$$

where b_W is the radius of the Watson sphere. The functions $R_L^{\text{out}}(E; r)$ are solutions of a radial Schrödinger equation similar to (4) for the spherical average of the potential in the outeratomic region. For localized molecular orbitals, these radial functions must decay exponentially at large distances from the molecule. The solutions are generated by inward Noumerov integration of the radial equation for trial values of E and l .

For the interatomic region we expand the molecular orbitals in the multicenter partial-wave representation

$$\begin{aligned} \psi_{\text{II}}(\vec{r}) = & \sum_L B_L^0 j_l(\kappa |\vec{r} - \vec{R}_0|) Y_L(\vec{r} - \vec{R}_0) \quad (b_0 \leq |\vec{r} - \vec{R}_0| \leq b_W) \\ & + \sum_{j=0}^4 \sum_L A_L^j f_l(\kappa |\vec{r} - \vec{R}_j|) Y_L(\vec{r} - \vec{R}_j) \quad (b_j < |\vec{r} - \vec{R}_j|) \\ & \quad \quad \quad (|\vec{r} - \vec{R}_0| \leq b_W) \end{aligned} \quad (6)$$

in which

$$\kappa = (E - V_0)^{\frac{1}{2}} \quad (7)$$

and

$$f_l(\kappa r) = \begin{cases} h_l^{(1)}(\kappa r) & (E < V_0 < 0; \kappa \text{ imaginary}) \\ n_l(\kappa r) & (V_0 < E < 0; \kappa \text{ real}) \end{cases} \quad (8)$$

In the above expressions, V_0 is the average interatomic potential, j_l is a spherical Bessel function, $h_l^{(1)}$ is a spherical Hankel function of the first kind, and n_l is a spherical Neumann function.

The composite molecular-orbital wavefunctions (3), (5) and (6) and their respective first derivatives are required to be continuous across the adjacent spherical boundaries. This is accomplished via the scattered-wave formalism described in

Refs. 1 and 2 and leads to the following relations among the multicenter and single-center partial-wave coefficients.

$$A_{L'}^j = -i\kappa b_j^2 [j_{\ell}(\kappa b_j), R_{\ell}^j(E; b_j)] C_{L'}^j \quad (9)$$

$$B_{L'}^0 = -i\kappa b_W^2 [R_{\ell}^{\text{out}}(E; b_W), f_{\ell}(\kappa b_W)] D_{L'}^0 \quad (10)$$

where

$$[j(x), R(x)] \equiv j(x) [dR(x)/dx] - R(x) [dj(x)/dx] \quad (11)$$

The secular equations which lead, in turn, to the molecular-orbital energies and independent partial-wave coefficients can be written in the linear, homogeneous form

$$\begin{aligned} \sum_{j'=0}^4 \sum_{L'} [T^{-1}(E)]_{LL'}^{jj'} A_{L'}^{j'} - \sum_{L'} S_{LL'}^{j0}(E) B_{L'}^0 &= 0 \\ \sum_{j'=0}^4 \sum_{L'} S_{LL'}^{0j'}(E) A_{L'}^{j'} - \sum_{L'} [g^{-1}(E)]_{LL'}^{00} B_{L'}^0 &= 0 \end{aligned} \quad (2)$$

in which

$$[T^{-1}(E)]_{LL'}^{jj'} \equiv \delta_{jj'} \delta_{LL'} [t_{\ell}^j(E)]^{-1} - (1 - \delta_{jj'}) G_{LL'}^{jj'}(E) \quad (13)$$

$$t_{\ell}^j(E) \equiv \frac{[j_{\ell}(\kappa b_j), R_{\ell}^j(E; b_j)]}{[f_{\ell}(\kappa b_j), R_{\ell}^j(E; b_j)]} \quad (14)$$

$$\begin{aligned} G_{LL'}^{jj'}(E) \equiv -4\pi i^{\ell-\ell'} \sum_{L''} i^{-\ell''} I_{L''}(L; L') \\ \times f_{\ell''}(\kappa R_{jj'}) Y_{L''}(\vec{R}_{jj'}) \end{aligned} \quad (15)$$

$$g_{LL'}^{00}(E) \equiv \delta_{LL'} \frac{[f_{\ell}(\kappa b_W), R_{\ell}^{\text{out}}(E; b_W)]}{[j_{\ell}(\kappa b_W), R_{\ell}^{\text{out}}(E; b_W)]} \quad (16)$$

$$\begin{aligned} S_{LL'}^{j0}(E) \equiv -4\pi i^{\ell-\ell'} \sum_{L''} i^{-\ell''} I_{L''}(L; L') \\ \times j_{\ell''}(\kappa R_{j0}) Y_{L''}(\vec{R}_{j0}) \end{aligned} \quad (17)$$

The vectors

$$\vec{R}_{jj'} \equiv \vec{R}_{j'} - \vec{R}_j \quad (18)$$

connect any two atoms of the molecule, and the vectors

$$\vec{R}_{j0} \equiv \vec{R}_0 - \vec{R}_j \quad (19)$$

connect each atom with the center of the cluster. The Gaunt integrals¹⁴

$$I_{L''}(L; L') \equiv \int Y_{L''}(\vec{r}) Y_L(\vec{r}) Y_{L'}(\vec{r}) d\Omega(\vec{r}) \quad (20)$$

occur in expressions (15) and (17). They are nonzero only if

$$|\ell - \ell'| < \ell'' < \ell + \ell' \quad (21)$$

$$\ell'' + \ell + \ell' = \text{even integer} \quad (22)$$

The Gaunt integrals can also be written as products of Clebsch-Gordon coefficients.

For the purposes of computation and compact exposition, the matrix elements as written above differ somewhat from the original form in which they were presented in Refs. 1 and 2. Real spherical harmonics are used throughout, so that under conditions (21) and (22), the matrix elements turn out to be real and symmetric, i. e.

$$G_{L'L}^{j'j}(E) = G_{LL'}^{jj'}(E) \quad (23)$$

$$S_{L'L}^{0j}(E) = S_{LL'}^{j0}(E) \quad (24)$$

It should also be noted from expression (17) that

$$S_{LL'}^{j0}(E) = -\delta_{LL'}(j=0) \quad (25)$$

For the purpose of computation, it is also useful to recall that the Bessel and Hankel functions of imaginary argument (which occur in the above formulae for the energy range $E < V_0 < 0$) can be written in the real, modified form

$$i_\ell(x) \equiv i^{-\ell} j_\ell(ix) \quad (26)$$

$$k_\ell^{(1)}(x) \equiv -i^{-\ell} h_\ell^{(1)}(ix) \quad (27)$$

As it stands, the matrix of the secular equations (12) is a 6×6 array for each partial-wave component $L = (\ell, m)$, because the atomic index $j = 0, 1, \dots, 4$. However, this matrix can be factorized considerably by exploiting the equilibrium tetrahedral symmetry of the sulfate ion. Instead of expanding the wavefunctions (3), (5) and (6) around each center j in ordinary spherical harmonics, we can expand them in linear combinations

$$K_{\ell n}^{\Gamma_S}(\vec{r}) = \sum_m C_{\ell n, m}^{\Gamma_0} Y_{\ell m}(\vec{r}) \quad (28)$$

and

$$K_{\ell n}^{\Gamma_O}(\vec{r}) = \sum_{j=1}^4 \sum_m C_{\ell n, m}^{\Gamma_j} Y_{\ell m}(\vec{r}) \quad (29)$$

of spherical harmonics which are a basis for the various irreducible representations Γ of the T_d (tetrahedral) point group. The summations are over allowed m -values and over equivalent oxygen atoms. The index n indicates that a particular value of ℓ may occur more than once in a given irreducible representation. The symmetry coefficients in (28) and (29) lead to compact symmetrized versions of the matrix elements in (12). For example, for the symmetrized version of the elements (15) which connect oxygen atoms, we can write

$$G_{\ell n; \ell' n'}^{\Gamma_O} \equiv \sum_{j=1}^4 \sum_{j'=1}^4 \sum_m \sum_{m'} C_{\ell n, m}^{\Gamma_j} G_{\ell m; \ell' m'}^{jj'} C_{\ell' n', m'}^{\Gamma_{j'}} \quad (30)$$

Symmetrized secular arrays of only 3×3 , 4×4 , and 5×5 dimensions are thereby obtained for the sulfate ion, if we include allowed partial wave components up to $\ell_{\max} = 3$ for the sulfur atom and outeratomic region and up to $\ell_{\max} = 1$ for the equivalent oxygen atoms.

We also have the option of partitioning¹⁵ and contracting the original set of secular equations (12) prior to symmetrization. This reduces the secular matrices even further and leads to a very interesting interpretation of the SCF-SW model. The contracted secular equations can be written in the form

$$\sum_{j'=0}^4 \sum_{L'} \{ \delta_{jj'} \delta_{LL'} [t_{\ell}^j(E)]^{-1} - W_{LL'}^{jj'}(E) \} A_{L'}^{j'} = 0 \quad (31)$$

where

$$W_{LL'}^{jj'}(E) \equiv (1 - \delta_{jj'}) G_{LL'}^{jj'}(E) + \sum_{L''} \sum_{L'''} S_{LL''}^{j0}(E) g_{L''L'''}^{00}(E) S_{L''L'}^{0j'}(E) \quad (32)$$

Expression (31) is just the partial-wave representation of the inverse of the "T-matrix"¹⁶ for a single electron multiply scattered among a system of nonoverlapping spherical potentials j ($j = 0, 1, \dots, 4$). The fact that this expression is set equal to zero is just the condition for the existence of bound single-particle states (the "T-matrix" itself has "poles" at these states). The "amplitude of scattering" at each potential for each partial-wave component ℓ of energy E is described by the individual "atomic t-matrix" $t_{\ell}^j(E)$ as defined in expression (14). The "propagation" of the partial waves between any two atoms j and j' is described by the matrix elements $W_{LL'}^{jj'}(E)$ as defined in Eq. (32). However, the latter is not equal solely to the partial-wave representation $G_{LL'}^{jj'}(E)$ of

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the "free-space" single-particle Green's function, as it would be for simple truncated "muffin-tin" type potentials. Through the partitioning and contraction of the original secular equations (12), the second term on the right side of (32) effectively "renormalizes" the free-space propagator $G_{L,L'}^{jj'}(E)$ to the original boundary condition placed on the cluster orbitals, in the case of SO_4^{2-} the solution of the Schrödinger equation in the interatomic region.

Although the matrix elements (13) through (16) look quite complicated, they are relatively straightforward to compute efficiently. This is due, in part, to the dependence of these quantities only on radial functions (e.g. $R_\ell^j(E; b_j)$, $f_\ell(\kappa b_j)$, etc.) and their first derivatives at appropriate sphere radii b_j , and on structure factors (e.g. $f_\ell(\kappa R_{jj'}) Y_L(\vec{R}_{jj'})$) which depend on the interatomic vectors $\vec{R}_{jj'}$. The zeros of the determinant of the secular equations (12) or their symmetrized contracted version, correspond to the bound molecular-orbital energies. Because the energy E is a parameter occurring in all matrix elements, the latter must be computed over a range of energies bracketing each eigenvalue and the determinant interpolated to zero. In our applications to SO_4^{2-} we have started with trial symmetrized wavefunctions consisting of only one or two allowed partial waves per atom, adding higher allowed partial waves until an increase in the size of the determinant produced no significant change in the molecular-orbital energies. One or two partial waves per atom is sufficient for convergence of the energies to ± 0.005 Hartree in the case of SO_4^{2-} . Accuracy greater than this is unwarranted, in view of the uncertainties in the SCF-SW potential for polyatomic molecules as complex as SO_4^{2-} .

The generation of a set of occupied molecular orbitals and energies for a model potential of the type described above is the starting point for a full SCF-SW calculation within the framework of the statistical $X\alpha^{10}$ exchange approximation. The initial set of orbitals leads to an electronic charge density which is used as the basis for generating a new potential. This potential is spherically averaged in the intraatomic and interatomic regions of the molecule, and is volume averaged in the interatomic region. This result, in turn, serves as the model potential for the first iteration. A new set of orbitals and energies is computed and the process is repeated until self consistency in the potential is attained. Five to ten iterations have been sufficient in most applications of the SCF-SW method, thus far, to yield convergence of the molecular-orbital energies to ± 0.005 Hartree. The total computation time per iteration for the case of SO_4^{2-} is approximately one minute on an IBM 360 Mod. 65 computer.

Calculated Results

It is possible to treat the more tightly bound "core" electrons separately from the more loosely bound "valence" electrons when one adopts the $X\alpha$ approximation to exchange correlation in a polyatomic molecule or solid¹⁰. While values of the exchange parameter α generally have to be optimized to yield valence one-electron energies which

are most consistent with experiment, it appears that the original Slater value of $\alpha = 1$ is most appropriate for the inner-electron levels¹⁰. Therefore, in our present work on SO_4^{2-} , we have calculated the SCF valence and core molecular energies in two stages. For the determination of the valence orbitals, the sulfur $1s^2 2s^2 2p^6$ and oxygen $1s^2$ core charge densities used to generate the starting molecular potential have been maintained through all SCF iterations (a "frozen core" approximation). The valence orbitals were calculated for two arbitrary choices of exchange parameter, namely $\alpha = 1$ and $\alpha = 2/3$, and for a Watson charge of +2. The resulting valence-orbital energies are listed in Table V. The core orbitals were then recomputed self consistently for a choice of $\alpha = 1$ on the basis of the calculated value of the electronic charge transfer between sulfur and oxygen atoms in the molecule (see Table VII). The resulting core-orbital energies are included in Table V. The quantities in parenthesis are the corresponding Hartree-Fock-Slater free-atom¹⁷ energy levels.

It is clear from Table V that the SCF-SW model leads to bound occupied molecular orbitals of negative energy, as anticipated for a sulfate anion stabilized by the electrostatic field of surrounding positive ions in a crystal such as K_2SO_4 or Na_2SO_4 . The effect of using a statistical exchange parameter $\alpha = 2/3$ for the valence electrons in place of the original Slater value $\alpha = 1$ is merely the reduction of the orbital eigenvalues by an approximately constant value of 0.2 Hartree. This too is not a surprising result, in view of previous applications of the $X\alpha$ statistical exchange approximation to atoms and crystals¹⁰.

We have also investigated the consequences of adopting a smaller value of positive stabilizing charge on the Watson sphere. In Table VI is a comparison of occupied valence-orbital energies obtained for respective stabilizing charges of +2 and +1. Only the initial non-self-consistent (NSCF) results are compared in this case, because the highest occupied orbital T_1 was "lost", i.e. it became effectively unbound, when we attempted to iterate the calculation to self consistency for the +1 charge. Thus the absolute magnitudes of the valence-orbital eigenvalues of SO_4^{2-} are rather critically dependent on the amount of charge we place on the Watson sphere. However, the relative spacing and ordering of energies are essentially unchanged.

It is also evident from Table V that the ordering of orbital energies is unaltered by adopting an exchange parameter $\alpha = 2/3$ in place of $\alpha = 1$. With this sequence, the highest occupied valence orbital is one having symmetry T_1 . ESR³ data on K_2SO_4 suggest that the symmetry of the SO_4^- ion in the sulfate or persulfate matrix is no greater than C_{2v} . This deviation from full tetrahedral symmetry T_d can be explained by the occurrence of a Jahn-Teller distortion of the ion. While the ordering of molecular orbitals which we have calculated for the tetrahedral sulfate ion is not absolutely certain, it is one for which a Jahn-Teller distortion to C_{2v} symmetry is allowed. To this extent, therefore, our theoretical results for SO_4^{2-} are consistent with ESR³ measurements. The

core-orbital energies in Table V, when compared with the free-atom core levels in parenthesis, are also in semiquantitative agreement with chemical shift data⁴.

In Table VII we have listed our calculated results for the distribution of electronic charge in the sulfate molecule. A comparison of initial and final SCF charge distributions for both choices of $X\alpha$ exchange parameter suggests a net transfer of approximately one unit of electronic charge from the sulfur atom to the four oxygen atoms. A net charge of between +0.4 and +0.5 is found in the sulfur sphere.

As we mentioned earlier, a number of molecular-orbital calculations, by ab initio, approximate, and semiempirical LCAO techniques, have already been published for the sulfate ion^{5,9}. These results are summarized in Tables VIII and IX. It is difficult for us to assess the significance of the latter work, because the results of the various LCAO applications are inconsistent with one another, both with respect to magnitudes and orderings of orbital energies, and with respect to the net charge on the sulfur atom. Our calculations by the SCF-SW method (see Table V) lead to an ordering of occupied orbital energies which is consistent with the ordering obtained by the ab initio SCF-LCAO method⁵ for a limited Gaussian basis set which included sulfur d-orbitals (see column 3 of Table VIII). Our calculation also effectively included sulfur d-orbitals, but through the $l=2$ component of the partial-wave expansion [see Eq. (3)] of the sulfur wavefunction. The core orbitals which we have calculated and listed in Table V also agree fairly well with those listed for the ab initio SCF-LCAO method⁵ in Table I. Core orbitals have not been determined in the other LCAO work. It is obvious from a comparison of Tables V and VIII that the SCF-SW model leads to more stable valence orbitals for SO_4^{2-} than do any of the LCAO calculations. The positive occupied orbital energies resulting from both the ab initio⁵ and approximate⁶ SCF-LCAO applications seem to be a peculiar feature of adopting limited atomic-orbital basis sets. It is doubtful that such energies have much physical significance, since one expects the orbitals to be stabilized by the crystal environment. Although the semiempirical, WH-LCAO method⁹ leads to occupied orbitals which all have negative energy, the ordering of these orbitals is inconsistent with the ordering obtained in our calculations and in the SCF-LCAO^{5,6} work.

Similar SCF-SW calculations are in progress on other polyatomic molecules, e. g., transition-metal complexes such as MnO_4^- and $\text{Fe}(\text{CN})_6^{4-}$. Work on these systems as well as further studies of sulfur and chlorine oxy-anions will be discussed in later reports and publications. The results of the present investigation suggest that the scattered-wave model is indeed a practical and reliable new approach to calculating the theoretical electronic structures of complex molecules where more conventional methods of quantum chemistry are difficult and costly to implement.

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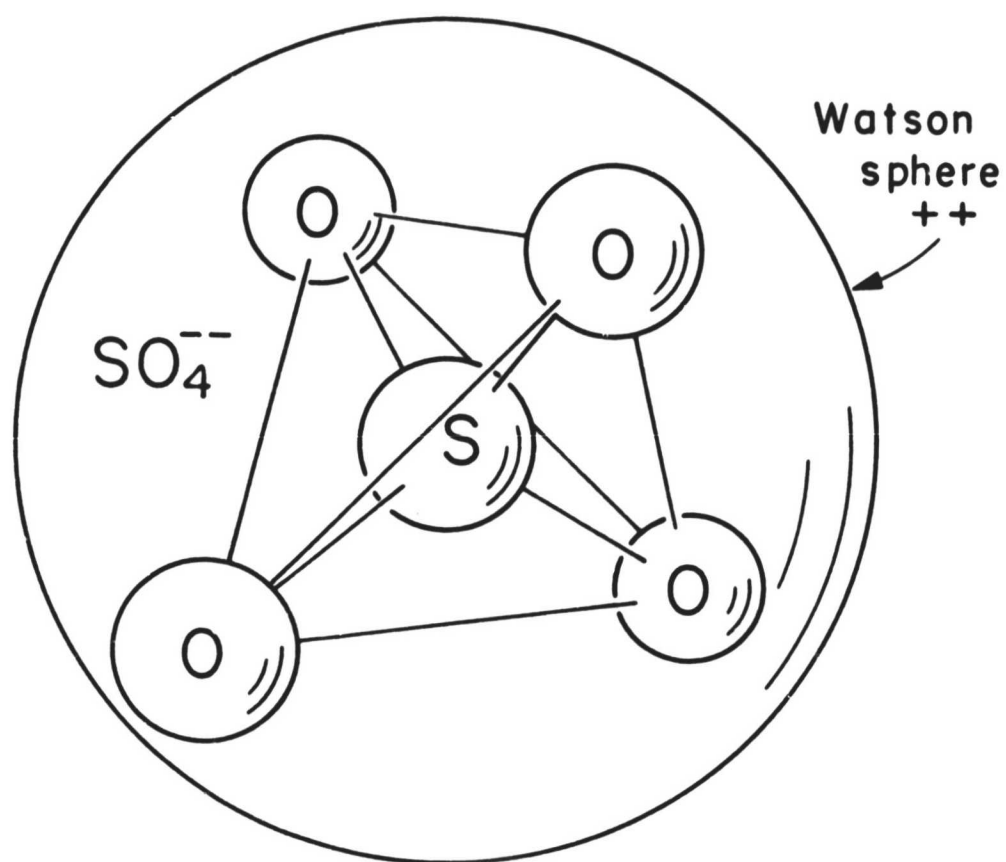


Fig. 1. Sulfate molecular ion

Table I. Initial and SCF molecular potentials around sulfur atom in SO_4^{2-} for $X\alpha$ exchange parameter $\alpha = 1$ and for Watson sphere of charge + 2

Mesh Point	Radius (au)	Initial Potential (Rydbergs)	SCF Potential (Rydbergs)
1	0.17567400-C2	-0.1813537D 05	-0.1813691D 05
5	0.8783699D-02	-0.3560731D 04	-0.3562274D 04
9	0.1581066D-01	-0.1940319D 04	-0.1941862D 04
13	0.2283762D-01	-0.1317004D 04	-0.1318547D 04
17	0.2986459D-01	-0.9872496D 03	-0.9887939D 03
21	0.3864827D-01	-0.7441401D 03	-0.7456855D 03
25	0.5270219D-01	-0.5246935D 03	-0.5262409D 03
29	0.6675611D-01	-0.3986323D 03	-0.4001804D 03
33	0.8081003D-01	-0.3171820D 03	-0.3187302D 03
37	0.9486395D-01	-0.2604566D 03	-0.2620043D 03
41	0.1124313D 00	-0.2101406D 03	-0.2116867D 03
45	0.1405392D 00	-0.1569388D 03	-0.1584816D 03
49	0.1686470D 00	-0.1225757D 03	-0.1241156D 03
53	0.1967548D 00	-0.9884327D 02	-0.1003810D 03
57	0.2248627D 00	-0.8160489D 02	-0.8314047D 02
61	0.2593575D 00	-0.6583152D 02	-0.6736398D 02
65	0.3162132D 00	-0.4870080D 02	-0.5022738D 02
69	0.3724288D 00	-0.3745376D 02	-0.3897399D 02
73	0.4286445D 00	-0.2966518D 02	-0.3117904D 02
77	0.4848602D 00	-0.2404042D 02	-0.2554814D 02
81	0.5551298D 00	-0.1894640D 02	-0.2044696D 02
85	0.6675611D 00	-0.1349295D 02	-0.1498312D 02
89	0.7799924D 00	-0.9996809D 01	-0.1147462D 02
93	0.8924238D 00	-0.7684194D 01	-0.9140981D 01
97	0.1004855D 01	-0.6110215D 01	-0.7534110D 01
101	0.1145394D 01	-0.4758054D 01	-0.6125307D 01
105	0.1370257D 01	-0.3398186D 01	-0.4632259D 01
109	0.1595120D 01	-0.2643424D 01	-0.3670972D 01

Table II. Initial and SCF molecular potentials around oxygen atom in SO_4^{2-} for $X\alpha$ exchange parameter $\alpha = 1$ and for Watson sphere of charge + 2

Mesh Point	Radius (au)	Initial Potential (Rydbergs)	SCF Potential (Rydbergs)
1	0.2213353D-C2	-0.7203131D 04	-0.7203020D 04
5	0.1106677D-01	-0.1419274D 04	-0.1419163D 04
9	0.1992018D-01	-0.7761358D 03	-0.7760252D 03
13	0.2877359D-01	-0.5285902D 03	-0.5284797D 03
17	0.3762701D-01	-0.3974847D 03	-0.3973743D 03
21	0.4869377D-01	-0.3006669D 03	-0.3005567D 03
25	0.6640060D-01	-0.2130376D 03	-0.2129279D 03
29	0.8410743D-01	-0.1625334D 03	-0.1624248D 03
33	0.1018143D 00	-0.1248181D 03	-0.1297112D 03
37	0.1195211D 00	-0.1059894D 03	-0.1068853D 03
41	0.1416546D 00	-0.8669632D 02	-0.8659699D 02
45	0.1770683D 00	-0.6513222D 02	-0.6504465D 02
49	0.2124819D 00	-0.5105745D 02	-0.5098730D 02
53	0.2478956D 00	-0.4122114D 02	-0.4117443D 02
57	0.2833092D 00	-0.3401775D 02	-0.3399591D 02
61	0.3275763D 00	-0.2741223D 02	-0.2743532D 02
65	0.3984036D 00	-0.2028447D 02	-0.2037225D 02
69	0.4692309D 00	-0.1564731D 02	-0.1578988D 02
73	0.5400582D 00	-0.1242743D 02	-0.1261885D 02
77	0.6108855D 00	-0.1007486D 02	-0.1031444D 02
81	0.6994197D 00	-0.7918274D 01	-0.8219119D 01
85	0.8410743D 00	-0.5600533D 01	-0.5997790D 01
89	0.9827289D 00	-0.4129217D 01	-0.4611382D 01
93	0.1124383D 01	-0.3166108D 01	-0.3712156D 01
97	0.1266038D 01	-0.2525044D 01	-0.3107091D 01

Table III. Initial and SCF molecular potentials in outeratomic region of SO_4^{2-} for $X\alpha$ exchange parameter $\alpha=1$ and for Watson sphere of charge +2

Mesh Point	Radius (au)	Initial Potential (Rydbergs)	SCF Potential (Rydbergs)
1	0.34528310 C1	-0.14675150 01	-0.93350690 00
5	0.40194500 C1	-0.88434340 00	-0.60799590 00
9	0.45860690 C1	-0.52117620 00	-0.36273670 00
13	0.51526870 C1	-0.32404210 00	-0.22240970 00
17	0.58609600 C1	-0.18872950 00	-0.12352660 00
21	0.69941970 C1	-0.86438870-01	-0.50034050-01
25	0.81274340 C1	-0.42299390-01	-0.21018860-01
29	0.92606710 C1	-0.21594520-01	-0.91447710-02
33	0.10393910 C2	-0.11304340-01	-0.41455890-02
37	0.11810450 C2	-0.51381010-02	-0.16750520-02
41	0.14076930 C2	-0.14998060-02	-0.53718600-03
45	0.16343400 C2	-0.44252510-03	-0.28188750-03
49	0.18609870 C2	-0.37728980-04	-0.20541500-03
53	0.20876350 C2	-0.53904460-04	-0.17733070-03
57	0.23709440 C2	-0.52989150-04	-0.15460380-03
61	0.28242390 C2	0.71819770-05	-0.12817510-03
65	0.32775340 C2	0.11143840-04	-0.11029310-03
69	0.37308280 C2	0.97884330-05	-0.96892600-04
73	0.41841230 C2	0.87308050-05	-0.86395470-04
77	0.47507420 C2	0.28548830-05	-0.76242210-04
81	0.56573310 C2	0.18975100-05	-0.64039990-04
85	0.65639210 C2	0.12255560-05	-0.55207780-04
89	0.74705100 C2	0.48890450-05	-0.48388870-04
93	0.83771000 C2	0.43609090-05	-0.43152080-04
97	0.95103370 C2	0.11755610-05	-0.38093450-04
101	0.11323520 C3	0.98783620-06	-0.21992710-04
105	0.13136690 C3	0.85108530-06	-0.27577830-04
109	0.14949870 C3	0.74765450-06	-0.24233090-04
113	0.16763050 C3	0.66625130-06	-0.21611930-04

Table IV. Various physical parameters used in SCF-SW calculation on SO_4^{2-} for $X\alpha$ exchange parameter $\alpha = 1$ and for a Watson sphere of charge + 2.

Equilibrium sulfur-oxygen distance ^a	= 2.72 au (1.44 Å)
Sulfur sphere radius	= 1.51 au
Oxygen sphere radius	= 1.21 au
Watson sphere radius	= 3.93 au
Initial average interatomic potential	= -1.203 Rydberg
SCF average interatomic potential	= -1.350 Rydberg

^a See Ref. 12.

Table V. Occupied molecular-orbital energies for SO_4^{2-} calculated by the SCF-SW method for two choices of $X\alpha$ exchange parameter and for a Watson sphere of charge + 2. Quantities in parenthesis are Hartree-Fock-Slater free-atom energy levels^a. Energies are in Hartrees.

Orbital Symmetry	Valence Orbitals	Core Orbitals	Valence Orbitals
	$\alpha = 1$	$\alpha = 1$	$\alpha = 2/3$
1T ₁	-0.490		-0.292
5T ₂	-0.510		-0.317
1E	-0.556		-0.369
4T ₂	-0.690		-0.502
5A ₁	-0.804		-0.596
3T ₂	-1.106		-0.890
4A ₁	-1.254		-1.046
2T ₂ (S2p)		-6.748 (-6.274)	
3A ₁ (S2s)		-8.688 (-8.215)	
1T ₂ (O1s)		-19.511 (-19.657)	
2A ₁ (O1s)		-19.511 (-19.657)	
1A ₁ (S1s)		-90.389 (-89.904)	

^a See Ref. 17. No Latter correction used.

Table VI. Comparison of occupied valence molecular-orbital energies of SO_4^{2-} calculated by the NSCF-SW method for a Watson sphere of charge +2 with those determined for a Watson sphere of charge +1. $X\alpha$ exchange parameter $\alpha = 1$. Energies are in Hartrees.

Orbital Symmetry	Charge +2	Charge +1
T_1	-0.359	-0.122
T_2	-0.371	-0.136
E	-0.427	-0.192
T_2	-0.518	-0.290
A_1	-0.574	-0.348
T_2	-0.938	-0.700
A_1	-1.027	-0.776

Table VII. Distribution of electronic charge in SO_4^{2-} for initial and final SCF-SW potentials. A Watson sphere of charge +2 is used. Two values of $X\alpha$ exchange parameter are considered.

Region of Molecule	Initial Charge		SCF Charge	
	$\alpha = 1$	$\alpha = 2/3$	$\alpha = 1$	$\alpha = 2/3$
Sulfur sphere	-12.9	-12.6	-12.4	-12.2
Oxygen sphere	-6.0	-5.7	-6.4	-6.1
Interatomic region	-10.6	-12.5	-11.3	-12.3
Outeratomic region	-2.5	-3.2	-0.8	-1.2

Table VIII. Occupied molecular-orbital energies of SO_4^{2-} calculated by various LCAO methods. Column headings indicate atomic-orbital basis functions adopted for the sulfur atom. Energies are in Hartrees.

Orbital Symmetry	Ab Initio SCF-LCAO ^a		Approximate SCF-LCAO ^b		SCCEI-LCAO ^c		WH-LCAO ^d	
	s, p	s, p, d	s, p	s, p	s, p	s, p, d	s, p, d	s, p, d
1T ₁	+0.2661	+0.112	+0.152	-0.070	+0.014	-0.323		
5T ₂	+0.2702	+0.0968	+0.172	-0.068	-0.044	-0.306		
1E	+0.2037	+0.0044	+0.093	-0.109	-0.076	-0.352		
4T ₂	-0.0291	-0.1366	-0.216	-0.259	-0.173	-0.426		
5A ₁	-0.1225	-0.2301	-0.276	-0.293	-0.214	-0.294		
3T ₂	-0.6842	-0.7922	-0.634	-0.805	-0.663	-0.991		
4A ₁	-0.9332	-1.0032	-0.848	-1.12	-0.856	-1.138		
2T ₂	-6.2235	-6.2709						
3A ₁	-8.5454	-8.5863						
1T ₂	-19.4377	-19.7580						
2A ₁	-19.4378	-19.7573						
1A ₁	-90.5899	-90.6766						

^a See Ref. 5.

^b See Ref. 6.

^c See Ref. 7.

^d See Ref. 9.

Table IX. Net electronic charge on sulfur ion in SO_4^{2-} calculated by various LCAO molecular-orbital methods.

Method	Sulfur Basis	Charge
Ab initio SCF-LCAO ^a	s, p s, p, d	+1.42 -0.55
Approx. SCF-LCAO ^b	s, p	+1.79
SCCEI-LCAO ^c	s, p s, p, d	+2.16 +1.18
CNDO-LCAO ^d	s, p s, p, d	+1.15 +0.51
WH-LCAO ^e	s, p, d	-0.09

^a See Ref. 5

^b See Ref. 6

^c See Ref. 7

^d See Ref. 8

^e See Ref. 9.

COMPUTATIONAL ASPECTS OF THE APW METHOD

Peter D. DeCicco

Now that we have reached the end of the first eighth of a century of calculation of energy bands on large scale computers by the APW (augmented plane wave) method, and find ourselves in a period of diminished financial support for computation, it is well to consider the efficiency with which we apply this method. Since the majority of past and current calculations involve crystals with cubic lattices, special consideration of this case is worth while. The reason for giving some special consideration to this case is found in the fact that the APW matrix elements depend strongly on the magnitudes of numerous wave vectors and it is only in the cubic lattices that the square magnitudes of reciprocal lattice vectors and the dot products of pairs of wave vectors are equal to a constant times an integer.

In the APW method one computes the determinant of a matrix M_{ij} and finds the zeros of this determinant. The matrix element M_{ij} of $(H-E)$ between APW's with wave vectors \vec{k}_i and \vec{k}_j is given by

$$\begin{aligned} \Omega M_{ij} = & [\vec{k}_i \cdot \vec{k}_j - E] \left[\Omega \delta_{ij} - \sum_{n=1}^N 4\pi R_{sn}^2 \frac{j_1(|\vec{k}_i - \vec{k}_j| R_{sn})}{|\vec{k}_i - \vec{k}_j|} e^{i(\vec{k}_j - \vec{k}_i) \cdot \vec{r}_n} \right] \\ & \times 4\pi R_{sn}^2 u'_{n\ell, E}(R_{sn}) / u_{n\ell, E}(R_{sn}) \\ & + v(\vec{k}_i - \vec{k}_j) \end{aligned} \quad (1)$$

where Ω is the volume of the unit cell which contains N atoms at positions \vec{r}_n . The function $U_{n\ell, E}(r)$ is the r -dependent part of the ℓ 'th partial wave of the Bloch function

and $v(\vec{K})$ is the Fourier coefficient of the "non-muffin tin" potential corresponding to the reciprocal lattice vector \vec{K} . (For Eq. (1) to be rigorous, one must require the "non-muffin tin" potential to be zero inside the APW spheres).

In most APW calculations one finds the zeros of the secular equation at a fixed point in the Brillouin zone (BZ) by calculating the determinant of (H-E) as a function of E and then employing an inverse interpolation scheme. The most repeated computational operations are therefore the setting up of the APW matrix and the calculations of its determinant using the technique of triangularization. The amount of computational effort involved in the evaluation of the determinant given the matrix is fairly well represented by the number of multiplication operations involved which is approximately $K^3/3$ for a $K \times K$ matrix. To see the computation involved in setting up the matrix M_{ij} ; let

$$F_{ij} = \Omega \delta_{ij} - \sum_{n=1}^N 4\pi R_{sn}^2 \frac{j_1(|\vec{k}_i - \vec{k}_j| R_{sn})}{|\vec{k}_i - \vec{k}_j|} e^{i(\vec{k}_j - \vec{k}_i) \cdot \vec{r}_n} \quad (2)$$

and

$$G_{ij\ell n} \equiv e^{i(\vec{k}_j - \vec{k}_i) \cdot \vec{r}_n} (2\ell + 1) P_\ell \left(\frac{\vec{k}_i \cdot \vec{k}_j}{|\vec{k}_i| |\vec{k}_j|} \right) j_\ell(k_i R_{sn}) j_\ell(k_j R_{sn}) \quad (3)$$

Then

$$\begin{aligned} \Omega M_{ij} &= (\vec{k}_i \cdot \vec{k}_j) F_{ij} - E \times F_{ij} \\ &+ \sum_{n=1}^N \sum_{\ell=0}^{\infty} G_{ij\ell n} \times [4\pi R_{sn}^2 u'_{n\ell, E}(R_{sn}) / u_{n\ell, E}(R_{sn})] \\ &+ v(\vec{k}_i - \vec{k}_j) \end{aligned} \quad (4)$$

where the (\times) signs indicate the multiplication which must be performed for each value of E. Since M_{ij} is hermitian, the number of distinct matrix elements is approximately $K^2/2$ and the number of multiplications required to set up the matrix is then approximately $(K^2/2)[N(\ell_{\max} + 1)]$ where $\ell \leq \ell_{\max}$. Thus the amount of computation involved in setting up the APW matrix should be greater than that involved in triangularization for $K \leq 3N(\ell_{\max} + 1)/2$. Thus for one atom/unit cell and ℓ -values the set-up time is greater than the triangularization time until $K \approx 18$. (This result also applies when the basis functions are symmetrized APW's rather than single APW's.) A closer examination would probably show that the comparative set-up time is even greater because it involves the 3 or 4 dimensional array $G_{ij\ell n}$.

[It has been shown that a considerable amount of the set-up time¹ as well as computer storage can be saved by an approach based on the nearly linear character of the logarithmic derivatives for the larger ℓ -values.^{2,3}]

Suppose that we evaluate the secular determinant 100 times in the course of finding 10 energy levels at a general point in the BZ with $K = 50$ and $l_{\max} = 9$. The following numbers represent estimates of the numbers of multiplications involved in various parts of the calculation:

$$\begin{array}{ll} F_{ij} : 4 \times 10^4 & u' / u : 2 \times 10^5 \\ P_l : 2.5 \times 10^4 & \text{SETUP } M_{ij} : 1.3 \times 10^6 \\ j_l : 0.5 \times 10^4 & \text{Triangularize } M_{ij} : 4 \times 10^6 \end{array}$$

Of the logarithmic derivatives u'/u it is assumed that 80 were previously tabulated on a fixed mesh in energy good for all points in the BZ so that 2×10^5 is the estimated number of multiplications needed to obtain u'/u at 20 additional energies chosen so as to "zero in" on the eigen energies. The reason why the quantities F_{ij} , P_l and j_l require relatively little computation is that they are calculated only once and are reused 100 times being stored in the arrays F_{ij} and G_{ijln} .

As long as the secular determinant is evaluated many times at each point in the BZ, it is clear from the above numbers that the computational effort involved for the quantities F_{ij} , P_l and j_l is of little importance. If, however, one wishes to search for zeros of the secular determinant at fixed E (say E_F) then it would appear that the computational effort required for each value of the secular determinant will more than double. Let us therefore see how this computational effort can be reduced.

The quantity F_{ij} does not depend on \vec{k}_i and \vec{k}_j separately but rather it depends on the reciprocal lattice vector $\vec{k}_i - \vec{k}_j$ whose magnitude is clearly less than or equal to twice that of the largest APW wave vector. If we assume 50 APW's per atom, $K = 50N$, then the number of such reciprocal lattice vectors is approximately $8K = 400N$. Thus we can calculate and store the 400N or fewer values of F_{ij} once for the entire calculation since F_{ij} is independent of the point in the BZ at which we are calculating. In general the reciprocal lattice vector $\vec{K} = \vec{k}_i - \vec{k}_j$ is specified by a triplet of integers which specify this vector in terms of 3 convenient translations of the reciprocal lattice. These integers can then serve as the indices of a 3 dimensional array $F(\vec{K})$. In cubic systems the situation is further simplified by the fact that $F(\vec{K})$ is trivially related to a quantity which depends only on the magnitude of \vec{K} . The square magnitude of \vec{K} in the appropriate units is then an integer which can serve as an index of a one or two dimensional array containing the quantity $4\pi R_{sn}^2 J_1(|\vec{K}|R_{sn})/|\vec{K}|$. The number of entries in this array would then be approximately $(400N)^{3/2} \approx 54N^{3/2}$.

The amount of computational effort required for $j_l(k_i R_{sn})$ is relatively small already because only one wave vector at a time is involved. However, in calculating these Bessel functions by downward recursion followed by normalization it is customary

to obtain $j_{\ell \max}$ to 8 figure accuracy or more while $j_{\ell \max + 1}$ is assumed in effect to be zero. If instead we required only 2-figure accuracy for $j_{\ell \max}$ the amount of computation would be roughly cut in half. To reduce the amount of computation further we could, in cubic systems at least, calculate and store all the j_{ℓ} 's which would be needed, given a mesh of points in the BZ. For example, in the CsCl structure with 8,000 points in the first BZ and 62 APW's per atom, the maximum value of $(\bar{k}_i)^2$ in the appropriate units (i.e., $(\pi/10a)^2$) is 3600 so that 36,000 storage location would suffice. Alternatively one could tabulate the 7200 values j_0 and j_1 and then calculate the j_{ℓ} 's for $\ell \geq 2$ by upward recursion at least for those \bar{k}_i lying outside the 1st BZ. (In the case of small $|\bar{k}_i|$, the downward recursion might be needed to get sufficient accuracy.)

Since the Legendre polynomial P_{ℓ} is generated by upward recursion requiring two multiplications per ℓ -value, the computation required is roughly twice that for the setting up of M_{ij} in the case of one atom/unit cell and relatively less with more atoms since the argument of P_{ℓ} does not depend on the atomic coordinate or sphere radii. Since the feasibility of the APW method is often space-limited by the size of the array $G_{ij\ell n}$, it will sometimes be better not to generate this array at all but rather calculate the Legendre polynomials each time M_{ij} is set up. If it is necessary to use even less storage space one might delete the storage of F_{ij} as indicated above as well as the storage of $\bar{k}_i \cdot \bar{k}_j \cdot F_{ij}$ noting that in cubic systems, the dot product $\bar{k}_i \cdot \bar{k}_j$ can be calculated using integer arithmetic. Furthermore, in cubic systems for which the potential outside the APW spheres is a lattice sum of spherical functions, $v(\bar{k}_i - \bar{k}_j)$ can be a one-dimensional array indexed by the squares magnitude of $(\bar{k}_i - \bar{k}_j)$ in the appropriate units. In the case of minimum storage of arrays, equation (4) becomes

$$\begin{aligned} \Omega m_{ij} &= (\bar{k}_i \cdot \bar{k}_j) \times F_{ij} - E \times F_{ij} \\ &+ \sum_{n=1}^N \sum_{\ell=0}^{\infty} e^{i(\bar{k}_j - \bar{k}_i) \cdot r_n} \times P_{\ell} \left(\frac{(\bar{k}_i \cdot \bar{k}_j)}{|\bar{k}_i| |\bar{k}_j|} \right) \times j_{\ell}(k_i R_{sn}) \\ &\times j_{\ell}(k_j R_{sn}) \times [4\pi (2\ell + 1) u'_{n\ell, E}(R_{sn}) / u_{n\ell, E}(R_{sn})] \\ &+ v(\bar{k}_i - \bar{k}_j) \end{aligned} \quad (5)$$

so that the set-up computation is about as long as the triangularization time for 50×50 matrix. However, the set-up time can be considered reduced by effectively making the sum on ℓ shorter as noted above.² Let us now consider the principal applications of the APW method under two categories:

- I. Calculations involving many energies and relatively few points in the BZ.
- II. Calculations involving many points in the BZ and relatively few energies.

Category I

1. Band calculations along symmetry directions using group theory.
2. Iterative self-consistent field calculations (including approximate determination of the Fermi energy).
3. Charge, spin and momentum density calculations.
4. Optical properties such as dielectric functions and photoemission (including momentum matrix elements).

Category II

1. Fermi Surface
2. Density of states at and near the Fermi Surface
3. De Haas - van Alphen and cyclotron resonance periods

In the case of materials with one or two atoms per unit cell, the relatively few points in the BZ for Category I calculations typically involves (or should involve) a mesh of from about 100 to about 1000 or perhaps 4000 points in the entire BZ. A Category II calculation involving comparable expense would involve roughly from 4000 to 2×10^5 points in the BZ at which the APW secular determinant would be evaluated. Since however, large regions of the BZ may be free of states in the energy interval of interest in Category II, the corresponding meshes in the BZ might well contain 2×10^4 to 2×10^6 points in the BZ.

From the above discussion it appears that the computationally most significant part of an APW calculation is or should be the triangularization of the (H-E) matrix. This fact supports the following suggestion for future APW calculations: Since the secular determinant $D(E, \vec{k})$ for a given E, \vec{k} represents a considerable amount of computational effort it would be worth-while to store the values of $D(E, \vec{k})$. In particular, one might consider the case of \vec{k} confined to a plane perpendicular to a symmetry axis. The solution of the secular equation for various values of E would then give a family of contours of constant energy in the plane useful for comparison with cyclotron resonance and de Haas-van Alphen measurements. For a fixed value of E , the function $D(E, \vec{k})$ is probably more easily interpolated with respect to \vec{k} than is the multi-valued function $E(\vec{k})$. Thus in future applications of the APW method it would be well to consider the problem of how to interpolate the function $D(E, \vec{k})$ onto a fine mesh of points in the BZ. In order to make $D(E, \vec{k})$ meaningful and a smooth function of \vec{k} , it would be necessary to hold fixed the set of reciprocal lattice vectors \vec{K}_i which specify the APW basis functions having wave vectors $\vec{k}_i = \vec{k} + \vec{K}_i$. If it is found feasible to interpolate $D(E, \vec{k})$ on \vec{k} as well as E within limited ranges of energy as is now done to find $E(\vec{k})$ at fixed \vec{k} , then the calculations in Category II above should be quite straight forward.

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1. John W. D. Connolly, M. I. T. SSMTG Semi-Annual Progress Report No. 72, 26 (1970).
2. The author is grateful to Professor P. DeCicco for pointing out this omission.
3. L. Kleinman and R. Shurtleff, Phys. Rev. 188, 1111 (1969).

A NON-SPHERICAL MODIFICATION TO THE AUGMENTED PLANE
WAVE METHOD II. Erratum and Addendum

John W. D. Connolly

In the last issue of the Semi-Annual Progress Report¹, we set forth a proposal for a modification of the A. P. W. method for the case of a non-spherical potential inside the muffin-tin spheres. The modified basis function took the form;

$$\phi_{\vec{k}}(\vec{r}) = \begin{cases} e^{i\vec{k} \cdot \vec{r}} & \text{outside} \\ \frac{1}{r} \sum_{\ell m} a_{\ell m} P_{\ell m}(r) Y_{\ell m}(\hat{r}) & \text{inside} \end{cases}$$

where the

$$a_{\ell m} = 4\pi R i^{\ell} j_{\ell}(kR) Y_{\ell m}(\hat{k}) / P_{\ell m}(R)$$

are chosen such that $\phi_{\vec{k}}$ is continuous at the sphere radius R and the radial functions $P_{\ell m}$ satisfy a set of coupled differential equations;

$$-(P_{\ell m})'' + \left[\frac{\ell(\ell+1)}{V^2} - E + V_0 \right] P_{\ell m} = - \sum_{\ell' m'} v_{\ell m; \ell' m'} P_{\ell' m'}$$

This led to a simple form of the matrix elements (Eq. (14) of Reference 1). However, there is a term which was inadvertently omitted from this equation² dependent on the coupling potentials $v_{\ell m; \ell' m'}$. Equation (14) should have the additional term;

28. NON-SPHERICAL MODIFICATION TO THE AUGMENTED PLANE WAVE METHOD

$$\sum_{\ell m, \ell' m'} \left\{ \xi_{\ell m \vec{g}}^* \xi_{\ell' m' \vec{g}'} - \xi_{\ell m \vec{g}}^* \xi_{\ell m \vec{g}'} \right\} \times \frac{1}{P_{\ell m}(R) P_{\ell' m'}(R)} \int_0^R P_{\ell m}(r) v_{\ell m; \ell' m'}(r) P_{\ell' m'}(r) dr$$

where the ξ - coefficients were defined as

$$\xi_{\ell m \vec{g}} = 4\pi i^\ell j_\ell(|\vec{k} + \vec{g}| R) Y_{\ell m}(\vec{k} + \vec{g})$$

The diagonal terms ($\ell m = \ell' m'$) in this summation vanish, but in the general (non-spherical) case, the off-diagonal terms do not. The solution of the set of coupled equations,

$$\frac{1}{r} \sum_{\ell m} P_{\ell m} Y_{\ell m}(\hat{r}),$$

represents the exact wave function for an electron in an unbounded (non-spherical) potential, i. e., in that case where $R \rightarrow \infty$. Therefore, one would expect that these modified APW's would be an especially suitable basis in the case where the radial functions are localized well inside the spheres.

Since the last Progress Report, a paper has appeared by Kleinman and Shurtleff³ in which a method similar to that proposed here is presented. They also suggest the use of a set of coupled differential equations to define the radial functions (cf. their Equation (13)). However, they were appalled by the number of coupled equations involved, i. e., if $\ell_{\max} = 12$, then there are $(\ell_{\max} + 1)^2 = 169$ equations. They therefore modified the APW basis to include only those ℓ -terms to the maximum valence value ($\ell_{\text{val}} = 2$ for transition elements). This was accomplished by allowing the plane wave $\exp(i\vec{k} \cdot \vec{r})$ to penetrate into the muffin-tin sphere in the APW basis function, equivalent to making

$$P_{\ell m}(r, E) = j_\ell(kr) \quad \text{for } \ell > \ell_{\text{val}}$$

in the ordinary APW basis, and leads to additional terms in the secular equation matrix elements. This complication we believe to be unnecessary for the following reasons;

(1) For satisfactory convergence of the energy eigenvalues, even in a transition element solid, it is not necessary to include terms up to $\ell = 12$. If one takes the summation up to $\ell = 5$ (corresponding to convergence of $< .005$ Ry.), then the number of coupled equations reduces to 36. For a non-transition element this reduction would be even greater.

(2) Symmetry will reduce the number of coupled equations further. For example, in a cubic solid, the first non-zero V_{LM} (cf. Equation (9) of Ref. 1) is for $L = 4$.

If we make the reasonable assumption that the $P_{\ell m}$ are unperturbed from their spherical values for $\ell > 2$, then the only coupling is among the $\ell = 2$ functions, and this can be removed by using cubic harmonics as has been noted³.

(3) Since the non-spherical perturbations are expected to have a small effect on the radial functions, we can use an iterative technique which essentially decouples the equations. If $P_{\ell m}^{(n)}$ represents the radial function after the n^{th} iteration, then we can solve the inhomogeneous equations:

$$(P_{\ell m}^{(n+1)})'' = g_{\ell m}(r) P_{\ell m}^{(n+1)} + \sum_{\ell' m' \neq \ell m} v_{\ell m; \ell' m'} P_{\ell' m'}^{(n)}$$

where

$$g_{\ell m}(r) = \frac{\ell(\ell+1)}{r^2} - E + V_0(r)$$

If the $n=0$ terms are set equal to the spherical solutions, then this set of equations should converge quickly. The Numerov integration method, currently used in most versions of the APW program, can also be used on this type of inhomogeneous equation, thereby taking advantage of the speed of this method and also minimizing the pain of re-programming. The Numerov method is usually applied to equations of the form;

$$P''(r) = g(r) P(r)$$

but it can also be used on equations of the form

$$P''(r) = g(r) P(r) + f(r)$$

In this latter case, the recursion relations for P becomes

$$P_{n+1} = (1 - h^2 g_{n+1} / 12)^{-1} [(2 + 5h^2 g_n / 6) P_n - (1 - h^2 g_{n-1} / 12) P_{n-1} + h^2 (f_{n+1} + 10f_n + f_{n-1}) / 12]$$

where only the last three terms have to be added in modifying the existing programs.

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References

1. John W. D. Connolly, M. I. T. SSMTG Semi-Annual Progress Report No. 72, 26 (1970).
2. The author is grateful to Professor P. DeCicco for pointing out this omission.
3. L. Kleinman and R. Shurtleff, Phys. Rev. 188, 1111 (1969).

INVARIANT OPERATORS I. CASIMIR INVARIANTS

Robert Gilmore

I. Introduction

There has been a great deal of interest in the invariant operators associated with a Lie group. These operators may be used to classify states belonging to an irreducible representation¹, to approximate spectra in atomic systems², and as models for Hamiltonians in nuclear systems³ and systems possessing phase transitions. Although the general properties of these invariant operators have been well-known for a long time^{1,4} and some have been constructed explicitly^{3,5,6}, they have not yet all been explicitly constructed for the simple classical Lie groups. Because of their widespread use, we feel that an explicit constructive determination of these operators is appropriate.

In the following sections, we construct the Casimir invariants for the unitary (A_n), symplectic (C_n), and orthogonal (B_n, D_n) groups. We also construct (some of) the invariants for non-semi-simple groups which may be constructed from semi-simple groups by Inonu-Wigner contraction.

II. Construction of Invariants

The Casimir invariants of a Lie algebra are functions of the generators which commute with all the generators. In short, they form a basis for the Lie algebra's universal enveloping algebra. Their general properties are well known^{1,4}:

1. They are symmetric homogeneous polynomial functions of the generators which are invariant under the automorphisms induced by the Weyl group of reflections.
2. The product of the orders of the n functionally independent and irreducible invariants of a simple rank n algebra is equal to the order of the Weyl group of reflections for that algebra.
3. On a compact algebra, the eigenvalue of the invariant \mathcal{C}_1 on an irreducible representation with highest weight \bar{M}^h is

$$\mathcal{C}_1(\bar{M}^h) = f_1(\bar{M}^h + \bar{R}) - f_1(\bar{R}) \quad (1)$$

Here f_1 consists of those terms in the polynomial invariant which contain only the mutually commuting generators H_i of the Cartan subalgebra, and \bar{R} is defined as usual:

$$\bar{R} = \frac{1}{2} \sum (\text{position roots}) \quad (2)$$

$f_1(\bar{H})$ are called the associated invariants.

4. The Jacobian $J(H) = \det \left\| \frac{\partial \mathcal{C}_i}{\partial H_j} \right\|$ is completely antisymmetric under the Weyl group.

We will make an explicit constructive determination of the invariants using the procedure outlined in steps 1'-4' below, then use observations 1-4 above to prove that the operators so constructed are in fact irreducible polynomial invariants.

1'. A faithful matrix representation of the generators X_α is determined:

$$X_\alpha \xrightarrow{\text{faithful}} M_\alpha \quad (3)$$

2'. The secular equation for the Lie algebra element $a^\alpha X_\alpha$, in this representation, is determined

$$\det \| a^\alpha M_\alpha - \lambda I \| = \sum \lambda^i f_i(a^\alpha) = 0 \quad (4)$$

3'. The symmetrized functions $f_i(M_\alpha)$, with the matrices M_α replacing arguments a^α , obey

$$[f_i(M_\alpha), M_\beta] = 0 \quad (5)$$

4'. The general polynomial invariants are then $f_i(X_\alpha)$, since they obey a commutation relation isomorphic to (5)

$$[f_i(X_\alpha), X_\beta] = 0 \quad (5')$$

III. Invariants of the Unitary Groups $U(n)$ (A_{n-1})

The generators of the group $U(n)$ are

$$\begin{aligned} U_i^i &= H_i \\ U_j^i &\cong E_{e_i - e_j} \quad i \neq j \\ [U_j^i, U_s^r] &= U_s^i \delta_j^r - U_j^r \delta_s^i \end{aligned} \quad (3)$$

A faithful $n \times n$ matrix representation of these generators is given by

$$U_j^i \rightarrow M_j^i : (M_j^i)_{rs} = \delta_{ir} \delta_{js} \quad (4)$$

The faithful matrix representative of the Lie algebra element $a_j^i U_j^i$ is

$$a_j^i U_j^i \rightarrow \| a_j^i \| \quad (5)$$

The determinant of this matrix is given by

$$\det \| a^i_j \| = \frac{\epsilon^{i_1 i_2 \dots i_n} a^{i_1}_{j_1} a^{i_2}_{j_2} \dots a^{i_n}_{j_n} \epsilon^{j_1 j_2 \dots j_n}}{n!} \quad (6)$$

The symbols $\epsilon^{i_1 \dots i_n}$, $\epsilon^{j_1 \dots j_n}$ are the usual Levi-Civita skew tensors

$$\epsilon^{j_1 j_2 \dots j_n} = \begin{array}{|c|} \hline j_1 \\ \hline j_2 \\ \hline \vdots \\ \hline j_n \\ \hline \end{array} \quad (7)$$

The secular equation of the matrix (5) is computed using the substitution

$$a^i_j \rightarrow a^i_j - \lambda \delta^i_j \quad (8)$$

The delta function serves to contract indices. The resulting secular equation is

$$\det \| a^i_j - \lambda I \| = \sum (-\lambda)^{n-r} f_r(a^i_j) \quad (9)$$

$$f_r(a^i_j) = \frac{\epsilon^{i_1 \dots i_r \ell_{r+1} \dots \ell_n} a^{i_1}_{j_1} \dots a^{i_r}_{j_r} \epsilon^{j_1 \dots j_r \ell_{r+1} \dots \ell_n}}{r! (n-r)!} \quad (9')$$

The corresponding invariants (neglecting an unimportant numerical factor) for the unitary groups $U(n)$, are

$$C_r^{U(n)}(U^i_j) = \epsilon^{i_1 \dots i_r \ell_{r+1} \dots \ell_n} U^{i_1}_{j_1} \dots U^{i_r}_{j_r} \epsilon^{j_1 \dots j_r \ell_{r+1} \dots \ell_n} \quad (10)$$

IV Invariants of the Symplectic Groups $US_p(2n): (\mathbb{C}_n)$

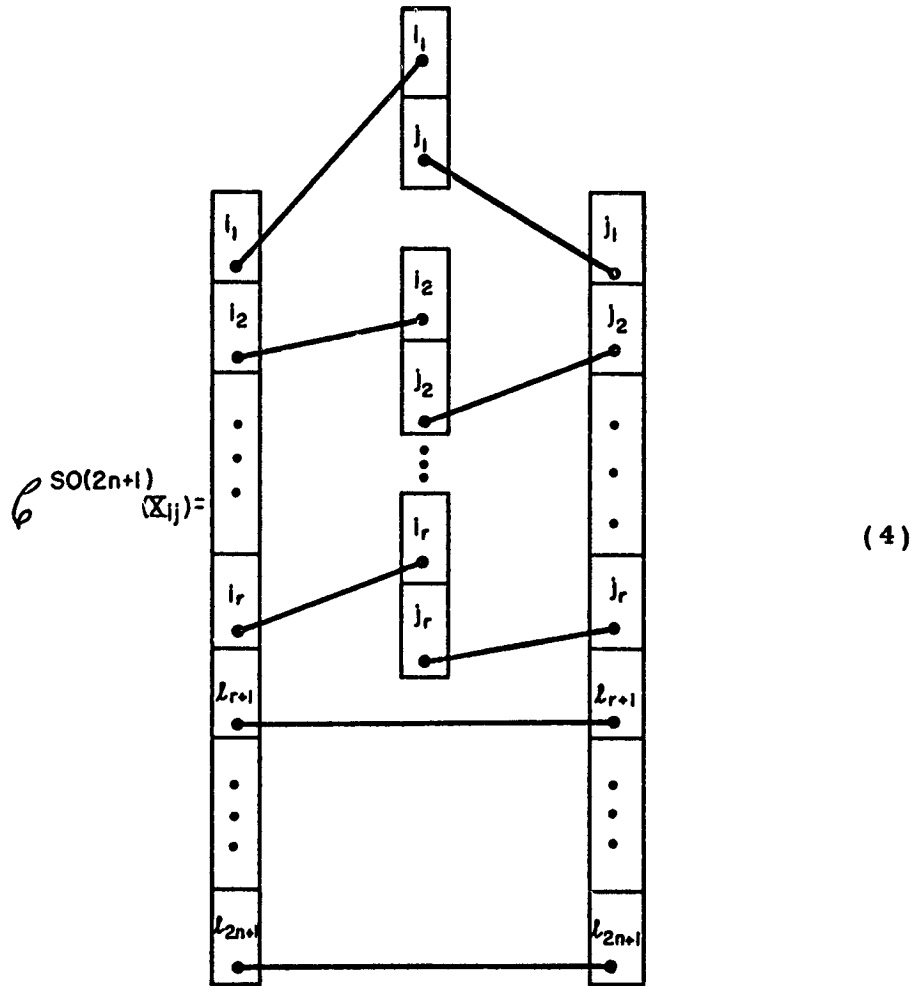
The group $US_p(2n)$ is a subgroup of $U(2n)$. This suggests the possibility that the invariants of $US_p(2n)$ might be 'subduced' from those of $U(2n)$. The

generators Z_j^i ($i, j = \pm 1, \pm 2, \dots, \pm n$) obey

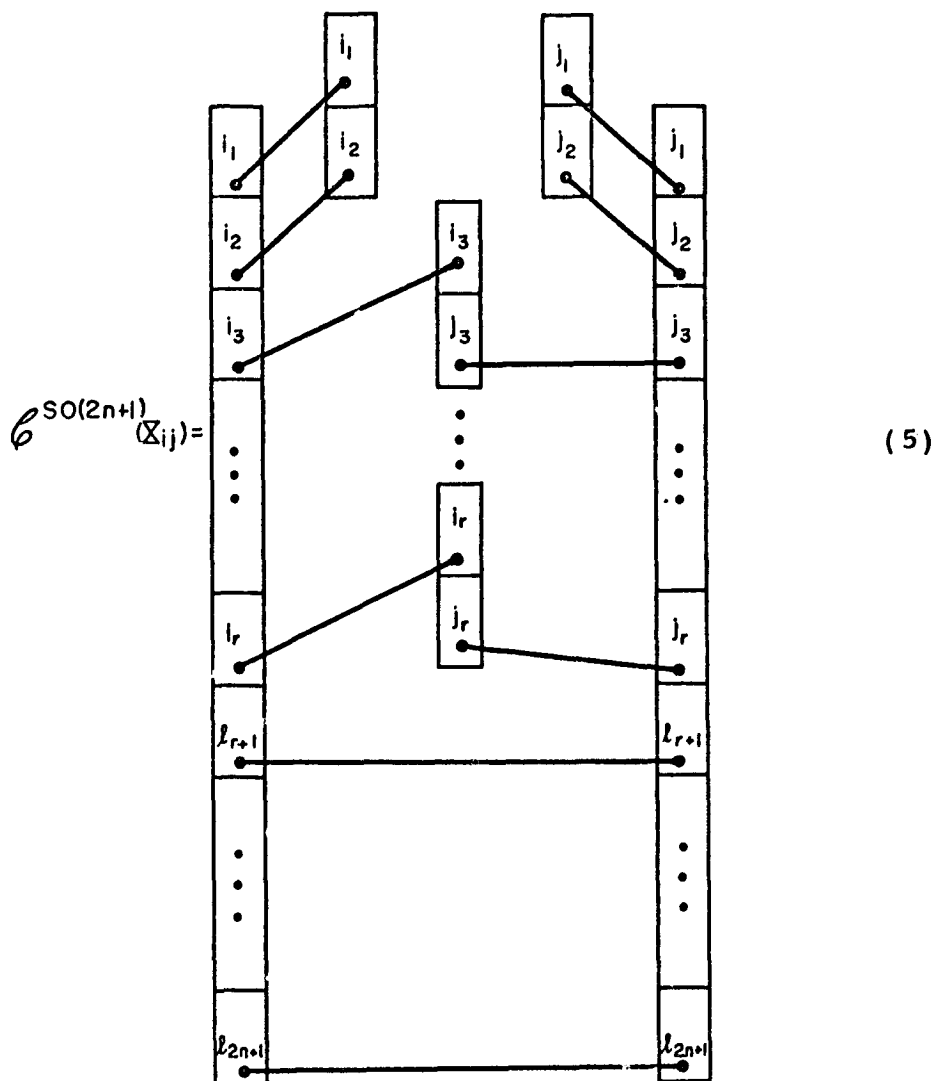
$$Z_j^i \Big|_{|r|} = H_r \tag{1}$$

$$Z_j^i = - \text{sign}(i) \text{sign}(j) Z_{-i}^{-j} \tag{2}$$

$$[Z_j^i, Z_s^r] = \text{sign}(jr) \left\{ Z_s^i \delta_{-j}^{-r} + Z_{-r}^{-j} \delta_i^s + Z_{-r}^i \delta_j^{-s} + Z_s^{-j} \delta_{-i}^r \right\} \tag{3}$$



Since $i_1 \neq j_1$, one of the other values of i is equal to j_1 . Without loss of generality, we can choose $i_2 = j_1$. Then the schematic contraction may be rearranged:



Proceeding by induction, we conclude

- 1) C_r vanishes if r is odd
- 2) The n invariants $C_r^{SO(2n+1)}$ of $SO(2n+1)$ ($r = 1, 2, \dots, n$) are

$$C_r^{SO(2n+1)}(X_{ij}) = \epsilon_{i_1 \dots i_{2r} l_{2r+1} \dots l_{2n+1}} X_{i_1 i_2} \dots X_{2r-1, 2r} \times \epsilon_{j_1 \dots j_{2r} l_{2r+1} \dots l_{2n+1}} X_{j_1 j_2} \dots X_{j_{2r-1}, j_{2r}} \quad (6)$$

$$\begin{array}{c}
 \begin{array}{|c|} \hline i_1 \\ \hline i_2 \\ \hline \vdots \\ \hline i_{2r-1} \\ \hline i_{2r} \\ \hline i_{2r+1} \\ \hline \vdots \\ \hline i_{2n+1} \\ \hline j_1 \\ \hline j_2 \\ \hline \vdots \\ \hline j_{2r-1} \\ \hline j_{2r} \\ \hline \end{array}
 \begin{array}{|c|} \hline i_1 \\ \hline i_2 \\ \hline \vdots \\ \hline i_{2r-1} \\ \hline i_{2r} \\ \hline i_{2r+1} \\ \hline \vdots \\ \hline i_{2n+1} \\ \hline j_1 \\ \hline j_2 \\ \hline \vdots \\ \hline j_{2r-1} \\ \hline j_{2r} \\ \hline \end{array}
 \end{array}
 \quad (6')$$

$\leftarrow \begin{matrix} SO(2n+1) \\ \varphi_r \end{matrix} (X_{ij}) =$

VI Invariants of the Orthogonal Groups $SO(2n) (D_n)$

The arguments of Sec. V for the algebras B_n may be repeated essentially verbatim for the algebras D_n . The only salient point is that $C_n^{SO(2n)}(X_{ij})$ is a perfect square, since there are no lines left to contract the skew tensors. The invariants $C_r^{SO(2n)}(X_{ij})$, $r = 1, 2, \dots, n-1$ are given by (V. 6), replacing l_{2n+1} by l_{2n} . The invariant $C_n^{SO(2n)}(X_{ij})$ is

$$C_n^{SO(2n)}(X_{ij}) = \epsilon^{i_1 i_2 \dots i_{2n-1} i_{2n}} X_{i_1 i_2} \dots X_{i_{2n-1} i_{2n}}. \quad (1)$$

$$\mathcal{C}_n^{SO(2n)}(\mathbb{X}_{ij}) = \begin{array}{|c|} \hline i_1 \\ \hline i_2 \\ \hline \vdots \\ \hline i_{2n-1} \\ \hline i_{2n} \\ \hline \end{array} = \begin{array}{|c|} \hline i_1 \\ \hline i_2 \\ \hline \square \\ \hline \vdots \\ \hline \square \\ \hline i_{2n-1} \\ \hline i_{2n} \\ \hline \end{array} \quad (1')$$

VII Irreducibility and Functional Independence

We observe that the operators given by expressions [III. 10, IV. 4, V. 6, VI. 1]

- 1) are symmetric homogeneous polynomials in the group generators
- 2) which commute with all the group generators
- 3) and are left invariant under automorphisms induced by the Weyl group.
- 4) The product of the orders of these invariants is in each case equal to the order of the appropriate Weyl group.
- 5) The number of invariants is equal to the rank of the algebra.

$SU(n) \cong A_{n-1}$ has $n-1$ invariants, since

$$C_1^{SU(n)}(U_j^i) = \sum_{i=1}^n H_i = 0 \quad (1)$$

These invariant operators fulfill observations (1) and (2), section II.

We also observe, from [III. 1 and III. 10], that the associated invariants* for the unitary groups are given by

$$f_k^{A_{n-1}}(\bar{H}) = \sum_{i_r \neq i_s} \prod_{r=1}^k H_{i_r} \quad k=1,2,\dots,n \quad (2)$$

The associated invariants for the algebras C_n, B_n, D_n can easily be determined from [IV. 1, IV. 4, V. 1, V. 6 and VI. 1]

$$f_k^{C_n, B_n, D_n}(\bar{H}) = \sum_{i_r \neq i_s} \prod_{r=1}^k H_{i_r}^2 \quad (k \neq n \text{ for } D_n)$$

$$f_n^{D_n}(\bar{H}) = \prod_{i=1}^n H_i \quad (3)$$

From (2) and (3) the value of the Jacobian $J(H) = \det \left\| \frac{\partial C_i}{\partial H_j} \right\|$ on any representation with highest weight \bar{M}^h may be determined:

$$\frac{J(\bar{M}^h + \bar{R})}{J(O + \bar{R})} = \dim \bar{M}^h \quad (4)$$

The invariants [III. 10, IV. 4, V. 6, VI. 1] or alternatively (2) and (3) therefore also satisfy observation (4), Sec. II. Therefore these invariants are the functionally independent irreducible polynomial invariants of the classical Lie groups.

The spectrum of these invariants on the compact real forms of these algebras has been determined⁸ using observation 3 of Sec. II.

VIII Invariants of Subgroups - A Caution

It is often possible to determine the invariants of a group \mathcal{G}' if it is embedded in a larger group \mathcal{G} whose invariants are known. Thus we were able to subduce the invariants of C_n, B_n and D_n using canonical embeddings. This technique may be used to suggest the structure of (subduced invariants), but these

* See above, Sec. II, observation 3.

operators may not belong to the center of the subgroup's universal enveloping algebra at all. In each case, the subduced operators must be shown to be invariant operators on the subgroups.

For example, $SO(3)$ has generators J_3, J_{\pm} :

$$\begin{aligned} [J_3, J_{\pm}] &= \pm J_{\pm} \\ [J_+, J_-] &= 2J_3 \end{aligned} \quad (1)$$

$$C_1^{SO(3)} = J_3^2 + \frac{1}{2}(J_+ J_- + J_- J_+) \quad (2)$$

The generators J_3, J_+ form a subalgebra of the original algebra. The 'invariant' of this algebra subduced from the well known Casimir invariant (2) is

$$C'_1(J_3, J_+) = J_3^2 \quad (3)$$

This is easily seen not to be an invariant of the subalgebra, for

$$[C'_1(J_3, J_+), J_+] = J_3 J_+ + J_+ J_3 \quad (4)$$

In fact, this particular algebra has no invariants at all.

IX Invariants of Contracted Groups

It is possible to form new group structures by the process of contraction^{8,9,10}. If the group \mathcal{G}' is a contraction of the group \mathcal{G} , then operators $C'_1(\bar{X}')$ may be subduced from the invariant operators $C_1(X)$ on \mathcal{G} . These operators $C'_1(X')$ may be or may not be invariant operators on \mathcal{G}' . If the contraction process used is the one proposed by Inonu and Wigner⁸, then operators subduced from invariants will remain invariant operators.

Example 1: The invariants of the group $SO(4)$ are

$$\begin{aligned} C_1^{SO(4)}(X) &= \sum_{i < j} X_{ij}^2 \\ C_2^{SO(4)}(X) &= X_{12}X_{34} + X_{23}X_{14} + X_{31}X_{24} \end{aligned} \quad (1)$$

Contracting with respect to the subalgebra $X_{ij} = J_k$ ($i, j, k = 1, 2, 3$) and defining

$$\begin{aligned} \lim_{\epsilon \rightarrow 0} \epsilon X_{i4} &= P_i \\ \lim_{\epsilon \rightarrow 0} \epsilon X_{ij} &= O \quad i, j = 1, 2, 3 \end{aligned} \quad (2)$$

we subduce the two invariants

$$\begin{aligned} e_1'(\bar{J}, \bar{P}) &= \lim_{\epsilon \rightarrow 0} \epsilon^2 C_1^{SO(4)}(X) \rightarrow \bar{P} \cdot \bar{P} \\ e_2'(\bar{J}, \bar{P}) &= \lim_{\epsilon \rightarrow 0} \epsilon C_2^{SO(4)}(X) \rightarrow \bar{J} \cdot \bar{P} \end{aligned} \quad (3)$$

Example 2: Either of the de Sitter groups $SO(+++ - \pm)$ may be contracted with respect to the $SO(+++ -)$ subgroup. The two invariants of the de Sitter groups are

$$\begin{aligned} C_1^{SO(5)}(X) &= \sum_{i < j} X_{ij}^2 \\ C_2^{SO(5)}(X) &= \sum V_i^2 \\ V_i &= \epsilon^{ijklm} X_{jk} X_{lm} \end{aligned} \quad i, j = 1, \dots, 5 \quad (4)$$

The generators are contracted by the following limiting process

$$\begin{aligned} \lim_{R \rightarrow \infty} \frac{1}{R} X_{\mu 5} &\rightarrow P_\mu = -\partial_\mu \\ \lim_{R \rightarrow \infty} \frac{1}{R} X_{\mu\nu} &\rightarrow O \quad \mu, \nu = 1, 2, 3, 4 \end{aligned} \quad (5)$$

The contracted invariants are

$$\begin{aligned} C_1^{IHLG}(X_{\mu\nu}, P_\lambda) &= \lim_{R \rightarrow \infty} \frac{1}{R^2} C_1^{SO(5)}(X) \rightarrow P_\mu^2 \\ C_2^{IHLG}(X_{\mu\nu}, P_\lambda) &= \lim_{R \rightarrow \infty} C_1^{SO(5)}(X) \rightarrow (W^\alpha)^2 \\ W^\alpha &= \lim_{R \rightarrow \infty} \frac{1}{R} V_\alpha \rightarrow \epsilon^{\alpha\mu\nu\lambda} X_{\mu\nu} P_\lambda \end{aligned} \quad (6)$$

These are the two well-known invariants of the Inhomogeneous Lorentz Group (IHLG).

Example 3: The Inhomogeneous Galilean Group (IHLG) may be contracted from the IHLG. It is the contraction of the IHLG with respect to the subgroup of rotations and time displacements, with generators $J_k = X_{ij} = x^i \partial_j - x^j \partial_i$ ($i, j, k = 1, 2, 3$) and $T = P_4 = -\partial_t$. The contracted generators⁸ are

$$\begin{aligned} \lim_{c \rightarrow \infty} \frac{1}{c} X_{i4} &= -t \partial_i = v_i \\ \lim_{c \rightarrow \infty} \frac{1}{c} P_i &= -\partial_i = p_i \end{aligned} \quad (7)$$

The contracted invariants are then

$$\begin{aligned} C_1^{\text{IHGG}}(\bar{J}, \bar{p}, \bar{v}, T) &= \lim_{c \rightarrow \infty} \frac{1}{c^2} C_1^{\text{IHLG}}(X_{\mu\nu}, P_\lambda) \rightarrow \bar{p} \cdot \bar{p} \\ C_2^{\text{IHGG}}(\bar{J}, \bar{p}, \bar{v}, T) &= \lim_{c \rightarrow \infty} \frac{1}{c^2} C_2^{\text{IHLG}}(X_{\mu\nu}, P_\lambda) \rightarrow (\bar{v} \times \bar{p}) \cdot (\bar{v} \times \bar{p}) \end{aligned} \quad (8)$$

It is clear from (7) that C_2^{IHGG} vanishes. The IHGG does have another invariant, though. It is

$$C_3^{\text{IHGG}}(\bar{J}, \bar{p}, \bar{v}, T) = \bar{J} \cdot \bar{p} \quad (9)$$

These three examples are physically useful cases in which invariants C_i of the group \mathcal{G} contract to invariants C_i' of the contracted group \mathcal{G}' , under Inonu-Wigner contraction. It is obvious, and apparent from example 3, that the contracted group may have additional invariants.

X Conclusion

The Casimir invariants for the simple classical Lie groups have been constructed. They are both irreducible and functionally independent. Their spectrum on any representation of a classical compact group has been determined. We have constructed invariants for non-semi-simple groups which may be constructed by Inonu-Wigner contraction of semi-simple groups. Several examples have been given.

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