SELECTED TOPICS ON THE ELECTRONIC STRUCTURE OF SMALL MOLECULES

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ABSTRACT

A systematic procedure is presented for constructing symmetrized functions of the coordinates of N fermion particles which may be used as trial wavefunctions in a quantum mechanical description of an N-electron molecular system. The functions are symmetrized with respect to the mathematical point group of operators which commute with the system's electronic Born-Oppenheimer Hamiltonian, as well as the permutation group. The procedure is particularly useful if the group of operators is non-Abelian, which results in multi-degenerate irreducible representations of the group. The procedure is essentially the Clebsch-Gordan geneological coupling method (which is well-known from its application to the coupling of angular momenta) applied to the finite groups which describe the symmetry operations of a molecule.

The coupling procedure is applied to the study of the electronic structure of several states of the diatomic molecule sulfur oxide. The advantage of the coupling procedure in this study is that it results in entirely real N-particle functions which are constructed from entirely real single-particle functions. Most other procedures which are capable of generating symmetrized functions of non-abelian groups require the use of or result in complex functions. The use of complex functions tends to be cumbersome from a computational point of view and should be avoided when possible.

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Also, a simple model is presented which provides insight into some of the electric and magnetic properties of small molecules. The probability distribution of the electrons in a molecule is approximated by that of a single particle moving in a three-dimensional anisotropic harmonic oscillator potential. Within this approximation the molecular electric polarizability, the magnetic susceptibility, and the magnetic shielding of a nuclear spin due to currents generated in the electron distribution by a magnetic field (the chemical shift) are computed using perturbation theory. The model exhibits Van Vleck paramagnetism for the last two properties. The predictions for the three properties provided by the model as applied to molecular hydrogen, H_2, are compared with experimental results.

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Dedication

To my wife, Mary, for her constant support.

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I. The Construction of Symmetrized N-particle Functions

A. Introduction

In quantum mechanics one is often confronted with the determination of eigenfunctions and corresponding eigenvalues of the time independent Schrödinger equation:

$$H\psi = E\psi \quad . \tag{IA.1}$$

The existence of any symmetry in the form of the Hamiltonian operator H can usually be exploited to facilitate the solution of (IA.1). Suppose, for example, there is an operator A which commutes with the Hamiltonian. Then it is well-known that functions may be found which simultaneously are eigenfunctions of both H and A. This fact may be used to help solve (IA.1) if it is easier to find eigenfunctions of A than H. One first solves for the eigenfunctions of A; denote by $\{\phi_i^a;\ i=1 \text{ to } g_a\}$ the g_a eigenfunctions of A with eigenvalue a. Since H and A commute, the eigenfunctions of H with eigenvalue a of A may be expressed as some linear combinations of the g_a eigenfunctions of A.

Consider now the slightly more complicated case of a collection of operators G = {A, B, C, ...} which all commute with H and with each other. One may then find functions which are eigenfunctions of all operators. If the collection of operators constitutes a group algebra, the requirement of mutual commutativity defines the group as an abelian group. Abelian groups are special in that their irreducible representations (IRs) are all one-dimensional. This means that the allowable eigenvalues

of the group of operators may be looked up in a character table in a reference book[1] if the group is isomorphic with any of commonly occuring groups. The eigenfunctions of the group which all have the same characters are identified by the label of the IR according to which they transform. By analogy with the case of one operator commuting with H, to solve (IA.1) when H commutes with an abelian group G of operators, one first finds the eigenfunctions of the group G. These are known as symmetrized functions and they are conventionally labelled by the standard label used for the IR according to which they transform. Each eigenfunction of H will transform according to a particular IR and can therefore be expressed as a linear combination of the corresponding symmetrized functions.

Finally, suppose H commutes with a collection G of operators which do not commute among themselves. One cannot find functions which simultaneously are eigenfunctions of H and every element of G. If G forms a group, however, one may still take maximum advantage of the commutation of H with each element of G. The result is that the eigenfunctions of H may be expressed as linear combinations of functions each of which transform as a given row of a given IR. Degeneracy of the IR implies a degeneracy of eigenvalues of H. This is, of course, a direct generalization of the preceeding two paragraphs. The demonstration will not be given here because it may be found in most group theory textbooks which discuss applications to quantum mechanics.[2]

It is important to note that if the Hamiltonian commutes with the elements of a non-abelian group, there will be degeneracies in energy. The fact that the elements of the group do not commute results in there being IRs with dimension higher than unity, and hence, corresponding

invariant subspaces of functions whose members have identical energy.

Proof: Suppose there are two elements A,B of a finite group G which do not commute. Since $ABA^{-1} \neq BAA^{-1} = B$, the class that contains B will contain other elements. The number of classes will therefore be less than the number of group elements. It is well-known for finite groups that the number of classes equals the number of IRs. Since the sum of the degeneracies of the IRs must equal the number of elements, and since the number of IRs is less than the number of elements, there is required to be an IR with a degeneracy greater than unity. It is already known[3] that functions which transform as different components of the same IR have the same energy. QED

In the study of the properties of small molecules, it is customary[4] to seek solutions to the time independent non-relativistic Schrödinger equation for a system of M nucleii and N electrons within the Born-Oppnheimer approximation:

$$H = H(\{\underset{\sim}{R}_i\}) = -\sum_{i=1}^{N} \frac{\nabla_i^2}{2} - \sum_{\substack{i=1,N \\ j=1,M}} \frac{Z_j}{|\underset{\sim}{r}_i - \underset{\sim}{R}_j|} + \sum_{i,j=1}^{M} \frac{Z_i Z_j}{|\underset{\sim}{R}_i - \underset{\sim}{R}_j|} + \sum_{i,j=1}^{N} \frac{1}{|\underset{\sim}{r}_i - \underset{\sim}{r}_j|} \qquad \text{(IA.2)}$$

where $\underset{\sim}{r}_i$ ($\underset{\sim}{R}_i$) represents the three coordinates of the $i^{\underline{th}}$ electron (nucleus), and Z_i the charge of the $i^{\underline{th}}$ nucleus. Within the Born-Oppenheimer approximation the energy and wavefunction depend parametrically

on the nuclear coordinates.

In seeking solutions to (IA.1) for the Hamiltonian given above it is natural to search for a set of operations which commute with it. Since H contains no dependence on the spin coordinates of any of the electrons, clearly

$$R^{-1}HR = H \tag{IA.3}$$

where R is a rotation of the spin coordinates of any or all of the electrons. Furthermore, for a specific choice of nuclear coordinates $\{R_i\}$ there may exist a set of operations $\{T_i\}$ on the spatial coordinates such that

$$T_i^{-1}\, H\, T_i = H \qquad i\forall \quad . \tag{IA.4}$$

It might seem that the application of group theory would only be useful in the "rare" occurances that the set of commuting operators forms a group. However, it is straightforward to show that the set of operators which commutes with H always constitutes a group.

Proof: If g_1 and g_2 commute with H then so does $g_3 = g_1g_2$ as can be seen from the following:

$$g_3^{-1}\, H\, g_3 = (g_1g_2)^{-1}H(g_1g_2) = (g_2^{-1}g_1^{-1})H(g_1g_2) = g_2^{-1}(g_1^{-1}Hg_1)g_2^{-1} = g_2^{-1}\, H\, g_2$$

$$= H \quad .$$

This demonstrates closure of the set. The presence of inverse elements is obvious. Since the identity operation trivially commutes with H, we may add it to the set generated by the above procedures of including all

unique products of operations. The resulting set thus satisfies the group axioms.

It may be assumed, therefore, that $\{T_i\}$, $\{R\}$ and also the set formed of their direct products are all groups. The determination of the eigenvalues and eigenvectors of H then becomes first a problem of determining the invariant subspaces of these groups of operators.

There is one other requirement on the eigenfunctions of H that comes not from any symmetry of H but from the fact that the electrons are fermions. The eigenfunctions must be antisymmetric on interchange of any pair of electrons.

$$\psi(\underset{\sim}{r}_1,\ldots,\underset{\sim}{r}_i,\ldots,\underset{\sim}{r}_j,\ldots,\underset{\sim}{r}_N) = -\psi(\underset{\sim}{r}_1,\ldots,\underset{\sim}{r}_j,\ldots,\underset{\sim}{r}_i,\ldots,\underset{\sim}{r}_N) \quad . \quad \text{(IA.5)}$$

There will be presumed to exist a self-adjoint operator, A, called the antisymmetrizer which yields an antisymmetrized N-particle function when operating on an arbitrary N-patricle function.

The form of the antisymmetrizer will depend on what form of N-particle function is to be used. The usual procedure[5] is to use a product of N single-particle functions or a linear combination of such products. This is a good starting point because the Hamiltonian (IA.2) would be separable in electronic coordinates, and a product of single-particle functions would be exact, if it weren't for the electron-electron repulsion term. It may be assumed that the single-particle functions are solutions of some approximate Hamiltonian (e.g., one obtained by neglecting the electron repulsion term of H) and, as such, constitute an orthonormalized basis for a Hilbert space. Each unique product of N single-particle

functions then is a basis function for an N-body direct product Hilbert space. The antisymmetrizer operates on an arbitrary function in this space and projects out the component in Fock Fermion space, the antisymmetric component. If the form of the wavefunction is an N-body direct product form, the resulting antisymmetrized form can always be written as a normalized linear combination of Slater determinants.[6]

Since operations on spin and space coordinates of an electron commute and the Hamiltonian (IA.1) has no spin dependence, the single-particle functions are expressed as a product of a space and a spin part, and the spin parts are the usual functions for a spin ½ fermion, $\gamma_i = \{\alpha,\beta\}$. The orthonormal space parts are finite in number for most practical applications, and will be denoted $\{f_i | i=1,m\}$. Thus,

$$\psi = \sum_i a_i \, \mathcal{A}[f_{1_i}(\underset{\sim}{r}_1)\ldots f_{N_i}(\underset{\sim}{r}_N)\gamma_{1_i}(1)\ldots\gamma_{N_i}(N)] \tag{IA.6}$$

is an acceptable form for ψ. With ψ in this form, $\mathcal{A}$ may be written

$$\mathcal{A} = (N!)^{-\frac{1}{2}} \sum_j \mathrm{sgn}(\sigma_j)\, P(\sigma_j) \tag{IA.7}$$

where σ_j is an element of the symmetric group of N particles. $P(\sigma_j)$ is an operator which produces a new function in the N-particle direct product space different than the operand by the permutation (σ_j) of particle indices. Recall that any permutation may be written as a product of transposition (simple exchange) permutations. The function $\mathrm{sgn}(\sigma_j)$ is +1 if the number of terms in such a product is even and -1 if the number is odd. The summation is over <u>all</u> permutations of the N electrons. The $(N!)^{-\frac{1}{2}}$ is for normalization and this form for $\mathcal{A}$ assumes

that the $\{f_i\}$ are orthonormalized.

The best set of $\{a_i\}$ and $\{f_i\}$ in (IA.6) is usually determined by a variational procedure, i.e., the functional E

$$E(\{a_i\},\{f_i\}) = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \quad , \quad \psi = \psi(\{a_i\},\{f_i\}) \quad , \tag{IA.8}$$

is minimized. The two procedures most common today in the field of electronic structure[4] are (a) the determination of the best set of spatial orbitals $\{f_i\}$ for a fixed and usually small number of a's, and (b) the determination of the best set of coefficients $\{a_i\}$ for a fixed set of orbitals $\{f_i\}$. Procedure (a) is known as the Hartree-Fock Self-Consistent Field (HFSCF) technique, and procedure (b) is known as the Configuration Interaction (CI) technique.

To use the theory of groups to help in solving (IA.1) it is required that ψ be symmetrized--i.e., that ψ transform as one component of some IR of the group of operators commuting with H. The terms of the sum in (IA.6) are Slater determinants which are not, in general, individually symmetrized. Linear combinations of Slater determinants arising from the same electron occupation (e.o.) of spatial orbitals (to be defined later) may be made which are properly symmetrized. These linear combinations will be called configurations.

The construction of configurations may simplify both the HFSCF and CI procedures. For ψ to transform as a particular component of a particular IR, it is sufficient that it be expressed as a linear combination of configurations that transform the same way. Thus, (IA.6) becomes

$$\psi = \sum_i c_i \psi_i \tag{IA.9}$$

where each ψ_i is a configuration given as

$$\psi_i = \sum_j d_j \times (\text{determinants of the } i^{\underline{th}} \text{ e.o.}) \quad . \tag{IA.10}$$

The sum in (IA.9) is generally much smaller than the one in (IA.6) and so the construction of configurations simplifies a CI procedure. Furthermore, since a configuration is the simplest symmetrized function of a given e.o., the construction of a configuration is necessarily the first step that should be taken in a HFSCF procedure to ensure that the wavefunction (and, hence, the energy) corresponds to the desired invariant subspace.

The remainder of this section will deal with the construction of configurations, the determination of the d_is of (IA.10).

B. The Coupling Procedure

In general there may be several determinants corresponding to the same electron occupation (e.o.) of spatial orbitals. The configurations, or various symmetrized functions, are constructed from these determinants. The e.o. numbers specify how many electrons are in each orbital of the molecule. For example, consider BH_3, which belongs to the spacial point group D_{3h}. The e.o. of the ground state is

$$1a_1'^2\ 2a_1'^2\ 1e'^4 \quad , \tag{IB.1}$$

while low-lying excited states might be expected to form from the e.o.

$$1a_1'^2\ 2a_1'^2\ 1e'^3\ 1a_1'' \quad . \tag{IB.2}$$

(The numbers which are neither superscripts nor subscripts, refer to the "principal quantum number" of the molecular spatial orbitals. The superscripts refer to the e.o. numbers, and the rest designates the IR according to which the molecular orbital transforms under the space group of the molecule. It will be assumed that the spatial orbitals, referred to previously as the $\{f_i\}$, transform appropriately as components of various IRs of the space group of the molecule.) Since the e' IR is two-fold degenerate, the determinants that can be constructed from the e.o. of (IB.2) are

$$D_1 = A[1a_1'^2\ 2a_1'^2\ 1e_a'^2\ 1e_b'\ 1a_1''\ \alpha\beta\alpha\beta\alpha\beta\alpha\alpha]$$

$$D_2 = \quad " \quad \alpha\beta]$$

$$D_3 = \quad " \quad \beta\alpha]$$

$$D_4 = \quad " \quad \beta\beta]$$

$$D_5 = A[1a_1'^2\ 2a_1'^2\ 1e_b'^2\ 1e_a'\ 1a_1''\ \alpha\beta\alpha\beta\alpha\beta\alpha\alpha]$$

$$D_6 = \quad " \quad \alpha\beta]$$

$$D_7 = \quad " \quad \beta\alpha]$$

$$D_8 = \quad " \quad \beta\beta] \quad . \tag{IB.3a-h}$$

In the above, several simplifications in notation have been introduced. $f_i(\underset{\sim}{r}_k)$ will be denoted simply by f_i, and it will be assumed that when a product of single particle functions is written the single particle

functions are functions of coordinates of successive electrons. Furthermore, f_i^2 will represent, naturally, $f_i(\underset{\sim}{r}_k)f_i(\underset{\sim}{r}_{k+1})$. It will be obvious from the order of f_i^2 in the product what k is. Sometimes $f_i(n)$ will be written to represent $f_i(\underset{\sim}{r}_n)$.

Thus, the e.o. numbers specify how the electrons are distributed among the spatial functions without reference to their spin component (α or β) or to the component of the spatial functionif it transforms as a degenerate IR. In the above example, the e' orbital is degenerate, having an e_a and an e_b component.

It should be clear that the set of eight determinants listed above form an invariant subspace under all the group operations. (All the a type orbitals transform to themselves. All the e_a orbitals transform to linear combinations of e_a and e_b orbitals, and so on.) This subspace is, in general, reducible and the linear combinations (of determinants) which transform according to the various IRs of the full group are the configurations. Thus, the specification of the e.o. is the first step in the construction of the configurations.

The e.o. numbers specify a partitioning of electrons into shells. The coupling procedure[7] will involve first the coupling of electrons within a shell, then the successive coupling of shells to produce an N-particle function which carries a particular IR, and finally, to antisymmetrize the N-particle function and express the result, a configuration, as a linear combination of determinants.

The possibility exists that an N-particle function symmetrized with respect to the space group <u>cannot</u> be made antisymmetric with respect to particle exchange. In this event, operation by $\hat{A}$ will kill the function, since $\hat{A}$ projects out the

component of the function in Fermion Fock space. For example, consider the two-particle function $\psi = (2)^{-\frac{1}{2}} f_1^2(\alpha\beta+\beta\alpha)$.

$$A\psi = \frac{1}{\sqrt{2}}\{\frac{1}{\sqrt{2}} f_1^2(\alpha\beta+\beta\alpha) - \frac{1}{\sqrt{2}} f_1^2(\beta\alpha+\alpha\beta)\} = 0 \quad . \qquad \text{(IB.4)}$$

These cases can be eliminated by consideration for fermion statistics only during the first step listed above: forming the intrashell couplings. The necessity for consideration for fermion statistics at this point only is a result of the fact that the Pauli exclusion principle will exclude particular couplings of electrons in the same shell, but not of electrons in different shells. An example of this is that for two s type electrons as in He, the $1s^2$ e.o. gives rise to only a ^1S whereas the 1s2s e.o. gives rise to both a ^1S and a ^3S state.

With this in mind, the coupling procedure for constructing the configurations of a given e.o. is as follows:

(i) Intrashell coupling. The possible space-spin states consistent with fermion statistics that can arise from each of the shells is determined. (see section D.)

(ii) For a particular ordering of shells, the direct product of the states of each shell with the states resulting from the cumulative coupling of all previous shells is decomposed. This decomposition is done without regard for fermion statistics in contrast to (i). Furthermore, the space and spin parts may be decomposed separately. The intermediate couplings which result in a state of the desired symmetry constitute a geneology.[7]

(iii) The geneologies are used in conjunction with a set of coupling coefficients to construct the symmetrized functions. (See

section C for the coupling coefficients.) If one e.o. gives rise to several symmetrized functions of the same symmetry through different geneologies, they are guaranteed to be orthogonal.[8]

(iv) The resulting function is symmetrized and if each shell function is written as a linear combination of determinants the product of such functions is trivially antisymmetrized.

To illustrate this procedure, consider a molecule with C_{3v} spatial operations, and an e.o. of $1a_1^2\ 2a_1^2\ 3a_1\ 1e^2\ 2e$. This might be an e.o. corresponding to some excited states of BH_3 which has a nonplanar geometry. Suppose configurations of space-spin symmetry $^3A_1$ are desired.

For this e.o., the shells and their allowed space-spin states are a_1^2: $^1A_1$; a_1: $^2A_1$; e^2: ^1E, $^1A_1$, $^3A_2$; and e: ^2E. Section D will explain how these are determined and also how to obtain the correct linear combination of one- and two-particle functions that transform appropriately.

For the ordering of shells as given, $1a_1^2(^1A_1)$ may be coupled only one way with $2a_1^2(^1A_1)$ to give a resulting state $^1A_1$. This may then be coupled only one way with $3a_1(^2A_1)$ to give $^2A_1$. The result may then be coupled four ways with $1e^2$: with $1e^2(^1E)$ to give ^2E, with $1e^2(^1A_1)$ to give $^2A_1$ and with $1e^2(^3A_2)$ to give $^2A_2$ and $^4A_2$. These four states may then be coupled with $2e(^2E)$ to give ^1E, ^3E, $^1A_1$, $^3A_1$, $^1A_2$, and $^3A_2$ (from the ^2E), ^1E and ^3E (from $^2A_1$), ^1E and ^3E (from $^2A_2$), and ^5E and ^3E (from $^4A_2$). There is, therefore, only one geneology resulting in the desired $^3A_1$ symmetry. The decomposition of direct products of spin IRs is given by the usual formula $S = |S_1+S_2|,\ldots,|S_1-S_2|$, and the decomposition of direct products of spacial IRs is given by the usual procedure[9]

$$a_j = \frac{1}{h} \sum_k \chi^{(j)}(C_k)^* \, \chi(C_k) N_K \tag{IB.5}$$

where a_j is the frequency index for the jth IR, $\chi^{(j)}(C_k)$ is the character of the jth IR for the kth class C_k of N_k elements in an h element group. $\chi(C_k)$ is the character of the reducible representation for the kth class of elements obtained by multiplying the characters of the two IRs whose direct product is being decomposed.[10]

The geneologies resulting from this procedure are illustrated in figure 1. Lines connect intermediate cumulative couplings, and above each line is listed the coupling of each of the shells.

To produce the configuration of symmetry $^3A_1$, the space couplings for products of e-type IRs are required. These will be derived in section C, but for now they will simply be presented:

$$\frac{1}{\sqrt{2}} [e_x(1)e_x(2) + e_y(1)e_y(2)] \quad \text{transforms like the } a_1 \text{ IR}$$

$$\frac{1}{\sqrt{2}} [e_x(1)e_y(2) - e_y(1)e_x(2)] \quad \text{transforms like the } a_2 \text{ IR}$$

$$\left\{ \begin{array}{l} \frac{1}{\sqrt{2}} [e_x(1)e_x(2) - e_y(1)e_y(2)] \\ \frac{1}{\sqrt{2}} [-e_x(1)e_y(2) - e_y(1)e_x(2)] \end{array} \right\} \text{transforms like the } \left\{ \begin{matrix} e_x \\ e_y \end{matrix} \right\} \text{ IR .} \tag{IB.6a-c}$$

In other words, the transformations of the two-particle functions on the left generate an IR of the type indicated on the right. The only spin couplings (Clebsch-Gordon combinations) needed are

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = |S=0;\ m_S=0\rangle$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = |S=1;\ m_S=0\rangle$$

$$\alpha(1)\alpha(2) = |S=1;\ m_S=1\rangle$$

$$\beta(1)\beta(2) = |S=1;\ m_S=-1\rangle$$

$$|S=0;\ m_S=0\rangle|S=0;\ m_S=0\rangle = |S=0;\ m_S=0\rangle \quad . \qquad \text{(IB.7a-e)}$$

Coupling the first four shells together yields the following seven-particle functions which have ^2E symmetry:

$$[\frac{1}{\sqrt{2}}\ 1a_1^2(\alpha\beta-\beta\alpha)][\frac{1}{\sqrt{2}}\ 2a_1^2(\alpha\beta-\beta\alpha)][3a_1\alpha][\frac{1}{2}\ (1e_x^2-1e_y^2)(\alpha\beta-\beta\alpha)]$$

$$\text{"} \qquad \text{"} \qquad [3a_1\beta] \qquad \text{"}$$

$$\text{"} \qquad \text{"} \qquad [3a_1\alpha][\frac{1}{2}(-1e_x1e_y - 1e_y1e_x)(\alpha\beta-\beta\alpha)]$$

$$\text{"} \qquad \text{"} \qquad [3a_1\beta] \qquad \text{"} \qquad \text{(IB.8a-d)}$$

The four functions (IB.8a-d) transform, respectively as $e_x \otimes \alpha$, $e_x \otimes \beta$, $e_y \otimes \alpha$, and $e_y \otimes \beta$. To obtain the highest spin component ($m_S=1$) for the desired geneology, $^3A_1$, the last shell is added with coupling given by (IB.6a) and (IB.7c). This produces the eight particle function:

$$[\frac{1}{\sqrt{2}}\ 1a_1^2(\alpha\beta-\beta\alpha)][\frac{1}{\sqrt{2}}\ 2a_1^2(\alpha\beta-\beta\alpha)][3a_1\alpha]$$

$$\times\ (\frac{1}{\sqrt{2}})\{[\frac{1}{2}(1e_x^2 - 1e_y^2)(\alpha\beta-\beta\alpha)][2e_x\alpha] + [\frac{1}{2}(-1e_x1e_y - 1e_y1e_x)(\alpha\beta-\beta\alpha)][2e_y\alpha]\}. \qquad \text{(IB.9)}$$

This function is the eight-particle symmetrized function which must now be written as a linear combination of determinants. To do this, each shell function is written as a linear combination of determinants:

$$[A(1a_1^2\alpha\beta)][A(2a_1^2\alpha\beta)][3a_1\alpha](\frac{1}{\sqrt{2}})\ \{\frac{1}{\sqrt{2}}[A(1e_x^2\alpha\beta) - A(1e_y^2\alpha\beta)][2e_x\alpha]$$

$$-\frac{1}{\sqrt{2}}[A(1e_x1e_y\alpha\beta) - A(1e_x1e_y\beta\alpha)][2e_y\alpha]\}\ . \tag{IB.10}$$

The configuration written as a linear combination of determinants is

$$\psi_{3_{A_1,m_S=1}} = \frac{1}{2}(D_1-D_2-D_3+D_4) \tag{IB.11}$$

where

$$D_1 = A[(1a_1^2\alpha\beta)(2a_1^2\alpha\beta)(3a_1\alpha)(1e_x^2\alpha\beta)(2e_x\alpha)]$$

$$D_2 = A[\qquad\quad " \qquad\quad (1e_y^2\alpha\beta)(2e_x\alpha)]$$

$$D_3 = A[\qquad\quad " \qquad\quad (1e_x1e_y\alpha\beta)(2e_y\alpha)]$$

$$D_4 = A[\qquad\quad " \qquad\quad (1e_x1e_y\beta\alpha)(2e_y\alpha)]\quad . \tag{IB.12a-d}$$

It may be seen by construction that the other eleven configurations arising from this same e.o. are orthogonal to the one above and also to each other.

The importance of the minus sign in (IB.6c) cannot be overemphasized. The minus sign of the two-particle function transforming as e_y ultimately resulted in the minus signs of the second and third determinants of the configuration (IB.11). The coupling method requires the partially coupled

shells to transform in precisely the same way as the basis functions of the IRs. However, if the relative phases of a set of two-particle functions (as in IB.6c) is selected arbitrarily, the functions will not transform according to exactly the same IRs as their constituent one-particle functions. In other words, the two-dimensional representation of the C_{3v} operations generated by the pair of functions (x,y) is different from that generated by (x,-y). The coupling coefficients generated by these two different representations would also differ. In practical applications of the coupling technique, care must also be taken that all degenerate partners of the set of one-particle spatial functions transform the same way. This point must be paid particular attention to because most HFSCF procedures which are used to generate the one-particle spatial functions produce these functions with random phases. This is usually the case because no aspect of the HFSCF procedure depends on the relative phases.

C. The Coupling Coefficients

This section will explain how coupling coefficients like those (IB.6) used in the previous section are derived and will illustrate with the derivation of coupling coefficients for the point group C_{3v}.

Let Γ^{α}, Γ^{β}, and Γ^{γ} be three IRs of a group G carried by the set of functions $\{f_i^{\alpha}\}$, $\{f_j^{\beta}\}$, and $\{f_k^{\gamma}\}$, respectively. The index i, for example, runs from one to $m(\alpha)$, the degeneracy of the αth IR. The coupling coefficients $c_{k\ell i}^{\alpha\beta\gamma}$ are defined as

$$f_i^{\gamma} = \sum_{k,\ell} c_{k\ell i}^{\alpha\beta\gamma} f_k^{\alpha} \otimes f_{\ell}^{\beta} \quad . \tag{IC.1}$$

If G = SU(2), the c's are the Clebsch-Gordon coefficients which are tabulated in most quantum mechanics textbooks. No such information is tabulated if G is a finite dimensional point group, however.

The most straightforward way to generate the coupling coefficients is with a projection operator technique like that described in many group theory texts[11] which discuss the generation of symmetry adapted functions for a single particle. The generalization to a two- or more-particle function space is straightforward.

Recall that for a space of single-particle functions, P_R is defined as

$$P_R f_i^\alpha = \sum_{j=1}^{m(\alpha)} f_j^\alpha \, \Gamma_{ji}^\alpha(R), \quad \forall R \in G \quad , \tag{IC.2}$$

where $\Gamma_{ji}^\alpha(R)$ is an element of the matrix that represents element R in G as described by the αth IR. It is a consequence of the great orthogonality theorem that

$$P_{ij}^\alpha f_k^\beta = \delta_{jk} \, \delta_{\alpha\beta} \, f_i^\alpha \quad , \tag{IC.3}$$

where P_{ij}^α is given by

$$P_{ij}^\alpha = \frac{m(\alpha)}{h} \sum_R \Gamma_{ij}^\alpha(R) P_R \quad . \tag{IC.4}$$

P_{ij}^α is called a projection operator because it projects out of an arbitrary function the part that corresponds to the ith component of the αth IR <u>if</u> the function contains a component that transforms like the jth component of the αth IR.

To extend this technique to a two-particle function space, we need only define P_R on a direct product space.

$$P_R(f_i^\alpha \otimes f_k^\beta) = \sum_{j=1}^{m(\alpha)} \sum_{\ell=1}^{m(\beta)} (f_j^\alpha \otimes f_\ell^\beta)\, \Gamma_{ji}^\alpha(R)\, \Gamma_{\ell k}^\beta(R) \quad . \tag{IC.5}$$

The coupling coefficients for the C_{3v} point group can be worked out by the projection operator technique. The character table[12] for this group is provided below.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

The representation matrices Γ_{ij}^α for the one-dimensional IRs are given trivially as the first two rows of the character table. The representation matrices for the E IR will be taken[13] as

$$\Gamma^E(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \Gamma^E(C_3) = \frac{1}{2}\begin{pmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}; \quad \Gamma^E(C_3^2) = \frac{1}{2}\begin{pmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix};$$

$$\Gamma^E(\sigma_{v1}) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \quad \Gamma^E(\sigma_{v2}) = \frac{1}{2}\begin{pmatrix} -1 & \sqrt{3} \\ \sqrt{3} & 1 \end{pmatrix}; \quad \Gamma^E(\sigma_{v3}) = \frac{1}{2}\begin{pmatrix} -1 & -\sqrt{3} \\ -\sqrt{3} & 1 \end{pmatrix}.$$

These matrices (a representation) are generated by the action of the group of operators on a vector space of functions. In fact they are generated by the functions (x,y) [where this notation specifies their ordering] as "operated on" by the operations of the group. "Operation" is defined for

the group elements as follows: the C_3 operations rotate the contours of a single-valued function in a left-handed sense about the +z-axis (clockwise in the xy plane), the σ_v operation reflects the contours of a function through the xz plane and the planes of reflection for σ_{v2} and σ_{v3} also contain the z-axis and are C_3 and C_3^2 rotations, respectively, of the σ_v plane. Thus, the notation "e_x, and e_y" will be used to denote pairs of functions which transform among themselves exactly like (x,y). This notation is being presented meticulously because there are so many different conventions in the literature.

Thus, from the matrix representing C_3, and the defining relations (IC.2) and (IC.5),

$$P_{C_3}[e_x(1)e_y(2)] = [-\frac{1}{2}e_x(1) - \frac{\sqrt{3}}{2}e_y(1)][\frac{\sqrt{3}}{2}e_x(2) - \frac{1}{2}e_y(2)]$$

$$= \frac{1}{4}[-\sqrt{3}\,e_x(1)e_x(2)+e_x(1)e_y(2)-3e_y(1)e_x(2)+\sqrt{3}\,e_y(1)e_y(2)]$$

and

$$P_{\sigma_{v1}}[e_x(1)e_y(2)] = -e_x(1)e_y(2) \quad . \qquad \text{(IC.7)}$$

Once the operation of all operators on all possible two-particle functions constructed from the direct product of two single-particle functions (each properly transforming as one component of one of the IRs) is determined, the projection operator technique may be used.

Suppose one wishes to determine the coupling coefficients for coupling two particles, each of which is in a single particle function transforming as the E IR. This situation provides the coupling coefficients for the e.o. 1e2e, which were given in (IB.6). One constructs the various

two-particle projection operators, guesses a two-particle function which has a component which transforms as desired, then projects out and normalizes the resulting function. Two inequivalent e particles can be coupled to A_1, A_2, and E. As an example of the procedure,

$$
\begin{aligned}
P^{A_1}(xx) = \frac{1}{6}\{&(1)xx + (1)(\tfrac{1}{4})(xx+\sqrt{3}\,xy+\sqrt{3}\,yx+3\,yy) \\
&+ (1)(\tfrac{1}{4})(xx-\sqrt{3}\,xy-\sqrt{3}\,yx+3\,yy) \\
&+(1)xx + (1)(\tfrac{1}{4})(xx+\sqrt{3}\,xy+\sqrt{3}\,yx+3\,yy) \\
&+ (1)(\tfrac{1}{4})(xx-\sqrt{3}\,xy-\sqrt{3}\,yx+3\,yy)\} \\
= \frac{1}{2}&(xx+yy) \quad . \qquad \text{(IC.8)}
\end{aligned}
$$

This must be normalized to $\frac{1}{\sqrt{2}}[e_x(1)e_x(1) + e_y(1)e_y(1)]$ to give (IB.6a). Similarly,

$$P^{A_2}(xx) = 0 \quad . \qquad \text{(IC.9)}$$

$$P^{E}_{xx}(xx) = \frac{1}{2}(xx-yy) \quad . \qquad \text{(IC.10)}$$

$$P^{E}_{yx}\left[\frac{1}{\sqrt{2}}(xx-yy)\right] = -\frac{1}{\sqrt{2}}(xy+yx) \quad . \qquad \text{(IC.11)}$$

$$P^{A_2}(xy) = \frac{1}{3}(xy-yx) \quad . \qquad \text{(IC.12)}$$

Note that the transverse projection operator, $P^{\alpha}_{ij}(i\neq j)$ must be used to give the correct relative phases of the various components of degenerate IRs.

After normalization, the e ⊠ e coupling coefficients are those presented in (IB.6):

$$\frac{1}{\sqrt{2}}(e_x e_x + e_y e_y) \qquad \text{transforms as the } a_1 \text{ IR}$$

$$\frac{1}{\sqrt{2}}(e_x e_y - e_y e_x) \qquad \text{transforms as the } a_2 \text{ IR}$$

$$\begin{Bmatrix} \frac{1}{\sqrt{2}}[e_x e_x - e_y e_y] \\ -\frac{1}{\sqrt{2}}[e_x e_y + e_y e_x] \end{Bmatrix} \quad \text{transforms as the} \begin{Bmatrix} e_x \\ e_y \end{Bmatrix} \text{IR.} \qquad \text{(IC.13a-c)}$$

Similar coupling coefficients may be obtained for a_2 ⊠ e,

$$\begin{Bmatrix} a_2 e_y \\ -a_2 e_x \end{Bmatrix} \quad \text{transforms as the} \begin{Bmatrix} e_x \\ e_y \end{Bmatrix} \text{IR} \quad , \qquad \text{(IC.14)}$$

and for a_1 ⊠ e,

$$\begin{Bmatrix} a_1 e_x \\ a_1 e_y \end{Bmatrix} \quad \text{transforms as the} \begin{Bmatrix} e_x \\ e_y \end{Bmatrix} \text{IR} \quad . \qquad \text{(IC.15)}$$

Actually, a_1 ⊠ (any IR) trivially decomposes to (any IR) and the components of a_1 ⊠ (any IR) match exactly with those of (any IR).

The projection operator technique may be used, of course, for any of the point groups. (Coupling coefficients for the 24 element T_d group have been derived and may be obtained from the author.) It should be obvious that if G is a group all of whose IRs are one-dimensional, each

direct product of functions transforming as these IRs may be decomposed into only <u>one</u> of the other IRs. Thus, each direct product of functions is already symmetrized. The coupling coefficients take on a particularly simple form for these abelian groups. (IC.1) reduces to the following:

$$f^{\gamma} = f^{\alpha} \otimes f^{\beta} \text{ if } \chi^{(\gamma)}(C_k) = \chi^{(\alpha)}(C_k)\cdot\chi^{(\beta)}(C_k), \quad \forall k \quad .$$

The subscripts of the f_i^{α} have been dropped because they are meant to refer to a component of the αth IR, and if G has only one-dimensional representations, the subscript is unnecessary. It is therefore seen that the coupling coefficients take on a particularly simple form:

$$C^{\alpha\beta\gamma} = \begin{cases} 1 \text{ if } \chi^{(\gamma)}(C_k) = \chi^{(\alpha)}(C_k)\cdot\chi^{(\beta)}(C_k), & \forall k \\ 0 \text{ otherwise} \end{cases} \quad .$$

D. Allowed Intrashell Couplings

As was mentioned in section IB, not all N-particle functions are allowed by fermi statistics. These functions cannot be antisymmetrized--the antisymmetrizer $\hat{A}$ annihilates them.

Consider the shell in the C_{3v} example which contained two equivalent e electrons. Without regard to fermi statistics, the six states that can be constructed are $^1A_1$, $^3A_1$, $^1A_2$, $^3A_2$, ^1E and ^3E. The corresponding wavefunctions are (maximum m_s value only)

$$^1A_1: \quad \frac{1}{2}(e_x e_x + e_y e_y)(\alpha\beta-\beta\alpha)$$

$$^3A_1: \quad \frac{1}{\sqrt{2}}(e_x e_x + e_y e_y)\alpha\alpha$$

$$^1A_2: \quad \frac{1}{2}(e_x e_y - e_y e_x)(\alpha\beta - \beta\alpha)$$

$$^3A_2: \quad \frac{1}{\sqrt{2}}(e_x e_y - e_y e_x)\alpha\alpha$$

$$^1E \quad \left\{ \begin{array}{l} \frac{1}{2}(e_x e_x - e_y e_y)(\alpha\beta - \beta\alpha) \\ \frac{1}{2}(-e_x e_y - e_y e_x)(\alpha\beta - \beta\alpha) \end{array} \right\}$$

$$^3E \quad \left\{ \begin{array}{l} \frac{1}{\sqrt{2}}(e_x e_x - e_y e_y)\alpha\alpha \\ \frac{1}{\sqrt{2}}(-e_x e_y - e_y e_x)\alpha\alpha \end{array} \right\} \quad . \qquad \text{(ID.1a-f)}$$

Operation by the antisymmetrizer, however, kills off all except the $^1A_1$, $^3A_2$ and ^1E states, leaving

$$^1A_1: \quad \frac{1}{\sqrt{2}} A(e_x e_x \alpha\beta) + \frac{1}{\sqrt{2}} A(e_y e_y \alpha\beta)$$

$$^3A_2: \quad A(e_x e_y \alpha\alpha)$$

and

$$^1E \quad \left\{ \begin{array}{l} \frac{1}{\sqrt{2}} A(e_x e_x \alpha\beta) - \frac{1}{\sqrt{2}} A(e_y e_y \alpha\beta) \\ -\frac{1}{\sqrt{2}} A(e_x e_y \alpha\beta) - \frac{1}{\sqrt{2}} A(e_x e_y \beta\alpha) \end{array} \right\} \quad . \qquad \text{(ID.2a-c)}$$

In constructing the allowable states arising from other occupations of shells, for example, e^3, a cumulative coupling procedure exactly like that which was used in section IB may be used, provided only antisymmetrized states are kept. In most of these cases the antisymmetrizer will kill off

all but a few couplings. Without regard for fermi statistics, for example, le^2le produces ^2E, $^2A_1$, $^2A_2$ (from coupling ^1E with ^2E), ^2E (from coupling $^1A_1$ with ^2E) and ^2E, ^4E (from coupling $^3A_2$ with ^2E). Of these six states, the antisymmetrizer kills all but one, the ^2E result of coupling $^1A_2$ with ^2E:

$$^2E: \quad \begin{Bmatrix} A(e_x e_x e_y \alpha\beta\alpha) \\ A(e_y e_y e_x \alpha\beta\alpha) \end{Bmatrix} \quad \text{transforms as} \begin{Bmatrix} e_x \\ e_y \end{Bmatrix} .$$

This is, of course, an overly simple example because it is generally well-known that "holes" may be coupled like electrons. The e^3 case can be treated like the e^1 case, which can only be coupled ^2E. There are situations, however, where the cumulative coupling procedure for coupling particles in the same shell (followed by antisymmetrization) is easier than constructing projection operators in a higher-particle space.[14] One such situation arises in the intrashell couplings of t^3.

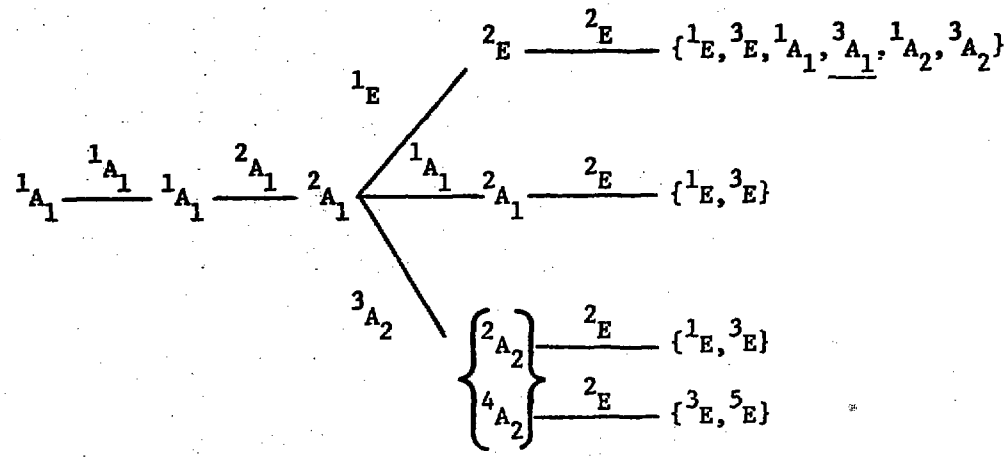

Figure 1

Caption: Diagram illustrating geneological couplings for an electron occupation $a_1^2 a_1^2 a_1 e^2 e$.

References

1. M. Tinkham, Group Theory and Quantum Mechanics (McGraw-Hill, San Francisco, 1969).
2. L. M. Falicov, Group Theory and Its Physical Applications (The University of Chicago Press, 1966) pp. 115-6. The proof involves showing that matrix elements of the Hamiltonian between functions which transform according to either different IRs or different components of the same IR are zero.
3. Ibid., p. 50.
4. H. F. Schaefer, The Electronic Theory of Atoms and Molecules (Addison-Wesley, Menlo Park, CA, 1972).
5. A. L. Fetter and J. D. Walecka, Quantum Theory of Many-Particle Systems (McGraw-Hill, San Francisco, 1971) p. 5.
6. Ibid., p. 16.
7. The geneological coupling procedure is well-known for angular momentum coupling [see R. Pauncz, Alternate Molecular Orbital Method (W. B. Saunders, Co., Philadelphia, PA, 1967) chapter 2], but not for the coupling of direct products of IRs of point groups. See D. R. Yarkony, Ph.D. thesis, University of California, Berkeley, 1975.
8. Proof of the orthogonality of spin eigenfunctions constructed by the geneological procedure is given by G. W. Pratt, Phys. Rev. 92, 278 (1953). This proof is easily generalized to include spacial couplings as discussed here.
9. L. M. Falicov, op. cit., p. 42.
10. Ibid., p. 73.

11. See, for example, F. A. Cotton, Chemical Applications of Group Theory, second edition (Wiley-Interscience, New York, 1971) p. 105.

12. M. Tinkham, op. cit., p. 325.

13. F. A. Cotton, op. cit., p. 109.

14. There is a procedure for generating a list of the allowable states arising from the coupling of n equivalent particles in a field of given symmetry. This procedure takes into account antisymmetrization on particle exchange (Fermi statistics) as well as spin and spatial symmetry. The discussion of this procedure is unnecessary here but may be found in the article by O. Goscinski and Y. Ohrn, Inter. Journal of Quantum Chemistry II, 845 (1968). This procedure is not discussed in the text because it does not lead to the n-particle symmetrized functions that are required here.

II. The Application of the Geneological Coupling Method to the Study of Sulfur Oxide

A. Introduction

In this section the geneological coupling procedure will be used to generate configurations for a configuration interaction (CI) study of the diatomic molecule sulfur oxide, SO.

In a single configuration scheme, SO has a ground state valence structure similar to both S_2 and O_2. Although S_2 and O_2 have been studied extensively both experimentally and theoretically,[1] the information available on SO is on considerably less stable ground. The ground state of SO arises from the electron occupation (e.o.)

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ 5\sigma^2\ 6\sigma^2\ 7\sigma^2\ 2\pi^4\ 3\pi^2 \quad . \qquad \text{(IIA.1)}$$

This e.o. gives rise to three possible couplings each of which exists in nature as a bound electronic state. They are: the ground state itself, $X^3\Sigma^-$, and two excited states, $a^1\Delta$ and $b^1\Sigma^+$. Three additional states will be studied which derive from the e.o.

$$\ldots\ 2\pi^3\ 3\pi^3 \quad . \qquad \text{(IIA.2)}$$

The states to be studied from this e.o. are $c^1\Sigma^-$, $^3\Delta$, and $^3\Sigma^+$. By analogy with the well-studied molecules S_2 and O_2 and also by direct experimental evidence[1] there is reason to believe the six states of the above two electron occupations are the lowest six electronic states of SO. Calculations will be performed on each of the states to determine various properties of the molecule.

The strategy for this study will be the usual one of a) constructing a configuration of the desired symmetry from one of the electron occupations, b) using a standard SCF-MO procedure to construct the best orbitals for this single configuration, c) generating a set of configurations obtained as all couplings with the same symmetry as that in (a) and derived from electron occupations that are substitutions of one and two electrons from the reference occupation, d) constructing Hamiltonian matrix over the reference configuration and all others generated in (c), and e) extracting the lowest eigenvalue and eigenvector from this matrix. This procedure, which is called a singles and doubles configuration interaction calculation, has been discussed at length in the literature.[2]

B. The Coupling Coefficients for the $C_{\infty v}$ Group

Both steps a) and c) above involve the generation of configurations from a given set of electron occupations. This involves, of course, the generation of coupling coefficients for the $C_{\infty v}$ group if the geneological procedure of part I is to be used.

The projection operator technique used for the derivation of coupling coefficients for the C_{3v} point group in the previous section is not readily applicable to infinite groups such as $C_{\infty v}$ or $D_{\infty h}$. Here, an alternate method will be used.

For the group $C_{\infty v}$, there are two common sets of symmetry functions, a complex set and a real set. The complex set is given by

$$\zeta_m = (2\pi)^{-\frac{1}{2}} \exp(im\phi), \quad m = 0, \pm 1, \pm 2, \ldots \qquad \text{(IIB.1)}$$

where $\phi = \arctan(y/x)$, and the real set is given by the linear combinations

$$\eta_o = (2\pi)^{-\frac{1}{2}}$$

$$\left.\begin{aligned} \eta_m &= (2)^{-\frac{1}{2}}\,(\zeta_m+\zeta_{-m}) = \pi^{-\frac{1}{2}}\cos m\phi \\ \eta_{-m} &= (-2)^{-\frac{1}{2}}\,(\zeta_m-\zeta_{-m}) = \pi^{-\frac{1}{2}}\sin m\phi \end{aligned}\right\} \quad m = 1,2,\ldots \quad . \qquad \text{(IIB.2)}$$

These two sets of functions each provide a basis for a representation of the group. The two representations supplied differ by an equivalence transformation. The coupling coefficients, of course, are different for the two representations.

It is usually more convenient from a computational standpoint to construct configurations, calculate integrals, etc., if real single-particle functions are employed. This demands the determination of coupling coefficients for basis functions transforming as (IIB.2) rather than (IIB.1). The coupling coefficients, however, are more easily determined from the representations provided by (IIB.1). The procedure to be used here will be to a) examine the transformation properties of the complex functions ζ, and of the real functions η, as well as the unitary transformation that relates them and their representations, b) derive the coupling coefficients of the complex functions, and c) utilize a unitary transformation to derive the coupling coefficients of the real functions from those of the complex ones.

The group $C_{\infty v}$ is generated by the operators $C(\theta)$ and σ_v. A coordinate system may be chosen so that the $C(\theta)$-axis is the z-axis and σ_v is a reflection in the xz plane. If one defines

$$\varepsilon_m = \exp(im\theta); \quad c_m = \cos m\theta; \quad s_m = \sin m\theta \quad , \qquad \text{(IIB.3)}$$

and "operation" as it was defined in part IC, the effects of the generating operators on the basis functions are

$$\begin{array}{lll} & \zeta_m & \eta_m \\ C(\theta) & \varepsilon_m\zeta_m & c_m\eta_m+s_m\eta_{-m} \\ \sigma_v & \zeta_{-m} & (\text{sign } m)\eta_m \end{array} \quad . \qquad \text{(IIB.4)}$$

This table is adequate to generate the representation supplied by either the complex or real functions.

From inspection, the pair $\{\zeta_m,\zeta_{-m}\}$ forms an invariant two-dimensional subspace which is irreducible, if $m \neq 0$. If $m = 0$, the subspace is one-dimensional and the function supplies the A_1 representation. For non-zero m, however, the representations are

$$C(\theta) : \begin{pmatrix} \varepsilon_m & 0 \\ 0 & \varepsilon_{-m} \end{pmatrix} ; \qquad \sigma_v : \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \qquad \text{(IIB.5)}$$

and the characters are 2 cosmθ and zero, respectively, identifying the E_m IR of $C_{\infty v}$.

Similarly for the real functions $\{\eta_m,\eta_{-m}\}$, the real function $m = 0$ supplies the A_1 representation and the pair for nonzero m supply the E_m IR. For completeness, the representation matrices are

$$C(\theta) : \begin{pmatrix} c_m & s_m \\ -s_m & c_m \end{pmatrix} ; \qquad \sigma_v : \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \text{(IIB.6)}$$

and these have the same traces as those above.

The two sets of basis functions are related by a transformation from ζ-space to η-space, $\underset{\sim}{\eta} = \underset{\approx}{U}\underset{\sim}{\zeta}$ where

$$\underset{\approx}{U} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} \quad , \quad \underset{\approx}{U}^{-1} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix} \quad . \tag{IIB.7}$$

An element of ζ-space, for example, is defined by $a\zeta_m + b\zeta_{-m}$ and is represented by the column vector $\begin{pmatrix} a \\ b \end{pmatrix}$. The transformation is also a similarity transformation which relates (IIB.5) and (IIB.6) by

$$\Gamma'(R) = U^{-1}\,\Gamma(R)U \quad , \quad R = C(\theta), \sigma_v \tag{IIB.8}$$

where Γ' is the representation supplied by ζ (IIB.5) and Γ is that supplied by η (IIB.6). Note that U is unitary, so $U^{\dagger}U = UU^{\dagger} = 1$.

The coupling coefficients for the set of complex basis functions are easily determined. The axial rotation group is a subgroup of the full rotation group, and both are discussed in many textbooks on angular momentum and quantum mechanics.[3] Consider first the direct products of the functions $\{\zeta_m, \zeta_{-m}\}$ and $\{\zeta_n, \zeta_{-n}\}$ for $m \geq n \geq 0$. This examination will provide coupling coefficients for $E_m \otimes E_n$, $E_m \otimes E_m$, $E_m \otimes A_1$, (for $n = 0$), and $A_1 \otimes A_1$. The four direct products are $\zeta_m\zeta_n$, $\zeta_m\zeta_{-n}$, $\zeta_{-m}\zeta_n$, and $\zeta_{-m}\zeta_{-n}$. With operations on single-particle functions, the pair of functions $\{\zeta_m\zeta_n, \zeta_{-m}\zeta_{-n}\}$ (in this order, of course) provides the representation matrices

$$C(\theta): \begin{pmatrix} \varepsilon_m\varepsilon_n & 0 \\ 0 & \varepsilon_{-m}\varepsilon_{-n} \end{pmatrix} = \begin{pmatrix} \varepsilon_{(m+n)} & 0 \\ 0 & \varepsilon_{-(m+n)} \end{pmatrix} ; \quad \sigma_v: \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{IIB.9}$$

Thus, this pair of functions transforms as $\{\zeta_{(m+n)}, \zeta_{-(m+n)}\}$. The pair of functions $\{\zeta_m\zeta_{-n}, \zeta_{-m}\zeta_n\}$ provides the representation

$$C(\theta): \begin{pmatrix} \varepsilon_{m-n} & 0 \\ 0 & \varepsilon_{-(m-n)} \end{pmatrix}; \quad \sigma: \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad . \tag{IIB.10}$$

Thus, if $m > n > 0$, the direct products of two E-type representations $E_m \otimes E_n$ provide functions which in turn provide representations for two more E-type representations, E_{m+n} and E_{m-n}.

If $m = n > 0$, the above representations correspond to E_{2m}, provided by $\{\zeta_m\zeta_m, \zeta_{-m}\zeta_{-m}\}$, and to the two one-dimensional representations A_1 and A_2, provided by $\{\frac{1}{\sqrt{2}}(\zeta_m\zeta_{-m} \pm \zeta_{-m}\zeta_m)\}$, respectively. This can be seen simply by examining the (reducible) representation matrices supplied by $\{\zeta_m\zeta_{-m}, \zeta_{-m}\zeta_m\}$:

$$C(\theta): \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \sigma_v: \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad . \tag{IIB.11}$$

The normalized sum and difference of the two products, however, provides

$$C(\theta): \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \sigma_v: \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad , \tag{IIB.12}$$

illustrating that this combination reduces the two-dimensional representation (IIB.11) to two one-dimensional ones with characters corresponding to A_1 and A_2.

If $m > n = 0$, or $m = n = 0$, the (trivial) coupling coefficients for $E_m \otimes A_1$ and $A_1 \otimes A_1$ are obtained. When direct products of functions

transforming both as one-dimensional IRs are taken (such as $A_1 \otimes A_1$, $A_2 \otimes A_2$, and $A_1 \otimes A_2$) the coupling coefficients are always trivial since another one-dimensional representation is obtained. The only coupling coefficients needed, therefore, are for $E_m \otimes A_2$, which will be a representation for E_m (as can be seen from a character table) provided by some linear combination of the functions $\zeta_m f_{a_2}$ and $\zeta_{-m} f_{a_2}$ where f_{a_2} is any function transforming as the A_2 IR. The matrices for the A_2 representation are the same as the characters, so the two functions provide

$$C(\theta): \begin{pmatrix} \varepsilon_m & 0 \\ 0 & \varepsilon_{-m} \end{pmatrix}; \qquad \sigma_v: \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \quad . \tag{IIB.13}$$

This representation does not correspond to the E_m IR, but that provided by the pair $\{\zeta_m f_{a_2}, -\zeta_{-m} f_{a_2}\}$ does.

The coupling coefficients are as follows:

$$\begin{pmatrix} \zeta_m \zeta_n \\ \zeta_{-m} \zeta_{-n} \end{pmatrix} \quad \text{transforms as} \quad \begin{pmatrix} \zeta_{m+n} \\ \zeta_{-(m+n)} \end{pmatrix} \text{ for } m \geq n > 0 \tag{IIB.14a}$$

$$\begin{pmatrix} \zeta_m \zeta_{-n} \\ \zeta_{-m} \zeta_n \end{pmatrix} \quad \text{"} \quad \begin{pmatrix} \zeta_{m-n} \\ \zeta_{-(m-n)} \end{pmatrix} \text{ for } m > n \geq 0 \tag{IIB.14b}$$

$$\frac{1}{\sqrt{2}}(\zeta_m \zeta_{-m} + \zeta_{-m} \zeta_m) \quad \text{"} \quad A_1 \quad \text{for } m > 0 \tag{IIB.14c}$$

$$\frac{1}{\sqrt{2}}(\zeta_m \zeta_{-m} - \zeta_{-m} \zeta_m) \quad \text{"} \quad A_2 \quad \text{for } m > 0 \tag{IIB.14d}$$

$$\begin{pmatrix} \zeta_m f_{a_2} \\ -\zeta_{-m} f_{a_2} \end{pmatrix} \quad \text{transforms as} \quad \begin{pmatrix} \zeta_m \\ \zeta_{-m} \end{pmatrix} \quad \text{for } m > 0 \quad . \qquad \text{(IIB.14e)}$$

To obtain the coupling coefficients for the representations provided by the real functions, the column vectors above need only be multiplied by a unitary matrix V which provides the transformation from a pair of complex functions to a pair of real functions. The transformation V is defined as

$$\begin{pmatrix} \eta_m \\ \eta_{-m} \end{pmatrix} = \underset{\approx}{V} \begin{pmatrix} \zeta_m \\ \zeta_{-m} \end{pmatrix} , \qquad \text{so} \qquad \underset{\approx}{V} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -i & i \end{pmatrix} .$$

Note that V is different than U, which is given by (IIB.7), because V transforms functions whereas U transforms vectors which are described in terms of basis functions $\{\eta_m, \eta_{-m}\}$ and $\{\zeta_m, \zeta_{-m}\}$. Application of V to the pair of functions (IIB.14a), gives

$$\underset{\approx}{V} \begin{pmatrix} \zeta_m \zeta_n \\ \zeta_{-m} \zeta_{-n} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} \zeta_m \zeta_n + \zeta_{-m} \zeta_{-n} \\ -i(\zeta_m \zeta_n - \zeta_{-m} \zeta_{-n}) \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} \eta_m \eta_n - \eta_{-m} \eta_{-n} \\ \eta_m \eta_{-n} + \eta_{-m} \eta_n \end{pmatrix} ,$$

which transforms as

$$\underset{\approx}{V} \begin{pmatrix} \zeta_{m+n} \\ \zeta_{-(m+n)} \end{pmatrix} = \begin{pmatrix} \eta_{m+n} \\ \eta_{-(m+n)} \end{pmatrix} , \qquad \text{for } m \geq n > 0 \quad , \qquad \text{(IIB.15)}$$

i.e., according to the representations (IIB.6) supplied by the real functions η. Continuation with this procedure results in the following:

$$\frac{1}{\sqrt{2}}\begin{pmatrix}\eta_m\eta_n-\eta_{-m}\eta_{-n}\\ \eta_m\eta_{-n}+\eta_{-m}\eta_n\end{pmatrix} \quad \text{transforms as} \quad \begin{pmatrix}\eta_{m+n}\\ \eta_{-(m+n)}\end{pmatrix} \quad \text{for } m \geq n > 0$$

$$\frac{1}{\sqrt{2}}\begin{pmatrix}\eta_m\eta_n+\eta_{-m}\eta_{-n}\\ \eta_{-m}\eta_n-\eta_m\eta_{-n}\end{pmatrix} \quad '' \quad \begin{pmatrix}\eta_{m-n}\\ \eta_{-(m-n)}\end{pmatrix} \quad \text{for } m > n \geq 0$$

$$\frac{1}{\sqrt{2}}(\eta_m\eta_m+\eta_{-m}\eta_{-m}) \quad '' \quad A_1$$

$$\text{for } m > 0$$

$$\frac{1}{\sqrt{2}}(\eta_{-m}\eta_m-\eta_m\eta_{-m}) \quad '' \quad A_2$$

$$\begin{pmatrix}\eta_{-m}f_{a_2}\\ -\eta_m f_{a_2}\end{pmatrix} \quad '' \quad \begin{pmatrix}\eta_m\\ \eta_{-m}\end{pmatrix} \quad \text{for } m > 0 \quad .\text{(IIB.16a-e)}$$

The functions (IIB.14c and d) yield (IIB.16c and d) directly after writing ζ_m in terms of η_m and normalizing, since the A_1 and A_2 representations are one-dimensional.

Configurations may now be constructed by the coupling procedure outlined in part I and either real orbitals $\eta_{\pm m}$ coupled according to (IIB.16) or complex orbitals $\zeta_{\pm m}$ coupled according to (IIB.14) may be used.

The coupling of two equivalent π electrons ($m=\pm 1$) may be done to produce functions transforming spatially as the Δ (E_2), Σ^+ (A_1) or Σ^- (A_2) IRs. The spin component may be coupled singlet (S=0) or triplet (S=1) for a possibility of six space-spin couplings (maximum m_s value only):

$$^1\Sigma^+ \ (^1A_1): \ \frac{1}{2}(\pi_x\pi_x+\pi_y\pi_y)(\alpha\beta-\beta\alpha)$$

$$^3\Sigma^+ \ (^3A_1): \ \frac{1}{\sqrt{2}}(\pi_x\pi_x+\pi_y\pi_y)\alpha\alpha$$

$$
\begin{aligned}
&{}^1\Sigma^- \ ({}^1A_2): \ \tfrac{1}{2}\,(\pi_y\pi_x-\pi_x\pi_y)(\alpha\beta-\beta\alpha)\\
&{}^3\Sigma^- \ ({}^3A_2): \ \tfrac{1}{\sqrt{2}}\,(\pi_y\pi_x-\pi_x\pi_y)\alpha\alpha\\
&{}^1\Delta_x \ ({}^1E_x): \ \tfrac{1}{2}\,(\pi_x\pi_x-\pi_y\pi_y)(\alpha\beta-\beta\alpha)\\
&{}^1\Delta_y \ ({}^1E_y): \ \tfrac{1}{2}\,(\pi_x\pi_y+\pi_y\pi_x)(\alpha\beta-\beta\alpha)\\
&{}^3\Delta_x \ ({}^3E_x): \ \tfrac{1}{\sqrt{2}}\,(\pi_x\pi_x-\pi_y\pi_y)\alpha\alpha\\
&{}^3\Delta_y \ ({}^3E_y): \ \tfrac{1}{\sqrt{2}}\,(\pi_x\pi_y+\pi_y\pi_x)\alpha\alpha \quad .
\end{aligned}
\tag{IIB.17}
$$

Application of the antisymmetrizer kills off all except three,

$$
\begin{aligned}
&{}^1\Sigma^+ \ \tfrac{1}{\sqrt{2}}\,A(\pi_x\pi_x\alpha\beta) + \tfrac{1}{\sqrt{2}}\,A(\pi_y\pi_y\alpha\beta)\\
&{}^3\Sigma^- \ A(\pi_x\pi_y\alpha\alpha)\\
&{}^1\Delta \ \left\{\begin{array}{l}\tfrac{1}{\sqrt{2}}\,A(\pi_x\pi_x\alpha\beta) - \tfrac{1}{\sqrt{2}}\,A(\pi_y\pi_y\alpha\beta)\\ \tfrac{1}{\sqrt{2}}\,A(\pi_x\pi_y\alpha\beta) + \tfrac{1}{\sqrt{2}}\,A(\pi_y\pi_x\alpha\beta)\end{array}\right\} \quad .
\end{aligned}
\tag{IIB.18}
$$

These functions are the analogs of (ID.2a-c) which represent the coupling of two equivalent e electrons in a C_{3v} molecule. The couplings are the same except for only one sign in the ${}^1\Delta_y$ function compared to the ${}^1E_y$ function.

If two nonequivalent π electrons are to be coupled, all six symmetry functions of (IIB.17) are permitted. By the particle-hole equivalence mentioned in the previous section, the coupling $\pi^3\pi^3$ produces the same

six states of (IIB.17) and the three of SO to be studied here (see IIA.2) are

$$
\begin{aligned}
{}^3\Sigma^+ \quad & \frac{1}{\sqrt{2}} A(1\pi_x^2\, 1\pi_y\, 2\pi_x^2\, 2\pi_y\, \alpha\alpha) + \frac{1}{\sqrt{2}} A(1\pi_y^2\, 1\pi_x\, 2\pi_y^2\, 2\pi_x\, \alpha\alpha) \\
{}^1\Sigma^- \quad & \frac{1}{2} A(1\pi_x^2\, 1\pi_y\, 2\pi_y^2\, 2\pi_x\, \alpha\beta) - \frac{1}{2} A(1\pi_x^2\, 1\pi_y\, 2\pi_y^2\, 2\pi_x\, \beta\alpha) \\
& -\frac{1}{2} A(1\pi_y^2\, 1\pi_x\, 2\pi_x^2\, 2\pi_y\, \alpha\beta) + \frac{1}{2} A(1\pi_y^2\, 1\pi_x\, 2\pi_x^2\, 2\pi_y\, \beta\alpha) \\
{}^3\Delta_x \quad & \frac{1}{\sqrt{2}} A(1\pi_y^2\, 1\pi_x\, 2\pi_y^2\, 2\pi_x\, \alpha\alpha) - \frac{1}{\sqrt{2}} A(1\pi_x^2\, 1\pi_y\, 2\pi_x^2\, 2\pi_y\, \alpha\alpha) \\
{}^3\Delta_y \quad & \frac{1}{\sqrt{2}} A(1\pi_y^2\, 1\pi_x\, 2\pi_x^2\, 2\pi_y\, \alpha\alpha) + \frac{1}{\sqrt{2}} A(1\pi_x^2\, 1\pi_y\, 2\pi_y^2\, 2\pi_x\, \alpha\alpha) \quad . \qquad \text{(IIB.19)}
\end{aligned}
$$

C. The Calculations

Using a wavefunction of the single configuration form as derived from the one of the two electron occupations of (IIA.1 and 2) and having the appropriate space-spin symmetries as given in (IIB.18 and 19), the best set of orbitals was determined by the SCF-MO procedure.[4] The orbitals generated by the SCF-MO procedure were constrained to be orthonormal and consisted of optimized (by the variational theorem) linear combinations of single-valued functions of three-space called basis functions. Each basis function is itself a fixed (i.e., not subject to variational optimization) linear combination of simple spherically symmetric radial gaussians of the form $\sum_i \exp[-\alpha_i(\underset{\sim}{r}-\underset{\sim}{R}_k)^2]$ multiplied by a cartesian spherical harmonic.[5] The gaussian functions that constitute a basis function are all centered at $\underset{\sim}{R}_k$ which is usually the position vector of one of the nuclei (the kth) of the molecule.

The calculation performed here employed thirty-eight basis functions, with twenty-three centered on the sulfur nucleus and fifteen on the oxygen nucleus. The basis set is denoted S[12s8p1d/6s4p1d] and O[9s5p1d/4s2p1d], meaning that centered on the sulfur nucleus there are six s-type basis functions, four triplets of functions of p-type symmetry, and one set of five functions of d-type symmetry. The six s-type functions are six different linear combinations of twelve simple gaussians, and similarly for the p- and d-type functions.[5] All the basis functions are real.

The SCF-MO procedure produces orbitals which transform according to the various IRs provided by the real function η_m and η_{-m}. The orbitals are thus identified by the IR according to which they transform: π_x,π_y if they transform as η_1,η_{-1}; δ_x,δ_y if as η_2,η_{-2}, and so on. It is thus at the SCF-MO stage that the symmetrized single-particle functions are generated. From thirty-eight functions, thirty-eight orbitals are produced. The molecular orbital basis set may be denoted [18σ8π2δ], 8π meaning there are eight π_x and eight π_y orbitals. Although there are thirty-eight orbitals, only thirteen are occupied at the SCF level of theory. The twenty-five unoccupied orbitals are called virtual orbitals.

From the SCF-MO wavefunction properties of the molecule may be computed such as the dipole moment and polarizabilities. If several calculations are performed at different internuclear distances, the resulting energies may be fitted to a curve an. vibrational properties may be predicted such as the classical vibrational frequency.

Following the generation of a set of molecular orbitals, a configuration interaction (CI) calculation may be performed. First, a set of

configurations is generated as all those couplings of the correct space-spin symmetry from a set of electron occupations. The set of electron occupations are usually generated as all excitations of one and two electrons from the occupied to the virtual set of orbitals generated by the SCF-MO calculation. Usually the configuration list consists of thousands of configurations.

The next step of the CI procedure is to construct a Hamiltonian matrix using the (orthonormal) configuration list as the basis. The lowest eigenvalue and eigenvector, which is a linear combination of configurations, may be extracted from the Hamiltonian by an interative procedure.[2] The resulting wavefunction may be used to compute properties of the molecule, and an electronic energy curve parameterized by internuclear distance may be constructed to compute vibrational properties, just as can be done with the SCF-MO wavefunctions and energies.

The results of this procedure are shown in the table together with the best available experimental information for comparison. The column labeled T_e provides excitation energies from the minimum of the ground state ($X^3\Sigma^-$) energy curve to the minimum of the excited state energy curve. In addition to the dipole moment, spectroscopic data usually supplied by infrared experiments are also given.

If the data provided by experiments are considered correct, it can be seen that the CI technique provides more accurage predictions than SCF. Also, by analysing the discrepancy between the molecular parameters predicted by the theories and those provided by the experiments, the accuracy of the theory can be determined. Thus, as provided by the few experimental results, the SCF level of theory gives excitation energies,

bond lengths, and stretching frequencies to 40%, 3%, and 20%, respectively, whereas CI gives the same to 15%, 1%, and 8%. This is in agreement with similar calculations[1] performed on S_2 and so these percentages are expected to be applicable to the states of SO for which there is no experimental information.

Comparison of Theoretical Predictions and Experimental[a] Results for SO

State	Method	Number of $C_{\infty v}$ Configurations	T_e[b], cm^{-1}	r_e, Å	ω_e, cm^{-1}	B_e, cm^{-1}	μ, Debye
$A''^3\Sigma^+$	CI	2349	26200	1.797	680	0.489	1.25
	SCF		18200	1.735	810	0.525	1.32
	Expt						
$A'^3\Delta$	CI	2615	25400	1.789	700	0.494	1.25
	SCF		17500	1.729	820	0.529	1.27
	Expt		28400[f]				
$c^1\Sigma^-$	CI	2041	24400	1.788	680	0.494	1.24
	SCF		16700	1.723	820	0.532	1.26
	Expt		27700[e]				
$b^1\Sigma^+$	CI	898	12400	1.518	1160	0.686	1.76
	SCF		16400	1.464	1350	0.738	2.10
	Expt		10509.97	1.5004	1067.66	0.7026	
$a^1\Delta$	CI	959	7140	1.506	1200	0.697	1.82
	SCF		8300	1.460	1260	0.742	2.23
	Expt		6150	1.4889[c]	1115.3[c]	0.709[c]	1.31[d]
$X^3\Sigma^-$	CI	1046	0	1.499	1200	0.7031	1.95
	SCF		0	1.457	1350	0.7446	2.42
	Expt		0	1.4810	1148.19	0.7208	

Table continued.

[a]From Données Spectroscopiques Relatives aux Molécules Diatomiques, edited by B. Rosen (Pergamon, Oxford, 1971), unless noted.

[b]All excitation energies are relative to the minimum energy of the ground state potential curve. This energy is -472.33354 at the SCF level of theory and -472.51170 at the CI level.

[c]From laser NMR experiments of C. Yamada, K. Kawaguchi and E. Hirota, J. Chem. Phys. 69, 1942 (1978).

[d]From C. R. Byfleet, A. Carrington and D. K. Russell, Mol. Phys. GB 20, 271 (1971).

[e]From Y.-P. Lee and G. C. Pimentel, J. Chem. Phys. 69, 3063 (1978).

[f]From D. E. Tevault and R. R. Smardzewski, J. Chem. Phys. 69, 3182 (1978).

[g]From T. Ishiwata and I. Tanaka, "Sensitized Chemiluminescence by SO ($^1\Delta$)", Thirteenth Informal Conference on Photochemistry. Clearwater Beach, Florida, 1978.

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2. Other than the construction of configurations from a given electron occupation, it is beyond the scope of this work to discuss the detailed workings of the SCF-MO and CI computer procedures employed. See, for example, R. R. Lucchese, B. R. Brooks, J. H. Meadows, W. C. Swope, and H. F. Schaefer, J. Comput. Phys. 26, 243 (1978), and B. R. Brooks and H. F. Schaefer, Int. J. Quantum Chem. (to be published).
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4. The SCF procedure used here was developed by C. C. J. Roothaan, Rev. Mod. Phys. 32, 179 (1960).
5. An excellent discussion of basis sets is by T. H. Dunning and P. J. Hay in Modern Theoretical Chemistry, Vol. 3, edited by H. F. Schaefer (Plenum, New York, 1977). The set used in this study centered on the sulfur nucleus is on page 24 of this volume. The basis set centered on the oxygen nucleus is to be found in an article of T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).

III. A Harmonic Oscillator Model for Electronic Properties

A. Introduction

The wavefunctions and eigenvectors describing a particle moving in a harmonic potential are almost as old as quantum mechanics itself. Indeed, this potential is one of the few for which exact analytic solutions to the time-independent Schrödinger equation can be found. In view of this, the approximation of real non-harmonic potentials by harmonic ones has been the basis of many theories and "back-of-the envelope" calculations. All of normal mode analysis for the study of the vibrational energies and corresponding wavefunctions of polyatomic molecules, for example, is based on the assumption that the complex motions of the nuclei of a molecule may be described as some linear combination of a collection of harmonic oscillators.

The following sections will deal with a harmonic oscillator model for the electronic properties of small closed-shell molecules. The attempt will be to approximate the electronic probability density of a molecule by the probability density of a particle moving in an anisotropic but harmonic potential. Three electronic properties will be investigated: the electric polarizability, the magnetic susceptibility, and the magnetic shielding of a nuclear spin by the electronic charge (chemical shift). The predictions given by the model for molecular hydrogen will be presented for comparison with experimental results.

B. Electric Polarizability

The application of a harmonic oscillator model in the study of electric polarizability is by no means a new idea. A classical treatment

of the oscillator toward this goal is given in many electrodynamic texts[1] and a quantum mechanical treatment is usually given as one problem in a problem set assigned in any first year quantum mechanics course.

For a system which may not be spherically symmetric, for small enough electric fields, $\underset{\sim}{\varepsilon}$, the energy may be expanded in a Taylor series in the field

$$E(\underset{\sim}{\varepsilon}) = E(0) + \sum_i \frac{\partial E(\underset{\sim}{\varepsilon})}{\partial \varepsilon_i}\Big|_{\underset{\sim}{\varepsilon}=0} \varepsilon_i + \sum_{i,j} \frac{1}{2} \frac{\partial^2 E(\underset{\sim}{\varepsilon})}{\partial \varepsilon_i \partial \varepsilon_j}\Big|_{\underset{\sim}{\varepsilon}=0} \varepsilon_i \varepsilon_j + \dots \quad . \qquad \text{(IIIB.1)}$$

This expression can be used to generate a definition for the polarizability when combined with the fact that for a point dipole in an electric field the energy is given as

$$E = E(0) - \underset{\sim}{p} \cdot \underset{\sim}{\varepsilon} \quad . \qquad \text{(IIIB.2)}$$

Apparently, the electric field induces a dipole moment in the charge distribution, p_{ind}. The total dipole moment will be a sum of a constant zero-field dipole moment, p_0, and the induced dipole moment which may also be written in a power series in the field:

$$\begin{aligned} \underset{\sim}{p}(\underset{\sim}{\varepsilon}) &= \underset{\sim}{p}_0 + p_{ind}(\underset{\sim}{\varepsilon}) \\ &= \underset{\sim}{p}_0 + \underset{\approx}{\alpha} \cdot \underset{\sim}{\varepsilon} + (\text{higher order terms in } \underset{\sim}{\varepsilon}) \quad . \end{aligned} \qquad \text{(IIIB.3)}$$

This is the usual definition for the polarizability, α. An expression for α in terms of the energy may be obtained by inserting (IIIB.3) into (IIIB.2) and equating "coefficients" of various powers of ε_i in (IIIB.1). One then finds

$$(\underset{\sim}{p}_0)_i = - \frac{\partial E(\underset{\sim}{\varepsilon})}{\partial \varepsilon_i}\Big|_{\varepsilon=0} \qquad \text{(IIIB.4)}$$

and

$$\alpha_{ij} = -\frac{1}{2}\frac{\partial^2 E(\underset{\sim}{\varepsilon})}{\partial\varepsilon_i\partial\varepsilon_j}\Big|_{\varepsilon=0} \quad . \tag{IIIB.5}$$

The procedure will be to use perturbation theory to develop an expression for $E(\underset{\sim}{\varepsilon})$ and then use (IIIB.5) to get a corresponding expression for α.

The Hamiltonian will be that of a three-dimensional anisotropic Harmonic oscillator with three different frequencies (hence the anisotropy) with a mass m and charge q. It is

$$H = [(\frac{1}{2m}p_x^2 + \frac{1}{2}m\omega_x^2x^2) + (\frac{1}{2m}p_y^2 + \frac{1}{2}m\omega_y^2y^2) + (\frac{1}{2m}p_z^2 + \frac{1}{2}m\omega_z^2z^2)]$$

$$- q\underset{\sim}{r}\cdot\underset{\sim}{\varepsilon} \tag{IIIB.6}$$

where $\underset{\sim}{r} = x\hat{x} + y\hat{y} + z\hat{z}$ is a vector which points from the origin to the particle. The part in brackets will be denoted H_0 and the rest H'. The eigenvalues and eigenfunctions of H_0 are known exactly. Since H_0 is separable in the three coordinates of the particle, its wavefunctions will be simply products of three one-dimensional wavefunctions,

$$\psi_{n_x,n_y,n_z}(\underset{\sim}{r}) = \psi_{n_x}(x)\ \psi_{n_y}(y)\ \psi_{n_z}(z) \quad , \tag{IIIB.7}$$

where n_x, n_y, and n_z represent quantum numbers for motion in each of the uncoupled directions. Dirac notation will sometimes be used.

$$\psi_{n_x,n_y,n_z}(\underset{\sim}{r}) = \langle\underset{\sim}{r}|n_x,n_y,n_z\rangle \tag{IIIB.8}$$

The use of functions of the form (IIIB.7) as the zeroth order wavefunctions, perturbation theory to second order gives

$$E_{\underset{\sim}{n}}(\underset{\sim}{\varepsilon}) = E_{\underset{\sim}{n}}(0) + \langle \underset{\sim}{n}|H'|\underset{\sim}{n}\rangle + \sum_{\underset{\sim}{n}'}{}' \frac{\langle \underset{\sim}{n}|H'|\underset{\sim}{n}'\rangle\langle \underset{\sim}{n}'|H'|\underset{\sim}{n}\rangle}{E_{\underset{\sim}{n}}(0)-E_{\underset{\sim}{n}'}(0)} \tag{IIIB.9}$$

where $\underset{\sim}{n}$ represents the ordered triplet of quantum numbers which specify the state of the oscillator and the zeroth order energies are given by the well-known expression

$$E_{\underset{\sim}{n}}(0) = \hbar\omega_x(n_x+\tfrac{1}{2}) + \hbar\omega_y(n_y+\tfrac{1}{2}) + \hbar\omega_z(n_z+\tfrac{1}{2}) \quad . \tag{IIIB.10}$$

The first order term of (IIIB.9) is zero due to symmetry. ($\psi^*(\underset{\sim}{r})\psi(\underset{\sim}{r})$ has even parity, whereas $\underset{\sim}{r}$ has odd parity, so the integrand of the first order term has odd parity.)

Substituting the form H' into IIIB.9, one obtains

$$E_{\underset{\sim}{n}}(\underset{\sim}{\varepsilon}) = E_{\underset{\sim}{n}}(0) + q^2 \sum_{i,j=1}^{3} \sum_{\underset{\sim}{n}'}{}' \frac{\langle \underset{\sim}{n}|r_i|\underset{\sim}{n}'\rangle\langle \underset{\sim}{n}'|r_j|\underset{\sim}{n}\rangle}{E_{\underset{\sim}{n}}(0)-E_{\underset{\sim}{n}'}(0)} \varepsilon_i\varepsilon_j \quad . \tag{IIIB.11}$$

From (IIIB.5) one finds that the polarizability is given by

$$\alpha_{ij} = -\frac{q^2}{2} \sum_{\underset{\sim}{n}'}{}' \frac{\langle \underset{\sim}{n}|r_i|\underset{\sim}{n}'\rangle\langle \underset{\sim}{n}'|r_j|\underset{\sim}{n}\rangle}{E_{\underset{\sim}{n}}(0)-E_{\underset{\sim}{n}'}(0)} \quad . \tag{IIIB.12}$$

Since the operator r_i has nonvanishing matrix elements only between states which differ by one in n_i quantum number, it is clear that unless i=j, either $\langle \underset{\sim}{n}|r_i|\underset{\sim}{n}'\rangle$ or $\langle \underset{\sim}{n}'|r_j|\underset{\sim}{n}\rangle$ is zero. Hence, $\underset{\approx}{\alpha}$ is diagonal.

In what follows, the model will be restricted to one describing molecules of axial symmetry, so $\omega_x = \omega_y = \omega$ and $\omega_z = \mu\omega$. Furthermore, only properties of the ground state of the molecule will be predicted, and it will be assumed that the charge distribution of the ground state of the molecule can be adequately described by that of a ground state oscillator ($\underset{\sim}{n} = 0$). This last assumption will certainly be better for some molecules than others. In particular one would think it to be best for molecules all of whose electrons are in nodeless orbitals, as is the case for molecular hydrogen.

The assumption that a ground state oscillator probability distribution adequately describes that of a real molecule makes the model at this point a purely geometrical one. That is, all the features of a real molecule such as the number of electrons and the shape and nodal character of the various orbitals are absorbed into two parameters, ω and ω_z, which define only the shape (geometry) of the oscillator distribution. Clearly a more elaborate model could be constructed where each orbital could be mimicked by an oscillator wavefunction with a similar nodal structure, and a total wavefunction built as an antisymmetrized product of orbitals (see section I). A less elaborate model than this, but still better than the purely geometric one, would be one where each orbital is described by a ground state oscillator distribution with a different size (different ω and ω_z). Clearly, the treating of molecular hydrogen is practically the same for all three levels of modeling since H_2 has only one orbital and that orbital is nodeless.

Incorporation of the above notation into (IIIB.12) gives

$$\alpha_{xx} = \alpha_{yy} = -\frac{q^2}{2} \sum_{\underset{\sim}{n}'}' \frac{\langle 0|x|\underset{\sim}{n}'\rangle\langle \underset{\sim}{n}'|x|0\rangle}{E_0 - E_{\underset{\sim}{n}'}}$$

$$= -\frac{q^2}{2\hbar} \sum_{\underset{\sim}{n}'}' \frac{|\langle 0|x|\underset{\sim}{n}'\rangle|^2}{-\omega(n_x' + n_y' + \mu n_z')} \quad . \qquad \text{(IIIB.13)}$$

Since matrix elements for the operator x are nonvanishing only between states which differ by one in quantum number n_x, the sum reduces to one term with $\underset{\sim}{n}' = (1,0,0)$. With $\langle 0|x|1\rangle = (\hbar/2m\omega)^{\frac{1}{2}}$,

$$\alpha_{xx} = q^2/4m\omega^2 \quad ,$$

and similarly

$$\alpha_{zz} = q^2/4m\mu^2\omega^2 \quad . \qquad \text{(IIIB.14)}$$

In order to use the above relations, as well as those which follow, to predict properties, some means must exist for determining the parameters of the model; q, m, ω and μ. The obvious choices for q and m are the charge and mass of the electron. The values to be used for ω and μ will be chosen based on the geometry of the molecule to be studied through the relationships

$$\langle 0|x^2|0\rangle = \hbar/2m\omega$$

$$\langle 0|z^2|0\rangle = \hbar/2m\mu\omega \quad . \qquad \text{(IIIB.15)}$$

From the literature[2] we obtain for H_2

$$\langle x^2\rangle = 1.533\ a_0^2$$

$$\langle z^2\rangle = 2.121\ a_0^2 \quad , \qquad \text{(IIIB.16)}$$

which when combined with (IIIB.15) gives μ=0.72 and values for α which are compared in the following table:

	Model	Experiment[3]	
α_{xx}	2.350	2.222	
α_{zz}	4.499	3.054	
α	3.066	2.499	(IIIB.17)

The units are a_0^3 where a_0 is the Bohr radius. The last line of the table is one-third the trace of the polarizability which is the average polarizability per molecule of a randomly oriented mixture.

Thus, the model gives values for the polarizability that differ by as much as 50% with the experimental values. Of course, the model values of the table above depend on the values for ω and μ used. These may be obtained many different ways. Values for ω to be used for H_2 may be obtained, for example, as the ones which give $\langle r \rangle$ or $\langle r^2 \rangle$ correctly for the hydrogen atom when modeled by a spherical (μ=1) oscillator. Values for μ may also be derived by various procedures. It is interesting to note here that for the harmonic oscillator $\mu = (\alpha_{xx}/\alpha_{zz})^{\frac{1}{2}}$. Experimental polarizabilities yield a value of 0.85 for μ.

C. Magnetic Susceptibility

Although the use of the oscillator model in predicting electric polarizabilities is quite old, its use in predicting magnetic susceptibilities is actually a relatively recent one. Apparently the first one to derive expressions for the susceptibility was the Russian worker Rebane[4] whose work was independently confirmed by Harris.[5]

The development of the expressions for the susceptibility of an oscillator parallels closely that for the electric polarizability. The unperturbed oscillator Hamiltonian will be the same H_0 as in the previous section. The Hamiltonian for a charged particle of mass m and charge q in the presence of a magnetic field $\underset{\sim}{B}$ derived from a vector potential $\underset{\sim}{A}$ is

$$H = \frac{1}{2m}\left(\underset{\sim}{p} - \frac{q}{c}\underset{\sim}{A}\right)^2 + (\text{h.o. potential})$$

$$= H_0 - \frac{q}{2mc}\left(\underset{\sim}{p}\cdot\underset{\sim}{A} + \underset{\sim}{A}\cdot\underset{\sim}{p}\right) + \frac{q^2}{2mc^2}\underset{\sim}{A}\cdot\underset{\sim}{A} \quad , \qquad \text{(IIIC.1)}$$

For a constant magnetic field $\underset{\sim}{B}$

$$\underset{\sim}{A} = \frac{1}{2}\underset{\sim}{B}\times\underset{\sim}{r} \qquad \text{(IIIC.2)}$$

and since $\underset{\sim}{p} \sim \underset{\sim}{\nabla}$,

$$\underset{\sim}{p}\cdot\underset{\sim}{A} \sim [\underset{\sim}{\nabla}\cdot(\underset{\sim}{B}\times\underset{\sim}{r})] + (\underset{\sim}{B}\times\underset{\sim}{r})\cdot\underset{\sim}{\nabla}$$

$$\sim \underset{\sim}{r}\cdot(\underset{\sim}{\nabla}\times\underset{\sim}{B}) - \underset{\sim}{B}\cdot(\underset{\sim}{\nabla}\times\underset{\sim}{r}) + (\underset{\sim}{B}\times\underset{\sim}{r})\cdot\underset{\sim}{\nabla}$$

$$\sim \underset{\sim}{A}\cdot\underset{\sim}{p} \quad . \qquad \text{(IIIC.3)}$$

The last proportionality holds because $\underset{\sim}{\nabla}\times\underset{\sim}{B} = 0$ ($\underset{\sim}{B}$ being constant) and $\underset{\sim}{\nabla}\times\underset{\sim}{r} = 0$. When we apply these facts to (IIIC.1), we obtain

$$H' = -\frac{q}{mc}(\underset{\sim}{A}\cdot\underset{\sim}{p}) + \frac{q^2}{2mc^2}\,\underset{\sim}{A}\cdot\underset{\sim}{A}$$

$$= -\frac{q}{2mc}(\underset{\sim}{B}\times\underset{\sim}{r})\cdot\underset{\sim}{p} + \frac{q^2}{8mc^2}\,(\underset{\sim}{B}\times\underset{\sim}{r})\cdot(\underset{\sim}{B}\times\underset{\sim}{r})$$

$$= -\frac{q}{2mc}\,\underset{\sim}{B}\cdot\underset{\sim}{L} + \frac{q^2}{8mc^2}\,\underset{\sim}{B}\cdot[\underset{\sim}{r}\cdot\underset{\sim}{r}\underset{\approx}{I} - \underset{\sim}{r}\underset{\sim}{r}]\cdot\underset{\sim}{B} \quad . \qquad \text{(IIIC.4)}$$

By exact analogy with section B, the susceptibility is defined as

$$\chi_{ij} = -\frac{1}{2}\frac{\partial^2 E(\underset{\sim}{B})}{\partial B_i \partial B_j}\Big|_{\underset{\sim}{B}=0} \quad . \qquad \text{(IIIC.5)}$$

Thus, a power series type expression for the energy needs to be derived. Only the terms quadratic in the field components are of interest, however, because terms of lower power will vanish by the second derivative and terms of higher power will vanish when the derivative is evaluated at zero field strength. As in the previous section perturbation theory provides the required energy expression. Retention of all terms of quadratic or lower order in the field yields

$$E(\underset{\sim}{B}) = E(0) - \frac{q}{2mc}\,\underset{\sim}{B}\cdot\langle 0|\underset{\sim}{L}|0\rangle + \frac{q^2}{8mc^2}\,\underset{\sim}{B}\cdot\langle 0|\underset{\sim}{r}\cdot\underset{\sim}{r}\underset{\approx}{I} - \underset{\sim}{r}\underset{\sim}{r}|0\rangle\cdot\underset{\sim}{B}$$

$$+ \frac{q^2}{4m^2c^2}\sum_{\underset{\sim}{n}}{}' \langle 0|\underset{\sim}{B}\cdot\underset{\sim}{L}|\underset{\sim}{n}\rangle\langle\underset{\sim}{n}|\underset{\sim}{B}\cdot\underset{\sim}{L}|0\rangle[E_0(0) - E_{\underset{\sim}{n}}(0)]^{-1} \quad , \qquad \text{(IIIC.6)}$$

where it has been assumed that the ground state is being perturbed.

The first first-order term is zero because the ground state is non-degenerate and therefore has no angular momentum. The remaining two terms of interest will be examined separately. The second first-order term will be called E^d because it will contribute to the diamagnetic

component of the susceptibility.

$$\underset{\approx}{\chi}^d \sim \langle 0|\underset{\sim}{r}\cdot\underset{\sim}{r}\underset{\approx}{I} - \underset{\sim}{r}\underset{\sim}{r}|0\rangle \quad . \tag{IIIC.7}$$

Since $\langle 0|r_i r_j|0\rangle = 0$ for $i \neq j$, it is clear that $\underset{\approx}{\chi}^d$ is a diagonal tensor. Also, due to the cylindrical symmetry, $\chi^d_{xx} = \chi^d_{yy}$. The independent components are, therefore,

$$\chi^d_x = -\frac{q^2}{8mc^2}\langle 0|y^2+z^2|0\rangle$$

$$\chi^d_z = -\frac{q^2}{8mc^2}\langle 0|x^2+y^2|0\rangle \quad , \tag{IIIC.8}$$

and since $\langle 0|r_i^2|0\rangle = h/2m\omega_i$, the model yields

$$\chi^d_x = -\frac{q^2 h}{16m^2c^2\omega}\left(1+\frac{1}{\mu}\right)$$

$$\chi^d_z = -\frac{q^2 h}{8m^2c^2\omega} \quad . \tag{IIIC.9}$$

The remaining (paramagnetic) component of χ, called χ^p, is

$$\underset{\approx}{\chi}^p \sim \sum_{\underset{\sim}{n}}{}' \langle 0|\underset{\sim}{L}|\underset{\sim}{n}\rangle\langle\underset{\sim}{n}|\underset{\sim}{L}|0\rangle\,[E_0(0) - E_{\underset{\sim}{n}}(0)]^{-1} \quad . \tag{IIIC.10}$$

It will be shown that $\underset{\approx}{\chi}^p$ is also diagonal: Consider an off-diagonal matrix element, say χ^p_{xy}. This element is a sum of terms each proportional to $\langle 0|yp_z - zp_y|\underset{\sim}{n}\rangle\langle\underset{\sim}{n}|zp_x - xp_z|0\rangle$. Owing to the selection rules for x and p_x in a harmonic oscillator basis, the first factor is zero unless $n_x = 0$

and $n_y = 1$. The second factor is zero unless $n_x = 1$ and $n_y = 0$. Since these conditions cannot be met for any $\underset{\sim}{n}$, $\chi^p_{xy} = 0$. A similar argument shows that all off-diagonal elements are zero.

Due to the cylindrical symmetry of the oscillator in its ground state $L_z|0\rangle = \langle 0|L_z = 0$. This is seen to be so by remembering that $L_z \sim \partial/\partial\phi$, where ϕ is the angle about the z-axis. $\psi_{\underset{\sim}{n}=0}$ has no ϕ dependence. This fact insures that $\chi^p_{zz} = 0$. The cylindrical symmetry further insures that $\chi^p_{xx} = \chi^p_{yy}$.

The only nonzero elements of χ^p are, therefore,

$$\chi^p_{xx} = \chi^p_{yy} = \frac{-q^2}{4m^2c^2} \sum_{\underset{\sim}{n}} |\langle 0|L_x|\underset{\sim}{n}\rangle|^2 \, [E_0(0) - E_{\underset{\sim}{n}}(0)]^{-1} \quad . \qquad \text{(IIIC.11)}$$

For $\langle 0|L_x|n\rangle$ to be nonzero it must be that $n_x=0$, $n_y=n_z=1$. Thus, the sum collapses to one term. If we write L_x in terms of annihilation and creation operators,[5] then operating on $|0,1,1\rangle$ we obtain

$$\begin{aligned}\langle 0,0,0|L_x|0,1,1\rangle &= \frac{\hbar}{2i} (\omega_z-\omega_y)/(\omega_y\omega_z)^{\frac{1}{2}} \\ &= \frac{\hbar}{2i} (\mu-1)/\sqrt{\mu} \quad . \qquad \text{(IIIC.12)}\end{aligned}$$

Thus, insertion of this into (IIIC.11) yields

$$\chi^p_{xx} = \frac{q^2}{4m^2c^2} \frac{\hbar^2}{4} \frac{(\mu-1)^2}{\mu} \frac{1}{\hbar(\omega+\mu\omega)} \quad . \qquad \text{(IIIC.13)}$$

The following equations for the susceptibility have been derived:

$$\underset{\approx}{\chi} = \underset{\approx}{\chi}^{p} + \underset{\approx}{\chi}^{d}$$

$$\chi^{d}_{zz} = -\frac{q^2\hbar}{8m^2c^2\omega}$$

$$\chi^{d}_{xx} = (1+\mu)\chi^{d}_{zz}/2\mu$$

$$\chi^{p}_{xx} = -(\mu-1)^2\chi^{d}_{zz}/2\mu(1+\mu)$$

$$\chi_{xx} = \chi^{p}_{xx} + \chi^{d}_{xx} = 2\,\chi^{d}_{zz}/(1+\mu) \quad . \qquad \text{(IIIC.1)}$$

Note that all diamagnetic terms are negative and all paramagnetic terms are positive. The components of the total susceptibility (paramagnetic plus diamagnetic) are always negative. Since the energy goes as $-\underset{\sim}{B}\cdot\underset{\approx}{\chi}\cdot\underset{\sim}{B}$ the separation of χ into a diamagnetic component which is negative and a paramagnetic component which is positive is in keeping with the usual definition that a diamagnetic substance is repelled by a magnetic field and a paramagnetic substance is attracted. The paramagnetism of most paramagnetic substances, however, is caused by a net magnetic moment in the ground state (as in the net spin moment of molecular oxygen whose ground state is $^3\Sigma_g^-$) which results in the first order term $\langle 0|L|0\rangle$ of (IIIC.6) being nonzero. Molecules of this type possess a molecular magnetic moment of $\frac{q}{2mc}\langle L\rangle$ which interacts in a first order way with the magnetic field. The oscillator model does not describe this type of paramagnetism, but a much smaller effect sometimes known as Van Vleck paramagnetism.[7]

What is the source of Van Vleck paramagnetism? Recall that if Larmor

theorem were fully valid, the effect of the applied magnetic field would be to induce all the electrons of a molecule to rotate about the field with an angular frequency $\omega = eB/2mc$. The extra kinetic energy of the electrons caused by this induced Lenz's law type current results in the diamagnetic component of the energy. Because of the anisotropy of the charge distribution of a molecule, however, some of the electronic charge will not be as free to rotate about the field. It is this "quenching" of the diamagnetic effect that is called Van Vleck paramagnetism.[8] This explains why there is a paramagnetic component to the susceptibility only when the field is applied perpendicular to the axis of the molecule. When the field is applied in the z-direction, the axial symmetry does not restrict the "Larmor rotation" of the electronic charge. Because the Van Vleck paramagnetism is only a reduction in the diamagnetism, it is clear that it can never dominate the diamagnetism to produce a truly paramagnetic molecule. This is seen from the model in that $|\chi^p/\chi^d| < 1$, for finite μ.

Proceeding with the application of the model to H_2, one again identifies q and m as the charge and mass of an electron and uses ω and μ from experimental data as was done in the previous section. The results are displayed in the table.

	Model	Experiment[3,8]	
$-\chi_{xx}$	0.446	0.427	
$-\chi_{zz}$	0.383	0.372	
$-\chi$	0.425	0.409	
$\lvert\chi^p_{xx}/\chi^d_{xx}\rvert$	0.027	0.026	(IIIC.15)

The units in the table above are $\alpha^2 a_0^3$, where α is the fine structure constant. The model predicts susceptibilities remarkably better than polarizabilities. The difference between model and experimental susceptibilities is about 4%. However, it should be noted that the "experimental data", $\langle x^2 \rangle$ and $\langle z^2 \rangle$, that were used to derive μ and ω are themselves derived from magnetic susceptibility experiments. To some extent, therefore, the model has been "rigged" to exhibit a size and shape that are superb for the modeling of susceptibility. The excellent agreement between model and experimental values of $|\chi^p/\chi^d|$ is to be noted, however.

By combining equations (IIIB.14) for the polarizability and (IIIC.14) for the susceptibility one obtains

$$\alpha = \frac{1}{3}\,[(1+2\mu^2)/\mu^2]q^2/4m\omega^2$$

$$\chi = -\frac{1}{3}\,[(5+\mu)/(1+\mu)]q^2\hbar/8m^2c^2\omega \quad . \qquad \text{(IIIC.16)}$$

These equations may be combined to eliminate ω and obtain a new relationship between the polarizability and the susceptibility,

$$\chi = -(e^2/4mc^2)\,f(\mu)\,\sqrt{\alpha}\;\; a_0^{\frac{1}{2}} \quad , \qquad \text{(IIIC.17)}$$

where the usual association of q and m with the electron has been made and

$$f(\mu) = \frac{5+\mu}{1+\mu}\;\frac{\mu}{[3(1+2\mu^2)]^{\frac{1}{2}}} \quad . \qquad \text{(IIIC.18)}$$

Due to the fact that the polarizability and the susceptibility represent responses of a system to extremely different types of perturbations, it would be indeed surprising if such a simple relation as (IIIC.17) were valid. However, a similar relation, known as the Kirkwood equation,[9] was developed for atoms by a variational argument in 1932. Note that for atoms, $\mu = 1$ and $f(1) = 1$. The fact that the oscillator model yields the same relation as the Kirkwood equation is truly remarkable even given that <u>any</u> relationship exists between these two properties.

D. Nuclear Magnetic Shielding (Chemical Shift)

The application of the oscillator model to the problem of estimating the shielding of a nuclear spin from an applied magnetic field is a new one. Indeed few non-trivial models exist that can shed light on and provide estimates for the magnitude of this phenomenon for systems more general than atoms.[10]

Consider first a bare nucleus with intrinsic angular momentum (spin) $\underset{\sim}{S}$ and a corresponding magnetic dipole moment of

$$\underset{\sim}{m} = g_N \left(\frac{eh}{2Mc}\right) \underset{\sim}{S} = g_N \beta_N \underset{\sim}{S} \qquad \text{(IIID.1)}$$

where e and M are the charge and mass of a proton, c is the speed of light. β_N is called the nuclear magneton and is a constant. g_N is a dimensionless quantity of the order of unity characteristic of the type of nucleus being considered.

If a magnetic field $\underset{\sim}{B}$ is applied to the bare nucleus, the energy of the system depends on the orientation of the spin relative to the field. In particular, the system is described by the Zeeman Hamiltonian,

$$H = -\underset{\sim}{m} \cdot \underset{\sim}{B} \quad . \tag{IIID.2}$$

Now if there are electrons around the nucleus, as there usually are, the energy levels characterized by the nuclear spin quantum numbers will be perturbed. The field will induce currents in the electronic distribution which will tend to screen the nucleus from the full effects of the applied field. The induced currents provide a field that is proportional to B and opposite to it. Thus, in the presence of an electronic distribution the nucleus actually feels a magnetic field which is smaller and given by

$$\underset{\sim}{B}_{eff} = (\underset{\approx}{1} - \underset{\approx}{\sigma}) \cdot \underset{\sim}{B} \quad , \tag{IIID.3}$$

where $\underset{\approx}{\sigma}$ is called the chemical shift tensor which describes the effects of the electrons in the molecule. The Zeeman Hamiltonian is thus modified to

$$H = H_{elec} - \underset{\sim}{m} \cdot (\underset{\approx}{1} - \underset{\approx}{\sigma}) \cdot \underset{\sim}{B} \quad , \tag{IIID.4}$$

where H_{elec} is the Hamiltonian of the electrons in the field of the nuclei, the applied field, and the fields of the other electrons, if there are others.

Consider now a particle bound to the origin with a harmonic force as before. The particle will be assumed to have a charge q and a mass m. The force will be degenerate in the x and y direction in order to produce an axially symmetric (diatomic-like) probability distribution. Near the origin, at $\underset{\sim}{R}$, will be fixed a nuclear spin $\underset{\sim}{S}$ with a magnetic moment

$\underset{\sim}{m}$. It should be emphasized that the spin at $\underset{\sim}{R}$ is not charged and so does not interact coulombically with the harmonically bound particle. In order to maintain axial symmetry, the spin will be placed on the z-axis so that $\underset{\sim}{R} = R\hat{z}$. This entire system is then to be placed in a magnetic field, $\underset{\sim}{B}$. The Hamiltonian for this is

$$H = \frac{1}{2m}\left(\underset{\sim}{p} - \frac{q}{c}\underset{\sim}{A}\right)^2 + (\text{h.o. potential}) - \underset{\sim}{m}\cdot\underset{\sim}{B} \quad . \tag{IIID.5}$$

Other than the last term, this Hamiltonian is just the same as that for the magnetic susceptibility (IIIC.1). However, in (IIIC.1) the vector potential produced only a constant magnetic field, whereas the vector potential referred to above produces both a constant magnetic field and the magnetic dipole of the nuclear spin.

$$A = \frac{1}{2}\underset{\sim}{B}\times\underset{\sim}{r} + \frac{\underset{\sim}{m}\times(\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3} = \underset{\sim}{A}_B + \underset{\sim}{A}_m \quad . \tag{IIID.6}$$

The Hamiltonian may be divided and perturbation theory used, as before. The unperturbed Hamiltonian H_0 will include the kinetic energy of the particle, the Harmonic potential and the $-\underset{\sim}{m}\cdot\underset{\sim}{B}$ term. This Hamiltonian is separable in particle and nuclear spin coordinates and the eigenvalues will be direct products of particle and spin (S^2, S_z) eigenfunctions. The perturbation is, then,

$$H' = -\frac{q}{mc}(\underset{\sim}{A}_B+\underset{\sim}{A}_m)\cdot\underset{\sim}{p} + \frac{q^2}{2mc^2}(\underset{\sim}{A}_B^2 + 2\underset{\sim}{A}_m\cdot\underset{\sim}{A}_B + \underset{\sim}{A}_m^2) \quad . \tag{IIID.7}$$

An expression for the energy is desired that is first order in both the field and the magnetic moment so that σ may be abstracted from it according to (IIID.4). This expression can come from perturbation theory only to second order and only perturbing terms that are zeroth or first order in B or m need be kept. This results in

$$H' = -\frac{q}{mc}(\underset{\sim}{A}_B + \underset{\sim}{A}_m)\cdot\underset{\sim}{p} + \frac{q^2}{mc^2}\,\underset{\sim}{A}_m\cdot\underset{\sim}{A}_B \quad . \tag{IIID.8}$$

The neglected terms are second order in either B or m and can never produce an energy expression of the form (IIID.4). First-order perturbation theory produces only one term of the desired form

$$E^1 = \left(\frac{q^2}{2mc^2}\right) \langle 0|\frac{\underset{\sim}{m}\times(\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3}\cdot(\underset{\sim}{B}\times\underset{\sim}{r})|0\rangle \quad . \tag{IIID.9}$$

By using vector manipulation and by extracting m and B outside the brackets, it is straightforward to identify a first-order contribution to the chemical shift tensor which will be called σ^d,

$$\underset{\approx}{\sigma}^d = \frac{q^2}{2mc^2}\langle 0|[(\underset{\sim}{r}-\underset{\sim}{R})\cdot\underset{\sim}{r}\underset{\approx}{I} - (\underset{\sim}{r}-\underset{\sim}{R})\underset{\sim}{r}]|\underset{\sim}{r}-\underset{\sim}{R}|^{-3}|0\rangle \quad . \tag{IIID.10}$$

From the fact that the nucleus lies along the z-axis, $\underset{\sim}{R} = R\hat{z}$, the symmetry of the situation yields only two independent nonzero elements of σ^d:

$$\sigma^d_{xx} = \sigma^d_{yy} = \frac{q^2}{2mc^2}\langle 0|[y^2 + z(z-R)]|\underset{\sim}{r}-\underset{\sim}{R}|^{-3}|0\rangle \quad ,$$

$$\sigma^d_{zz} = \frac{q^2}{mc^2}\langle 0|\frac{x^2}{|\underset{\sim}{r}-\underset{\sim}{R}|^3}|0\rangle \quad . \tag{IIID.11}$$

Second-order perturbation theory produces only one kind of sum all of whose terms are first-order in both B and m. This is

$$E^2 = \frac{q^2}{m^2c^2} \sum_{\underset{\sim}{n}}' \left[\langle 0| \tfrac{1}{2} \underset{\sim}{B} \times \underset{\sim}{r} \cdot \underset{\sim}{p} |\underset{\sim}{n}\rangle\langle \underset{\sim}{n}| \underset{\sim}{p} \cdot \frac{\underset{\sim}{m} \times (\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3} |0\rangle + \text{c.c.} \right] \frac{1}{E_0 - E_n} \quad . \qquad \text{(IIID.12)}$$

Again, use of vector identities and extraction of m and B outside the brackets yields the second-order contribution to the chemical shift,

$$\underset{\approx}{\sigma}^p = \frac{-q^2}{2m^2c^2} \sum_{\underset{\sim}{n}}' \left[\langle 0| \underset{\sim}{\ell} |\underset{\sim}{n}\rangle\langle \underset{\sim}{n}| \frac{(\underset{\sim}{r}-\underset{\sim}{R}) \times \underset{\sim}{p}}{|\underset{\sim}{r}-\underset{\sim}{R}|^3} |0\rangle + \text{c.c.} \right] (E_n - E_0)^{-1} \quad , \qquad \text{(IIID.13)}$$

where $\underset{\sim}{\ell} = \underset{\sim}{r} \times \underset{\sim}{p}$. It is obvious from the form of σ^p that it is real and symmetric. Also, for the choice of $\underset{\sim}{R}$ along the z-axis, σ^p is diagonal with only two unique components. Furthermore, since $\ell_z|0\rangle = \langle 0|\ell_z = 0$, as was discussed in the section on susceptibilities, $\sigma^p_{zz} = 0$. This leaves only

$$\sigma^p_{xx} = \sigma^p_{yy} = \frac{-q^2}{m^2c^2} \sum_{\underset{\sim}{n}}' \langle 0| \ell_x |\underset{\sim}{n}\rangle\langle \underset{\sim}{n}| \frac{yp_z - (z-R)p_y}{|\underset{\sim}{r}-\underset{\sim}{R}|^3} |0\rangle (E_{\underset{\sim}{n}} - E_0)^{-1} \qquad \text{(IIID.14)}$$

As for the previous properties, the sum above reduces to one term. This is because when ℓ_x operates on the ground state the resulting state is proportional to one of the excited states of the oscillator. In fact, using a ladder operator technique it is easy to show that

$$\langle 0|\ell_x = \langle 0|(yp_z - zp_y) = -\frac{i\hbar}{2} \frac{\omega_z - \omega_y}{\sqrt{\omega_y \omega_z}} \langle 011| \quad , \qquad \text{(IIID.15)}$$

so that only the term $\underset{\sim}{n} = (0,1,1)$ remains. Furthermore, since

$$p_x|0\rangle = im\omega_x x|0\rangle \quad , \tag{IIID.16}$$

which can also be proven simply using ladder operators, σ^p_{xx} may be written as an expectation value of a function of coordinates only. The result is

$$\sigma^p_{xx} = -\frac{q^2}{m^2c^2}\langle 0|\ell_x \cdot \frac{yp_z-(z-R)p_y}{|\underset{\sim}{r}-\underset{\sim}{R}|^3}|0\rangle\ [\hbar(\omega_y+\omega_z)]^{-1} \tag{IIID.1}$$

$$= \frac{q^2}{\hbar c^2}\ \frac{(\omega_y-\omega_z)}{(\omega_y+\omega_z)}\ \langle 0|\frac{\omega_z y^2z^2-\omega_y y^2 z(z-R)}{|\underset{\sim}{r}-\underset{\sim}{R}|^3}|0\rangle \quad .$$

To simplify the three equations above for σ^d_{xx}, σ^d_{zz}, and σ^p_{xx}, they will be normalized to the spherical limit (μ=1, R=0) chemical shift. This gets rid of the excess baggage of constants that preface each expression. In the spherical limit, the well-known[11] expression for the chemical shift is

$$\sigma_0 = \frac{q^2}{3m^2c^2}\langle 0|\frac{1}{r}|0\rangle$$

$$= \frac{2}{3}\frac{q^2}{c^2}\left(\frac{\omega}{m\pi\hbar}\right)^{\frac{1}{2}} \quad , \qquad \text{for an oscillator.} \tag{IIID.1}$$

Furthermore, a dimensionless length parameter is defined as $d^2 \equiv (m\omega/\hbar)R^2$ to simplify the equations.

Since the integrals to be evaluated involve integrands which are essentially Gaussian functions multiplied by simple functions of spatial coordinates, they may be simplifed using Gaussian transform techniques[12] from three-dimensional to one-dimensional form. The results are

$$\frac{\sigma^d_{zz}}{3\sigma_0} = \mu^{3/2} \int_0^1 x^2 \exp[-\mu d^2 x^2][1-(1-\mu)x^2]^{-2} dx$$

$$\frac{\sigma^d_{xx}}{3\sigma_0} = \frac{\mu^{1/2}}{2} \int_0^1 \exp[-\mu d^2 x^2][1-(1-\mu)x^2]^{-2}[1-x^2-2d^2\mu x^2(1-(1-\mu)x^2)]dx$$

$$\frac{\sigma^p_{xx}}{3\sigma_0} = -\frac{\mu^{1/2}}{2}\frac{(1-\mu)}{(1+\mu)} \int_0^1 x^2 \exp[-\mu d^2 x^2][1-(1-\mu)x^2]^{-1}$$

$$\times \{1-(1+2\mu d^2+2\mu^2 d^2)x^2 + 2\mu d^2 x^4 + 2\mu - \frac{4\mu^2 x^2}{[1-(1-\mu)x^2]}\}dx \quad . \qquad (11)$$

Unfortunately, these integrals cannot be performed analytically. However, they are well behaved in the region of integration and this allows them to be easily evaluated for particular values of μ and d^2 by any of several numerical procedures. In what follows, the Gaussian quadrature procedure[13] was used.

It should be remarked at this point that an experiment cannot determine separately the paramagnetic and diagmagnetic contributions to the chemical shift, but only the sum of the two. The diamagnetic component may be determined indirectly by a measurement of the size ($\langle x^2\rangle$, $\langle z^2\rangle$) of the molecule as determined by a different type of experiment. The paramagnetic component is then determined by subtracting the diamagnetic component from the total shift as determined by a standard magnetic resonance experiment. It may be argued that this procedure is ambiguous.

This model, as well as other theories of magnetic resonance, cannot escape this same ambiguity. This is because only the <u>total</u> chemical shift, the sum of the diamagnetic and paramagnetic components, is gauge

invariant.[2] The individual components are not gauge invariant. For example, in the model developed here, the external constant magnetic field was generated by a vector potential $\underset{\sim}{A} = \frac{1}{2}\underset{\sim}{B}\times\underset{\sim}{r}$, where $\underset{\sim}{r}$ was measured from the origin. One could just as well have used $\underset{\sim}{A}' = \frac{1}{2}\underset{\sim}{B}\times\underset{\sim}{r}_s$, where $\underset{\sim}{r}_s = \underset{\sim}{r}-\underset{\sim}{R}$ locates the Harmonic oscillator particle relative to the nuclear spin. This different choice of vector potential, or different gauge, produces the same magnetic field and the same total chemical shift. However, the paramagnetic and diamagnetic contributions to σ are different. (One advantage of the use of the vector potential A', however, is that the paramagnetic term is explicitly negative and the diamagnetic term is explicitly positive. This is in keeping with the usual definition of diamagnetism and paramagnetism since $E \sim \underset{\sim}{m}\cdot\underset{\approx}{\sigma}\cdot\underset{\sim}{B}$.) Since only the total chemical shift is observable, individual contributions will not be calculated.

In applying the model to the hydrogen molecule, the first problem is the determination of the three parameters R, ω and μ. Clearly, since the oscillator should be centered between the nuclei, R will be half the equilibrium bond length of 1.4 a_0. For μ the value of 0.72 will be used as was done for the polarizability and susceptibility. Also as before, ω will be determined by $\langle x^2\rangle$ data and equations B.15 and 16. These assignments give

$$d^2 = \left(\frac{m\omega}{\hbar}\right)\left(\frac{1.4\ a_0}{2}\right)^2 = 0.16 \quad . \qquad \text{(IIID.21)}$$

These parameters provide enough information to evaluate the integrals (IIID.20), but this only gives chemical shifts scaled to the "spherical limit". To determine the actual components of σ, σ_0 needs to be determined.

Clearly, there are many ways to do this. One way is to use equation (IIID.19) for the shift of the spherical oscillator and insert a frequency ω determined from $\langle x^2 \rangle$, as above. However, ω_z could also be used for the frequency, and in keeping with the idea of σ_0 being a "spherical limit" shift, an ω determined from $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$ might also be considered. The fact is, however, that since H_2 is so close to spherical ($\mu = \langle x^2 \rangle / \langle z^2 \rangle = 0.72$) these procedures give substantially the same results.

An equally valid way to determine the spherical limit chemical shift is to consider the chemical shifts of various atoms. The united atom limit of H_2 (helium) immediately comes to mind. However, since the nuclear charge is larger, helium has a much more localized probability distribution than would be needed here. What is desired is the shift in some limit where the charge distribution becomes spherical without "shrinking" much as it would if the nuclear charge increased. Thus, an appropriate value of σ_0 could be that of <u>two</u> electrons in a hydrogen 1s orbital. Since the chemical shift of hydrogen, which may be calculated analytically, is $\sigma = 17.76$ ppm, a good value for σ_0 for H_2 is 2 x 17.76 ppm = 35.52 ppm. Using this and the above values for ω, μ, and R, the values of the following table are obtained:

	Model	Experiment[2,14]
σ_{xx}	18.3 ppm	27.3 ppm
σ_{zz}	29.8 ppm	34.9 ppm
σ_{xx}/σ_{zz}	0.61	0.78
σ	22.1 ppm	25.3 ppm

Thus, the model gives values correct to within about 20%.

The model has also been solved[15] for the chemical shift i case of $\mu \geq 1$ (where the probability distribution is oblate, shaped) and $\underset{\sim}{R} = R\hat{x}$. In this form the oscillator may be used the proton or (for different R) the ^{13}C chemical shift of ben Another use which comes to mind is the modeling of the situat nuclear spin at the active site inside a porphyrin ring (R=0, as in hemoglobin and chlorophyll.

E. Comments

As can be deduced from the three tables, the oscillator not predict accurate values of properties of molecular hydro was repeatedly mentioned above, however, that there are choosing values for the several parameters of the model, some may give better predictions for properties than were derived Indeed, in some cases where experimental information is unava the accuracy of the model as used above may be enough.

However, the real value of the model is not in the accur predictions but in the insight it provides to the complex inter of an electronic wavefunction with electric and magnetic field nuclear spins. Although simple enough to provide analytic exp for several properties, the model can exhibit a complex phenom Van Vleck paramagnetism in both the magnetic susceptibility and chemical shift.

There is every reason to believe that the model is general to total anisotropy ($\omega_x \neq \omega_y \neq \omega_z$) so that less-than-axially-sy molecules could be mimicked. It is also probable that other mo

properties may be predicted, such as the spin-rotation coupling of nuclear (or electronic) spin with molecular rotation.

Another line of investigation, which could prove fruitful, is the generalization of the theory to an oscillator in other than its ground state. These excited states could then be used to model the various orbitals of a molecule by providing states of the correct nodal structure. Even more simply, each orbital of a large molecule could be modeled by a ground state oscillator with different ω and μ. It is quite likely, however, that the model is most valuable in its simplest form, as presented here.

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