Calculation of force constants and dipole-moment derivatives

During the course of my research for a Ph.D. degree under the supervision of Professor I.M. Mills, I developed a set of perturbed Hartree-Fock equations for calculation of the derivatives of molecular orbitals with respect to a nuclear coordinate. We applied this theory to the calculation of force constants and dipole moment derivatives of the LiH, BH, and HF molecules in their $X^1\Sigma^+$ states using the minimum basis set. SCF wavefunctions of Ransil (Revs. Mod. Phys. 32, 245, (1960)). These were meant only as pilot calculations to demonstrate the feasibility and numerical stability of the equations. There were indeed no such numerical problems, and the work was later published (Gerratt and Mills, J. Chem. Phys., 49, 1719, 1730, (1968)). I enclose reprints of these papers.

Since that time I have become deeply involved in other work, such as the calculation of molecular properties from spin-coupled wavefunctions which is supported by the S.R.C. However I now have had an application from a Dr. R. Waddell who is very keen indeed to work on this project, and it is for this reason that I now apply for a Postdoctoral Fellowship for 2 years in order to enable him to do so. In fact Dr. Waddell has already been working on this project for several months at his own expense, and I am well satisfied with his progress and general approach.

The basic aim of this project is to calculate directly from large basis set LCAO-SCF-MO wavefunctions the various spectroscopic constants that characterise the infrared spectra of molecules. There are now of course near Hartree-Fock calculations available in the literature for a number of first-row diatomic molecules and small polyatomic molecules. However, most of these (such as LiH, Li_2, HF, H_2O, CH_4) are no longer of great interest in vibrational spectroscopy. Of far greater interest are small polyatomic molecules such as formaldehyde or formyl fluoride HCOF, which do not have a great deal of symmetry, and for which it is difficult to determine all the force constants (see below). My students and I have succeeded in getting to run on the IBM 360/195 computer at the Rutherford High Energy Laboratory the complete multicentre Slater integral package written by R.M. Stevens at Harvard University. This package includes a complete SCF section, which Stevens has used in a very large basis-set calculation on the NH_3 molecule in order to determine the height of the barrier to inversion (R.M. Stevens, J.Chem. Phys., 55, 1725, (1971)). With this program we propose to produce LCAO-MO-SCF wavefunctions for the H_2CO and HCOF and then to perform perturbed Hartree-Fock calculations. We propose to examine the quality of the basis sets, not only from the point of view of energy, but also as to how well the Hellmann-Feynman theorem and the electron-nucleus cusp conditions are satisfied. If necessary, we propose to add to the basis functions such as a 2p STO with exponent about equal to the 1s exponent in order to ensure a good balance of forces. A 2p Slater function with such a large exponent will no doubt alter the total energy very little, but will affect the forces significantly. In other words, the addition of this function will bring the whole wavefunction closer to the Hartree-Fock limit in this particular respect. Although there is a good minimum basis set calculation on H_2CO in the literature (Foster and Boys, Revs. Mod. Phys., 32, 303, (1960)), there is no Slater basis calculation for HCOF, and no extended basis set for either molecule.

Since publication, our work has been taken up by a group of workers under Dr. P. Swanstrøm in Denmark (e.g. Swanstrom, Thomsen and Yde, Mol. Phys., 20, 1135, (1971). I enclose a Xerox copy of their paper). However they are firmly committed to the use of basis sets consisting of floating Gaussian orbitals, and propose to apply these to small diatomic molecules. We propose on the other hand to use large Slater basis-set functions with some modification as described above, since I regard it as vital for the calculation of force constants that the wave-functions have the correct behaviour close to the nuclei.

There are three main reasons why one should attempt to calculate the force constants and dipole-moment derivatives of small molecules from perturbed Hartree-Fock theory.

1. Consider a closed-shell molecule consisting of 2n electrons and A nuclei. The electrons are described by n M.O.'s ϕ_μ ($\mu = 1, =2, \ldots, n$). Let the potential experienced by electron μ be v_μ,

$$v_\mu = -\sum_{J=1}^{A} \frac{Z_J}{r_J}, \qquad \text{(in a.u.)} \qquad (1)$$

where $r_\mu \equiv | r_\mu - R_J |$, r_μ, R_J being the position vectors of electron μ and nucleus J respectively. Then the force constant $f_{\alpha\beta}^{JK}$ is given by

$$f_{\alpha\beta}^{JK} = 2 \sum_{\mu=1}^{n} \{ \langle \phi_\mu | \frac{\partial^2 v_\mu}{\partial R_J^\alpha \partial R_K^\beta} | \phi_\mu \rangle$$

$$+ 2 \langle \frac{\partial \phi_\mu}{\partial R_J^\alpha} | \frac{\partial v_\mu}{\partial R_K^\beta} | \phi_\mu \rangle \} , \qquad (2)$$

where R_J^α is the α-component of R_J ($= x, y,$ or z). The essential quantities to be calculated are thus the $\partial \phi_\mu^J / \partial R_J^\alpha$, the derivatives of the M.O.'s with respect to components of the nuclear coordinates.

Now the Hartree-Fock wavefunction provides a _finite model_ for the behaviour of the electrons in molecules, and once having calculated the $f_{\alpha\beta}^{JK}$ from equation (2), one has a _physical interpretation_ of the result in terms of which M.O.'s distort the most easily and contribute so much. No such interpretation is possible if a complete SCF calculation were to be repeated at several nuclear configurations, and a potential surface constructed from these results.

Furthermore, we expect to obtain from a near Hartree-Fock wavefunction good results for a force constant calculation by equation (2) as accurate as the prediction of one-electron properties. The proof of this statement was given in our paper (Gerratt and Mills, J. Chem. Phys. -enclosed), and a similar proof is also given by Swanstrøm et al. (paper enclosed). A more sophisticated proof has also been given by K. Freed using diagrammatic Rayleigh-Schrödinger perturbation theory (J. Chem. Phys., 52, 253, (1970). This is in spite of the fact that a closed-shell Hartree-Fock function

virtually always predicts incorrect dissociation products; the nuclear displacements considered here are only of infinitesimal magnitude.

2. The usual method of calculating vibrational spectroscopic constants is by repeating entire SCF calculations at a number of nuclear configurations. This is an extremely laborious method and requires a very great deal of computer time. It is necessary to reoptimise exponents each time as otherwise the force constants are much too high. Even so, this is an unstable method numerically. The results obtained by fitting a curve to a number of points depend upon the number and spread of the points. This does not seem to be widely realised in the literature. Thus, for example, Meyer and Pulay (J. Chem. Phys., 56, 2109, (1972)) criticise our estimate of an accuracy of 1-2% for force constants from Hartree Fock functions, and give error estimates of 10-20%. However, shortly afterwards (J. Chem. Phys., 57, 3337, (1972)), they correct themselves and obtain much more accurate values, stating that "the errors were in fact produced by a numerically unstable curve-fitting procedure"!. In addition, as pointed out above, the results do not permit any physical interpretation.

3. For a non-linear molecule, the number of normal modes, $N_Q = 3N-6$, and hence the number of independent force constants is $k_Q = \frac{1}{2}N_Q(N_Q+1)$. Unless there is a great deal of symmetry present, it is not possible to determine the harmonic force field uniquely from infra-red data alone. Extra information may be available from vibration-rotation interactions or centrifugal stretching deduced from high resolution IR or microwave spectra, but often one has to make assumptions about the harmonic force field. This is particularly true of the small "off-diagonal" force constants $f_{\alpha\beta}^{JK}$ ($\alpha \neq \beta$), whose signs may of course also be negative. Reliable theoretical calculations of these quantities would therefore be of help to spectroscopists working in this field, particularly if a physical interpretation of the force constants enabled one to transfer values between chemically similar molecules. This is also true of the dipole moment derivatives, $(\partial\mu_\alpha / \partial Q)$. Only the squared moduli of these quantities can be obtained from IR spectra, the signs which are often of interest, hence remaining undetermined. Occasionally, the band shapes of high-resolution vibration-rotation spectra enable one to relate the relative signs of several dipole moment derivatives, but the absolute sign of one of them remains to be determined.

The derivation of the perturbed Hartree-Fock equations takes into account the movement of the basis functions with the nuclei upon which they are centred. If we denote the Slater basis functions by χ_p, this process gives rise to integrals of the form

$$< \frac{\partial \chi_p}{\partial R_J^\alpha} | f | \chi_q >, \quad < \frac{\partial \chi_p}{\partial R_J^\alpha} \chi_q | \frac{1}{r_{12}} | \chi_r \chi_s >, \tag{3}$$

where f is a one-electron operator. The presence of these non-standard integrals are the major problem in the applicability of the theory. The most efficient way of calculating these would be to do so simultaneously with the standard integrals. However, this would mean either writing from the start a new integral package, or altering in a major way existing packages. Either of these alternatives is a daunting prospect.

As mentioned above, we now have the Stevens multicentre integral package working on the Rutherford IBM 360/195 machine (and also the fast diatomic integral package written by D.M. Silvers). It seems therefore a reasonable compromise to use these packages to calculate the standard integrals and use some other method to calculate the integrals (3).

For this purpose, I wrote such a special integral package as part of my Ph.D. research work. The orbitals $\partial\chi_p/\partial R_\alpha^J$ can always be written as a linear combination of (non-standard) Slater orbitals. For example $\partial\chi(1s)/\partial R_\alpha \chi(1p)$. My integral package uses the Barnett-Coulson method and is written in Algol 60. Dr. Waddell is now in the course of converting this to Fortran, a task which I hope will be completed within the next few months.

A few remarks about the Barnett-Coulson method are necessary since it is occasionally the subject of criticism in the literature. I made an extensive study of the numerical instabilities, and have corrected several of them. These are fully described in my Ph.D. thesis. In addition, I have collected from M.P. Barnett a considerable amount of unpublished material in which he has himself undertaken several studies, and proposed remedies. For example, for certain combinations of orbital exponents, the series for the exchange integrals converges badly. Barnett has shown that the series which arises in his method asymptotically approach the form $T_n = \frac{1}{k^n}$. He shows that this last series can be "filled onto" the expansion and rapidly summed to infinity. This technique, as far as I am aware, has never been tried on any scale.

From a more theoretical point of view, D.F. Tuan has shown that multi-configuration interaction calculations (MCI calculations) also satisfy the Hellmann-Feynman theory (J. Chem. Phys. 51, 607, (1969)). The entire theoretical development described above then goes through for this type of wavefunction also. Thus it is possible to derive perturbation equations for the orbitals, and moreover these will be of the same form as the equations derived by Hinze and Roothaan (Prog. Theor. Phys. Japan. Suppl. No. 40, 37, (1967). See also S. Fuzinaga, Prog. Theor. Phys. Japan, 41, 307, (1969)). These last equations however, were originally derived for the purpose of improving the convergence of the MCI calculations. We propose to study the possibility of using this kind of wavefunction in which the extra configurations are just those required to predict the correct dissociation products. Several wavefunctions of this type have already been published by A. Wahl (see e.g. Adv. Quantum Chem., 5, 261, (1970)).

We propose to carry out most of this work on the Rutherford IBM 360/195 mcahine, working mainly through the terminal that is to be installed in the Physics Department at this University, hopefully, at the end of January, 1973. I would therefore like to request a total of twelve hours for this project on this machine over the proposed 2 year period.

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