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Localized Orbitals. II. Expanded Basis Sets

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Two methods are presented to delineate localized orbitals defined on large basis sets. These methods calculate equivalent orbitals for polyatomic molecules which are accurate enough for precise quantum mechanical calculations. The localized orbitals are defined in terms of parameters that can be readily visualized by the chemist, yet allow changes in electronic structure during molecular bond formation and substituent exchange reactions to be determined. It is shown that these equivalent orbitals constitute a foolproof starting point for self-consistent field (LCAO-MO-SCF) calculations. The results of calculations on the water molecule using Gaussian basis functions are presented along with a discussion of numerical and computational techniques.

INTRODUCTION

This series of papers presents a representation for the accurate mathematical description of the electronic structure of polyatomic molecules, which is defined in terms of concepts and parameters that have an intuitive appeal to the chemist. (The first paper¹ in this series deals with the definition of *equivalent orbitals* of a system of σ bonds defined in terms of minimal basis sets.) The representation includes all of the parameters necessary to trace the changes in the electronic structure that take place in molecular bond formation and the changes in bonds during substituent interchange reactions. Further, this representation allows the definition of molecular wavefunctions of sufficient accuracy to consider their use in a broad spectrum of quantum mechanical calculations of molecular properties.

This paper is a study of the application of this technique to a space spanned by an incomplete, yet not minimal, set of Gaussian-type orbitals (GTO's).² However, the technique is not restricted specifically to these functions.

Initializing self-consistent field (SCF) calculations with functions where each coefficient is set to zero or with functions chosen by crude techniques often produces instabilities in the numerical procedure that causes a divergence of the calculation. (An example of

this is when a 73|73|3 basis set was chosen³ for CH_2O , a divergence resulted requiring hand manipulation of the starting eigenfunctions.) This results from the fact that the guessed initial wavefunctions differ too greatly from those that would be calculated in the SCF procedure. Therefore, if the equivalent orbitals calculated by the procedure described herein are an excellent *approximation* to the SCF wavefunctions, then the equivalent orbitals should constitute a foolproof starting point for the SCF procedures. This should not only cut down cycling time significantly, but also obviate the possibility of a divergence.

The study of the electronic structure of families of molecules in terms of a set of simple parameters should uncover regularities in the variation of these parameters during chemical reactions. It should then be possible to derive a set of "über-quantum mechanical rules" that subsumes the framework and mathematical terms used to derive the values of the parameters. The technique presented herein, coupled with the rules yet to be discerned, will uniquely determine the molecular electronic wavefunction. The parameters sought are the bond polarity coefficients (a measure of the ionicity of the bond), hybridization parameters (if necessary), and the proper atomic orbital (A.O.) basis functions. (A more complete discussion is given in Ref. 4, pp. 95-167. Note, however, a slight change in the definition

of h_z .) In other words, the change in the atomic orbitals and ionicity of bonds, the net charge on each atom, etc., due to substituent exchange reactions and molecular bond formation are determinable. Within the mathematical framework of this technique, it is also possible to see the change in the calculated expectation values of physical quantities as a result of variations in each defined parameter. Moreover, it is hoped that optimization of only a limited set of parameters by fitting to experimental data will produce meaningful results.

Throughout this study, the water molecule has been used to demonstrate this mathematical technique as the molecule has a well-known geometry (bond angle = 104.5° , O-H distance = 0.95721 \AA), has good symmetry, is composed of sigma systems alone, and is small enough for descriptive purposes and calculational simplicity.

THE DEFINITION OF EQUIVALENT ORBITALS USING EXPANDED BASIS SETS

The *localized orbitals* of any polyatomic system are specified by the techniques derived in other publications.⁴⁻⁷ The localized orbitals represent the bonding orbitals that would occur in a one- or two-center two electron bond as if only those two atoms (those two on which the bond is defined) existed in the molecular system. In other words, orbital overlap between different centers is neglected allowing a definition of bonding orbital systems with the important property that the angular momentum of the bonding orbital hybrids, measured about that bond axis, has only integral values. Previous papers offered the techniques for delineating localized orbitals dealing with sigma systems alone,¹ sigma and pi systems,⁴⁻⁷ and the use of *d* orbitals in $pi^{4,5}$ bonding. Nonetheless, the equivalent orbitals of any polyatomic system are given in terms of the matrix of the localized orbital coefficients, Γ_0 , specified in terms of a minimal basis set, Φ_m (a column matrix of functions), the overlap matrix, Δ_m , and the overlap matrix expressed in center block diagonal form, Δ_{0m} (that in which all intercenter overlap is set to zero). These were given by the following:

$$\Psi_{E0} = \Gamma_0 \Delta_{0m}^{0.5} \Delta_m^{-0.5} \Phi_m \equiv \Gamma_m \Phi_m, \quad (1)$$

where

$$\Psi_{E0} \Psi_{E0}^T = \Gamma_0 \Delta_{0m} \Gamma_0^T = 1. \quad (2)$$

However, we now wish to express the equivalent orbitals in terms of basis sets which are larger than minimal. We define the matrix expressing the expansion coefficients, Q , of the minimal basis set orbital in terms of the expanded basis set by the relationship

$$\Phi_m = Q\Phi. \quad (3)$$

The overlap matrix Δ over the extended basis functions is given by $\Delta = \Phi\Phi^T$. The center block diagonal form overlap matrix, Δ_0 , is defined in terms of Δ by setting all overlap between centers equal to zero. Thus,

the *equivalent orbitals* are $\Psi_{E0} \equiv \Gamma_0 \Phi$. These have the property expressed by Eq. (2).

The extension of the above to handle extended basis sets is not unique. At least two methods are possible which obey all of the dictates of the *localized representation*. The first, referred to as Method 1, is that the equivalent orbitals are given by

$$\Gamma_G = \Gamma_0 [Q_1 \Delta Q_1^T]^{-1/2} Q_1. \quad (4)$$

The second, referred to as Method 2, is given by the following:

$$\Gamma_G = \Gamma_0 Q_2 \Delta_0^{1/2} \Delta^{-1/2}. \quad (5)$$

Unlike the Q_1 matrix of Method 1, the Q_2 matrix is constrained to have the property

$$Q_2 \Delta_0 Q_2^T = 1. \quad (6)$$

[In order to convert an arbitrary matrix, \bar{Q} , with the proper dimensionality into a matrix obeying Eq. (6), it is necessary to determine the real, symmetric, and necessarily positive definite matrix $S = Q \Delta_0 Q^T$. An orthogonal transformation exists that diagonalizes S to produce S_D , a diagonal matrix, by the equation $U^T S U = S_D$, where $U^T U = U U^T = 1$. The matrix Q is therefore given by $U S_D^{-1/2} U^T \bar{Q} = Q$ where $(S_D^{-1/2})_{ii} = (S_D)_{ii}^{-1/2}$. If S is not positive definite (all positive elements on the diagonal of S_D), a linear dependence exists in the

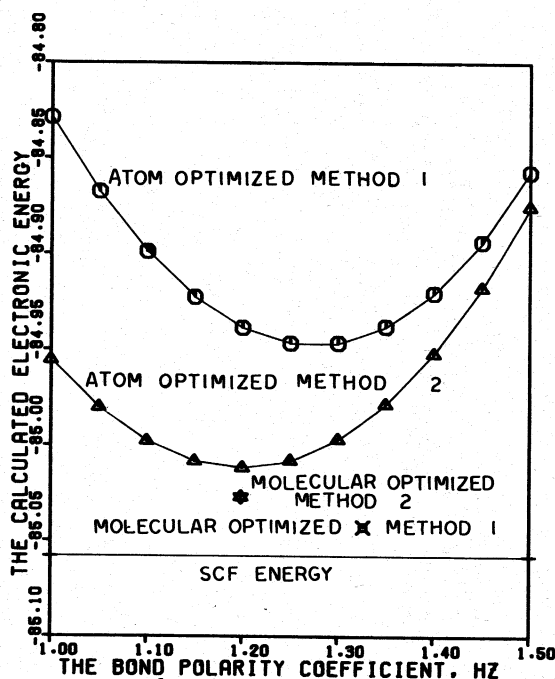


FIG. 1. A plot of the Q matrix elements representing the atom optimized ($\square = 01s$, $\circ = 02s$, $\triangle = 02p$), the Method 1 molecular optimized ($\diamond = 01s$, $+$ $= 02s$, $\times = 02p$), and the Method 2 molecular optimized ($\gamma = 01s$, $\varkappa = 02s$, $\varkappa = 02p$) coefficients versus the logarithm of the GTO orbital exponent. The $02s$ and $02p$ molecular values are shifted as explained in the text.

TABLE I. The calculated values of the atomic orbital expansion coefficients, and bond polarity coefficients, h_Z , for the two types of regression objective functions for Method 1 and Method 2.

Basis orbitals		Atom optimized ^a expansion coefficient	Molecular optimized expansion coefficients			
			$\chi^2 = \text{energy} = \text{minimum}$		$\chi^2 = \sum \Gamma_G - \Gamma ^2 = \text{minimum}$	
			Method 1 ^b	Method 2 ^c	Method 1 ^d	Method 2 ^e
O 1s	2200.	0.0056905	0.00560020	0.00565963	0.00597832	0.00258446
	332.2	0.0416845	0.04108432	0.04147895	0.04240754	0.03381572
	76.93	0.1802574	0.17770527	0.17944961	0.18083784	0.16550481
	21.74	0.4568924	0.45445548	0.45608017	0.45979618	0.43981247
	6.773	0.4414585	0.44764652	0.44410411	0.45195510	0.43885621
	1.103	0.0362224	-0.03027089	0.01001790	-0.03915050	0.06644444
	0.3342	-0.0087322	-0.09937294	-0.03883358	-0.11774267	-0.01850274
O 2s	2200.	-0.0012856	-0.00111838	-0.00143130	-0.00005230	-0.01203547
	332.2	-0.0097375	-0.00751682	-0.00773884	-0.00267910	-0.03214586
	76.93	-0.0431581	-0.03800747	-0.04363449	-0.01654913	-0.07936922
	21.74	-0.1371344	-0.12473147	-0.11948880	-0.07285914	-0.14404537
	6.773	-0.1937388	-0.18530559	-0.20404317	-0.13183490	-0.19255958
	1.103	0.3821590	0.49148061	0.52987292	0.40975074	0.72954958
	0.3342	0.6418389	0.68112305	0.61226036	0.65528994	0.66010571
O 2p ^f	8.356	0.1193404	0.11371348	0.11371348	0.11371348	0.11371348
	1.719	0.4707758	0.43183250	0.43183250	0.43183250	0.43183250
	0.3814	0.6223083	0.66179180	0.66179180	0.66179180	0.66179180
H 1s	4.239	0.0748200	0.19495215	0.09040911	0.15908125	0.11179900
	0.6577	0.4159000	0.63903676	0.42496232	0.44647008	0.55074024
	0.4183	0.6365000	0.33248188	0.57252355	0.59125398	0.60701806

^a The oxygen exponents were obtained from Whitman (Ref. 10). The hydrogen coefficients were chosen by the author.

^b $h_Z(\text{calculated}) = 1.3270119$, energy (final) = -85.0432623, energy (SCF) = -85.058144296.

^c $h_Z(\text{calculated}) = 1.19905231$, energy (final) = -85.0273505 (note: this

has not converged fully).

^d $h_Z(\text{calculated}) = 1.26904456$, $\chi^2 = 9.48 \times 10^{-5}$, $E(\text{final}) = -80.621414$.

^e $h_Z(\text{calculated}) = 1.20565352$, $\chi^2 = 1.393 \times 10^{-4}$.

^f These coefficients are the same as the SCF due to the form of the SCF molecular orbital completely filling one O_p A.O.

proposed basis set.] The molecular geometry and bond polarity coefficients usually determine the localized orbital coefficient matrix uniquely, the orbital exponents fully determine the expanded set basis function to be used, and the basis function expansion coefficients fully specify the matrix Q . Therefore, the *equivalent orbitals* are determined in terms of these parameters in addition to the hybridization parameters (if needed).

Molecular geometry can be obtained with excellent accuracy from microwave spectroscopy and other techniques. However, it is not obvious that any experimental technique can yield directly the values that should be used in determining the proper bond polarity coefficients and atomic orbital expansion coefficients for use in quantum mechanical calculations where great accuracy is needed. In contradistinction to this statement, there exists a series of papers^{8,9} striving to perform the extraction of the proper localized orbital bond polarity coefficients from experimental data. See in particular Ref. 8.

The atomic orbital coefficients (the elements of the Q matrix) are those that have been calculated¹⁰ as optimal for the respective atoms in their ground state. Further, the basis set orbital exponents are the atom optimized orbital exponents. Consider the data of Whit-

man,¹⁰ who optimized several basis sets for each of the first row elements. To good accuracy, his predicted orbital exponents $\{\xi_i\}$ are given in terms of the atomic number, N , by the relationship

$$\log \xi_i = m \log N + b_i, \quad (7)$$

where the slope m is 2.23 ± 0.12 and the intercept values $\{b_i\}$ are readily calculable from the orbital exponents listed for oxygen in Table I. If the value of his atomic orbital expansion coefficient is plotted against the logarithm of the orbital exponent, a group of curves appear that have shapes similar to the radial plot of customary $2s$ and $2p$ orbitals (see Fig. 1). Later in this work it will be shown that it is possible to relate the change in the predicted values of the Q matrix coefficients to a shift in the valence orbital nuclear charge due to the effect of the bond polarity coefficients upon the total charge of an atom.

The remaining set of parameters are the bond polarity coefficients, which express the total charge resident on one atom of a two atom bond in the *localized representation*. (This is exclusive of hybridization parameters which are discussed more fully elsewhere.^{4,7} These are undefined in the water molecule.) As an example, consider a two center bond $\Psi = \alpha \Psi_A(s) + \gamma_1 \psi_A(p) +$

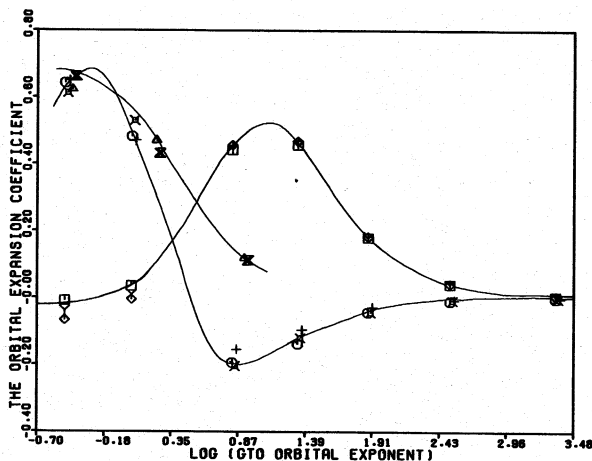


FIG. 2. A plot of the calculated molecular electronic energy as a function of h_z value using atom optimized orbital exponents and expansion coefficients for equivalent orbitals calculated by Method 1 and Method 2. Also shown are the results of complete molecular optimization of the Q matrix as well as the h_z value.

$\gamma_2\psi_B(s, p)$; the total charge residing on atom A is given by $h_z = \alpha^2 + \gamma_1^2$, since overlap between orbitals on different centers is nonexistent. Once sufficient data on a sufficient number of molecules is obtained it is possible to calculate the bond polarity coefficients from quantities, χ , which for historical reasons shall be called electronegativities, by the relationship

$$h_z = h_{AB} = 1.0 + K(\chi_A - \chi_B). \quad (8)$$

h_{AB} determines the relative proportion of charge residing in the hybrid orbital on center A. Clearly, in a two electron bond, the net charge to reside on center B is $(2 - h_{AB}) = h_{BA}$ (which in the above example is γ_2^2). A population analysis in the *localized representation* depends solely (presuming molecular geometry is well known) upon the values of the bond polarity coefficients and hybridization parameters. Moreover, this representation offers an outstanding visual picture since the charge and bond order matrix in the *localized representation* is always unique and often diagonal.

THE USE OF GAUSSIAN EQUIVALENT ORBITALS AS STARTING EIGENFUNCTIONS IN HARTREE-FOCK (SCF) CALCULATIONS

If the *equivalent orbitals* are good approximations to the wavefunctions predicted by Hartree-Fock techniques, then these functions should constitute an excellent starting platform from which to initiate SCF calculations. The technique described herein has been applied successfully to over 30 different large molecules.¹¹⁻¹³ In every instance the calculation proceeded quickly to completion without a divergence or even any hint of numerical instability.

To show the effect of using each of the methods described in this paper in starting a self-consistent field

calculation, the water molecule was run using (a) zero eigenfunctions (those with all coefficients preset to zero), (b) a set of molecular optimized *equivalent orbitals* (described fully in the next section of this paper), and (c) *equivalent orbitals* calculated from atom optimized Q matrix coefficients using three examples of Method 1 and three examples of Method 2. In (c) the values of h_z that minimized the calculated electronic energy and the atom optimized Q matrix were used. The remaining two examples of each method are those in which the values of h_z are taken to be 0.2 in magnitude on either side of the atom optimum value. How the optimum values differ between Method 1 and Method 2 can be seen in Fig. 2. In every case, convergence was obtained in half the time taken by using the zero eigenfunction starting point. Further, convergence after the first two cycles proceeded at a rate depending solely upon the energy difference between that calculated in that cycle and the SCF energy. In no instance was an attempt made to use any of the interpolation schemes that had been shown to hasten convergence¹⁴ since this is irrelevant to the issues at point. Table II is a summary of the results of the calculations described above.

THE CALCULATION OF MOLECULAR OPTIMIZED EQUIVALENT AND LOCALIZED ORBITALS

Having the results of the LCAO-MO-SCF calculation, it is possible to ask the question: What values should have been chosen in the *localized representation* for the bond polarity coefficient(s), and atomic orbital coefficients (the Q matrix elements) to give the best possible "fit" to the SCF wavefunctions, subject to the constraints of the limited basis set? The basis truncation error (that error in the wavefunction due to the fact that an incomplete basis set is used, or equivalently, one which would not exist had a complete set been used) will introduce errors in the calculated values of these coefficients that will tend to mask the regularities that could have been shown in a straightforward manner had the truncation errors not existed. The SCF procedure minimizes the calculated total electronic energy while subjecting itself to the limited basis constraint. It compensates by shifting values that would have been calculated with complete basis sets simply to force the energy to be as low as possible. The techniques of the *localized representation* offer rather stern constraints on the form of the wavefunctions. If it is possible to exactly match the SCF functions using complete basis sets, one should not expect an energy for the highly constrained equivalent orbitals over the limited basis set LCAO-MO-SCF functions to be as low as the SCF energy. However, the calculated energy should be a direct measure of the validity of the chosen equivalent orbitals. Therefore, it is possible to take as variables in a multiparameter nonlinear regression analysis, the bond polarity coefficient and the Q matrix elements, using as a single objective function in a minimization

of squares, the expression

$$\chi^2 = |\text{energy}_{E_0}(h_Z, Q) - E_{\text{SCF}}|^2. \quad (9)$$

Details of the calculational and numerical techniques are given in the Appendix of this paper.

It is also proper to investigate the regression of the parameters of the *localized representation* on an objective function

$$\chi^2 = \sum_{i,j} |(\Gamma_{\text{SCF}})_{ij} - (\Gamma_{E_0})_{ij}|^\alpha,$$

where the power, α , to which each term is raised, is 1, 2, and 4.

The resulting coefficients and final objective function values of the totally unconstrained problem are given in Table I for key examples of each calculation.

The results for $\alpha=1$ and 4 did not differ significantly from the $\alpha=2$ calculation so these were deleted from the table. In each case, the calculated energies of the final equivalent orbitals ($\alpha=1, 2, 4$) were so high that it is concluded that this specific technique is unsuitable for the calculation of the proper values of these parameters if these are defined as the "molecular optimized *localized representation* coefficients."

A calculation was done varying only the h_Z values using Method 1 or Method 2; the minimum energy was obtained for $h_Z=1.274$ and 1.200, respectively. The dependence of the calculated energy upon h_Z with each method is shown in Fig. 2. Figure 2 also shows the final "molecular optimized" h_Z values. It should be noted that if partial optimization (e.g., varying h_Z alone) is all that is performed, Method 1 is *absolutely* unsatisfactory, whereas Method 2 is satisfactory. This has been demonstrated in calculations on much more complicated molecules.¹³

Figure 1 is a plot of the expansion coefficients as predicted by an atom optimized problem vs the logarithm of the orbital exponent. Also given on this plot are the results of the complete optimization calculation in which the points referring to valence orbitals are shifted along the abscissa. To good accuracy, the procedure given in the following paragraph can be used to advantage.

The orbital expansion coefficients to be used are identical to those of the atom optimized values. However, the set of orbital exponents are shifted from the atom optimized set by an amount that is calculated from Eq. (7), thereby taking into account the change in net nuclear charge. This change is due to the fact that the sum of all of the h_Z values for each atom do not sum to give the number which are present in the ground state atoms. In water, there are two abortive bonds (unshared electron pairs) as well as the net charge of h_Z in each of the two C-H sigma bonds. The total charge in the valence orbitals plus that of the inner orbitals (in this case, two electrons) is $6+2h_Z$. Had h_Z been calculated to be 1.000, the atomic configuration would have been achieved. However, we see a

net shift in "atomic number," N , in the amount $2(h_Z-1)$. This shift in N is related to a shift in the optimal orbital exponents by the relationship [derived from Eq. (7)]

$$\log \xi_i - \log \xi_i^0 = 2.23 \{ \log [8 + 2(h_Z - 1)] - \log 8 \}. \quad (10)$$

Essentially equivalently, coefficients can be chosen from the original curve using the atom optimized orbital exponents taking into account the shift along the curve due to the deviation of the calculated sum of h_Z values from the atomic case. In a sense, this may be interpreted as an exponent optimization. The inner shell orbitals are seemingly unaffected by the shift in charge except for slight changes in the coefficients of the lower magnitude orbital exponents due probably to the induced nonorthogonality between the valence and inner shell orbitals.

It can be seen that Method 1 and Method 2 yield *equivalent orbitals* of sufficient accuracy to consider their use in precise quantum mechanical calculations as long as complete optimization is accomplished. It is felt that Method 2 will prove to be extremely useful when optimization with respect to the bond polarity coefficients alone is accomplished. Even though the regression techniques (outlined in the Appendix) are considered to be quite efficient, the cycling required for convergence is roughly two orders of magnitude slower than the SCF procedure, even without interpolation schemes that would speed the SCF calculations even further. Larger molecules could take an unreasonable amount of computer time even on today's largest and finest computers (for water on a CDC 6400, the SCF cycling takes approximately 300 sec; the regression, roughly 30 000 sec).

The primary result of this study is that to good accuracy, molecules can be described mathematically in the *localized representation*, and in this representation the parameters normally used in conversation between working chemists are the parameters used in the quantum mechanical calculations and the variation of these parameters upon molecular bond formation is consistent with current notions.

ACKNOWLEDGMENTS

The author would like to express his appreciation to Professor Victor J. Law for helpful discussions on nonlinear programming.

APPENDIX: ROTATIONAL DISCRIMINATION NONLINEAR REGRESSION ANALYSIS¹⁵

Consider a single-valued differentiable function, Q , given in terms of a sum of squares of differentiable real functions $\{f_j\}$, $j=1, \dots, n$ of a set of real variables \mathbf{x} [$x_i = (\mathbf{x})_i$] and a set of constants $\{f_{0j}\}$, $j=1, \dots, m$, such that

$$Q = \frac{1}{2} \sum_j [f_j(\mathbf{x}) - f_{0j}]^2. \quad (A1)$$

When a set of initial values is known for \mathbf{x} , i.e., \mathbf{x}_0 , it is possible to calculate a new set $\mathbf{x}' = \mathbf{x}_0 + h\delta\mathbf{x}$, h a constant, giving a lower value of Q by use of the equation

$$(\partial^2 Q / \partial \mathbf{x}^2) \delta \mathbf{x} = -\partial Q / \partial \mathbf{x}. \quad (\text{A2})$$

Differentiation of Eq. (A1) twice yields

$$[\partial Q / \partial \mathbf{x}]_i = \sum_j [f_j(\mathbf{x}) - f_{0j}] (\partial f_j / \partial x_i), \quad (\text{A3})$$

$$[\partial^2 Q / \partial \mathbf{x}^2]_{ik} = \sum_j (\partial f_j / \partial x_i) (\partial f_j / \partial x_k) + (f_j - f_{0j}) (\partial^2 f_j / \partial x_i \partial x_k). \quad (\text{A4})$$

Employing the Gauss-Newton approximation (the sum of all of the second terms the right-hand side in the above equation is zero), we define a matrix \mathbf{G} such that

$$(\mathbf{G})_{ik} = \sum_j (\partial f_j / \partial x_i) (\partial f_j / \partial x_k) \approx [\partial^2 Q / \partial \mathbf{x}^2]_{ik} \quad (\text{A5})$$

which we call the approximate Hessian matrix. Since \mathbf{G} is a real positive semidefinite matrix, there exists an orthogonal matrix \mathbf{U} which diagonalizes \mathbf{G} ; thus,

$$\mathbf{U}^T \mathbf{G} \mathbf{U} = \mathbf{G}_D, \quad (\text{A6})$$

where \mathbf{G}_D is a diagonal matrix. Equation (A2) is now expressed

$$\mathbf{G} \delta \mathbf{x} = -\partial Q / \partial \mathbf{x}. \quad (\text{A7})$$

Therefore,

$$[\mathbf{U}^T \mathbf{G} \mathbf{U}][\mathbf{U}^T \delta \mathbf{x}] = -[\mathbf{U}^T (\partial Q / \partial \mathbf{x})] \quad (\text{A8})$$

which allows definition of two matrices $\delta \mathbf{y} \equiv \mathbf{U}^T \delta \mathbf{x}$ and $\partial Q / \partial \mathbf{y} \equiv \mathbf{U}^T (\partial Q / \partial \mathbf{x})$, so that Eq. (A8) is expressed: $\mathbf{G}_D \mathbf{y} = -\partial Q / \partial \mathbf{y}$. A diagonal matrix \mathbf{G}_D^P can be defined where $(\mathbf{G}_D^P)_{ii} = 1.0 / (\mathbf{G}_D)_{ii}$ if and only if $(\mathbf{G}_D)_{ii}$ is not zero (or above a defined threshold for numerical reasons), and $(\mathbf{G}_D^P)_{ii} = 0.0$ otherwise. Further, $(\delta \mathbf{y})_i$ and $(\partial Q / \partial \mathbf{y})_i$ are defined to be zero when $(\mathbf{G}_D^P)_{ii} = 0.0$. Then, $\delta \mathbf{y} = -\mathbf{G}_D^P (\partial Q / \partial \mathbf{y})$ so that

$$\delta \mathbf{x} = \mathbf{U} \mathbf{G}_D^P \mathbf{U}^T (\partial Q / \partial \mathbf{x}). \quad (\text{A9})$$

In the Fariss and Law treatment¹⁵ an upper limit, h (consistent with the definition $\mathbf{x}' = \mathbf{x}_0 + h\delta\mathbf{x}$ calculated from the previous iteration) was placed on the magnitude of each $(\delta \mathbf{y})_i$, necessitating a single parameter minimization on h . For the single parameter search, it

is assumed that $Q = Q(h)$ takes the form

$$Q = (h - h_0)^\beta + Q_0. \quad (\text{A10})$$

The evaluation by central differences, of Q , $\partial Q / \partial h \equiv D_1$, $\partial^2 Q / \partial h^2 \equiv D_2$, and $\partial^3 Q / \partial h^3 \equiv D_3$ at a base point h_0 is then carried out. It is not difficult to show that

$$h - h_0 = D_1 D_2 / (D_2^2 - D_1 D_3) \quad (\text{A11})$$

and

$$\beta = (2D_2^2 - D_1 D_3) / (D_2^2 - D_1 D_3). \quad (\text{A12})$$

Using the above, convergence can be rapidly achieved. The derivatives are evaluated numerically by the following:

$$D_1 = [f(h_0 + \delta h) - f(h_0 - \delta h)] / 2\delta h, \quad (\text{A13})$$

$$D_2 = [f(h_0 + \delta h) - 2f(h_0) + f(h_0 - \delta h)] / \delta h^2, \quad (\text{A14})$$

$$D_3 = [f(h_0 + 2\delta h) - 3f(h_0 + \delta h) + 3f(h_0) - f(h_0 - \delta h)] / \delta h^3. \quad (\text{A15})$$

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² A Gaussian basis function is defined as follows:

$$\Phi_{\text{GTO}} = (2\zeta/\pi)^{0.75} f(x, y, z) \exp(-\zeta r^2),$$

where $f(x, y, z) = 1$ for an s orbital and $f(x, y, z) = 2(\zeta)^{0.5} \{x, y, z\}$ for a p_x, p_y, p_z orbital, respectively.

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