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Pathology in Force-Field Computation Associated with Hartree Fock Symmetry-Breaking Instability[1]

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Energy gradients are easy to compute, in the restricted SCF model, provide an insight into reaction mechanisms, and make possible the efficient computation of force constants, equilibrium geometries, and the structures of transition states.[3-6] However, there are some serious hazards in the routine use of the gradient programs now becoming widespread, associated with the instability of symmetry-restricted SCF solutions to symmetry-breaking. Lowering of the electronic energy associated with the symmetry breaking in the wave functions may be induced deliberately by choice of the basis set, or unintentionally by the nuclear distortions which are introduced in the course of calculations of force constants. If the latter, an artificially low, and perhaps negative force constant will be computed, associated with a »normal coordinate« which breaks the molecular symmetry. This will produce false conclusions on the ease of symmetry breaking distortions. We show by reference to a model two-electron system that this problem is frequently encountered in twixtyl or diradical systems, and can be overcome by choosing a wavefunction which is not symmetry or spinrestricted, without the need for extensive configuration mixing.

INTRODUCTION

Energy gradients are not very difficult to compute, particularly in semi-empirical SCF-MO theory, and add a great deal of information to the accompanying energy computation.[3-6] For example, the energy gradient

$$\mathbf{G} = -\sum_i \frac{\partial E}{\partial x_i} \mathbf{u}_i, \tag{1}$$

where x_i is a nuclear coordinate and $\mathbf{u}_i$ is a unit vector in the direction of increasing x_i, points toward the nearest extremum in the energy surface. Extreme points on the energy surface, which are of prime importance in the theoretical discussion of chemical reaction mechanisms, are specified by the condition $\frac{\partial E}{\partial x_i} = 0$ (all i). Thus the gradient can guide the search for these extreme points very efficiently.

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If one confines attention to computations in the restricted SCF formalism, which is the foundation of the vast majority of computations, the gradient can be written in a compact way

$$\frac{\partial E}{\partial x_i} = \frac{\partial}{\partial x_i} \{\Sigma P_{\mu\nu} h_{\mu\nu} + \Sigma [\mu\lambda \mid \upsilon\sigma] (2 P_{\mu\lambda} P_{\mu\sigma} - P_{\mu\sigma} P_{\nu\lambda})\} \tag{2}$$

Since one may presume that the wave function is optimized within the limitations of the basis, $\partial P_{\mu\nu}/\partial x_i = \frac{\partial S_{\mu\nu}^{(5)}}{\partial x_i}$ and one need only evaluate derivatives of the integrals. In semi-empirical ZDO theories in which $S_{\mu\nu} = \delta_{\mu\nu}$ and only one- and two-center integrals are retained, these derivatives are known in analytic form, and there are rather few new integral computations required to obtain energy gradients. In ab initio theories many more two-electron integrals occur and the gradient computations become more time-consuming. However, if a Gaussian basis is chosen, many of the derivatives can be expressed as a combination of integrals previously evaluated in the course of the energy computation, with great saving of time. Due to the high information content and low cost of the gradient computations, such computations are becoming more and more widespread. After the pioneering work of McIver[3], the use of a number of CNDO- and MINDO-based gradient programs has been reported and some are available through QCPE[4]. Parallel ab initio work using gradients has been described by Pulay[5], and the program POLYGRAD based on POLYATOM is available[6].

Since we can anticipate wide use of these programs, it is worthwhile to make clear any circumstances when the gradient calculation may give misleading results. Since the most dramatic triumph of the gradient calculation has been in their description of molecular force fields, a failure in this area would be particularly disappointing. In this report we wish to describe, by the use of a model system, a pitfall in SCF gradient computation which will lead to a false prediction of symmetry breaking in the nuclear framework. This pathology is closely related to the Hartree-Fock instabilities investigated by Čizek and Paldus[7], and Koutecky[8]. For completeness, we describe this phenomenon briefly.

HARTREE-FOCK INSTABILITIES AND THE SYMMETRY DILEMMA

Čizek and Paldus considered the variations in energy in the neighborhood of a Hartree-Fock solution, and found it convenient to describe the small variations in a basis of one-electron excitations Φ_{kl}. Although the Hartree-Fock wave function is chosen so to produce an energy invariant to *first order* in these excitations, second order terms arise. Through second order in single excitations, the energy may be written

$$E = E_0 + \sum_{klmn} E_{klmn} \delta\Phi_{kl} \delta\Phi_{mn} \tag{3a}$$

This expression looks very much like a vibrational force field, and similarly a transformation to »normal excitational modes« parallel to normal vibrational modes can be found.

$$E = E_0 + \Sigma E_{\mu\nu,\,\mu\nu} \Phi_{\mu\nu} \Phi_{\mu\nu} \tag{3b}$$

If a specific $E_{\mu\nu,\mu\nu}$ is negative, the Hartree-Fock solution is unstable, and the total energy will be lowered by mixing Φ_μ with Φ_ν. The resulting wave function can be written

$$\Psi = |\Phi_1^2 \ldots (\Phi_\mu + \lambda \Phi_\nu)^2 \ldots \Phi_N^2| \tag{4}$$

for the »singlet instability« retaining the single-determinant form. If Φ_μ is of different symmetry from Φ_ν, the new determinant is of mixed symmetry. The symmetry breaking or charge fluctuation from the symmetric reference determinant stabilizes the system, in a manner of speaking. A. Toyota, T. Tanaka, and T. Nakajima[9] have reported a series of PPP computations on pentalenes and annulenes which show that, indeed, the SCF energy *does* decrease when the nuclear framework is distorted in the sense implied in the charge density waves associated with broken symmetry solutions. However, one must be cautious in concluding that such a symmetry breaking nuclear distortion is necessarily stabilizing or even easy. Although the exact wavefunction is symmetry adapted, there is no need that an approximate function restricted to a single-determinant form must also be symmetry adapted. Indeed, the symmetry breaking may be the only way that a more realistic multi-configurational wave function can be introduced. The following expansion of the broken-symmetry solution will make the last statement more clear.

$$|\Phi_1^2 \ldots \frac{(\Phi_\mu + \lambda \Phi_\nu)^2}{(1+\lambda^2)} \ldots \Phi^2| = \frac{|\Phi_1^2 \ldots \Phi_\mu^2 \ldots \Phi_N^2|}{(1+\lambda^2)} + \frac{\lambda^2}{1+\lambda^2} |\Phi_1^2 \ldots \Phi_\nu^2 \ldots \Phi_N^2| +$$

$$\frac{\lambda}{1+\lambda^2} \left(|\Phi_1^2 \ldots \Phi_\mu^\alpha \Phi_\nu^\beta \ldots \ldots \Phi_N^2| - |\Phi_1^2 \ldots \Phi_\mu^\beta \Phi_\nu^\alpha \ldots \Phi_N^2|\right) \tag{5}$$

The first two terms resemble a particular CI wave function wherein a doubly excited state is mixed with the reference state. The coefficients are not CI--optimal, since the singly excited state of distinct symmetry is inescapably mixed into the function so to maintain the single determinant form. Nevertheless the energy gain from this non-optimal CI offsets any penalty associated with the introduction of the singly excited state, in the case of singlet instability. The energy of the wave function of broken symmetry can be written

$$\frac{E(\Phi_\mu^2) - \lambda^2 K_{\mu\nu}}{(1+\lambda^2)^2} + \frac{\lambda^2}{(1+\lambda^2)^2} E({}^1\Phi_\mu \Phi_\nu) + \Theta\left[\frac{\lambda^4}{(1+\lambda^2)^2}\right] \tag{6}$$

It is equally likely that the energy lowering arises from the introduction of a relatively *stable* openshell state $\Phi_\mu \Phi_\nu$ rather than any advantage of CI between the closed shell states.

In all these remarks, we have assumed that the nuclei remain in the original symmetric arrangement. The symmetry breaking occurs in the single--determinant wavefunction only. We stress once more that there is no implication that the nuclei must move so to break the symmetry of the Hamiltonian. However, one way to remove the symmetry constraint on the *wave function* is to break the symmetry of the Hamiltonian. Then even within the restricted Hartree Fock formalism the Φ_μ^2 state and the Φ_ν^2 states may mix with the ${}^1\Phi_\mu\Phi_\nu$ state. If the symmetry of the Hamiltonian is broken, the response of the

system has two components. One response is the mixing due to the passage from restricted to unrestricted wave function; the other response is the change in energy due to the change in position of nuclei in the force field as determined in a consistently unrestricted computation. If the system is HF singlet-unstable the observed *energy change* upon symmetry breaking will be anomalously low.

If the *gradient* is computed without consideration of the possibility of changes in LCAO coefficients — that is, with the assumption that the wave function is fully optimized within the constraints of its form — the initially presumed symmetry of the nuclei will never be broken. That is to say, if $x_m = \Sigma_1 a_{km} q_k$ is a coordinate of less than total symmetry, $\partial E/\partial x_m|_0 = 0$. However, the gradient evaluated when the symmetry of the nuclei is broken by a non-totally symmetric displacement x_n, $\partial E/\partial x_m|_{x_n}$ will refer to a very different density matrix $\mathbf{P}(x_n)$ than did the gradient $\partial E/\partial x_m$, if the reference SCF solution is unstable with respect to symmetry breaking.

The usual presumption that

$$P_{\mu\nu}(x_n) \sim P_{\mu\nu}(0) + \sum_n \left.\frac{\partial P}{\partial x_n}\right|_0 x + \Theta(x_n^2)$$

$$\sim P_{\mu\nu}(0) + \Theta(x_n^2) \tag{7}$$

while not strictly false, is misleading in that the correction on the order of the displacement — squared will not generally be small when $P_{\mu\nu}(x_n)$ can be very different from $P_{\mu\nu}(0)$.

To illustrate the problem we construct a model system, described in the following section.

AN UNSTABLE MODEL SYSTEM

We quote the energy for an unrestricted (different orbitals for different spins) single determinant.[8]

$$E = \sum_{\mu\nu} P_{\mu\nu}{}^T h_{\mu\nu} + 1/4 \sum_{\mu\nu\rho\sigma} [\mu\sigma \,|\, \upsilon\varrho] \{2 P_{\mu\sigma}{}^T P_{\nu\varrho}{}^T - P_{\mu\varrho}{}^T P_{\nu\sigma}{}^T - P_{\mu\varrho}{}^- P_{\nu\sigma}{}^-\} \tag{8}$$

Here $P_{\mu\nu}{}^T = P_{\mu\nu}{}^\alpha + P_{\mu\nu}{}^\beta$ and $P_{\mu\nu}{}^- = P_{\mu\nu}{}^\alpha - P_{\mu\nu}{}^\beta$ where $P_{\mu\nu}{}^\sigma$ is the density matrix for spin σ. Let the wave function be $|\Psi_\alpha \Psi_\beta|$, a single determinant with orbitals expressed in the $\Phi_1{}^\alpha$, $\Phi_1{}^\beta$, $\Phi_2{}^\alpha$, $\Phi_2{}^\beta$ basis.

$$\Psi_\alpha(x_\alpha) = \cos x_\alpha \, \Phi_1{}^\alpha + \sin x_\alpha \, \Phi_2{}^\alpha$$

$$\Psi_\beta(x_\beta) = \cos x_\beta \, \Phi_1{}^\beta + \sin x_\beta \, \Phi_2{}^\beta \tag{9}$$

Here $\langle \Phi_1 \,|\, \Phi_2 \rangle = 0$, $\langle \Phi_1 \,|\, \Phi_1 \rangle = \langle \Phi_2 \,|\, \Phi_2 \rangle = 1$.

We presume that $\Phi_1{}^\sigma$ ($\sigma = \alpha$ or β) is of different symmetry from $\Phi_2{}^\sigma$. If we choose $h_{11} = 0$, $h_{12} = h_{21} = 0$ (by symmetry) $h_{22} = \Delta$, then

$$E(x_\alpha x_\beta) = (\sin^2 x_\alpha + \sin^2 x_\beta)\,\Delta + (\sin x_\alpha \cos x_\alpha + \sin x_\beta \cos x_\beta)\, V_1 +$$
$$+ \cos^2 x_\alpha \cos^2 x_\beta \, J_{11} + \sin^2 x_\alpha \sin^2 x_\beta \, J_{22} + (\cos^2 x_\alpha \sin^2 x_\beta +$$
$$+ \cos^2 x_\beta \sin^2 x_\alpha) \, J_{12} + 4 K_{12} \cos x_\alpha \cos x_\beta \sin x_\alpha \sin x_\beta \tag{10}$$

In the above expression we have introduced a non-symmetric one electron perturbation V_1 which we may use to describe a symmetry breaking nuclear

motion. Now consider the stability of the energy to symmetry breaking in the wave function.

$$\text{at } (x_\alpha, x_\beta) = (0, 0) \quad \frac{\partial E}{\partial x_\alpha} = V_1, E = J_{11} \text{ (or 0 if } V_1 \text{ is 0)}$$

$$(0, \pi/2) \quad \frac{\partial E}{\partial x_\alpha} = V_1;\ E = \Delta + J_{12}$$

$$0\ (\pi/2, 0) \quad \frac{\partial E}{\partial x_\alpha} = -V_1;\ E = \Delta + J_{12}$$

$$(\pi/2, \pi/2) \quad \frac{\partial E}{\partial x_\alpha} = -V_1;\ E = 2\Delta + J_{22} \tag{11}$$

If V_1 is zero, we find at least four extreme points. At these points $\frac{\partial^2 E}{\partial x_\alpha^2} = E_{\alpha\alpha}$ becomes

$$\begin{aligned}(x_\alpha, x_\beta) = \quad & (0, 0) \quad 2(\Delta - J_{11} + J_{12}) = E_{\alpha\alpha} \\ & (0, \pi/2) = 2(\Delta + J_{22} - J_{12}) = E_{\alpha\alpha} \\ & (\pi/2, 0) = -2(\Delta - J_{11} + J_{12}) = E_{\alpha\alpha} \\ & (\pi/2, \pi/2) = -2(\Delta + J_{22} - J_{12}) = E_{\alpha\alpha}\end{aligned} \tag{12}$$

The $E_{\beta\beta}$ are related to these expressions by symmetry, since one may exchange α with β in $E(\alpha, \beta)$. Finally

At

$$\begin{aligned}(x_\alpha, x_\beta) = \quad & (0, 0) \quad E_{\alpha\beta} = 4K_{12} \\ & (0, \pi/2) = -4K_{12} \\ & (\pi/2, 0) = -4K_{12} \\ & (\pi/2, \pi/2) = 4K_{12}\end{aligned} \tag{13}$$

If the wave function is spin-restricted ($x_\alpha = x_\beta = x$) then $\frac{\partial E}{\partial x} = 0$ at $x = 0$, $\frac{\pi}{2}$ and may $= 0$ when the following expressions vanishes.

$$\Delta + \sin^2 x\,[J_{22} + J_{11} - 2(J_{12} + K_{12})] - J_{11} + J_{12} + 2K_{12} = 0; \tag{14}$$

this occurs when

$$\sin^2 x = \frac{J_{11} - J_{12} - 2K_{12} - \Delta}{J_{22} + J_{11} - 2(J_{12} + 2K_{12})}$$

We find a solution to equation 14 for real x when $J_{11} > J_{12} + 2K_{12} + \Delta$. The energy curvature at this value of x is

$$E_{xx} = 8 \sin^2 x \cos^2 x\,(2J_{22} + 2J_{11} - 4J_{12} - 8K_{12}) \tag{15}$$

If $J_{11} + J_{22} > 2J_{12} + 4K_{21}$, the point x corresponds to a broken-symmetry minimum energy spin restricted solution. Further analysis shows that this solution is unstable with respect to relaxing the spin equivalence. That is, a different-orbital-different spin solution lies lower in energy.

The situation may be summarized in a figure, constructed with the following assumptions.

At

$$(0, 0),\ E_{\alpha\alpha} = 2(\Delta - J_{11} + J_{12}) < 0\ \ E_{\beta\beta} = 2(J_{12} - J_{22}\ \Delta) < 0$$
$$(\pi/2, \pi/2)\ E_{\alpha\alpha} = 2(J_{12} - J_{22} - \Delta) < 0\ \ E_{\beta\beta} = 2(J_{12} - J_{11} + \Delta) < 0$$
$$(\pi/2, 0)\ E_{\alpha\alpha} = 2(J_{11} - \Delta - J_{12}) > 0\ \ E_{\beta\beta} = 2(J_{22} + \Delta - J_{12}) > 0 \qquad (16)$$

and at these points

$(E_{\alpha\alpha}E_{\beta\beta} - E_{\alpha\beta}^2) > 0$ so that these points are relative maxima or minima rather than saddle points. The reader may verify that if J_{11} and J_{22} are large compared with Δ, J_{12} and K_{12} these criteria are easily met, and under the same circumstances, that $E_{xx} > 0$ implying that the spin-restricted determinant defined above is a minimum within the spin-restricted subspace.

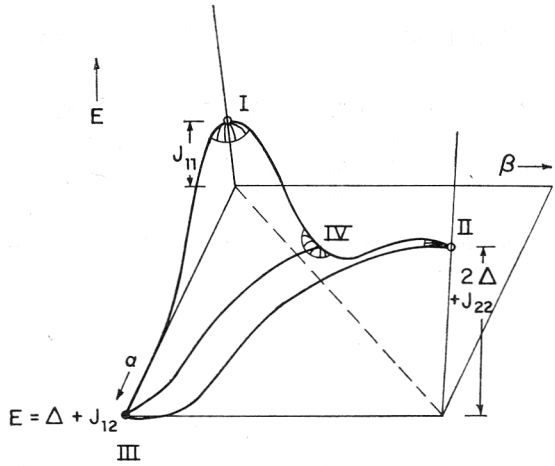

Figure 1. A section of the energy surface for the model system described in the text is displayed. The surface is symmetric with respect to exchange of the variational parameters x_α and x_β. Several extrema are found for the parameters chosen in the text; I corresponds to the state Φ_1^2, and II to the state Φ_2^2. III is an openshell $\Phi_1\Phi_2$ state, with energy equal to the average of the $\Phi_1\Phi_2$ triplet and singlet states. IV is a symmetry-broken spin-restricted state lying below state I and II but above state III; its energy is defined by equations 12 and 18.

GRADIENT AND CURVATURE IN THE MODEL SYSTEM

The gradient will maintain the symmetry of a system, implying $\frac{\partial E(0)}{\partial q_l} = 0$ if q_l is a displacement such that $\Gamma_k \neq \Gamma_l$ where Γ_z is the symmetry species of displacement z.

$\frac{\partial E(q_k)}{\partial q_l} \equiv 0$ likewise if q_k maintains symmetry while q_l breaks symmetry.

However, $\frac{\partial E(q_l)}{\partial q_k}$, which might be used in the finite difference estimate of the value of $\frac{\partial^2 E}{\partial q_l\, \partial q_k}$, will in general be different from zero, because the density matrix defining $E(q_k)$ will no longer be totally symmetric. In the model system $E(q_k)$ will be evaluated with a parameter x near the value given in equation 14; $E(q_l)$ will be evaluated with the restriction that x be near zero.

This symmetry breaking, so that x passes abruptly from 0 or $\pi/2$ to an intermediate value, will have the effect of coupling symmetric and symmetry--breaking modes when the numerically constructed cartesian force constant matrix is diagonalized, and will be recognizable *before* the diagonalization by a degree of asymmetry in the matrix not accountable by simply numerical (roundoff or SCF convergance) imprecision.

For a numerical illustration we assign parameters as follows, taken from our CNDO computation on the norcaradiene circumambulation[10].

$$J_{11} = 0.7 \quad J_{12} = 0.1 \quad \Delta = 0.2$$
$$J_{22} = 1.0 \quad K_{12} = 0.05 \tag{17}$$

TABLE I

Energy Values and Curvature Near Extrema

$E\,(0, 0) = 0.7$	$E_{\alpha\alpha} = -0.8$	$E_{\beta\beta} = -0.8$
$E\,(\pi/2, \pi/2) = 1.4$	-2.2	-2.2
$E\,(\pi/2, 0) = 0.3$	$+0.8$	2.2
$E\,(x = 0) = 0.7$	$E\,(x = \pi/2) = 1.4$	$E\,(x_{opt}) = 0.63$
$\sin^2 x_{opt} = 0.231$	$(x_{opt} \sim 28.7^0)$	E (CI between $x = 0$, $x = \pi/2$) $= .696$

The force matrix, for a symmetry maintaining mode q_k and a symmetry breaking mode, q_l is

$$\begin{bmatrix} \left[\frac{\partial E(q_k)}{\partial q_k} - \frac{\partial E(-q_k)}{\partial q_k}\right]/2\,q_k & \left[\frac{\partial E(q_k)}{\partial q_l} - \frac{\partial E(-q_k)}{\partial q_l}\right]/2\,q_l \\ \left[\frac{\partial E(q_l)}{\partial q_k} - \frac{\partial E(-q_l)}{\partial q_k}\right]/2\,q_k & \left[\frac{\partial E(q_l)}{\partial q_l} - \frac{\partial E(-q_l)}{\partial q_l}\right]/2\,q_l \end{bmatrix}$$

$$\cong \begin{vmatrix} \frac{\partial^2 E_2(x_o)}{\partial q_k} & \frac{\partial^2 E(x_o)}{\partial q_l\,\partial q_k} \equiv 0 \\ \frac{\partial^2 E(x_{opt})}{\partial q_k\,\partial q_l} & \frac{\partial^2 E(x_{opt})}{q_l^2} \end{vmatrix}$$

$$= \begin{vmatrix} a - \lambda & 0 \\ c & b - \lambda \end{vmatrix}$$

Depending on details of the computation, and (if a prepackaged program is used) sheer *chance*, the eigenvalues will be computed by matrix diagonalization

of a diagonal (upper triangle) or nondiagonal (lower triangle) matrix in a standard subroutine. Either a symmetry-correct set of force constants (a and b) will emerge, or a symmetry broken set will emerge. If c is sufficiently large, ($\simeq a$ and b) negative eigenvalues can emerge, *even in an equilibrium geometry,* due to the instability of the HF wave function.

Even if symmetry adapted, numerically apparently reasonable roots are computed, the force constants a and b *cannot be compared with validity,* since they refer to different reference wave functions. One is, in effect, using a better wave function for the class of symmetry breaking modes than one is using for symmetry maintaining modes. This is an expression of Löwdin's »symmetry dilemma«, and is a consequence of the choice of the Hartree Fock reference points.

One may evade this problem even within the Hartree-Fock formalism, at least in part, by using a symmetry unrestricted different — orbital different spins function throughout the computation. A well tested direct minimization method is described by Koutecky[8] for semi-empirical computation and by Ruedenberg[11] for ab initio applications. In the model system, the direct minimization technique would produce the stable open shell state, which corresponds to the energy minimum. Identification of the crossover point where a closed shell state becomes minimal in energy would be easy, and gradients would be as easy to compute as in the RHF computation. One problem will be that while one may prefer to describe a particular spin state or electronic state, the direct minimization method tends to produce mixed spin states, even when the Hamiltonian is spin free.

Clearly the widely available gradient programs must be used with caution whenever a region of HF instability may be encountered. A quick diagnosis of this hazard can be obtained by computation of E_{xx} equation 15, or the expression for $\sin^2 x$, equation 14. In these equations the label 1 could refer to the SCF HOMO, 2 to the SCF LUMO. In the regions of HF instability, one is obliged to perform 2×2 CI to describe the totally symmetric state correctly, and a computation on the singly excited non-totally symmetric state would be highly informative, if not absolutely essential to an understanding of the surface.

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SAŽETAK

Patološko ponašanje računa potencijalnog polja uslijed nestabilnosti Hartree-Fockove metode zbog smanjene simetrije

C. Trindle

Rutinska upotreba programa za računanje gradijenata energije nekoga molekulskog sistema krije u sebi neke opasnosti. One su posljedica nestabilnosti Hartree-Fockove metode s obzirom na smanjenje simetrije. To se posebno često može dogoditi u računima potencijalnog polja, gdje se kao rezultat mogu dobiti negativne potencijalne konstante. Predložena je jednostavna metoda primjenom koje se spomenute teškoće mogu izbjeći.

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