

Handling of intrinsic divergence in the orthogonal gradient method of orbital optimization in an MC-SCF framework and geometry optimization in pathological cases: I (propynal in excited states)

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Abstract. It is demonstrated that a generalized version of the orthogonal gradient method of orbital optimization may sometimes encounter a specific divergence problem which may be termed intrinsic to the first order method. Instead of switching over to a more sophisticated second order method one can cure the divergence problem at the first order level itself by suitably tailoring the MC-SCF operator or the MC-SCF energy matrix. Results of complete geometry optimization of propynal in $1,3n\pi^*$ and $3\pi\pi^*$ states (pathological cases) are reported to demonstrate the usefulness of the method at an INDO-MCSCF level of approximation. The results of structure calculations are further rationalized from generalized quantum chemical bond order indices.

Keywords. Orthogonal gradient method; orbital optimization.

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1. Introduction

The occurrence of convergence difficulties has not been uncommon in the context of SCF calculations by the traditional repeated diagonalization procedure of Roothaan [1]. In fact, such difficulties have been encountered even in closed-shell SCF calculation during the pioneering work of Hartree. A host of remedial measures has been suggested from time to time with varying degrees of success. Of these, mention may be made of the Aitken's procedure [2, 3, 3a], level shifting techniques [4], corresponding orbital methods [5], and the DIIS procedure [6]. The list is by no means exhaustive.

Recently, attention has been drawn to the existence of what has been called intrinsic divergence problem in traditional SCF calculations [7, 8]. The problem is intrinsic in the sense that a better choice of the starting wavefunction would not automatically cure the divergence. Stanton recently used the fixed point iteration theory to clarify the conditions of convergence in closed-shell SCF calculations, and in the process demonstrated the existence of intrinsic divergence in a series of SCF problems [9]. The analysis of Stanton, however, has no bearing on the orthogonal gradient method (OGM) of solving the SCF problem [10, 11, 12, 13]. Intrinsic divergence problems

in the context of OGM or variants of it were recently analysed by us [14, 15] and techniques were suggested to circumvent the problem. However, our earlier works were confined to closed-shell or unrestricted open-shell calculations. We now propose to extend the analysis to the more general case.

Root of convergence problems in the first order SCF theories can frequently be traced to either (i) a poor choice of the starting wavefunction (extrinsic problem), or (ii) the existence of strong coupling between the orbital and configuration spaces which is neglected in the first order theories (intrinsic problem).

Thus, if the observed divergence is independent of the starting wavefunction, one suspects that the problem must be intrinsic to the first order method itself. Two alternatives exist at this point: switch over to a second order (MC) SCF procedure [16, 17, 18, 18a] which is computationally a much more involved problem or look for a suitable divergence-curing device that can force the first order method to converge. The layout of the paper is as follows. In § 2 we briefly describe the orthogonal gradient method while § 3 describes the proposed schemes for tackling the pathological cases. Some examples for the efficacy of the methods proposed are included in §§ 4 and 5. Although the calculations are done at the INDO level of approximation introduced by Pople, the suggested technique would remain perfectly valid in an ab-initio framework.

2. The orthogonal gradient method

In the master equation approach of McWeeny [19] based on the first order variational procedure, one alternately solves the orbital equation (1) and the linear variational problem involving the CI coefficients (equation 2)

$$hT^0 P_1 + Z(P_2) = V(T^0) = ST^0 \varepsilon \quad (1)$$

$$HC = CE \quad (2)$$

where h represents the one-electron part of the interaction, P_1 represents the one-electron density matrix in the MO basis and Z is the two-electron part of the interaction in the AO-MO basis [18], T^0 is an $n \times m$ matrix, n representing the dimensionality of the AO basis set and m the number of occupied molecular orbitals. Let T^t represent the total coefficient matrix ($n \times n$). Using (1) and its hermitian conjugate we have

$$(T^t)^\dagger V = (T^t)^\dagger ST^0 \varepsilon \quad (3)$$

$$V^\dagger (T^t) = \varepsilon^\dagger (T^0)^\dagger S (T^t). \quad (4)$$

The orthonormality condition in the total space demands

$$(T^t)^\dagger S (T^t) = 1 \quad (5)$$

which in turn proves that (if T^t is invertible)

$$S^{-1} = (T^t)(T^t)^\dagger. \quad (6)$$

Combining equations (3) and (4) and using (6) we have

$$V^\dagger T^t (T^t)^\dagger V = \varepsilon^\dagger [T^{0\dagger} S T^t (T^t)^\dagger S T^0] \varepsilon = \varepsilon^\dagger \varepsilon. \quad (7)$$

The condition at convergence demands the hermiticity of ε which allows us to write [10]

$$\varepsilon = (V^\dagger S^{-1} V)^{1/2}. \quad (8)$$

Equation (8) can now be used to eliminate ε from (1) which permits us to write [12, 13, 14, 15].

$$V = ST^0(V^\dagger S^{-1}V)^{1/2}. \quad (9)$$

Equation (9) at once leads to the following iterative scheme for the optimization of orbitals

$$T_n^0 \Rightarrow T_{n+1}^0 = S^{-1}V_n(V_n^\dagger S^{-1}V_n)^{-1/2}. \quad (10)$$

One can arrive at (10) from a slightly different line of reasoning. Away from the stationary point, the lagrangian multiplier matrix is not hermitian. Let ε_n be the slightly non-hermitian lagrangian multiplier matrix at the n th step. One can, then define a unitary transformation matrix U_n ($m \times m$) and use it to transform the coefficient matrix for the occupied orbitals T^0 as $T_{n+1}^0 \Rightarrow T_n^0 U_n$. If we now postulate that this transforms $\varepsilon_n \Rightarrow U_n^\dagger \varepsilon_n$. We immediately arrive at the conclusion that the form of the unitary transformation matrix U_n is $U_n = \varepsilon_n(\varepsilon_n^\dagger \varepsilon_n)^{-1/2}$. This is equivalent to the content of equation (10).

Usually, iterations based on (10) converge fast. This has been verified in ab-initio as well as semiempirical calculations [12, 20]. Nevertheless one may occasionally encounter convergence problem in some cases. In a previous communication [15] we dealt with the problem of convergence in closed-shell SCF calculations within the framework of the orthogonal gradient method (OGM). It was shown there that the OGM could encounter pathological cases of divergence even in closed-shell SCF calculations if the magnitude of eigenvalue of even one orbital in the unoccupied subspace happened to be larger than the eigenvalue of largest modulus in the occupied subspace. Similar problems may crop up in a general open shell calculation as well.

3. Pathological cases of divergence

Let us consider a particular example where iterations based on equation (10) fail to converge for any reasonable choice of the starting wavefunction. In the course of our recent investigations on the structural features of a series of carbonyl and thiocarbonyl molecules in low-lying excited states by using the orthogonal gradient method of orbital optimization in an INDO/MCSCF framework [21,22] we found that $(\text{CN})_2\text{CO}$ is a pathological case. Table 1 displays convergence profiles obtained in the course of orbital optimization in the ${}^3n\pi^*$ state of $(\text{CN})_2\text{CO}$. Divergence was encountered for all the different types of input vectors tried. Hartree type damping was found to be ineffective.

Several other interpolation techniques were tried without success (results not included in table 1). We may, therefore, categorize this as a truly pathological case within the realm of the orthogonal gradient method. Recalling the analysis made earlier [14, 13, 15] one may conjecture that the energy matrix V for this particular problem (cf eqn. 10) has the particular kind of eigenvalue spectrum which was shown to be responsible for the onset of intrinsic divergence in a number of closed-shell SCF problems [15]. If this conjecture were correct, the remedy would be to replace V in equation (9) by an appropriately root-shifted or level-shifted V matrix (say, \tilde{V}) at every iteration. The dressed V is forced to have the eigenvalue structure which ensures convergence. One must note, however, that the shifting requires additional labour in the present context. This is because the V matrix in (9) is in the mixed

Table 1. Convergence profiles for the $^3n\pi^*$ state orbital optimization of $(\text{CN})_2\text{CO}$ for different input orbitals.

Iteration No. (n)	Electronic energy at the nth iteration (E_n) in a.u. for different types of inputs (I-V)				
	I	II	III	IV	V
0	-138.728207	-138.719567	-138.745881	-138.839461	-138.728207
1	-138.760006	-138.642760	-138.768359	-138.841348	-138.760006
2	-138.770608	-138.350082	-138.783678	-138.842674	-138.770608
3	-138.765135	-137.633612	-138.796290	-138.843603	-138.765135
4	-138.724518		-138.805712	-138.844254	-138.695375
5	-138.600376	diverges	-138.809856	-138.844708	-138.022183
6	-138.204329		-138.803453	-138.845019	-133.335322
7	-137.266025		-138.771857	-138.845217	
8				-138.845301	
9	diverges		diverges	-138.845217	diverges
10				-138.844792	
11				-138.843566	
12				diverges	

Notes: I. Closed-shell ground state vectors as input; II. Eigenvectors of h_{core} as input; III. V_{N-1} potential orbitals as input; IV. Partially optimized orbitals as input; V. Input as in I and two point (Hartree) damping [3a].

(AO-MO) basis and therefore, requires to be transformed into purely AO or MO basis before resorting to eigenvalue shifting technique. After introducing the required degree of level-shifting, V is to be transformed back into its original representation and used in (9) for updating the orbitals. We indicate below the sequence of transformations for root-shifted (case a) and level-shifted (case b) iteration:

Case a: root-shifted iterations

step 1: construction of the V matrix

$$V_i = hT_i P_1^i + Z_i$$

step 2: transformation of V_i into the AO basis

$$\bar{V}_i = V_i T_i^\dagger$$

step 3: formation of the root-shifted $\bar{V}_i (= V_i^s)$

$$(V_i^s)_{pq} = (V_i)_{pq} + \lambda_{pq} \delta_{pq}$$

step 4: transformation of V_i^s back to the mixed AO-MO basis

$$\tilde{V}_i = \bar{V}_i^s T_i$$

step 5: updation of $T_i \Rightarrow T_{i+1}$ as

$$T_{i+1} = S^{-1} \tilde{V}_i^s (\tilde{V}_i^s \dagger S^{-1} \tilde{V}_i^s)^{-1/2}$$

and return to step 1.

Case b: level-shifted iterations

In this scheme the steps to be executed are as follows:

step 1: construction of the V matrix

$$V_i = hT_i P_1^i + Z_i,$$

step 2: transformation of V_i into the AO basis

$$V_i^a = V_i T_i^\dagger,$$

step 3: generation of the level-shifted V matrix in the AO basis

$$V_i^b = V_i^a + \lambda P,$$

where P is the matrix representation of the projector into the occupied space ($P = \sum_i^{\text{occ}} |\phi_i\rangle\langle\phi_i|$) in AO basis. If λ is a sufficiently large negative quantity the shifting in step 3 ensures that there are no unoccupied orbitals having eigenvalues large (in absolute sense) than their orbital counterparts.

step 4: transformation of V_i^b back in AO-MO basis

$$\bar{V}_i^l = V_i^b T_i^\dagger.$$

step 5: update $T_i \Rightarrow T_{i+1}$ as follows

$$T_{i+1} = S^{-1} \bar{V}_i^l (\bar{V}_i^{l\dagger} S^{-1} \bar{V}_i^l)^{-1/2}$$

and return to the step 1.

4. Examples of curing divergence problem

In all the cases of intrinsic divergence encountered so far, the shifted iterations based on scheme *a* or *b* smoothly converged irrespective of the choice of starting orbitals. In table 2 we have summarized root-shifted convergence profiles for the pathological case where unaided iterations failed to converge (see table 1). It is clearly demonstrated that root-shifting eliminates the divergence problem and iterations now smoothly converge to the desired level of self-consistency with any reasonable choice of the starting wavefunction. In a pathological case as the one described in the previous section even a small error in the wavefunction tends to get magnified at every iteration unless one resorts to shifting. That this conclusion is inescapable is amply demonstrated by the convergence profile in figure 1. The shifting procedure was invoked right from the first iteration and was allowed to continue until the computed energy monotonically converged to within 10^{-4} a.u. (the point (a) in figure 1). Shifting was withdrawn at this point. After a few iterations in which the energy decreases, the point (b) is reached where divergence sets in again. However, if shifted iterations and allowed to continue beyond the point (a) energy decreases monotonically and convergence ($\epsilon < 10^{-6}$ a.u.) is ultimately achieved (branch a-c of figure 1). To test the stability of the solution, shifting was again withdrawn at the point (c) and iterations were allowed to continue. No divergence was encountered. Thus we may start with any reasonable choice of the wavefunction and invoke the shifting procedure instead

Table 2. Convergence profiles for a pathologically divergent SCF calculation when root-shifting is used with different types of input ($\epsilon < 10^{-4}$ a.u.).

Iteration No. (<i>n</i>)	Electronic energy at <i>n</i> th root-shifted iteration (E_n) for different types of input (a.u.)			
	I	II	III	IV
0	-138.728207	-138.719567	-138.753343	-138.745881
1	-138.753330	-138.789092	-138.814765	-138.760590
2	-138.764409	-138.807970	-138.824312	-138.768933
3	-138.773143	-138.816671	-138.828846	-138.776317
4	-138.780849	-138.822229	-138.831749	-138.783231
5	-138.787901	-138.826389	-138.833875	-138.789763
6	-138.794423	-138.929723	-138.835560	-138.795905
7	-138.800447	-138.832453	-138.836951	-138.801632
8	-138.805976	-138.834712	-138.838128	-138.806918
9	-138.811011	-138.836584	-138.839135	-138.811748
10	-138.811556	-138.838140	-138.840006	-138.816121
15	-138.831601	-138.842741	-138.842920	-138.831656
24		-138.845186		
25	-138.842994	-138.845285	-138.845115	-138.843333
30	-138.844547		-138.845237	
34	-138.845141			
35	-138.845239			-138.845217

For details of the inputs I-IV see the footnotes to table 1.

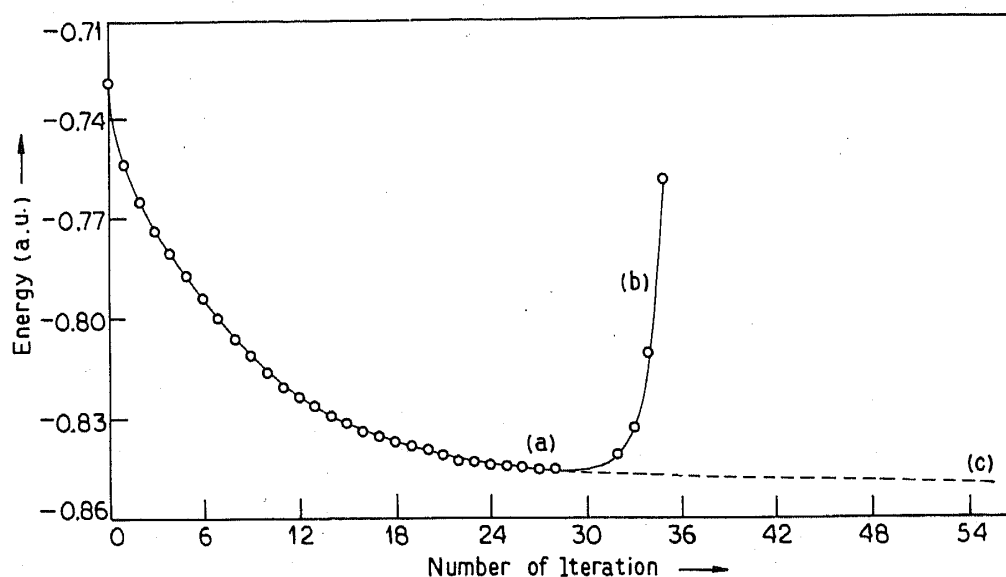


Figure 1. Energy convergence profile in a typical pathological case of orbital optimization in OGM when shifting is used (a-c) and when shifting is withdrawn after a few iterations (a-b).

of looking for a better starting point or switching over to the more laborious second order MCSCF methods even when a pathological problem is encountered [23]. Now the question is: how good are the energies computed this way? To show that they are indeed reliable we report here the results of complete geometry optimization carried out on a pathologically diverging case by our orthogonal gradient method.

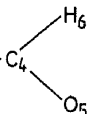
5. Geometry optimization in a pathologically divergent case

At the particular level of approximation the propynal in the $n\pi^*$ state is a pathological case just like the $(\text{CN})_2\text{CO}$ molecule. The reason for focussing our attention on propynal instead of $(\text{CN})_2\text{CO}$ is the lack of availability of experimental data for the latter. The near-uv spectrum of propynal has received considerable attention of spectroscopists [24]. Since the molecule fluoresces as well as phosphoresces it has naturally become an important subject of laser photochemical or photophysical studies. Molecular dimensions in the ground state have been determined by microwave spectroscopy which confirmed planar ground state structure. Partial analysis of the many banded absorption spectrum ranging from 3000 Å to 4000 Å was made by Howe and Goldstein [25] who identified the band system associated with $n\pi^*$ transition typical of a $\lambda\text{C}=\text{O}$ chromophore. Brand *et al* [26] (BCW) made detailed ro-vibronic studies of the $^1A' \rightarrow ^1A''$ band system having the origin at 3820 Å and were able to assign with a fair degree of certainty eleven of the twelve fundamental modes of the upper electronic state ($^1A''$). From the anharmonic nature of the ν'_{10} , the out-of-plane wagging mode of the aldehydic hydrogen, BCW concluded that propynal is non-planar in this coordinate by at most 3° . They attributed this quasi-planarity of propynal in the $^1A''$ state to π conjugation effects arising from the ethyne group.

Since our OGM based INDO/MC-SCF method [21, 22] has been found to furnish fairly reliable structural parameters of small carbonyl systems in the low-lying excited states we have carried out geometry optimization for propynal in $^{1,3}n\pi^*$ and $^3\pi\pi^*$ states by using the proposed root shifted or level shifted OGM in a MC-SCF framework. These results are summarized in table 3. The molecule is predicted to be planar in the $n\pi^*$ states in conformity with the experimental findings of Brand *et al*

Table 3. Computed structural parameters of propynal in the $^{1,3}n\pi^*$ and $^3\pi\pi^*$ states. The pathological divergence was cured by resorting to the use of a root-shifted version of the orthogonal gradient method of orbital optimization. A constant value of 1.0 a.u. was used for shifting at all the points on the energy surface.

Geometrical parameters [†]	$^1n\pi^*$ state ($^1A''$)	$^3n\pi^*$ state ($^3A''$)	$^3\pi\pi^*$ state ($^3A'$)	Available experimental data ($^3A''$) [26]
$r(\text{C}_2-\text{H}_1)$ Å	1.095	1.092	1.095	
$r(\text{C}_2-\text{C}_3)$ Å	1.215	1.210	1.220	1.23
$r(\text{C}_3-\text{C}_4)$ Å	1.396	1.400	1.374	1.445 ± 0.046
$r(\text{C}_4-\text{O}_5)$ Å	1.340	1.320	1.385	1.31
$r(\text{C}_4-\text{H}_6)$ Å	1.130	1.110	1.114	
$\text{C}_3-\text{C}_4-\text{O}_5$ deg	117.0	119.0	120.3	123 ± 2
$\text{H}_6-\text{C}_4-\text{C}_3$ deg	128.0	128.0	125.8	
$\text{H}_1-\text{C}_2-\text{C}_3$ deg	176.4	180.0	180.0	180 ± 3
$\text{C}_2-\text{C}_3-\text{C}_4$ deg	180.0	180.0	180.0	178 ± 10
ϕ (out of plane angle at C_4)	~ 0.0	~ 0.0	~ 0.0	0.0

[†] The numbering of the atoms is: $\text{H}_1-\text{C}_2 \equiv \text{C}_3-\text{C}_4$ 

[26] and Lin and Moule [27]. The C-C≡C group is found to retain its linear configuration upon excitation. This finding also agrees with the experimental finding of Brand *et al* [26]. The other notable features of the computed excited state geometrical parameters include lengthening of the C=O bond, decrease in the C-C length and an increase of the C≡C bond distance all of which nicely mirror experimental findings [26]. The $^3\pi\pi^*$ state is also predicted to be planar. The C=O bond is, however, much more elongated in the $^3\pi\pi^*$ state compared to $n\pi^*$ state. The C-C bond on the other hand is predicted to be shortened considerably following the $\pi\pi^*$ excitation.

The pattern of changes in bond lengths observed upon excitation can be rationalized in terms of changes in quantum chemical bond order (BO) between different pairs of atoms following excitation and classical idea of resonance among canonical structures. The BOs are derived from the one electron density (OED) matrix P (in MO basis) which can be partitioned into P_1^D and P_1^S where P_1^D denotes the one electron density component due to the doubly occupied orbitals (core) and P_1^S that due to the singly (or less) occupied orbitals (valence). The OED in MO basis is then converted into OED in the AO basis

$$P^D = TP_1^D T^\dagger,$$

$$P^S = TP_1^S T^\dagger.$$

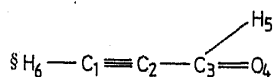
The bond order between a pair of atoms A and B is then defined as follows [28]

$$B_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} (P_{\mu\nu}^D P_{\nu\mu}^D) + \sum_{\mu \in A} \sum_{\nu \in B} (P_{\mu\nu}^S P_{\nu\mu}^S).$$

Table 4 summarises computed bond orders between different pairs of atoms of propynal and charge densities in different atoms in the ground and three excited states of propynal. The computed C≡C BO in the ground ($^1A'$) state of propynal is a bit less than what would be expected for a carbon-carbon triple bond while the C=O BO is somewhat smaller than that expected for a carbon-oxygen double bond. On the other hand, the computed C-C BO in the ground state is about 10% larger

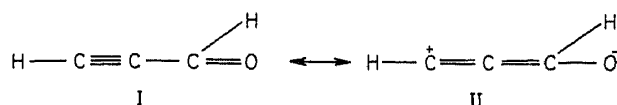
Table 4. Computed bond orders between different atoms and net charge densities on each atom in the ground and excited states of propynal[§].

State	Bond orders				Net charges on atoms				
	C ₁ -C ₂	C ₂ -C ₃	C ₃ -O ₄	C ₁ -H ₆ (C ₃ -H ₅)	C ₁	C ₂	C ₃	O ₄	H ₅₍₆₎
ground ($^1A'$)	2.84	1.11	1.88	0.98 (0.92)	-0.02	-0.05	0.34	-0.28	-0.05 (0.06)
$^1n\pi^*$ ($^1A''$)	2.70	1.19	1.10	0.98 (0.90)	-0.08	0.01	0.11	-0.12	0.02 (0.06)
$^3n\pi^*$ ($^3A''$)	2.78	1.16	1.12	0.97 (0.90)	-0.09	0.01	0.08	-0.10	0.04 (0.06)
$^3\pi\pi^*$ ($^3A'$)	2.60	1.34	0.97	0.98 (0.94)	-0.04	0.01	0.15	-0.16	-0.03 0.07

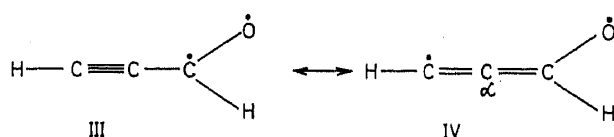


Intrinsic divergence in orthogonal gradient MC-SCF method

than that expected for a C-C single bond. One can rationalize the observed ground state BOs of propynal in terms of mixing of the following canonical structures (I and II).



From table 4 we can see further that $n\pi^*$ excitation causes a further decrease in the C \equiv C BO, an increase in C-C BO, and about 40% decrease in the C=O BO. These changes are much more pronounced in the $^3\pi\pi^*$ state. We can again invoke the classical valence concept of chemistry to interpret the observed changes in the BOs caused by $n\rightarrow\pi^*$ excitation in terms of mixing among canonical structures (III & IV).



The allene structure (IV) which results from electronic charge transfer will have the effect of decreasing the C-C BO and increasing the C \equiv C BO significantly. In the $^3\pi\pi^*$ state, canonical structure (IV) is expected to have higher weightage. These expectations are in conformity with the structural data given in table 3.

6. Conclusion

The shifted orthogonal gradient method of orbital optimization has been found to be quite efficacious in handling pathologically divergent cases occasionally encountered in the excited state calculations of SCF or MCSCF wavefunctions. Instead of requiring one to go over to computationally more involved techniques, the method allows one to work at the first order level but at the same time circumvent the divergence problem. Further improvement is established by invoking the Padé-MCSCF strategy [23].

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