CONFIGURATION INTERACTION ENERGY DERIVATIVES

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ABSTRACT. Building upon the Hamiltonian expansion of Helgaker and the MCSCF energy derivative developments of Jørgensen, an analysis of the geometrical derivatives of the CI energy is performed. Combining the geometry variation of the Hamiltonian with that of the molecular orbitals (as given by the MCSCF orbital response of Jørgensen) allows the variation of the CI configuration expansion coefficients to also be handled by response theory. After developing the form of the CI energy derivatives, a few observations are made concerning their computational practicality.

1. INTRODUCTION

In the two preceding papers, Helgaker and Jørgensen have set the stage for examining configuration interaction (CI) energy derivatives. In particular, Helgaker demonstrated how an especially clever atomic orbital (ao) parameterization and orthonormalization process[1] allows for efficient treatment of the geometry dependence of the electronic Hamiltonian (H) and directly results in expressions which are in the molecular orbital basis. The resulting expressions for geometrical derivatives of the Hamiltonian contain ao integral derivatives as well as undifferentiated integrals which have been subjected to so called one-index transformations (using derivatives of the ao overlap matrix as transformation matrices (see his Eq. (19))). P. Jørgensen's paper shows how to use the resulting geometry dependence of H to develop expressions for geometrical derivatives of the MCSCF energy. His analysis is carried out in terms of exponential unitary operators which describe the responses of the molecular orbital (mo) and configuration-space expansion coefficients to geometrical displacements.

In the present paper, analogous methods are utilized to express the derivative of the CI energy with respect to geometry. Relative to the MCSCF case, two fundamental changes must be made in deriving the CI expressions:

1) The molecular orbital expansion coefficients can not be assumed to be fully variationally optimized; only the configuration-space can

P. Jørgensen and J. Simons (eds.), Geometrical Derivatives of Energy Surfaces and Molecular Properties, 27–34.

be taken to obey the generalized Brillouin theorem[2] (GBT).

2) The two-step procedures by which the molecular orbital and configuration-space wavefunction amplitudes are chosen must be properly represented in the derivation.

Although a few remarks pertinent to the computational implementation of the working equations are made here, these matters are covered in substantial detail in later papers by R. Shepard and H.J.Aa. Jensen. The focus of the present paper is a clear development of the CI energy derivative expressions building upon the preceding papers by Helgaker and Jørgensen. The strategy to be used can be described as follows:

1) The molecular orbital and configuration-space response techniques introduced earlier by Jørgensen are used in two separate steps to describe the geometrical responses of the mo's (which are assumed to be SCF- or MCSCF-optimized orbitals) and of the configuration-space wavefunction amplitudes (which are assumed to be CI-optimized).

2) The mo responses thus obtained are combined with Helgaker's Hamiltonian derivative expressions to define and analyze the geometry dependence of an effective Hamiltonian $\bar{H}$. Isolating the mo responses in the Hamiltonian $\bar{H}$ makes the CI energy function identical in form to the MCSCF form treated in the preceeding papers. This connection to the MCSCF development allows the CI energy derivatives to be written directly from Jørgensen's MCSCF expressions by simply replacing H by $\bar{H}$.

3) The resulting CI energy derivatives are then written in a manner which elucidates several aspects of their computational implementation and which permits interchange-theorem-like methods to be implemented.

2. DEVELOPMENT

2.1. The Orbital Response.

The orthonormal molecular orbitals are assumed to have been variationally optimized at a molecular geometry denoted $\underline{X}_o$. This optimization may have involved either an MCSCF or SCF wavefunction either of which is denoted $|o\rangle$. The requirement that the orbital and configuration amplitudes of $|o\rangle$ are optimized at $\underline{X}_o$ results in the generalized Brillouin theorem for both the orbital and configuration spaces[3] of $|o\rangle$ (see Eqs. (20), (24) of Jørgensen)

$$F_n \equiv \langle o|[P_n,H]|o\rangle = 0 \tag{1a}$$

$$F_{\bar{P}q} \equiv \langle o|[E_{\bar{P}q},H]|o\rangle = 0 \tag{1b}$$

where P_n and $E_{\bar{P}q}$ are the state transfer operators[4]

$$P_n = |n\rangle\langle o| - |o\rangle\langle n| \tag{2a}$$

and unitary group generators[4]

$$E^{-}_{pq} = \sum_{\sigma} (a^{+}_{p\sigma}a_{q\sigma} - a^{+}_{q\sigma}a_{p\sigma}) \qquad (2b)$$

described in the preceeding paper. It should be noted that the Hamiltonian H and wavefunction $|o\rangle$ are evaluated at $\underline{X}_o$ in Eqs. (1) and that the functions $\{|n\rangle\}$ span the orthogonal complement space of the MCSCF (or SCF, in which case there are no $|n\rangle$ and hence no P_n) function.

To express the response of the mo's and configuration amplitudes to a displacement of the geometry from $\underline{X}_o$ to $\underline{X}_o + \underline{X}$, Jørgensen's Eq. (23) is combined with Helgaker's order-by-order (in $\underline{X}$) expansion of H (see his Eq. (30)). These orbital responses, denoted $\kappa^{(n)}_{pq}$ have been explicitly given by Jørgensen and Simons[5] through second order (n = 2) and by Simons, Jørgensen, and Helgaker[6] through n = 4. For example, the first-order response parameters $\kappa^{(1)}_{pq}$ are obtained by solving

$$\underline{\underline{G}}^{o} \begin{pmatrix} \kappa^{(1)} \\ \underline{S}^{(1)} \end{pmatrix} = \begin{pmatrix} \underline{F}^{(1)} \end{pmatrix} \qquad (3)$$

where $F^{(1)}_{pq}$ and $F^{(1)}_{n}$ are GBT elements as in Eq. (1) but with the Hamiltonian H replaced by Helgaker's first Hamiltonian H (in Eq. (19)). The matrix $\underline{\underline{G}}^{o}$ is Jørgensen's Hessain matrix (see his Eq. (21)) which contains both orbital- and state-function components; the parameters $S^{(1)}_{n}$ describe responses of the MCSCF configuration amplitude. It should be noted that solution of the above orbital response problem involves simultaneous treatment of the orbital and configuration responses in situations where MCSCF orbitals are used.

2. 2. The Effective Hamiltonian.

Now that the molecular orbitals' responses to geometrical displacements have been formulated, it is possible to address the CI wavefunction amplitude response problem. Given a CI wavefunction $|CI\rangle$ constructed from orbitals which have been optimized as described above and whose orbital response parameters $\kappa^{(n)}_{pq}$ are taken as known, attention is to be focused on the CI energy function

$$E_{CI} = \langle CI|H|CI\rangle \qquad (4)$$

In particular, the variation of E_{CI} with geometry must be related to variation in the state-space expansion coefficients and those in the mo's and in H.

Combining Helgaker's expansion of H in powers of $\underline{X}$ with the above molecular orbital responses and Jørgensen's unitary exponential parameterizations of the configuration amplitudes and orbital variations (see Jørgensen's Eq. (16)) allows all of the $\underline{X}$-dependence of E_{CI} to be displayed

$$E_{CI} = \langle CI | \exp(\sum_{n} S_n P_n) \exp(\sum_{pq} \kappa_{pq} E^-_{pq})$$

$$H \exp(-\sum_{rs} \kappa_{rs} E^-_{rs}) \exp(-\sum_{m} S_m P_m) | CI \rangle$$

$$= \langle CI | \exp(\hat{S}) \exp(\hat{\kappa}) H \exp(-\hat{S}) \exp(-\hat{S}) | CI \rangle \qquad (5)$$

where $|CI\rangle$ denotes the CI function at $\underline{X}_o$. In Eq. (5) as in all of the subsequent equations the $\hat{S}$ operator and its S_n parameters refer to the CI state-space. This space is likely to be quite large compared to the state-space used in Sec. 2.1 in treating the MCSCF response problem. The, as yet undetermined, S_n parameters can be isolated from the known geometry dependence of κ_{pq} and of H by introducing the effective Hamiltonian

$$\bar{H} \equiv \exp(\sum_{pq} \kappa_{pq} E^-_{pq}) H \exp(-\sum_{rs} \kappa_{rs} E^-_{rs}) \qquad (6)$$

This allows the E_{CI} function of Eq. (5) to be cast into a form in which only the configuration amplitude variations are explicitly displayed

$$E_{CI} = \langle CI | \exp(S) \bar{H} \exp(-S) | CI \rangle \qquad (7)$$

The essential point to be made concerning the introduction of $\bar{H}$ is that the geometry dependences of H (given earlier by Helgaker) and of $\hat{\kappa}$ (as outlined above and explicitly given through fourth order in refs. (5) and (7)) combine to provide an order-by-order expansion for $\bar{H}$, which appears through fourth order in ref. (6). The lowest three such terms in the $\underline{X}$-dependence of $\bar{H}$ are

$$\bar{H}_o = H, \text{ the Hamiltonian at } \underline{X}_o \qquad (8a)$$

$$\bar{H}_1 = H_1 - [\kappa^{(1)}, H] \qquad (8b)$$

$$\tfrac{1}{2}\bar{H}_2 = \tfrac{1}{2}H_2 - [\kappa^{(1)}, H_1] - \tfrac{1}{2}[\kappa^{(1)}, \kappa^{(1)}, H] - \tfrac{1}{2}[\kappa^{(2)}, H] \qquad (8c)$$

It should be stressed that these expressions for the $\bar{H}_n$ are not simply disguising difficult-to-evaluate factors. Quite to the contrary, they are actually suggestive of computationally practical strategies. For example, each of the commentators $[\kappa^{(1)}, H_m]$ can be reexpressed in terms of a one-and-two-body Hamiltonian whose integrals (or integral derivatives) have been subjected to the one-index transformation introduced earlier by Helgaker (but with the $\kappa^{(1)}_{pq}$ array as the transformation matrix). The net result is that $\bar{H}_n$ is, in effect, a one-and two-body Hamiltonian whose "integrals" have been one-index transformed one or more times. H.J.Aa. Jensen's, R. Shepard's and T. Helgaker's later papers more fully treat the computational aspects of these transformations. For now it should be sufficient to observe that the $\bar{H}_n$ can be viewed as computationally tractable one-and two electron

operators which contain the explicit geometry dependence of both the ao basis orbitals and the MCSCF (or SCF/mo's).

2.3. CI Energy Derivatives.

The developments given in the preceeding paper by Jørgensen for MCSCF wavefunctions can now be applied to Eq. (7) to immediately write the desired expressions for the CI energy derivatives. Jørgensen's MCSCF development, when restricted to contain only the state-function response parameters $\{S_n\}$ as Eq. (7) and with H replaced by the above $\bar{H}$, yields the appropriate CI derivatives, the first two of which are given below:

$$E_1 = \langle CI|\bar{H}_1|CI\rangle = \langle CI|H_1|CI\rangle - \langle CI|[\kappa^{(1)},H]|CI\rangle \tag{9a}$$

$$\begin{aligned} \tfrac{1}{2}E_2 &= \tfrac{1}{2}\langle CI|\bar{H}_2|CI\rangle + \tfrac{1}{2}\sum_n \bar{F}_n^{(1)}S_n^{(1)} \\ &= \tfrac{1}{2}\langle CI|H_2|CI\rangle - \langle CI|[\kappa^{(1)},H_1]|CI\rangle \\ &\quad -\tfrac{1}{2}\langle CI|[\kappa^{(1)},\kappa^{(1)},H]|CI\rangle - \tfrac{1}{2}\langle CI|[\kappa^{(2)},H]|CI\rangle \\ &\quad +\tfrac{1}{2}\sum_n\{\langle CI|H_1|n\rangle - \langle CI|[\kappa^{(1)},H]|n\rangle\}S_n^{(1)} \end{aligned} \tag{9b}$$

where $S_n^{(1)}$ are the CI state-space amplitude responses obtained by solving the first order piece of Jørgensen's Eq. (23):

$$\sum_m G_{nm}\, S_m^{(1)} = \bar{F}_n^{(1)} = \langle CI|H_1|n\rangle - \langle CI|[\kappa^{(1)},H]|n\rangle \tag{10}$$

The matrix element G_{nm} is the state-space Hessian matrix (see Jørgensen's Eq. (21)):

$$G_{nm} = \langle n|H|m\rangle - E_{CI}\delta_{nm} \tag{11}$$

and $\bar{F}_n^{(1)}$ is the state-space GBT element defined with respect to the first-order effective Hamiltonian $\bar{H}_1$.

2.4. Observations on Implementation of the E_n.

As written in Eqs. (9), the evaluation of the first two CI energy derivatives would appear to require the following steps:

1) The computation of CI expectation values of the Hamiltonian derivatives H_1 and H_2 given earlier by Helgaker.

2) The solution of the first- and second-order orbital response equations (e.g. Eq. 3)) for $\kappa_{rs}^{(1)}$ and $\kappa_{rs}^{(2)}$.

3) Carrying out one-index transformations on the integrals defining H or H_1, followed by calculation of CI expectation values for the resultant operators (to compute, for example, $\langle CI|[\kappa^{(n)},H_m]|CI\rangle$ (n,m = 0,1,2) and $\langle CI|[\kappa^{(1)},\kappa^{(1)},H]|CI\rangle$.

4) Solution of the first-order CI-space response equation (Eq.

(10)) for $S_n^{(1)}$ followed by contraction of $S_n^{(1)}$ with the corresponding GBT element $\bar{F}_n^{(1)}$.

Although the computational evaluation of the above CI energy derivatives is more difficult than in the MCSCF case, the four-step outline given above presents an overly pessimistic view of the situation. Calculation of the CI expectation values of H_1 and H_2 are in fact required, but are by no means the bottleneck in the calculations. Moreover, solution of the state-space response equations, which may involve $\sim 10^6$ configurations, can be evaluated using direct-CI like methods by first expressing G_{nm} and $\bar{F}_n^{(1)}$ of Eq. (10) within the primitive configuration space as demonstrated in refs. (6) and (8). The later paper by H.J.Aa. Jensen deals explicitly with the matter and show that even very large configuration spaces can be handled.

Evaluation of the second term in Eq. (9a) and the second, third, and fourth terms in Eq. (9b) requires further analysis. The use of one-index transformations with $\kappa_{pq}^{(1)}$ or $\kappa_{pq}^{(2)}$ as the transformation matrix can be used to evaluate $\langle CI|[\kappa^{(1)},\bar{H}]|CI\rangle$, $\langle CI|[\kappa^{(1)},H_1]|CI\rangle$ and $\langle CI|[\kappa^{(2)},H]|CI\rangle$ as CI expectation values and two successive one-index transformations would allow $\langle CI|[\kappa^{(1)},\kappa^{(1)},H]|CI\rangle$ to be computed likewise. The disadvantages of such an approach are that one must solve the MCSCF response equations described earlier for <u>each</u> of the 3 N cartesian displacement directions in $\underline{X}$ and that one must carry out the one-index transformations for each of these 3 N directions. The primary advantage of the above approach is that, once the one-index transformations are carried out, only CI average values need be evaluated.

Handy and Schaefer[9] have suggested that contributions such as those treated above via one-index transformations can be more efficiently handled by introducing interchange-theorem-like methods. For example, they correctly point out that $\langle CI|[\kappa^{(n)},H_m]|CI\rangle$ can be reexpressed in a form whose implementation does not require the solution of $(3N)^n$ linear response equations. They use the fact that the equations which determine the $\kappa_{pq}^{(n)}$ parameters are of the form

$$\underline{\underline{G}}^{o}\ (\frac{\underline{\kappa}^{(1)}}{\underline{S}^{(n)}}) = (I^{(n)}) \tag{12}$$

where the $I^{(n)}$ vector involves lower order $\underline{\kappa}^{(\ell)}$ and $\underline{S}^{(\ell)}$ ($\ell < n$) parameters (see Eqs. (63) - (66) of ref. (6)) and $\underline{\underline{G}}^{o}$ is the full (i.e. orbital- and configuration-space) Hessian of the MCSCF problem which characterizes the orbital responses. This allows $\kappa_{pq}^{(n)}$ to be written (formally):

$$\kappa_{pq}^{(n)} = \sum_{rs} (\underline{\underline{G}}^{o})^{-1}_{pq,rs}\ T_{rs}^{(n)} + \sum_{k} (\underline{\underline{G}}^{o})^{-1}_{pq,k}\ T_{k}^{(n)} \tag{13}$$

in terms of the orbital-orbital and orbital-configuration components $(\underline{\underline{G}}^{o})^{-1}_{pq,rs}$ and $(\underline{\underline{G}}^{o})^{-1}_{pq,k}$ of the MCSCF Hessian matrix. Using Eq. (13) allows one to write

$$\langle CI|[\kappa^{(n)},H_m]|CI\rangle = \sum_{\substack{pq\\rs}} \langle CI|[E^-_{pq},H_m]|CI\rangle$$

$$(\underline{\underline{G}}^o)^{-1}_{pq,rs}\, T^{(n)}_{rs} + \sum_{pq,k} \langle CI|[E^-_{pq},H_m]|CI\rangle\, (\underline{\underline{G}}^o)^{-1}_{pq,k}\, T^{(n)}_k$$

which can be rewritten as

$$= \sum_{rs} \tilde{\kappa}_{rs}\, T^{(n)}_{rs} + \sum_k \tilde{\kappa}_k\, T^{(n)}_k \qquad (14)$$

Here $(\tilde{\kappa}_{rs}, \tilde{\kappa}_k)$ is the vector obtained by solving the linear response equations

$$\underline{\underline{G}}^o\, \underline{\tilde{\kappa}} = (\underline{{}^{CI}F}_o) \qquad (15)$$

where

$${}^{CI}F_{rs} \equiv \langle CI|[E^-_{rs},H_m]|CI\rangle \qquad (16)$$

is the orbital-space GBT vector for the Hamiltonian H_m but involving the CI wavefunction. Eqs. (15) would have to be solved only $(3N)^m$ times which, if $m < n$, results in potentially less work than solving for the $\kappa^{(n)}$. For example, for $m = o$, Eq. (15) is only a single linear equation whose dimension is equal to that of the combined MCSCF orbital and configuration parameter spaces.

In summary, the computational implementation of Eqs. (9) for E_1 and E_2 is likely feasible when the full power of direct-CI type methods (for Eq. (10)) and one-index transformations are utilized. Even the third CI energy derivative E_3 given in ref. (6) may be within reach because it still only requires the $S^{(1)}_n$ CI-space response parameters (although it also requires $\kappa^{(3)}$ or the use of a Handy-Schaefer-type rearrangement). However, the evaluations of E_4 (see ref. (6)) requires that the second-order CI response equations be solved for $S^{(2)}_n$; This is a considerably more difficult task, so it will be some time before CI fourth energy derivatives are obtained for substantial configuration expansion lengths.

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