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First and second anharmonicities of the MCSCF energy

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In an earlier paper¹ we demonstrated how to obtain analytical expressions for potential energy forces (gradients) and curvatures (Hessians) relevant to a wide range of *ab initio* electronic wave functions. In this Note we extend our earlier development to obtain expressions for third and fourth order energy derivatives with respect to nuclear displacement for a multiconfigurational self-consistent field (MCSCF) wave function. These higher derivatives relate to the anharmonicities of potential energy surfaces and are therefore of direct relevance to the interpretation of vibrational spectra. We restrict our attention to the MCSCF case because it is for this situation that one obtains the most compact and tractable working equations.

The development of analytical expressions for energy derivatives involves three steps. First, one must have available expressions for the geometry dependence of the electronic Hamiltonian²

$$H(\mu) = H_0 + \mu H_1 + \frac{\mu^2}{2} H_2 + \frac{\mu^3}{3!} H_3 + \dots \quad (1)$$

Here μ represents the, in general $3N-6$ component, vector describing the displacements of the molecule's nuclei. Explicit formulas for the derivatives H_1 and H_2 of H are given in Eqs. (13)–(16) of Ref. 1; H_3 can be obtained straightforwardly in a similar manner by differentiating H once more with respect to the components of μ . H_1 , H_2 , and H_3 are nothing but the electronic Hamiltonian in which all one and two electron integrals are differentiated once, twice, or three times. The second necessary ingredient is the implicit μ dependence of the electronic wave function $|0\rangle$. By variationally optimizing the wave function with a Hamiltonian which contains an infinitesimal nuclear displacement [Eq. (1)], one obtains a set of equations to be solved for the variational parameters appearing in $|0\rangle$. For example, the response of the MCSCF wave function being considered here can be described¹ in terms of orbital (κ_{rs}) and configuration (S_{no}) variational parameters appearing in the unitary operators $\exp(i\hat{k})$ and $\exp(i\hat{S})$ which act on $|0\rangle$ to describe the wave function's response. By making

$$E = \langle 0 | \exp(-i\hat{S}) \exp(-i\hat{k}) H(\mu) \exp(i\hat{k}) \exp(i\hat{S}) | 0 \rangle \quad (2)$$

stationary with respect to variations in the κ_{rs} and S_{no} parameters, one obtains a set of equations for these parameters which depend upon μ and which can be solved in an order-by-order fashion.¹ One thereby obtains the μ dependence of κ_{rs} and S_{no}

$$(\kappa_{rs}, S_{no}) \equiv (\lambda_i) = \sum_{k=0}^{\infty} \lambda_i^{(k)} \mu^k \quad (3)$$

Expressions for the parameters $\lambda_i^{(1)}$ and $\lambda_i^{(2)}$ are given in Eqs. (46) and (47) of Ref. 1; an extension of the result for $\lambda_i^{(3)}$, as contained in Eq. (32) of Ref. 3, is shown below to be unnecessary for the present treatment. All of these low-order $\lambda_i^{(k)}$ parameters are expressed^{1,3} in terms of generalized Brillouin ($F_i^{(k)}$) and Hessian ($G_{ij}^{(k)}$) matrices and the supercurvature matrix $K_{ijk}^{(k)}$ in which either H_0 , H_1 , or H_2 (corresponding to $k=0, 1, 2$) is used. These matrices are fully defined in Ref. 1.

Given the explicit μ dependence of $|\bar{0}\rangle \equiv \exp(i\hat{R}) \times \exp(i\hat{S}) | 0 \rangle$, the third and final step involves computing

$$E(\mu) = \langle \bar{0} | H(\mu) | \bar{0} \rangle = \sum_{k=0}^{\infty} \mu^k E^{(k)} \quad (4)$$

as a power series in μ . The gradient, Hessian, and higher derivatives can then be identified from this power series:

$$E(\mu) = E(0) + \mu \frac{dE}{d\mu} + \frac{1}{2} \mu^2 \frac{d^2E}{d\mu^2} + \frac{1}{6} \frac{d^3E}{d\mu^3} \mu^3 + \dots \quad (5)$$

Expressions for $dE/d\mu$ and $d^2E/d\mu^2$ are given for this MCSCF case and for other cases in Ref. 1.

In the notation of Ref. 1, the terms in Eq. (4) which are third order in μ are as follows (Einstein summation notation is used for repeated indices):

$$E^{(3)} = \frac{1}{6} \langle 0 | H_3 | 0 \rangle + \frac{1}{2} F_i^{(1)} \lambda_i^{(2)} + \frac{1}{2} F_i^{(2)} \lambda_i^{(1)} + \frac{1}{4} \lambda_i^{(2)} G_{ij}^0 \lambda_j^{(1)} + \frac{1}{4} \lambda_i^{(1)} G_{ij}^0 \lambda_j^{(2)} + \frac{1}{2} \lambda_i^{(1)} G_{ij}^{(1)} \lambda_j^{(1)} + \frac{1}{6} K_{ijk}^0 \lambda_i^{(1)} \lambda_j^{(1)} \lambda_k^{(1)} \quad (6)$$

Substituting Eqs. (46) and (47) of Ref. 1 for $\lambda^{(1)}$ and $\lambda^{(2)}$

allows $E^{(3)}$ to be rewritten as

$$\frac{1}{6} \frac{d^3 E}{d\mu^3} = E^{(3)} = \frac{1}{6} \langle 0 | H_3 | 0 \rangle + \frac{1}{2} F_i^{(2)} \lambda_i^{(1)} + \frac{1}{2} G_{ij}^{(1)} \lambda_i^{(1)} \lambda_j^{(1)} + \frac{1}{6} K_{ijk}^0 \lambda_i^{(1)} \lambda_j^{(1)} \lambda_k^{(1)}. \quad (7)$$

The second anharmonicity can be obtained in like fashion:

$$\frac{1}{4!} \frac{d^4 E}{d\mu^4} = E^{(4)} = \frac{1}{4!} \langle 0 | H_4 | 0 \rangle + \frac{1}{3!} F_i^{(3)} \lambda_i^{(1)} + \frac{1}{2!2!} \lambda_i^{(1)} G_{ij}^{(2)} \lambda_j^{(1)} + \frac{1}{3!} K_{ijk}^{(1)} \lambda_i^{(1)} \lambda_j^{(1)} \lambda_k^{(1)} + \frac{1}{4!} L_{ijkl}^0 \lambda_i^{(1)} \lambda_j^{(1)} \lambda_k^{(1)} \lambda_l^{(1)} - \frac{1}{2!2!2!} \lambda_i^{(2)} G_{ij}^0 \lambda_j^{(2)}, \quad (8)$$

where from Ref. 1

$$\lambda_i^{(1)} = - (G^0)^{-1}_{ij} F_j^{(1)} \quad (9)$$

and

$$\lambda_i^{(2)} = - (G^0)^{-1}_{ij} F_j^{(2)} - 2(G^0)^{-1}_{ij} G_{jk}^{(1)} \lambda_k^{(1)} - (G^0)^{-1}_{ij} K_{jkl}^0 \lambda_k^{(1)} \lambda_l^{(1)}. \quad (10)$$

Equations (7) and (8) thus represent our working equations for the first and second anharmonicities. Their evaluation requires generalized Brillouin $F^{(i)}$, $i=1, 2, 3$ Hessian $G^{(i)}$, $i=0, 1, 2$, and generalized Hessian L^0 , K^0 , $K^{(1)}$ matrices^{1,3} as well as the derivatives of one- and two-electron integrals which appear in the H_i , $i=0, 1, 2, 3, 4$. In Refs. 1 and 3 it is shown how to efficiently evaluate matrix products such as those appearing in $E^{(3)}$ and $E^{(4)}$.

Admittedly, the fully *ab initio* evaluation of $E^{(3)}$ and $E^{(4)}$ will require large amounts of computer time and

storage primarily because of the third and fourth derivatives of the integrals appearing in H_3 and H_4 . Although analytical expressions for the third and fourth energy derivative of the other wave functions treated in Ref. 1 may also be obtained, far less simplification occurs in these cases. Only for the MCSCF wave function, whose orbital and configuration amplitudes have been variationally optimized in a fully coupled manner, do the generalized Brillouin theorem ($F_i^{(0)}=0$) and Eqs. (9) and (10) hold. It is thus our opinion that attempts to implement these new third and fourth derivative results should first be directed towards the MCSCF case.

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This paper also contains a good survey of the literature on *ab initio* molecular gradients and Hessians, so we will not reproduce that here.

²We should point out that only by using (symmetrically) orthogonalized atomic orbitals as a basis in terms of which to evaluate H and its μ derivatives are we able to isolate all of the explicit μ dependence in H . Density matrices which arise in evaluating the MCSCF energy are only μ dependent through the implicit μ dependence contained in the variational parameters of the MCSCF function.

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Supplemental basis functions for the second transition row elements

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Huzinaga¹ has published GTO basis sets for the second transition row elements (Y–Cd). These basis sets are comparable in quality to the basis sets for the first transition row elements developed by Wachters² and Huzinaga.¹ For molecular calculations, these basis sets need to be augmented by (i) $5p$ functions to describe the $5s \rightarrow 5p$ near degeneracy; (ii) by a diffuse $4d$ function to provide for a balanced description of the $5s^2 4d^n$, $5s^1 4d^{n+1}$, and $4d^{n+2}$ states of the atom; and (iii)

by a set of $4f$ functions to correlate the $4d$ functions. The diffuse $4d$ function here is similar in function to the diffuse $3d$ function for the first transition row elements recommended by Hay.³

Table I gives the optimized values for the diffuse $4d$, the $5p$, and $4f$ (STO exponent) functions. The diffuse $4d$ function and the $5p$ functions were optimized at the SCF level based on the $5s^1 4d^{n+1}$ state (except for Pd which