Geometrical Derivatives of Dipole Moments and Polarizabilities

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Abstract

Molecular dipole moments and polarizabilities, as well as their geometrical derivatives, are given analytical expressions for multiconfiguration self-consistent-field and configuration interaction wavefunctions. By considering the response of the electronic wavefunction induced by electric field and geometrical displacement terms in the Hamiltonian, the response of the total electronic energy to these terms is analyzed. The dipole moment and polarizability are then identified through the factors in the energy which are linear and quadratic in the electric field, respectively. Derivatives with respect to molecular deformation are obtained by identifying factors in these moments which are linear, quadratic, etc., in the distortion parameter. The analytical derivative expressions obtained here are compared to those which arise through finite-difference calculations, and it is shown how previous configuration-interaction-based finite difference dipole moment and polarizability derivatives are wrong. The proper means of treating such derivatives are detailed.

1. Introduction

In a recent publication [1] we demonstrated how to obtain analytical expressions for potential energy forces (gradients) and curvatures (Hessians) appropriate to a wide range of *ab initio* quantum mechanical wavefunctions. By using symmetrically orthogonalized atomic basis functions, all of the explicit geometry dependence (μ), including the basis set dependence, can be isolated in the electronic Hamiltonian $H(\mu)$, and unitary exponential operators $\exp(i\hat{\kappa})$ $\exp(i\hat{S})$ can be used to treat the implicit variations in the electronic wavefunction. Expressions for the dependence of the energy on the $3N$ nuclear displacements $\mu = \{X_i, Y_i, Z_i; i = 1, \ldots, N\}$ (N is the number of atoms in the molecule):

$$E(\mu) = E(0) + \frac{\partial E}{\partial \mu}\mu + \frac{1}{2}\frac{\partial^2 E}{\partial \mu^2}\mu^2 + \cdots, \tag{1}$$

could then be derived. In that one paper we were able to cover most of the previously existing* gradient and Hessian expressions as well as to obtain several new results.

In the present paper, we turn our attention to the geometry dependence of those molecular properties which arise as responses of the energy to an externally applied field. In particular,† we consider the effect of an external electric field

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* Reference 1 contains a review of gradient and Hessian results which have been obtained by others.
† The derivation and results obtained here remain valid for any external perturbation which appears in the Hamiltonian in a linear fashion.

of strength ε on the electronic energy E. By utilizing the machinery of Ref. 1, but with a Hamiltonian which includes the electric dipole interaction $H + \boldsymbol{\varepsilon} \cdot \mathbf{r}$, we are able to determine the ε and μ dependence* of $E(\varepsilon, \mu)$. According to

$$E(\varepsilon) = E(0) + \boldsymbol{\varepsilon} \cdot \mathbf{M} - \tfrac{1}{2}\boldsymbol{\varepsilon} \cdot \tilde{\alpha} \cdot \boldsymbol{\varepsilon} + \cdots , \tag{2}$$

the dipole moment ($\mathbf{M}$) and polarizability ($\tilde{\alpha}$) functions can easily be identified once the ε dependence of E is analyzed. Furthermore, by studying the μ dependence of $E(\varepsilon, \mu)$, we are able to extract the μ dependence of $\mathbf{M}$ and $\tilde{\alpha}$:

$$\mathbf{M}(\mu) = \mathbf{M}(0) + \frac{d\mathbf{M}}{d\mu}\mu + \frac{1}{2}\frac{d^2\mathbf{M}}{d\mu^2}\mu^2 + \cdots , \tag{3}$$

$$\tilde{\alpha}(\mu) = \tilde{\alpha}(0) + \frac{d\tilde{\alpha}}{d\mu}\mu + \frac{1}{2}\frac{d^2\tilde{\alpha}}{d\mu^2}\mu^2 + \cdots . \tag{4}$$

The μ derivatives of $\mathbf{M}$ and $\tilde{\alpha}$ are of great importance in molecular spectroscopy [2, 3]. The sizes of $d\mathbf{M}/d\mu$ and $d^2\mathbf{M}/d\mu^2$ govern the strengths of infrared fundamental and (first) overtone transitions, respectively, whereas $d\tilde{\alpha}/d\mu$ determines Raman fundamental intensities.

In Sec. 2 we describe how the electronic Hamiltonian depends on the electric field and on nuclear displacement and how the use of orthogonalized atomic basis orbitals is especially useful. In Sec. 3 we discuss how the electronic wave function $|0\rangle$ and energy E depend on the combined presence of an external electric field and an infinitesimal nuclear displacement. The orbital and configuration amplitudes of $|0\rangle$ are varied to make $E(\varepsilon, \mu)$ stationary in Sec. 4 thereby obtaining ε- and μ-dependent expressions for the optimal orbital and configuration amplitudes. The explicit ε and μ dependencies of $H + \boldsymbol{\varepsilon} \cdot \mathbf{r}$ is combined with the implicit dependence of the MCSCF or configuration interaction (CI) functions $|0\rangle$ in Sec. 5 to generate the full ε and μ dependencies of $E(\varepsilon, \mu)$. This then allows us to obtain new analytical results for the dipole moment and polarizability derivatives. In Sec. 6 the relationships between our analytical expressions and results obtained by finite difference approaches are clarified. Section 7 contains our concluding remarks.

2. Dependence of Electronic Hamiltonian on ε and μ

When an electric field is applied to a molecule, the total electronic energy E contains an explicit dependence on both the electric field (ε) and the nuclear positions (μ) which appear in the Hamiltonian and an implicit dependence arising through the variational parameters characterizing the wave function. Let us first describe how to express the Hamiltonian dependence on the electric field and the nuclear position.

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* ε is the (static) electric field strength, and μ is a $3N$-dimensional vector containing the displacements of each of the coordinates of the molecule's nuclei.

The Hamiltonian of the molecule in the presence of the field may be written as

$$H = H + \varepsilon \cdot r \tag{5}$$

where r is the position operator and H is the nonrelativistic electronic Hamiltonian of the molecule in the absence of the electric field. In a finite-basis calculation the above Hamiltonian can be conveniently expressed in terms of a basis of orthogonalized atomic orbitals $\{\phi_i\}$. When such an orthonormalized set of atomic orbitals is used, all basis set effects are isolated [4] in the one- and two-electron integrals which occur in the Hamiltonian. All annihilation and creation operator dependencies on nuclear position can be neglected in this case without loss of generality, as was explicitly demonstrated in Ref. 1. Within this basis of orthogonalized atomic orbitals, whose precise nature we discuss later, the Hamiltonian H becomes [5]

$$H = \sum_{pq} h_{pq} a_p^+ a_q + \frac{1}{2} \sum_{pqtu} \langle \phi_p \phi_q | \phi_t \phi_u \rangle a_p^+ a_q^+ a_u a_t, \tag{6}$$

where the integrals are

$$\langle \phi_p \phi_q | \phi_t \phi_u \rangle = \int \phi_p^*(1) \phi_q^*(2) \frac{1}{r_{12}} \phi_t(1) \phi_u(2) \, d\tau_1 \, d\tau_2, \tag{7}$$

$$h_{pq} = \langle \phi_p | h_1 | \phi_q \rangle, \tag{8}$$

and h_1 contains all of the usual one-electron operators

$$h_1 = -\frac{1}{2} \nabla_r^2 - \sum_A \frac{Z_A}{|r - R_A|} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|R_A - R_B|}, \tag{9}$$

and Z_A denotes the charge and R_A is the position of nucleus A.

The electric dipole operator may also be expressed in the basis of these atomic orbitals

$$\varepsilon \cdot M = \varepsilon \cdot \sum_{p,q} M_{pq} a_p^+ a_q, \tag{10}$$

where

$$M_{pq} = \langle \phi_p | r | \phi_q \rangle - \sum_A Z_A R_A \delta_{pq}. \tag{11}$$

The Hamiltonian depends on nuclear position through the second and third terms in Eq. (9) and through the fact that the basis functions appearing in the integrals are combinations of primitive atomic orbitals which sit on the nuclear centers. In what follows, we will suppress the vector notations r, M, R_A, ε, etc., for notational ease and simply keep in mind that the electric field is a vector quantity.

To explore how the Hamiltonian changes as the nuclei are moved, let us consider the infinitesimal nuclear displacement

$$R^0 \to R^0 + \mu, \tag{12}$$

where μ is a row vector

$$\mu = (\mu_A^x \mu_A^y \mu_A^z \mu_B^x \mu_B^y \cdots), \tag{13}$$

containing the (small) magnitudes of displacements in the X, Y, and Z components of all nuclei A, B, etc.

The Hamiltonian in Eq. (6) at the displaced coordinates can be written as the Hamiltonian at the undisplaced coordinates H_0 plus terms that are linear, quadratic, cubic, etc., in the nuclear displacement μ. In Ref. 1 the dependence of H on μ is written

$$H(R^0 + \mu) = H_0 + \mu H_1 + \tfrac{1}{2}\mu H_2 \mu + \cdots, \tag{14}$$

and explicit expressions are given for H_1 and H_2. The electric dipole operator's dependence on μ may be written in a similar manner

$$M(R^0 + \mu) = M_0 + \mu M_1 + \tfrac{1}{2}\mu M_2 \mu + \cdots, \tag{15}$$

where

$$M_1 = \sum_{pq} \nabla \left[\langle \phi_p | r - \left(\sum_A Z_A R_A \right) | \phi_q \rangle \right] a_p^+ a_q, \tag{16}$$

$$M_2 = \sum_{pq} \nabla\nabla \left[\langle \phi_p | r - \left(\sum_A Z_A R_A \right) | \phi_q \rangle \right] a_p^+ a_q. \tag{17}$$

The vector ∇ contains derivatives with respect to all coordinates of the nuclei

$$\nabla = \{\nabla_A, \nabla_B, \ldots\}. \tag{18}$$

The full Hamiltonian, including the electric dipole term, at the displaced coordinates may thus be written as a power series expansion in ε and μ

$$\mathrm{H}(\varepsilon, \mu) = \sum_{l=0}^{1} \sum_{k=0}^{\infty} H_{l,k} \varepsilon^l \mu^k \tag{19}$$

where, for example, $H_{0,2} = \tfrac{1}{2} H_2$ and $H_{1,2} = \tfrac{1}{2} M_2$.

3. Dependence of the Wavefunction and Energy on μ and ε

Let us consider a multiconfiguration wavefunction [6]

$$|0\rangle = \sum_i C_{i0} |\Phi_i\rangle, \tag{20}$$

where $|\Phi_i\rangle$ denotes a configuration state function that consists of a simple linear combination of determinants $\{|\phi_f^D\rangle\}$

$$|\phi_f^D\rangle = \prod_{r\in f} a_r^+ |\mathrm{vac}\rangle. \tag{21}$$

The product $\prod_{r\in f} a_r^+$ is an ordered product of creation operators which relates to the set of orthonormal molecular orbitals occupied in $|\phi_f^D\rangle$. For the sake of

simplicity we assume in the following development that all orbitals and states are real. Note that now we have made a specification of the nature of the orthonormal orbitals used to express H.

The multiconfiguration state function $|\tilde{0}\rangle$ at the displaced geometry $R^0 + \mu$ may be expressed as a unitary transformation of the wavefunction $|0\rangle$ at the undisplaced geometry R^0:

$$|\tilde{0}\rangle = \exp{(i\hat{\kappa})} \exp{(i\hat{S})}|0\rangle, \tag{22}$$

where the operators

$$\hat{\kappa} = i \sum_{r>s} \kappa_{rs}(a_r^+ a_s - a_s^+ a_r), \tag{23}$$

$$\hat{S} = i \sum_k S_{k0}(|k\rangle\langle 0| - |0\rangle\langle k|), \tag{24}$$

are discussed in detail in Refs. 1 and 6. $\hat{\kappa}$ contains all nonredundant orbital excitation operators of the orbital optimization problem [6]. In $\hat{S}$, the states $\{|k\rangle\}$ denote the set of orthogonal complement states to $|0\rangle$, each of which is also some combination of the same configuration state functions

$$|k\rangle = \sum_i C_{ik}|\Phi_i\rangle. \tag{25}$$

The coefficient matrix $\mathbf{C}$ of Eqs. (20) and (25) obviously forms a unitary matrix.

At the displaced geometry, the total electronic energy of the molecular system in the presence of an electric field may be written [1]

$$E(\kappa, S, \varepsilon, \mu) = \langle \tilde{0}|H(\varepsilon, \mu)|\tilde{0}\rangle \tag{26}$$

Expanding this total energy in powers of S and κ around the point $(\kappa, S) = (0, 0)$ gives

$$
\begin{aligned}
E(\kappa, S, \mu) = \langle 0|H(\varepsilon, \mu)|0\rangle &- i\langle 0|[\hat{S} + \hat{\kappa}, H(\varepsilon, \mu)]|0\rangle \\
&- \tfrac{1}{2}\langle 0|[S, S, H(\varepsilon, \mu)]|0\rangle - \tfrac{1}{2}\langle 0|[\hat{\kappa}, \hat{\kappa}, H(\varepsilon, \mu)]|0\rangle \\
&- \langle 0|[\hat{S}, [\hat{\kappa}, H(\varepsilon, \mu)]]|0\rangle + \tfrac{1}{6}i\langle 0|[\hat{S}, \hat{S}, \hat{S}, H(\varepsilon, \mu)]|0\rangle \\
&+ \tfrac{1}{6}i\langle 0|[\hat{\kappa}, \hat{\kappa}, \hat{\kappa}, H(\varepsilon, \mu)]|0\rangle + \tfrac{1}{2}i\langle 0|[\hat{S}, \hat{S}, [\hat{\kappa}, H(\varepsilon, \mu)]]|0\rangle \\
&+ \tfrac{1}{2}i\langle 0|[S, [\hat{\kappa}, \hat{\kappa}, H(\varepsilon, \mu)]]|0\rangle + \cdots, \tag{27}
\end{aligned}
$$

where we have introduced the n-tuple symmetric commutators discussed in Ref. 1. The role of these commutators is to make the matrices shown below in Eqs. (32)–(34) symmetric under permutation of their indices. By now introducing a notation in which the variational parameters κ_{rs} and S_{k0} as well as the operators

$$Q_{rs}^+ = \{a_r^+ a_s\}, \quad r > s; \qquad R_{k0}^+ = \{|k\rangle\langle 0|\},$$

multiplying these parameters in $\hat{\kappa}$ and $\hat{S}$ [see Eqs. (23) and (24)] are collected together as column vectors

$$\{\lambda_i\} = \lambda = \begin{pmatrix} \kappa_{rs} \\ S_{k0} \end{pmatrix}, \tag{28}$$

$$\{T_i\} = T = \begin{pmatrix} Q_{rs}^+ - Q_{rs} \\ R_{k0}^+ - R_{k0} \end{pmatrix}, \tag{29}$$

we can write the total energy as (Einstein summation convention is used with respect to the subscripts i, j, k)

$$E(\lambda, \mu) = E + F_i\lambda_i + \tfrac{1}{2}G_{ij}\lambda_i\lambda_j + \tfrac{1}{6}K_{ijk}\lambda_i\lambda_j\lambda_k + \cdots. \tag{30}$$

Here the Hamiltonian average value

$$E = \langle 0|H(\varepsilon, \mu)|0 \rangle, \tag{31}$$

the generalized Brillouin matrix [6]

$$F = \langle 0|[T, H(\varepsilon, \mu)]|0 \rangle, \tag{32}$$

the Hessian matrix

$$G = \langle 0|[T, T, H(\varepsilon, \mu)]|0 \rangle, \tag{33}$$

and the cubic derivative matrix

$$K = \langle 0|[T, T, T, H(\varepsilon, \mu)]|0 \rangle, \tag{34}$$

are all ε and μ dependent. In defining the matrices G and K, the Hamiltonian always operates first on the orbital-space excitation operators and then on the orbital-space excitation operators and then on the state transfer operators [1]. Because the matrices G and K are symmetric under permutation of their indices, their explicit indices need not be written out as in Eq. (30); this shorthand device will be used from now on.

4. Wave Function Optimization

A. MCSCF Case

To obtain a useful expression for how the total energy of an MCSCF wavefunction depends upon electric field strength (ε) and nuclear displacement (μ), we need to first determine how the MCSCF wavefunction response parameters (λ) depend on ε and μ. Equations for determining the λ_i as functions ε and μ can be obtained by differentiating Eq. (30) for $E(\lambda)$ with respect to λ and setting the resultant expression equal to zero

$$F + G\lambda + \tfrac{1}{2}K\lambda\lambda + \cdots = 0. \tag{35}$$

Recall that because the Hamiltonian of Eq. (5) depends on ε and μ, the matrices F, G, and K, each of which contains this Hamiltonian once, depend on ε and μ in a parallel manner. In particular, we can express F, G, and K as power

series in ε and μ

$$F = \sum_{l=0}^{1} \sum_{k=0}^{\infty} F^{l,k} \varepsilon^{l} \mu^{k}, \tag{36}$$

$$G = \sum_{l=0}^{1} \sum_{k=0}^{\infty} G^{l,k} \varepsilon^{l} \mu^{k}, \tag{37}$$

$$K = \sum_{l=0}^{1} \sum_{k=0}^{\infty} K^{l,k} \varepsilon^{l} \mu^{k}, \tag{38}$$

in which each of the terms arises from the ε and μ dependence of H. For example,

$$G^{l,k} = \langle 0 | [T, T, H_{l,k}] | 0 \rangle, \tag{39}$$

and $H_{l,k}$ is given in Eq. (19).

By introducing Eqs. (36)–(38) into Eq. (35) and assuming that the λ response parameters can also be expanded in powers of ε and μ

$$\lambda = \sum_{l=0}^{\infty} \sum_{k=0}^{\infty} \varepsilon^{l} \mu^{k} \lambda^{l,k}, \tag{40}$$

we can obtain an order-by-order solution of Eq. (35). The lowest order equation obtained in this way reads as follows:

$$F^{0,0} + G^{0,0} \lambda^{0,0} + \tfrac{1}{2} K^{0,0} \lambda^{0,0} \lambda^{0,0} + \cdots = 0. \tag{41}$$

This is nothing but the parameter optimization equation appropriate to the situation with $\mu = 0$ and $\varepsilon = 0$. Because the MCSCF wavefunction has been optimized at $\mu = 0$, $\varepsilon = 0$ we have $F^{0,0} = 0$ and, hence $\lambda^{0,0} = 0$. The next few low-order equations are as follows:

$$F^{1,0} + G^{0,0} \lambda^{1,0} = 0, \tag{42}$$

$$F^{0,1} + G^{0,0} \lambda^{0,1} = 0, \tag{43}$$

$$F^{1,1} + G^{1,0} \lambda^{0,1} + G^{0,1} \lambda^{1,0} + G^{0,0} \lambda^{1,1} + K^{0,0} \lambda^{1,0} \lambda^{0,1} = 0. \tag{44}$$

These equations allow the low-order $\lambda^{l,k}$ to be evaluated in terms of the F, G, and K matrices.

The matrices $G^{0,0}$ and $K^{0,0}$ are nothing but the Hessian and third derivative matrices which appear in MCSCF energy optimization [7]. The vectors $F^{0,1}$ and $\lambda^{0,1}$ relate to the response of the system to the μ variation; explicit expressions for these quantities are given in Eqs. (39) and (46) of Ref. 1 and in Ref. 6. The vectors $F^{1,0}$ and $\lambda^{1,0}$ describe the response of the system to the electric field and are treated in Ref. 8. $G^{1,0}$ and $G^{0,1}$ are Hessian matrices but with the Hamiltonian operator replaced by M_0 and H_1, respectively. Finally, $F^{1,1}$ is a generalized Brillouin vector with the Hamiltonian replaced by M_1. Once the integral derivatives appearing in H_1 and M_1 are available, the evaluation of all of these quantities requires no more effort than needed to evaluate the generalized Brillouin and Hessian matrices which arise in conventional MCSCF energy calculations. Even

the seemingly formidable third term of Eq. (44) can be handled straightforwardly as described in Ref. 9.

B. The CI Case

Equations (35) cannot be directly used to express the optimal κ and S parameters appropriate to the CI wavefunction. This is so because a CI calculation is carried out in two steps. In the first step, the orbitals are determined by a SCF or MCSCF orbital optimization and in the second step the configuration amplitudes are optimized through the CI calculation. The response of $|\text{CI}\rangle$ to a nuclear displacement may therefore be parametrized as

$$|\tilde{\text{CI}}\rangle = \exp(i\,^{MC}\hat{\kappa}) \exp(i\,^{CI}\hat{S})|\text{CI}\rangle, \tag{45}$$

where the $^{MC}\kappa$ coefficients are first obtained in an MCSCF or SCF calculation via Eq. (35) and subsequently the ^{CI}S coefficients are obtained as we now describe. The response of the orbitals ($^{MC}\kappa^{l,k}$) is fixed at values entirely determined from the MCSCF orbital optimization prior to the CI calculation. The configuration amplitude responses ^{CI}S are determined by making the energy expression

$$E(S) = \langle \text{CI}| \exp(-i\,^{CI}\hat{S}) \exp(-i\,^{MC}\hat{\kappa}) H(\varepsilon, \mu) \exp(i\,^{MC}\hat{\kappa}) \exp(i\,^{CI}\hat{S})|\text{CI}\rangle \tag{46}$$

stationary with respect to variations in the ^{CI}S parameters only. Introducing the shorthand notation

$$\bar{H}(\varepsilon, \mu) = \exp(-i\,^{MC}\hat{\kappa}) H(\varepsilon, \mu) \exp(i\,^{MC}\hat{\kappa}) \tag{47}$$

in Eq. (46) and expanding the $\exp(i\,^{CI}\hat{S})$ operator in powers of $^{CI}\hat{S}$, allows us to write the total energy in Eq. (46) as

$$E(S, \mu) = \bar{E} + {}^{C}\bar{F}\,^{CI}S + \tfrac{1}{2}{}^{C}\bar{G}\,^{CI}S\,^{CI}S + \tfrac{1}{6}{}^{C}K\,^{CI}S\,^{CI}S\,^{CI}S + \cdots, \tag{48}$$

where the $\bar{E}$, $^{C}\bar{F}$, $^{C}\bar{G}$, and $^{C}\bar{K}$ are defined through Eqs. (31)–(34), but with the modified Hamiltonian $\bar{H}(\varepsilon, \mu)$ of Eq. (47) replacing $H(\varepsilon, \mu)$ of Eq. (19). The upper left subscript C on $^{C}\bar{F}$, $^{C}\bar{G}$, and $^{C}\bar{K}$ is introduced to remind us that these matrices only have configuration-space components. Setting the first derivative with respect to ^{CI}S of Eq. (48) equal to zero then gives:

$$0 = {}^{C}\bar{F} + {}^{C}\bar{G}\,^{CI}S + \tfrac{1}{2}{}^{C}\bar{K}\,^{CI}S\,^{CI}S + \cdots. \tag{49}$$

A power series expansion of the parameters ^{CI}S similar to that used for the λ parameters of Eq. (40) may now be introduced

$$^{CI}S = \sum_{l=0}^{\infty} \sum_{k=0}^{\infty} \varepsilon^l \mu^k \,^{CI}S^{l,k}, \tag{50}$$

and Eq. (49) solved order-by-order in ε and μ. To do so we must also decompose $\bar{H}(\varepsilon, \mu)$ into various orders in ε and μ. Knowing the $^{MC}\kappa^{l,k}$ from the orbital optimization step and using the ε and μ expansions of $H(\varepsilon, \mu)$ given in Eq. (19)

gives

$$\bar{H}(\varepsilon, \mu) = \sum_{l,k=0}^{\infty} \varepsilon^l \mu^k \bar{H}_{l,k}, \tag{51}$$

where, for example,

$$\bar{H}_{00} = H_{00}; \tag{52}$$

$$\bar{H}_{10} = H_{10} - i[^{MC}\hat{\kappa}^{1,0}, H_{00}], \tag{53}$$

$$\bar{H}_{01} = H_{01} - i[^{MC}\hat{\kappa}^{01}, H_{00}], \tag{54}$$

$$\bar{H}_{11} = H_{11} - i[^{MC}\hat{\kappa}^{1,1}, H_{0,0}] - i[^{MC}\hat{\kappa}^{1,0}, H_{0,1}] - i[^{MC}\hat{\kappa}^{0,1}, H_{1,0}], \tag{54a}$$

etc. The quantities $\bar{E}$, $^C\bar{F}$, $^C\bar{G}$, and $^C\bar{K}$ contain $\bar{H}(\varepsilon, \mu)$ in a linear fashion and they can be expressed in power series in ε and μ:

$$\bar{E} = \sum_{l=0}^{1} \sum_{k=0}^{\infty} \bar{E}^{l,k} \varepsilon^l \mu^k, \tag{55}$$

$$^C\bar{F} = \sum_{l=0}^{1} \sum_{k=0}^{\infty} {}^C\bar{F}^{l,k} \varepsilon^l \mu^k, \tag{56}$$

$$^C\bar{G} = \sum_{l=0}^{1} \sum_{k=0}^{\infty} {}^C\bar{G}^{l,k} \varepsilon^l \mu^k, \tag{57}$$

$$^C\bar{K} = \sum_{l=0}^{1} \sum_{k=0}^{\infty} {}^C\bar{K}^{l,k} \varepsilon^l \mu^k, \tag{58}$$

in which each term arises from the ε and μ dependence of $\bar{H}$. For example,

$$^C\bar{F}^{l,k} = \langle CI|[^{CI}R^+ - {}^{CI}R, \bar{H}_{l,k}]|CI\rangle. \tag{59}$$

Using Eqs. (55)–(58), Eq. (49) can be written in an order-by-order fashion:

$$^C\bar{F}^{1,0} + {}^C\bar{G}^{0,0}\,{}^{CI}S^{1,0} = 0, \tag{60}$$

$$^C\bar{F}^{0,1} + {}^C\bar{G}^{0,0}\,{}^{CI}S^{0,1} = 0, \tag{61}$$

$$^C\bar{F}^{1,1} + {}^C\bar{G}^{1,0}\,{}^{CI}S^{0,1} + {}^C\bar{G}^{0,1}\,{}^{CI}S^{1,0} + {}^C\bar{G}^{0,0}\,{}^{CI}S^{1,1} + {}^C\bar{K}^{0,0}\,{}^{CI}S^{0,1}\,{}^{CI}S^{0,1} = 0, \tag{62}$$

etc., which are the working response equations for this CI case. Note that the CI response equations in Eqs. (60)–(62) are identical in form to the MCSCF response equations of Eqs. (42)–(44) when F, G, and K are replaced by $^C\bar{F}$, $^C\bar{G}$, and $^C\bar{K}$ and λ by ^{CI}S.

5. Electric-Field and Nuclear-Displacement Dependence of E

Given the above procedure for computing the λ_i parameters, we now return to our expression for the energy $E(\varepsilon, \mu)$ in order to identify the desired molecular properties (dipole moment and polarizability) and their nuclear-displacement derivatives. We accept as the definition of the dipole moment M and polarizability

α the electric-field expansion of $E(\varepsilon, \mu)$ given in Eq. (2). The dipole moment as a function of nuclear displacement $M(\mu)$ is therefore obtained by finding all terms in $E(\varepsilon, \mu)$ which are linear in ε. The polarizability function $\alpha(\mu)$ is calculated as -2 times the sum of all terms in $E(\varepsilon, \mu)$ which are quadratic in ε. The dipole moment and its μ derivatives* at $\mu = 0$ are then obtained by finding terms in $E(\varepsilon, \mu)$ which are first order in ε and zeroth, first, etc., orders in μ. In a similar fashion $-\frac{1}{2}\alpha(0)$ and its μ derivatives are obtained by writing all terms in $E(\varepsilon, \mu)$ which are quadratic in ε and zeroth, first, etc., orders in μ.

A. The Dipole Moment for the MCSCF Wavefunction

Using the expressions for the $\lambda^{l,k}$ in Eq. (40) and $F^{l,k}$, $G^{l,k}$, and $K^{l,k}$ of Eqs. (36)–(38) in the total MCSCF energy expression in Eq. (30), the following results are obtained for the dipole moment and its derivatives:

$$M(0) = E^{1,0} = \langle 0|r|0\rangle, \tag{63}$$

$$\left.\frac{dM}{d\mu}\right|_{\mu=0} = E^{1,1} + F^{1,0}\lambda^{0,1} + F^{0,1}\lambda^{1,0} + G^{0,0}\lambda^{1,0}\lambda^{0,1}$$
$$= E^{1,1} + F^{1,0}\lambda^{0,1}, \tag{64}$$

$$\left.\frac{1}{2}\frac{d^2M}{d\mu^2}\right|_{\mu=0} = E^{1,2} + F^{1,0}\lambda^{0,2} + F^{1,1}\lambda^{0,1} + F^{0,1}\lambda^{1,1}$$
$$+ F^{0,2}\lambda^{1,0} + G^{0,0}\lambda^{1,0}\lambda^{0,2} + G^{0,0}\lambda^{1,1}\lambda^{0,1}$$
$$+ \tfrac{1}{2}G^{1,0}\lambda^{0,1}\lambda^{0,1} + G^{0,1}\lambda^{0,1}\lambda^{1,0}$$
$$+ \tfrac{1}{2}K^{0,0}\lambda^{1,0}\lambda^{0,1}\lambda^{0,1}$$
$$= E^{1,2} + F^{1,1}\lambda^{0,1}$$
$$+ F^{0,2}\lambda^{1,0} + \tfrac{1}{2}G^{1,0}\lambda^{0,1}\lambda^{0,1} + G^{0,1}\lambda^{0,1}\lambda^{1,0}$$
$$+ \tfrac{1}{2}K^{0,0}\lambda^{1,0}\lambda^{0,1}\lambda^{0,1}. \tag{65}$$

In simplifying the above equations, use has been made of Eqs. (42) and (43). The simple form of the dipole moment expression in Eq. (63) is because the Hellmann–Feynman theorem is fulfilled in the MCSCF case. Although more will be said later about the relationships of these expressions to those obtained via finite difference calculations at slightly displaced molecular geometries, the above expressions can be viewed as practical working equations for evaluating M and its μ derivatives analytically.

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* In considering which nuclear displacements to use in an actual implementation of the equations we derive here, care must be taken to remove the translation and rotations from the 3N primitive displacements. Pulay et al. make this point clearly in Ref. 3.

B. The Polarizability for the MCSCF Wave Function

In an analogous manner, the polarizability and its first μ derivative can be expressed as follows:

$$-\tfrac{1}{2}\alpha(0) = F^{1,0}\lambda^{1,0} + \tfrac{1}{2}\lambda^{1,0}\lambda^{1,0}G^{0,0} = \tfrac{1}{2}F^{1,0}\lambda^{1,0}, \qquad (66)$$

$$
\begin{aligned}
-\frac{1}{2}\frac{d\alpha}{d\mu}\bigg|_{\mu=0} &= F^{1,0}\lambda^{1,1} + G^{0,0}\lambda^{1,1}\lambda^{1,0} + F^{0,1}\lambda^{2,0} + G^{0,0}\lambda^{2,0}\lambda^{0,1} \\
&\quad + F^{1,1}\lambda^{1,0} + \tfrac{1}{2}G^{0,1}\lambda^{1,0}\lambda^{1,0} + G^{1,0}\lambda^{1,0}\lambda^{0,1} \\
&\quad + \tfrac{1}{2}K^{0,0}\lambda^{1,0}\lambda^{1,0}\lambda^{0,1} \\
&= F^{1,1}\lambda^{1,0} + \tfrac{1}{2}G^{0,1}\lambda^{1,0}\lambda^{1,0} + G^{1,0}\lambda^{1,0}\lambda^{0,1} \\
&\quad + \tfrac{1}{2}K^{0,0}\lambda^{1,0}\lambda^{1,0}\lambda^{0,1}.
\end{aligned}
\qquad (67)
$$

Again Eqs. (42) and (43) have been used to simplify the above equations.

C. The Dipole Moment for the CI Wave Function

The calculation we now consider assumes that an MCSCF calculation has been carried out in a configuration space consisting of the presumed dominant configurations and, subsequently, a larger CI calculation has been carried out using the resultant MCSCF orbitals and a configuration list that is larger than that used in the MCSCF calculation. Because the orbital and configuration amplitudes of the final $|\text{CI}\rangle$ wavefunction have not been optimized simultaneously, each component of the response vector must be viewed as having been determined from separate calculations. The orbital responses $^{MC}\kappa^{1,0}$, $^{MC}\kappa^{0,1}$, $^{MC}\kappa^{1,1}$, ..., should be determined from Eqs. (42)–(44) using the MCSCF state and its orthogonal complement set of states to describe the configuration space part of these equations. The configuration responses $^{CI}S^{1,0}$, $^{CI}S^{0,1}$, $^{CI}S^{1,1}$ should be determined from Eqs. (60)–(62). Given these $^{MC}\kappa$ and ^{CI}S responses, one can obtain an order-by-order decomposition of the total energy in Eq. (30). The dipole moment corresponding to a CI calculation may be identified by collecting those terms in Eq. (30) which are first order in ε and zeroth order in μ:

$$M(0) = \bar{E}^{1,0} = \langle \text{CI}|r|\text{CI}\rangle + \sum_{r>s} \langle \text{CI}|[a_r^+ a_s - a_s^+ a_r, H_{0,0}]|\text{CI}\rangle {}^{MC}\kappa_{rs}^{1,0}. \qquad (68)$$

To derive Eq. (61) we have used the fact that $^{C}\bar{F}^{0,0}$ vanishes

$$\langle \text{CI}|[R^+ - R, H_{0,0}]|\text{CI}\rangle = 0,$$

because the CI state has had its configuration amplitudes variationally determined. The last term in Eq. (68) denotes the non-Hellmann–Feynman contribution to the dipole moment caused by the fact that the orbitals and configuration amplitudes are optimized in separate calculations. Equation (68) has previously been derived by Tuan [10] and discussed by Nerbrant [11]. Diercksen et al. [12] have shown the importance of the last term of Eq. (68) when correlation effects are

important for describing the dipole moment. Diercksen et al. evaluated the last term in Eq. (68) by initially determining the total dipole moment using energy finite differences and then subtracting the first term of Eq. (68) from the finite difference total dipole moment. The second term may be evaluated more simply by carrying out a simple one index transformation of the integrals [1, 8].

The dipole moment derivative with respect to nuclear displacement may similarly be written as [see Eq. (48)]

$$\left. \frac{dM}{d\mu} \right|_{\mu=0} = \bar{E}^{1,1} + {}^C\bar{F}^{1,0\ CI}S^{0,1} + {}^C\bar{F}^{0,1\ CI}S^{1,0} + {}^C\bar{G}^{0,0\ CI}S^{1,0\ CI}S^{0,1}$$
$$= \bar{E}^{1,1} + {}^C\bar{F}^{1,0\ CI}S^{0,1}. \tag{69}$$

To derive Eq. (69) use has been made of Eq. (60) and ${}^C\bar{F}^{00} = 0$. Note that the CI dipole moment first derivative is identical in structure to the MCSCF expression for the dipole moment first derivative with E, F, G, and K replaced by $\bar{E}$, ${}^C\bar{F}$, ${}^C\bar{G}$, and ${}^C\bar{K}$ and with λ replaced by ${}^{CI}S$. In fact, such replacements will, in general, bring the MCSCF expressions into the corresponding CI results. For this reason we need not give explicit expressions for the CI second dipole moment derivative, the CI polarizabilities, and the CI first polarizability derivative, but refer to appropriate substitutions of the MCSCF equations in Eqs. (65)–(67). The additional work involved in carrying out a CI calculation compared to an MCSCF calculation thus consists of carrying out the Hamiltonian transformations in Eqs. (51)–(54) and determining the required CI response parameters from Eqs. (60)–(62).

6. Relationships between Finite-Difference and Analytical M and α Derivatives

It is of interest to examine whether finite difference [13]* estimates of the μ derivatives of $M(\mu)$ and $\alpha(\mu)$ adequately replicate the results of the analytical M and α derivative calculations described above. Such calculations are done [14, 15] by evaluating $M(\mu)$ or $\alpha(\mu)$ at closely spaced geometries and, for example, utilizing finite-difference fit techniques such as those outlined clearly by Bartlett and Purvis [13].

A. The MCSCF Case

Let us consider how the results of such finite-difference MCSCF calculations would relate to those obtained using our analytical expressions. The orbital and configuration dependence of the wavefunction $|\tilde{0}\rangle$ at a slightly displaced geometry μ for the MCSCF function can be represented as

$$|\tilde{0}\rangle = \exp\left[i(\mu\,\hat{\kappa}^{0,1} + \tfrac{1}{2}\mu^2\,\hat{\kappa}^{0,2} + \cdots)\right]\exp\left[i(\mu\hat{S}^{0,1} + \tfrac{1}{2}\mu^2\hat{S}^{0,2} + \cdots)\right]|0\rangle. \tag{70}$$

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* Bartlett and Purvis [13] do not necessarily advocate use of finite-difference methods; their article is, in our opinion, one of the clearest descriptions of the intracacies of the finite-difference approach.

The finite difference first derivatives of M and α can be thought of as arising from using $|\tilde{0}\rangle$ and $|0\rangle$ in our expressions for M and α given in Eqs. (63) and (66):

$$\frac{dM}{d\mu} \cong \lim_{\mu \to 0} \mu^{-1}[\langle \tilde{0}|r(R^0 + \mu)|\tilde{0}\rangle - \langle 0|r(R^0)|0\rangle], \tag{71}$$

$$-\frac{d\alpha}{d\mu} \cong \lim_{\mu \to 0} \tfrac{1}{2}\mu^{-1}\{\langle \tilde{0}|[\tilde{T}, r(R^0 + \mu)]|\tilde{0}\rangle\langle \tilde{0}|[\tilde{T}, \tilde{T}, H(R^0 + \mu)]|\tilde{0}\rangle^{-1}\langle \tilde{0}|[\tilde{T}, r(R^0 + \mu)]|\tilde{0}\rangle$$
$$- \langle 0|[T, r(R^0)]|0\rangle\langle 0|[T, T, H(R^0)]|0\rangle^{-1}\langle 0|[T, r(R^0)]|0\rangle\}. \tag{72}$$

$\tilde{T}$ refers to the orbital excitation $(\tilde{Q}^+ - \tilde{Q})$ and state transfer $(\tilde{R}^+ - \tilde{R})$ operators at the displaced geometry $R^0 + \mu$, which may be expanded in terms of the orbitals and states at the undisplaced geometry as

$$\tilde{Q}^+ = \exp[i(\mu\hat{\kappa}^{0,1} + \tfrac{1}{2}\mu^2\hat{\kappa}^{0,2} + \cdots)]Q^+ \exp[-i(\mu\hat{\kappa}^{0,1} + \tfrac{1}{2}\mu^2\hat{\kappa}^{0,2} + \cdots)], \tag{73}$$

$$\tilde{R}^+ = \exp[i(\mu\hat{\kappa}^{0,1} + \tfrac{1}{2}\mu^2\hat{\kappa}^{0,2}\cdots)]\exp[i(\mu\hat{S}^{0,1} + \tfrac{1}{2}\mu^2\hat{S}^{0,2} + \cdots)]$$
$$R^+\exp[-i(\mu\hat{\kappa}^{0,1} + \tfrac{1}{2}\mu^2\hat{\kappa}^{0,2} + \cdots)]\exp[-i(\mu\hat{S}^{0,1} + \tfrac{1}{2}\mu^2\hat{S}^{0,2} + \cdots)]. \tag{74}$$

The μ dependence of $r(R^0 + \mu)$ and $H(R^0 + \mu)$ is given in Eqs. (14) and (15). Higher derivatives such as $d^2M/d\mu^2$ can be obtained by identifying coefficients of higher powers of μ.

Let us consider first the finite difference evaluation of $dM/d\mu$. By expanding the exponential operators in Eq. (70) and collecting terms which are first order in μ, we obtain

$$\langle \tilde{0}|r(R^0 + \mu)|\tilde{0}\rangle = \mu\langle 0|r_1|0\rangle + \langle 0|r|0\rangle - i\mu\lambda^{0,1}\langle 0|[T, r]|0\rangle + \cdots$$
$$= \mu\langle 0|r_1|0\rangle + \mu\lambda^{0,1}F^{1,0} + \langle 0|r|0\rangle, \tag{75}$$

so

$$\frac{dM}{d\mu} \cong E^{1,1} + F^{1,0}\lambda^{0,1}, \tag{76}$$

which is in agreement with our analytical result [Eq. (64)].

The analogous treatment of $d\alpha/d\mu$ is a little more tedious. We begin by analyzing the μ dependence of each of the factors appearing in Eq. (72):

$$\langle \tilde{0}|[\tilde{T}, r(R^0 + \mu)]|\tilde{0}\rangle = F^{1,0} + \mu F^{1,1} + \mu G^{1,0}\lambda^{0,1} + \cdots, \tag{77}$$

$$\langle \tilde{0}|[\tilde{T}, \tilde{T}, H(E^0 + \mu)]|\tilde{0}\rangle^{-1}$$
$$= [G^{0,0} + \mu G^{0,1} + \mu K^{0,0}\lambda^{0,1} + \cdots]^{-1}$$
$$= (G^{0,0})^{-1} - (G^{0,0})^{-1}[\mu G^{0,1} + \mu K^{0,0}\lambda^{0,1} + \cdots](G^{0,0})^{-1} + \cdots. \tag{78}$$

Using these two expressions in our finite-difference formula [Eq. (72)] for $d\alpha/d\mu$, we obtain

$$\frac{d\alpha}{d\mu} = \lambda^{1,0}G^{1,0}\lambda^{0,1} + \lambda^{1,0}F^{1,1} + \frac{1}{2}K^{0,0}\lambda^{1,0}\lambda^{0,1}\lambda^{1,0} + \frac{1}{2}\lambda^{1,0}G^{0,1}\lambda^{1,0}, \quad (79)$$

which again is identical to our analytical expression.

The above analysis makes it clear that finite-difference methods can be used to determine the geometry dependence of M and α. Of course, in carrying out such finite-difference calculations, care must be taken to ensure that the geometrical displacement step size μ is indeed small enough to permit the derivatives to be accurately described as a finite difference and yet large enough to ensure that energy differences are computed accurately enough to determine the derivative.

B. The CI Case

To demonstrate both that an analysis similar to that employed above can be used for the CI response and that more care must be taken in the CI case, let us examine the finite difference simulation of $dM/d\mu$. The CI expression [Eq. (68)] for M at a small displacement μ gives

$$\tilde{M}(\mu) = \langle \tilde{CI}|r(R^0+\mu) - i[^{MC}\tilde{\kappa}^{1,0}, H(R^0+\mu)]|\tilde{CI}\rangle, \quad (80)$$

where the tilde denotes the operators and states at the displaced geometry. The nuclear dependence of each individual factor in Eq. (80) will now be analyzed. The CI state at the displaced geometry may be written through first order in μ as

$$|\tilde{CI}\rangle = \exp(i\mu^{MC}\hat{\kappa}^{0,1})\exp(i\mu^{CI}\hat{S}^{0,1})|CI\rangle. \quad (81)$$

The nuclear dependence of the operator

$$^{MC}\tilde{\kappa}^{1,0} = i\sum_{r>s}{}^{MC}\tilde{\kappa}_{rs}^{1,0}(\tilde{Q}_{rs}^+ - \tilde{Q}_{rs}), \quad (82)$$

is determined through the dependence of the orbital excitation operators in Eq. (73) and the $^{MC}\tilde{\kappa}^{1,0}$ parameters of Eq. (42). To determine the μ dependence of $^{MC}\tilde{\kappa}^{1,0}$ requires both components of Eq. (42) to be μ expanded:

$$^{MC}\tilde{\lambda}^{1,0} = -(\tilde{G}^{0,0})^{-1}\tilde{F}^{1,0}. \quad (83)$$

Using the expansions for $\tilde{F}^{1,0}$ and $(\tilde{G}^{0,0})^{-1}$ found in Eqs. (77) and (78) allows us to obtain

$$^{MC}\tilde{\lambda}^{1,0} = -(G^{0,0})^{-1}[F^{1,0} + \mu F^{1,1} + \mu\lambda^{0,1}G^{1,0} + \mu G^{0,1}\lambda^{1,0} + \mu K^{0,0}\lambda^{0,1}\lambda^{1,0}]. \quad (84)$$

By now recognizing that the last four terms in Eq. (84) appear in Eq. (44) for $\lambda^{1,1}$, we can write

$$^{MC}\tilde{\lambda}^{1,0} = -(G^{0,0})^{-1}[F^{1,0} - \mu G^{0,0}\lambda^{1,1}]$$

$$= \lambda^{1,0} + \mu\lambda^{1,1}, \quad (85)$$

and so

$$^{MC}\tilde{\kappa}^{1,0} = {}^{MC}\kappa^{1,0} + \mu \, {}^{MC}\kappa^{1,1}. \tag{86}$$

The μ dependence of $\tilde{M}(\mu)$ in Eq. (80) may now, using Eqs. (14), (15), (73), (79), and (81), be written

$$\tilde{M}(\mu) = \langle \text{CI}| \exp\left(-i\mu \, {}^{CI}\hat{S}^{0,1}\right)\{r_{1,0} + \mu r_{11} - i\mu[{}^{MC}\hat{\kappa}^{0,1}, r_{1,0}] + \cdots$$
$$- i[{}^{MC}\hat{\kappa}^{1,0}, H_{0,0}] - i\mu[{}^{MC}\hat{\kappa}^{1,1}, H_{0,0}]$$
$$- i\mu[{}^{MC}\hat{\kappa}^{1,0}, H_{0,1}] + \cdots\} \exp\left(\mu i \, {}^{CI}\hat{S}^{0,1}\right)|\text{CI}\rangle, \tag{87}$$

and simplified using Eqs. (53), (54a), (55), and (56)

$$\tilde{M}(\mu) = \langle \text{CI}| \exp\left(-i \, {}^{CI}\hat{S}^{0,1}\right)(\bar{H}_{1,0} + \mu \bar{H}_{1,1} + \cdots) \exp\left(i \, {}^{CI}\hat{S}^{0,1}\right)|\text{CI}\rangle$$
$$= {}^{C}\bar{E}^{1,0} + \mu \, {}^{C}\bar{E}^{1,1} + \mu \, {}^{C}\bar{F}^{1,0}S^{0,1}\cdots. \tag{88}$$

Equation (88) clearly shows that the finite-difference CI expression for $dM/d\mu$ is identical to the analytical expression in Eq. (69).

In summary, the CI method can also be used within the finite-difference approach to compute $dM/d\mu$. However, one must use the CI expression for $M(\mu)$ [Eq. (68)]; one *cannot* use the MCSCF formula $\langle \text{CĨ}|\tilde{r}(R^0 + \mu)|\text{CĨ}\rangle$. Only the CI dipole moment expression of Eq. (68) is a correct expression to use when computing CI dipole moments. The expression $\langle \text{CĨ}|r(R^0 + \mu)|\text{CĨ}\rangle$ would only be correct if exactly the same molecular orbitals were used at R^0 and $R^0 + \mu$. However, finite-difference CI dipole moment derivatives have conventionally been evaluated using different SCF orbitals at R^0 and $R^0 + \mu$, and using only the first term of Eq. (68) [14]. As a result, CI finite-difference dipole moment derivatives have been incorrectly evaluated and cannot be trusted, in particular, for cases where the second term of Eq. (68) is important for describing the dipole moment [12]. Care must also be taken to use the correct expression for the polarizability in evaluating CI-based finite-difference polarizability derivatives. Such has not in general been the case, as a result of which CI polarizability derivatives have been incorrectly evaluated [14, 15].

7. Concluding Remarks

We have shown how to use modern energy and wavefunction response theory to generate analytical expressions for molecular dipole moments and polarizabilities as well as for their geometrical gradients. Our developments have been carried out explicitly for multiconfigurational self-consistent-field and configuration interaction wavefunctions.

The relationships between our analytical results for dipole moment and polarizability derivatives and derivatives obtained by finite-difference methods were analyzed in some detail. We found that finite-difference techniques could be used to generate derivatives which agree with our analytical expressions, but only if the quantity whose finite difference is taken is a consistent representation of the dipole moment or polarizability for the particular wavefunction (MCSCF

or CI) under consideration. Previous finite-difference nuclear displacement dipole moment and polarizability derivatives for CI wavefunctions have used incorrect representations [14, 15] of the dipole moment and the polarizability, and thus their nuclear derivatives have been incorrectly evaluated.

Acknowledgments

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