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ABSTRACT

Equations providing the first and second derivatives of a configuration interaction (CI) energy with respect to an external parameter are provided. We assume no restriction on the form of the CI expansion built from molecular orbitals obtained in a multiconfiguration Hartree-Fock (MCHF) calculation. Also the coupled perturbed multi-configuration Hartree-Fock formalism is presented for a general MCHF wavefunction and provides the first order and second order changes of the molecular orbital expansion coefficients with respect to an external parameter.

INTRODUCTION

The capability of efficiently calculating the gradient of the energy with respect to nuclear coordinates for single configuration (HF) or multi-configuration Hartree-Fock (MCHF) wavefunctions[1-5] has had a significant impact on molecular structure determination in recent years. It is now feasible to calculate near Hartree-Fock structures of molecules containing more than a few heavy atoms, and to predict their vibrational spectra. Recently, Morokuma et al.[6] and Schaefer et al.[7] have reported applications of gradient techniques for MCHF wavefunctions of the Generalized Valence Bond type, and the same formalism is commonly used in this laboratory.[8] The use of the gradient for general MCHF wavefunctions has been hampered by the complexity of methods which generate the MCHF wavefunction, but this is bound to change as the MCHF formalism is better understood[9,10] and more entrenched among quantum chemists as a tool necessary for quantitative predictions of chemical structures and reactivity.[11,12]

Going one step further, Schaefer et al.[13] and Pople et al.[14] have reported the implementation of computational methods, which provide the energy gradient for correlated wavefunctions of the Configuration Interaction (CI) type and of Moller Plesset (MP) type. However, a serious restriction of both programs lies in the nature of the molecular orbitals which can be used to construct the correlated wavefunction: the molecular orbitals from a closed-shell (HF) calculation or from a spin-unrestricted HF calculation (UHF). Tachibana et al.[15] have given the epxression of the energy gradient for CI wavefunctions constructed from spin restricted open shell HF calculations.

In addition, Pople et al.[5] showed that the analytic calculation of the energy second derivative for closed-shell HF and UHF wavefunctions is now practical.

The difficulty in carrying out the calculation of the gradient for correlated wavefunctions or the second derivative for HF or UHF wavefunctions lies in the need to know the derivatives of the molecular orbital (MO) coefficients, with respect to the nuclear coordinates. The Coupled Perturbed Hartree-Fock (CPHF) method described by Garrett and Mills,[16] and used by several research groups[17-19] to calculate atomic and molecular properties (such as polarizabilities) provides a formalism by which one can obtain the MO coefficient derivatives. CPHF formulas used in open-shell HF wavefunctions are given by Tachibana,[15] while Sadley et al.[20] extended the CPHF formalism for MCHF wavefunction in which a pair of electrons is excited from a closed shell to another closed shell.

The first objective of this paper is to present a global formalism giving the first and second derivatives of the energy for CI wavefunctions constructed from MCHF orbitals without any restrictions on the form of the CI and MCHF wavefunctions. The second objective is to reformulate the coupled perturbed multi-configuration Hartree-Fock theory applied to the most general MCHF wavefunctions. Working equations for the first and second derivatives of the MO coefficients with respect to an external parameter are provided.

WAVEFUNCTION AND ENERGY

Let us consider a molecule consisting of nuclei and n electrons and describe the wavefunction of the molecule with the aid of the Configuration Interation (CI) method. The CI theory is based on an n-electron wavefunction Ψ expressed as a linear combination of n-electron configuration state functions (CSF). Each CSF is a linear combination of Slater determinants built from an orthonormal set of one-particle spin-orbitals (one-electron functions of spatial and spin coordinates). In the expansion regime (LCAO), the spin-orbitals are written as linear combinations of atomic basis functions of one-electron spatial and spin space.

We represent the set of wavefuntions describing the ground and excited states of the molecule by

$$\underset{\sim}{\Psi} = \{\Psi_1, \Psi_2, \ldots \Psi_M\} \ , \tag{1}$$

the set of CSF's used to expand the wavefunction by

$$\underset{\sim}{\Phi} = \{\phi_1, \phi_2, \ldots \Phi_M\} \ , \tag{2}$$

the set of spin-orbitals used in the construction of the CSF's by

$$\phi = \{\phi_1, \phi_2, \ldots \phi_N\} \ , \tag{3}$$

and the set of atomic basis functions used in the expansion of the spin orbitals by

$$\underset{\sim}{\chi} = \{\chi_1, \chi_2, \ldots \chi_N\} \ , \tag{4}$$

The molecular energy is the expectation value of the non-relativistic electronic Hamiltonian of the molecule. The latter may be written:

$$H = -\tfrac{1}{2}\sum_{\mu=1}^{n} \nabla_\mu^2 + \sum_{\mu=1}^{n} v_\mu + \sum_{\mu>\nu}^{n} r_{\mu\nu}^{-1} + V_{\text{nuclear}} \quad , \tag{5}$$

where $-\tfrac{1}{2}\nabla_\mu^2$ is the kinetic energy operator of electron μ, v_μ is the potential experienced by electron μ in the field of all the nuclei, $r_{\mu\nu}^{-1}$ is the Coulomb electron repulsion operator between electron μ and ν, and V_{nuclear} is the nuclear repulsion operator.

We denote by $\underset{\sim}{\mathbb{H}}$ the CI matrix in the $\underset{\sim}{\Phi}$ basis

$$\underset{\sim}{\mathbb{H}} = \langle \underset{\sim}{\Phi}^+ | H | \underset{\sim}{\Phi} \rangle \quad , \tag{6}$$

by $\mathbb{C}$ the matrix of coefficients of the ground and excited states of the molecule in the $\underset{\sim}{\Phi}$ basis

$$\underset{\sim}{\Psi} = \underset{\sim}{\Phi}\,\mathbb{C} \quad , \tag{7}$$

by $\underset{\sim}{\mathbb{E}}$ the diagonal matrix of the ground and excited states energies. The matrices $\underset{\sim}{\mathbb{C}}$ and $\underset{\sim}{\mathbb{E}}$ are solutions of the secular equation

$$\underset{\sim}{\mathbb{H}}\,\underset{\sim}{\mathbb{C}} = \underset{\sim}{\mathbb{C}}\,\underset{\sim}{\mathbb{E}} \quad , \tag{8}$$

and satisfy the orthonormality condition

$$\underset{\sim}{\mathbb{C}}^+\,\underset{\sim}{\mathbb{C}} = \underset{\sim}{\mathbb{I}}_M \quad , \tag{9}$$

where $\underset{\sim}{\mathbb{I}}_M$ represents the unit matrix of order M. Furthermore, we denote $\underset{\sim}{C}$ the expansion matrix of the spin orbitals $\underset{\sim}{\phi}$ in the spatial-spin atomic basis $\underset{\sim}{\chi}$:

$$\underset{\sim}{\phi} = \underset{\sim}{\chi}\,\underset{\sim}{C} \quad . \tag{10}$$

Let $\underset{\sim}{S}$ be the metric matrix of the one-electron spatial-spin space

$$\underset{\sim}{S} = \langle \underset{\sim}{\chi}^+ | \underset{\sim}{\chi} \rangle \quad . \tag{11}$$

The orthonormality condition for the spin-orbitals $\underset{\sim}{\phi}$ has the form

$$\underset{\sim}{C}^{\dagger}\,\underset{\sim}{S}\,\underset{\sim}{C} = \underset{\sim}{\mathbb{I}}_N \quad , \tag{12}$$

where $\underset{\sim}{\mathbb{I}}_N$ represents the unit matrix of order N.

CI ENERGY DERIVATIVES

Let us suppose that we have solved the secular equation for the molecule in some conditions, and that the molecule is subjected to a small one-electron perturbation characterized by a parameter λ. Without loss of generality we assume that the energy and wavefunction of the system are known for $\lambda = 0$, and we wish to find the solution of the secular equation for a neighboring value of λ.

For the unperturbed case ($\lambda = 0$), we have

$$\underset{\sim}{\mathbb{H}}(0)\,\underset{\sim}{\mathbb{C}}(0) = \underset{\sim}{\mathbb{C}}(0)\,\underset{\sim}{\mathbb{E}}(0) \quad , \tag{13}$$

$$\underset{\sim}{\mathbb{C}}(0)^{\dagger}\,\underset{\sim}{\mathbb{C}}(0) = \underset{\sim}{\mathbb{I}}_M \quad . \tag{14}$$

In the perturbed conditions, the secular equation has the form

$$\underset{\sim}{\mathbb{H}}(\lambda)\,\underset{\sim}{\mathbb{C}}(\lambda) = \underset{\sim}{\mathbb{C}}(\lambda)\,\underset{\sim}{\mathbb{E}}(\lambda) \quad , \tag{15}$$

and the orthonormality condition is

$$\underset{\sim}{\mathbb{C}}(\lambda)\,\underset{\sim}{\mathbb{C}}(\lambda) = \underset{\sim}{\mathbb{I}}_M \quad . \tag{16}$$

Let us expand the various matrices in a power series in λ:

$$\underset{\sim}{\mathbb{H}}(\lambda) = \underset{\sim}{\mathbb{H}}(0) + \lambda \underset{\sim}{d\mathbb{H}}(0) + \tfrac{1}{2}\,\lambda^2 \underset{\sim}{d^2\mathbb{H}}(0) + \ldots \quad , \tag{17}$$

$$\underset{\sim}{\mathbb{C}}(\lambda) = \underset{\sim}{\mathbb{C}}(0) + \lambda \underset{\sim}{d\mathbb{C}}(0) + \tfrac{1}{2}\,\lambda^2 \underset{\sim}{d^2\mathbb{C}}(0) + \ldots \quad , \tag{18}$$

$$\underset{\sim}{\mathbb{E}}(\lambda) = \underset{\sim}{\mathbb{E}}(0) + \lambda \underset{\sim}{d\mathbb{E}}(0) + \tfrac{1}{2}\,\lambda^2 \underset{\sim}{d^2\mathbb{E}}(0) + \ldots \quad . \tag{19}$$

Note that $d\underset{\sim}{\mathbb{E}}(0)$, $d^2\underset{\sim}{\mathbb{E}}(0)$, ... are all diagonal matrices since $\underset{\sim}{\mathbb{E}}(\lambda)$ and $\underset{\sim}{\mathbb{E}}(0)$ are both diagonal. In addition, if $\underset{\sim}{\mathbb{S}}(\lambda)$ represents the metric matrix in the $\underset{\sim}{\Phi}$ basis, then we have $\underset{\sim}{\mathbb{S}}(\lambda) = \underset{\sim}{\mathbb{I}}_M$ for any value of λ. It follows that in an expansion similar to (17), we have

$$d\underset{\sim}{\mathbb{S}}(0) = d^2\underset{\sim}{\mathbb{S}}(0) = \ldots = \underset{\sim}{0} \quad .$$

We substitute Eqs. (17)-(19) into Eq. (15)and collect the terms of the same order in λ. In first-order we get

$$\underset{\sim}{\mathbb{H}}(0)\, d\underset{\sim}{\mathbb{C}}(0) + d\underset{\sim}{\mathbb{H}}(0)\, \underset{\sim}{\mathbb{C}}(0) = \underset{\sim}{\mathbb{C}}(0)\, d\underset{\sim}{\mathbb{E}}(0) + d\underset{\sim}{\mathbb{C}}(0)\, \underset{\sim}{\mathbb{E}}(0) \quad , \tag{20}$$

while the second-order terms give

$$d^2\underset{\sim}{\mathbb{H}}(0)\, \underset{\sim}{\mathbb{C}}(0) + 2d\underset{\sim}{\mathbb{H}}(0)\, d\underset{\sim}{\mathbb{C}}(0) + \underset{\sim}{\mathbb{H}}(0)\, d^2\underset{\sim}{\mathbb{C}}(0)$$

$$= d^2\underset{\sim}{\mathbb{C}}(0)\, \underset{\sim}{\mathbb{E}}(0) + 2d\underset{\sim}{\mathbb{C}}(0) d\underset{\sim}{\mathbb{E}}(0) + \underset{\sim}{\mathbb{C}}(0)\, d^2\underset{\sim}{\mathbb{E}}(0) \quad . \tag{21}$$

Similarly, substitution into the orthonormality condition gives in first order

$$d\underset{\sim}{\mathbb{C}}(0)^{\dagger}\underset{\sim}{\mathbb{C}}(0) + \underset{\sim}{\mathbb{C}}(0)\, d\underset{\sim}{\mathbb{C}}(0) = \underset{\sim}{0} \quad . \tag{22}$$

Focusing one's attention on the P^{th} column of Eq. (20), we get after rearrangement

$$\left[\underset{\sim}{\mathbb{H}}(0) - \mathbb{E}_p(0)\, \underset{\sim}{\mathbb{I}}\right] d\underset{\sim}{\mathbb{C}}_p(0) = -\left[d\underset{\sim}{\mathbb{H}}(0) - d\mathbb{E}_p(0)\, \underset{\sim}{\mathbb{I}}\right] \mathbb{C}_p(0) \quad , \tag{23}$$

and after multiplication by $\underset{\sim}{\mathbb{C}}_p(0)^{\dagger}$ on the left,

$$d\mathbb{E}_p(0) = \underset{\sim}{\mathbb{C}}_p(0)^{\dagger}\, d\underset{\sim}{\mathbb{H}}(0)\, \underset{\sim}{\mathbb{C}}_p(0) \quad . \tag{24}$$

The second-order equation gives

$$d^2\mathbb{E}_p(0) = \underset{\sim}{\mathbb{C}}_p^{\dagger}(0)\, d^2\underset{\sim}{\mathbb{H}}(0)\, \underset{\sim}{\mathbb{C}}_p(0) + 2\underset{\sim}{\mathbb{C}}_p^{\dagger}(0) \left[d\underset{\sim}{\mathbb{H}}(0) - d\mathbb{E}_p(0)\, \underset{\sim}{\mathbb{1}} \right] d\underset{\sim}{\mathbb{C}}_p(0) \quad . \tag{25}$$

Using (23), the final expression for $d^2\mathbb{E}_p(0)$ is

$$d^2\mathbb{E}_p(0) = \underset{\sim}{\mathbb{C}}_p^{\dagger}(0)\, d^2\underset{\sim}{\mathbb{H}}(0)\, \underset{\sim}{\mathbb{C}}_p(0) - 2d\underset{\sim}{\mathbb{C}}_p^{\dagger}(0) \left[\underset{\sim}{\mathbb{H}}(0) - \mathbb{E}_p\, \underset{\sim}{\mathbb{1}} \right] d\underset{\sim}{\mathbb{C}}_p(0) \quad . \tag{26}$$

Alternatively we can expand $d\underset{\sim}{\mathbb{C}}(0)$ and $d^2\underset{\sim}{\mathbb{C}}(0)$ along the orthonormal basis of states

$$d\underset{\sim}{\mathbb{C}}(0) = \underset{\sim}{\mathbb{C}}(0)\, \underset{\sim}{V} \quad , \tag{27}$$

$$d^2\underset{\sim}{\mathbb{C}}(0) = \mathbb{C}(0)\, \underset{\sim}{W} \quad . \tag{28}$$

Equations (20) and (21) become

$$\underset{\sim}{\mathbb{E}}(0)\underset{\sim}{V} - \underset{\sim}{V}\,\underset{\sim}{\mathbb{E}}(0) = d\,\underset{\sim}{\mathbb{E}}(0) - \underset{\sim}{\mathbb{C}}(0)^{\dagger}\, d\underset{\sim}{\mathbb{H}}(0)\, \underset{\sim}{\mathbb{C}}(0) \quad , \tag{29}$$

$$\begin{aligned} \underset{\sim}{\mathbb{E}}(0)\,\underset{\sim}{W} - \underset{\sim}{W}\,\underset{\sim}{\mathbb{E}}(0) &= d^2\underset{\sim}{\mathbb{E}}(0) - \underset{\sim}{\mathbb{C}}(0)^{\dagger}\, d^2\underset{\sim}{\mathbb{H}}(0)\, \underset{\sim}{\mathbb{C}}(0) + 2\underset{\sim}{V}\, d\,\underset{\sim}{\mathbb{E}}(0) \\ &\quad - 2\underset{\sim}{\mathbb{C}}(0)^{\dagger}\, d\underset{\sim}{\mathbb{H}}(0)\, \underset{\sim}{\mathbb{C}}(0)\, \underset{\sim}{V} \quad , \end{aligned} \tag{30}$$

while the orthonormality condition gives

$$\underset{\sim}{V} + \underset{\sim}{V}^{\dagger} = \underset{\sim}{0} \quad . \tag{31}$$

Equation (29) provides the following expression for V_{PQ} when $P \neq Q$,

$$V_{PQ} = - \frac{\underset{\sim}{\mathbb{C}}_p^{\dagger}(0)\, d\underset{\sim}{\mathbb{H}}(0)\, \underset{\sim}{\mathbb{C}}_Q(0)}{\mathbb{E}_p(0) - \mathbb{E}_Q(0)} \quad , \tag{32}$$

while from (31) we get

$$V_{PP} = 0 \quad . \tag{33}$$

It follows that

$$d^2\mathbb{E}_p(0) = \underset{\sim}{\mathbb{C}}_p(0)^\dagger \, d^2\underset{\sim}{\mathbb{H}}(0) \, \underset{\sim}{\mathbb{C}}_p(0) - 2 \sum_{P \neq Q} \frac{\left| \underset{\sim}{\mathbb{C}}_p(0)^\dagger d\underset{\sim}{\mathbb{H}}(0) \, \underset{\sim}{\mathbb{C}}_Q(0) \right|^2}{\mathbb{E}_Q(0) - \mathbb{E}_p(0)} \, . \tag{34}$$

Equations (24) and (26) are in accord with well known properties of perturbation theory: the first order correction to the energy can be obtained from the knowledge of zeroth-order wavefunction, while the second-order correction to the energy requires the knowledge of the first-order correction to the wavefunction. The calculation of $d\underset{\sim}{\mathbb{C}}_p(0)$ can be carried out using the inhomogeneous system of coupled equations (23). Even for large CI expansions of several thousand configurations, (23) can be solved by some iterative process.

It what follows, we will proceed in determining the first and second derivatives of the CI matrix elements necessary to calculate $d\mathbb{E}_p(0)$ and $d^2\mathbb{E}_p(0)$.

DERIVATIVES OF CI MATRIX ELEMENTS

For a value λ of the perturbation parameter, the general formula for the interaction energy between configurations I and J can be written

$$\mathbb{H}_{IJ}(\lambda) = \sum_{i,j}^{occ} \gamma_{IJ}^{ij} \langle \phi_i(\lambda) | h(\lambda) | \phi_j(\lambda) \rangle + \tfrac{1}{2} \sum_{i,j,k,\ell}^{occ} \Gamma_{IJ}^{ijk\ell} \langle \phi_i(\lambda)\phi_j(\lambda) \left| \frac{1}{r_{12}} \right| \phi_i(\lambda)\phi_\ell(\lambda) \rangle \tag{35}$$

In (35), $h(\lambda)$ represents the usual one-electron bare nucleus operator, and "occ" represents the set of molecular orbitals denoted i, j, k and ℓ occupied in both configurations. The quantities γ_{IJ}^{ij} and $\Gamma_{IJ}^{ijk\ell}$ are the structure constants which depend only on the formal expression of the two configurations. In what follows, we will delete the subscripts I and J

for sake of clarity, and will adhere to the following conventions: we will represent the one-electron integrals $\langle\phi_i(\lambda)|\phi_j(\lambda)\rangle$ by $(i|j)$, $\langle\phi_i(\lambda)|h(\lambda)|\phi_j(\lambda)\rangle$ by $(i|h|j)$, and the two-electron repulsion integrals $\langle\phi_i(\lambda)\phi_j(\lambda)|1/r_{12}|\phi_k(\lambda)\phi_\ell(\lambda)\rangle$ by $(\phi_i\phi_j||\phi_k\phi_\ell)$ or $(ij||k\ell)$ when there is no possibility of confusion. The symbols $i,j,k,\ell\ldots$ will represent molecular orbitals occupied in at least one configuration; $a,b,c,d\ldots$ will represent molecular orbitals occupied in none of the configurations; $p,q,r,s\ldots$ will be used as summation indices; $\mu,\nu,\rho,\sigma\ldots$ will represent basis functions, and the short-hand notation $(\mu|\nu)$, $(\mu|h|\nu)$ and $(\mu\nu||\rho\sigma)$ will be used for the one- and two-electron integrals over basis functions $\underset{\sim}{\chi}$.

It is convenient to define the new quantities

$$F^{ij} = h\,\gamma^{ij} + \sum_{k,\ell}^{occ} V_{k\ell}\,\Gamma^{ijk\ell} \quad , \tag{36}$$

usually called the "generalized Fock operator" for the orbitals i and j, where $V_{k\ell}$ is the electron potential operator given by

$$V_{k\ell}(1) = \int \frac{1}{r_{12}}\,\phi_k^{(2)}\,\phi_\ell^{(2)}\,\underset{\sim}{dr}_2 \quad . \tag{37}$$

Using Eq. (36), the energy expression (35) can be written

$$\mathbb{H}(\lambda) = \tfrac{1}{2}\sum_{i,j}^{occ}\{\langle\phi_i(\lambda)|F^{ij}(\lambda)|\phi_j(\lambda)\rangle + \gamma^{ij}\,\langle\phi_i(\lambda)|h(\lambda)|\phi_j(\lambda)\rangle\} \quad . \tag{38}$$

In the spatial-spin function basis $\underset{\sim}{\chi}(\lambda)$, we denote by $\underset{\sim}{S}(\lambda)$, $\underset{\sim}{H}^{ij}(\lambda)$, $\underset{\sim}{G}^{ij}(\lambda)$, and $\underset{\sim}{F}^{ij}(\lambda)$ the matrices of the overlap, $\gamma^{ij}h(\lambda)$, $\sum_{k,\ell}^{occ}\Gamma^{ijk\ell}V_{k\ell}(\lambda)$, and $F^{ij}(\lambda)$ operators respectively:

$$\underset{\sim}{S}(\lambda) = \langle\underset{\sim}{\chi}^{\dagger}(\lambda)|\underset{\sim}{\chi}(\lambda)\rangle \quad , \tag{39}$$

$$\underset{\sim}{H}^{ij}(\lambda) = \langle \underset{\sim}{\chi}^{\dagger}(\lambda) \left| \gamma^{ij} h(\lambda) \right| \underset{\sim}{\chi}(\lambda) \rangle \quad , \tag{40}$$

$$\underset{\sim}{G}^{ij}(\lambda) = \langle \underset{\sim}{\chi}^{\dagger}(\lambda) \left| \sum_{k\ell}^{occ} \Gamma^{ijk\ell} V_{k\ell}(\lambda) \right| \underset{\sim}{\chi}(\lambda) \rangle \quad ,$$

$$\underset{\sim}{F}^{ij}(\lambda) = \langle \underset{\sim}{\chi}^{\dagger}(\lambda) \left| F^{ij}(\lambda) \right| \underset{\sim}{\chi}(\lambda) \rangle \quad . \tag{42}$$

Let $\underset{\sim}{C}(\lambda)$ be the matrix of coefficients of the orbitals $\underset{\sim}{\phi}(\lambda)$ in the spatial-spin basis $\underset{\sim}{\chi}(\lambda)$. The orthonormality condition between spin-orbitals is valid for all values of λ:

$$\underset{\sim}{C}^{\dagger}(\lambda)\ \underset{\sim}{s}(\lambda)\ \underset{\sim}{C}(\lambda) = \underset{\sim}{\mathbb{1}} \quad . \tag{43}$$

To obtain the derivative of $\mathbb{H}(\lambda)$ given by Eq.(38), it is convenient to define a modified spatial-spin basis, denoted $\bar{\underset{\sim}{\chi}}(\lambda)$ corresponding to the unperturbed spin-orbitals:

$$\bar{\underset{\sim}{\chi}}(\lambda) = \underset{\sim}{\chi}(\lambda)\ \underset{\sim}{C}(0) \quad . \tag{44}$$

In this basis we write the spin-orbitals $\underset{\sim}{\phi}(\lambda)$ as

$$\underset{\sim}{\phi}(\lambda) = \bar{\underset{\sim}{\chi}}(\lambda)\ \underset{\sim}{U}(\lambda) \quad , \tag{45}$$

which implies that

$$\underset{\sim}{C}(\lambda) = \underset{\sim}{C}(0)\ \underset{\sim}{U}(\lambda) \quad . \tag{46}$$

Equation (45) is used as a means to separate the variations of the orbitals and the variations of the basis set of functions. Clearly $\underset{\sim}{U}(0) = \underset{\sim}{\mathbb{1}}$. In the modified spatial-spin basis $\bar{\underset{\sim}{\chi}}(\lambda)$, we denote by $\underset{\sim}{S}(\lambda)$, $\underset{\sim}{H}^{ij}(\lambda)$, $\underset{\sim}{G}^{ij}(\lambda)$ and $\underset{\sim}{F}^{ij}(\lambda)$ the matrices corresponding to $\underset{\sim}{S}$, $\underset{\sim}{H}^{ij}$, $\underset{\sim}{G}^{ij}$, and $\underset{\sim}{F}^{ij}$ respectively:

$$\underset{\sim}{S}(\lambda) = \langle \bar{\underset{\sim}{\chi}}(\lambda) | \bar{\underset{\sim}{\chi}}(\lambda) \rangle = \underset{\sim}{C}^{\dagger}(0)\ \underset{\sim}{S}(\lambda)\ \underset{\sim}{C}(0) \quad , \tag{47}$$

$$\underset{\sim}{H}^{ij}(\lambda) = \langle \bar{\underset{\sim}{\chi}}(\lambda) | \gamma^{ij} h(\lambda) | \bar{\underset{\sim}{\chi}}(\lambda) \rangle = \underset{\sim}{C}^{\dagger}(0)\ \underset{\sim}{H}^{ij}(\lambda)\ \underset{\sim}{C}(0) \quad , \tag{48}$$

$$\underset{\sim}{G}^{ij}(\lambda) = \langle \bar{\underset{\sim}{\chi}}(\lambda) | \sum_{k,\ell}^{occ} \Gamma^{ijk\ell} V_{k\ell}(\lambda) | \bar{\underset{\sim}{\chi}}(\lambda) \rangle = \underset{\sim}{C}^{\dagger}(0)\ \underset{\sim}{G}^{ij}(\lambda)\ \underset{\sim}{C}(0) \quad , \tag{49}$$

$$\underset{\sim}{F}^{ij}(\lambda) = \langle \bar{\underset{\sim}{\chi}}(\lambda) | F^{ij}(\lambda) | \bar{\underset{\sim}{\chi}}(\lambda) \rangle = \underset{\sim}{C}^{\dagger}(0)\ F^{ij}(\lambda)\ \underset{\sim}{C}(0) \quad . \tag{50}$$

From Eq. (48) we get

$$\{ \underset{\sim}{S}(\lambda) \}_{pq} = \sum_{\mu,\nu}^{N} C_{\mu p}(0)\ C_{\nu q}(0)\ \langle \chi_{\mu}(\lambda) | \chi_{\nu}(\lambda) \rangle \quad ; \tag{51}$$

Note that

$$\{ S(0) \}_{pq} = \langle \phi_p(0) | \phi_q(0) \rangle = \delta_{pq} \quad . \tag{52}$$

From Eq. (49) we get

$$\{ \underset{\sim}{H}^{ij}(\lambda) \}_{pq} = \gamma^{ij} \sum_{\mu,\nu}^{N} C_{\mu p}(0)\ C_{\nu q}(0)\ \langle \chi_{\mu}(\lambda) | h(\lambda) | \chi_{\nu}(\lambda) \rangle \quad ; \tag{53}$$

Note that

$$\{ \underset{\sim}{H}^{ij}(0) \}_{pq} = \gamma^{ij} \langle \phi_p(0) | h | \phi_q(0) \rangle \quad . \tag{54}$$

Similarly from Eq. (50) get get

$$\{ \underset{\sim}{G}^{ij}(\lambda) \}_{pq} = \sum_{k\ell}^{occ} \Gamma^{ijk\ell} \langle \bar{\chi}_p(\lambda) \bar{\chi}_q(\lambda) \| \phi_k(\lambda) \phi_{\ell}(\lambda) \rangle \quad ,$$

$$= \sum_{k,\ell}^{occ} \Gamma^{ijk\ell} \sum_{r,s}^{N} \langle \bar{\chi}_p(\lambda) \bar{\chi}_q(\lambda) \| \bar{\chi}_r(\lambda) \bar{\chi}_s(\lambda) \rangle\ U_{rk}(\lambda)\ U_{s\ell}(\lambda) \quad , \tag{55}$$

where

$$\langle \bar{\chi}_p(\lambda)\bar{\chi}_q(\lambda) \| \bar{\chi}_r(\lambda)\bar{\chi}_s(\lambda) \rangle = \sum_{\mu\nu\rho\sigma}^{N} C_{\mu p}(0)\, C_{\nu q}(0)\, C_{\rho r}(0)\, C_{\sigma s}(0) \times \langle \chi_\mu(\lambda)\chi_\nu(\lambda) \| \chi_\rho(\lambda)\chi_\sigma(\lambda) \rangle \quad . \tag{56}$$

Note that

$$\{ \underset{\sim}{G}^{ij}(0) \}_{pq} = \sum_{k,\ell}^{occ} \Gamma^{ijk\ell} \langle \phi_p(0)\phi_q(0) \| \phi_k(0)\phi_\ell(0) \rangle \quad . \tag{57}$$

In order to obtain the first-order and second-order contributions to the energy, we expand the various matrices in power series of λ, as well as the energy scalar:

$$\underset{\sim}{S}(\lambda) = \underset{\sim}{\mathbb{1}} + \lambda\, d\underset{\sim}{S}(0) + \tfrac{1}{2}\lambda^2 d^2\underset{\sim}{S}(0) + \ldots \quad , \tag{58}$$

$$\underset{\sim}{H}^{ij}(\lambda) = \underset{\sim}{H}^{ij}(0) + \lambda\, d\underset{\sim}{H}^{ij}(0) + \tfrac{1}{2}\lambda^2 d^2\underset{\sim}{H}^{ij}(0) + \ldots \quad , \tag{59}$$

$$\underset{\sim}{G}^{ij}(\lambda) = \underset{\sim}{G}^{ij}(0) + \lambda\, d\underset{\sim}{G}^{ij}(0) + \tfrac{1}{2}\lambda^2 d^2\underset{\sim}{G}^{ij}(0) + \ldots \quad , \tag{60}$$

$$\underset{\sim}{F}^{ij}(\lambda) = \underset{\sim}{F}^{ij}(0) + \lambda\, d\underset{\sim}{F}^{ij}(0) + \tfrac{1}{2}\lambda^2 d^2\underset{\sim}{F}^{ij}(0) + \ldots \quad , \tag{61}$$

$$\underset{\sim}{U}(\lambda) = \underset{\sim}{\mathbb{1}} + \lambda\, d\underset{\sim}{U}(0) + \tfrac{1}{2}\lambda^2 d^2\underset{\sim}{U}(0) + \ldots \quad , \tag{62}$$

$$\mathbb{H}(\lambda) = \mathbb{H}(0) + \lambda\, d\mathbb{H}(0) + \tfrac{1}{2}\lambda^2 d^2\mathbb{H}(0) + \ldots \quad . \tag{63}$$

In the modified spatial-spin basis, the energy expression and orthonormality condition take the form:

$$\mathbb{H}(\lambda) = \tfrac{1}{2} \sum_{i,j}^{occ} \underset{\sim}{U}_i^{\dagger}(\lambda) \{ \underset{\sim}{F}^{ij}(\lambda) + \underset{\sim}{H}^{ij}(\lambda) \} \underset{\sim}{U}_j(\lambda) \quad , \tag{64}$$

$$\underset{\sim}{U}^{\dagger}(\lambda) \; S(\lambda) \; \underset{\sim}{U}(\lambda) = \underset{\sim}{\mathbb{1}} \quad . \tag{65}$$

In (64), $\underset{\sim}{U}_i(\lambda)$ denotes the i^{th} column of $\underset{\sim}{U}(\lambda)$.

Let us substitute Eq. (58) through (63) into Eq. (64) and (65), and let us collect the terms of same order in λ. In zeroth order we obtain Eq. (64) for the value $\lambda = 0$ of the perturbation parameter, which is the energy of the unperturbed system.

The first- and second-order equations are:

$$d\mathbb{H}(0) = \tfrac{1}{2} \sum_{i,j}^{occ} \Big[d\underset{\sim}{U}_i^{\dagger}(0) \{ \underset{\sim}{F}_j^{ij}(0) + \underset{\sim}{H}_j^{ij}(0) \} + \{ \underset{\sim}{F}_i^{ij\dagger}(0) + \underset{\sim}{H}_i^{ij\dagger}(0) \} \; d\underset{\sim}{U}_j(0) + \{ d\underset{\sim}{F}_{ij}^{ij}(0) + d\underset{\sim}{H}_{ij}^{ij}(0) \} \Big], \tag{66}$$

$$\begin{aligned} d^2\mathbb{H}(0) = \tfrac{1}{2} \sum_{i,j}^{occ} \Big[& d^2\underset{\sim}{U}_i(0) \{ \underset{\sim}{F}_j^{ij}(0) + \underset{\sim}{H}_j^{ij}(0) \} \\ & + \{ \underset{\sim}{F}_i^{ij}(0) + \underset{\sim}{H}_i^{ij\dagger}(0) \} \; d^2\underset{\sim}{U}_j(0) + \{ d^2\underset{\sim}{F}_{ij}^{ij}(0) + d^2\underset{\sim}{H}_{ij}^{ij}(0) \} \\ & + 2d\underset{\sim}{U}_i^{\dagger}(0) \{ d\underset{\sim}{F}_j^{ij}(0) + d\underset{\sim}{H}_j^{ij}(0) \} + 2 \{ d\underset{\sim}{F}_i^{ij\dagger}(0) + d\underset{\sim}{H}_i^{ij\dagger}(0) \} \; d\underset{\sim}{U}_j(0) \\ & + 2d\underset{\sim}{U}_i^{\dagger}(0) \{ \underset{\sim}{F}^{ij}(0) + \underset{\sim}{H}^{ij}(0) \} \; d\underset{\sim}{U}_j(0) \Big] \end{aligned} \tag{67}$$

In a similar fashion, from the orthonormality condition Eq. (65), we get

$$d\underset{\sim}{U}^{\dagger}(0) + d\underset{\sim}{S}(0) + d\underset{\sim}{U}(0) = \underset{\sim}{0} \quad , \tag{68}$$

$$d^2\underset{\sim}{U}^{\dagger}(0) + d^2\underset{\sim}{S}(0) + d^2\underset{\sim}{U}(0) + 2 \left[d\underset{\sim}{U}^{\dagger}(0) \; d\underset{\sim}{S}(0) + d\underset{\sim}{U}^{\dagger}(0) \; d\underset{\sim}{U}(0) + d\underset{\sim}{S}(0) d\underset{\sim}{U}(0) \right] = \underset{\sim}{0} \; . \tag{69}$$

From (54) and (56) we get the derivatives of $H^{ij}_{pq}(\lambda)$ and $G^{ij}_{pq}(\lambda)$,

$$\{\underset{\sim}{dH}^{ij}(0)\}_{pq} = \gamma^{ij} \sum_{\mu,\nu}^{N} C_{\mu p}(0)\, C_{\nu q}(0)\, d(\mu|h|\nu)_{\lambda=0} \quad , \tag{70}$$

$$\{\underset{\sim}{d^2H}^{ij}(0)\}_{pq} = \gamma^{ij} \sum_{\mu,\nu}^{N} C_{\mu p}(0)\, C_{\nu q}(0)\, d^2(\mu|h|\nu)_{\lambda=0} \quad , \tag{71}$$

$$\begin{aligned}\{\underset{\sim}{dG}^{ij}(0)\}_{pq} = {} & \sum_{k,\ell}^{occ} \Gamma^{ijk\ell} \sum_{\mu,\nu,\rho,\sigma}^{N} C_{\mu p}(0)\, C_{\nu q}(0)\, C_{\rho k}(0)\, C_{\sigma \ell}(0)\; d(\mu\nu\|\rho\sigma)_{\lambda=0} \\ & + 2 \sum_{k\ell}^{occ} \Gamma^{ijk\ell} \sum_{r}^{N} \langle\!\langle \phi_p(0)\phi_q(0) \| \phi_k(0)\phi_r(0) \rangle\!\rangle\, dU_{r\ell}(0) \quad ,\end{aligned} \tag{72}$$

$$\begin{aligned}\{\underset{\sim}{d^2G}^{ij}(0)\}_{pq} = {} & \sum_{k,\ell}^{occ} \Gamma^{ijk\ell} \sum_{\mu\nu\rho\sigma}^{N} C_{\mu p}(0)\, C_{\nu q}(0)\, C_{\rho k}(0)\, C_{\sigma \ell}(0)\; d^2(\mu\nu\|\rho\sigma)_{\lambda=0} \\ & + 2 \sum_{k,\ell}^{occ} \Gamma^{ijk\ell} \sum_{r}^{N} \langle\!\langle \phi_r(0)\phi_q(0) \| \phi_k(0)\phi_r(0) \rangle\!\rangle\, d^2U_{r\ell}(0) \\ & + 2 \sum_{k,\ell}^{occ} \Gamma^{ijk\ell} \sum_{r,s}^{N} \langle\!\langle \phi_p(0)\phi_q(0) \| \phi_r(0)\phi_s(0) \rangle\!\rangle\, dU_{rk}(0)\, dU_{s\ell}(0) \\ & + 4 \sum_{k,\ell}^{occ} \Gamma^{ijk\ell} \sum_{r}^{N} \sum_{\mu\nu\rho\sigma}^{N} C_{\mu p}(0)\, C_{\nu q}(0)\, C_{\rho k}(0)\, C_{\sigma r}(0)\; d(\mu\nu\|\rho\sigma)_{\lambda=0}\, dU_{r\ell}(0)\end{aligned} \tag{73}$$

Straightforward algebraic manipulation gives the final expressions for $d\mathbb{H}(0)$ and $d^2\mathbb{H}(0)$:

$$d\mathbb{H}(0) = \sum_{i,j}^{occ} \sum_{\mu,\nu}^{N} \gamma^{ij}\, C_{\mu i}(0)\, C_{\nu j}(0)\; d(\mu|h|\nu)_{\lambda=0}$$

$$+ \tfrac{1}{2} \sum_{i,j,k,\ell}^{occ} \sum_{\mu,\nu,\rho,\sigma}^{N} \Gamma^{ijk\ell}\, C_{\mu i}(0)\, C_{\nu j}(0)\, C_{\rho k}(0)\, C_{\sigma \ell}(0)\; d(\mu\nu\|\rho\sigma)_{\lambda=0}$$

$$+ 2 \sum_{i}^{occ} \sum_{r}^{N} dU_{ri}(0)\; \varepsilon^{ri}(0) \quad , \tag{74}$$

$$d^2\mathbb{H}(0) = \sum_{ij}^{occ} \sum_{\mu,\nu}^{N} \gamma^{ij}\, C_{\mu i}(0)\, C_{\nu j}(0)\; d^2(\mu|h|\nu)_{\lambda=0}$$

$$+ \tfrac{1}{2} \sum_{i,j,k,\ell}^{occ} \sum_{\mu\nu\rho\sigma}^{N} \Gamma^{ijk\ell}\, C_{\mu i}(0)\, C_{\nu j}(0)\, C_{\rho k}(0)\, C_{\sigma \ell}(0)\; d^2(\mu\nu\|\rho\sigma)_{\lambda=0}$$

$$+ 4 \sum_{i}^{occ} \sum_{r}^{N} dU_{ri}(0)\; d\varepsilon^{ri}(0)$$

$$+ 2 \sum_{i}^{occ} \sum_{r}^{N} d^2U_{ri}(0)\; \varepsilon^{ri}(0)$$

$$+ 2 \sum_{i,j}^{occ} \sum_{r,s}^{N} dU_{ri}(0)\, \langle r|F^{ij}|s\rangle\, dU_{sj}(0)$$

$$+ 4 \sum_{i,j,k,\ell}^{occ} \sum_{r,s}^{N} \Gamma^{ijk\ell}\, dU_{ri}(0)\, \langle rj\|s\ell\rangle\, dU_{sk}(0) \tag{75}$$

where $\varepsilon^{ri}(0)$ and $d\varepsilon^{ri}(0)$ are given by

$$\varepsilon^{ri}(0) = \sum_{j}^{occ} \sum_{\mu\nu}^{N} \gamma^{ij} C_{\mu r}(0) C_{\nu j}(0) (\mu|h|\nu)_{\lambda=0}$$

$$+ \sum_{j,k,\ell}^{occ} \sum_{\mu\nu\rho\sigma}^{N} \Gamma^{ijk\ell} C_{\mu r}(0) C_{\nu j}(0) C_{\rho k}(0) C_{\sigma \ell}(0) (\mu\nu\|\rho\sigma) \quad , \tag{76}$$

$$d\varepsilon^{ri}(0) = \sum_{j}^{occ} \sum_{\mu\nu}^{N} \gamma^{ij} C_{\mu r}(0) C_{\nu j}(0) d(\mu|h|\nu)_{\lambda=0}$$

$$+ \sum_{j,k,\ell}^{occ} \sum_{\mu\nu\rho\sigma}^{N} \Gamma^{ijk\ell} C_{\mu r}(0) C_{\nu j}(0) C_{\rho k}(0) C_{\sigma \ell}(0) d(\mu\nu\|\rho\sigma)_{\lambda=0} \quad . \tag{77}$$

Equation (76) can be rewritten as

$$\varepsilon^{ri}(0) = \langle \phi_r(0) \Big| \sum_{j}^{occ} \{\gamma^{ij} h(0) + \sum_{k,\ell}^{occ} \Gamma^{ijk\ell} V_{k\ell}(0)\} \Big| \phi_j(0) \rangle \quad ,$$

$$= \langle \phi_r(0) \Big| \sum_{j}^{occ} F^{ij}(0) \Big| \phi_j(0) \rangle \tag{78}$$

Note that Eq. (77) is analogous to Eq. (76), but is constructed from the derivative integrals rather than the normal integrals. We will see later that these quantities $\varepsilon^{ri}(0)$ are identical to the Lagrange multipliers to be introduced as a means to enforce the orthonormality constraint on $\underset{\sim}{\phi}$, if we are to minimize the energy of a CI wavefunction by variation of the spin-orbital coefficients.

Conclusion: We have derived compact formulas Eq. (74)-(77), for the first- and second-derivatives of CI matrix elements. These derivatives can be easily calculated from the first and second derivatives of the one-electron and two-electron integrals, the Lagrange multipliers, and the first and second derivatives of the spin-orbital coefficients with respect to the perturbation parameter λ.

MULTI-CONFIGURATION HARTREE-FOCK WAVEFUNCTION: FIRST AND SECOND ENERGY DERIVATIVES

A multi-configuration Hartree-Fock wavefunction (MCHF) is a CI wavefunction for which the energy has been minimized with respect to variations of the spin-orbital coefficients, within the orthonormality constraint of the spin-orbitals. Following Hinze,[21] one can show that upon convergence, the spin-orbitals satisfy the following equations:

$$\sum_{j}^{occ} F^{ij} |\phi_j\rangle = \sum_{k}^{occ} |\phi_k\rangle \varepsilon^{ki} \quad , \tag{79}$$

where F^{ij} is defined by Eq. (36), and ε^{ki}'s are the Lagrange multipliers, given by Eq.(78). Furthermore, $\varepsilon^{ki} = \varepsilon^{ik}$ if i and k represent a pair of occupied orbitals, and $\varepsilon^{ki} = 0$ if k represents a virtual orbital and i an occupied orbital. This property of the Lagrangian matrix makes it possible to further simplify the expressions for $d\mathbb{H}(0)$ and $d^2\mathbb{H}(0)$.

The third contribution in Eq. (74) can be written

$$2 \sum_{i}^{occ} \sum_{r}^{N} dU_{ri}(0)\, \varepsilon^{ri}(0) = 2 \sum_{i}^{occ} \sum_{r}^{occ} dU_{ri}(0)\, \varepsilon^{ri}(0)$$

$$= \sum_{i}^{occ} \sum_{r}^{occ} [dU_{ri}(0) + dU_{ir}(0)]\, \varepsilon^{ri}(0) \,. \tag{80}$$

The orthonormality condition Eq. (65), expanded up to second-order as in Eqs. (68) and (69), implies

$$dU_{pp}(0) = -\tfrac{1}{2}\, dS_{pp}(0) \quad , \tag{81}$$

$$dU_{pq}(0) + dU_{qp}(0) = -dS_{pq}(0) \quad , \tag{82}$$

$$d^2U_{pq}(0) + d^2U_{qp}(0) = -d^2S_{pq}(0) - 2 \sum_{r}^{N} \{dU_{rp}(0) dS_{rq}(0)$$

$$+ dU_{rp}(0) dU_{rq}(0) + dS_{pr}(0) dU_{rq}(0)\} \tag{83}$$

with

$$S_{pq}(0) = \sum_{\mu\nu}^{N} C_{\mu p}(0)\, C_{\nu q}(0)\, (\mu|\nu)_{\lambda=0} \quad , \tag{84}$$

$$dS_{pq}(0) = \sum_{\mu,\nu}^{N} C_{\mu p}(0)\, C_{\nu q}(0)\, d(\mu|\nu)_{\lambda=0} \quad , \tag{85}$$

$$d^2S_{pq}(0) = \sum_{\mu,\nu}^{N} C_{\mu p}(0)\, C_{\nu q}(0)\; d^2(\mu|\nu)_{\lambda=0} \quad . \tag{86}$$

Using Eq. (84), we get for Eq. (80),

$$2 \sum_{i}^{occ} \sum_{r}^{N} dU_{ri}(0)\, \varepsilon^{ri}(0) = - \sum_{i,r}^{occ} \sum_{\mu\nu}^{N} \varepsilon^{ri}(0)\, C_{\mu i}(0)\, C_{\nu r}(0)\, d(\mu|\nu)_{\lambda=0} \quad . \tag{87}$$

Equation (87) shows that for a fully variational wavefunction, the energy derivative can be calculated from the knowledge of the wavefunction alone, without requiring the knowledge of $\underset{\sim}{dU}(0)$, the variation of the spin-orbital coefficients.

Similarly the fourth contribution to $d^2\mathbb{H}(0)$ in Eq. (75) can be written

$$2 \sum_{i}^{occ} \sum_{r}^{N} d^2U_{ri}(0)\, \varepsilon^{ri}(0) = \sum_{i}^{occ} \sum_{r}^{occ} [d^2U_{ri}(0) + d^2U_{ir}(0)]\, \varepsilon^{ri}(0) \tag{88}$$

which can be simplified using Eq. (83),

$$2 \sum_{i}^{occ} \sum_{r}^{N} d^2U_{ri}(0)\, \varepsilon^{ri}(0) = - \sum_{i,r}^{occ} \sum_{\mu,\nu}^{N} \varepsilon^{ri}(0)\, C_{\mu i}(0)\, C_{\nu r}(0)\; d^2(\mu|\nu)_{\lambda=0}$$

$$- 2 \sum_{i,r}^{occ} \Bigg\{ 2 \sum_{s}^{N} \sum_{\mu,\nu}^{N} \varepsilon^{ri}\, dU_{si}(0)\, c_{\mu s}(0)\, c_{\nu r}(0)\; d(\mu|\nu)_{\lambda=0}$$

$$+ \sum_{s}^{N} \varepsilon^{ri}\, dU_{si}(0) dU_{sr}(0) \Bigg\} \quad . \tag{89}$$

In the case of a fully variational wavefunction, the second-order derivative can be calculated from $d\underset{\sim}{U}(0)$, the first-order derivatives of the spin-orbital coefficients. It is clear then that first derivatives of a CI energy and second-derivatives of a MCHF energy require $d\underset{\sim}{U}(0)$. When the wavefunction is a Hartree-Fock wavefunction (HF), $d\underset{\sim}{U}(0)$ is obtained by the method of coupled-perturbed Hartree-Fock theory (CPHF). The first energy derivative of a CI wavefunction constructed from a single configuration orbital can then be readily calculated. In what follows, we shall present an extension of the CPHF theory to a MCHF wavefunction, referred to as Coupled Perturbed Multi-Configuration Hartree-Fock theory.

COUPLED PERTURBED MULTICONFIGURATION HARTREE-FOCK THEORY

In matrix notation, the Lagrangian matrix $\underset{\sim}{E}(\lambda)$ for a perturbation λ is given by

$$\underset{\sim}{U}^{+}(\lambda)\left\{\sum_{j}^{occ} \underset{\sim}{F}^{ij}(\lambda)\,\underset{\sim}{U}_{j}(\lambda)\right\} = \underset{\sim}{E}^{i}(\lambda) \quad , \quad \text{for all } i \ , \tag{90}$$

with $\underset{\sim}{E}^{i}(\lambda)$ denoting the i^{th} column of $\underset{\sim}{E}(\lambda)$. We expand $\underset{\sim}{E}(\lambda)$ in a power series in λ

$$\underset{\sim}{E}(\lambda) = \underset{\sim}{E}(0) + \lambda d\underset{\sim}{E}(0) + \tfrac{1}{2}\lambda^{2}\, d^{2}\underset{\sim}{E}(0) + \ldots \quad . \tag{91}$$

We substitute Eqs. (91) and (61), (62) into Eq. (90) and collect terms of the same order in λ:

$$\sum_{j}^{occ} \underset{\sim}{F}_{j}^{ij}(0) = \underset{\sim}{E}^{i}(0) \quad , \tag{92}$$

$$\underset{\sim}{dU}^{\dagger}(0)\ \underset{\sim}{E}^{i}(0) + \sum_{j}^{occ} [\underset{\sim}{dF}_{j}^{ij}(0) + \underset{\sim}{F}^{ij}(0)\ \underset{\sim}{dU}_{j}(0)] = \underset{\sim}{dE}^{i}(0) \qquad (93)$$

$$\underset{\sim}{d^2U}^{\dagger}(0)\ \underset{\sim}{E}^{i}(0) + \sum_{j}^{occ} [\underset{\sim}{d^2F}_{j}^{ij}(0) + \underset{\sim}{F}^{ij}(0)\ \underset{\sim}{d^2U}_{j}(0)]$$
$$+ 2\ \underset{\sim}{dU}^{\dagger}(0) \{ \sum_{j}^{occ} [\underset{\sim}{dF}_{j}^{ij}(0) + \underset{\sim}{F}^{ij}(0)\ \underset{\sim}{dU}_{j}(0)] \}$$
$$+ 2 \sum_{j}^{occ} \underset{\sim}{dF}^{ij}(0)\ \underset{\sim}{dU}_{j}(0) = \underset{\sim}{d^2E}^{i}(0) \quad ; \qquad (94)$$

Equations (92)-(94) are valid for all i.

When the energy of the wavefunction has converged to a stationary point, then $E(\lambda)$ is a hermitian matrix, and

$$\begin{aligned} E^{ik} &= E^{ki} \quad \text{for i occupied, k occupied} \quad , \\ E^{ik} &= 0 \quad \text{for i virtual, k occupied} \quad , \\ E^{ii} &\neq 0 \quad \text{for i virtual.} \end{aligned} \qquad (95)$$

The above property of $E(\lambda)$ is true for any value of λ, therefore $\underset{\sim}{dE}(0)$ and $\underset{\sim}{d^2E}(0)$ satisfy the same equations, i.e.,

$$\begin{aligned} dE^{ik} &= dE^{ki} \ , \quad d^2E^{ik} = d^2E^{ki} \quad \text{for i occupied, k occupied,} \\ dE^{ik} &= 0 \ , \quad d^2E^{ik} = 0 \quad \text{for i virtual, k occupied ,} \\ dE^{ii} &\neq 0 \ , \quad d^2E^{ii} \neq 0 \quad \text{for i virtual.} \end{aligned} \qquad (96)$$

After substitution of Eqs. (70) and (72), the first-order equations (95) and (96) become:

$$\sum_{r}^{N} \left[dU_{rk}(0)\, E^{ri}(0) - dU_{ri}(0)\, E^{rk}(0) \right]$$

$$+ \sum_{j}^{occ} \sum_{mn}^{occ} \sum_{r}^{N} 2 \left[\Gamma^{ijmn} (kj||mr) - \Gamma^{kjmn} (ij||mr) \right] dU_{rn}(0)$$

$$+ \sum_{j}^{occ} \sum_{r}^{N} \left[\langle k|F^{ij}|r\rangle - \langle i|F^{kj}|r\rangle \right] dU_{rj}(0)$$

$$= - \sum_{j}^{occ} \sum_{\mu\nu}^{N} \left(\gamma^{ij} c_{\mu k}(0)\, c_{\nu j}(0) - \gamma^{kj} c_{\mu i}(0)\, c_{\nu j}(0) \right) d(\mu|h|\nu)_{\lambda=0}$$

$$- \sum_{j}^{occ} \sum_{mn}^{occ} \sum_{\mu\nu\rho\sigma}^{N} \left(\Gamma^{ijmn}\, c_{\mu k}(0)\, c_{\nu j}(0)\, c_{\rho m}(0)\, \sigma_{n}(0) \right.$$

$$\left. - \Gamma^{kjmn}\, c_{\mu i}(0)\, c_{\nu j}(0)\, c_{\rho m}(0)\, c_{\sigma n}(0) \right) d(\mu\nu||\rho\sigma)_{\lambda=0} \qquad (97)$$

for i occupied and k occupied, and

$$\sum_{r}^{N} dU_{ri}(0)\, E^{rk}(0) + \sum_{j}^{occ} \sum_{mn}^{occ} \sum_{r}^{N} 2\Gamma^{kjmn} (ij||mr)\, dU_{rn}(0)$$

$$+ \sum_{j}^{occ} \sum_{r}^{N} \langle i|F^{kj}|r\rangle\, dU_{rj}(0)$$

$$= - \sum_{j}^{occ} \sum_{\mu\nu}^{N} \gamma^{kj} c_{\mu i}(0)\, c_{\nu j}(0)\, d(\mu|h|\nu)_{\lambda=0}$$

$$- \sum_{j}^{occ} \sum_{mn}^{occ} \sum_{\mu\nu\rho\sigma}^{N} \Gamma^{kjmn}\, c_{\mu i}(0)\, c_{\nu j}(0)\, c_{\rho m}(0)\, c_{\sigma n}(0)\, d(\mu\nu\|\rho\sigma)_{\lambda=0} \qquad (98)$$

for i virtual and k occupied.

Equation (94) can be written

$$\underset{\sim}{d^2U^\dagger}(0)\ \underset{\sim}{E^i}(0) + \sum_j^{occ} \left[\underset{\sim}{d^2F^{ij}_j}(0) + \underset{\sim}{F^{ij}}(0)\ \underset{\sim}{d^2U_j}(0)\right]$$

$$+\ 2\ \sum_j^{occ} \left[\underset{\sim}{dF^{ij}}(0)\ \underset{\sim}{dU_j}(0)\right] + 2\ \underset{\sim}{dU^\dagger}(0)\left(\underset{\sim}{dE^i}(0) - \underset{\sim}{dU^\dagger}(0)\ \underset{\sim}{E^i}(0)\right)$$

$$= \underset{\sim}{d^2E^i}(0) \qquad (99)$$

and after substitution of Eqs. (71) and (73) into Eqs. (95 and (96) we get:

$$\sum_{r}^{N}\left[d^2U_{rk}(0)E^{ri}(0) - d^2U_{ri}(0)E^{rk}(0)\right]$$

$$+ \sum_{j}^{occ}\sum_{mn}^{occ}\sum_{r}^{N} 2\left[\Gamma^{ijmn}(kj\|mr) - \Gamma^{kjmn}(ij\|mr)\right] d^2U_{rn}(0)$$

$$+ \sum_{j}^{occ}\sum_{r}^{N}\left[<k|F^{ij}|r> - <i|F^{kj}|r>\right]d^2U_{rj}(0)$$

$$= -\sum_{j}^{occ}\sum_{\mu\nu}^{N}\left(\gamma^{ij}c_{\mu k}(0)c_{\nu j}(0) - \gamma^{kj}c_{\mu i}(0)c_{\nu j}(0)\right) d^2(\mu|h|\nu)_{\lambda=0}$$

$$- \sum_{j}^{occ}\sum_{mn}^{occ}\sum_{\mu\nu\rho\sigma}^{N}\Big(\Gamma^{ijmn}\, c_{\mu k}(0)c_{\nu j}(0)c_{\rho m}(0)c_{\sigma n}(0)$$

$$- \Gamma^{kjmn}\, c_{\mu i}(0)c_{\nu j}(0)c_{\rho m}(0)c_{\sigma n}(0)\Big)\, d^2(\mu\nu\|\rho\sigma)_{\lambda=0}$$

$$- \sum_{j}^{occ}\sum_{r}^{N}\sum_{\mu\nu}^{N} 2\left(\gamma^{ij}c_{\mu k}(0)c_{\nu r}(0) - \gamma^{kj}c_{\mu i}(0)c_{\nu r}(0)\right) dU_{rj}(0)d(\mu|h|\nu)_{\lambda=0}$$

$$- \sum_{j}^{occ}\sum_{mn}^{occ}\sum_{r}^{N}\sum_{\mu\nu\rho\sigma}^{N} 2\Big(\Gamma^{ijmn}\, c_{\mu k}(0)c_{\nu r}(0)c_{\rho m}(0)c_{\sigma n}(0)$$

$$- \Gamma^{kjmn}\, c_{\mu i}(0)c_{\nu r}(0)c_{\rho m}(0)c_{\sigma n}(0)\Big)\, dU_{rj}(0)\, d(\mu\nu\|\rho\sigma)_{\lambda=0}$$

$$- \sum_{j}^{occ}\sum_{mn}^{occ}\sum_{r}^{N}\sum_{\mu\nu\rho\sigma}^{N} 4\Big(\Gamma^{ijmn}\, c_{\mu k}(0)c_{\nu j}(0)c_{\rho m}(0)c_{\sigma r}(0)$$

$$- \Gamma^{kjmn}\, c_{\mu i}(0)c_{\nu j}(0)c_{\rho m}(0)c_{\sigma r}(0)\Big)\, dU_{rn}(0)\, d(\mu\nu\|\rho\sigma)_{\lambda=0}$$

$$- \sum_{j}^{occ}\sum_{mn}^{occ}\sum_{r,s}^{N} 4\Big(\Gamma^{ijmn}(kr\|ms) - \Gamma^{kjmn}(ir\|ms)\Big) dU_{rj}(0)\, dU_{sn}(0)$$

$$- \sum_{j}^{occ}\sum_{mn}^{occ}\sum_{r,s}^{N} 2\Big(\Gamma^{ijmn}(kj\|rs) - \Gamma^{kjmn}(ij\|rs)\Big) dU_{rm}(0)\, dU_{sn}(0)$$

$$- \sum_{r}^{N} 2\left(dU_{rk}(0)dE^{ri}(0) - dU_{ri}(0)dE^{rk}(0)\right)$$

$$+ \sum 2\left(dU_{rk}(0)dU_{sr}(0)E^{si}(0) - dU_{ri}(0)dU_{sr}(0)E^{sk}(0)\right) \quad , \quad (100)$$

for i occupied, k occupied, and

$$\sum_r^N d^2U_{ri}(0)E^{rk}(0) + \sum_j^{occ}\sum_{mn}^{occ}\sum_r^N 2\,\Gamma^{kjmn}(ij\|mr)\,d^2U_{rn}(0)$$

$$+ \sum_j^{occ}\sum_r^N \langle i|F^{kj}|r\rangle\; d^2U_{rj}(0)$$

$$= -\sum_j^{occ}\sum_{\mu\nu}^N \gamma^{kj}c_{\mu i}(0)c_{\nu j}(0)\; d^2(\mu|h|\nu)_{\lambda=0}$$

$$-\sum_j^{occ}\sum_{mn}^{occ}\sum_{\mu\nu\rho\sigma}^N \Gamma^{kjmn}\,c_{\mu i}(0)c_{\nu j}(0)c_{\rho m}(0)c_{\sigma n}(0)\; d^2(\mu\nu\|\rho\sigma)_{\lambda=0}$$

$$-\sum_j^{occ}\sum_r^N\sum_{\mu\nu}^N 2\gamma^{kj}\,c_{\mu i}(0)c_{\nu r}(0)\; dU_{rj}(0)\; d(\mu|h|\nu)_{\lambda=0}$$

$$-\sum_j^{occ}\sum_{mn}^{occ}\sum_r^N\sum_{\mu\nu\rho\sigma}^N 2\Gamma^{kjmn}\,c_{\mu i}(0)c_{\nu r}(0)c_{\rho m}(0)c_{\sigma n}(0)\; dU_{rj}(0)\; d(\mu\nu\|\rho\sigma)_{\lambda=0}$$

$$-\sum_j^{occ}\sum_{mn}^{occ}\sum_r^N\sum_{\mu\nu\rho\sigma}^N 4\Gamma^{kjmn}\,c_{\mu i}(0)c_{\nu j}(0)c_{\rho m}(0)c_{\sigma r}(0)\; dU_{rn}(0)\; d(\mu\nu\|\rho\sigma)_{\lambda=0}$$

$$-\sum_j^{occ}\sum_{mn}^{occ}\sum_{rs}^N 4\Gamma^{kjmn}\,(ir\|ms)\;\; dU_{rj}(0)\; dU_{sn}(0)$$

$$-\sum_j^{occ}\sum_{mn}^{occ}\sum_{rs}^N 2\Gamma^{kjmn}\,(ij\|rs)\;\; dU_{rm}(0)\; dU_{sn}(0)$$

$$-\sum_r^N 2dU_{ri}(0)\; dE^{rk}(0) + \sum_{r,s}^N 2dU_{ri}(0)\; dU_{sr}(0)\; E^{sk}(0) \quad , \qquad (101)$$

for i virtual and k occupied.

We want to determine $\underset{\sim}{dU}(0)$ and $\underset{\sim}{d^2U}(0)$. The set of N(N-1)/2 equations (97),(98) and (100),(101), along with the orthonormality conditions (81) and (82) form two well defined systems of linear equations for $\underset{\sim}{dU}(0)$ and $\underset{\sim}{d^2U}(0)$. These linear systems can be solved by an iterative process described by Pople et al.[5] Note that only the inhomogeneous contribution to the equations differ for $\underset{\sim}{dU}(0)$ and $\underset{\sim}{d^2U}(0)$, and that $\underset{\sim}{d^2U}(0)$ depends on $\underset{\sim}{dU}(0)$. For completeness, we repeat Pople's iterative method.

Let us denote by $\underset{\sim}{B}$ the supervector of unknowns ($\underset{\sim}{dU}(0)$ or $\underset{\sim}{d^2U}(0)$), then the set of coupled equations Eqs. (97) and (100) can be written in the form

$$(\underset{\sim}{1} - \underset{\sim}{A})\underset{\sim}{B} = \underset{\sim}{B}_0 \quad , \tag{102}$$

where $\underset{\sim}{A}$ is a non-symmetric square matrix, and $\underset{\sim}{B}_0$ is a vector formed with the terms of the right-hand side in Eqs. (97), (98), (100), and and (101).

Let us define an increasing set of orthogonal vectors,

$$\underset{\sim}{\mathcal{B}} = \left\{ \underset{\sim}{B}_0, \underset{\sim}{B}_1, \ \cdots \ \underset{\sim}{B}_n, \underset{\sim}{B}_{n+1} \right\} \quad , \tag{103}$$

with $\underset{\sim}{B}_0$ the inhomogeneous part of Eq. (102) with

$$\underset{\sim}{B}_{n+1} = \underset{\sim}{A}\ \underset{\sim}{B}_n - \sum_{\alpha=0}^{n} \underset{\sim}{B}_\alpha \frac{\langle \underset{\sim}{B}_\alpha | A | \underset{\sim}{B}_n \rangle}{\langle \underset{\sim}{B}_\alpha | \underset{\sim}{B}_\alpha \rangle} \quad . \tag{104}$$

The number of expansion vectors n increases by one for each iteration. The solution vector $\underset{\sim}{B}$ is approximated by $\underset{\sim}{\bar{B}}$ where

$$\underset{\sim}{\bar{B}} \cong \sum_{\alpha}^{n} b_\alpha \underset{\sim}{B}_\alpha \quad , \tag{105}$$

with the b's solution of the $n \times n$ set of coupled equations

$$\sum_{\beta}^{n} \langle \underset{\sim}{B}_{\alpha} | \underset{\sim}{1} - \underset{\sim}{A} | \underset{\sim}{B}_{\beta} \rangle \; b_{\beta} = \langle \underset{\sim}{B}_{\alpha} | \underset{\sim}{B}_{0} \rangle \quad , \tag{106}$$

for $\alpha = 1 \ldots n$.

CONCLUSION

We have derived equations which provide the first and second derivatives of the energy of a molecule, with respect to an external parameter. These formulas apply when the wavefunction is described with a HF, MCHF or CI expression. We note that the formalism presented here deals with spin-orbitals, which are the product of a spatial orbital and a spin function of either α or β spin. In the restricted scheme, spin-orbitals are grouped by pairs formed with one spatial orbital multiplied by spin α for one member of the pair, and by spin β for the other member. However, the same formulas can be used for spatial orbitals only if we introduce new reduced density matrix elements:

$$\underset{\sim}{\gamma}^{ij} = \gamma^{i_\alpha j_\alpha} + \gamma^{i_\beta j_\beta} \quad , \tag{107}$$

$$\underset{\sim}{\Gamma}^{ijk\ell} = \Gamma^{i_\alpha j_\alpha k_\alpha \ell_\alpha} + \Gamma^{i_\alpha j_\alpha k_\beta \ell_\beta} + \Gamma^{i_\beta j_\beta k_\alpha \ell_\alpha} + \Gamma^{i_\beta j_\beta k_\beta \ell_\beta} \quad , \tag{108}$$

where i_α, i_β ... represent the spatial orbital i associated with spin α and β respectively.

It is anticipated that the availability of programs providing the first and second energy derivatives for wavefunctions of quantitative accuracy will result in extended capabilities for calculations and

predictions of molecular properties, for the determination of reaction paths, and for the calculation of potential energy surfaces used in chemical kinetics studies.

Implementation of the formulas is in progress, and applications to chemical problems will be reported in subsequent publications.

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