Derivative studies in configuration–interaction theory

R. Krishnan, H. B. Schlegel,[a] and J. A. Pople

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

The use of analytic gradient techniques in electronic structural calculations has been an important recent development in molecular quantum theory. Most of the work on energy derivatives has been carried out with Hartree–Fock (HF) wave functions[1-5] and has been recently extended to multiconfiguration SCF theories.[6,12] Very little work on energy derivatives has been done with wave functions including fuller effects of electron correlation. Recently we have calculated the analytical first derivatives of the second-order Møller–Plesset perturbation energy.[7] However, higher order effects of electron correlation could be important in a number of chemical problems. To take this into account, we have now formulated the spin–orbital equations for the analytical derivatives of the configuration–interaction energy[8,9,13] including all double substitutions (CID) and have developed an efficient computer program for their evaluation.

Let Ψ_0 be the HF determinantal wave function with n occupied spin orbitals $\chi_1 \cdots \chi_n$. These are eigenfunctions of the Fock operator, the corresponding eigenvalues being $\epsilon_1 \cdots \epsilon_n$. If there are N atomic spin orbital basis functions, there will be a finite number of unoccupied (virtual) spin orbitals $\chi_{n+1} \cdots \chi_N$. Labels $i, j, k \ldots$ denote occupied spin orbitals, $a, b, c \ldots$ denote virtual spin orbitals, and $p, q, r \ldots$ denote general spin orbitals.

The CID wave function can be written in an unnormalized form as

$$\Psi_{\mathrm{CID}} = \sum_s a_s \Psi_s = \Psi_0 + \frac{1}{4} \sum_{ijab} a_{ij}^{ab} \Psi_{ij}^{ab} , \qquad (1)$$

where Ψ_{ij}^{ab} is a determinant in which the spin orbitals χ_i and χ_j are replaced by spin orbitals χ_a and χ_b, respectively. The energy $\mathscr{E}_{\mathrm{CID}}$ is obtained by variationally optimizing the coefficients a_{ij}^{ab}. This is given by the expectation value

$$\mathscr{E}_{\mathrm{CID}} = \frac{\langle \Psi_{\mathrm{CID}} | \mathcal{H} | \Psi_{\mathrm{CID}} \rangle}{\langle \Psi_{\mathrm{CID}} | \Psi_{\mathrm{CID}} \rangle} = \frac{\sum_{st} a_s \mathcal{H}_{st} a_t}{\sum_s a_s^2} . \qquad (2)$$

Since the expansion coefficients a_{ij}^{ab} have been optimized variationally we have $\partial \mathscr{E}_{\mathrm{CID}} / \partial a_{ij}^{ab} = 0$ in (2). Differentiation of (2) with respect to an external parameter x now gives

$$(\partial \mathscr{E}_{\mathrm{CID}} / \partial x) = T^{-1} \sum_{st} [a_s (\partial \mathcal{H}_{st} / \partial x) a_t] , \qquad (3)$$

where $T = (\sum_s a_s^2)$ is the normalization factor. Hence the energy derivative can be reduced to the derivative of the Hamiltonian matrix which in turn is given in part by the set of antisymmetrized two-electron integrals

$$(pq\|rs) = \int \int \chi_p^*(1) \chi_q^*(2)(r_{12})^{-1} \\ \times [\chi_r(1)\chi_s(2) - \chi_s(1)\chi_r(2)] d\tau_1 d\tau_2 . \qquad (4)$$

These can be expressed in terms of the basis functions as

$$(pq\|rs) = \sum_{\mu\nu\lambda\sigma}^{N} c_{\mu p}^{(0)} c_{\nu q}^{(0)} c_{\lambda r}^{(0)} c_{\sigma s}^{(0)} (\mu\nu\|\lambda\sigma) , \qquad (5)$$

where $c^{(0)}$ denotes the molecular orbital coefficients and $(\mu\nu\|\lambda\sigma)$ are antisymmetrized two-electron integrals over the atomic spin orbital basis functions. Differentiation of (5) leads to two kinds of terms. The first involves the derivatives of the basis function two-electron integrals $(\partial / \partial x)(\mu\nu\|\lambda\sigma)$ which are calculated by the regular integral gradient procedures.[7] The second involves the derivatives of the molecular orbital coefficients $c_{\mu p}^{(1)} = (\partial / \partial x)(c_{\mu p})$. This is conveniently handled in the space of the unperturbed molecular spin orbitals.

$$c_{\mu p}^{(1)} = \sum_q c_{\mu q}^{(0)} u_{qp}^{(1)} . \qquad (6)$$

The derivatives $u_{qp}^{(1)}$ can be solved iteratively by coupled-perturbed Hartree–Fock theory[10,7] (CPHF) and can be given in terms of the derivatives of the Fock matrix $\mathcal{F}_{qp}^{(1)}$ and the overlap matrix $S_{qp}^{(1)}$ in the space of the unperturbed molecular spin orbitals[7,10]

$$u_{qp}^{(1)} = [\mathcal{F}_{qp}^{(1)} - S_{qp}^{(1)} \epsilon_p]/(\epsilon_p - \epsilon_q) . \qquad (7)$$

Note that in case of degeneracy, $u_{qp}^{(1)}$ may have a zero denominator if p and q are both occupied orbitals or virtual orbitals. However, such terms can be reformulated to formally cancel the $(\epsilon_p - \epsilon_q)$ term and this avoids the problems in such degenerate cases. Details of such a process will be given elsewhere.[11]

After some algebraic manipulation, the final energy derivative in terms of spin orbitals can be given by

$$(\partial \mathscr{E}_{\mathrm{CID}} / \partial x) = (\partial \mathscr{E}_{\mathrm{HF}} / \partial x) + T^{-1} \sum_{ijab} a_{ij}^{ab} z_{ij}^{ab} , \qquad (8)$$

where

$$z_{ij}^{ab} = \frac{1}{2}(ij\|ab)_x^\dagger + \frac{1}{8}\sum_{cd} a_{ij}^{cd}(ab\|cd)_x^\dagger + \frac{1}{8}\sum_{kl} a_{kl}^{ab}(kl\|ij)_x^\dagger - \sum_{kc} a_{kj}^{cb}(ka\|ic)_x^\dagger + \frac{1}{2}\sum_c a_{ij}^{cb}[\mathcal{F}_{ca}^{(1)} - \epsilon_a S_{ca}^{(1)}] - \frac{1}{2}\sum_k a_{kj}^{ab}[\mathcal{F}_{ki}^{(1)} - \epsilon_i S_{ki}^{(1)}]$$

$$+ \sum_e u_{ei}^{(1)}\left[(ej\|ab) + \frac{1}{2}\sum_{kl} a_{kl}^{ab}(ej\|kl) - 2\sum_{kc} a_{kj}^{cb}(ka\|ec)\right] + \sum_m u_{ma}^{(1)}\left[(ij\|mb) + \frac{1}{2}\sum_{cd} a_{ij}^{cd}(mb\|cd) - 2\sum_{kc} a_{kj}^{cb}(km\|ic)\right]$$

$$+ \sum_m S_{mi}^{(1)}\left[-\frac{1}{2}w_{mj}^{ab} + \frac{1}{4}\sum_{cd}(ab\|cd)a_{mj}^{cd} - \sum_{kc}(kb\|jc)a_{mk}^{ac}\right] + \sum_e S_{ea}^{(1)}\left[-\frac{1}{2}w_{ij}^{eb} + \frac{1}{4}\sum_{kl}(kl\|ij)a_{kl}^{eb} - \sum_{kc}(kb\|jc)a_{ik}^{ec}\right] . \qquad (9)$$

Here

$$(pq \parallel rs)_x^{\ddagger} = \sum_{\mu\nu\lambda\sigma}^{N} c_{\mu p}^{(0)} c_{\nu q}^{(0)} c_{\lambda r}^{(0)} c_{\sigma s}^{(0)} (\partial/\partial x)(\mu\nu \parallel \lambda\sigma) \tag{10}$$

and w_{ij}^{ab} is an array which is used in the evaluation of the coefficients a_{ij}^{ab} in the iterative CID process[9]

$$w_{ij}^{ab} = (ab \parallel ij) + \frac{1}{2}\sum_{cd}(ab \parallel cd)a_{ij}^{cd} + \frac{1}{2}\sum_{kl}(kl \parallel ij)a_{kl}^{ab} + \sum_{kc}[-(kb \parallel jc)a_{ik}^{ac} + (ka \parallel jc)a_{ik}^{bc} - (ka \parallel ic)a_{jk}^{bc} + (kb \parallel ic)a_{jk}^{ac}] \quad . \tag{11}$$

To illustrate the applicability of the CI-derivative program, we have optimized the geometry of ethylene at the CID level with the 6-31G* basis[14] ($r_{CC} = 1.328$ Å, $r_{CH} = 1.084$ Å, HCH $= 116.4°$). 12 086 nonvanishing coefficients a_{ij}^{ab} having values greater than 10^{-8} were processed in each CID calculation. The computer time required to do the CID derivatives (143 min on a VAX 11/780 computer) is less than that required for the preceding CID calculation (156 min). This should make the program widely applicable in searches for stationary points on potential energy surfaces. Extension of the technique to the CISD method is straightforward and is currently in progress.

[a] Present address: Merck Sharp, and Dohme Research Labs, Rahway, NJ 07000.

[1] P. Pulay, Mol. Phys. 17, 197 (1969).

[2] P. Pulay, in Modern Theoretical Chemistry, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 4.

[3] P. Pulay and W. Mayer, J. Mol. Spectrosc. 40, 59 (1971).

[4] H. B. Schlegel, S. Wolfe, and F. Bernardi, J. Chem. Phys. 63, 3632 (1975).

[5] K. Ishida, K. Morokuma, and A. Komornicki, J. Chem. Phys. 66, 2153 (1977).

[6] J. D. Goddard, N. C. Handy, and H. F. Schaefer III, J. Chem. Phys. 71, 1525 (1979).

[7] J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. S13, 1979 (to be published).

[8] I. Shavitt, in Modern Theoretical Chemistry, edited by H. F. Schaefer III (Plenum, New York, 1977).

[9] J. A. Pople, R. Seeger, and R. Krishnan, Int. J. Quantum Chem. S11, 149 (1977).

[10] J. Gerratt and I. M. Mills, J. Chem. Phys. 49, 1719 (1968).

[11] R. Krishnan, H. B. Schlegel, and J. A. Pople (to be published).

[12] S. Kato and K. Morokuma, Chem. Phys. Lett. 65, 19 (1979).

[13] A. Tachibana, K. Yamashita, T. Yamabe, and K. Fukui, Chem. Phys. Lett. 59, 255 (1978).

[14] P. C. Hariharan and J. A. Pople, Mol. Phys. 27, 209 (1974).

NOTES

Reactions of fast cesium atoms with polymers of antimony pentafluoride and gold pentafluoride

R. N. Compton and P. W. Reinhardt

Chemical Physics Section, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

There is considerable evidence from thermochemical[1,2] and gas phase reaction studies[3-5] that the electron affinities of many hexafluorides are well in excess of 5 eV. Recent theoretical calculations confirm some of these estimates.[6,7] The extremely large electron affinities for these hexafluorides are expected to strongly influence gas phase reaction processes involving these molecules. In this note, we report the observation of SbF_6^- and AuF_6^- produced in collisional ionization reactions of fast (1-40 eV) Cs atoms with polymers of SbF_5 and AuF_5.

Antimony pentafluoride mixed with HF is a very strong acid in the Lewis sense and is often referred to as "magic acid." For many years, SbF_5 has been used to produce organic cations in solution via the assumed reaction $RX + SbF_5 \rightarrow R^+ + SbF_5X^-$. Liquid antimony pentafluoride has an extremely large viscosity and is known to be highly associated in the gas phase.[8,9] Consequently, in our experiments, gaseous $(SbF_5)_n$ polymers were introduced directly into the collisional ionization chamber through a multichannel hole array from the liquid vapor at room temperature.

A molecular beam of $(AuF_5)_n$ polymers was prepared using the method of Vasile et al.[10] A Ni tube containing $[O_2][AuF_6]$ salt was resistively heated to ~ 170 to 190 °C. The gaseous products O_2 and $(AuF_5)_n$ polymers effused from a small hole drilled in the Ni tube. The molecular beam crossed the fast Cs beam and was terminated by a liquid N_2 filled cold trap located ~ 5 cm away. The $[O_2]$