Direct analytical calculation of first-order density matrix elements through third order

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A theory which permits the analytical calculation of atomic and molecular first-order density matrices in a computationally tractable manner is developed. Contour integral techniques are used to derive an equation relating the first-order density matrix γ to certain eigenvectors which arise in our earlier theory of molecular ionization potentials and electron affinities. By analytically evaluating the resulting contour integral, we obtain a closed expression giving γ in terms of Hartree–Fock orbital energies and two-electron integrals.

I. INTRODUCTION

Knowledge of the first-order density matrix[1,2] γ belonging to the wavefunction $|g\rangle$ is sufficient to determine the expectation value $\langle g|f|g\rangle$ of any one-electron operator f

$$\langle g|f|g\rangle = \mathrm{Tr}(\gamma f), \tag{1}$$

where f is the representation of f in an arbitrary basis. In most calculations γ and f are expressed in the basis of the Hartree–Fock (HF) spin orbitals φ_i of the atom or molecule:

$$f_{ij} = \langle \varphi_i | f | \varphi_j \rangle, \tag{2}$$

$$\gamma_{ij} = \langle \varphi_i | \gamma | \varphi_j \rangle. \tag{3}$$

In terms of the creation $\{C_i^+\}$ and annihilation $\{C_i\}$ operators referring to the spin orbitals $\{\varphi_i\}$, γ can also be written as[3]

$$\gamma_{ij} = \langle g | C_i^+ C_j | g \rangle. \tag{4}$$

If the wavefunction $|g\rangle$ were known, γ could be calculated from Eq. (4) and any expectation value would follow naturally from Eq. (1).

The eigenfunctions η_i and eigenvalues λ_i of γ are known as natural spin orbitals (NSO's) and occupation numbers (ON's), respectively:

$$\gamma \eta_i = \lambda_i \eta_i. \tag{5}$$

These NSO's have proven to be quite useful as a basis for atomic and molecular configuration interaction (CI) calculations, primarily because they lead to the most rapidly convergent CI expansion.[1]

Considering the great deal of information which is so compactly stored in the first-order density matrix, it is very logical and important to seek methods which permit the direct calculation[4-6] of γ, without having to obtain the wavefunction $|g\rangle$. The difficulty which consistently plagues such methods is the N-representability problem[4,7,8]; how can one know whether a density matrix which is calculated by an approximate theory belongs to a properly antisymmetric N-electron wavefunction?

Because a practical solution of the N-representability problem is not presently available, we do not attempt to deal further with this difficulty. Rather, we present here a new theory which allows the direct calculation of γ in a computationally tractable fashion, but which ignores the consequences of N representability.

In Sec. II, the connection between the first-order density matrix and a complete set of positive-ion states is established. Section III contains a derivation of a contour-integral expression for γ, which is analytically evaluated to third order in the electronic interactions r_{ij}^{-1} in Sec. IV. Our concluding remarks are presented in Sec. V.

II. RELATION OF γ TO POSITIVE-ION STATES

Representing the ground state of the N-electron atom or molecule of interest by $|g^N\rangle$ and inserting an orthornormal complete set $\{|\lambda^{N-1}\rangle\}$ of $(N-1)$-electron eigenstates in Eq. (4) gives

$$\gamma_{ij} = \sum_\lambda \langle g^N | C_i^+ | \lambda^{N-1} \rangle \langle \lambda^{N-1} | C_j | g^N \rangle. \tag{6}$$

In an earlier publication,[9] we developed a theory of molecular electron affinities and ionization potentials in which the positive-ion eigenstates $|\lambda^{N-1}\rangle$ are related to $|g^N\rangle$ by the operators Ξ_λ^+:

$$\Xi_\lambda^+ | g^N \rangle = | \lambda^{N-1} \rangle, \tag{7}$$

where

$$\Xi_\lambda^+ = \sum_i X_i(\lambda) C_i + \sum_{\substack{m<n \\ \alpha}} Y_{n\alpha m}(\lambda) C_m C_\alpha^+ C_n$$
$$+ \sum_{\substack{\alpha<\beta \\ m}} Y_{\alpha m \beta}(\lambda) C_\beta C_m^+ C_\alpha. \tag{8}$$

In Ref. (9), which is hereafter referred to as I, and in the present paper, the wavefunction $|g^N\rangle$ will be taken from Rayleigh–Schrödinger perturbation theory and all quantities will be calculated through third order[10] in the electronic interaction r_{ij}^{-1}.

By inserting Eqs. (7) and (8) into Eq. (6) and

using the following property of Ξ_λ^+:

$$\Xi_\lambda \big| g^N \rangle = 0, \tag{9}$$

one can express γ in terms of the expansion coefficients $X_i(\lambda)$ appearing in Eq. (8) as

$$\gamma_{ij} = \sum_\lambda X_i(\lambda) X_j^*(\lambda). \tag{10}$$

Notice that the index λ runs over only the states of the positive ion; the vectors $\mathbf{X}(\lambda)$ belonging to negative-ion states, which also occur in our earlier theory, are not included in Eq. (10). This result constitutes the starting point of the theory presented herein.

According to the formal developments presented in I, the $X_i(\lambda)$ can be obtained as eigenvectors of the pseudoeigenvalue problem

$$\mathbf{H}(E_\lambda)\mathbf{X}(\lambda) = E_\lambda \mathbf{X}(\lambda), \tag{11}$$

where the matrix $\mathbf{H}(E)$ is defined in Eq. (37) of I and the E_λ are equal to electron affinities and ionization potentials of the molecule. The normalization of the vectors $\mathbf{X}(\lambda)$ is dictated by the condition that the functions $|\lambda^{N-1}\rangle$ be normalized to unity:

$$\langle \lambda^{N-1} | \lambda^{N-1} \rangle = \langle g^N | \{\Xi_\lambda, \Xi_\lambda^+\}_+ | g^N \rangle = 1. \tag{12}$$

Substituting Eq. (8) into Eq. (12) and making use of Eq. (27) of I, one obtains the normalization condition for the $\mathbf{X}(\lambda)$ which can be written as

$$1 = \sum_k X_k^*(\lambda) X_k(\lambda) + \sum_{k,l} X_k^*(\lambda) \Big\{ \sum_{\substack{m<n \\ \alpha}} [B_{k,n\alpha m}^* B_{l,n\alpha m} /$$

$$(E_\lambda - E_\alpha^{mn})^2] + \sum_{\substack{\alpha<\beta \\ m}} [B_{k,\alpha m\beta}^* B_{l,\alpha m\beta}/(E_\lambda + E_{\alpha\beta}^m)^2] \Big\}$$

$$\times X_l(\lambda). \tag{13}$$

This result should be kept in mind, as it is used later to derive the principal equation of this paper. In order to obtain a convenient expression for the sum appearing in Eq. (10), it is necessary to formally solve Eq. (11) for the vectors $\mathbf{X}(\lambda)$ which obey the above normalization condition. This task is accomplished by contour integration techniques[11] in the following section.

III. DERIVATION OF THE CONTOUR INTEGRAL FORMULA FOR γ

The pseudoeigenvalue problem given in Eq. (11) can be formally solved in the manner described below. If Eq. (37) of I is considered to define a matrix $\mathbf{H}(z)$ for any value of the *parameter z*, then the (normalized) eigenvectors $\{\mathbf{V}_\alpha(z)\}$ and eigenvalues $\{E_\alpha(z)\}$ of $\mathbf{H}(z)$ are functions of z:

$$\mathbf{H}(z)\mathbf{V}_\alpha(z) = E_\alpha(z)\mathbf{V}_\alpha(z). \tag{14}$$

If Eq. (14) were solved repeatedly as z is varied

from $-\infty$ to $+\infty$, at certain values of z (call these $z_1, z_2, \cdots$) one of the above eigenvalues $\{E_\alpha(z)\}$ would be identically equal to z:

$$E_{\alpha\lambda}(z_\lambda) = z_\lambda \quad \lambda = 1, 2, 3, \cdots. \tag{15}$$

The roots $\{z_\lambda\}$ are the desired pseudoeigenvalues $\{E_\lambda\}$ of Eq. (11) and the corresponding normalized vectors $\{\mathbf{V}_{\alpha\lambda}(z_\lambda)\}$ are proportional to the $\mathbf{X}(\lambda)$:

$$\mathbf{H}(z_\lambda)\mathbf{V}_{\alpha\lambda}(z_\lambda) = z_\lambda \mathbf{V}_{\alpha\lambda}(z_\lambda), \tag{16}$$

$$\mathbf{X}_\lambda = N_\lambda^{-1/2} \mathbf{V}_{\alpha\lambda}(z_\lambda). \tag{17}$$

Of course the $\{\mathbf{V}_{\alpha\lambda}(z_\lambda)\}$ are not mutually orthogonal because they are eigenvectors of different $\mathbf{H}(z_\lambda)$ matrices.

By making use of Eq. (14), the spectral resolution of the inverse matrix $[z\mathbf{1} - \mathbf{H}(z)]^{-1}$ can be written as follows:

$$[z\mathbf{1} - \mathbf{H}(z)]^{-1} = \sum_\alpha (z - E_\alpha(z))^{-1} \mathbf{V}_\alpha(z)\mathbf{V}_\alpha^+(z). \tag{18}$$

Notice that the poles of $[z\mathbf{1} - \mathbf{H}(z)]^{-1}$ are equal to the electron affinities (EA's) and ionization potentials (IP's) appearing in Eq. (11). From the structure of $\mathbf{H}(z)$ given in Eq. (37) of I, one can see that the IP's lie to the left (lower energy) of the EA's on the energy (z) axis. Therefore, the integral of $(2\pi i)^{-1}[z\mathbf{1} - \mathbf{H}(z)]^{-1}$ over the contour shown in Fig. 1 yields the following important equation[12]:

$$(2\pi i)^{-1} \int_C [z\mathbf{1} - \mathbf{H}(z)]^{-1} dz$$

$$= \sum_\lambda \{1 - [dE_{\alpha\lambda}(z_\lambda)/dz]\}^{-1} N_\lambda \mathbf{X}(\lambda)\mathbf{X}^+(\lambda), \tag{19}$$

where the index λ runs only over the energy differences corresponding to IP's of the molecule.

To make the connection between Eq. (19) and the expression for γ given in Eq. (10), one must evaluate the proportionality constant N_λ and the derivative $dE_{\alpha\lambda}(z_\lambda)/dz$. It follows from Eqs. (13)
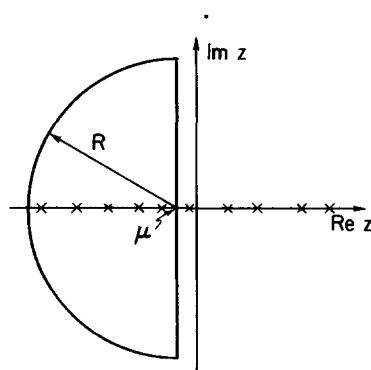

FIG. 1. The contour in the complex z plane over which the integration in Eq. (19) is performed. The value of μ is chosen to separate the ionization potentials ($E_\lambda < \mu$) from the electron affinities ($E_\lambda > \mu$).

and (17) that N_λ is given by

$$N_\lambda = 1 + \sum_{k,l} (\mathbf{V}_{\alpha\lambda}^*)_k \left\{ \sum_{\substack{m<n \\ \alpha}} [B_{k,n\alpha m}^* B_{l,n\alpha m}/(E_\lambda - E_\alpha^{mn})^2] \right.$$

$$\left. + \sum_{\substack{\alpha<\beta \\ m}} [B_{k,\alpha m\beta}^* B_{l,\alpha m\beta}/(E_\lambda + E_{\alpha\beta}^m)^2] \right\} (\mathbf{V}_{\alpha\lambda})_l. \quad (20)$$

By using the Hellmann–Feynman theorem[13]

$$dE_{\alpha\lambda}/dz = \mathbf{V}_{\alpha\lambda}^+ (d\mathbf{H}/dz) \mathbf{V}_{\alpha\lambda} \quad (21)$$

and the definition of $\mathbf{H}(z)$ given in Eq. (37) of I, one can obtain the following identity:

$$dE_{\alpha\lambda}(z_\lambda)/dz = 1 - N_\lambda, \quad (22)$$

where N_λ is expressed in Eq. (20). These results allow Eqs. (10) and (19) to be combined to give the relation between γ and the contour integral of $[z\mathbf{1} - \mathbf{H}(z)]^{-1}$:

$$\gamma = (2\pi i)^{-1} \int_C [z\mathbf{1} - \mathbf{H}(z)]^{-1} dz. \quad (23)$$

In the following section, a technique which allows the numerical evaluation of γ according to Eq. (23) is developed and the above contour integral is calculated analytically through third order.

IV. ANALYTICAL CALCULATION OF γ

For notational convenience, Eq. (37) of I is written in shorthand as follows:

$$\mathbf{H}(z) = \mathbf{A} + \mathbf{B}[z\mathbf{1} + \Delta]^{-1}\mathbf{B}^+, \quad (24)$$

where the diagonal matrix Δ contains the energy differences $\{E_\alpha^{mn}\}$ and $\{E_{\alpha\beta}^m\}$ defined in Eqs. (34) and (35) of I. The contribution to γ arising from the integral over the arc shown in Fig. 1 can easily be reduced to the simple expression shown below:

$$\gamma^{\text{arc}} = (2\pi i)^{-1} \lim_{R \to \infty} \int_{\pi/2}^{3\pi/2} iR \exp(i\theta)([\mu + R\exp(i\theta)]\mathbf{1}$$

$$- \mathbf{A} - \mathbf{B}\{[\mu + R\exp(i\theta)]\mathbf{1} + \Delta\}^{-1}\mathbf{B}^+)^{-1} d\theta$$

$$= \tfrac{1}{2}\mathbf{1}. \quad (25)$$

In carrying out the above integration, the locus of the arc is described by

$$z = \mu + R\exp(i\theta) \quad \pi/2 \leq \theta \leq 3\pi/2. \quad (26)$$

The value of μ is arbitrary except that it must separate the EA roots of Eq. (11) from the IP roots. With the result of Eq. (25), the task of calculating γ from Eq. (23) is reduced to the evaluation of the integral along the line from $\mu - i\infty$ to $\mu + i\infty$:

$$\gamma^{\text{line}} = (2\pi)^{-1} \int_{-\infty}^{\infty} \{(\mu + iy)\mathbf{1} - \mathbf{A}$$

$$- \mathbf{B}[(\mu + iy)\mathbf{1} + \Delta]^{-1}\mathbf{B}^+\}^{-1} dy. \quad (27)$$

Decomposing the matrix whose inverse appears in Eq. (27) into real and imaginary parts, one obtains

$$[(\mu + iy)\mathbf{1} - \mathbf{H}(\mu + iy)]_{ij}$$

$$= \delta_{ij}(\mu - \epsilon_i) - A_{ij}^3 - \sum_{\substack{\alpha<\beta \\ m}} \{B_{i,\alpha m\beta}(\mu + E_{\alpha\beta}^m)B_{j,\alpha m\beta}^*/$$

$$[y^2 + (\mu + E_{\alpha\beta}^m)^2]\} - \sum_{\substack{m<n \\ \alpha}} \{B_{i,n\alpha m}(\mu - E_\alpha^{mn})B_{j,n\alpha m}^*/$$

$$[y^2 + (\mu - E_\alpha^{mn})^2]\} + iy\left[\delta_{ij} + \sum_{\substack{\alpha<\beta \\ m}} \{B_{i,\alpha m\beta}B_{j,\alpha m\beta}/\right.$$

$$[y^2 + (\mu + E_{\alpha\beta}^m)^2]\} + \sum_{\substack{m<n \\ \alpha}} \{B_{i,n\alpha m}B_{j,n\alpha m}^*/$$

$$\left.[y^2 + (\mu - E_\alpha^{mn})^2]\}\right], \quad (28)$$

where A_{ij}^3 is the third-order component of A_{ij} which is defined in Eq. (31d) of I. To simplify the treatment of the algebraic manipulations which follow, the right side of Eq. (28) is more compactly written as

$$[(\mu + iy)\mathbf{1} - \mathbf{H}(\mu + iy)]_{ij} = \delta_{ij}(\mu - \epsilon_i) - V_{ij}(y^2)$$

$$+ iy\{\delta_{ij} + U_{ij}(y^2)\}, \quad (29)$$

where $V_{ij}(y^2)$ and $U_{ij}(y^2)$ are defined by analogy with Eq. (28) and are, as discussed in I, correct through third order in the electron interactions r_{ij}^{-1}. Denoting the matrix whose elements are $\delta_{ij}(\mu - \epsilon_i)$ by $\mathbf{a}$, the real part of the inverse matrix appearing in Eq. (27) is given by

$$\text{Re}[z\mathbf{1} - \mathbf{H}(z)]_{\text{line}}^{-1}$$

$$= \{\mathbf{a} - \mathbf{V} + y^2(\mathbf{1} + \mathbf{U})[\mathbf{a} - \mathbf{V}]^{-1}(\mathbf{1} + \mathbf{U})\}^{-1}; \quad (30)$$

the imaginary component is an odd function of y which does not contribute to γ^{line}. Numerical integration techniques can be used to accomplish the integration shown in Eq. (27). Reinhardt and Doll[6] have successfully employed similar methods in their second-order Green's function calculations of atomic first-order density matrices. Clearly, the principal drawback of such an approach is the expense involved in calculating the two inverse matrices in Eq. (30) for each of the many values of y needed to perform the numerical integration. Because this problem may severely limit the range of problems to which this numerical approach can be applied, it is essential that an alternative theory which avoids the above-mentioned difficulty be developed. This is achieved through third order by the formal analysis presented below.

By expanding both of the inverse matrices appearing in Eq. (30) and neglecting terms which are higher than third order in r_{ij}^{-1}, one obtains the following useful result:

$$\text{Re}[(\mu + iy)\mathbf{1} - \mathbf{H}(\mu + iy)]_{ij}^{-1}$$

$$= \delta_{ij}(\mu - \epsilon_i)[y^2 + (\mu - \epsilon_i)^2]^{-1} + \{V_{ij}[(\mu - \epsilon_i)(\mu - \epsilon_j)$$

$$-y^2] - y^2 U_{ij}(\mu - \epsilon_i + \mu - \epsilon_j)\}\{[y^2 + (\mu - \epsilon_i)^2]$$
$$\times [y^2 + (\mu - \epsilon_j)^2]\}^{-1}. \quad (31)$$

Because the functions $V_{ij}(y^2)$ and $U_{ij}(y^2)$ do not have any singularities along the real y axis, there is no reason to expect that the above expansion will be divergent for any value of y. A similar argument can be made in the case of Reinhardt and Doll's expansion of the Dyson equation[6] in powers of the self-energy $\Sigma(z)$ for values of z along the vertical axis $z = \mu + iy$. The principal difference between the present results and the so-called Born approximation of Ref. (6) is that γ is obtained through one higher order (3rd) in this work.

The integration of Eq. (31) can be carried out analytically to give the desired γ^{line}. The zeroth-order contribution to γ^{line} combines with the previously calculated γ^{arc} to give:

$$[\gamma^{\text{arc}} + {}^0\gamma^{\text{line}}]_{ij} = \delta_{ij}[\tfrac{1}{2} + \tfrac{1}{2}(\mu - \epsilon_i)/|\mu - \epsilon_i|]$$
$$= \delta_{ij}\begin{cases} 1 & \text{if } \mu > \epsilon_i \\ 0 & \text{if } \mu < \epsilon_i \end{cases} \quad (32)$$

which can be written symbolically in terms of the unit step function $\theta(x)$ as $\delta_{ij}\theta(\mu - \epsilon_i)$. Notice that this result is simply the single-determinant component of γ; all of the effects of electron correlation are contained in that portion of γ^{line} discussed below.

By analytically integrating the expression for the second- and third-order components of $[(\mu + iy)\mathbf{1} - \mathbf{H}(\mu + iy)]^{-1}$ given in Eq. (31), one obtains the following contributions to γ:

$$\gamma'_{ii} = \frac{1}{2}\sum_{\substack{\alpha<\beta \\ m}}[|B_{i,\alpha m\beta}|^2(1 - S_i)/(\epsilon_i + E_{\alpha\beta}^m)^2]$$
$$- \frac{1}{2}\sum_{\substack{m<n \\ \alpha}}[|B_{i,n\alpha m}|^2(1 + S_i)/(\epsilon_i - E_\alpha^{mn})^2], \quad (33)$$

$$\gamma'_{ij} = \frac{1}{2}\sum_{\substack{\alpha<\beta \\ m}}B_{i,\alpha m\beta}B^*_{j,\alpha m\beta}\{(E_{\alpha\beta}^m + \epsilon_i)^{-1}(E_{\alpha\beta}^m + \epsilon_j)^{-1}$$
$$+ (\epsilon_i - \epsilon_j)^{-1}[S_i(E_{\alpha\beta}^m + \epsilon_i)^{-1} - S_j(E_{\alpha\beta}^m + \epsilon_j)^{-1}]\}$$
$$- \frac{1}{2}\sum_{\substack{m<n \\ \alpha}}B_{i,n\alpha m}B^*_{j,n\alpha m}\{(\epsilon_i - E_\alpha^{mn})^{-1}(\epsilon_j - E_\alpha^{mn})^{-1}$$
$$- (\epsilon_i - \epsilon_j)^{-1}[S_i(\epsilon_i - E_\alpha^{mn})^{-1} - S_j(\epsilon_j - E_\alpha^{mn})^{-1}]\}$$
$$\text{for } i \neq j, \quad (34)$$

where S_i is defined by

$$S_i = \begin{cases} 1 & \text{if } \mu > \epsilon_i \\ -1 & \text{if } \mu < \epsilon_i \end{cases}. \quad (35)$$

Equations (33) and (34), when combined with Eq. (32), give our final third-order analytical expression for the elements of the first-order density matrix γ. It should be noticed that no numerical

integrations remain in our result; γ has been expressed in closed form in terms of the HF orbital energies ϵ_i and the two-electron integrals $\langle ij|kl\rangle$. To calculate γ, one need only carry out a *single* computation of the terms contained in Eqs. (32)–(34); this is a significant advantage over the numerical-integration approach discussed earlier.

If the diagonal elements of γ are interpreted as the electron occupation numbers of the HF spin orbitals φ_i, an interesting deduction can be inferred from Eqs. (32) and (33). Except in pathological cases, the chemical potential μ can be chosen such that the occupied HF spin orbitals $\{\varphi_\beta\}$ obey $\mu > \epsilon_\beta$ and the unoccupied spin orbitals $\{\varphi_p\}$ obey $\mu < \epsilon_p$. In this case, the diagonal elements of γ reduce to

$$\gamma_{\beta\beta} = 1 - \sum_{\substack{m<n \\ \alpha}}|B_{\beta,n\alpha m}|^2/(\epsilon_\beta - E_\alpha^{mn})^2, \quad (36)$$

$$\gamma_{pp} = \sum_{\substack{\alpha<\beta \\ m}}|B_{p,\alpha m\beta}|^2/(\epsilon_p + E_{\alpha\beta}^m)^2. \quad (37)$$

The meaning of the above equations is quite easy to see. The occupation probability of the function $\{\varphi_\beta\}$ is decreased from its single-determinant value of 1, the result of which is to transfer electron density to the spin orbitals $\{\varphi_p\}$ which were unoccupied in zeroth order. This, of course, is exactly what we would expect, based on our experience with density matrices of CI wavefunctions.[14]

V. CONCLUSION

In this paper, an analytical evaluation of the elements of atomic and molecular first-order reduced density matrices has been achieved through third order in the electronic interactions r_{ij}^{-1}. To compute γ for any molecule of interest, one must carry out a single calculation using Eqs. (32)–(34), which contain sums of terms involving only Hartree-Fock orbital energies and two-electron integrals. The analytical result of this paper has significant computational advantages over the numerical integration approaches described herein and used in Refs. (6) and (11). Because γ is written in a simple closed form here, the present theory also offers better possibilities for gaining physical insight into the structure of γ for correlated systems. We are currently in the process of adding a subroutine, which embodies the content of Eqs. (32)–(34), to our computer program for calculating molecular electron affinities and ionization potentials. The initial results for several diatomic molecules of immediate interest should become available in the near future.

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