

# An analysis of the natural orbital theory of ionization potentials

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A perturbation approach is used to analyze the natural transition orbital method proposed by Smith and Day for computing ionization potentials. The results are carried to third order in the electronic interaction and a comparison is made with the diagrammatic method of Cederbaum. Two of the third-order terms included in the natural transition orbital method which contribute to the "particle part" of the self-energy are found to differ from Cederbaum's diagrammatic terms by multiplicative factors.

## I. INTRODUCTION

Direct methods for the calculation of ionization potentials have been a very active area of research in recent years.<sup>1-8</sup> Several different methods have received attention in the form of analysis and comparison. Purvis and Öhrn<sup>9</sup> and Simons and Jørgensen<sup>10</sup> have shown how the equation-of-motion (EOM) method can be made to contain all the second- and third-order self-energy diagrams which are obtained diagrammatically by Cederbaum.<sup>5</sup> Smith and Day<sup>11</sup> have compared their natural transition orbitals (NTO) theory to the EOM technique by analyzing the form of the equations used in these methods. The theories of Parr *et al.*<sup>1</sup> and Smith and Day<sup>2</sup> have been shown to be formally identical, thus our analysis applies equally to both for a single electron ionization.

Within the NTO methods, the quality of the reference wavefunction is of utmost importance. In this paper, an evaluation of the NTO theory is achieved by using a second-order Rayleigh-Schrödinger perturbation theory wavefunction. This choice of reference function permits an order-by-order comparison with other methods in which perturbation theory is used to treat ionization energies.

## II. THEORY

Following the development of Smith and Day,<sup>2</sup> and assuming that the wavefunction for the  $N-1$  electron system,  $|\phi^{N-1}\rangle$ , can be accurately described by the removal of a specific spin orbital from the wavefunction of  $N$  electron system,  $|\phi^N\rangle$ , we write

$$|\phi^{N-1}\rangle = \Omega_j |\phi^N\rangle, \quad (1a)$$

where

$$\Omega_j = \sum_i C_i c_{ij} \quad (1b)$$

and  $C_i$  is an annihilation operator corresponding to the Hartree-Fock spin orbital  $\phi_i$ . The difference between the energy of the  $N$  electron system,  $E^N$ , and the energy of the  $N-1$  system,  $E^{N-1}$ , can be expressed as follows,

$$-[H, \Omega] |\phi^N\rangle = \Delta E \Omega |\phi^N\rangle = -(E^{N-1} - E^N) \Omega |\phi^N\rangle. \quad (2)$$

Taking the matrix element of Eq. (2) with the complex conjugate of the  $N-1$  electron wavefunction,  $\langle \phi^{N-1} | = \langle \phi^N | \Omega^\dagger$ , leads to a matrix equation of the eigenvalue

form

$$\mathbf{V}^c \mathbf{c}^c = \mathbf{S}^c \mathbf{c}^c \Delta E, \quad (3a)$$

where

$$V_{ij}^c = -\langle \phi^N | C_j^\dagger [H, C_i] | \phi^N \rangle \quad (3b)$$

and

$$S_{ij}^c = \langle \phi^N | C_j^\dagger C_i | \phi^N \rangle. \quad (3c)$$

Using the second quantized form of the Hamiltonian,

$$H = \sum_{ij} \langle i|h|j \rangle C_i^\dagger C_j + \frac{1}{4} \sum_{ijkl} \langle ij||kl \rangle C_i^\dagger C_j^\dagger C_l C_k, \quad (4)$$

with antisymmetrical two-electron integrals  $\langle ij||kl \rangle$ , the  $ij$  matrix element of  $\mathbf{V}^c$  becomes

$$V_{ij}^c = \langle \phi^N | \sum_k \langle i|h|k \rangle C_j^\dagger C_k + \frac{1}{4} \sum_{g,h,l} \langle ig||kl \rangle C_j^\dagger C_g^\dagger C_l C_k | \phi^N \rangle. \quad (5)$$

When the wavefunction is exact (e.g., equal to a full CI function),  $\mathbf{V}^c$  is Hermitian; however, this may not be the case for an arbitrary trial wavefunction. For this reason Smith and Day have chosen to use the Hermitian component,

$$\begin{aligned} \bar{V}_{ij} &= \langle \phi^N | \frac{1}{2} \sum_k \{ \langle i|h|k \rangle C_j^\dagger C_k + \langle k|h|j \rangle C_k^\dagger C_i \} \\ &+ \frac{1}{4} \sum_{g,h,l} \{ \langle ig||kl \rangle C_j^\dagger C_g^\dagger C_l C_k + \langle kl||jg \rangle C_k^\dagger C_l^\dagger C_g C_i \} | \phi^N \rangle \\ &= \frac{1}{2} (V_{ij}^c + V_{ji}^{c*}). \end{aligned} \quad (6)$$

This form of  $\bar{\mathbf{V}}$  will be used throughout our analysis.

The second-order correlated wavefunction chosen for use in our work is given by

$$\begin{aligned} |0\rangle &= N^{-1/2} \left\{ 1 + \sum_{p\delta} (K_{p\delta}^p C_p^\dagger C_\delta) + \sum_{\substack{m<n \\ \alpha<\beta}} (K_{\alpha\beta}^{mn} C_m^\dagger C_n^\dagger C_\beta C_\alpha) \right. \\ &+ \left. \sum_{\substack{m<n<p \\ \alpha<\beta<\gamma}} (K_{\alpha\beta\gamma}^{mnp} C_m^\dagger C_n^\dagger C_p^\dagger C_\gamma C_\beta C_\alpha) + \dots \right\} |HF\rangle, \end{aligned} \quad (7)$$

where the correlation coefficients,  $K_{\alpha\beta\gamma}^{mnp} \dots$ , are determined by Rayleigh-Schrödinger perturbation theory,  $N$  is the appropriate normalization constant, indices  $g, i, j, k, l$  are unspecified Hartree-Fock spin-orbitals, and the indices  $\alpha, \beta, \delta, \gamma$  ( $m, n, p, q$ ) are occupied (unoccupied) spin-orbitals. Using only the first- and second-order components of this wavefunction, which is sufficient to compute  $\bar{\mathbf{V}}$  through third order, the required

expansion coefficients<sup>12</sup> are:

$$K_{\delta}^p = \sum_{\substack{m < n \\ \gamma}} \frac{\langle \gamma p | | mn \rangle \langle mn | | \delta \gamma \rangle}{(\epsilon_{\delta} - \epsilon_p)(\epsilon_{\delta} + \epsilon_{\gamma} - \epsilon_m - \epsilon_n)} + \sum_{\alpha < \beta} \frac{\langle \alpha \beta | | \delta q \rangle \langle q p | | \alpha \beta \rangle}{(\epsilon_{\delta} - \epsilon_p)(\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_q - \epsilon_p)}, \quad (8)$$

$$K_{\alpha\beta}^{mn} = \frac{\langle mn | | \alpha \beta \rangle}{(\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_m - \epsilon_n)} + \frac{1}{2} \sum_{\delta\gamma} \frac{\langle mn | | \delta \gamma \rangle \langle \delta \gamma | | \alpha \beta \rangle}{(\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_m - \epsilon_n)(\epsilon_{\delta} + \epsilon_{\gamma} - \epsilon_m - \epsilon_n)} + \frac{1}{2} \sum_{pq} \frac{\langle mn | | p q \rangle \langle p q | | \alpha \beta \rangle}{(\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_m - \epsilon_n)(\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_p - \epsilon_q)}$$

$$+ p_{\alpha\beta}^{mn} \sum_{\delta p} \frac{\langle \delta n | | \beta p \rangle \langle p m | | \delta \alpha \rangle}{(\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_m - \epsilon_n)(\epsilon_{\alpha} + \epsilon_{\delta} - \epsilon_m - \epsilon_p)}, \quad (9)$$

$$K_{\alpha\beta\gamma}^{mnp} = \text{2nd order terms}, \quad (10)$$

$$K_{\alpha\beta\gamma\delta}^{mnpq} = \text{2nd order terms}, \quad (11)$$

where  $p_{\alpha\beta}^{mn}$  is an operator which sums over the cyclically permuted upper and lower indices independently, the sign being determined by  $(-1)$  parity. It turns out that the evaluation of  $K_{\alpha\beta\gamma}^{mnp}$  and  $K_{\alpha\beta\gamma\delta}^{mnpq}$  is not necessary if one is interested in computing  $\tilde{V}$  through third order.

By choosing the perturbation to be the exact nonrelativistic Hamiltonian [Eq. (4)] minus the Hartree-Fock Hamiltonian, and employing the above second-order reference state [Eqs. (7)–(11)] in Eq. (6), one obtains:

$$\begin{aligned} \tilde{V}_{ij} = & \delta_{ij} \epsilon_i - \frac{1}{2} \sum_{\substack{m < n \\ \gamma}} |K_{\gamma i}^{mn} K_{\gamma j}^{mn}| (\epsilon_i \delta_{i\delta} + \epsilon_j \delta_{j\delta'}) (1 - \delta_{ij}) + \sum_{p\delta} \langle i\delta | | j p \rangle K_{\delta}^p + \sum_{p\delta} \langle i p | | j \delta \rangle K_{\delta}^{p*} + \frac{1}{2} \sum_{\substack{m < n \\ \gamma}} \langle i \gamma | | mn \rangle K_{j\gamma}^{mn} \\ & + \frac{1}{2} \sum_{\substack{m < n \\ \gamma}} K_{i\gamma}^{mn*} \langle mn | | j \gamma \rangle - \frac{1}{2} \sum_{\substack{\alpha < \beta \\ m < n \\ \gamma}} |K_{\alpha\beta}^{mn} K_{\gamma j}^{mn}| \langle i \gamma | | \alpha \beta \rangle - \frac{1}{2} \sum_{\substack{\alpha < \beta \\ m < n \\ \gamma}} |K_{\gamma i}^{mn} K_{\alpha\beta}^{mn}| \langle \alpha \beta | | j \gamma \rangle - \frac{1}{2} \sum_{\substack{m, n, p \\ \gamma, \delta}} |K_{\gamma\delta}^{mn} K_{\gamma j}^{pn}| \langle i m | | p \delta \rangle \\ & - \frac{1}{2} \sum_{\substack{m, n, p \\ \gamma, \delta}} |K_{\gamma i}^{mn} K_{\gamma\delta}^{pn}| \langle \delta m | | j p \rangle + \sum_{\substack{\alpha < \beta \\ m, n, p}} |K_{\alpha\beta}^{mn} K_{\alpha\beta}^{pn}| \langle i m | | j p \rangle + \sum_{\substack{m < n \\ \alpha, \beta, \gamma}} |K_{\alpha\beta}^{mn} K_{\alpha\gamma}^{mn}| \langle i \gamma | | j \beta \rangle, \end{aligned} \quad (12)$$

where we have used the notation

$$|K_{\alpha\beta}^{mn} K_{\alpha\beta}^{mn}| \equiv K_{\alpha\beta}^{mn*} K_{\alpha\beta}^{mn}, \quad (12a)$$

and  $\delta_{i\delta}$  is used to indicate that the spin-orbital  $\phi_i$  must be occupied. The terms in Eq. (12) which contain only one Rayleigh-Schrödinger double excitation expansion coefficient contribute in both second- and third-order since  $K_{\alpha\beta}^{mn}$  contains both first- and second-order parts. In analyzing the third-order parts in Eq. (12) one can see that we have obtained Cederbaum's diagrams<sup>5</sup> labeled A<sub>1</sub>–A<sub>6</sub> as well as contributions from the diagrams representing the "particle-part" of the self-energy which Cederbaum labels C<sub>1</sub>–C<sub>3</sub> and D<sub>1</sub>–D<sub>3</sub>. However, only one-half of C<sub>1</sub> and C<sub>3</sub> are included in Eq. (12).

All of Cederbaum's second-order diagrams for the "particle part" of the self-energy are included in Eq. (12). However, an additional off-diagonal second-order contribution

$$\left[ -\frac{1}{2} \sum_{\substack{m < n \\ \gamma}} |K_{\gamma i}^{mn} K_{\gamma j}^{mn}| (\epsilon_i \delta_{i\delta} + \epsilon_j \delta_{j\delta'}) (1 - \delta_{ij}) \right]$$

appears in Eq. (12) but does not appear in Cederbaum's diagrams. The NTO theories thus give the diagonal "particle part" of the self-energy complete through second order, but not third order. The off-diagonal components of the NTO self-energy are in error in second order.

### III. CONCLUSIONS

By taking a perturbation theory approach to the natural transition orbital method of Smith and Day, which

is equivalent to Parr's theory, we have shown that only the "particle part" of the self-energy is obtained in the NTO method for calculating ionization potentials. With this restriction, the NTO theories are complete in second order except for off-diagonal terms in  $\tilde{V}_{ij}$  and in third order except for the fact that the NTO equation contains only one-half of Cederbaum's C<sub>1</sub> and C<sub>3</sub> diagrams.

Ionization potential theories which employ a more extensive operator space than shown in Eq. (1b) together with the Hartree-Fock ground state have been investigated and are shown to introduce spurious terms which are cancelled by using a correlated wavefunction.<sup>13</sup> The results of current work from this group indicate that all second order and most, but not all, third-order diagrams of Cederbaum can be generated by keeping all (Hermitian and non-Hermitian) terms and using a Hartree-Fock reference state and an inner projection manifold which includes  $h_1$ ,  $h_3$ , and  $h_5$ .<sup>14</sup> It has also been shown that the contributions of  $h_5$  are of fourth order<sup>15,16</sup> if the spurious non-Hermitian terms are eliminated. This shows that the inclusion of  $h_5$  is not needed in a complete third-order theory. Thus it seems that both the NTO method, which employs a small operator space  $\{C_1\}$  and a high quality reference state, and an approach which uses a large operator space ( $h_1, h_3, h_5$ ) together with a poorer reference state (Hartree-Fock) give "most" of Cederbaum's third-order diagrams. However, knowing that the exact energy difference requires both the exact wavefunction and the exact ionization operator, we are led to conclude that results of a given quality require a corresponding quali-

ty in both the operator and the wavefunction approximations. We feel that an operator space including  $h_1$  and  $h_3$  and a wavefunction including first- and second-order corrections can most conveniently give a theory which is complete through third-order.

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<sup>15</sup>Evidence is presented in both Ref. 13 and 16 that these terms can be ignored in that higher correlation eliminates them and the equations without the non-Hermitian terms can be used for calculation.

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