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Theoretical Studies of Negative Molecular Ions

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I. Introduction

In a recent review article on negative molecular ions (Simons, 1977), coverage was concentrated on *results* of quantum chemical calculations on specific anions; very little discussion was devoted to the methods used to carry out these calculations. Because the present series is devoted to covering developments in theoretical chemistry, it is perhaps more appropriate to direct the present review, toward explaining the quantum mechanical *techniques* that are currently used to study molecular anions. A more complete overview of the current status of theoretical research on negative ions can be obtained by reading this article and the author's other review (Simons, 1977).

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To understand why one needs rather sophisticated methods to study negative ions reliably, one need only to consider the results of our calculations (Smith *et al.* 1974) on the vertical ($R = 1.718$ a.u.) electron detachment energy ($X^1\Sigma^-$ OH^- $\rightarrow X\,^2\pi_i$ OH) of OH^-. Using an atomic orbital basis consisting of twenty Slater-type orbitals (STO's), we obtained a Koopmans' theorem approximation to the electron detachment energy equal to 3.06 eV. The energy difference between two separate self-consistent field (SCF) calculations (ΔSCF), one on OH^- and one on OH, carried out within the same basis was equal to -0.20 eV; the difference between Koopmans' theorem and ΔSCF represents the effects of allowing the orbitals to relax upon removal of the π electron. Finally, our best-computed energy difference, which contains effects of electron correlation through third order, was 1.76 eV, which is in good agreement with both Branscomb's early experiments (Branscomb, 1966) and Lineberger's more recent laser detachment results (Hotop *et al.*, 1974). The difference between 1.76 eV and the ΔSCF value of -0.2 eV represents the effects of electron correlation. These effects are indeed as large as the entire electron affinity of OH; moreover, this result is not atypical.

Because the treatment of both orbital relaxation and electron correlation effects in a sufficiently rigorous manner is an absolute necessity in any reliable scheme for computing properties of anions, theoretical progress toward understanding negative ions has been made rather slowly. Quite simply put, it is difficult to include correlation effects to a high enough order to guarantee precision of ± 0.2 eV in computed ion-neutral energy differences. In Berry's 1968 review article (Berry, 1969), his assessment of the state of quantum chemical research on anions involved briefly mentioning the works of Pekeris (1958) on H^-; Weiss (1968) on Li^-, Na^-, and K^-; Clementi (1964), Clementi and McLean (1964), and Clementi *et al.* (1964) on several atomic ions; Sinanoğlu and Oksuz (1968) on C^-, O^-, and F^-; Taylor and Harris (1963) on H_2^-; Wahl and Gilbert (1965) on halogen diatomics; and Cade (1967a,b) on OH^-, CH^-, SiH^-, SH^-, and PH^-. Therefore, in 1968 it would have been fair to say that negative molecular ions were not yet within the class of species that could conveniently be studied by existing quantum chemical methods. On the other hand, the development of modern laser technology was making available to the experimentalist new tools to use in carrying out high precision photodetachment and photoelectron spectroscopy studies of gas-phase anions. Thus, even in 1968, a great deal of experimental progress was beginning to be made. These experimental developments made a parallel development of theoretical methods and models aimed at better understanding negative ions a necessary and quite natural step in the scientific progress in this area.

In 1973 Simons and Smith published an article in which they attempted to use equations of motion (EOM) techniques to express the vertical electron affinity (EA) or detachment energy (DE) of a closed-shell species in a manner that treated orbital relaxation and electron correlation through third order in perturbation theory (the difference between the Coulombic interaction and the Hartree–Fock interaction being the perturbation). This developmental paper was followed by other formal papers by Simons (1974), Jørgensen (Jørgensen and Simons, 1975), and Jordan (Jordan *et al.*, 1976b), in which small deficiencies in the original theory were corrected and connection was made with the recent Green's function developments of Cederbaum (1973), Pickup and Goscinski (1973), Purvis and Öhrn (1974), and Freed (Tsui and Freed. 1975). The result of these papers was a method that permits the direct calculation of EA's and DE's of closed-shell species that are accurate through third order. Because the work of Doll and Reinhardt (1972) indicated that a second-order treatment of electron correlation effects was inadequate, this extension to third order was quite important. With this historical perspective in mind let us now turn our attention toward developing a unifying framework in whose terms we can understand the different techniques which are currently in use in this area of research.

II. The One-Electron Green's Function

The electron propagator or the one-electron Green's function has been used for some time.(Cederbaum, 1973; Cederbaum *et al.*, 1971, 1973; Pickup and Goscinski, 1973; Purvis and Öhrn, 1974, 1975; Tsui and Freed, 1975; Griffing and Simons, 1975, 1976; Kenney and Simons, 1975; Andersen and Simons, 1976, 1977a,b; Griffing *et al.*, 1975; Jordan *et al.*, 1976a; Linderberg and Öhrn, 1967, 1973; Doll and Reinhardt, 1972; Schneider *et al.*, 1970; Yarlagadda *et al.*, 1973) in the study of electron spectroscopy. The advantages of using the electron propagator arise because the transition energies and the transition strengths are obtained directly as poles and residues of the propagator, respectively. Several alternative procedures for decoupling the equation of motion for the electron propagator have been developed. In this review we use the superoperator formalism of Goscinski and Lukman (1970) as the framework for our development.

The time-dependent Green's function $G_{ij}(t)$ is defined in terms of the spin-orbital annihilation (a_i) and creation (a_i^+) operators as follows:

$$G_{ij}(t) = (1/i)\{\langle a_i^+(t)a_j\rangle\theta(t) - \langle a_j a_i^+(t)\rangle\theta(-t)\}, \qquad (1)$$

where $\theta(t)$ is the Heaviside step function and the bracket $\langle\ \rangle$ indicates an average over some reference state. By introducing the identity $\exp(iHt)a^+ \exp(-iHt) = \exp(-i\hat{H}t)a^+$, where $\hat{H}$ is the superoperator Hamiltonian ($\hat{H}a^+ \equiv a^-, H$), and Fourier transforming Eq. (1), one obtains

$$\mathsf{G}(E) = (\mathbf{a}(E\hat{I} - \hat{H})^{-1}\mathbf{a}) \qquad (2)$$

where $\hat{I}$ and $\hat{H}$ are the superoperator identity and Hamiltonian respectively, and the **a** are the set of annihilation operators $\mathbf{a} = a_i$, which are arranged in a super row vector. The superoperator scalar product is defined in the conventional fashion, $(A|\hat{H}|B) \equiv \langle A^+(\hat{H}B) + (\hat{H}B)A^+ \rangle$. The superoperator resolvent $(E\hat{I} - \hat{H})^{-1}$ can be approximated via the inner projection technique in which case the propagator then takes the form

$$G(E) = (\mathbf{a}|\mathbf{h})(\mathbf{h}|E\hat{I} - \hat{H}|\mathbf{h})^{-1}(\mathbf{h}|\mathbf{a}), \tag{3}$$

where **h** is a projection manifold which, if chosen to be complete and orthonormal, makes Eqs. (2) and (3) identical. The operator space

$$\begin{aligned} &\{\mathbf{h}_1, \mathbf{h}_3, \mathbf{h}_5 \cdots\} \\ &= \{a_i, a_i^+ a_k a_l, a_i^+ a_j^+ a_k a_l a_r, \cdots\}, \qquad k > l, i > j, k > l > r \cdots \end{aligned} \tag{4}$$

spans the manifold **h**. We now discuss appropriate selections of **h** which, in conjunction with a choice of the reference state, ensure that the electron propagator is calculated correctly through third order in the electronic interaction. The development is limited to third order primarily because currently used methods have not been extended, except for selective summation of higher order terms, to fourth and higher order. Moreover, results (Griffing and Simons, 1975, 1976; Kenney and Simons, 1975; Andersen and Simons, 1976; Griffing *et al.* 1975; Jordan *et al.* 1976a; Andersen and Simons, 1977a,b) of third-order calculations seem to be very reliable (±0.2 eV).

[illegible] the Hartree–Fock (HF) ground state is able to give the electron propagator correct through second order in the electronic interaction. Such second-order calculations [illegible] Hamiltonians [illegible] and [illegible] 1975 [illegible] of EA's are not sufficiently [illegible] except in well-understood [illegible]. Thus we choose to demonstrate how, using a correlated ground state and the above projection manifold, we are able to get the electron propagator correct through third [illegible] from correlation effects in the ground state.

The effect of including $\mathbf{h}_5$ in the projection manifold, where the HF ground state is used as reference state, has been discussed by Tyner-Redmon *et al.* (1975) and from their analysis it is clear that $\mathbf{h}_5$ introduces terms which are at least fourth order in the electronic interaction, independent of the choice of reference state. This conclusion is not easily reached in a rigorous derivation because the superoperator Hamiltonian, $\hat{H}$, is not hermitian $[(\mathbf{h}_5|\hat{H}|\mathbf{h}_1) = 0$, but $(\mathbf{h}_1|\hat{H}|\mathbf{h}_5) \neq 0]$. However, Purvis *et al.* (1976) have shown that although $\hat{H}$ is not rigorously hermitian, the nonhermitian terms are introduced by the improved (higher order) reference state. Thus, if one is careful to avoid the nonhermitian parts of $\hat{H}$, one can show, as Tyner-Redmon has, that the $\mathbf{h}_5$ operators cannot contribute to G^{-1} through third order. We therefore concentrate on using $\mathbf{h}_1, \mathbf{h}_3$ as our projection manifold in our search for a theory that is consistent through third order.

As the reference state in our analysis we use a correlated wave function given by

$$|0\rangle = N^{-1/2}\Big\{1 + \sum_{p\delta} (K^p_\delta a^+_p a_\delta) + \sum_{\substack{m>n\\ \alpha>\beta}} (K^{mn}_{\alpha\beta} a^+_m a^+_n a_\beta a_\alpha) + \sum_{\substack{m>n>p\\ \alpha>\beta>\delta}} (K^{mnp}_{\alpha\beta\delta} a^+_m a^+_n a^+_p a_\alpha a_\beta a_\delta) + \cdots\Big\}|\mathrm{HF}\rangle \tag{5}$$

where the $\mathbf{a}^+$ are a set of HF creation operators and where indices m, n, p, q ($\alpha, \beta, \delta, \gamma$) refer to unoccupied (occupied) spin orbitals in the HF ground state and i, j, k, l, r are unspecified spin orbitals. We then take the correlation coefficients from Rayleigh–Schrödinger perturbation theory

$$\begin{aligned} K^p = \sum_{\substack{m>n\\ \alpha>\beta}} \{&\langle p\alpha||mn\rangle\delta_{\delta\beta}\langle p\beta||mn\rangle\delta_{\alpha\delta} \\ &+ \langle\beta\alpha||\delta m\rangle\delta_{np} - \langle\beta\alpha||\delta n\rangle\delta_{pm}\} \\ &\times \frac{\langle mn||\alpha\beta\rangle}{(\varepsilon_\delta - \varepsilon_p)(\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_n - \varepsilon_m)} + \text{higher order terms} \\ &\text{in the electronic interaction} = K^p_\delta(2, 3, \ldots) \end{aligned} \tag{6}$$

$$\begin{aligned} K^{mn}_{\alpha\beta} = \frac{\langle mn||\alpha\beta\rangle}{\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_m - \varepsilon_n} &+ \text{higher order terms in the} \\ &\text{electronic interaction} = K^{mn}_{\alpha\beta}(1, 2, \ldots) \end{aligned} \tag{7}$$

$$K^{mnp}_{\alpha\beta\delta} = K^{mnp}_{\alpha\beta\delta}(2, 3, \ldots) \tag{8}$$

where the numbers in the bracket indicate the orders in the electronic interaction contributing to K^p_δ, $K^{mn}_{\alpha\beta}$, and $K^{mnp}_{\alpha\beta\delta}$. The ε_i indicate HF orbital energies and the two-electron integral $\langle mn|\alpha\beta\rangle$ refers to the charge densities $m\alpha$ and $n\beta$ and

$$\langle mn||\alpha\beta\rangle = \langle mn|\alpha\beta\rangle - \langle mn|\beta\alpha\rangle. \tag{9}$$

In the remainder of our analysis we employ the projection manifold $\{\mathbf{h}_1, \mathbf{h}_3\}$

where the $\mathbf{h}_3$ space for convenience has been redefined as

$$\mathbf{h}_3 = \{a_i^+ a_k a_l + \langle a_i^+ a_l \rangle a_k - \langle a_i^+ a_k \rangle a_l\}. \tag{10}$$

This choice of the subspace $\mathbf{h}_3$ ensures the space is orthogonal to $\mathbf{h}_1$

$$(\mathbf{h}_1 | \mathbf{h}_3) = 0, \tag{11}$$

even for a correlated reference state. We also have the following orthogonality relations:

$$(\mathbf{h}_1 | \mathbf{h}_1) = 1, \qquad (\mathbf{h}_3 | \mathbf{h}_3) = \mathsf{S}(0, 2, 3, \ldots). \tag{12}$$

Using Eqs. (11) and (12). Eq. (3) can be partitioned into the form

$$\begin{aligned} \mathsf{G}^{-1}(E) &= (\mathbf{h}_1 | E\hat{I} - \hat{H} | \mathbf{h}_1) - (\mathbf{h}_1 | \hat{H} | \mathbf{h}_3)(\mathbf{h}_3 | \hat{E}I - H | \mathbf{h}_3)^{-1}(\mathbf{h}_3 | \hat{H} | \mathbf{h}_1) \\ &= E\mathsf{1} - \mathsf{A} - \mathsf{B}\mathsf{D}^{-1}\mathsf{C} \end{aligned} \tag{13}$$

where the matrices ABC and D are defined as

$$\begin{aligned} \mathsf{A} &= (\mathbf{h}_1 | \hat{H} | \mathbf{h}_1) \qquad & \mathsf{B} &= (\mathbf{h}_1 | \hat{H} | \mathbf{h}_3) \\ \mathsf{D} &= (\mathbf{h}_3 | \hat{E}I - \hat{H} | \mathbf{h}_3) \qquad & \mathsf{C} &= (\mathbf{h}_3 | \hat{H} | \mathbf{h}_1). \end{aligned} \tag{14}$$

We are now prepared to make an order-by-order analysis of Eq. (13) in which we retain only those terms which are zeroth, first, second, or third order in the electronic interaction. Since, as will be seen shortly, the B and C matrices are at least of first order, we need to consider only that part of the D matrix that is zeroth and first order. This constrains the indices in the projection manifold $\mathbf{h}_3$ to be of the form $a_m^+ a_\alpha a_\beta \; \alpha > \beta$ or $a_\alpha^+ a_m a_n \; m > n$ since operators such as $a_m^+ a_n a_\alpha$ lead to matrix elements in the D matrix that are at least of second order. The resulting subspace $\mathbf{h}_3$ is thus identical to that used in calculating the electron propagator through second order in the electron repulsions (Doll and Reinhardt, 1972), although we now need to obtain the B and C matrices through second order, the D matrix through first order, and the A matrix through third order.

Previous attempts (Schneider *et al.*, 1970; Yarlagadda *et al.*, 1973) to obtain the electron propagator correct through third order have used the reference state

$$|0\rangle = N_0^{-1/2}\left(1 + \sum_{\substack{m>n \\ \alpha>\beta}} K_{\alpha\beta}^{mn} a_m^+ a_n^+ a_\alpha a_\beta\right) |\mathrm{HF}\rangle \tag{15}$$

where the $K_{\alpha\beta}^{mn}$ are determined from first-order Rayleigh–Schrödinger perturbation theory. In calculating the B, C, and D matrix elements correct through second and first order, respectively, no changes are obtained from considering the higher correlated ground state in Eq. (5). The matrix elements of B, C, and D are given, either for the reference state of Eq. (5) or for the state shown in Eq. (15) as

$$B_{i,\alpha m\beta} = -\langle im||\alpha\beta\rangle - \frac{1}{2}\sum_{p,q}\langle im|pq\rangle K^{pq}_{\alpha\beta} + \sum_{\gamma,p}[\langle i\gamma|p\alpha\rangle K^{mp}_{\beta\gamma} - \langle i\gamma|p\beta\rangle K^{mp}_{\alpha\gamma}] \tag{16}$$

$$B_{i,n\alpha m} = \langle i\alpha|mn\rangle + \frac{1}{2}\sum_{\gamma\delta}\langle i\alpha|\delta\gamma\rangle K^{mn}_{\delta\gamma} + \sum_{\gamma p}[\langle ip|\gamma n\rangle K^{mp}_{\alpha\gamma} - \langle ip|\gamma m\rangle K^{np}_{\alpha\gamma}] \tag{17}$$

C = B (through second order)

$$D_{n\alpha m,\delta p\gamma} = 0. \tag{18}$$

$$D_{n\alpha m,q\beta p} = \delta_{nq}\delta_{\alpha\beta}\delta_{mp}(\varepsilon_m + \varepsilon_n - \varepsilon_\alpha - E) - \delta_{qn}\langle m\beta||p\alpha\rangle - \delta_{pm}\langle n\beta||q\alpha\rangle + \delta_{qm}\langle n\beta||p\alpha\rangle + \delta_{\alpha\beta}\langle mn||pq\rangle + \delta_{pn}\langle m\beta||q\alpha\rangle, \tag{19}$$

$$D_{\delta p\gamma,\alpha q\beta} = -\{\delta_{\delta\alpha}\delta_{pq}\delta_{\gamma\beta}(\varepsilon_p - \varepsilon_\delta - \varepsilon_\gamma + E)\} - \delta_{\gamma\beta}\langle\delta q||\alpha p\rangle + \delta_{\delta\alpha}\langle\gamma q||\beta p\rangle + \delta_{\gamma\alpha}\langle\delta q||\beta p\rangle + \delta_{pq}\langle\delta\gamma||\beta\alpha\rangle + \delta_{\delta\beta}\langle\gamma q||\alpha p\rangle. \tag{20}$$

In the A matrix we need to include all terms up to third order. The A matrix elements obtained by using Eq. (15) as a reference state need to be modified by third-order terms that result from the interaction between the singly excited states of Eq. (5) and the HF ground state. The triply excited states of Eq. (5), which also result from a second-order Rayleigh–Schrödinger perturbation calculation, do not introduce third-order terms in A. We thus have to add to the A matrix elements given by Simons (Simons and Smith, 1973), which employed the reference state of Eq. (15), the terms δA_{ij}

$$\begin{aligned}\delta A_{ij} = &\sum_{\substack{\delta\beta\\ pmn}}\frac{\langle jp||i\delta\rangle\langle\delta\beta||mn\rangle\langle mn||p\beta\rangle}{(\varepsilon_\delta - \varepsilon_p)(\varepsilon_\delta + \varepsilon_\beta - \varepsilon_m - \varepsilon_n)}\\ &+ \sum_{\substack{\delta\beta\\ pmn}}\frac{\langle j\delta||ip\rangle\langle p\beta||mn\rangle\langle mn||\delta\beta\rangle}{(\varepsilon_\delta - \varepsilon_p)(\varepsilon_\delta + \varepsilon_\beta - \varepsilon_m - \varepsilon_n)}\\ &+ \sum_{\substack{\delta\alpha\beta\\ pn}}\frac{\langle jp||i\delta\rangle\langle\delta n||\beta\alpha\rangle\langle\alpha\beta||pn\rangle}{(\varepsilon_\delta - \varepsilon_p)(\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_p - \varepsilon_n)}\\ &+ \sum_{\substack{\delta\alpha\beta\\ pn}}\frac{\langle j\delta||ip\rangle\langle\beta\alpha||\delta n\rangle\langle pn||\alpha\beta\rangle}{(\varepsilon_\delta - \varepsilon_p)(\varepsilon_\alpha + \varepsilon_\beta - \varepsilon_p - \varepsilon_n)}.\end{aligned} \tag{21}$$

The A matrix originally given by Simons (Simons and Smith, 1973) is

$$A_{ij} = \delta_{ij}\varepsilon_i + \sum_{k,l} \langle ik \| jl \rangle F_{kl}, \tag{22}$$

where

$$F_{kl} = \sum_{\alpha>\beta,\,p} K^{pk}_{\alpha\beta} K^{pl}_{\alpha\beta} - \sum_{p<q,\,\alpha} K^{pq}_{\alpha l} K^{pq}_{\alpha k}. \tag{22a}$$

The results shown in Eqs. (16–22a) constitute a superoperator derivation of the electron propagator through third order. With these general results in hand, let us now turn to the analysis of various approximations that have been introduced for $\mathsf{G}(E)$.

III. Approximations to $\mathsf{G}(E)$

A. CEDERBAUM'S DIAGRAMMATIC METHOD

In a series of papers aimed at developing an accurate and tractable quantum mechanical approach to principal and shake-up ionization energies and photoelectron intensities, Cederbaum (1973) and Cederbaum *et al.* (1971, 1973) has made use of Feynman diagram techniques to derive an approximation to the self-energy $\Sigma(E)$ appearing in the Dyson equation

$$\mathsf{G}^{-1}(E) = \mathsf{G}_0^{-1}(E) - \Sigma(E). \tag{23}$$

A comparison of Eqs. (13) and (23) shows that $\Sigma(E)$ can be written as $\mathsf{B}\mathsf{D}^{-1}\mathsf{C} + \mathsf{A}^{(3)}$, where $\mathsf{A}^{(3)}$ is the third-order part of A if $\mathsf{G}_0^{-1}(E)$ is identified as $(E - \varepsilon_i\delta_{ij})$. In Figs. 1 and 2 are shown the diagrams that constitute the second- and third-order components of $\Sigma(E)$, respectively. The reader should consult the papers of Cederbaum for a review of the rules for writing, in terms of two-electron integrals and orbital energies, the values of Feynman diagrams. The (second-order) diagrams of Fig. 1 arise in our Eq. (13) for $G^{-1}(E)$ when the first-order components of B and C are combined with the zeroth order (diagonal) component of $\mathsf{D}^{-1}(-\mathsf{B}^{(1)}(\mathsf{D}^0)^{-}\mathsf{C}^{(1)})$. The explicit expressions for B, C, A, and D given in Eqs. (16–22) allow these second-order components to be evaluated in a straightforward manner.

The third-order diagrams in Fig. 2 labeled A1–A6 arise in Eq. (13) from the third-order components of A with diagrams A1 and A2 coming from matrix elements involving the first-order Rayleigh–Schrödinger component of the wave function $|0\rangle$ and diagrams A3–A6 resulting from elements involving the second-order component of $|0\rangle$. Diagrams C1–C6 and D1–D6 arise in Eq. (13) from three sources: (1) by combining the second-order parts of C, the zeroth-order parts of D^{-1}, and the first-order parts of B; (2) by combining the first-order parts of C, the zeroth-order parts of D^{-1}, and the second-order parts of B; and (3) by combining the first-order parts of B and C with the first-order parts of D^{-1}. Because D contains zeroth- and first-order components $D^0 + D^1$ [see Eqs. (19) and (20)], D^{-1} can be approximated, through first order, and $(D^0)^{-1} - (D^0)^{-1}D^1(D^0)^{-1}$; the second term in this expression is that referred to above as the first-order part of D^{-1}.

In solving the Dyson equation (23) for $G(E)$, Cederbaum must evaluate the contribution to $\sum_{ij}(E)$ made by each diagram in Figs. 1 and 2 for each value of the variable E. The evaluation of the third-order diagrams C1–C6 and D1–D6 involves the summation over five indices, e.g.,

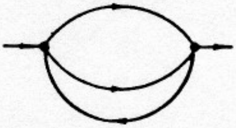

Fig. 1. The second-order self-energy diagrams of Cederbaum.

$$\mathrm{C1} = \sum_{\substack{\alpha \\ p<q,\, r<s}} \langle pq||i\alpha\rangle\langle rs||pq\rangle\langle j\alpha||rs\rangle \times (\varepsilon_\alpha - \varepsilon_p - \varepsilon_q + E)^{-1}(\varepsilon_\alpha - \varepsilon_r - \varepsilon_s + E)^{-1}. \qquad (24)$$

The computation time involved in calculating such terms clearly depends upon the number of Hartree–Fock spin orbitals to the fifth power. This N^5 dependence is obviously a severely limiting aspect of the Green's function method as implemented in the above manner. Nevertheless, Cederbaum (1973) and his collaborators (1971, 1973) have carried out high precision

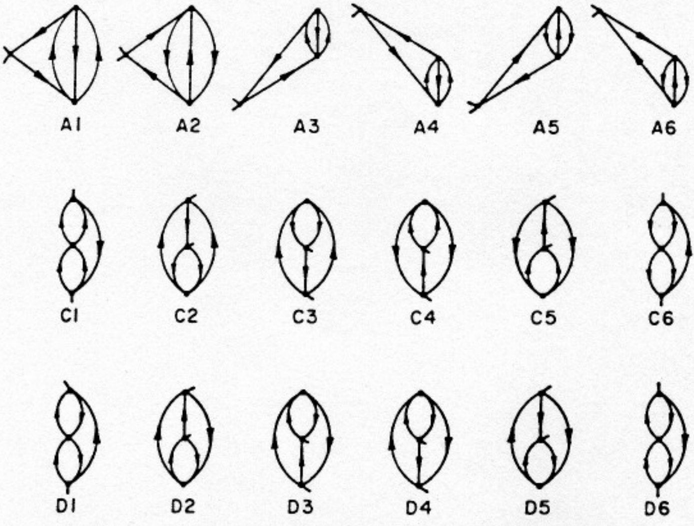

Fig. 2. The third-order self-energy diagrams of Cederbaum.

studies of reasonably large molecules using this complete third-order treatment of $\Sigma(E)$.

B. SIMONS' APPROACH AND THE TECHNIQUE OF PURVIS AND ÖHRN

To accomplish a reduction in the computational effort required to compute $\Sigma(E)$ through third order, Simons and Smith (1973) introduced, in an *ad hoc* manner, simplifications of $\Sigma(E)$ that have now been wisely used in their studies of molecular anions (Smith *et al.*, 1974; Griffing and Simons, 1975, 1976; Kenney and Simons, 1975; Andersen and Simons, 1976; Griffing *et al.*, 1975; Jordan *et al.*, 1976a; Andersen and Simons, 1977a). These authors approximated the D matrix appearing in Eq. (13) by its diagonal component only; all off-diagonal components of D contribute to the third-order parts of $\Sigma(E)$ through terms of the form $-\mathrm{B}^{(1)}(\mathrm{D}^0)^{-1}\mathrm{D}^1(\mathrm{D}^0)^{-1}\mathrm{C}^1$, therefore this approximation causes errors in $\Sigma(E)$ which are of third order. Purvis and Öhrn (1974, 1975) and P. Jørgensen and G. Purvis (private communication) have been involved in attempting to develop more systematic approximations to D^{-1}. Their emphasis has been directed toward finding computationally tractable schemes that allow one to replace the full D matrix by a smaller sub-block of D. Thus far there have not been many calculations carried out using such block diagonalization techniques, although their implementation is certainly worth pursuing.

In the approaches of Simons *et al.* and of Purvis and Öhrn, the self-energy $\Sigma(E)$ contains, as it should, only simple poles; only D is E-dependent. Thus the first- and second-order components of B and C, which are not E-dependent, need be calculated only once. Only D^{-1} has to be formed for each value of E. If D is taken, as Simons has done, to be diagonal, this is a trivial step. In contrast, as is shown in Eq. (24), the diagrammatic representation of $\Sigma(E)$, although very closely related to the algebraic superoperator approach given in Section II, requires each contribution to $\Sigma(E)$ to be calculated for each value of E. Thus the more rigorous treatment of Cederbaum involves carrying out fivefold summations for each value of E and for each element $\sum_{ij}(E)$ of the self energy [see Eq. (24), for example]. If D is taken to be diagonal, the approach described in Section II involves doing a threefold summation for each element of $\Sigma(E)$, once the E-independent quantities A, B, and C are computed (once-and-for-all). The replacement of fivefold sums by threefold sums represents an important savings.

C. CHONG'S THIRD-ORDER PERTURBATION THEORY APPROACH

In a recent series of formal and computational papers, Chong *et al.* (1974a,b,c) has employed third-order Rayleigh–Schrödinger perturbation theory with geometric approximations to higher order terms and doublezeta quality basis sets to study the low-lying states of molecular ions (primarily cations). This approach involves the separate calculation, via third-order perturbation theory, of the energies of both the neutral molecule and the ion. Such perturbation calculations have yielded ionization potentials that are precise to ±0.5 eV. In studying anions, this level of accuracy is not adequate. It is our feeling that much of the error resulting in Chong's calculations is due to the quality of his basis sets. A critical evaluation of this third-order perturbation theory approach in which extended basis sets are employed would be most welcome. Once the basis set question is resolved, one can attempt to evaluate the inherent limitations of the perturbation theory method.

D. THE IONIZATION ENERGY METHODS OF PARR AND OF SMITH

Parr (Morrell *et al.*, 1975) and Smith (Smith and Day, 1974; Day *et al.*, 1975) have independently developed a technique for computing ionization potentials that is closely related to the Green's function approach described in Section II. The implementation of this theory involves construction of a matrix V whose elements are given (for IP calculations) by

$$V_{ij} = \tfrac{1}{2}\langle 0|a_i^+[H, a_j] + [a_j^+, H]a_i|0\rangle, \tag{25}$$

where the reference state $|0\rangle$ is assumed to be a high quality (correlated) approximation to the ground electronic state of the system. The (approximate) ionization energies $\{\varepsilon_\mu\}$ are obtained by solving

$$\mathsf{V}g_\mu = \varepsilon_\mu \mathsf{S}g_\mu, \tag{26}$$

with

$$S_{ij} \equiv \langle 0|a_i^+ a_j|0\rangle. \tag{27}$$

This approach has been applied to a few atomic systems; the results are sufficiently encouraging to warrant further investigation of the idea. Andersen (Andersen and Simons, 1976) has carried out an order-by-order analysis of the elements of V by using a second-order Rayleigh–Schrödinger approximation to the reference state in Eq. (25). He finds that the (primary) ionization energies generated by the method of Parr and Smith contain almost all second- and third-order corrections to the Koopmans' theorem approximation. if the second-order reference state is used for $|0\rangle$ in Eq. (25). The method therefore seems to also have a good deal of formal justification. However. it is not at all clear how well this approach will do when it is applied to shake-up ionization processes. It is our feeling that formal and