PHYSICAL REVIEW A VOLUME 14, NUMBER 6 DECEMBER 1976

Algebraic approximation in many-body perturbation theory

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(Received 7 June 1976)

Many-body perturbation theory is developed within the algebraic approximation, i.e., parametrization of state functions by expansion in a finite basis set. This considerably extends the applicability of the theory to molecules, allowing all two-, three-, and four-body contributions to the energy to be evaluated through third order. Within this context, a comparison is presented between perturbation calculations and previously reported configuration-interaction calculations which employed the same basis sets. The [2/1] Padé approximants to the energy are constructed and upper bounds to the energy expectation values are determined. Two zeroth-order Hamiltonians are used, and the convergence of the resulting perturbation series is compared. Both of these perturbation expansions yield Padé approximants to the energy which are within 0.9% of the corresponding configuration-interaction results. The variation-perturbation upper bounds for the energy are all within 3.2% of the corresponding configuration-interaction bounds. Considering this agreement and the tractability of the diagrammatic perturbative scheme, it appears that the perturbation expansion is highly competitive.

I. INTRODUCTION

The determination of the electronic structure of atoms and molecules containing N electrons involves the evaluation of an appropriate eigenvalue and eigenfunction of a semibounded self-adjoint Hamiltonian operator $\mathcal{H}$ in Hilbert space. A tractable scheme for solving such equations is the algebraic approximation in which eigenfunctions are parametrized by expansion in a finite set of functions. Differential equations thus become algebraic equations for expansion coefficients. The algebraic approximation results in the restriction of the domain of the operator $\mathcal{H}$ to a finite-dimensional subspace S of Hilbert space. The algebraic approximation may be implemented by defining a suitable orthonormal basis set of $M(>N)$ one-electron spin orbitals and constructing all unique N-electron determinants $|\mu\rangle$ using the M one-electron functions. The number of unique determinants that can be formed is $\eta = \binom{M}{N}$, and η is the dimension of the subspace S spanned by the set of determinants. The algebraic approximation restricts the domain of $\mathcal{H}$ to this η-dimensional subspace.

Within the algebraic approximation, the Schrödinger equation may, in principle, be solved by the method of configuration interaction. The wave function is expressed as a superposition of configurations $|\mu\rangle$ with linear coefficients C_μ, and the optimal expansion coefficients determined by the variation principle. In practice, difficulties arise in setting up and solving secular equations of high order. Thus, only a small subset of the $|\mu\rangle$ is usually employed in the expansion.

Diagrammatic many-body perturbation theory[1,2] may also be formulated within the algebraic approximation. Thus the domain of the perturbation theory operators is restricted to the η-dimensional space spanned by the $|\mu\rangle$ and consequently the perturbation-theory wave function is generated in terms of an η-dimensional representation. The results of many-body perturbation theory, when carried through infinite order, are identical to those of configuration interaction if the same basis set is used. However, the perturbation-theory expansions must be truncated at some finite order n, and in this case, the degree of agreement with the configuration interaction result is a measure of the convergence of the perturbation series through nth order.

The primary purpose of this work is to demonstrate that full third-order many-body perturbative energy calculations can produce results that are within a few percent of singly and doubly excited configuration-interaction results, when each is performed within the same basis set. This has not been previously demonstrated and hence should provide some new insight into the quality of the perturbation expansions. The choice of an atomic or molecular test system is immaterial except that it must be a convenient, nontrivial system where configuration-interaction results are available. The object is to compare the perturbative results with the singly and doubly excited configuration-interaction limit, and not necessarily to attempt to find a more accurate energy value for the system than that obtained in previous studies. Therefore, in the present work, third-order perturbative calculations are compared with various configuration-interaction results of Barr and Davidson[3] for the ground ${}^1S$ state of the neon atom. More accurate calculations exist for neon; however, the results of Barr and Davidson are chosen because they report various configuration-interaction calculations for each of several basis sets, which can each be employed for the perturbation calculations. The other results which have been reported for neon[4-6] are not directly comparable with the present work.

The many-body perturbation theory[1,2] provides a convenient diagrammatic formulation of Rayleigh-Schrödinger perturbation theory. The diagrams not only offer a pictorial description of correlation effects but also give rise to an extremely efficient algorithm for the numerical determination of the terms in the many-body expansion. This is particularly true when the algebraic approximation is invoked, and allows the range of applicability to be considerably extended for molecules.

Many-body perturbation calculations, using the numerical solution of the Hartree-Fock equations, have been limited to atoms[7] and small hydrides,[8] in which the relatively light hydrogen atoms are treated as further perturbations. Within the algebraic approximation, many-body calculations have been reported for atoms,[9] the hydrogen molecule[10] and some other diatomic molecules.[11] These calculations have all been restricted to the calculation of two-body contributions through third order and, in some cases, a partial or approximate evaluation of both many-body contributions and higher-order terms. The model calculations reported here for the Ne atom are complete through third order within the space spanned by the various basis sets. All two-, three-, and four-body terms are rigorously evaluated. This also allows the determination of an upper bound by substituting the truncated many-body wave function in the Rayleigh quotient.

Section II contains a description of the many-body perturbation theory and its relationship to the method of configuration interaction within the algebraic approximation. The many-body perturbative wave function and the determination of upper bounds are described. In Sec. III, the Ne-atom calculations are described. A comparison of two-body perturbative and certain pair-restricted configuration-interaction calculations is presented first. This comparison is presented because the two-body results are obtained simultaneously as a by-product of the full many-body calculations, because pair configuration-interaction calculations are quite common, and because a pair-by-pair analysis can be made. However, this comparison is only incidental and subordinate to the further comparison that is presented between the full many-body results and the unrestricted singly and doubly excited configuration-interaction results. A short discussion is given in Sec. IV.

II. THEORETICAL CONSIDERATIONS

A. Effective Hamiltonian in a finite subspace

Let S denote the subspace of N-electron Hilbert space spanned by the orthonormal set $\{|\mu\rangle\}$ of N-electron functions which can be constructed from a given set of one-electron basis functions. The projector onto this subspace is

$$I_S=\sum_{\mu=0}^{\eta}|\mu\rangle\langle\mu|,\qquad I_S|\nu\rangle=|\nu\rangle,\quad |\nu\rangle\in S, \tag{1}$$

and the effective Hamiltonian operator[12] in S is $\hat{\mathcal{H}}=I_S\mathcal{H}I_S$. Carets are used to identify operators which have been outer projected onto S. The electronic Hamiltonian is

$$\mathcal{H}=\sum_p h(p)+\sum_{p<q}v(p,q), \tag{2}$$

in which p and q denote electronic coordinates. The one-electron operator h is a sum of the electronic kinetic energy and nuclear-electronic attraction, while v is the two-electron Coulomb repulsion term. The Schrödinger equation, within the algebraic approximation, has the form $\hat{\mathcal{H}}|\psi\rangle=E|\psi\rangle$; $|\psi\rangle\in S$.

The solutions of the effective Schrödinger equation may be written as a superposition of configurations

$$|\psi\rangle=\sum_{\mu=0}^{\eta}C_\mu|\mu\rangle,\quad |\mu\rangle\in S, \tag{3}$$

where the expansion coefficients may be determined in principle by the solution of a secular equation. The method of configuration interaction essentially entails preparing and diagonalizing the matrix $\langle\mu|\hat{\mathcal{H}}|\nu\rangle$ to find its lowest eigenvalue E. In practice, the expansion (3) contains many terms and some arbitrary criterion has to be invoked to truncate it.

The many-body perturbation expansion may be related to the method of configuration interaction as follows. Let P denote the projector onto some model or reference space S_P; let Q denote the projector onto the orthogonal complement S_Q; and then

$$I_S=P+Q;\quad S=S_P\oplus S_Q\,. \tag{4}$$

Substituting Eq. (4) into $\hat{\mathcal{H}}|\psi\rangle=E|\psi\rangle$, multiplying from the left by P or Q and eliminating $Q|\psi\rangle$ from the two resulting equations, yields

$$\hat{G}|\chi\rangle=E|\chi\rangle;\quad |\chi\rangle=P|\psi\rangle;\quad |\chi\rangle\in S_P, \tag{5}$$

with the reference operator

$$\hat{G}=P[\mathcal{H}P+P\mathcal{H}Q(E-Q\mathcal{H}Q)^{-1}Q\mathcal{H}]P\,. \tag{6}$$

Although the eigenfunctions of the reference operator $\hat{G}$ are in the model space S_P of dimension d, the d eigenvalues of $\hat{G}$ are coincident with d of the eigenvalues of $\hat{\mathcal{H}}$. In the many-body perturbation theory, S_P is taken to be one-dimensional and to consist of the lowest-energy configuration $|0\rangle$, in the set $\{|\mu\rangle\}$. The corresponding lowest eigenvalue E is identical to that obtained by dividing the Hamiltonian into two parts, $\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1$, expanding the inverse operator in Eq. (6), and rearranging terms.[13]

B. Closed-shell matrix Hartree-Fock reference functions

Within the algebraic approximation, the integro-differential Hartree-Fock equations become a set of algebraic equations for the orbital expansion coefficients.[14] The N-electron, closed-shell model wave function is $|K\rangle = \det|\varphi_a(1)\varphi_b(2)\ldots\varphi_n(N)|$, where the φ's are spin orbitals, which within the algebraic approximation are expanded in a finite set of basis functions. The ket $|K\rangle$ is an eigenfunction of the model (i.e., matrix Hartree-Fock) Hamiltonian

$$\hat{\mathcal{H}}_{\text{model}} = I_S\left(\sum_p h(p) + \sum_p V^N(p)\right) I_S\,, \tag{7}$$

where V^N is the one-electron self-consistent potential in S.

$$V^N(1) = \sum_{j=1}^{\eta} \int \varphi_j(2)\, O\varphi_j(2)\, dr_2\,, \tag{8}$$

where

$$O = [1-(12)]r_{12}^{-1} \tag{9}$$

and (12) permutes the coordinates of electrons 1 and 2. Thus

$$\hat{\mathcal{H}}_{\text{model}}|K\rangle = \mathcal{E}_K|K\rangle;\quad K\geq 0;\quad \mathcal{E}_K = \sum_k^{\text{in } K} \epsilon_k \tag{10}$$

where ϵ_k is the orbital energy corresponding to φ_k.

The reference state $|0\rangle$ is the eigenfunction having the lowest eigenvalue $\mathcal{E}_0 \equiv E_0$. The functions φ_i in $|0\rangle$ are the occupied orbitals or hole states, and are identified with the set of indices $\{ijk\ldots\}$; the remaining functions are the unoccupied, excited orbitals, or particle states, and are identified with indices $\{abc\ldots\}$. Any determinant $|K\rangle$ is related to $|0\rangle$ by the number of occupied orbitals $\varphi_i\ldots$ that are replaced by unoccupied orbitals $\varphi_a\ldots$ on changing $|0\rangle$ into $|K\rangle$. If this number is t, $|K\rangle$ is a t-tuple excitation. The number of distinct t-tuple excitations is $\binom{N}{t}\binom{M-N}{t}$ where M is the number of spin orbitals in the basis set. Of course summing this product over t gives $\binom{M}{N}=\eta$.

C. Diagrammatic perturbation theory

The many-body perturbation expansion is obtained from Eqs. (5) and (6) using the projectors

$$P = |0\rangle\langle 0|;\quad Q = \sum_{K=1}^{\eta} |K\rangle\langle K|\,. \tag{11}$$

In general, $\hat{\mathcal{H}}_0$ must have the form $\sum |K\rangle\langle K|T|K\rangle\langle K|$, where T is arbitrary. There are an infinite number of possibilities of which two are considered here.

(a) *The model Hamiltonian* is defined by

$$\hat{\mathcal{H}}_0 \equiv \hat{\mathcal{H}}_{\text{model}};\quad \hat{\mathcal{H}}_1 = I_S\left(\sum_{p<q} v(p,q) - \sum_p V^N(p)\right) I_S\,. \tag{12}$$

Clearly $\hat{\mathcal{H}}_{\text{model}}$ of Eq. (7) is diagonal in S since the $|K\rangle$ satisfy Eq. (10). The perturbative expansion for $E = \langle 0|\hat{G}|0\rangle$ can be rearranged to form a power series in $\hat{\mathcal{H}}_1$:

$$E = \sum_{n=0}^{\infty} E_n\,, \tag{13}$$

where the nth-order energy term E_n is proportional to the nth power of matrix elements over $\hat{\mathcal{H}}_1$.

The perturbation series of Eq. (13) has a diagrammatic representation exclusively in terms of linked graphs.[1] The first-order contribution E_1 is given in Fig. 1 and has the value

$$E_1 = \langle 0|\mathcal{H}_1|0\rangle = -\tfrac{1}{2}\sum_{ij}\langle ij|O|ij\rangle\,. \tag{14}$$

By using the operator O defined in Eq. (9), only one diagram from a given set of diagrams related by electron exchange is required. The bracket notation has the usual meaning, i.e.,

$$\langle pq|O|rs\rangle = \int d\tau_1 \int d\tau_2\, \varphi_p^*(1)\,\varphi_q^*(2)\, O\varphi_r(1)\,\varphi_s(2)\,. \tag{15}$$

The use of self-consistent matrix Hartree-Fock orbitals gives rise to an exact cancellation of all single-particle insertions other than in E_1 as shown, diagrammatically in Fig. 2. The ensuing

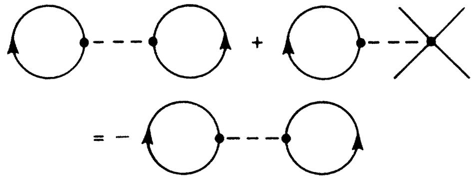

FIG. 1. First-order energy corrections. X represents $-V^N$, where V^N is the Hartree-Fock potential. Interaction lines represent the operator O defined in Eq. (9).

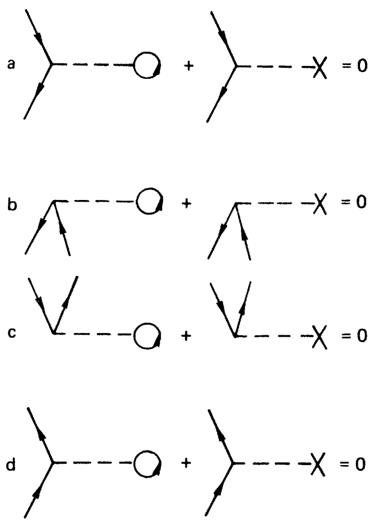

FIG. 2. Single-particle insertions which cancel when the Hartree-Fock model is used in zeroth order. Interaction lines represent the operator O defined in Eq. (9).

simplification is significant for high-order terms, but is already evident for second order where, as shown in Fig. 3, four out of five diagrams vanish leaving

$$E_2=\frac{1}{4}\sum_{ij}\sum_{ab}\langle ij\,|\,O|\,ab\rangle\langle ab|\,O|\,ij\rangle/D_{ijab} \qquad (16)$$

with the denominator

$$D_{ijab}=\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b\,. \qquad (17)$$

The third-order graphs are shown in Fig. 4. The first of these, the particle-particle graph, Fig. 4 A , arises exclusively from two-body interactions:

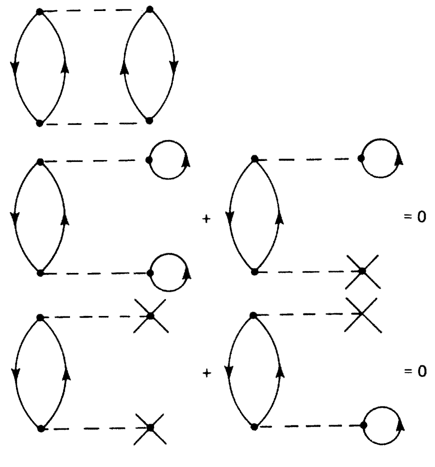

FIG. 3. Second-order energy diagrams. Interaction lines represent the operator O defined in Eq. (9).

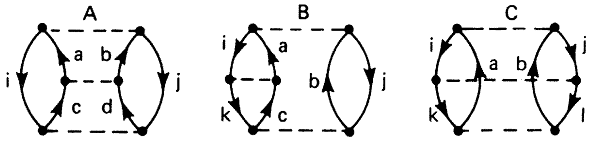

FIG. 4. Third-order energy diagrams. Interaction lines represent the operator O defined in Eq. (9). Hole lines are labeled i j,k,l; particle lines are labeled a, b,c,d. The number of distinct hole lines determine the number of interacting bodies described by the diagram. A is the particle-particle (pp) diagram, B is the hole-particle (hp) diagram, and C is the hole-hole (hh) diagram.

$$E_3(pp)=\frac{1}{8}\sum_{ij}\sum_{abcd}\langle ij\,|\,O|\,ab\rangle\langle ab|\,O|\,cd\rangle \times\langle cd|\,O|\,ij\rangle/D_{ijab}D_{ijcd}\,. \qquad (18)$$

Only two occupied orbitals are involved in this contribution. The hole-particle graph, Fig. 4 B , has both two-body and three-body components

$$E_3(hp)=-\sum_{ijk}\sum_{abc}\langle ij\,|\,O|\,ab\rangle\langle ka|\,O|\,ic\rangle \times\langle cb|\,O|\,kj\rangle/D_{ijab}D_{jkbc}\,. \qquad (19)$$

Three-body terms correspond to the case where i, j, and k are distinct, whereas the two-body contribution arises when $i=k$. The hole-hole graph, Fig. 4 C , involves two-, three-, or four-body interactions depending on the coincidence of the hole indices:

$$E_3(hh)=\frac{1}{8}\sum_{ijkl}\sum_{ab}\langle ij\,|\,O|\,ab\rangle \times\langle kl|\,O|\,ij\rangle\langle ab|\,O|\,kl\rangle/D_{ijab}D_{klab}\,. \qquad (20)$$

Two-body terms arise when $i=k$ and $j=l$ or $i=l$ and $j=k$, while for three-body terms $i=k$, $i=l$, $j=k$ or $j=l$. Four-body terms are those for which i, j, k, l are all distinct.

(b) *The shifted Hamiltonian* is defined by

$$\mathcal{H}'_0\equiv\mathcal{H}_{\text{shifted}}=\mathcal{H}_{\text{model}}+\sum_{K=0}^{\eta}|K\rangle\langle K|\mathcal{H}_1|K\rangle\langle K|\,. \qquad (21)$$

Hence,

$$\mathcal{H}'_0=\sum_{K=0}^{\eta}|K\rangle\langle K|\mathcal{H}|K\rangle\langle K|\,;$$
$$\mathcal{H}'_1=\sum_{K\neq L=0}^{\eta}|K\rangle\langle K|\mathcal{H}|L\rangle\langle L|\,. \qquad (22)$$

The following relations follow immediately,

$$E=\sum_{n=0}^{\infty}E'_n;\quad E'_0=E_0+E_1;\quad E'_1=0\,. \tag{23}$$

Obviously, the infinite-order result does not depend on the choice of $\hat{\mathcal{H}}_0$. By using a second division of $\hat{\mathcal{H}}$, a qualitative measure of the convergence of the series is obtained. The shifted diagrammatic expansion is the same as that outlined above except that (i) all diagonal scattering is excluded and (ii) the denominator factors D_{ijab} are "shifted":

$$\begin{aligned}D'_{ijab}=\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b&-\langle ij\,|\,O|\,ij\rangle-\langle ab|\,O|\,ab\rangle\\&-\langle ai\,|\,O|\,ia\rangle-\langle bi\,|\,O|\,ib\rangle\\&-\langle aj\,|\,O|\,ja\rangle-\langle bj\,|\,O|\,jb\rangle\,.\end{aligned}\tag{24}$$

Two-, three-, and four-body graphs arise as discussed in the preceding section. However, the two-body hole-hole graphs vanish since these diagrams all arise from diagonal interactions.

It should be noted that both perturbation schemes are defined with respect to single-determinant states $|K\rangle$. Although the individual determinants may not necessarily be eigenfunctions of the spin or orbital angular momentum operators of interest, the summations over K are not truncated and therefore range over all permitted values. Hence, the correct linear combination of determinants is always obtained corresponding to the use of proper angular momentum eigenfunctions. This choice of reference states $|K\rangle$ causes the specifically defined energy denominators of Eqs. (17) and (24) to accompany the perturbation schemes. Of course, in infinite order, this choice is equivalent to choosing multideterminantal angular momentum eigenfunctions for $|K\rangle$, assuming the perturbation series are convergent.

D. Many-body perturbative wave function. Upper bounds to the energy.

The many-body perturbation theory generates a wave function having the form

$$|\psi\rangle=\sum_{m=0}^{\infty}|\psi_m\rangle\,, \tag{25}$$

where the mth-order correction $|\psi_m\rangle$ is proportional to the mth power of matrix elements over $\hat{\mathcal{H}}_1$, and $|\psi_0\rangle$ is the reference state $|0\rangle$. The diagrammatic representation of $|\psi\rangle$ contains only linked graphs: contributions through second order are given in Fig. 6. Truncation of this infinite series for $|\psi\rangle$ after n terms produces an approximate wave-function $|\Phi_n\rangle$. In general, the function $|\Phi_n\rangle$ is not normalized, although a normalization factor can be introduced.[15] Inserting $|\Phi_n\rangle$ into the Rayleigh quotient yields a variational upper bound for the eigenvalue[16]

$$E_{\text{exact}}\leq E_{\text{var}}=\langle\Phi_n|\hat{\mathcal{H}}|\Phi_n\rangle/\langle\Phi_n|\Phi_n\rangle\,. \tag{26}$$

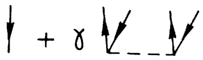

FIG. 5. Diagrammatic representation of Eq. (27).

In the present work, the wave function is truncated at first-order $|\Phi_1\rangle$. Since this wave function has a simple form, an additional variational parameter γ is easily incorporated:

$$|\Phi_1\rangle=|0\rangle+\gamma|\psi_1\rangle, \tag{27}$$

which is given the diagrammatic representation shown in Fig. 5. After some manipulation, Eq. (26) becomes

$$\begin{aligned}E_{\text{exact}}\leq E_{\text{var}}(\gamma)=E_0+E_1&\\+[(2\gamma-\gamma^2)E_2+\gamma^2E_3]/(1+\gamma^2\Delta_{11})&\end{aligned}\tag{28}$$

where the overlap term Δ_{11} is

$$\Delta_{11}=\frac{1}{4}\sum_{ij}\sum_{ab}\langle ij\,|\,O|\,ab\rangle\langle ab|\,O|\,ij\rangle/D^2_{ijab}\,. \tag{29}$$

A different wave function corresponds to each perturbation scheme. Hence there is a $|\Phi_1\rangle$ corresponding to the model scheme and another $|\Phi'_1\rangle$ corresponding to the shifted perturbation procedure. The optimal value of the parameter γ is obtained from the variation principle

$$\gamma_{\text{optimal}}=\Delta_{11}^{-1}[\pm(\zeta^2+\Delta_{11})^{1/2}-\zeta];\quad\zeta=\tfrac{1}{2}[1-(E_3/E_2)]\,. \tag{30}$$

III. A STUDY OF THE NEON ATOM

A. Basis sets

Three different one-electron basis sets were used. These sets have been used previously for detailed configuration-interaction studies.[3] The real normalized Slater basis functions are given in Table I, together with the corresponding matrix Hartree-Fock energies and values of η. Set A is a "double-zeta" basis,[17] Set B is a "Hartree-Fock" basis,[18] and Set C is composed of Set A plus additional s, p, and d functions.[3] Set B gives the lowest matrix Hartree-Fock energy while Set C gives the best description of the correlation of the electrons. Set C includes d functions and these have an important effect in describing electron correlation. These basis sets are quite modest in size and are not flexible enough to yield high absolute accuracy. However, they are adequate for comparitive purposes. The values of η, the dimension of the space S for each of the basis sets given in Table I, take no account of orthogonalities. Spin and spatial symmetry orthogonalities

TABLE I. Basis sets of real normalized Slater functions for neon.

Basis set	Ref.	Matrix Hartree-Fock energy (hartrees)	Function	Exponents	η, dimension of subspace S
A	a	−128.534 80	1s	8.9141, 12.3545	1.8×10^5
			2s	2.1839, 3.4921	
			2p	2.0514, 4.6748	
B	b	−128.547 01	1s	9.5735, 15.4496	2.5×10^8
			2s	1.9550, 2.8462, 4.7746, 7.7131	
			2p	1.4700, 2.3717, 4.4545, 9.4550	
C	c	−128.538 72	1s	8.9141, 12.3545	8.5×10^8
			2s	2.1839, 3.4921, 8.9141	
			3s	2.1839	
			2p	2.0514, 4.6748, 12.3545	
			3d	4.6748	

[a] E. Clementi, J. Chem. Phys. 40, 1944 (1964).

[b] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. 127, 1618 (1962).

[c] T. L. Barr, and E. R. Davidson, Phys. Rev. A 1, 664 (1970).

greatly reduce the number of terms which have to be included in a complete configuration interaction expansion for the ground state.

The use of matrix Hartree-Fock orbitals leads to the cancellation of the class of diagrams shown in Fig. 2 and eliminates the entry through third order in the energy of any single excitation determinant $|K'\rangle$, where K' denotes the excitation from an occupied orbital i to an excited orbital a. The only determinants that can enter the perturbation series through third order in the energy are doubly excited states $|K''\rangle$, where K'' denotes the simultaneous excitation from two occupied orbitals i and j to two excited orbitals a and b (denoted by $ij\rightarrow ab$). In Fig. 7 the structure of the configuration interaction matrix and its relationship to the terms in the perturbation expansion is illustrated. The number of possible double excitations obtainable from the three basis sets is ~2×10^3, 15×10^3, and 20×10^3 respectively; however, spin and spatial orthogonalities reduce these numbers to ~140, 925, and 1750.

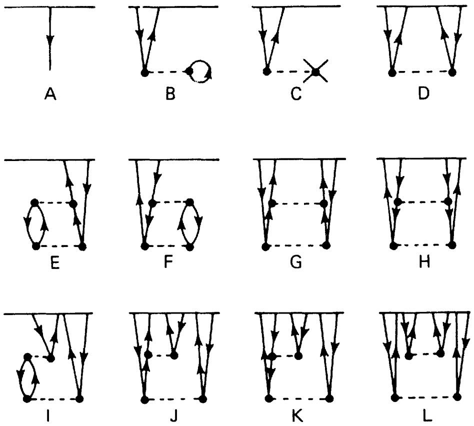

FIG. 6. Contributions to the many-body perturbative wave function through second order where interaction lines represent O defined in Eq. (9). Diagram A is zeroth order, B-D are first order, and E-K are second order. If X represents $-V^N$, where V^N is the Hartree-Fock potential, diagrams B and C cancel. Of the second-order diagrams, E and F involve single-excitations, G, H, and I involve doubly-excited states, J and K involve triply-excited states, and L involves quadruple excitations. Second-order diagrams which mutually cancel are not given.

B. Results of perturbation calculations

The energy contributions corresponding to the diagrams of Figs. 3 and 4 and Eqs. (14)–(20) are given in Table II. Values of the overlap Δ_{11}, Eq. (29), are also given. The relative importance of the various components is evident.

Intra-pair contributions involve, exclusively, a single pair of hole states and therefore represent two-body effects. The intrapair diagonal terms arise from diagrams having not only a single pair of hole lines but also a single pair of particle lines (i.e., diagonal scattering). When the zeroth-order Hamiltonian is $\hat{\mathcal{H}}_{\text{shifted}}$, all such diagonal terms are identically zero. The intra-pair, non-diagonal terms correspond to interactions between two states $ij\rightarrow ab$ and $ij\rightarrow cd$ both involving excitations from the same ij pair.

The two-body terms, especially the diagonal ones, make the major contribution to the energy correction. Three- and four-body terms are associated with inter-pair interactions. Three-body effects arise from inter-pair interactions involving pairs with a common occupied orbital, for instance, $ij\rightarrow ab$ and $ik\rightarrow ac$. If two pairs have no

TABLE II. Components of the perturbation expansions for neon.[a]

Basis set[b]	A		B		C	
$\hat{\mathcal{H}}_0$	$\hat{\mathcal{H}}_{\text{model}}$	$\hat{\mathcal{H}}_{\text{shifted}}$	$\hat{\mathcal{H}}_{\text{model}}$	$\hat{\mathcal{H}}_{\text{shifted}}$	$\hat{\mathcal{H}}_{\text{model}}$	$\hat{\mathcal{H}}_{\text{shifted}}$
Intra-pair energies: diagonal terms (two-body)						
E_2^2	−0.137 14	−0.165 12	−0.179 18	−0.207 70	−0.250 52	−0.290 56
$E_3^2(pp)$	+0.014 98	0.0	+0.012 89	0.0	+0.021 11	0.0
$E_3^2(hp)$	−0.052 74	0.0	−0.060 01	0.0	−0.076 00	0.0
$E_3^2(hh)$	+0.014 87	0.0	+0.023 17	0.0	+0.021 28	0.0
Total	−0.160 03	−0.165 12	−0.203 13	−0.207 70	−0.284 13	−0.290 56
Intra-pair interactions: nondiagonal terms (two-body)						
$E_3^2(pp)$	+0.000 93	+0.001 36	+0.007 90	+0.010 88	+0.005 78	+0.007 81
$E_3^2(hp)$	−0.000 29	−0.000 34	−0.012 43	−0.017 57	−0.003 02	−0.003 94
Total	+0.000 64	+0.001 02	−0.004 53	−0.006 69	+0.002 76	+0.003 87
Inter-pair interactions between pairs having a common hole state (three body)						
$E_3^3(hp)$	+0.024 18	+0.036 14	+0.031 82	+0.046 22	+0.029 89	+0.043 48
$E_3^3(hh)$	+0.000 05	+0.000 06	+0.000 11	+0.000 12	+0.000 10	+0.000 11
Total	+0.024 23	+0.036 20	+0.031 92	+0.046 34	+0.029 99	+0.043 59
Inter-pair interactions between pairs having no common hole states (four body)						
$E_3^4(hh)$	+0.001 07	+0.001 62	+0.001 45	+0.002 01	+0.001 58	+0.002 21
Overlap Δ_{11}	+0.015 21	+0.022 85	+0.023 29	+0.033 87	+0.021 20	+0.030 58

[a] The energy terms are labelled with subscripts to denote order and superscripts to denote number of interacting bodies. Energies are in hartrees.

[b] From Table I.

common orbital, $ij \rightarrow ab$ and $kl \rightarrow ab$, then a four-body inter-pair interaction arises. Although the contribution from a given set ijk, or $ijkl$, may be small the total sum of such many-body terms can by no means be ignored, since the number of such terms is in general large.

The convergence of the perturbation series is displayed both as a function of number of interacting bodies and of increasing order in Table III. The convergence with the number of interacting bodies needs to be examined with caution, however, since only contributions through third order have been included in a given term E^b. As higher orders are computed, additional contributions are obtained for each $b \geq 2$. On the other hand, all two-, three-, and four-body contributions to the terms for a given order have been included and the convergence by order is exact. For all three

TABLE III. Convergence of the perturbation series.[a]

Basis set[b]	A		B		C	
$\hat{\mathcal{H}}_0$	$\hat{\mathcal{H}}_{\text{model}}$	$\hat{\mathcal{H}}_{\text{shifted}}$	$\hat{\mathcal{H}}_{\text{model}}$	$\hat{\mathcal{H}}_{\text{shifted}}$	$\hat{\mathcal{H}}_{\text{model}}$	$\hat{\mathcal{H}}_{\text{shifted}}$
Convergence with increasing number of interacting bodies.						
E^1	−74.418 35	−128.534 80	−74.509 42	−128.547 01	−74.475 64	−128.538 72
E^2	−54.275 82	−0.164 10	−54.245 24	−0.214 39	−54.344 44	−0.286 69
E^3	+0.024 23	+0.036 20	+0.031 92	+0.046 34	+0.029 99	+0.043 59
E^4	+0.001 07	+0.001 62	+0.001 45	+0.002 01	+0.001 58	+0.002 21
Convergence with increasing order.						
E_0	−74.418 35	−128.534 80	−74.509 42	−128.547 01	−74.475 64	−128.538 72
E_1	−54.116 44	0.0	−54.037 59	0.0	−54.063 08	0.0
E_2	−0.137 14	−0.165 12	−0.179 18	−0.207 70	−0.250 52	−0.290 56
E_3	+0.003 05	+0.038 85	+0.004 90	+0.041 67	+0.000 72	+0.049 67

[a] The energy E^m is a sum of all m-body contributions through third order; E_n is the nth-order energy. Energies are in hartrees.

[b] From Table I.

TABLE IV. Comparison of perturbation two-body pair energies and pair-excited configuration interaction energies for neon.[a]

Basis set[b]	*A*			*B*			*C*		
Method $\hat{\mathcal{H}}_0$	Perturbation theory $\hat{\mathcal{H}}_{\text{model}}$	Perturbation theory $\hat{\mathcal{H}}_{\text{shifted}}$	Configuration interaction[c]	Perturbation theory $\hat{\mathcal{H}}_{\text{model}}$	Perturbation theory $\hat{\mathcal{H}}_{\text{shifted}}$	Configuration interaction[c]	Perturbation theory $\hat{\mathcal{H}}_{\text{model}}$	Perturbation theory $\hat{\mathcal{H}}_{\text{shifted}}$	Configuration interaction[c]
1*s*-1*s* *K* shell	−0.011 96	−0.011 97	−0.011 97	−0.028 16	−0.028 21	−0.028 21	−0.031 59	−0.031 64	−0.031 70
1*s*-2*s*	−0.001 81	−0.001 81	−0.001 81	−0.003 71	−0.003 72	−0.003 70	−0.003 98	−0.003 99	−0.003 98
1*s*-2*p*	−0.001 91	−0.001 92	−0.001 89	−0.006 28	−0.006 31	−0.006 21	−0.012 79	−0.012 85	−0.012 66
K-*L* interaction	−0.003 72	−0.003 73	−0.003 70	−0.009 99	−0.010 03	−0.009 91	−0.016 77	−0.016 84	−0.016 64
2*s*-2*s*	−0.003 98	−0.004 06	−0.004 06	−0.005 07	−0.005 14	−0.005 14	−0.008 23	−0.008 29	−0.008 38
2*s*-2*p*	−0.041 62	−0.043 05	−0.040 51	−0.048 41	−0.049 91	−0.047 02	−0.051 23	−0.052 61	−0.050 29
2*p*-2*p*	−0.098 10	−0.101 28	−0.096 07	−0.116 02	−0.121 10	−0.113 45	−0.173 54	−0.177 31	−0.169 66
L shell	−0.143 70	−0.148 39	−0.140 64	−0.169 50	−0.176 15	−0.165 61	−0.233 00	−0.238 21	−0.228 33
Sum of pairs	−0.159 38	−0.164 09	−0.156 31	−0.207 65	−0.214 39	−0.203 73	−0.281 36	−0.286 69	−0.276 67

[a] Energies are in hartrees.

[b] From Table I.

[c] T. L. Barr and E. R. Davidson, Phys. Rev. A 1, 644 (1970).

basis sets, the use of $\hat{\mathcal{H}}_0 = \hat{\mathcal{H}}_{\text{model}}$ gives more rapid convergence.

C. Comparison of pair energies

The pair energies obtained from two-body perturbation calculations are compared with the pair-excited configuration interaction results of Barr and Davidson[3] in Table IV. Each calculation uses the matrix Hartree-Fock orbitals for a particular basis set and use the corresponding matrix Hartree-Fock energy as a reference for the energy correction.

The perturbation result is obtained by restricting the calculation to the inclusion of all two-body components arising in second and third order (Figs. 3 and 4) for a given orbital pair. The $1s-1s$ and $2s-2s$ terms each consist of a single spin-orbital pair, while the $1s-2s$ term consists of a sum of the four corresponding component spin-orbital pairs. Terms involving the $2p$ orbitals contain an additional sum over the spatial components of this function. Only doubly excited configurations enter the perturbation series through third order.

The configuration-interaction pair excitation energies were obtained[3] by performing a separate calculation for each orbital pair with a wave function of the form

$$|\psi_{ij}\rangle = |0\rangle + \sum_a C_{ia}|i\rightarrow a\rangle + \sum_b C_{jb}|j\rightarrow b\rangle + \sum_{ab} C_{ijab}|ij\rightarrow ab\rangle . \tag{31}$$

The energies given in Table IV are the differences between the eigenvalues corresponding to $|\psi_{ij}\rangle$ and $|0\rangle$. Equation (31) includes contributions from single excitations $i\rightarrow a$ and refers to orbital pairs rather than spin-orbital pairs. The latter has no consequence for the terms $1s-1s$ and $2s-2s$. For terms such as $1s-2s$ having more than one spin component, this includes some interactions between different spin-orbital pairs; for example, $1s\alpha, 1s\beta, 2s\alpha$ and $1s\alpha, 1s\beta, 2s\alpha, 2s\beta$: these are three- and four-body contributions, respectively.

The present work is concerned only with a numerical comparison of results obtained from the above two definitions, although other definitions of pair energies exist.[19]

For a given basis set, the perturbation and configuration-interaction pair results in Table IV are in remarkable agreement for the $1s-1s$, $1s-2s$, $1s-2p$, and $2s-2s$ terms. Thus, the higher-order effects and single excitations are negligible for these pairs when compared to the two-body third-order perturbation result. For the $2s-2p$

and $2p-2p$ terms the perturbation results are consistently lower than configuration interaction and the model scheme is closer to configuration interaction than the shifted scheme. The inclusion of the positive three- and four-body contributions within an orbital pair must account for this difference.

The total "sum-of-pairs" energy is within 0.005 Hartrees for the model perturbation and pair configuration-interaction schemes, the source of the deviation arising within the treatment of the $2p$ orbital. The shifted scheme gives a "sum-of-pairs" energy that is another 0.005 Hartree lower than the model scheme. Since none of these pair calculations are bounded, the variation principle cannot be invoked to choose one or another of these results to be the best one. Indeed, in view of the magnitude of many-body terms the "sum-of-pairs" energy is not particularly useful. However pair analyses do provide a means of making detailed comparisons of methods.

D. Comparison of many-body perturbation and configuration interaction calculations

The basis sets of Table I have been used by Barr and Davidson[3] to perform configuration-interaction calculations, which they refer to as "total pair excitation block" (TPEB) calculations. It should be noted that these calculations correspond to the general configuration-interaction procedure, Eq. (3), with the single restriction of including all singly and doubly excited states. A comparison of these calculations with the perturbation results is given in Table V.

The two-body energy corrections overestimate the configuration-interaction values by 14–23%. The three- and four-body effects in third order account for most of this difference and the total third-order perturbation results are within 0.2–5.5% of the configuration-interaction results. Half the perturbation results overestimate and the other half underestimate the configuration-interaction values. The model scheme gives closer agreement in each case.

It has been suggested[20] that the $[n+1/n]$ Padé approximants form a more appropriate approximation to the energy expectation value than the $(2n+1)$th-order Taylor series, although both have residual contributions of order $2n+2$. From the third-order expansion, the $[2/1]$ Padé approximant may be written in terms of the energy coefficients

$$E[2/1]=E_0+E_1+\frac{E_2}{1-(E_3/E_2)}\,, \tag{32}$$

TABLE V. Comparison of full single- and double-excitation configuration-interaction energy corrections for neon with many-body perturbation values, the [2/1] Padé approximants and the many-body upper bounds.[a]

Basis set[b]	*A*		*B*		*C*	
$\hat{\mathcal{H}}_0$	$\hat{\mathcal{H}}_{\text{model}}$	$\hat{\mathcal{H}}_{\text{shifted}}$	$\hat{\mathcal{H}}_{\text{model}}$	$\hat{\mathcal{H}}_{\text{shifted}}$	$\hat{\mathcal{H}}_{\text{model}}$	$\hat{\mathcal{H}}_{\text{shifted}}$
	Configuration interaction[c] (single and double excitations)					
(CI)	−0.133 56		−0.174 65		−0.247 60	
	Restricted perturbation (two-body)					
$E_2+E_3^2$	−0.159 38	−0.164 09	−0.207 65	−0.214 39	−0.281 36	−0.286 69
(% CI)	(119.3)	(122.9)	(118.9)	(122.8)	(113.6)	(115.8)
	Full many-body perturbation (two-, three-, and four-body)					
E_2+E_3	−0.134 08	−0.126 27	−0.174 28	−0.166 04	−0.249 79	−0.240 89
(% CI)	(100.4)	(94.5)	(99.8)	(95.1)	(100.9)	(97.3)
	Padé approximant for many-body perturbation					
$E[2/1]$	−0.134 15	−0.133 67	−0.174 41	−0.173 00	−0.249 79	−0.248 14
(% CI)	(100.4)	(100.1)	(99.9)	(99.1)	(100.9)	(100.2)
	Many-body perturbative upper bound					
$E_{\text{var}}(\gamma=1)$	−0.132 07	−0.123 45	−0.170 31	−0.160 60	−0.244 61	−0.233 74
(% CI)	(98.9)	(92.4)	(97.5)	(92.0)	(98.8)	(94.4)
	Optimized many-body perturbative upper bound					
γ optimal	0.964 38	0.797 77	0.952 82	0.814 21	0.976 94	0.835 77
$E_{\text{var}}(\gamma=\text{opt})$	−0.132 25	−0.131 72	−0.170 72	−0.169 11	−0.244 74	−0.242 84
(% CI)	(99.0)	(98.6)	(97.7)	(96.8)	(98.8)	(98.1)

[a] Energies are in hartrees.

[b] From Table I.

[c] T. L. Barr and E. R. Davidson, Phys. Rev. A 1, 644 (1970).

which has the form of a sum of a geometric series and is, therefore, often referred[10] to as the "geometric approximation." However, this name does not reflect the nature of the perturbation expansion since higher-order terms obtained by expanding the denominator in Eq. (32) *do not* correspond to higher-order terms in the perturbation expansion.

The [2/1] Padé approximants to the energy expansion are within 0.9% of the configuration interaction results. The use of this approximant gives a significant change in the results obtained for the shifted scheme, which has the effect of bringing the model and shifted scheme in closer agreement. This agreement is suggestive that the result is independent of the particular splitting of $\mathcal{H}$ chosen for the calculations and is a measure of the rapid convergence of the perturbation series.

Rigorous many-body upper bounds to the expectation value of the energy are also reported in Table V. These were obtained by evaluating the Rayleigh quotient as discussed in Sec. II D. Results are given for both $\lambda = 1$ and the optimal value given by Eq. (30). In all cases, the $\mathcal{H}_{\text{model}}$ scheme gives a result closer to the configuration interaction number, and an optimal value of λ closer to one.

There are two sources of the deviation between the many-body upper bounds and configuration interaction results: (i) the inclusion of single-excitation configurations in configuration interaction; (ii) the inclusion of higher-order effects in the configuration interaction expansion. However, these effects are seen to be very small.

IV. DISCUSSION

In the present study, the evaluation within the algebraic approximation of all diagrams in the many-body perturbation series for the energy through third order, including all two-, three-, and four-body contributions, is discussed. The absolute accuracy of the results obtained is dependent upon the quality of the basis set employed. The present model calculations are concerned with the comparison of the method of configuration interaction and many-body perturbation theory when the same basis set is used in both schemes.

Two-body perturbation calculations and pair configuration-interaction results are found to be in good agreement. The analysis in terms of pair energies permits a detailed comparison of these methods. The major source of deviation in Table IV arises from the inclusion of some three- and four-body effects in the pair configuration-interaction calculation arising from the use of spatial orbital configurations in the latter.

Three-body effects in many-body perturbation theory have been discussed for atoms and molecules.[21] For nuclear matter, such components have been estimated to have a magnitude of 3–6% of the two-body energy.[22] The inclusion of three- and four-body contributions in the present work changes the two-body correction by as much as 28%. Many-body terms are clearly important for the correct evaluation of the energy and are most probably equally important for other properties.

The [2/1] Padé approximants for the model and shifted perturbation schemes have been found to be in closer agreement with each other than the corresponding Taylor series. Since the infinite-order result is independent of the choice of zeroth-order Hamiltonian, this suggests that the $[n+1/n]$ Padé approximant provides a more rapidly convergent representation of the energy.

The inclusion of all many-body effects through third order permits the determination of rigorous upper bounds to the total energy. The agreement of the many-body upper bounds with the singly and doubly excited configuration-interaction results to within 3% is demonstrated. The major source of deviation is the inclusion of single-excitation configurations in the configuration-interaction calculations. If the perturbation series were car-

	$\lvert 0\rangle$	$\lvert K'\rangle$	$\lvert K''\rangle$	$\lvert K'''\rangle$	$\lvert K''''\rangle$
$\lvert 0\rangle$	0	–	2	–	–
$\lvert K'\rangle$	–	5	4	5	–
$\lvert K''\rangle$	2	4	3	4	4
$\lvert K'''\rangle$	–	5	4	5	5
$\lvert K''''\rangle$	–	–	4	5	5

FIG. 7. Relationship of configuration interaction matrix to terms in the perturbation expansion. $\lvert 0\rangle$ denotes the ground state configuration; $\lvert K'\rangle$, $\lvert K''\rangle$, $\lvert K'''\rangle$, and $\lvert K''''\rangle$ denote singly-, doubly-, triply-, and quadruply-excited configurations. The figures indicate the order in the perturbation series at which a given block of the configuration-interaction matrix first contribute. Thus, for example, matrix elements of the form $\langle K'\lvert\mathcal{H}\rvert K''\rangle$ first arise in fourth order in the perturbation expansion.

ried through fifth order, this would correspond to a second-order many-body wave function and would include the effect of single, double, triple, and quadruple excitations as shown in Fig. 6.

The shifted scheme arose in many-body perturbation theory as an attempt to include higher-order diagonal diagrams in low-order terms through denominator shifts. The shifted scheme represents the case of a different splitting of $\hat{\mathcal{H}}$ which produces a better unperturbed energy result than the model scheme. Nevertheless, the $\hat{\mathcal{H}}_{\text{model}}$ procedure gives closer agreement with configuration interaction than the shifted scheme in all of the present calculations.

Many-body effects are found to be larger when $\hat{\mathcal{H}}_{\text{shifted}}$ is used as a zeroth-order Hamiltonian. Two-body effects are also larger for this scheme; the total third-order results from the two perturbation schemes being in relatively close agreement. Two-body perturbation calculations using $\hat{\mathcal{H}}_{\text{shifted}}$ have been observed to be "closer to experiment." This is obviously because the positive many-body terms being neglected are larger. It is interesting to note the agreement between the second-order energies and the full third-order values. These figures differ by only 2–3% for the $\hat{\mathcal{H}}_{\text{model}}$ scheme, whereas the corresponding numbers for the $\hat{\mathcal{H}}_{\text{shifted}}$ scheme differ by 20–25%. However, such behavior can only be observed *after* a third-order calculation has been performed.

It is important to remember that the perturbation calculations are not iterative and are computationally tractable. The calculations reported here were performed on an IBM 360/91 computer, in a multiprogramming environment. Some computer CPU time requirements are given below to illustrate the efficiency of the diagrammatic scheme. The integrals[23] over the basis sets A, C of Table I are computed in ~0.2, 0.9 sec respectively. The self-consistent field procedure[24] and transformation[24] of integrals to the matrix Hartree-Fock orbital basis take ~1.5, 7 sec and processing of the integrals on external storage takes ~2.5, 4 sec for Sets A, C. Finally, the evaluation of all the diagrams[25] through third-order including many-body contributions and overlap terms for both perturbation expansions together takes ~2, 6 sec for Sets A, C respectively. The time requirements for Set B are only slightly less than for Set C.

The present results have been obtained for an atom. However, just as for the method of configuration interaction within the algebraic approximation, there is no difference between an atomic and molecular problem once the integrals over the operators in $\mathcal{H}$ with respect to the basis set have been evaluated. Since these integrals can be evaluated for functions centered on the various nuclei in a molecule, the algebraic approximation introduces an enormous flexibility into the range of applicability of many-body perturbation theory to molecular problems.

ACKNOWLEDGMENT

The efficient service of the computer center at The Johns Hopkins University Applied Physics Laboratory is gratefully acknowledged. This work was supported by the Department of the Navy, Naval Sea Systems Command, under Contract No. N00017-72-C4401.

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[1] K. A. Brueckner, Phys. Rev. 100, 36 (1955); J. Goldstone, Proc. R. Soc. A 239, 267 (1957).

[2] N. H. March, W. H. Young, and S. Sampanthar, *The Many-Body Problem in Quantum Mechanics*, (Cambridge U. P., London, 1967).

[3] T. L. Barr and E. R. Davidson, Phys. Rev. A 1, 644 (1970).

[4] R. K. Nesbet, T. L. Barr, and E. R. Davidson, Chem. Phys. Lett. 4, 203 (1969); J. W. Viers, F. E. Harris, and H. F. Schaefer, Phys. Rev. A 1, 24 (1970); C. F. Bunge and E. M. A. Peixota, Phys. Rev. A 1, 1277 (1970); A. Weiss, Phys. Rev. A 3, 126 (1971); F. Sasaki and M. Yoshimine, Phys. Rev. A 9, 17 (1974); R. Ahlrichs, F. Driessler, V. Staemmler, and W. Kutzelnigg, J. Chem. Phys. 62, 1235 (1974).

[5] R. K. Nesbet, Phys. Rev. 155, 56 (1967); 175, 2 (1968); C. Matsubara, Phys. Rev. A 1, 561 (1970); C. M. Moser and R. K. Nesbet, Phys. Rev. A 6, 1710 (1972).

[6] H. P. Kelly, Phys. Rev. 144, 39 (1966); D. A. Micha, Phys. Rev. A 1, 755 (1970); T. Lee, N. C. Dutta, and T. P. Das, Phys. Rev. A 4, 1410 (1971).

[7] H. P. Kelly, Phys. Rev. 131, 684 (1963); 136, B896 (1964); E. S. Chang, R. T. Pu, and T. P. Das, Phys. Rev. 174, 16 (1968); N. C. Dutta, C. Matsubara, R. T. Pu, and T. P. Das, Phys. Rev. 177, 33 (1969); T. Lee, N. C. Dutta, and T. P. Das, Phys. Rev. A 1, 995 (1970).

[8] H. P. Kelly, Phys. Rev. 23, 455 (1969); Phys. Rev. A 1, 274 (1970); J. H. Miller and H. P. Kelly, Phys. Rev. Lett. 26, 679 (1971); T. Lee, N. C. Dutta, and T. P. Das, Phys. Rev. Lett. 25, 204 (1970); C. M. Dutta, N. C. Dutta, and T. P. Das, Phys. Rev. Lett. 25, 1695 (1970); T. Lee and T. P. Das, Phys. Rev. A 6, 968 (1972).

[9] U. Kaldor, Phys. Rev. A 7, 427 (1973); J. S. Binkley and J. A. Pople, Int. J. Quant. Chem. 9, 229 (1975).

[10] J. M. Schulman and D. N. Kaufman, J. Chem. Phys. 53, 477 (1970); U. Kaldor, Phys. Rev. Lett. 31, 1338 (1973); J. Chem. Phys. 62, 4634; 63, 2199 (1975).

[11] R. J. Bartlett and D. M. Silver, Int. J. Quant. Chem. Symp. 8, 271 (1974); 10, 185 (1976); Phys. Rev. A 10, 1927 (1974); 13, 912 (1976); Chem. Phys. Lett. 29,

199 (1974); 37, 198 (1976); J. Chem. Phys. 62, 3258 (1975); 64, 1260, 4578 (1976); D. M. Silver and R. J. Bartlett, Phys. Rev. A 13, 1 (1976); P. Stern and U. Kaldor, J. Chem. Phys. 64, 2002 (1976); D. L. Freeman and M. Karplus, J. Chem. Phys. 64, 2641 (1976).

[12] A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1970), Vol. 2, Chapter 18.

[13] P.-O. Löwdin, Phys. Rev. 139, A357 (1968).

[14] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

[15] J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Adv. Quant. Chem. 1, 255 (1964).

[16] W. H. Young and N. H. March, Phys. Rev. 109, 1854 (1958); A. Dalgarno and A. L. Stewart, Proc. Phys. Soc. Lond. 77, 467 (1961); O. Goscinski and E. Brandas, Chem. Phys. Lett. 2, 299 (1968); R. J. Bartlett and D. M. Silver, Int. J. Quant. Chem. Symp. 9, 183 (1975).

[17] E. Clementi, J. Chem. Phys. 40, 1944 (1964).

[18] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. 127, 1618 (1962).

[19] O. Sinanoğlu, J. Chem. Phys. 36, 706, 3198 (1962); R. K. Nesbet, Adv. Chem. Phys. 9, 321 (1965); Phys. Rev. 155, 51 (1967); 175, 2 (1968); H. F. Schaefer III, *The Electronic Structure of Atoms and Molecules* (Addison-Wesley, Reading, Ma., 1972).

[20] S. Wilson, D. M. Silver, and R. A. Farrell, Special Invariance Properties of the $[N+1/N]$ Padé Approximants in Rayleigh-Schrödinger Perturbation Theory (to be published).

[21] H. P. Kelly, Advan. Chem. Phys. 14, 129 (1969); K. Freed, Phys. Rev. 173, 1 (1968); Ann. Rev. Phys. Chem. 22, 313 (1971); N. C. Dutta and C. M. Dutta, Phys. Rev. A 6, 959 (1972).

[22] H. A. Bethe, Phys. Rev. 138, B804 (1965); R. Rajaraman and H. A. Bethe, Rev. Mod. Phys. 39, 745 (1967).

[23] D. M. Silver, J. Phys. (Paris) 32, 129 (1971).

[24] R. M. Stevens, J. Chem. Phys. 52, 1397 (1970); R. K. Nesbet, Rev. Mod. Phys. 35, 552 (1963).

[25] D. M. Silver, Diagrammatic Many-Body Perturbation Expansion for Atoms and Molecules: General Organization, and Second-Order and Third-Order Ladder Energies (to be published); S. Wilson, Diagrammatic Many-Body Perturbation Expansion for Atoms and Molecules: Third-Order Hole-Particle Energies (to be published).