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# Modified potentials in many-body perturbation theory: Three-body and four-body contributions

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Three-body and four-body contributions to the third-order diagrammatic perturbative energy expansion are evaluated for the electronic energy, using both the standard self-consistent-field potential $V^N$ and a modified potential $V^{N-1}$ to determine the unoccupied states. The [2/1] Padé approximants to the energy are constructed and first-order perturbative wave functions are inserted into the Rayleigh quotient to yield rigorous upper bounds for the energy. The results indicate that the standard $V^N$ potential generates a more suitable virtual orbital basis for the calculations.

## I. INTRODUCTION

For an $N$-electron system, the Hartree-Fock self-consistent-field (SCF) procedure invokes the variation principle to determine an SCF potential $V^N$ and a self-consistent orthonormal set of $N$ one-electron orbitals $\varphi_i$ which are optimal within the particular function space $S$ in which the orbitals are expanded. That is, the expectation value of the electronic Hamiltonian $\mathcal{H}$, with respect to the $N$-electron single-determinant constructed from these optimal orbitals, has a minimum value relative to the energy corresponding to any other single-determinant constructed from other combinations of $N$ elements of $S$. In addition to the set of self-consistent optimal occupied orbitals $\varphi_i$, the SCF potential can be used to generate an orthonormal set of unoccupied orbitals $\varphi_a$ which are orthogonal to each of the $\varphi_i$. Although the variation principle is used to partition the space $S$ into occupied and unoccupied subspaces, the elements of the unoccupied space have neither a self-consistent nor optimal property. The unoccupied orbitals are merely those orbitals that diagonalize the Hartree-Fock operator in the unoccupied subspace. The unoccupied orbitals can be subjected to a unitary transformation among themselves by the use of a modified potential. This provides additional degrees of freedom in the choice of a set of unoccupied orbitals which may, for example, lead to improved convergence properties when these orbitals are used to calculate a correlated wavefunction. On the other hand, it is possible that the original set of unmodified unoccupied orbitals is as suitable as any modified set; and hence, such a redetermination of these orbitals might be superfluous for certain applications.

In a previous paper,[1] various aspects of the use of modified potentials were examined by performing two-body third-order perturbation calculations. The present work investigates the three-body and four-body contributions to the third-order energy when a modified potential is used. In particular, results are given for the $X^1\Sigma^+$ state of hydrogen fluoride at its equilibrium internuclear distance using the previously reported[2] 46 orbital Slater-type basis set ($F$: $12\sigma$, $7\pi$, $3\delta$; $H$: $6\sigma$, $3\pi$, $1\delta$). Many-body perturbative wave functions, truncated after first order, are also obtained. Rigorous upper bounds to the energy are obtained by using these wave functions in the Rayleigh quotient.

## II. THEORY

The diagrammatic many-body formulation[3] of Rayleigh-Schrödinger perturbation theory is employed. The reader is referred to the previous paper[1] for further background, notation, and definitions. The diagrams contributing to the correlation energy through third order are shown in Fig. 1. Explicit expressions have been given[1] for the two-body portions of these diagrams.

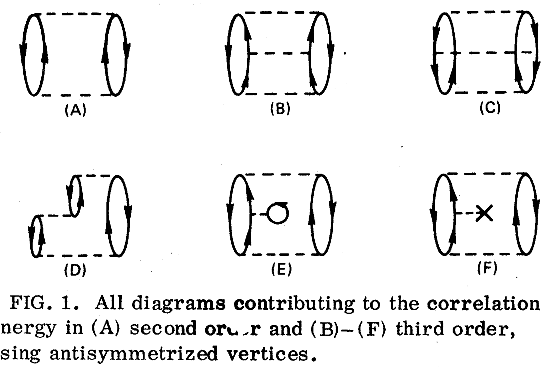

FIG. 1. All diagrams contributing to the correlation energy in (A) second order and (B)–(F) third order, using antisymmetrized vertices.

Three-body terms arise in the third-order diagrams (C) and (D); while four-body terms arise in diagram (C):

$$E_3(C)=\frac{1}{8}\sum_{ijkl}\sum_{ab}\frac{\langle ab\,\|\,ij\rangle\langle ij\,\|\,kl\rangle\langle kl\,\|\,ab\rangle}{D(ijab)D(klab)}\,, \tag{1}$$

$$E_3(D)=\sum_{ijk}\sum_{abc}\frac{\langle ij\,\|\,ab\rangle\langle ic\,\|\,ak\rangle\langle jk\,\|\,bc\rangle}{D(ijab)D(jkbc)}\,. \tag{2}$$

The number of distinct occupied orbital labels ($ijkl$) is equal to the number of interacting bodies that give rise to the energy term. Three-body effects in many-body perturbation theory have often been discussed for atoms and molecules[1,2,4] as well as for nuclear matter.[5] Using expansions in a finite set of basis functions, the evaluation of three- and four-body contributions to the energy has become quite tractable for atoms and molecules.[6]

The standard energy denominators $D$ employed with the diagrams of Fig. 1 and Eqs. (1) and (2) are defined in terms of the orbital energies

$$D(ijab)=\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b\,. \tag{3}$$

The potential-shift denominator $D^{VS}$ is obtained by shifting the standard denominator with the diagonal elements of the potential-interaction diagrams, Fig. 1 ($E+F$):

$$D^{VS}(ijab)=D(ijab)-\Delta^{VS}(ijab)\,, \tag{4}$$

where the denominator shift is given by

$$\Delta^{VS}(ijab)=\langle a\,|(V^N-V)\,|\,a\rangle+\langle b\,|(V^N-V)\,|\,b\rangle\,. \tag{5}$$

The fully shifted denominator $D^S$ corresponds to shifting the denominator with the diagonal elements of all the third-order diagrams in Fig. 1:

$$D^S(ijab)=D(ijab)-\Delta^S(ijab)\,, \tag{6}$$

where

$$\Delta^S(ijab)=\langle ab\,\|\,ab\rangle+\langle ij\,\|\,ij\rangle+\langle ai\,\|\,ia\rangle+\langle bi\,\|\,ib\rangle+\langle aj\,\|\,ja\rangle+\langle bj\,\|\,jb\rangle+\Delta^{VS}(ijab)\,. \tag{7}$$

The basis functions $\varphi$ are simultaneous diagonal states of the matrix equation

$$\langle\varphi\,|H|\,\varphi\rangle=\epsilon \tag{8}$$

containing the operator[7]

$$H(1)=h(1)+V^N(1)+P[V(1)-V^N(1)]P\,, \tag{9}$$

where $h$ is the sum of kinetic-energy and nuclear attraction operators, $P$ is the projector for the orthonormal complement to the occupied space

$$P=1-\sum_{i=1}^{N}|\varphi_i\rangle\langle\varphi_i|\,, \tag{10}$$

the SCF potential is $V^N$:

$$V^N(1)=\sum_{k=1}^{N}\int d\tau_2\,\varphi_k^*(2)r_{12}^{-1}(1-P_{12})\varphi_k(2)\,, \tag{11}$$

and the modified potential is denoted by $V$. In the present work, $V$ is taken to be either $V^N$ itself or the $V^{N-1}$ potential of Kelly,[8]

$$V^{N-1}(1)=\sum_{k=1}^{N-1}\int d\tau_2\,\varphi_k^*(2)r_{12}^{-1}(1-P_{12})\varphi_k(2)\,, \tag{12}$$

although several other choices for $V$ had been considered previously.[1]

## III. RESULTS

An analysis of the correlation corrections is given in Table I, where the contributions from various diagrams are compared. The magnitudes of the three- and four-body interactions are largest for the $V^{N-1}$ calculation using the standard denominator $D$. The calculation using $V^N$ with the denominator $D$ gives energies comparable with those corresponding to the use of the potential $V^{N-1}$ with denominator $D^{VS}$. Finally, the two calculations using the $D^S$ denominator give results which are quite similar to one another. Even for the calculation using $V^N$ with denominator $D$, which has the smallest three- and four-body effects, the many-body energy amounts to a significant fraction of the total two-body energy through third-order and in an absolute sense contributes ~31 kcal/mole, which is certainly not negligible.

The perturbative energy components are summarized in Table II. The three- and four-body effects are quite important as evidenced by the differences between the two-body and many-body results through third order, $E_2+E_3$. It is interesting to note that the total many-body third-order contribution is quite small when the potential $V^N$ is used with denominator $D$. Thus, the difference between $E_2$ and $E_2+E_3$ (many body) is ~0.7% of the mean value of these energies. For all of the other cases, a lower $E_2$ value is obtained than by using $V^N$ with denominator $D$; however, the positive three- and four-body effects are largest for these other cases and the results through third order lie above that obtained by using $V^N$ with denominator $D$.

The [2/1] Padé approximant[9] to the correlation energy is also given in Table II:

$$[2/1]\ \text{Padé}=\frac{E_2}{1-E_3/E_2}\,, \tag{13}$$

where $E_3$ includes all many-body components. This alternative third-order representation of the energy has a fourth-order residual. In addition to its scale-invariance property,[10] the [2/1] Padé

TABLE I. Components of the perturbation expansion for hydrogen fluoride ($R=1.7328$ bohr).[a]

| Potential | $V^N$ | $V^N$ | $V^{N-1}$ | $V^{N-1}$ | $V^{N-1}$ |
|---|---|---|---|---|---|
| Denominator | $D$ | $D^S$ | $D$ | $D^{VS}$ | $D^S$ |
| Intrapair energies (two body) | | | | | |
| $E_2^2(A)$ | −0.305 49 | −0.353 55 | −0.385 68 | −0.317 47 | −0.370 09 |
| $E_3^2(B)$ | +0.046 93 | +0.032 58 | +0.082 65 | +0.051 37 | +0.036 61 |
| $E_3^2(C)$ | +0.041 06 | 0.0 | +0.078 05 | +0.045 19 | 0.0 |
| $E_3^2(D)$ | −0.135 13 | −0.042 77 | −0.247 49 | −0.148 81 | −0.049 55 |
| $E_3^2(E+F)$ | 0.0 | 0.0 | +0.109 68 | +0.012 68 | +0.018 15 |
| Total | −0.352 63 | −0.363 74 | −0.362 78 | −0.357 04 | −0.364 89 |
| Interpair interactions between pairs having a common occupied orbital (three body) | | | | | |
| $E_3^3(C)$ | −0.000 03 | −0.000 08 | −0.000 24 | −0.000 06 | −0.000 14 |
| $E_3^3(D)$ | +0.046 35 | +0.067 49 | +0.088 11 | +0.051 82 | +0.077 06 |
| Total | +0.046 31 | +0.067 41 | +0.087 86 | +0.051 77 | +0.076 93 |
| Interpair interactions between pairs having no common occupied orbital (four body) | | | | | |
| $E_3^4(C)$ | +0.002 97 | +0.004 01 | +0.005 30 | +0.003 25 | +0.004 49 |
| %(3.4 body/2 body)[b] | 14.0 | 19.6 | 25.7 | 15.4 | 22.3 |
| Overlap[c] | +0.050 73 | +0.073 15 | +0.097 92 | +0.055 98 | +0.082 77 |

[a] The energy terms are labelled with subscripts to denote order and superscripts to denote number of interacting bodies. The potentials are defined in Eqs. (9)–(12); the denominators are defined in Eqs. (3)–(7). Energies are in hartrees.

[b] Defined by $100\times[E_3^3(C+D)+E_3^4(C)]/|E_2(A)+E_3^2(B \text{ to } F)|$.

[c] Defined in Eq. (17).

approximant brings a uniformity to the results; that is, the spread in energies has been reduced from ~34 mhartree for $E_2+E_3$ to ~7 mhartree for the Padé approximants.

In addition to generating an energy series, the many-body perturbation theory generates a wave function having the form of a power series in the perturbation operator $\mathcal{H}_1$. This wave function, truncated after first order, is depicted in Fig. 2. Since the orbital basis set is first determined as a

TABLE II. Comparison of perturbative energy corrections for hydrogen fluoride ($R=1.7328$ bohr) with the empirical correlation energy $E_{\text{corr}}=-0.381$ hartree.[a]

| Potential | $V^N$ | $V^N$ | $V^{N-1}$ | $V^{N-1}$ | $V^{N-1}$ |
|---|---|---|---|---|---|
| Denominator | $D$ | $D^S$ | $D$ | $D^{VS}$ | $D^S$ |
| $E_2$ | −0.305 49 | −0.353 55 | −0.385 68 | −0.317 47 | −0.370 09 |
| (% $E_{\text{corr}}$) | (80.2) | (92.8) | (101.2) | (83.3) | (97.1) |
| $E_2+E_3$ (two body) | −0.352 63 | −0.363 74 | −0.362 78 | −0.357 04 | −0.364 89 |
| (% $E_{\text{corr}}$) | (92.6) | (95.5) | (95.2) | (93.7) | (95.8) |
| $E_2+E_3$ (many body) | −0.303 34 | −0.292 31 | −0.269 62 | −0.302 02 | −0.283 47 |
| (% $E_{\text{corr}}$) | (79.6) | (76.7) | (70.8) | (79.3) | (74.4) |
| [2/1] Padé[b] | −0.303 36 | −0.301 35 | −0.296 47 | −0.302 74 | −0.299 90 |
| (% $E_{\text{corr}}$) | (79.6) | (79.1) | (77.8) | (79.5) | (78.7) |

[a] All energies are in hartrees. The potentials are defined in Eqs. (9)–(12); the denominators are defined in Eqs. (3)–(7).

[b] Defined in Eq. (13).

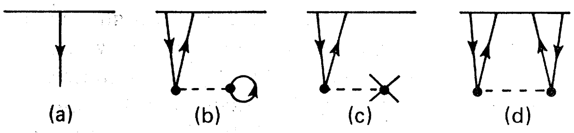

FIG. 2. Components of the many-body perturbative wave function through first-order using antisymmetrized vertices. (a) The zero-order function; (b)–(d) first-order corrections. (b) and (c) mutually cancel if × represents $-V^N$, where $V^N$ is the Hartree-Fock potential. (d) Sum over all doubly excited states.

solution to the matrix Hartree-Fock equation using $V^N$, and since the redetermination of the unoccupied orbitals corresponding to $V$ involves a unitary transformation within the space of unoccupied orbitals, the exact cancellation of the single-excitation diagrams (b) and (c) is preserved. Thus the first-order wave function consists of (a) the reference single determinant $\Phi_0$ and (d) the double-excitation diagram $\Phi_1$. Different wave functions are generated by different choices of potential $V$ or by different choices of energy denominator $D$, $D^{VS}$, or $D^S$.

Since the first-order many-body wave function has a simple form, an additional variational parameter $\gamma$ is easily incorporated:

$$\psi_1 = \Phi_0 + \gamma \Phi_1 . \tag{14}$$

This wave function can be inserted into the Rayleigh quotient to produce a rigorous upper bound for the energy[11]

$$E_{\text{true}} \leq E_{\text{var}}(\gamma) = \langle \psi_1 | \mathcal{H} | \psi_1 \rangle / \langle \psi_1 | \psi_1 \rangle . \tag{15}$$

The perturbative energy terms through third-order can be used for this evaluation:

$$\begin{aligned} E_{\text{true}} &\leq E_{\text{var}}(\gamma) \\ &= E_0 + E_1 + [(2\gamma - \gamma^2)E_2 + \gamma^2 E_3]/(1 + \gamma^2 S_{11}) , \end{aligned} \tag{16}$$

where the overlap integral has the explicit form

$$S_{11} = \tfrac{1}{4} \sum_{ij} \sum_{ab} \frac{\langle ij \| ab \rangle^2}{D(ijab)^2} . \tag{17}$$

The perturbative variational upper-bounds are presented in Table III. Changing $\gamma$ from unity to its optimal value has the greatest effect for the cases having the highest-energy bound. The use of the potential $V^N$ with denominator $D$ leads to the lowest energy for either choice of $\gamma$ and an optimal value of $\gamma$ closest to one. This implies that the corresponding perturbation wave function is variationally well suited to describe the hydrogen fluoride molecule. The use of an optimal $\gamma$ brings the results for the five cases into good agreement with one another; the largest difference in this case is only ~8 mhartree.

The upper-bounds to the total energy are also presented in Table III for the five cases. These results should be compared with the best previous configuration interaction upper bound of −100.351 hartree, obtained by Bender and Davidson.[12]

## IV. DISCUSSION

Although there have been mathematical demonstrations[7] that a proper perturbation scheme can be constructed making use of a modified potential for the determination of excited-state orbitals, a mathematical analysis has never been given to prove that the use of a modified potential is more efficacious than the standard $V^N$ potential for the perturbative calculation of electronic energies and wave functions. Instead the advantages of modified potentials have been advanced through the use of numerical example.

In contrast, the possibility that equivalent results might be obtained whether $V^N$ or a modified potential is used for the determination of excited-

TABLE III. Comparison of many-body perturbative variational upper bounds $E_{\text{var}}$ for hydrogen fluoride ($R = 1.7328$ bohr) with the empirical correlation energy $E_{\text{corr}} = -0.381$ hartree.[a]

| Potential | $V^N$ | $V^N$ | $V^{N-1}$ | $V^{N-1}$ | $V^{N-1}$ |
|---|---|---|---|---|---|
| Denominator | $D$ | $D^S$ | $D$ | $D^{VS}$ | $D^S$ |
| $E_{\text{var}}$ ($\gamma = 1$) | −0.288 70 | −0.272 39 | −0.245 57 | −0.286 01 | −0.261 80 |
| (% $E_{\text{corr}}$) | (75.8) | (71.5) | (64.5) | (75.1) | (68.7) |
| $\gamma$ optimal | 0.947 77 | 0.811 33 | 0.728 71 | 0.909 46 | 0.770 51 |
| $E_{\text{var}}$ ($\gamma$ = optimal) | −0.289 53 | −0.286 84 | −0.281 05 | −0.288 72 | −0.285 16 |
| (% $E_{\text{corr}}$) | (76.0) | (75.3) | (73.8) | (75.8) | (74.8) |
| $E_{\text{tot}}$ [b] | −100.359 | −100.356 | −100.350 | −100.358 | −100.354 |

[a] All energies are in hartrees. The potentials are defined in Eqs. (9)–(12); the denominators are defined in Eqs. (3)–(7).

[b] The total energy is defined by $E_{\text{ref}} + E_{\text{var}}$ ($\gamma$ = optimal), where $E_{\text{ref}}$ is the SCF reference energy corresponding to these calculations (−100.069 hartree).

state orbitals can be established from the following argument. The problem of interest is the Schrödinger equation

$$\mathcal{H}\psi = E\psi \,. \qquad (18)$$

Using the unperturbed solvable problem

$$\mathcal{H}_0\phi_m = \epsilon_m\phi_m \,, \qquad (19)$$

the perturbation operator is defined

$$\mathcal{H}_1 = \mathcal{H} - \mathcal{H}_0 \,, \qquad (20)$$

so that the perturbation expansions are relevant only when the expansion parameter $\lambda$ is unity:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1\lambda \,, \qquad (21)$$

$$\psi_{\mathrm{PT}} = \sum_{K=0}^{\infty} \Phi_K\lambda^K \,, \qquad (22)$$

$$E_{\mathrm{PT}} = \sum_{P=0}^{\infty} E_P\lambda^P \,. \qquad (23)$$

The perturbation-theory expansions for $\psi_{PT}$ and $E_{PT}$ must converge in order to be valid, and furthermore these expansions must converge to the exact $\psi$ and $E$ satisfying Eq. (18). Since $\mathcal{H}$ is totally independent of $\mathcal{H}_0$, then $\psi$ and $E$ must be independent of $\mathcal{H}_0$ also. Therefore when convergence is reached, the perturbative solutions $\psi_{PT}$ and $E_{PT}$ must also be independent of $\mathcal{H}_0$ and hence they must be independent of the particular choice of potential employed in $\mathcal{H}_0$. Thus, the correct result is obtained when the perturbative scheme has converged and at that point there must be an equivalence between the results obtained using either $V^N$ or $V$.

Having established that the correct final result must be independent of the choice of potential, it is necessary to realize that the rate of convergence of the perturbative expansions might depend on the choice of $V$. The usefulness of a modified potential lies in the possibility of obtaining a converged result at the lowest order of calculation.

The foregoing arguments assume that a *complete* basis set is used for the expansion of the orbitals and that therefore the perturbative results should converge to the exact $\psi$ and $E$. If the basis set is *not* complete, then the perturbative results can only be expected to converge to the "basis-set limit." The basis-set limit is a quantity which must be determined from some evidence of convergence. One such test is to compare different $P$th-order representations of the energy for a given perturbative scheme, like $E_2+E_3$ and $E[2/1]$. Another test is to compare a particular $P$th-order representation of the energy for different schemes, like $E_2+E_3$ using the various potentials and denominators. Since the converged result must be independent of these differences, these comparisons indicate whether the $P$th-order results share this independence property and therefore show some evidence of convergence. Ideally these comparisons and other convergence tests would be performed using high-order results. Of course, as the basis set approaches completeness, the basis-set limit should approach the exact result.

The quality of a result should be judged by its proximity to the basis-set limit. Nevertheless, the ability to obtain an energy close to the exact value from a second-order calculation using a modified potential has been regarded as an attractive feature of the method. In our previous paper,[1] we demonstrated by numerical example that a certain arbitrariness is introduced into the calculations through use of a modified potential with the standard denominator $D$ such that *any* desired energy can be obtained by manipulating the potential. Although this might be a useful feature in the context of a semiempirical approach, it is not desirable for strict *ab initio* calculations. To avoid this difficulty, we showed[1] that the use of either the denominator $D^{VS}$ or $D^S$ can ensure the negative definite character of the resolvent and thus a proper perturbative scheme can be guaranteed.

The present calculations are performed in the $N$-electron space restricted to the reference configuration and all other configurations which can be formed by double excitations. In previous work on the neon atom,[6] the third-order perturbative cacalculations had been shown to give an accuracy comparable with that afforded by the method of configuration interaction, including all singly and doubly excited configurations with respect to a closed-shell matrix Hartree-Fock reference function, if the same basis set is employed. The present third-order results would therefore be expected to be close to the corresponding doubly excited configuration interaction results for hydrogen fluoride obtainable with the present basis set. The extent to which the energies corresponding to the various cases in Table II agree with one another is taken as a measure of how close these results are to the doubly excited basis set limit for the correlation energy. The most uniform results are obtained from the [2/1] Padé approximants for the five cases in Table II. In addition, the best agreement between the third-order results, $E_2+E_3$ (many body) and [2/1] Padé, is obtained for the two cases $V^N$ with denominator $D$ and $V^{N-1}$ with denominator $D^{VS}$. The second-order energy in closest agreement with these third-order results is $E_2$ using $V^N$ with denominator $D$.

The perturbative expansion for $\psi$ can be examined in terms of the Rayleigh quotient of Eq. (15). These results, given in Table III, represent rigorous variational upper bounds on the energy. The near equivalence of these results, especially for optimal $\gamma$, is a measure of the convergence of the perturbative expansion for $\psi$ to the basis-set limit.

On the basis of the near equivalence of the results presented here in Tables II and III, the most reasonable conclusion to draw is that the $V^N$ and $V^{N-1}$ potentials are equally efficacious in producing third-order results of uniform quality. Although $E_2$ using potential $V^N$ and denominator $D$ is very close to the third-order limit, the ease with which the third-order energies can be obtained within the algebraic approximation[6] would suggest that $E_2 + E_3$ (many body) is the most suitable low-order energy result. Another advantage is that the upper bounds of Eq. (16) can be derived from the components of a third-order calculation.

The results and conclusions in this paper pertain strictly to the hydrogen fluoride molecule within the particular basis set employed. Although this basis set is far from complete, it is nevertheless a large set for a molecular calculation and its quality is high enough to produce more accurate upper bounds for the energy than any previous attempt. Thus, the present results are probably indicative of the general situation for arbitrary molecular systems. If considerably larger basis sets could be employed for molecules, it would of course be desirable to examine various aspects of such calculations: two-body versus many-body effects, convergence with respect to perturbative order, determination of the basis-set limit, and the influence of a modified potential on the rate of convergence of the perturbative series.

Just as the canonical unoccupied orbitals can be subjected to a unitary transformation within the unoccupied space by using a modified potential, the occupied orbitals may be subjected to an arbitrary unitary transformation within the occupied space. There are many arbitrary criteria, such as localization criteria, which can be invoked to determine this transformation.[13] The converged infinite-order perturbation expansion should be invariant to the separate unitary transformation of both the occupied and unoccupied orbitals, within their respective subspaces. The determination of the effect of transformations on the occupied orbitals in a truncated perturbation expansion would require numerical experiment. In view of the close agreement of the third-order results obtained with different modifications of the unoccupied orbitals in the present work, it is anticipated that a similar degree of agreement might be obtained when modified occupied orbitals are employed in calculations taken completely through third order. The use of localized occupied orbitals would, of course, change the relative magnitudes of the various components of the energy.

The present results have demonstrated the importance of three- and four-body effects in the evaluation of the electronic energy of hydrogen fluoride. The results vindicate the use of the standard SCF $V^N$ potential for the determination of the unoccupied virtual states when using finite basis sets. Of course, the effects of modified potentials on properties other than energy remain to be determined.

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