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Fourth-order Møller–Plessett perturbation theory in the local correlation treatment. I. Method

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Fourth-order Møller–Plesset perturbation theory (MP4) is formulated for localized internal orbitals of closed-shell systems. Unlike previous localized perturbation theories, our formulation is strictly identical with canonical MP4 theory if no further approximations are made. In the local treatment, large savings can be achieved by two techniques: (1) neglecting or treating at a lower (second order) level pair correlation between distant pairs, and (2) restricting the correlation basis to the atomic orbitals in the spatial vicinity of the correlated pair. These techniques have been used in our previous local correlation treatment for variational CI, coupled electron pair (CEPA), and approximate coupled cluster (ACCD) wave functions. The MP4 method is more economical than these techniques because of the absence of iterative cycles. Implementation with single, double, and quadruple substitutions is discussed.

I. INTRODUCTION

Perturbative many-body techniques provide the most economical way of calculating correlated wave functions for ground-state molecules. Experience shows that, among variants of many-body perturbation theory,[1,2] the Møller–Plesset partitioning (i.e., the Fock operator as the zeroth-order Hamiltonian) yields the best results for closed-shell molecules. Although the second order of this theory (MP2) is very old,[3] and the third order was generally understood in the 60's, acceptance of perturbational methods was slow, for two reasons. First, the lack of the variational upper bond property was thought to be a significant shortcoming. Only the painful realization that the upper bond property is incompatible with simultaneous size consistency and computational simplicity made perturbational techniques generally acceptable. Second, it was thought that variational methods and other iterative (e.g., coupled cluster) methods are not significantly more expensive than their perturbational counterparts. For instance, Kutzelnigg[4] argues that the cost of an MP3 calculation should be about the same as that of variational CI with double substitutions, since the same Hamiltonian matrix elements are needed in both. This argumentation is not valid, however, for the direct CI-type methods[5] which are used almost exclusively for large scale CI calculations today. If the initial integral transformation is not counted, the cost of such iterative methods is directly proportional to the number of cycles which is usually 6–12. Thus while it is true that the computational dependence of perturbative methods is the same as their variational and coupled cluster analogs, practically there is an order of magnitude difference in favor of perturbation theory. The terms included in iterative methods are usually higher order contributions from unlinked double substitutions, summed selectively to infinite order. From the point of view of perturbation theory it is not evident why such terms should be included when other, more important terms involving higher substitutions are omitted. Practical calculations[6,7] show that MP theory, particularly when carried to fourth order, provides an excellent approximation for dynamical correlation effects. An important contribution to the popularity of MP theory is the availability of the efficient GAUSSIAN 80 program package.[8]

The steep increase of the computational effort with increasing molecular size still restricts the applicability of MBPT to relatively small molecules. The dominant computational step in MP2 scales as nN^4; MP3, and MP4 restricted to single, double and quadruple substitutions (MP4-SDQ) contain n^2N^4 and n^3N^3 terms; and triple substitutions in MP4 give rise to terms which scale with n^3N^4. Here n is the number of occupied MO's and N is the total number of basis functions. It is evident that truncation of the correlation space is inevitable for any efficient correlation method for larger molecules. Random configuration selection using estimated correlation contributions has not become popular for ground-state surfaces, for several reasons: (1) Due to the very slow convergence of the traditional canonical CI expansion, the combined effect of countless small contributions is not necessarily small; (2) it is difficult to generate microscopically smooth surfaces by this method, precluding gradient evaluation; and (3) random configuration selection introduces an undesirable dependence on the virtual orbitals, as well as expensive logic.

Perhaps the only way to avoid the steep increase of computing costs with molecular size, and the disadvantages of random configuration selection procedures, is to make use of the localizability of ground-state electronic structure. Recently we have suggested a localized correlation treatment.[9–11] This method uses localized internal orbitals, and atomic basis functions to describe the virtual space, in the spirit of the SCEP method.[12] Originally[10] it was implemen-

ted for variational CI, CEPA,[13] and ACCD[14] many-body methods. There are two significant sources of savings in the local correlation treatment:

(1) In the localized description, pair correlation between distant orbitals is very small. Depending on the intended application, these *weak pairs* can be neglected,[10] or treated at a lower (second order) level. The neglect of distant correlation is trivial but the more appealing approximate treatment has been developed recently, and we shall discuss it in some detail.

(2) Due to the localization, one may restrict the virtual space for a given pair to a subset of the atomic orbitals (AO's). Our prescription for the local correlation space will be given later; the program is quite flexible in this respect. Obviously, the correlation space for a localized MO should include the AO's located in the spatial vicinity of the MO. The local correlation space restriction brings a large reduction in both storage requirement and computational effort; at the same time, it recovers ~97% of the correlation energy of the full basis with double-zeta-plus polarization basis sets. As discussed previously,[10,11] we believe that the local approach results in a more consistent treatment of electron correlation effects than the usual all-doubles approach. In particular, it eliminates both intra- and intermolecular basis set superposition artifacts[11]: the use of the tails of basis functions located on distant atoms for describing correlation. Intermolecular basis set superposition effects are particularly bothersome in the calculation of weak dispersion forces. We shall discuss the latter in a forthcoming paper.[15]

In a typical case (butadiene with the 5-31G** basis)[10] the speed-up in the CI loop due to the local restriction varies between 17 and 40, depending on whether the weak pairs are retained or not. As we usually need 8 cycles for sharp convergence while a full basis MP4-SDQ is computationally equivalent to 1.5–2 cycles, the local correlation method is only a few times more efficient than a nonlocal MP4-SDQ computation in this case. (Asymptotically, however, the local correlation treatment should win by a large margin.) This situation is now remedied with the introduction of the local MP4 method. Previously, we have formulated local Møller–Plesset perturbation theory to third order[11,16]; applications have been reported to molecules as large as oxetane[11,17] and benzene.[18] MP4-SDQ has several advantages over MP3: it is not significantly more expensive[19]; it includes the singles which are important for properties; and it can be formulated as an energy functional: the latter property means that the one-particle density matrix can be defined in a unique way (see, e.g., Ref. 16). Triple substitutions have not yet been included. However, it is evident that the savings offered by the local treatment are even more important for the expensive triple substitutions than for the other terms.

The local correlation treatment has two further advantages over canonical orbital based theories: (1) it provides a natural decomposition of the correlation energy into chemically significant contributions; (2) electron correlation in spectator groups can be omitted if it is clear that they will not contribute significantly. Not all orbitals in all molecules are localizable. However, most orbitals in most ground-state molecules can be localized very well. Orbitals which are

genuinely delocalized must be treated globally; our method reverts to the customary correlation methods for these cases.

Variational CI and coupled-pair methods can be formulated easily for localized orbitals.[13,20-23] Many-body perturbation theory (MBPT) is, however, more difficult to express in localized form. With the exception of ours, none of the previous formulations[24-27] of localized perturbation theories yields results identical with the canonical Møller–Plesset theory. We consider this a serious deficiency. Not only is a new and untested many-body method introduced, but the model results of Kapuy *et al.*[27] show that these methods are inferior to MP theory, even at fourth order. Previous local perturbation theories[24-29] contain a substantial one-particle perturbation which apparently requires the inclusion of contributions higher than fourth order. Computational savings using these methods have not yet been reported.

In the present paper, we give a detailed description of our local correlation treatment, emphasizing the local fourth order Møller–Plesset theory. With the exception of MP4, these methods have been implemented for two years on various computers, from supermicros to class VI computers, and we have performed numerous computations with them. In a paper under preparation we shall provide computational times and examples, with emphasis on class VI (supercomputer) performance.

Several other groups are working on local correlation theories.[28-34] Because of the ease of formulation, most of these methods are based on variational CI, coupled-pair, or coupled-cluster (i.e., iterative) methods. Laidig *et al.*[28,29] include perturbational results along with coupled-cluster ones but their zeroth-order Hamiltonian is not defined exactly; it is presumably the diagonal part of the Fock operator. Some of these methods[28-31] replace the Hartree–Fock reference function by a crudely localized (PCILO-type[24]) wave function. We have strong reservations against such methods at the *ab initio* level, as the arbitrariness of the reference function will manifest itself in any finite order of PT, as shown by the results of Laidig *et al.*[28] This arbitrariness may prevent the reliable calculation of small energy differences. The motivation behind the work of Laidig *et al.*[28-30] is efficiency for large molecules. Computational savings have not yet been demonstated, however.

The recent results of Förner *et al.*[32] are somewhat similar to our previous treatment,[10] in that a restricted local correlation subspace is used. The latter is defined in terms of localized virtual orbitals, not in terms of atomic orbitals as in our treatment. We see two disadvantages in this: Localizability in the virtual space, in contrast to the occupied space, is doubtful, particularly for extended basis sets, and the results depend on the virtual orbitals which is undesirable for gradient calculation. As a further approximation, the correlation energy is first calculated independently in arbitrarily defined local regions, and added as in IEPA.[4] In a next step, calculations on pairs of regions are performed and the simple additive results are corrected by them. Such manipulations are obviously undesirable because they involve additivity assumptions, much extra computation, and do not converge towards the nonlocal results with the relaxation of the local basis restriction. Moreover, as the results of Ref. 32 show,

intersystem energies are by no means negligible as compared with intrasystem ones, requiring the extension of their procedure to triples of regions: this however, would negate the computational advantages of the local treatment. In contrast to our results where a very high percentage of the correlation energy was recovered (relative to the full virtual space calculation), the percentage of the correlation energy recovered by Förner et al.[32] is much less. We attribute this to their small basis set: the lack of a suitable virtual space leads to the utilization of the tails of functions located on neighboring centers as correlation functions. Reference 32 has been formulated only for iterative (coupled cluster) many-body techniques, and provides few technical details and no timing information.

We shall discuss the very recent paper of Stollhoff and Vasilopoulos,[33] as its unusual nomenclature (e.g., "state" for orbital), and unconventional techniques may cause difficulties for the reader used to mainstream quantum chemistry. In this method, the local correlation space is defined by functions which are roughly a 1:1 linear combination of occupied and virtual orbitals: $g \simeq N(\phi_i + \phi_a)$; only substitutions $i \rightarrow a$ are permitted. The functions g are defined as simple atomic hybrid orbitals; unfortunately, this introduces much arbitrariness. The many-body method used by Stollhoff et al.[33] is based on L-CPMET (CEPA-0),[4,35] i.e., it is iterational, too. However, in order to achieve computational efficiency, a series of further approximations is introduced in the spirit of the IEPA (independent electron pair approximation) method,[4] i.e., pair couplings are omitted. The error caused by this is approximately corrected by a series of calculations in which only two pairs are considered; the resulting double count of certain terms is then corrected. Finally, intraatomic correlation is taken into account only at a second order-like level. As a result of these manipulations, it is not possible to judge the quality of the approximation by the percentage of the correlation energy recovered, and indeed the latter is given in Ref. 33 only as an estimate. This contrasts with our method which goes over smoothly to the traditional results with the enlargement of the local correlation space. For functional formulated many-body methods (variational CI, L-CPMET, MP2, and MP4) our correlation energies must be strict upper bounds to the corresponding full basis results. A feature of the method of Stollhoff and Vasilopoulos is that different basis sets are used at the SCF and the correlation levels. This is probably desirable, although it further complicates the input and the definition of the wave function.

The very recent paper of Kirtman and Dykstra[34] combines the local correlation treatment[10] with Kirtman's local SCF method[36]. We expect that this will lead to further significant economies.

II. THEORY

Our method is based on the SCEP technique[12,37,38] for closed shells: the latter is an efficient matrix-formulated direct CI-type method; in its original form,[12] and in the form used by us, the virtual space is described directly in terms of atomic orbitals. Although the MO form of SCEP is somewhat more efficient for full basis set calculations, only the

AO form is applicable in the local treatment.[10] We use our simple and efficient generator state formalism.[39] We emphasize that the calculation of the pair coupling terms is asymptotically twice as efficient in the generator-state form[39] as in previous *spin-adapted* formulations of the closed-shell CI problem (Ahlrichs and Zirz[40] have developed a similar but less efficient method in an unpublished conference contribution). We are working on an extension of the generator state formalism to spin-adapted open-shell wave functions. Note that Cizek's CPMET[41] method was implicitly formulated in terms of generator states. However, the computational efficiency of the latter was not realized at that time and later formulations reverted to orthogonal spin functions. Generator states have long been advocated by Matsen.[42] He does not use, however, a biorthogonal basis, and therefore could not realize the simplifications of the generator state spin coupling. Our doubly substituted configuration states are defined as

$$\psi_{ij}^{pq} = \phi_{ij}^{pq} + \phi_{ij}^{\bar{p}\bar{q}} + \phi_{ij}^{\bar{p}q} + \phi_{ij}^{p\bar{q}}. \tag{1}$$

Here $i \geqslant j$ are occupied orbital indices and p, q denote, in the general case, AO's. We refer to Ref. 39 for the definition of the singles and for further details. The doubly substituted wave function is written as

$$\psi = \psi_0 + \Sigma_{i > j} \psi_{ij},$$

where the pair correlation function is defined as

$$\psi_{ij} = \Sigma_{p,q} (C_{ij})_{pq} \psi_{ij}^{pq};$$

note the unrestricted summation with respect to p and q. The CI coefficients are collected in N_p matrices C_{ij} where N_p is the number of correlated pairs; in the full case, this is $n(n+1)/2$. Besides diminishing the number of operations, the square matrices of the generator state formalism are more advantageous than the triangular matrices of previous formulations[12,37,38] for modern vector and array processors.

In a previous paper,[16] we derived the localized form of MP2 and MP3 starting with the Hylleraas variation principle.[43] An alternative derivation is given here. The zeroth-order Hamiltonian is the sum of the Fock operators. Unlike in the canonical formulation, however, we do not assume that the orbitals are eigenfunctions of the Fock operator; consequently, the zeroth-order Hamiltonian is not diagonal on the basis of our states. Using standard notation, the first-order wave function is given by

$$\psi^{(1)} = - (H_0 - E_0)^{-1} H' \psi_0.$$

The condition for the first-order wave function and the corresponding pair coefficients $C^{(1)}$ to satisfy this equation can be stated by requiring that the second-order residuum function vanishes:

$$T^{(2)} = (H_0 - E_0)\psi^{(1)} + H'\psi_0 = 0.$$

The coefficients of $T^{(2)}$, expanded in our configuration states, Eq. (1), are easily shown[16] to be given by the matrices

$$T_{ij}^{(2)} = K_{ij} + FC_{ij}S + SC_{ij}F$$
$$- S\Sigma_k [F_{ik}C_{kj} + F_{kj}C_{ik}]S = 0. \tag{2}$$

Here only C is written for the first-order pair coefficients $C^{(1)}$; we shall use the latter only if the order is not clear from the context. The matrix element T_{ij}^{pq} corresponds to the pro-

jection of the residuum onto the function ψ_{ij}^{pq}, and **K** is the internal exchange operator, $(K_{ij})_{pq} = (pi|jq)$; **F** and **S** are the AO Fock and overlap matrices, respectively. This expression is part of the full CPMET residuum formula given in Ref. 39. The determination of the first-order wave function requires an iterative procedure[16]: The residuum is transformed to a temporary MO-like basis and it is divided by estimated energy denominators to yield corrections to the coefficients until the residuum vanishes. Using a conjugate-gradient-type convergence acceleration (see below), this procedure converges very well (in four to six steps); it is equivalent to the iterative inversion of the operator $(H_0 - E_0)$. At first the iterative nature of this procedure may appear to be a significant disadvantage. However, the computational work involved in this procedure scales only as $n^2 N^3$, against the integral transformation nN^4; as for realistic calculations N/n is large (>5), this is not too serious; in the local basis set approximation the extra work is insignificant. Even for a full MP2 calculation, there are advantages in the proposed formalism, particularly for gradient evaluation[16]; note that Handy et al.[44] have recently formulated MP2 gradients and second derivatives in a similar way, to avoid small energy denominators which plague the canonical formalism.

The second order energy is given by

$$E^{(2)} = \langle \psi^{(1)}|H'\psi_0\rangle = \Sigma_{i>j}\langle K_{ij}\widetilde{C}_{ji}^{(1)}\rangle , \quad (3)$$

where $\widetilde{C}_{ij} = (1 + \delta_{ij})^{-1}(4C_{ij} - 2C_{ji})$ is the contravariant coefficient matrix[39]; C_{ji} is the transpose of C_{ij}, and $\langle...\rangle$ denotes a matrix trace.

Using standard perturbation theory, the third order energy is given as

$$E^{(3)} = \langle \psi^{(1)}|H - E_r|\psi_0 + \psi^{(1)}\rangle = \Sigma_{i>j}\langle T_{ij}^{(3)}\widetilde{C}_{ji}^{(1)}\rangle . \quad (4)$$

Here E_r is the reference (SCF) energy $E_r = E_0 + E^{(1)}$ and $T^{(3)}$ is the CEPA-0 (L-CPMET) doubles residuum matrix,[39] evaluated with the first-order coefficients:

$$T_{ij}^{(3)} = K_{ij} + K[C_{ij}] + FC_{ij}S + SC_{ij}F$$
$$+ Q_{ij}S + SQ_{ji}^\dagger + S(G_{ij} + G_{ji}^\dagger)S . \quad (5)$$

Here **C** stands for $C^{(1)}$; the definition of the external exchange matrix **K**[C], and the pair coupling matrices **Q** and **G**, as well as the Coulomb matrix **J** is as follows:

$$K(X)_{qr} = \Sigma_{st}(qs|rt)X_{st} , \quad (6)$$

$$Q_{ij} = \Sigma_k \{(K_{ik} - \tfrac{1}{2}J_{ik})(2C_{kj} - C_{jk})$$
$$- \tfrac{1}{2}J_{ik}C_{jk} - J_{jk}C_{ik}\} , \quad (7)$$

$$G_{ij} = \Sigma_{k>l}(1 + \delta_{kl})^{-1}\{(ik|jl) - \delta_{ij}F_{ik} - \delta_{ki}F_{jl}\}C_{kl} . \quad (8)$$

$$J_{ij}^{pq} = (ij|pq) .$$

To establish connection with other formulations, we note that the external exchange matrix **K**(C) describes couplings with four external labels; the **Q**'s describe couplings with two external and two internal labels; and the **G**'s contain terms with four internal labels.

The general expression for the fourth order energy is

$$E^{(4)} = \langle \psi^{(1)}|H' - E^{(1)}|\psi^{(2)}\rangle - E^{(2)}\|\psi^{(1)}\|^2 , \quad (9)$$

where

$$\psi^{(2)} = -(H_0 - E_0)^{-1}(H' - E^{(1)})\psi^{(1)} . \quad (10)$$

$E^{(4)}$ can be evaluated by expanding $\psi^{(2)}$ in a configuration basis. The expansion contains singly, doubly, triply, and quadruply substituted configurations relative to the reference configuration ψ_0. The coefficients of single, double, and triple substitutions arise from connected[1,2] diagrams and the corresponding coefficients have to be explicitly evaluated by means of an iterative procedure similar to the one used for the first-order wave function. The quadruple substitutions, which arise from the disconnected products of doubles, can be evaluated solely from the first-order wave function. We shall discuss the evaluation of these contributions in order.

A. Singles

The singles part of the second-order wave function ψ_S satisfies the equation

$$(H_0 - E_0)\psi_S + [(H' - E^{(1)})\psi^{(1)}]_S = 0 ,$$

where the notation $[...]_S$ means projection on the singles subspace. The expansion coefficients of this function in terms of our singly substituted configuration states[39] are collected in the singles residuum matrix **R**. We give **R** in AO form here. By rearranging some terms in the singles residuum formula of Ref. 39 we obtain

$$R = F + SdF - FdS - \Sigma_{j,k}K_{jk}(2C_{kj} - C_{jk})S$$
$$+ S\Sigma_{k,j}D_{jk}\{F(2C_{kj} - C_{jk})S$$
$$+ 2K[C_{kj}] - K^\dagger[C_{kj}]\} = 0 . \quad (11)$$

Here **d** is the singles coefficient matrix in AO form[39]: $d = Ud^{MO}U^\dagger$, and **U** is the SCF coefficient matrix. $(d^{MO})_{ia}$ is the coefficient of the singly substituted configuration state ψ_i^a. The factor $(1 + \delta_{kj})$ in Eq. (33) of Ref. 39 is not needed in the correct formula. The matrix D_{jk} is defined as

$$D_{jk} = UE_{jk}U^\dagger ,$$

where $(E_{jk})_{il} = \delta_{ij}\delta_{kl}$. In Eq. (11), the first-order doubles coefficient matrix $C^{(1)}$ is denoted by **C** for brevity. In orbital basis, only the occupied-virtual elements of **R**, R_{ia}, are significant: they correspond to the overlap of the residuum function with the singly substituted configuration ψ_i^a. For Hartree–Fock orbitals, the contributions of the Fock matrix to **R** vanishes because of the Brillouin theorem; it has been retained, however, for generality. As in the doubles cases, iterative updating of the singles coefficients converges quickly to yield the fourth-order singles coefficients. The energy contribution of the singles is given by

$$E_S = 2\langle dFd^\dagger S + dSd^\dagger F\rangle . \quad (12)$$

Because of the slight computational requirement of single substitutions, we do not normally use the local basis set approximation for them.

B. Doubles

Calculation of the doubles coefficients for the second-order wave function and fourth-order energy is entirely analogous to the calculation of the first-order wave function, Eq. (2). The only difference is that $T^{(3)}$, the third-order residu-

um matrix [Eq. (5)] replaces the internal exchange matrix **K**. The equation to be solved iteratively is

$$\mathbf{T}_{ij}^{(4)} = \mathbf{T}_{ij}^{(3)} + \mathbf{FC}_{ij}\mathbf{S} + \mathbf{SC}_{ij}\mathbf{F}$$

$$- \mathbf{S}\Sigma_k [F_{ik}\mathbf{C}_{kj} + F_{kj}\mathbf{C}_{ik}]\mathbf{S} = 0 . \tag{13}$$

Here we have written simply **C** for the doubles coefficients in the second-order wave function, $\mathbf{C}^{(2)}$. $\mathbf{T}^{(3)}$ in this equation is constant, and is evaluated using the first-order coefficients, $\mathbf{C}^{(1)}$. The energy contribution from the fourth-order doubles is

$$E_D = \Sigma_{i>j} \langle \mathbf{T}_{ij}^{(3)}\widetilde{\mathbf{C}}_{ji}^{(2)} \rangle .$$

C. Triples

It is now generally accepted that the contribution of triple substitutions is important at the fourth-order level.[6,7] In this paper, only the general computational features for triples are discussed here; expressions will be given in a separate publication. A major problem with an iterational procedure, similar to the doubles and the singles case, is the large number of triple substitutions in a full calculation. In order to be efficient, the coefficients in an iterative scheme must be accomodated in the fast storage. This is normally not a problem with doubles and singles but becomes prohibitive for triples. Of course, the local treatment is expected to cut back the number of triples dramatically. However, the truncation scheme for triples has yet to be established empirically. For instance, do we have to include substitutions from triplets (ijk) where (ij) is a strong pair but (ik) and (jk) are weak? Is it sufficient to include substitutions $(ijk) \rightarrow (pqr)$ in which p belongs to the domain of i, q to the domain of j, and r to the domain of k, or do we have to use the union of the three domains? Although we have some intuitive answers to these questions, they have to be confirmed experimentally. A minor difficulty with triples is that the symmetrical generator state formulation is redundant[45]: six generator state configurations can be defined for a general triple substitution, corresponding to the six permutations of the virtual labels pqr, but there are only five independent singlet spin functions. In spite of this, the explicit spin adaptation of the generator state formulation still brings substantial savings[46] compared to an elementary spin-orbital formulation, and also compared to an orthogonal formulation.[45]

D. Quadruples

The fourth-order quadruples contribution, and the renormalization contribution [the last term in Eq. (9)] to the energy should be treated together because of the cancellation between them. These terms can be easily obtained from CPMET[41] (also called coupled cluster doubles, CCD) contributions to the residuum matrix, given in the spin-adapted generator state formulation[39]:

$$E_Q = \Sigma_{i>j} \langle \mathbf{v}_{ij}\mathbf{S}\widetilde{\mathbf{C}}_{ji}^{(1)}\mathbf{S} \rangle . \tag{14}$$

The formula for **v** has been derived in Ref. 39 from Hurley's[47] spin-orbital equations. The evaluation of **v** has been traditionally regarded as a fairly expensive part of the calculation. In the generator state formulation, however, it requires only $3n^3$ matrix multiplications where n is the num-

ber of the (correlated) internal orbitals, i.e., $3n^3N^3$ multiplications; it is thus only 1.5 times more expensive than the evaluation of the doubles pair coupling terms Q in Eq. (5). The generator state formulation provides a savings by a factor of 2 for these terms as well as for the Q's over previous *explicitly spin-adapted* formulations.

It is convenient to classify the four terms in **v** (and in E_Q) as the ACCD[14] terms, and the non-ACCD terms. The latter are omitted in the ACCD approximation, introduced by Chiles and Dykstra.[14] The ACCD terms are given by

$$\mathbf{w}_{ij} = \Sigma_{k>l}(1 + \delta_{kl})^{-1}(\alpha_{kl,ij}\mathbf{C}_{kl} + \alpha_{kl,ji}\mathbf{C}_{lk})$$

$$- \Sigma_k(\beta_{jk}\mathbf{C}_{ik} + \beta_{ik}\mathbf{C}_{kj}) , \tag{15}$$

where

$$\alpha_{kl,ij} = \langle \mathbf{K}_{kl}\mathbf{C}_{ji} \rangle ,$$

$$\beta_{jk} = \Sigma_l(2\alpha_{kl,jl} - \alpha_{kl,lj}) .$$

The non-ACCD terms of **v** are[10]

$$\mathbf{x}_{ij} = \tfrac{1}{2}\Sigma_k\{\mathbf{C}_{ki}\mathbf{B}_{kj} + 2(\mathbf{C}_{ki}\mathbf{B}_{kj})^\dagger + (2\mathbf{C}_{ik} - \mathbf{C}_{ki})\widetilde{\mathbf{B}}_{kj}\}$$

$$- \mathbf{C}_{ij}\mathbf{A}^\dagger - \mathbf{AC}_{ij} . \tag{16}$$

Here

$$\mathbf{A} = \tfrac{1}{2}\Sigma_{k>l}(\widetilde{\mathbf{C}}_{lk}\mathbf{K}_{kl} + \widetilde{\mathbf{C}}_{kl}\mathbf{K}_{lk}) ,$$

$$\mathbf{B}_{kj} = \Sigma_l \mathbf{K}_{lk}\mathbf{C}_{jl} ,$$

$$\widetilde{\mathbf{B}}_{kj} = \Sigma_l(2\mathbf{K}_{kl} - \mathbf{K}_{lk})(2\mathbf{C}_{lj} - \mathbf{C}_{jl}) .$$

E. Application to UHF reference functions

The theory described above is applicable, with trivial modifications, to UHF reference functions. The formulas in this case are simpler but computationally more demanding. At the suggestion of the Referee, this formalism is summarized below. The indices i,j,k denote here occupied *spin orbitals*, and the dimension of all matrices is $2N$ by $2N$.

The equation for the first-order coefficients is identical with Eq. (2), except that $\overline{\mathbf{K}}_{ij} = \mathbf{K}_{ij} - \mathbf{K}_{ji}$ replaces $\mathbf{K}_{ij}$. The coefficients $\mathbf{C}_{ij}^{pq}$ are antisymmetric in both pairs of indices. The second-order energy is given by

$$E^{(2)} = \tfrac{1}{4}\Sigma_{i,j} \langle \overline{\mathbf{K}}_{ij}\mathbf{C}_{ji}^{(1)} \rangle . \tag{17}$$

The third-order residuums, the analogs of Eq. (5), are

$$\mathbf{T}_{ij}^{(3)} = \mathbf{T}_{ij}^{(2)} + \mathbf{K}(C_{ij}) + 2\Sigma_k\{(\mathbf{K}_{ik} - \mathbf{J}_{ik})\mathbf{C}_{kj}\mathbf{S}$$

$$- \mathbf{SC}_{jk}(\mathbf{K}_{ki} - \mathbf{J}_{ki}) - (\mathbf{K}_{jk} - \mathbf{J}_{jk})\mathbf{C}_{ki}\mathbf{S} + \mathbf{SC}_{ik}$$

$$\times (\mathbf{K}_{kj} - \mathbf{J}_{kj})\} + \Sigma_{k,l}\{(ki|lj) - (kj|li)\}\mathbf{SC}_{kl}\mathbf{S} , \tag{18}$$

where **C** stands for $\mathbf{C}^{(1)}$.

The third-order energy is

$$E^{(3)} = \tfrac{1}{8}\Sigma_{i,j} \langle \mathbf{T}_{ij}^{(3)}\mathbf{C}_{ji}^{(1)} \rangle . \tag{19}$$

The fourth-order singles residuum can be evaluated as

$$\mathbf{R}_{ia} = (\mathbf{SdF} - \mathbf{FdS} - \tfrac{1}{2}\Sigma_{j,k}\overline{\mathbf{K}}_{jk}\mathbf{C}_{kj})_{ia} - \tfrac{1}{2}\Sigma_j\mathbf{K}(\mathbf{C}_{ij})_{ja} . \tag{20}$$

The fourth-order doubles residuum formula is identical with Eq. (13). The fourth-order doubles energy is

$$E_D = \tfrac{1}{4}\Sigma_{i,j} \langle \mathbf{T}_{ij}^{(3)}\mathbf{C}_{ji}^{(2)} \rangle . \tag{21}$$

Finally, the energy expression for the fourth-order quadru-

ples is obtained simply by rewriting the formulas of Pople *et al.*[6] or Bartlett and Purvis[7] in matrix form; they can also be derived from the spin-orbital formulation of the CCD theory[47]:

$$E_Q = \tfrac{1}{8}\Sigma_{i,j}\langle(\mathbf{v}_{ij} - \mathbf{v}_{ji})\mathbf{S}\mathbf{C}_{ji}^{(1)}\mathbf{S}\rangle , \qquad (22)$$

where

$$\mathbf{v}_{ij} = \Sigma_{k,l}\{\langle\overline{\mathbf{K}}_{kl}\mathbf{C}_{ij}\rangle\mathbf{C}_{kl}$$
$$- 4\mathbf{C}_{ij}\overline{\mathbf{K}}_{kl}\mathbf{C}_{lk} - 4\langle\overline{\mathbf{K}}_{kl}\mathbf{C}_{lj}\rangle\mathbf{C}_{ik} + 8\mathbf{C}_{ik}\overline{\mathbf{K}}_{kl}\mathbf{C}_{lj}\} . \qquad (23)$$

These formulas can be made more appropriate for implementation by introducing explicit (α,β) spin blocking and restricting the summations.

III. COMPUTATIONAL METHOD

The paramount consideration in organizing our computer code was to retain the major advantage of SCEP[12]: the absence of logic in the inner loops, and consequently the high efficiency, particularly on vector and array processors. The code is organized around matrix manipulation routines. Although the use of local basis sets requires a considerable amount of logic, all logic is in the outer loops. As explained in our previous paper,[10] the (doubles) coefficient matrices $\mathbf{C}$ and the residuals $\mathbf{T}$ are compactly stored in the fast memory in matrices of variable dimension. Considering the drastic reduction in memory requirement due to the local restriction, and the fact that computers with large memories and efficient virtual memory are commonplace nowadays, this poses virtually no limitation on the systems we can treat. The partially transformed integrals are stored externally in the form of the Coulomb and exchange matrices $\mathbf{J}$ and $\mathbf{K}$[12].

We discuss various aspects of our program below.

A. Localization

We use our traditional SCF routine with Boys[48] localization. There are provisions to exclude orbitals from the localization procedure: this is needed if the core orbitals are not correlated, and also for genuinely delocalized systems, like benzene.

B. The local basis set

As mentioned in the Introduction, our local basis is defined as a subset of atomic basis functions (AO's). We have performed extensive tests on the selection of the local correlation basis sets. For simplicity, local basis sets are not defined for individual pairs of orbitals; rather, we assign subspaces, called domains,[10] to occupied orbitals; the domain of orbital i is denoted by $D(i)$. The most consistent local basis definition appears to be this:

(1) For a bicentric bond localized on atoms A and B, use the valence AO's of A and B.

(2) For a lone pair localized on A, use the valence AO's of A. This is easily extended to the comparatively rare case of tricentric bonds. For the pair (ij) we prefer now to use the union of the local bases of i and j, although we have the option of using an asymmetrical local basis, i.e., one in which only substitutions $i \rightarrow D(i), j \rightarrow D(j)$ are permitted. As noted

previously,[39] these substitutions describe directly the dipole–dipole part of the dispersion force between orbitals i and j. We have found, however, that ionic contributions to the dispersion force are significant,[15] up to 30% at typical van der Waals distances; the latter can only be described if the substitutions $j \rightarrow D(i)$ and $i \rightarrow D(j)$ are also permitted.

To guarantee the strong orthogonality of the correlation function to ψ_0, the local basis sets are projected against the internal (occupied) orbitals; the projected AO's are the correlation functions actually used. The local correlation space is checked for linear dependence or quasidependence and dependent functions are removed until the smallest root of the overlap matrix (built with normalized functions) exceeds a limit ($\sim 10^{-5}$).

We have experimented with various schemes to select the local correlation space on the basis of estimated contribution. These schemes are unsatisfactory because the constancy of the local correlation space across the potential surface cannot be guaranteed.

C. Calculation of pair coupling terms

In our previous paper,[10] we have briefly discussed the calculations of these terms, $\mathbf{Q}$ and $\mathbf{G}$, in Eq. (5); the calculation of the quadruples contributions, Eq. (15), is analogous. To minimize input–output, the calculation of the $\mathbf{Q}_{ij}$ matrices is operator driven. A pair of (full) $\mathbf{J}_{ij}$, $\mathbf{K}_{ij}$ matrices is read in the memory, and all contributions from them are calculated and added to the residuum vector $\mathbf{T}$. To a given residuum $\mathbf{T}_{kj}$, only the appropriate submatrices of $\mathbf{J}$, $\mathbf{K}$, and $\mathbf{S}$ contribute. These submatrices are extracted and stored compactly (a *gather* operation); subsequent matrix operations are performed on these packed matrices, with no logic or reference to the local basis. For the calculation of the $\mathbf{G}_{ij}$ type pair couplings, Eq. (5), a packed coefficient matrix is multiplied by the appropriate factor and added to the appropriate position of a full matrix $\mathbf{G}_{ij}$, a *scatter* operation. The required small submatrix of $\mathbf{S}\mathbf{G}_{ij}\mathbf{S}$ is then calculated and added to $\mathbf{T}_{ij}$. The logic-intensive parts of these operations are of order $O(N_L^2)$ where N_L is the (average) local basis dimension, while the computationally demanding $O(N_L^3)$ matrix multiplications are logic-free, and vectorize excellently on the CRAY.

D. The treatment of distant pairs

Pair correlations between distant orbitals are weak, and it is intuitively clear that higher-order contribution to them can be neglected with virtually no loss of accuracy. For ordinary bicentric localized orbitals and decent basis sets, intrapair correlation energies usually amount to ~ 30 mE_h. Interpair correlation energy between two orbitals sharing an atom is usually ~ 10 mE_h while orbitals separated by one bond have pair correlation energies in the 1 mE_h range. The latter already satisfy our criterion for a distant (or weak) pair: the pair correlation energy is less than 3 mE_h. Our following paper contains calculations which illustrate the fast convergence of the perturbation series for weak pairs.

The situation is somewhat more complex in the case when all pairs are correlated because there are coupling terms between strong and weak pairs. These terms are re-

tained in our treatment of the weak pairs, along with coupling terms between the weak pairs (ik) and (jk) if the pair (ij) is strong, which are of the same order of magnitude. These strong couplings between weak pairs are analogous to the Axilrod–Teller[49] triple–dipole terms in the theory of dispersion forces and will be discussed separately.[15] A formal summary of our treatment of weak pairs is given below:

(1) All pairs which are explicitly correlated are included at the second-order level.

(2) At the third-order level, the following diagonal pair contributions are omitted from the residuum matrix $\mathbf{T}_{ij}$ and therefore from the third-order energy, Eq. (5):

$$\mathbf{K}(\mathbf{C}_{ij}) - \mathbf{J}_{jj}\mathbf{C}_{ij}\mathbf{S} - \mathbf{S}\mathbf{C}_{ij}\mathbf{J}_{ii} + (ii|jj)\mathbf{S}\mathbf{C}_{ij}\mathbf{S}. \qquad (24)$$

It is easy to see that if the pair (ij) is distant, these terms approximately cancel.[15]

(3) The only other third-order terms dropped are contributions to $\mathbf{Q}_{ik}$ from $\mathbf{C}_{jk}$ if the pairs (ik), (jk), and (ij) are all weak.

(4) The doubles contribution to the fourth-order energy is neglected for weak pairs.

(5) In the quadruples contribution to the fourth-order energy the following approximations are made: $\alpha_{ij,kl}$ is set to zero if both (ij) and (kl) are weak pairs. The **B** terms in Eq. (16) are neglected if both (ij) and (ik) are weak pairs. Similarly, the contribution of the **A** term in Eq. (16) is neglected if (ij) is a weak pair.

The validity of these approximations is illustrated in the next paper of this series.

E. The external exchange operator

The most complex and computationally most demanding part in our previous implementation[10] of the local correlation treatment was the evaluation of the external exchange matrix $\mathbf{K}(\mathbf{C})$ of Eq. (6). The complexity derives from the necessity to guarantee strong orthogonality to ψ_0. Because of the orthogonalization of the local basis set to the occupied subspace, all AO integrals are needed to evaluate the external **K** matrices. The approach described in Ref. 10 is quite efficient but suffers from the need to generate many partially transformed integral files which require very large temporary storage space. In addition, the sorting step does not vectorize well on class VI computers.

This problem is much less acute in MP4 than in iterative methods because MP4 requires a single evaluation of $\mathbf{K}_{ext}$ per pair while iterative methods require ~ 10 evaluations. In addition, the external **K** matrix is not needed for weak pairs. In a molecule with the usual connectivity, the number of strong pairs grows only linearly with molecular size. We can therefore evaluate the external K matrix in the full AO basis, by the formula

$$\mathbf{K}[\mathbf{C}_{ij}] = \mathbf{P}_i\mathbf{K}[\mathbf{P}_i^\dagger\mathbf{C}_{ij}\mathbf{P}_j]\mathbf{P}_j^\dagger.$$

Here **K** is the external exchange matrix evaluated with projected local basis functions and $\mathbf{P}_i$ is an $N_i \times N$ projector matrix of the basis function in the domain $D(i)$ to the virtual space (N_i is the local dimension); **P** is simply the appropriate submatrix of $\mathbf{1}-\mathbf{SUU}^\dagger$; recall that **U** denotes the SCF coefficients.

As mentioned in Ref. 10, the calculation of integrals in triplets $i_1 = (pq|rs)$, $i_2 = (pr|qs)$, $i_3 = (ps|qr)$, as recommended by Meyer[50] can be used to speed up the evaluation of the external K matrix by a factor of 2 relative to older implementations.[23] To do this we have to construct the symmetrical and antisymmetrical parts of the coefficient matrix: $\mathbf{C}^{\pm} = 0.5(\mathbf{C} \pm \mathbf{C}^\dagger)$, and the six integral combinations $P^{\pm} = (i_2 \pm i_3)$; $Q^{\pm} = (i_3 \pm i_1)$; $R^{\pm} = (i_1 \pm i_2)$. The symmetrical and antisymmetrical external exchange matrix elements are obtained by the following algorithm:

$$K_{pq}^{\pm} \leftarrow P^{\pm}C_{rs}^{\pm}; \quad K_{rs}^{\pm} \leftarrow P^{\pm}C_{pq}^{\pm};$$

and the similarly for Q and the indices (pr), (qs); R and (ps), (qr). We believe that this algorithm is identical with the one mentioned briefly by Ahlrichs.[51] The computational dependence of this algorithm is only $\frac{1}{4}n^2N^4$.

The external K matrix is calculated for as many pairs at the same time as memory will allow, with the innermost loop running over the pairs. This makes the time spent on label decoding and the construction of the integral combinations P,Q,R is negligible; the inner loop also vectorizes efficiently.

F. Convergence

Convergence acceleration is very important in the iterative methods (variational CI, CEPA, CPMET, and ACCD). It is less important at the MP4 level, although in the local basis there are iterative parts. The same convergence acceleration is used in all iterative programs, whether it is an eigenvalue problem (e.g., variational CI), functional minimization problem (e.g., MP2) or a system of equations (CPMET). This method is closely related to the variation-perturbation method,[5,52,53] Davidson's matrix diagonalization technique,[54] and the method used by Roos and Siegbahn,[55] and by Pople et al.[56] for the solution of large systems of linear equations. A similar method, DIIS (direct inversion in the iterative subspace) has proved useful for accelerating the convergence of SCF[57,58] and small MC-SCF[59] wave functions. As pointed out by, e.g., Wormer et al.,[60] these methods are all derivatives of the conjugate gradient technique, and therefore can be simplified somewhat by using a three-term recurrence relation. There is little incentive to do this, e.g., in the SCF problem, as the computational effort and storage requirements of convergence acceleration are minimal, and the use of three-term recursion formulas was found empirically to slow down convergence somewhat for these highly nonlinear problems.[59] In the present case, the large number of variational parameters, and the near linearity of the problem make the use of three-term recursion much more desirable. Collecting the coefficients in the vector **C** and the residuums in **T**, and denoting the step index by a superscript, the extrapolation procedure used can be formulated as

$$\mathbf{C}^n \leftarrow \alpha_0\mathbf{C}^n + \alpha_1\mathbf{C}^{n-1} + \alpha_2\mathbf{C}^{n-2}. \qquad (25)$$

The coefficients α are determined from the condition that the projection of the extrapolated residuum $\mathbf{T}^n$ on $\mathbf{C}^n$, $\mathbf{C}^{n-1}$, and $\mathbf{C}^{n-2}$ vanishes; it is assumed here that **T** is a linear func-

tion of the coefficients C, i.e., small nonlinearities in T are neglected. This condition leads to a 3×3 system of equations,

$$\Sigma_m A_{km}\alpha_m = b_k ,$$

where

$$A_{km} = \Sigma_{ij}\langle(T_{ij}^k - K_{ij})\widetilde{C}_{ji}^m\rangle , \qquad (26)$$

$$b_k = \Sigma_{ij}\langle K_{ij}\widetilde{C}_{ji}^k\rangle .$$

These expressions correspond to the approximate minimization of the energy in the subspace of the last three iterates. In Eqs. (25) and (26), the *extrapolated* coefficient matrices and residuals are used for steps $(n-1)$ and $(n-2)$; it follows from the theory of conjugate gradient methods that, for a linear system, this yields results which are equivalent to the inclusion of all previous iterations. Although the equations to be solved are strictly linear only for L-CPMET (CEPA-0), and for MP2 and MP4, the algorithm outlined above works for variational CI as well as Davidson's[54] method does, and requires significantly less disk storage.

G. Symmetry

As first pointed out by Dykstra et al.,[37] symmetry handling is actually simpler in a localized orbital basis than in a canonical one. Our program calculates the residual matrices only for one member of an equivalent set, and generates the image of this for the rest.

H. A representative application: Oxalic acid

Energies and timings for a representative application, oxalic acid with the 6-311G** basis set[61] are given in Table I. The internal valence orbitals were localized using Boys' procedure.[48] The local basis for the orbitals was defined in the standard way as the valence AOs of the atoms on which the orbital is localized. We used the union of the local basis sets for orbitals $|i\rangle$ and $|j\rangle$ to describe the interpair correlation (ij). With the frozen core approximation oxalic acid has 153 correlating pairs; out of this 102 nonadjacent pairs were treated as weak.

TABLE I. Energies and timings for oxalic acid.[a]

Program step	Energy (E_h)	Time (s)[b]
Integrals + SCF	− 376.455 232	281.1
Integral transformation		267.5
Local MO basis		73.9
Iterative MP2 (eight iterations)	− 1.045 829	103.2
MP3 (51 strong and 102 weak pairs)	0.013 203	279.8
MP3 (weak pair contribution only)	− 0.059 233	⋯
MP4 (Q)	0.017 059	195.0
MP4 (S)	− 0.010 458	⋯
MP4 (D) (six iterations)	− 0.023 243	65.9
Total	− 377.504 500	1266.9

[a] 6-311G* basis (Ref. 61), experimental geometry [D. D. Danielson and K. Hedberg, J. Am. Chem. Soc. 101, 3730 (1979)], C_{2v} symmetry. The total number of CI coefficients is 304 236; the number of independent configurations is slightly less than this number, as the intrapair coefficient matrices are stored in full quadratic form.
[b] On the CRAY XMP-24.

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